

Volume 16 (1968)

1. **The Aldol Condensation** - Arnold T. Nielsen and William J. Houlihan

THE ALDOL CONDENSATION

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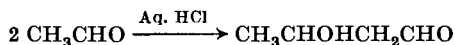
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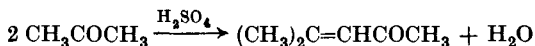
INTRODUCTION

The aldol condensation takes its name from aldol (3-hydroxybutanal), a name introduced by Wurtz who first prepared this β -hydroxy aldehyde from acetaldehyde in 1872.¹ The aldol condensation includes reactions producing β -hydroxy aldehydes (β -aldols) or β -hydroxy ketones (β -ketols)

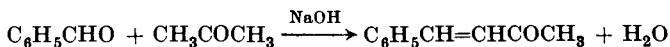
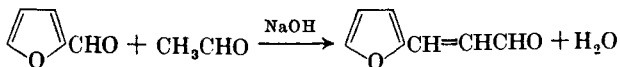


¹ A. Wurtz, *Bull. Soc. Chim. France*, [2] 17, 436 (1872); *Ber.*, 5, 326 (1872); *Compt. Rend.*, 74, 1361 (1872).

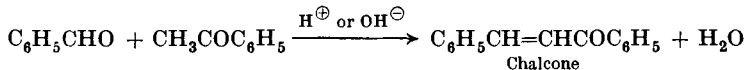
by self-condensations or mixed condensations of aldehydes and ketones, as well as reactions leading to α,β -unsaturated aldehydes or α,β -unsaturated ketones, formed by dehydration of intermediate β -aldols or β -ketols. Formation of mesityl oxide by self-condensation of acetone, a reaction discovered by Kane in 1838, is the first known example of ketone self-condensation.²



The Claisen-Schmidt condensation is an aldol condensation discovered by Schmidt³ in 1880 (condensation of furfural with acetaldehyde or acetone) and developed by Claisen (1881–1899).^{4–6} It is most often taken to be the condensation of an aromatic aldehyde with an aliphatic aldehyde or ketone to yield an α,β -unsaturated aldehyde or ketone, usually in the presence of a basic catalyst.



However, the term has been extended to include many types of aldehyde-ketone condensations (e.g., chalcone formation⁵) employing either acidic



or basic catalysts. Schmidt was first to employ a basic catalyst for the aldol condensation.³

The term aldol condensation has sometimes been applied to many so-called "aldol-type" condensations involving reaction of an aldehyde or ketone with a substance R_2CHX or RCH(X)Y (X or Y = an activating group such as CO_2R , CONHR , CN , NO_2 , SO_2CH_3 ; R = alkyl, aryl or hydrogen). Mechanistically, of course, these reactions are like aldol condensations. They produce a hydroxyl compound or its dehydration product and include the Claisen,^{7, 8} Knoevenagel,^{9, 9a} Doebner,^{9, 9a}

² R. Kane, *Ann. Physik Chem.*, [2] **44**, 475 (1838); *J. Prakt. Chem.*, **15**, 129 (1838).

³ J. G. Schmidt, *Ber.*, **13**, 2342 (1880); **14**, 1459 (1881).

⁴ L. Claisen and A. Claparède, *Ber.*, **14**, 349 (1881).

⁵ L. Claisen, *Ber.*, **20**, 655 (1887).

⁶ L. Claisen, *Ann.*, **306**, 322 (1899).

⁷ C. R. Hauser and B. E. Hudson, Jr., *Org. Reactions*, **1**, 266–302 (1942).

⁸ C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 59–196 (1954).

⁹ J. R. Johnson, *Org. Reactions*, **1**, 210–265 (1942).

^{9a} G. Jones, *Org. Reactions*, **15**, 204–599 (1967).

Perkin,⁹ Stobbe,¹⁰ and Reformatsky¹¹ reactions.¹² However, since the products are not aldols or ketols or dehydration products thereof, it is believed that the term aldol condensation should not be applied to reactions forming them. The present review includes examples where X and Y = CHO or COR only, i.e., solely condensation reactions of aldehydes and ketones. Included are 1,3-diketones, β -keto aldehydes, and α - and γ - ω -keto compounds (e.g., RCH_2COCO_2H and $RCH_2CO(CH_2)_nX$; $n > 1$, X = any group); some of these reactions might be described as both Knoevenagel and aldol condensations.

Excluded arbitrarily from this review, with few exceptions, are certain Knoevenagel-aldol condensations involving β -keto compounds, $RCOCH_2X$, where the α -methylene group of a ketone is activated *additionally* by some activating group other than the carbonyl group (e.g., β -keto esters). With few exceptions, reaction sequences starting with aldehydes or ketones which involve transient aldol intermediates that are not isolated are excluded; an example would be the formation of certain heterocyclic compounds as in the Robinson-Schöpf reaction.¹³ Most reactions of aldehydes or ketones leading indirectly through other reactions to an aldol condensation product are also arbitrarily excluded. One exception is the Michael reaction¹⁴ which may generate 1,5-diketones or keto aldehydes which, *in situ*, undergo an aldol condensation to a cyclic product. Except for a few important and closely related methods, syntheses of β -aldols and β -ketols and their dehydration products by alternative methods of preparation are not discussed. One such method is the Wittig reaction¹⁵ which may be applied to syntheses of α,β -unsaturated aldehydes and ketones.

In France, the term β -hydroxycarbonylation¹⁶ has been applied to condensations leading to β -aldols and β -ketols. However, this terminology has not been used extensively elsewhere.

MECHANISM

Simple Base Catalysis. The aldol condensation is catalyzed by acids and bases, the latter being more frequently employed. The

¹⁰ W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1-73 (1951).

¹¹ R. L. Shriner, *Org. Reactions*, **1**, 1-37 (1942).

¹² For recent summaries of aldol condensation and related reactions, cf. H. O. House, *Modern Synthetic Reactions*, pp. 216-256, Benjamin, New York, 1965; R. L. Reeves, in *The Chemistry of the Carbonyl Group*, ed. by S. Patai, pp. 580-600, Interscience, New York, 1966.

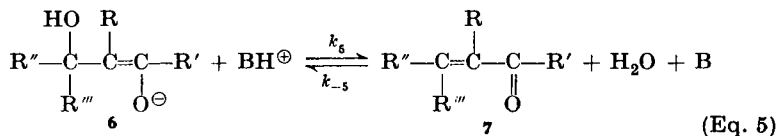
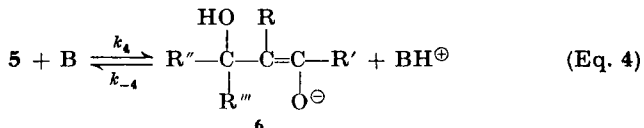
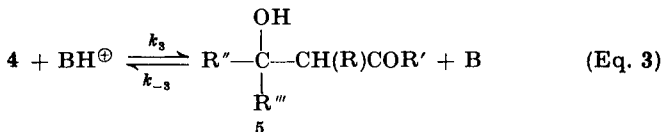
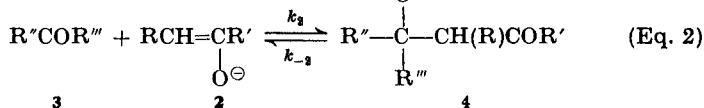
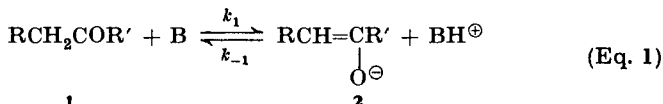
¹³ L. A. Paquette and J. W. Heimaster, *J. Am. Chem. Soc.*, **88**, 763 (1966).

¹⁴ E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179-555 (1959).

¹⁵ A. Maercker, *Org. Reactions*, **14**, 332-334 (1965).

¹⁶ H. Gault, *Bull. Soc. Chim. France*, 302 (1955); "*L'Hydroxycarbonylation*," *Colloques Internationaux du Centre National de la Recherche Scientifique*, Paris, May 31-June 5, 1954. A group of 26 papers published in *Bull. Soc. Chim. France*, 250-302 (1955).

base-catalyzed mechanism, which has received much study,^{17, 18} may be pictured by the following steps (R and R'' = alkyl or aryl; R' and R''' = alkyl, aryl, or hydrogen).



The question of the rate-limiting step for aldol and ketol formation has been examined.¹⁷⁻²⁰ For formation of an aldol in concentrated solutions (from acetaldehyde,^{19, 21} propanal,²² and butanal²³) the proton removal step (Eq. 1) is rate-limiting ($k_1 < k_2$). However, at low aldehyde concentrations the rate of ionization is not much greater than the rate of condensation, and the reaction becomes second order in aldehyde.¹⁹⁻²⁷

¹⁷ C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, pp. 676-699, Cornell University Press, Ithaca, New York, 1953.

¹⁸ A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, 2nd ed., pp. 335-350, Wiley, New York, 1961.

¹⁹ R. P. Bell, *The Proton in Chemistry*, pp. 137-138, Cornell University Press, Ithaca, New York, 1959.

²⁰ J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **87**, 5050 (1965).

²¹ A. Broche and R. Gibert, *Bull. Soc. Chim. France*, 131 (1955).

²² J. Jimenez and A. Broche, *Bull. Soc. Chim. France*, 1499 (1961).

²³ S. E. Rudakova and V. V. Zharkov, *Zh. Obshch. Khim.*, **33**, 3617 (1963) [*C.A.*, **60**, 7883 (1964)].

²⁴ H. Matsuyama, *Proc. Japan Acad.*, **27**, 552 (1951) [*C.A.*, **46**, 3838 (1952)].

²⁶ J. Hine, J. G. Houston, and J. H. Jensen, *J. Org. Chem.*, **30**, 1184, 1328 (1965).

²⁶ R. P. Bell and M. J. Smith, *J. Chem. Soc.*, 1691 (1958).

²⁷ R. P. Bell and P. T. McTigue, *J. Chem. Soc.*, 2983 (1960).

For condensations of certain aldehydes with ketones the reaction is first order in aldehyde at low concentrations, but zero order in aldehyde at high concentrations: examples are the reaction of *p*-nitrobenzaldehyde with 2-butanone, cyclohexanone, and desoxybenzoin.^{28, 29} However, for many condensations involving ketones, at a wide range of concentrations, the slow step is the condensation step in which the new carbon-carbon bond is formed (Eq. 2); $k_1 > k_2$. Kinetic evidence supporting this view has been presented for the formation of diacetone alcohol from acetone,^{26, 30} and for the condensations of aromatic aldehydes with acetophenone,³¹ of formaldehyde^{32, 33} and acetaldehyde³³ with 1,3-diketones, and of formaldehyde³⁴ with acetone. When the first step (Eq. 1) is rate-limiting, general base catalysis may be important.³⁵ When the second step (Eq. 2) is relatively slow, specific solvent anion (hydroxide, ethoxide) catalysis is observed.

The α, β -unsaturated aldehydes and ketones (7) often found as reaction products can arise from the aldol or ketol 5 by a carbanion elimination (E1cb) mechanism which requires an initial proton removal, followed by elimination of hydroxide ion (Eqs. 4 and 5). The equilibrium of Eq. 4 may lie far to the left ($k_{-4} \gg k_4$; $K_{\text{eq}}^{(4)} \ll 1$) and deuterium exchange into 5 would be expected to occur readily during formation of 7 in cases where $k_{-4} \gg k_5$.^{36, 37} In certain examples, rates k_4 and k_5 appear to be of the same order of magnitude. Factors met in certain aldol condensations (R = alkyl, R' = aryl; protic solvents) and favoring facile loss of hydroxide ion³⁷ from 6 could also disfavor proton removal^{38, 39} from 5. A comparison of the overall rate of base-catalyzed dehydration ($5 \rightarrow 7$; rate = $K_{\text{eq}}^{(4)}k_5$) for 1-hydroxy-1-phenyl-3-pentanone (5a)⁴⁰ with rates of proton removal of certain aliphatic ketones under similar reaction

²⁸ S. F. Nelsen and M. Stiles, unpublished results. We are indebted to Professor Stiles for making some of his results available to us prior to publication.

²⁹ This situation is illustrated by the lack of deuterium incorporation into *threo*- and *erythro*-4-O₂NC₆H₄CHOHCH(C₆H₅)COC₆H₅ in D₂O—NaOD during their interconversion; L. Traynor, Ph.D. thesis, University of Michigan, 1964; *Dissertation Abstr.*, **25**, 6972 (1965).

³⁰ D. S. Noyce and W. L. Reed, *J. Am. Chem. Soc.*, **81**, 624 (1959).

³¹ E. Coombs and D. P. Evans, *J. Chem. Soc.*, 1295 (1940).

³² P. Rumpf and M. Diard, *Compt. Rend.*, **248**, 823 (1959).

³³ M. Laloi, *J. Rech. Centre Natl. Rech. Sci. Lab. Bellevue (Paris)*, **55**, 141 (1961) [*C.A.*, **58**, 4393 (1963)].

³⁴ S. Nagase, *Kogyo Kagaku Zasshi*, **64**, 1008 (1961) [*C.A.*, **57**, 2064 (1963)].

³⁵ D. C. Gutsche, R. S. Buriks, K. Nowotny, and H. Grassner, *J. Am. Chem. Soc.*, **84**, 3775 (1962).

³⁶ R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

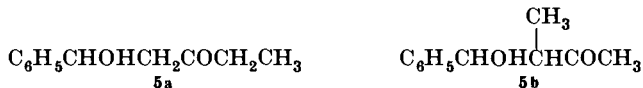
³⁷ J. F. Bunnett, *Angew. Chem., Intl. Ed. Engl.*, **1**, 225 (1962).

³⁸ A. K. Mills and A. E. Wilder Smith, *Helv. Chim. Acta*, **43**, 1915 (1960).

³⁹ H. Shechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Am. Chem. Soc.*, **84**, 2905 (1962).

⁴⁰ M. Stiles, D. Wolf, and G. V. Hudson, *J. Am. Chem. Soc.*, **81**, 628 (1959).

conditions³⁸ suggests that k_4 and k_5 could be comparable. The observation that 3-methyl-4-hydroxy-4-phenyl-2-butanone (**5b**) undergoes retrogression to reactants rather than dehydration in basic medium⁴⁰ suggests



that k_4 is relatively slow ($k_4 \ll k_{-3}k_{-2}/k_3$) in this case; k_5 is not, however, necessarily slow relative to k_4 .^{40a} The rate of retrogression of **5b** to reactants is about four times faster than that of **5a**,⁴⁰ under conditions where the rate of proton removal (k_4) from **5b** would be expected to be 10^2 to 10^3 times slower than from **5a**.^{29, 36, 39} Although α,β -unsaturated ketones may be hydrated in basic media, their formation is effectively irreversible in most instances ($k_5 \gg k_{-5}$). This circumstance may offset previous unfavorable equilibria and allow the condensation to proceed to completion (formation of 7). A detailed understanding of the mechanism of the base-catalyzed dehydration of aldols and ketols awaits further study.

In protic solvents (water, ethanol) the aldol condensation is reversible and the various equilibria are often quite sensitive to the nature of substituents.⁴⁰⁻⁴² Since in practice the preparations are generally so conducted that thermodynamic control determines the products, the effects of substituents on the several equilibria are of great importance. In aprotic solvents (ethers, hydrocarbons) equilibration occurs exceedingly slowly, particularly with lithium and magnesium enolates.⁴³⁻⁴⁵ Thus kinetically controlled aldol condensations should be more favorable under these conditions.

Amine Catalysis. Primary and secondary amines (especially in the presence of added acid) exert a pronounced catalytic effect on condensation of aldehydes and ketones with active methylene compounds (Knoevenagel condensation).^{9a, 46} Pyrrolidine and piperidine are very effective. Tertiary amines are without effect or are very poor aldol catalysts except when general base catalysis is observed.^{35, 47, 48} Because of their weak base strength most amines provide only low concentrations

^{40a} P. Carsky, P. Zuman, and V. Horak, *Collection Czech. Chem. Commun.*, **30**, 4316 (1965).

⁴¹ J. E. Dubois and H. Viellard, *Tetrahedron Letters*, 1809 (1964).

⁴² D. S. Noyce and L. R. Snyder, *J. Am. Chem. Soc.*, **81**, 620 (1959).

⁴³ H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 1341 (1965).

⁴⁴ H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965).

⁴⁵ H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

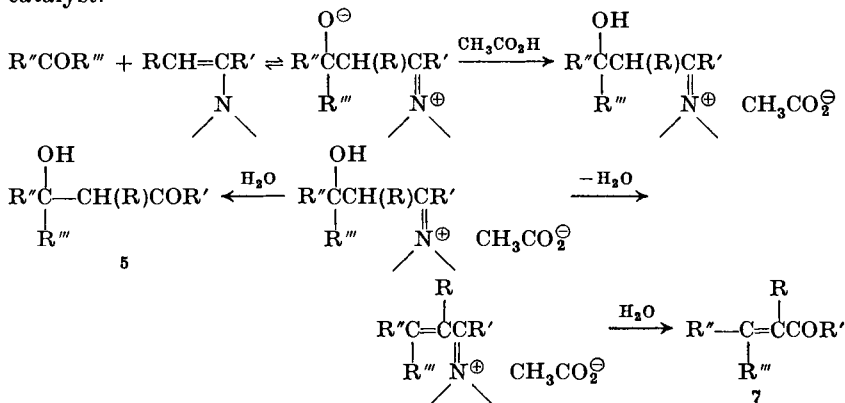
⁴⁶ E. Knoevenagel, *Ann.*, **281**, 25 (1894).

⁴⁷ F. H. Westheimer and H. Cohen, *J. Am. Chem. Soc.*, **60**, 90 (1938).

⁴⁸ T. A. Spencer, H. S. Neel, T. W. Flechtner, and R. A. Zayle, *Tetrahedron Letters*, 3889 (1965).

of solvent anion base (hydroxide, ethoxide), and the marked catalytic effect of primary and secondary amines must be explained on another basis.

At least two mechanisms appear to be operative for most amine-catalyzed aldol condensations. Many of these reactions, especially those involving secondary amines and reactive aldehydes or ketones capable of forming enamines, require an enamine intermediate in the condensation step leading to an aldol, as well as in the step leading to an α,β -unsaturated carbonyl compound.⁴⁹⁻⁵⁶ Evidence supporting an enamine mechanism has been presented for the self-condensation of propanal to 2-methyl-2-pentenal^{50, 54-56} and for certain Robinson annelation reactions.⁴⁸ Enamines have been condensed with aldehydes and ketones to give aldol condensation products.^{53a-56b} An acid catalyst (preferably acetic acid), usually employed in an amount equivalent to the amine, is required to effect the condensation. It is reported that enamines fail to undergo aldol condensation with aldehydes in the absence of an added acid catalyst.⁵⁶



⁴⁹ T. A. Spencer and K. K. Schmiegel, *Chem. Ind. (London)*, 1765 (1963).

⁵⁰ I. V. Mel'nichenko and A. A. Yasnikov, *Ukr. Khim. Zh.*, **30**, 838 (1964) [*C.A.*, **61**, 14490 (1964)].

⁵¹ D. J. Goldsmith and J. A. Hartman, *J. Org. Chem.*, **29**, 3520, 3524 (1964).

⁵² J. Szmuzkovicz, *Advan. Org. Chem.*, **4**, 1-114 (1963).

⁵³ G. Stork, A. Brizzolara, H. Landesman, J. Szmuzkovicz, and R. Torrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

^{53a} L. Birkofer, S. M. Kim, and H. D. Engels, *Chem. Ber.*, **95**, 1495 (1962).

⁵⁴ A. A. Yasnikov and K. I. Matkovskii, *Ukr. Khim. Zh.*, **28**, 210 (1962). [*C.A.*, **58**, 3306 (1963)].

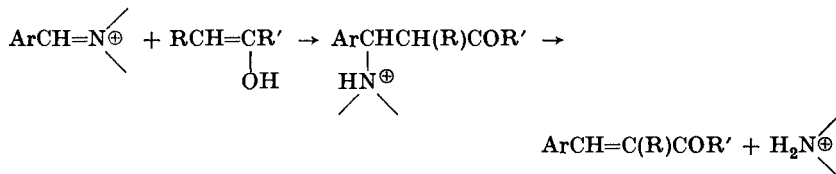
⁵⁵ T. S. Boiko, N. V. Volkova, and A. A. Yasnikov, *Ukr. Khim. Zh.*, **29**, 1179 (1963) [*C.A.*, **60**, 3964 (1964)].

⁵⁶ N. V. Volkova and A. A. Yasnikov, *Dokl. Akad. Nauk SSSR*, **149**, 94 (1963) [*C.A.*, **59**, 5011 (1963)].

^{56a} L. A. Paquette and H. Stucki, *J. Org. Chem.*, **31**, 1232 (1966).

^{56b} F. T. Bond and W. E. Musa, *Chem. Ind. (London)*, 1380 (1966).

A second amine-catalyzed mechanism, involving attack of an iminium ion on the methylene group (enol) of an aldehyde or ketone, is important in certain aldol condensations (Knoevenagel-aldol);⁵⁶ see p. 43.^{12, 13, 56c-e} This process is favored by use of primary amines with aldehydes or ketones which readily form imines and in condensations with carbonyl compounds of high enol content such as 1,3-diketones.^{56, 57} Aldimines⁵⁸ and ketimines⁵⁹ condense readily with certain active methylene compounds, including ketones⁵⁸ ("alkylidenation reaction"⁵⁹); α,β -unsaturated ketones may be prepared by this reaction which is catalyzed by acids.⁵⁸



A third mechanism is possible, that of condensation of an immonium ion with an enamine. An immonium ion-dienamine reaction step is postulated in the pyrrolidinium perchlorate-catalyzed self-condensation of 2-cyclohexen-1-one.^{59a} The formation of α,β -unsaturated ketones by self-condensation of enamines derived from methyl alkyl ketones may involve such a reaction (see p. 20);⁶⁰ a dienamine intermediate can be isolated. An immonium ion-enamine reaction may occur in the condensation of acetone with 1-propenylpiperidine (added acetic acid) to yield 2,4,5-trimethyl-2,4-hexadienal (see p. 27).⁵⁴

Acid Catalysis. The mechanism of the acid-catalyzed reaction^{17, 18} is similar to that of the base-catalyzed reaction in that an initial proton removal step (Eq. 7) is involved, though from a protonated intermediate 8 (R and R'' = alkyl or aryl; R' and R''' = alkyl, aryl, or hydrogen). The intermediate enol 9 reacts in a rate-limiting step (Eq. 8)⁴² with a second (protonated) carbonyl molecule to produce an aldol or ketol 5. However, α,β -unsaturated carbonyl compounds 7 (rather than aldols

^{56c} J. Hine, B. C. Merron, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **88**, 3367 (1966).

^{56d} M. L. Bender and A. Williams, *J. Am. Chem. Soc.*, **88**, 2502 (1966).

^{56e} J. Hine, F. C. Kokesh, K. G. Hampton, and J. Mulders, *J. Am. Chem. Soc.*, **89**, 1205 (1967).

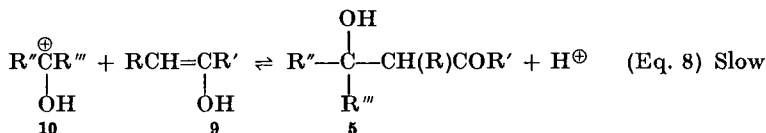
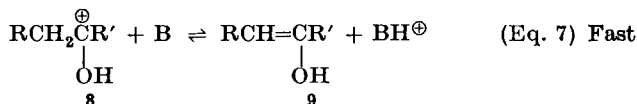
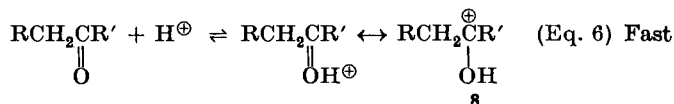
⁵⁷ A. A. Yasnikov, K. I. Matkovskii, and E. M. Gaivoronskaya, *Ukr. Khim. Zh.*, **28**, 88 (1962) [*C.A.*, **58**, 1326 (1963)].

⁵⁸ A. H. Blatt and N. Gross, *J. Org. Chem.*, **29**, 3306 (1964).

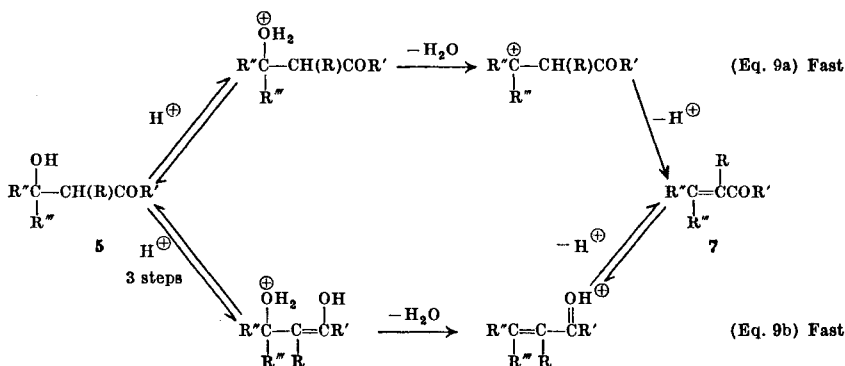
⁵⁹ G. Charles, *Bull. Soc. Chim. France*, 1559 (1963).

^{59a} N. J. Leonard and W. J. Musliner, *J. Org. Chem.*, **31**, 639 (1966).

⁶⁰ G. Bianchetti, P. Dalla Croce, and D. Pocar, *Tetrahedron Letters*, 2039 (1965).



or ketols) are the most frequently encountered products, because acid-catalyzed dehydration is very rapid and in most instances not easily reversed. The dehydration step (Eq. 9) involves protonation of the hydroxyl group, followed by loss of water and then loss of a proton. The dehydration may proceed, in kinetically distinguishable paths, via a carbonium ion or enol intermediate (Eqs. 9a and 9b).^{61-62a} Dehydration



is generally more rapid than reversal of the rate-determining condensation step (Eq. 8).⁴² The course of the acid-catalyzed reaction, unlike the base-catalyzed process, is not characterized by the influence of reversibility in all steps, but principally by reactivity and stability of intermediate enols.⁴²

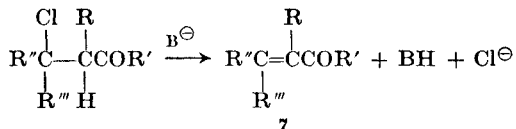
An important and useful acid-catalyzed procedure employs hydrogen chloride in the absence of solvent, or in an aprotic solvent such as benzene,

⁶¹ D. S. Noyce and W. L. Reed, *J. Am. Chem. Soc.*, **80**, 5539 (1958).

⁶² M. Stiles and A. Longroy, *Tetrahedron Letters*, 337 (1961).

^{62a} S. Cabani and N. Ceccanti, *J. Chem. Soc., Phys. Org.*, 77 (1966).

to produce a β -chloroketone which may be dehydrohalogenated stereoselectively to the more stable *trans* 7 (*trans* disposition of bulkier β -group and α -carbonyl group).⁶³



Stereochemistry. Present knowledge of the stereochemistry of the aldol condensation is limited.^{48, 64-75c} Aldols and ketols are susceptible to retrogression to form the reactants or to dehydration to yield the corresponding α,β -unsaturated carbonyl compounds. The facile equilibration of aldols through their enolate anions, as well as by retrogression, contributes to the paucity of examples of kinetically controlled aldol formation.^{64-72, 76} Available data suggest a general lack of stereo-electronic control or stereospecificity in the C—C bond-forming process. Mixtures of epimers often result under kinetically controlled conditions in condensations leading to acyclic⁶⁴ or alicyclic^{66, 69-71} products. In the two ketols and the aldol shown,^{66, 69, 70} mild conditions and short reaction times lead to mixtures of epimers involving substituents about the bond shown by a broken line. Slightly more vigorous conditions or longer reaction times result in complete conversion to the most stable epimer in each example.^{66, 69, 70} In the formation of acyclic products, equilibration may lead to mixtures of epimers different from the mixtures formed

⁶³ H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 2428 (1958).

⁶⁴ M. Stiles, R. R. Winkler, U. Chang, and L. Traynor, *J. Am. Chem. Soc.*, **86**, 3337 (1964).

⁶⁵ A. C. Huitric and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 1147 (1956).

⁶⁶ A. T. Nielsen, *J. Org. Chem.*, **30**, 3650 (1965).

⁶⁷ J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

⁶⁸ T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

⁶⁹ I. Vogel, *J. Chem. Soc.*, 594 (1927).

⁷⁰ M. B. Rubin, *J. Org. Chem.*, **29**, 3333 (1964).

⁷¹ W. S. Johnson, J. J. Korst, R. A. Clement, and J. Dutta, *J. Am. Chem. Soc.*, **82**, 614 (1960).

⁷² W. S. Johnson, J. Ackerman, J. F. Eastham, and H. A. DeWalt, *J. Am. Chem. Soc.*, **78**, 6302 (1956).

⁷³ W. F. Johns, *J. Org. Chem.*, **26**, 4583 (1961).

⁷⁴ K. Tanabe and Y. Morisawa, *Chem. Pharm. Bull. (Tokyo)*, **11**, 536 (1963) [*C.A.*, **59**, 7600 (1963)].

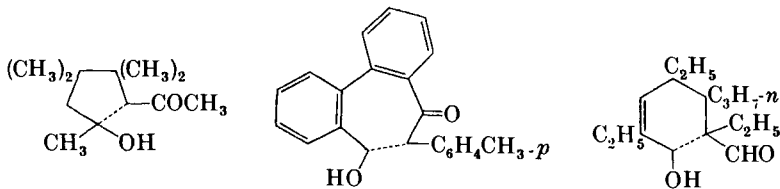
⁷⁵ K. Tanabe, R. Hayashi, and R. Takasaki, *Chem. Pharm. Bull. (Tokyo)*, **9**, 1 (1961) [*C.A.*, **60**, 9331 (1964)].

^{75a} J. J. Basselier, C. Guerey, and S. Julia, *Bull. Soc. Chim. France*, 2988 (1965).

^{75b} G. L. Buchanan and G. W. McLay, *Tetrahedron*, **22**, 1521 (1966).

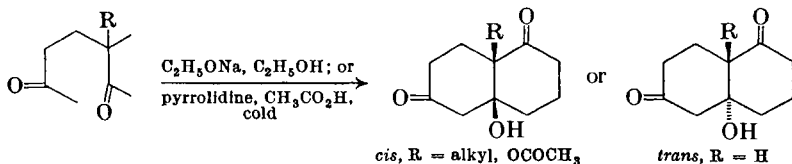
^{75c} F. Johnson, N. A. Starkovsky, and A. A. Carlson, *J. Am. Chem. Soc.*, **87**, 4612 (1965).

⁷⁶ T. A. Spencer, H. S. Neel, D. C. Ward, and K. L. Williamson, *J. Org. Chem.*, **31**, 434 (1966).



under kinetic control.^{64, 65} These observations suggest that the transition state for the condensation has a relatively long developing C—C bond and does not resemble the products.

Other asymmetric centers in the reactant(s) may influence the stereochemistry of the aldol condensation leading to very stereoselective processes as in certain examples of the Robinson annelation reaction;^{67, 68, 76, 77} it is not known to what extent these results represent kinetic control.⁶⁸



In many cases the aldol condensation appears to be more stereoselective under conditions of thermodynamic control (except in certain acyclic systems)^{64, 65} than under conditions of kinetic control.

Another important stereochemical question concerns *cis-trans* isomerism of α,β -unsaturated carbonyl compounds derived from ketols and aldols. It is clear from the known examples^{63, 78-90a} that the most highly favored (and often the most stable) product is the *trans* isomer (*trans* disposition of the bulkier β -group and the α -carbonyl group); the formation of

⁷⁷ T. A. Spencer and T. W. Flechtner, unpublished results; we wish to thank Professor Spencer for making some of his results available to us prior to publication.

⁷⁸ C. Y. Chen and R. J. W. Le Fèvre, *J. Chem. Soc.*, 5528 (1965).

⁷⁹ S. V. Tsukerman, A. I. Artemenko, and V. F. Lavrushin, *Zh. Obshch. Khim.*, **34**, 3591 (1964) [*C.A.*, **62**, 4736 (1965)].

⁸⁰ A. Hassner and T. C. Mead, *Tetrahedron Letters*, 1223 (1962).

⁸¹ R. Heilmann, *Bull. Soc. Chim. France*, [5] **4**, 1064 (1937).

⁸² J. E. Dubois and M. Dubois, *Compt. Rend.*, **256**, 715 (1963).

⁸³ H. Kwart and L. G. Kirk, *J. Org. Chem.*, **22**, 116 (1957).

⁸⁴ R. A. Abramovitch and A. Obach, *Can. J. Chem.*, **37**, 502 (1959).

⁸⁵ R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

⁸⁶ L. Crombie, *Quart. Rev. (London)*, **6**, 101 (1962).

⁸⁷ R. E. Buckles, G. V. Mock, and L. Locatelli, Jr., *Chem. Rev.*, **55**, 659 (1955).

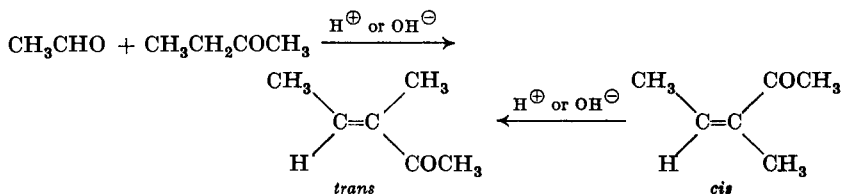
⁸⁸ G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).

⁸⁹ G. Gamboni, V. Theus, and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

⁹⁰ V. Theus, W. Surber, L. Colombi, and H. Schinz, *Helv. Chim. Acta*, **38**, 239 (1955).

^{90a} J. Sotiropoulos and P. Bédos, *Compt. Rend.*, **263**, Ser. C, 1392 (1966).

3-methyl-*trans*-3-penten-2-one is illustrative.⁶³ *cis* Isomers may sometimes be isomerized to *trans* isomers with acid or basic catalysts^{63, 82, 91};

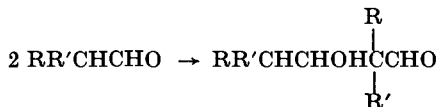


the reverse transformation is frequently effected by irradiation with ultraviolet light.^{92, 93} The mechanism of the heterolytic isomerization can involve hydration of the olefinic double bond,^{63, 91} or formation of a dienolate anion if a γ hydrogen atom is present, followed by equilibration of the α,β - and the β,γ -unsaturated ketones.⁹⁴

SCOPE AND LIMITATIONS

Self-Condensation of Aldehydes

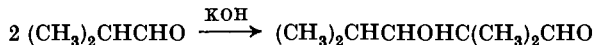
The aldol condensation produces β -hydroxy aldehydes from saturated aliphatic aldehydes having at least one α hydrogen atom. Formaldehyde



undergoes self-condensation to polyhydroxyaldehydes (Butlerow reaction),^{95-99a} although the initial step leading to glycolaldehyde is not an aldol condensation,⁹⁷ subsequent steps do constitute an aldol condensation.



Aldols produced from aldehydes having only one α hydrogen atom (e.g., isobutyraldol) cannot be dehydrated to α,β -unsaturated aldehydes.



⁹¹ D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **83**, 2525 (1961).

⁹² L. v. Hahn and J. F. Miguel, *Compt. Rend.*, **257**, 1948 (1963).

⁹³ R. E. Lutz and R. H. Jordan, *J. Am. Chem. Soc.*, **72**, 4090 (1950).

⁹⁴ H. C. Volger and W. Brackman, *Rec. Trav. Chim.*, **84**, 1017 (1965).

⁹⁵ A. M. Butlerow, *Ann.*, **120**, 295 (1861).

⁹⁶ E. Pfeil and H. Ruckert, *Ann.*, **641**, 121 (1961).

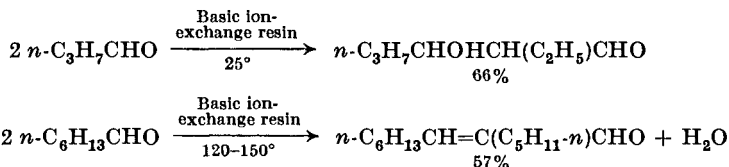
⁹⁷ H. W. Wanzlick, *Angew. Chem., Intl. Ed. Engl.*, **1**, 79 (1962).

⁹⁸ J. F. Walker, *Formaldehyde*, 3rd ed., pp. 215-217, Reinhold, New York, 1964.

⁹⁹ H. Ruckert, E. Pfeil, and G. Scharf, *Chem. Ber.*, **98**, 2558 (1965).

^{99a} K. Runge and R. Mayer, Ger. (East) pat., 44,094 [*C.A.*, **64**, 17426 (1966)].

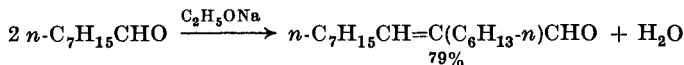
Unbranched homologs of acetaldehyde (*n*-alkanals) up to hexanal produce aldols in a normal manner with basic catalysts if reaction conditions are mild; for this particular reaction basic ion-exchange resins appear to be the most effective catalysts.¹⁰⁰ Propanal and butanal have been condensed to aldols in good yields, but the more vigorous conditions (higher temperature, stronger base) needed to effect condensation of higher homologs often cause extensive dehydration of the aldols, leading to α,β -unsaturated aldehydes. For example, heptanal with a mild basic ion-exchange catalyst reacts only at elevated temperature to produce 2-pentyl-2-nonenal, not the aldol.¹⁰¹ Yields of aldols decrease as the



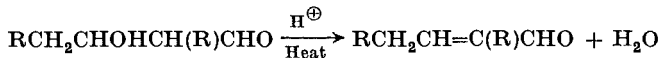
carbon chain increases in length. Phosphorus oxychloride and thionyl chloride have been reported to condense heptanal to the aldol in 41–46% yield at 0–10°.^{102, 103}

Numerous side reactions (discussed on pp. 61–62) frequently accompany attempts to apply vigorous conditions to the self-condensation of alkanals. Aldols dimerize to 1,3-dioxane derivatives on standing and should be redistilled immediately before use (see p. 59).

Although general procedures are not available to form aldols in good yields from *n*-alkanals of more than six carbon atoms, the derived α,β -unsaturated aldehydes have been obtained in excellent yields in all cases reported.^{103a} The condensation of octanal to 2-hexyl-2-decenal is an example.¹⁰⁴



Aldols having a hydrogen atom α to the carbonyl group may readily be dehydrated, by heating with an acid catalyst such as iodine or oxalic acid, to α,β -unsaturated aldehydes in good yield.¹⁰⁰ Heating strongly in



¹⁰⁰ M. J. Astle and J. A. Zaslowsky, *Ind. Eng. Chem.*, **44**, 2869 (1952).

¹⁰¹ G. Durr, *Ann. Chim. (Paris)*, [13] **1**, 84 (1956).

¹⁰² M. Backès, *Compt. Rend.*, **196**, 277 (1933).

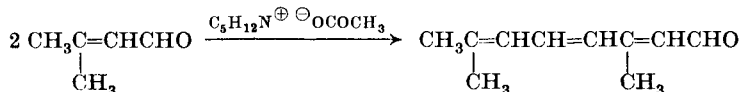
¹⁰³ M. Backès, *Bull. Soc. Chim. France*, [5] **9**, 60 (1942).

^{103a} W. J. Porter, Jr., J. A. Wingate, and J. A. Hanan, U.S. pat., 3,248,428 [C.A., **65**, 2128 (1966)].

¹⁰⁴ F. J. Villani and F. F. Nord, *J. Am. Chem. Soc.*, **69**, 2605 (1947).

the absence of a catalyst may dissociate aldols to form the parent aldehydes.

The self-condensation of α,β -unsaturated aliphatic aldehydes is an important synthetic route to conjugated polyenals, although yields are often low. The condensation products isolated have been formed by attack on the γ rather than the α carbon atom;¹⁰⁵⁻¹¹³ mild basic catalysts, such as piperidinium acetate, are preferred.¹¹⁴ With amine catalysts dienamine intermediates are probably involved. These are attacked preferentially on the α position in many reactions, including Michael addition and alkylation.⁵² The attack on the γ position observed in aldol condensation suggests a thermodynamically controlled product composition favoring a linear, rather than a cross-conjugated, polyene. 3-Methyl-2-butenal forms dehydrocitrinal in 14.5% yield.¹¹⁵ Polyenals



have been prepared in this manner from benzaldehyde and 2-butenal.¹¹⁶ The Wittig reaction is a useful alternative route to polyenals.¹⁵

Mixed Condensation of Aldehydes

The condensation of formaldehyde with aliphatic aldehydes (Tollens condensation^{117, 118}) can readily produce methylol aldehydes in which all α hydrogen atoms have been replaced by methylol groups. It is difficult to prevent complete methylolation; the second methylol group is evidently introduced more rapidly than the first,¹¹⁹ and the equilibrium also

¹⁰⁵ F. G. Fischer and K. Löwenberg, *Ann.*, **494**, 263 (1932).

¹⁰⁶ F. G. Fischer and K. Hultsch, *Ber.*, **68**, 1726 (1935).

¹⁰⁷ T. Reichstein, C. Ammann, and G. Trivelli, *Helv. Chim. Acta*, **15**, 261 (1932).

¹⁰⁸ K. Bernhauer, K. Irrgang, K. Adler, M. Mattauch, P. Miller, and F. Neiser, *Ann.*, **525**, 43 (1936).

¹⁰⁹ F. G. Fischer, K. Hultsch, and W. Flaig, *Ber.*, **70**, 370 (1937).

¹¹⁰ R. Kuhn and C. Grundmann, *Ber.*, **71**, 2274 (1938).

¹¹¹ C. Grundmann, *Chem. Ber.*, **81**, 510 (1948).

¹¹² D. N. Kursanov and Z. N. Parnes, *Dokl. Akad. Nauk SSSR*, **103**, 847 (1955) [*C.A.*, **50**, 9326 (1956)].

¹¹³ D. N. Kursanov and Z. N. Parnes, *Dokl. Akad. Nauk SSSR*, **91**, 1125 (1953) [*C.A.*, **48**, 10549 (1954)].

¹¹⁴ H. Shingu and T. Okazaki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **27**, 69 (1951) [*C.A.*, **47**, 2124 (1953)].

¹¹⁵ I. N. Nazarov and Z. A. Krasnaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 238 (1958) [*C.A.*, **52**, 12792 (1958)].

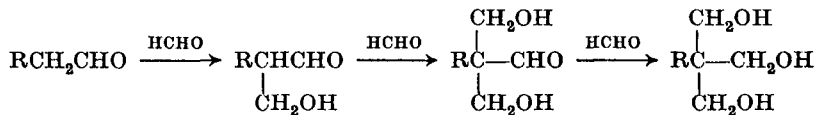
¹¹⁶ J. Schmitt, *Ann.*, **547**, 270 (1941).

¹¹⁷ B. Tollens and P. Wigand, *Ann.*, **265**, 316 (1891).

¹¹⁸ P. Rave and B. Tollens, *Ann.*, **276**, 58 (1893).

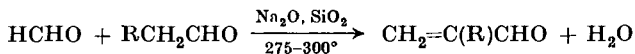
¹¹⁹ Y. Ishikawa and T. Minami, *Kogyo Kagaku Zasshi*, **63**, 277 (1960) [*C.A.*, **56**, 2322 (1962)].

favors the polymethylol product. Monomethylolalkanals can be obtained from branched (α - and/or β -substituted) and higher alkanals ($>C_5$) under mild conditions (e.g., potassium carbonate, aqueous ether, low temperature).¹²⁰ *n*-Alkanals (butanal through nonanal) have been condensed with formaldehyde to yield 2,2-bis-methylol alkanals.^{121, 122}



Unless reaction conditions are sufficiently mild, however, reduction of the aldehyde group by formaldehyde often leads, irreversibly, to diols or triols (crossed Cannizzaro reaction),^{123, 123a} lower-molecular-weight aliphatic aldehydes are apparently most susceptible to this reduction which is also favored by excess formaldehyde. Although basic condensing agents (hydroxides) are most frequently employed, the reaction is also effected by sulfuric acid.¹²⁴

α -Alkylacroleins are obtained in 46–62% yield by vapor-phase condensation of formaldehyde with *n*-alkanals;¹²⁵ the subject has been reviewed.¹²⁶



The condensation of pentanal and hexanal with formaldehyde in water at 100° (18–20 hr.) in the absence of added catalyst has been reported to yield α -*n*-propyl- and α -*n*-butyl-acrolein in 64–66% yield.¹²⁷ Dehydration of monomethylolalkanals by means of an acid catalyst usually leads to polymers and low yields of α -alkylacroleins.¹²⁰ α -Alkylacroleins are more conveniently prepared from Mannich intermediates, $\text{R}'\text{CH}(\text{CH}_2\text{NR}_2)\text{CHO}$.^{120, 128}

¹²⁰ C. S. Marvel, R. L. Myers, and J. H. Saunders, *J. Am. Chem. Soc.*, **70**, 1694 (1948).

¹²¹ T. Shono, H. Ono, and R. Oda, *Kogyo Kagaku Zasshi*, **59**, 960 (1951) [*C.A.*, **52**, 9952 (1958)].

¹²² O. Neunhoeffer and H. Neunhoeffer, *Ber.*, **95**, 102 (1962).

¹²³ T. A. Geissman, *Org. Reactions*, **2**, 94–113 (1944).

^{123a} K. Ko, S. Kunimoto, Y. Shimono, and T. Yamaguchi, Japan pat., 8769 [*C.A.*, **65**, 12109 (1966)].

¹²⁴ D. Bertin, H. Fritel, and L. Nedelec, *Bull. Soc. Chim. France*, 1068 (1962).

¹²⁵ S. Malinowski, H. Jablezynska-Jedrzejska, S. Basinski, and S. Benbenek, *Chim. Ind. (Paris)*, **85**, 885 (1961) [*C.A.*, **56**, 2321 (1962)].

¹²⁶ G. S. Mironov and M. I. Farberov, *Usp. Khim.*, **33**, 649 (1964) [*C.A.*, **61**, 6912 (1964)].

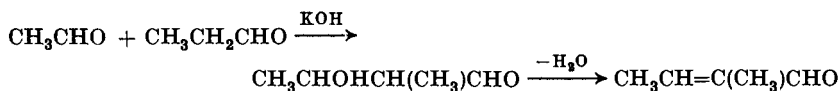
¹²⁷ L. M. Korobova and I. A. Livshits, *Zh. Obshch. Khim.*, **34**, 3419 (1964) [*C.A.*, **62**, 2699 (1965)].

¹²⁸ F. F. Blicke, *Org. Reactions*, **1**, 303–341 (1942).

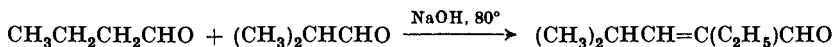
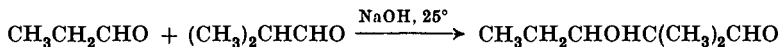
Mixed condensations of hydroxy aldehydes have been used for sugar syntheses.^{35, 95-98, 129-132}



In mixed condensations of aliphatic aldehydes four different aldol products are possible, but one often predominates. Concurrent formation of α,β -unsaturated aldehydes often leads to more complex mixtures. From the limited number of examples available it appears that, at least for most simple aliphatic aldehydes reacting at ambient temperature, the aldol results from attack by the aldehyde with the lesser number of α substituents on the α carbon atom of the aldehyde having the greater



number of α substituents¹³³⁻¹³⁹ (Lieben's rule).^{140, 141} At higher temperatures different behavior may be expected. Isobutyraldehyde, for example, forms aldols (which cannot dehydrate) according to Lieben's rule under mild conditions (25°),¹³³ but more vigorous conditions (80°) produce α,β -unsaturated aldehydes formed by condensation at the isobutyraldehyde carbonyl group (e.g., 2-ethyl-4-methyl-2-pentenal from butanal).¹³⁶ Since the formation of α,β -unsaturated carbonyl compounds



is usually irreversible, this orientation is to be expected from mixed condensations effected under vigorous conditions (thermodynamic control). Some β,γ -unsaturated isomer may be expected in carbonyl products having both α and γ substituents.¹⁴²

¹²⁹ L. Hough and J. K. N. Jones, *J. Chem. Soc.*, 3191 (1951).

¹³⁰ R. Schaffer and A. Cohen, *J. Org. Chem.*, **28**, 1929 (1963).

¹³¹ W. Pigman, *The Carbohydrates*, pp. 113-114, Academic, New York, 1957.

¹³² M. L. Wolfrom, *Advan. Carbohydrate Chem.*, **11**, 193-196 (1956).

¹³³ M. Kohn, *Monatsh. Chem.*, **22**, 21 (1901).

¹³⁴ A. Lilienfeld and S. Tauss, *Monatsh. Chem.*, **19**, 61 (1898).

¹³⁵ E. Swoboda and W. Fosseck, *Monatsh. Chem.*, **11**, 383 (1890).

¹³⁶ Badische Anilin- und Soda-Fabrik, A.-G., Brit. pat. 734,000 [*C.A.*, **50**, 7845 (1956)].

¹³⁷ V. Grignard and P. Abelmann, *Bull. Soc. Chim. France*, [4] **7**, 638 (1910).

¹³⁸ M. B. Green and W. J. Hickinbottom, *J. Chem. Soc.*, 3262 (1957).

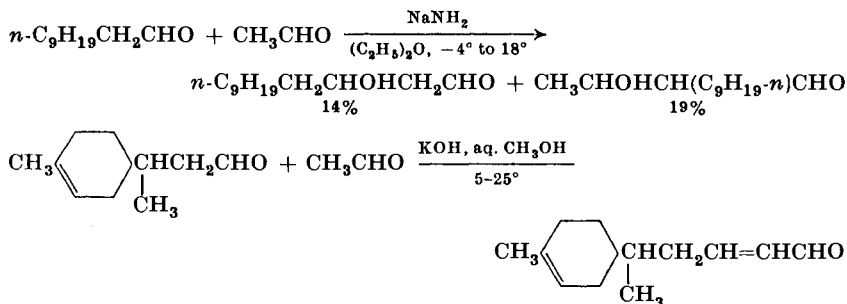
¹³⁹ L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

¹⁴⁰ A. Lieben, *Monatsh. Chem*, **22**, 289 (1901).

¹⁴¹ J. E. Dubois, *Bull. Soc. Chim. France*, [5] **20**, C17 (1953).

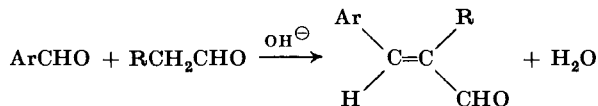
¹⁴² H. Gilman, *Organic Chemistry*, Vol. I. 2nd ed., pp. 1041-1043, Wiley, New York, 1943.

It appears that increased substitution of bulky groups in the β position of one reactant favors attack at the less substituted aldehyde carbonyl group even at low temperatures. For example, condensation of acetaldehyde with undecanal (sodium amide in ether) leads to nearly equal amounts of the two possible mixed aldols;¹⁴³ this result may be due in part to use of the aprotic solvent ether which prevents rapid enolate equilibration.⁴³⁻⁴⁵ 3-(4-Methyl-3-cyclohexenyl)butanal has been reported to condense with acetaldehyde at the methyl group (potassium hydroxide in aqueous methanol).¹⁴⁴ Careful quantitative analyses of product mixtures obtained from mixed aliphatic aldehyde condensations are evidently limited in number, and the subject deserves further study.



Roles of solvent, catalyst, and temperature as well as structure are important in determining product composition. Equilibration of substrate protons (in protic solvents) relative to non-equilibration (in aprotic solvents), which affects concentrations of intermediate enolates and alkoxides, is a factor in these experiments.

Aromatic aldehydes condense with aliphatic ones to produce cinnamaldehydes in fair to good yields. Aldols seldom are isolated. Basic catalysts are employed most frequently. Electron-withdrawing groups in the aromatic ring generally favor the condensation; electron-releasing groups

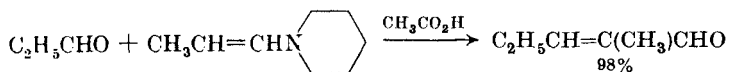


disfavor it. As the alkyl group R of the alkanal becomes bulkier, yields decrease. The product has been shown to have the β -aryl group *trans* to the carboxaldehyde group for R = H or C₆H₅.^{88, 89}

¹⁴³ M. Stoll, *Helv. Chim. Acta*, **30**, 991 (1947).

¹⁴⁴ R. B. Wearn and C. Bordenca, U.S. pat. 2,519,327 [*C.A.*, **45**, 649 (1951)].

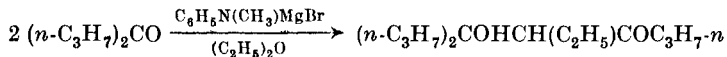
An aldehyde enamine has been condensed with propanal in the presence of acetic acid to give a 98% yield of 2-methyl-2-pentenal.⁵⁶ This reaction



is of potential value in aldol condensations because it could be applicable to mixed aldehyde condensations if equilibration of the enamine and the aldehyde could be prevented. The Wittig reaction is applicable to the preparation of α,β -unsaturated aldehydes, $\text{RCH}=\text{C}(\text{R}')\text{CHO}$.¹⁵

Self-Condensation of Ketones

The self-condensation of ketones may lead to ketols or α,β -unsaturated ketones. Diacetone alcohol is best prepared by condensing acetone using barium oxide catalyst.¹⁴⁵ The best yield (75%)^{146, 147} is secured by employing a Soxhlet extractor to separate the catalyst from the ketol as it is formed. Mesityl oxide may be prepared in 79% yield by heating acetone under reflux with a basic ion-exchange resin.¹⁴⁸ (Phorone and isophorone are by-products of acetone self-condensation.) It is also readily prepared by dehydration of diacetone alcohol (iodine catalyst).¹⁴⁹ More vigorous conditions are needed for the self-condensation of symmetrical homologs of acetone such as 3-pentanone and 4-heptanone; catalysts such as sodium ethoxide, aluminum *t*-butoxide, isopropylmagnesium chloride, zinc chloride, and phosphorus oxychloride have been used. Acid catalysts lead to unsaturated ketones. Methylanilinomagnesium bromide in ether-benzene solvent is an excellent catalyst for ketol preparation;¹⁵⁰ it catalyzes self-condensation of 4-heptanone to the ketol in 45% yield and 3-pentanone to the ketol in 60% yield. Attempts to effect self-condensation of diisopropyl and diisobutyl ketones have failed.¹⁵¹



Unsymmetrical aliphatic ketones undergo self-condensation by attack of the carbonyl group on the less hindered α carbon atom (anti-Lieben's

¹⁴⁵ J. Herscovioi, T. Bota, and D. Siriteaunu, *Rev. Chim. (Bucharest)*, **15**, 736 (1964) [*C.A.*, **62**, 11679 (1965)].

¹⁴⁶ J. Colonge, *Bull. Soc. Chim. France*, [4] **49**, 441 (1931).

¹⁴⁷ J. B. Conant and N. Tuttle, *Org. Syntheses, Coll. Vol.*, **1**, 199 (1941).

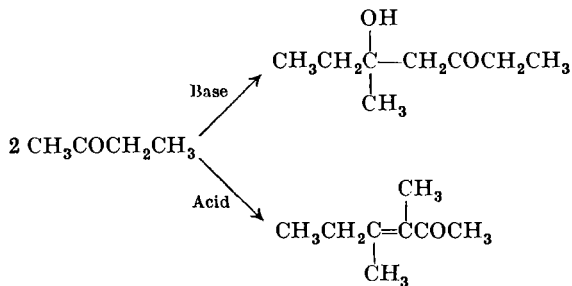
¹⁴⁸ N. B. Lorette, *J. Org. Chem.*, **22**, 346 (1957).

¹⁴⁹ J. B. Conant and N. Tuttle, *Org. Syntheses, Coll. Vol.*, **1**, 345 (1941).

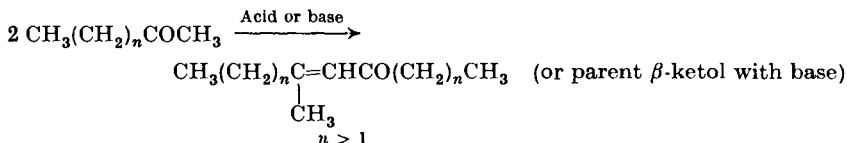
¹⁵⁰ V. Grignard and J. Colonge, *Compt. Rend.*, **194**, 929 (1932).

¹⁵¹ W. Wayne and H. Adkins, *J. Am. Chem. Soc.*, **62**, 3401 (1940).

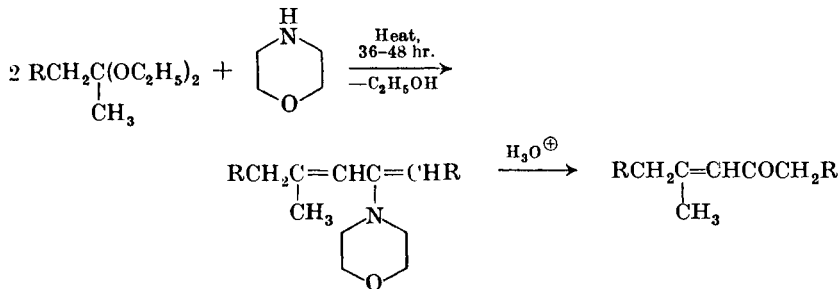
Rule.). One known exception is 2-butanone which undergoes self-condensation on the ethyl group with acid catalysis.¹⁵²⁻¹⁵⁴ All other



methyl ketones, including branched ones, undergo primarily 1-condensation (on the methyl group) with acid *or* basic catalysts;¹⁵¹⁻¹⁵⁸ either ketols or unsaturated ketones may result with base. A very small amount of 3-condensation may also result in certain instances.^{152, 156}



The self-condensation of enamines derived from methyl alkyl ketones (generated *in situ* from the ketals and morpholine) ultimately produces α,β -unsaturated ketones resulting from condensation at the methyl group.⁶⁰



¹⁵² V. Grignard and J. Colonge, *Compt. Rend.*, **190**, 1349 (1930).

¹⁵³ J. Colonge and K. Mostafavi, *Bull. Soc. Chim. France*, [5] **5**, 1478 (1938).

¹⁵⁴ A. E. Abbott, G. A. R. Kon, and R. D. Satchell, *J. Chem. Soc.*, 2514 (1928).

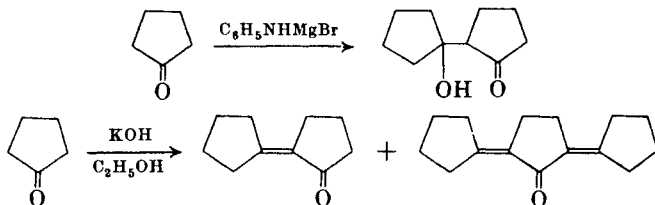
¹⁵⁵ H. Thoms and C. Mannich, *Ber.*, **38**, 2555 (1903).

¹⁵⁶ J. Colonge, *Bull. Soc. Chim. France*, [4] **49**, 426 (1931).

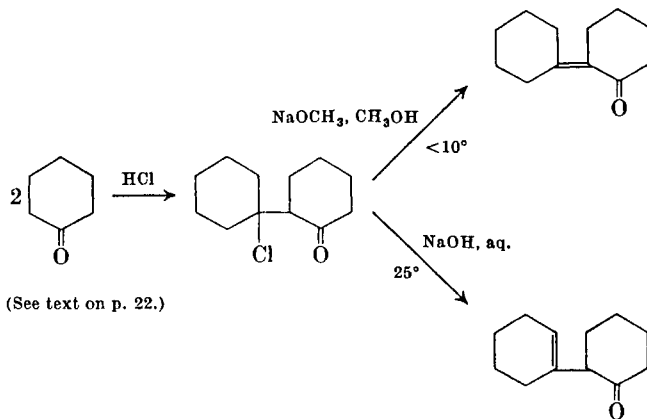
¹⁵⁷ J. E. Dubois, *Compt. Rend.*, **224**, 1018 (1947).

¹⁵⁸ J. E. Dubois and M. Chastrette, *Tetrahedron Letters*, 2229 (1964).

Self-condensation of alicyclic ketones proceeds normally; cyclopentanone, cyclohexanone, and cycloheptanone form ketols or α,β -unsaturated ketones; the ketols derived from cyclopentanone dehydrate most easily. Ketol formation is favored with anilinomagnesium bromide in ether.¹⁵⁹ 2-Cyclobutylidenecyclobutanone has been prepared from cyclobutanone and its enamines.^{56b}



Acid catalysts favor the monosubstituted unsaturated ketone.^{160, 161} With cyclohexanones the double bond in the product may appear in the endocyclic β,γ position as well as the α,β position.¹⁶¹⁻¹⁶⁴ The use of ethanolic potassium hydroxide as a catalyst leads to mixtures of mono- and bis-condensation products.^{165-167a}



¹⁵⁹ J. Colonge, *Compt. Rend.*, **196**, 1414 (1933).

¹⁶⁰ J. Plesek, *Collection Czech. Chem. Commun.*, **21**, 368 (1956); *Chem. Listy*, **50**, 246 (1956) [*C.A.*, **50**, 7732 (1956)].

¹⁶¹ W. Hüchel, O. Neunhoeffer, A. Gerecke, and E. Frank, *Ann.*, **477**, 110 (1930).

¹⁶² O. Wallach, *Ber.*, **40**, 70 (1907).

¹⁶³ J. Reese, *Ber.*, **75**, 384 (1942).

¹⁶⁴ E. Wenkert, S. K. Bhattacharya, and E. M. Wilson, *J. Chem. Soc.*, 5617 (1964).

¹⁶⁵ J. Stanek, *Chem. Listy*, **46**, 110 (1952).

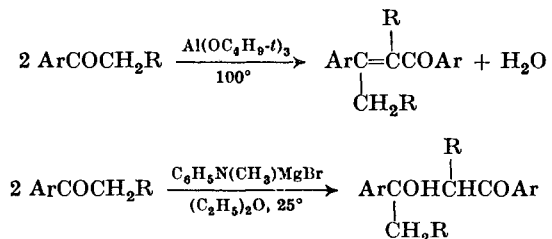
¹⁶⁶ J. Plesek, *Collection Czech. Chem. Commun.*, **21**, 375 (1956); *Chem. Listy*, **50**, 252 (1956) [*C.A.*, **50**, 7732 (1956)].

¹⁶⁷ D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. France*, 1662 (1965).

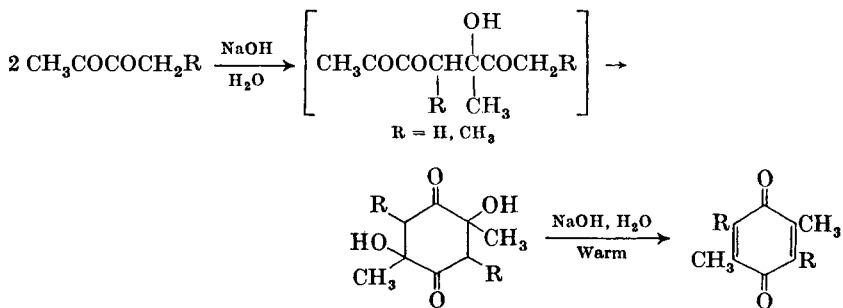
^{167a} T. A. Favorskaya, A. S. Lozhenitsyna, G. A. Kalabin, and V. M. Vlasov, *Zh. Org. Khim.*, **2**, 739 (1966) [*C.A.*, **65**, 8772 (1966)].

The intermediate β -chloroketone, 2-(1-chlorocyclohexyl)cyclohexanone,^{162, 164} prepared from cyclohexanone and hydrogen chloride, may be dehydrohalogenated to the α,β -unsaturated ketone (methanolic sodium methoxide at low temperature, $<10^\circ$) or the endocyclic β,γ isomer (with aqueous sodium hydroxide at room temperature).^{163, 164}

Alkyl aryl ketones undergo self-condensation to substituted styryl aryl ketones (dypnones). Aluminum *t*-butoxide¹⁵¹ and hydrogen bromide¹⁵² are effective catalysts for these condensations. Methylanilinomagnesium bromide in ether produces ketols.¹⁵⁹



The 1,2-diketones, 2,3-butanedione and 2,3-pentanedione, undergo base-catalyzed self-condensation, in low yield, to *p*-benzoquinone derivatives.¹⁶⁸⁻¹⁷¹ The intermediate cyclic ketol has been isolated from 2,3-butanedione after reaction with dilute aqueous sodium hydroxide at low temperature,^{168, 170} more concentrated base at higher temperature produces the benzoquinone.



In aqueous acetic acid, 2,3-butanedione undergoes self-condensation to a dihydrofuranone.^{171a} Self-condensation has been effected with one

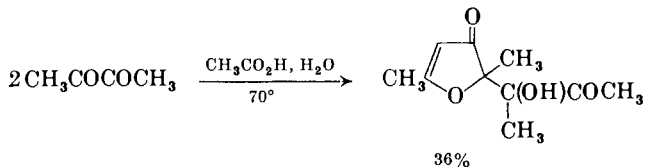
¹⁶⁶ O. Diels, W. M. Blanchard, and H. v.d. Heyden, *Ber.*, **47**, 2355 (1914).

¹⁶⁹ G. Machell, *J. Chem. Soc.*, 683 (1960).

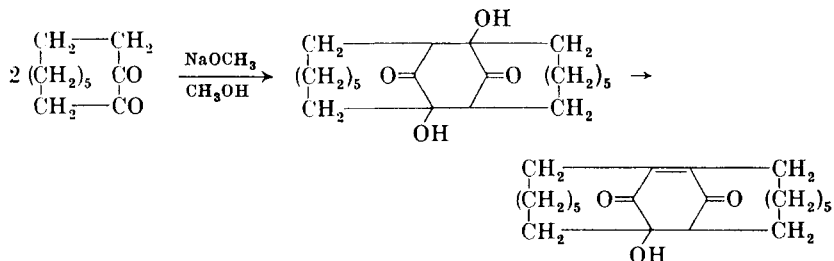
¹⁷⁰ H. v. Pechmann and E. Wedekind, *Ber.*, **28**, 1845 (1895).

¹⁷¹ H. v. Pechmann, *Ber.*, **21**, 1411 (1888).

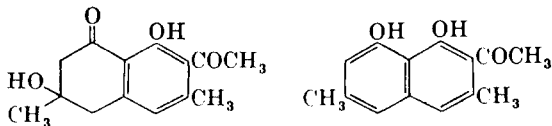
^{171a} R. Shapiro, J. Hackmann, and R. Wahl, *J. Org. Chem.*, **31**, 2710 (1966).



cyclic 1,2-diketone; the ketol formed could not be completely dehydrated to a benzoquinone,¹⁷² presumably because of the strain that would be present in the product.



Few examples of self-condensation of 1,3-diketones are known. 2,4,6-Heptanetrione was condensed under carefully controlled conditions (aqueous sodium hydroxide and a potassium acid phosphate buffer) to a tetralone (at *pH* 7.1–7.2) or a naphthalene derivative (*pH* 8.2).¹⁷³ Attempts to effect self-condensation of other 1,3-diketones have failed.¹⁷⁴



Diketones having carbonyl groups separated by two or more carbons have not been observed to undergo intermolecular condensation. Those which have been examined readily condense intramolecularly to form cycloalkenones or acyl cycloalkenes (discussed on pp. 49–56).

Mixed Condensation of Ketones

The condensation of two different ketones produces ketols or α,β -unsaturated ketones. The reaction has seldom been applied to two

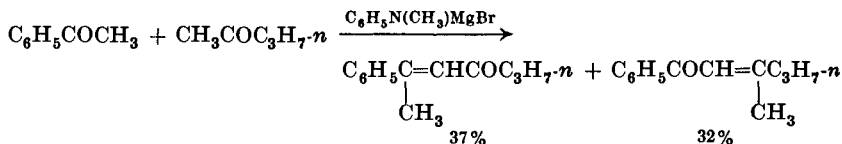
¹⁷² R. A. Raphael and A. I. Scott, *J. Chem. Soc.*, 4566 (1952).

¹⁷³ J. R. Bethell and P. Maitland, *J. Chem. Soc.*, 3751 (1962).

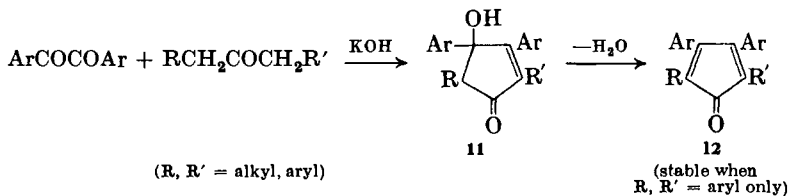
¹⁷⁴ E. E. Blaise, *Compt. Rend.*, **158**, 708 (1914).

and cyclopentanone¹⁸¹⁻¹⁸³ condense with acetone to form isopropylidene derivatives.¹⁸⁴ The relative reactivities of ketones to nucleophilic attack (rates and equilibria) appear to be important here and have been evaluated for the formation of acetals,¹⁸⁵ semicarbazones,¹⁸⁶ cyanohydrins,¹⁸⁷⁻¹⁹¹ and bisulfite addition compounds,^{192, 193} as well as for sodium borohydride reduction.^{194, 195} The relative reactivities of ketone enolates may also be pertinent; cf. alkylation rates.^{196, 197}

Acetophenone condenses with 2-butanone or 2-pentanone to give mixtures of products.¹⁹⁸



The condensation of benzils with simple aliphatic ketones leads to the interesting cyclopentenone ketols, "anhydroacetonebenzils (**11**),"¹⁹⁹⁻²⁰¹ which do not dehydrate to stable cyclopentadienones. The ketols



¹⁸¹ G. A. R. Kon and J. H. Nutland, *J. Chem. Soc.*, 3101 (1926).

¹⁸² O. Wallach, *Ann.*, **394**, 362 (1912).

¹⁸³ L. Bouveault, *Compt. Rend.*, **130**, 415 (1900).

¹⁸⁴ P. Hudry and P. Cordier, *Compt. Rend.*, **261**, 468 (1965).

¹⁸⁵ J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.*, **30**, 4284 (1965).

¹⁸⁶ J. B. Conant and P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2881 (1932).

¹⁸⁷ W. J. Svirbely and J. F. Roth, *J. Am. Chem. Soc.*, **75**, 3106 (1953).

¹⁸⁸ D. P. Evans and J. R. Young, *J. Chem. Soc.*, 1310 (1954).

¹⁸⁹ A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2533 (1928).

¹⁹⁰ A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 1976 (1930).

¹⁹¹ K. L. Servis, L. K. Oliver, and J. D. Roberts, *Tetrahedron*, **21**, 1827 (1965).

¹⁹² K. Shinra, K. Ishikawa, and K. Arai, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 661 (1954) [*C.A.*, **49**, 5084 (1955)].

¹⁹³ M. A. Gubareva, *Zh. Obshch. Khim.*, **17**, 2259 (1947) [*C.A.*, **42**, 4820 (1948)].

¹⁹⁴ H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, **87**, 1280 (1965).

¹⁹⁵ H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

¹⁹⁶ J. M. Conia, *Ann. Chim. (Paris)* [12] **8**, 709 (1953).

¹⁹⁷ H. D. Zook and W. L. Rellahan, *J. Am. Chem. Soc.*, **79**, 881 (1957).

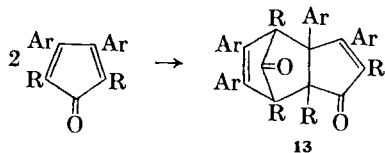
¹⁹⁸ V. V. Chelinstev and A. V. Pataraya, *Zh. Obshch. Khim.*, **11**, 461 (1941) [*C.A.*, **35**, 6571 (1941)].

¹⁹⁹ F. R. Japp and C. I. Burton, *J. Chem. Soc.*, **51**, 431 (1887).

²⁰⁰ F. R. Japp and T. S. Murray, *J. Chem. Soc.*, **71**, 144 (1897).

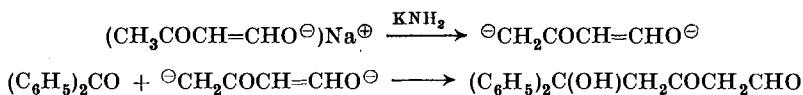
²⁰¹ P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958).

derived from dibenzyl ketone do dehydrate to produce tetraphenylcyclopentadienones (tetracyclones, **12**).²⁰²⁻²⁰⁶ The cyclopentadienones derived from dialkyl ketones are unstable and readily form carbonyl



bridged dimers such as **13**.^{205, 206} Condensation of benzils with cyclohexanones leads to ketols²⁰⁷ and with acetophenones to β -benzoyl chalcones.²⁰⁸

By employing 2 molecular equivalents of potassium amide (in liquid ammonia) with certain 1,3-dicarbonyl compounds to produce a dicarbanion, condensations may be effected at the γ position.^{209-212c} Alkylations and acylations also occur at the γ position of the dianion. The dicarbanions are most conveniently prepared from the monoenolate salt of the dicarbonyl compound by treatment with 1 molecular equivalent of



potassium amide.²¹² The method has been applied to 1-aryl-1,3,5-hexanetriones (*tris*-anion intermediate) whereby condensation of a carbonyl compound (benzophenone, benzaldehyde) occurs on the terminal methyl group to produce a ketol.²¹³

²⁰² C. G. Henderson and R. H. Corstorphine, *J. Chem. Soc.*, **79**, 1256 (1901).

²⁰³ W. Dilthey, O. Trösken, K. Plum, and W. Schommer, *J. Prakt. Chem.*, [2] **141**, 331 (1934).

²⁰⁴ J. R. Johnson and O. Grummitt, *Org. Syntheses, Coll. Vol.*, **3**, 806 (1955); L. F. Fieser, *Org. Syntheses*, **46**, 45 (1966).

²⁰⁵ C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945); C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **20**, 315 (1955).

²⁰⁶ M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

²⁰⁷ C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **16**, 716 (1951).

²⁰⁸ C. F. H. Allen and H. B. Rosener, *J. Am. Chem. Soc.*, **49**, 2110 (1927).

²⁰⁹ T. M. Harris and C. R. Hauser, *J. Am. Chem. Soc.*, **84**, 1750 (1962).

²¹⁰ J. F. Wolfe, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **29**, 3249 (1964).

²¹¹ R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

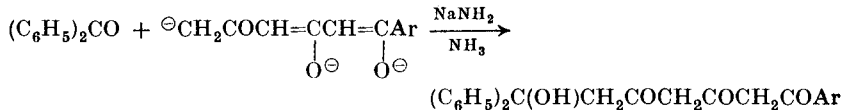
²¹² T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **87**, 3186 (1965).

^{212a} K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **31**, 663 (1966).

^{212b} S. Boatman and C. R. Hauser, *J. Org. Chem.*, **31**, 1785 (1966).

^{212c} T. M. Harris and C. M. Harris, *Org. Reactions*, **17**, in press.

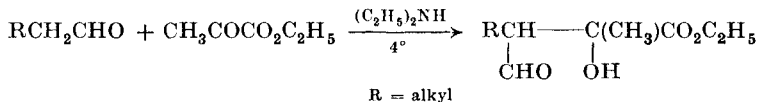
²¹³ K. G. Hampton, T. M. Harris, C. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 4263 (1965).



An unexplored, but potentially useful, synthetic route to α,β -unsaturated ketones might involve condensation of a ketone with a ketone enamine (acetic acid catalyst).^{54, 56} The Wittig reaction may be employed for synthesis of α,β -unsaturated ketones.¹⁵

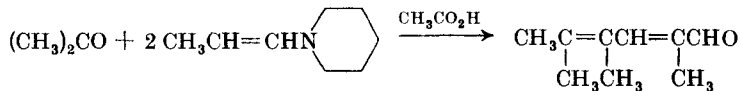
Condensation of Aldehydes with Acyclic Ketones

The condensation of aldehydes with ketones to yield ketols or α,β -unsaturated ketones is a reaction of broad utility and applicability. A significant limitation results from the greater reactivity of aldehydes, which will undergo self-condensation or will condense at the α carbon atom of ketones.¹⁸⁶⁻¹⁹³ Ketones, however, will not condense intermolecularly at the α carbon atom of aldehydes to form aldols with simple base or acid catalysts. By employing certain enamine or imine intermediates this limitation may be circumvented. Condensation of ethyl pyruvate with butanal and higher alkanals^{214, 215} in the presence of diethylamine at 4° leads to aldols and probably involves the more readily formed aldehyde enamine. (Pyruvic acid under the same conditions with the same aldehydes forms alkylidene derivatives, $\text{RCH}_2\text{CH}=\text{CHCOCO}_2\text{H}$.^{215a})



Intramolecular condensations of ketonic carbonyl groups on the α carbon atom of aldehydes (via aldehyde enamine intermediates) to produce cycloalkene carboxaldehydes are known and are discussed on p. 57.

An intermolecular condensation of a ketone with an aldehyde enamine has been reported. Acetone reacts with 1-propenylpiperidine (added acetic acid) to produce, ultimately, 2,4,5-trimethyl-2,4-hexadienal in unstated yield;⁵⁴ the second molecule of enamine entering the reaction



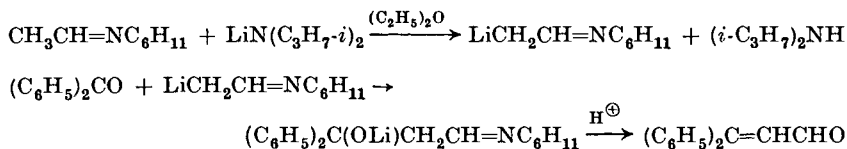
²¹⁴ P. Cordier, J. Schreiber, and C. G. Wermuth, *Compt. Rend.*, **250**, 1668, 2587 (1960).

²¹⁵ J. Schreiber and C. G. Wermuth, *Bull. Soc. Chim. France*, 2242 (1965).

^{215a} C. G. Wermuth *Bull. Soc. Chim. France*, 1435 (1966).

may be attacked by an immonium ion intermediate such as $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}=\overset{\oplus}{\text{N}}\text{C}_5\text{H}_{10}$. This type of reaction would appear to be of much potential synthetic value if it could be extended to other ketones and enamines derived from an aldehyde or ketone, particularly if condensation with only one molecule of enamine could be achieved by proper choice of reaction conditions. Employment of preformed enamines (under mild conditions), rather than those generated *in situ*, appears to be necessary. In each of the few known examples where secondary amine catalysts have been employed in condensations of aldehydes (having α hydrogen atoms) with ketones, the products have been α,β -unsaturated ketones.²¹⁶⁻²²⁰

By employing an aldehyde imine anion, condensation with ketones can be directed to produce α,β -unsaturated aldehydes (a directed Wittig aldol condensation).^{221-221b} In this synthesis the imine is metalated with a lithium amide in ether, then treated with a ketone to produce an isolable lithium salt; hydrolysis of this salt in dilute sulfuric acid provides the α,β -unsaturated aldehyde in excellent yield—78% overall in the example shown in the accompanying equations.



The Wittig reaction itself is not applicable to the preparation of α,β -unsaturated aldehydes from ketones and formylalkylidene triphenylphosphoranes.^{15, 221b, c}

The entire discussion of aldehyde-ketone condensations that follows applies principally to condensations conducted in protic solvents under equilibrium conditions.

Symmetrical Ketones. Only acetone and 3-pentanone are very reactive in condensations with aldehydes in the presence of ethanolic potassium or sodium hydroxide or ethoxide catalysts. 4-Heptanone and

²¹⁶ M. E. McEntee and A. R. Pinder, *J. Chem. Soc.*, 4419 (1957).

²¹⁷ G. B. Payne, *J. Org. Chem.*, **24**, 1830 (1959).

²¹⁸ K. Eiter, *Ann.*, **658**, 91 (1962).

²¹⁹ G. Wermuth, *Compt. Rend.*, **251**, 391 (1960).

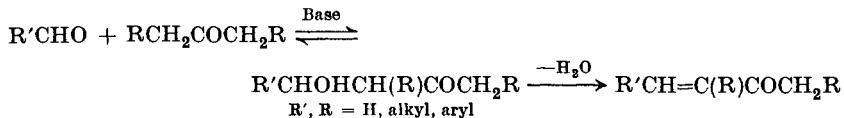
²²⁰ B. D. Wilson, *J. Org. Chem.*, **28**, 314 (1963).

²²¹ G. Wittig and H. D. Frommeld, *Ber.*, **97**, 3548 (1964).

^{221a} G. Wittig and P. Suchanek, *Tetrahedron, Suppl.* **8**, Part **1**, 347 (1966).

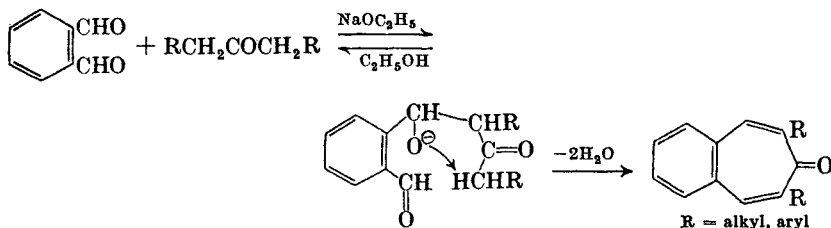
^{221b} G. Wittig, *Record Chem. Prog. (Kresge-Hooker Sci. Lib.)*, **28**, 45 (1967).

^{221c} S. Tripett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).



higher *n*-alkanones condense with most monocarboxaldehydes with great difficulty, and yields are poor; no procedure has yet been developed for satisfactorily effecting condensations of this type.²²² However, it appears that several approaches might be applicable to such condensations. For example, a modification of the directed Wittig aldol synthesis^{221b} might be applied, namely, addition of an aldehyde to the required ketimine anion. Another approach could make use of a slowly equilibrating lithium enolate (in a solvent such as 1,2-dimethoxyethane, with rigorous exclusion of proton donors),⁴⁴ followed by addition of the aldehyde. Alternatively, condensation of an aldehyde with a ketone enamine, or the Wittig reaction,¹⁵ might be employed.

It is interesting that, although most monocarboxaldehydes give very poor yields (usually <20%) of condensation product with 4-heptanone and higher non-methyl *n*-alkanones, *o*-phthalaldehyde is exceptional and reacts readily with these ketones to give excellent yields (73–97%) of 2,7-di-*n*-alkyl-4,5-benzotropones.²²³ It is known that intramolecular base-catalyzed enolization is an efficient process;²²⁴ this fact suggests that intramolecular aldol-derived alkoxide-catalyzed enolization of the second α proton may be strongly favored when R is a large group, and may contribute to the success of these condensations. When R is a branched alkyl group, yields are lower, suggesting that in these examples the initial equilibrium favors reactants.



The very unreactive diisopropyl and diisobutyl ketones may be converted into their enolate ions with a strong base such as methylanilino-magnesium bromide. These ions, in contrast to those of *n*-alkanones, do

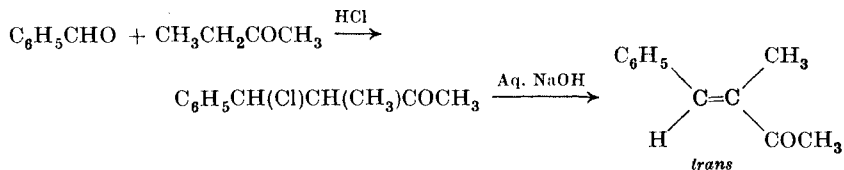
²²² S. G. Powell and A. T. Nielsen, *J. Am. Chem. Soc.*, **70**, 3627 (1948).

²²³ D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 2220 (1958).

²²⁴ E. T. Harper and M. L. Bender, *J. Am. Chem. Soc.*, **87**, 5625 (1965).

Ketones of the type $\overset{1}{\text{C}}\overset{2}{\text{H}_3}\overset{3}{\text{COCHR}}\text{R}'$ ($\text{R}' = \text{alkyl, aryl, or H}$; $\text{R} = \text{alkyl or aryl}$) may condense with aldehydes at carbon 1 (*1-condensation*) or carbon 3 (*3-condensation*). Four principal factors determine the structure of the product obtained at equilibrium: (1) catalyst; (2) nature of substituents R and R' in the ketone; (3) structure of the aldehyde; and (4) the solvent, which has received little study. These factors have been reviewed briefly for 2-butanone.²³¹ Although mixtures of 1- and 3-condensation products are possible and to be expected, few studies of the exact composition of products have been reported; a single substance appears to predominate in most reactions.

Acid catalysts favor 3-condensation except where steric factors prevent it. The most highly branched enol $[\text{CH}_3\text{C}(\text{OH})=\text{CHR}]$ derived from the ketone reacts preferentially with the aldehyde to produce an α,β -unsaturated ketone⁴² (see equations, p. 10). It is primarily the direction of enolization which determines the course of the acid-catalyzed condensation. The dehydration of the intermediate ketol is rapid (relative to the condensation step), and ketols seldom result from acid-catalyzed condensations.^{30, 40} Anhydrous hydrogen chloride is often employed as acid catalyst; the intermediate β -halo ketone may be dehydrohalogenated by treatment with aqueous or ethanolic alkali hydroxide²³² or carbonate,



pyridine, or quinoline, or by heating. In the α,β -unsaturated product the larger β -substituent and the α carbonyl group are oriented *trans*.²³³⁻²³⁵

All methyl *n*-alkyl ketones studied are reported to produce 3-condensation with acid catalysts.^{236, 237} Examples of acid-catalyzed condensation at carbon atom 3 with ketones of the type $\text{CH}_3\text{COCHR}\text{R}'$ ($\text{R}, \text{R}' = \text{alkyl or aryl but not hydrogen}$) are rare. Since the expected intermediate ketol cannot dehydrate and ketol is not a favored product, one would

²³¹ H. Haeussler and J. Dijkema, *Ber.*, **77**, 601 (1944).

²³² C. Harries and G. H. Müller, *Ber.*, **35**, 966 (1902).

²³³ M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim.*, **84**, 17 (1965).

²³⁴ M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim.*, **84**, 979 (1965).

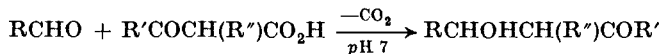
²³⁵ M. E. Kronenberg and E. Havinga, to be published. We are indebted to Prof. Havinga and Dr. Kronenberg for providing us with their data prior to publication.

²³⁶ M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **54**, 334 (1932).

²³⁷ K. Iwamoto and T. Kato, *Sci. Rept. Tohoku Imp. Univ., First Ser.*, **19**, 689 (1930) [*C.A.*, **25**, 2132 (1931)].

predict the major condensation product to be an α,β -unsaturated ketone derived by condensation of the methyl group, $RCH=CHCOCHR'R'$. The only reported exceptions to 3-condensation using an acid catalyst are found with methyl isobutyl ketone which condenses at the methyl group with aromatic aldehydes (benzaldehyde,^{238, 239} salicylaldehyde,²³⁹ and 4-methoxybenzaldehyde²⁴⁰). Acetaldehyde²⁴¹ and chloral²⁴² are reported to undergo 3-condensation with methyl isobutyl ketone. Condensation of benzaldehyde with 2-heptanone (concentrated hydrochloric acid catalyst) produced 91% 3-condensation and 9% 1-condensation.²⁴³ It is likely that small percentages of 1-condensation accompany many examples of reported 3-condensation. Gas-liquid chromatography and nuclear magnetic resonance spectra would aid in assay of condensation mixtures, but until recently, they have not been extensively employed for this purpose.⁶³

Synthesis of β -ketols of known structure (including those derived by 3-condensation from methyl ketones) may be achieved by decarboxylation of a β -keto ester at pH 7 (phosphate buffer, 25°, several days) in water or aqueous methanol, presumably to generate the required ketone enol intermediate which condenses with the aldehyde present (Schöpf condensation).^{40, 244}



The course of the base-catalyzed condensation of aldehydes with unsymmetrical ketones is much more responsive to reaction conditions which influence the condensation (solvent, catalyst, temperature) than is the acid-catalyzed reaction. The reaction sequence is in some ways similar to that of the acid-catalyzed reaction, but relative rates for the steps are different.^{40, 42} The rate-determining step with either catalyst is usually the condensation step,^{18, 26, 245, 246} but the dehydration step in the base-catalyzed reaction is much slower and more easily reversed (relative to the condensation step) than in the acid-catalyzed reaction^{30, 40} (see p. 10). Ketols are frequently produced in the base-catalyzed reaction, especially under mild conditions.

²³⁸ C. V. Gheorghiu and B. Arwentiew, *J. Prakt. Chem.*, [2] **118**, 295 (1928).

²³⁹ I. M. Heilbron and F. Irving, *J. Chem. Soc.*, 936 (1929).

²⁴⁰ C. V. Gheorghiu and B. Arwentiew, *Bull. Soc. Chim. France*, [4] **47**, 195 (1930).

²⁴¹ J. E. Dubois, R. Luft, and F. Week, *Compt. Rend.*, **234**, 2289 (1952).

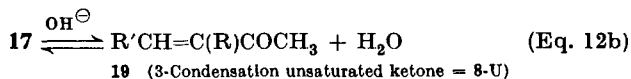
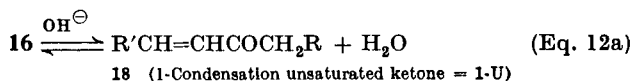
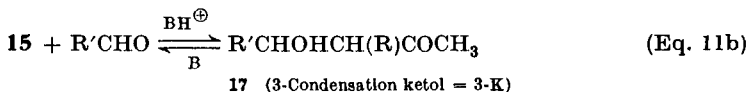
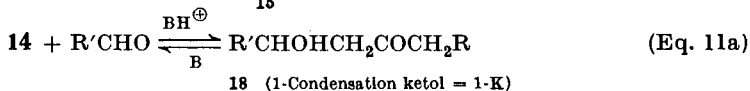
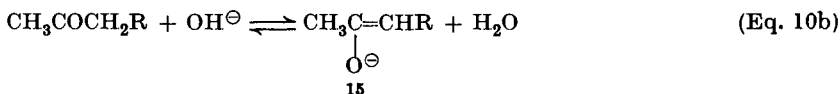
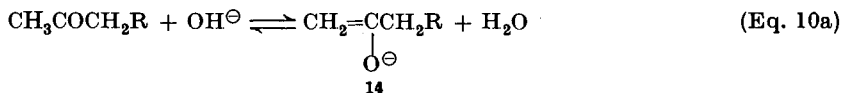
²⁴² J. S. Buck and I. M. Heilbron, *J. Chem. Soc.*, **121**, 1198 (1922).

²⁴³ M. Metayer, *Rec. Trav. Chim.*, **71**, 153 (1952).

²⁴⁴ C. Schöpf and K. Thierfelder, *Ann.*, **518**, 127 (1935).

²⁴⁵ G. Kresze and B. Gnauck, *Z. Elektrochem.*, **60**, 174 (1956).

²⁴⁶ G. Sipos, A. Furka, and T. Szell, *Monatsh. Chem.*, **91**, 643 (1960).



The composition of the equilibrium mixture of methyl alkyl ketone-derived enolate anions **14** and **15** is affected by the solvent and by the structure of the ketone. It is pertinent to attempt an evaluation of the composition of this mixture in order to interpret the composition of aldol condensation product mixtures. Few systematic studies of such enolate compositions have been made for protic solvents (water, ethanol) which are commonly employed in most aldol condensations.^{246a-c} Direct measurements of enolate composition in 1,2-dimethoxyethane (quenching in deuterium oxide-deuterioacetic acid) indicate a stability order $n\text{-C}_4\text{H}_9\text{CH}=\underset{\text{O}^\ominus}{\text{C}}\text{CH}_3 > n\text{-C}_4\text{H}_9\text{CH}_2\underset{\text{O}^\ominus}{\text{C}}=\text{CH}_2$;^{43, 247} the amount of more

highly substituted enolate at equilibrium (58–87%) depends on the cation and the solvent. A more highly branched alkyl group favors the less highly substituted enolate (67–82% **14** when $\text{R} = \text{C}_3\text{H}_7$);^{43, 247} The more highly substituted enolate derived from 2-methylcyclopentanone and 2-methylcyclohexanone is the more favored.^{43, 247–248c} Alkylation

^{246a} C. Rappe, *Acta Chem. Scand.*, **20**, 376, 1721, 2236, 2305 (1966).

^{246b} J. Warkentin and O. S. Tee, *Chem. Commun.*, 190 (1966); *J. Am. Chem. Soc.*, **88**, 5540 (1966).

^{246c} A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967).

²⁴⁷ H. O. House, *Record Chem. Progr.*, **28**, 98 (1967).

²⁴⁸ D. Caine, *J. Org. Chem.*, **29**, 1868 (1964).

^{248a} G. Subrahmanyam, S. K. Malhotra, and H. Ringold, *J. Am. Chem. Soc.*, **88**, 1332 (1966).

^{248b} H. O. House, W. L. Roelofs, and B. M. Trost, *J. Org. Chem.*, **31**, 646 (1966).

^{248c} D. Caine and B. J. L. Huff, *Tetrahedron Letters*, 4695 (1966).

of equilibrated methyl *n*-alkyl ketone enolates favors attack on the more highly substituted enolate,^{43, 247, 249-251} as does Michael addition.^{14, 252-254} (With non-methyl unsymmetrical acyclic ketones, alkylation occurs preferentially on the less highly substituted enolate,^{45, 250} in agreement with the findings for the composition of the enolate.^{43, 45}) The enol contents of pure 2-butanone (0.012%) and other methyl alkyl ketones have been found to be greater than that of acetone (0.00015%).²⁵⁵⁻²⁵⁷ (The enol contents of the pure liquids parallel the values in alcohol and water.^{249, 256, 258, 259}) These considerations all suggest that for methyl *n*-alkyl ketones in all solvents the more highly substituted enolate is the more stable.^{246a-c, 260, 261} [The greater rate of proton removal (in water) from isobutyraldehyde relative to acetaldehyde (corrected factor ca. 6.7),²⁰ combined with the predicted slower C-protonation rate for isobutyraldehyde enolate relative to that of acetaldehyde enolate,^{36, 248a} suggests the stability order: $(\text{CH}_3)_2\text{C}=\text{CHO}^\ominus > \text{CH}_2=\text{CHO}^\ominus$.]

The composition of the equilibrium mixture **16** and **17** (1-ketol and 3-ketol) is determined by several factors which are difficult to assess quantitatively but may be expressed in terms of equilibrium constants (Eq. 13). [In weakly basic media an additional equilibrium exists between enolate ion and enol, which favors 3-condensation.^{246a-c}] The more

$$\frac{[\text{1-ketol}]}{[\text{3-ketol}]} = \frac{K_{10a}K_{11a}}{K_{11b}K_{10b}} \quad (\text{Eq. 13})$$

highly substituted enolate anion **15** leads to the 3-condensation ketol with simple aldehydes and ketones ($\text{R}, \text{R}' = \text{CH}_3, n\text{-alkyl}$); that is, the ratio [1-ketol]/[3-ketol] appears to be determined principally by the relative concentrations of the ketone enolate ions and enols. When R' (in the aldehyde) and particularly R (in the ketone) both become large, branched, and bulky alkyl groups (*i*-butyl, heptyl, etc.), 1-condensation ketol is

²⁴⁹ J. M. Conia, *Bull. Soc. Chim. France*, 1392 (1956).

²⁵⁰ J. M. Conia, *Record Chem. Progr.*, **24**, 43 (1963).

²⁵¹ S. K. Malhotra and F. Johnson, *J. Am. Chem. Soc.*, **87**, 5513 (1965).

²⁵² L. B. Barkley and R. Levine, *J. Am. Chem. Soc.*, **72**, 3699 (1950).

²⁵³ A. D. Campbell, C. L. Carter, and S. N. Slater, *J. Chem. Soc.*, 1741 (1948).

²⁵⁴ G. R. Zellars and R. Levine, *J. Org. Chem.*, **13**, 911 (1948).

²⁵⁵ A. Gero, *J. Org. Chem.*, **26**, 3156 (1961); **19**, 1960 (1954).

²⁵⁶ N. L. Allinger, L. W. Chow, and R. W. Ford, *J. Org. Chem.*, **32**, 1994 (1967).

²⁵⁷ J. E. Dubois and G. Barbier, *Bull. Soc. Chim. France*, 682 (1965).

²⁵⁸ C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, pp. 554-566, Cornell University Press, Ithaca, New York, 1953.

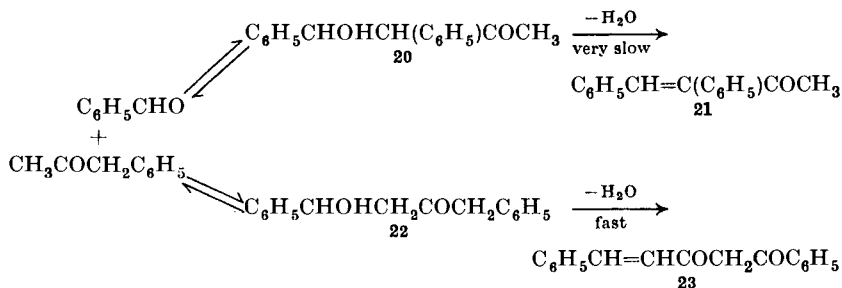
²⁵⁹ G. S. Hammond, in *Steric Effects in Organic Chemistry*, ed. by M. S. Newman, pp. 442-454, Wiley, New York, 1956.

²⁶⁰ H. M. E. Cardwell and A. E. H. Kilner, *J. Chem. Soc.*, 2430 (1951).

²⁶¹ H. M. E. Cardwell, *J. Chem. Soc.*, 2442 (1951).

avored for two reasons: bulky groups facilitate cleavage of **17** to reactants,^{30, 40, 262, 263} relative to **16**; and the less highly substituted enolate anion becomes more stable as R in the ketone becomes more branched and bulkier.^{43, 45}

The composition of the product at the α,β -unsaturated ketone stage (**18** = 1-U and **19** = 3-U) introduces a third pair of equilibria, Eqs. 12a and 12b (actually, two steps are involved in the ketol \rightarrow unsaturated ketone transformation; see p. 5). It is known that more vigorous reaction conditions favor unsaturated ketone and also often result in an increase in the total percentage of 1-condensation products (1-K and 1-U). It has been established in certain examples that retrogression of **17** to reactants may be favored over dehydration (e.g., **19** is not produced from **17** in basic medium when $R' = C_6H_5$, $R = CH_3$, whereas under the same conditions **16** dehydrates to **18** when $R' = C_6H_5$, $R = H$).⁴⁰ In another example, the sodium hydroxide-catalyzed condensation of benzaldehyde with phenylacetone favors 1-condensation.²⁶⁴ The favored enolate, $C_6H_5CH=C(CH_3)O^\ominus$, would lead to **20**, but retrogression of **20** to reactants occurs faster than dehydration and **21** is not formed. Less favored ketol **22** dehydrates, effectively irreversibly, to yield the product



23. In contrast, the piperidine-catalyzed condensation of aldehydes with phenylacetone produces condensation on the methylene group.²⁶⁵⁻²⁶⁷ It is known that α -substituents favor β,γ unsaturation in ketones at equilibrium,¹⁴² again suggesting the α,β form **18** (1-U) to be the most stable. It appears likely that $K_{12a}/K_{12b} > 1$. The ratio of unsaturated ketone products is given by Eq. 14.

$$\frac{[1-U]}{[3-U]} = \frac{K_{10a}K_{11a}K_{12a}}{K_{10b}K_{11b}K_{12b}} \quad (\text{Eq. 14})$$

²⁶² M. R. F. Ashworth and J. E. Dubois, *Bull. Soc. Chim. France*, 147 (1955).

²⁶³ C. S. Rondestvedt and M. E. Rowley, *J. Am. Chem. Soc.*, **78**, 3804 (1956).

²⁶⁴ G. Goldschmidt and G. Knöpfer, *Monatsh.*, **18**, 437 (1897).

²⁶⁵ H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

²⁶⁶ R. Dickinson, *J. Chem. Soc.*, 2234 (1926).

²⁶⁷ I. M. Heilbron and F. Irving, *J. Chem. Soc.*, 931, 936 (1929).

Table I summarizes the known condensations¹⁴¹ (solvent water, ethanol, or aqueous ethanol in most cases) of aldehydes with methyl ketones to form ketol and α,β -unsaturated ketone products. Only formaldehyde

TABLE I. SUMMARY OF REPORTED KETOL AND α,β -UNSATURATED KETONE 1:1 PRODUCTS FORMED IN BASE-CATALYZED CONDENSATIONS OF ALDEHYDES WITH METHYL KETONES ($\overset{1}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{OCHRR}'$ and $\overset{1}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{OCH}_2\text{R}$)

| Principal Product | Aldehyde | Ketone |
|-------------------------------|--|--|
| 3-Condensation | Formaldehyde | All |
| | Acetaldehyde | All except methyl isobutyl and neopentyl ketones |
| 1- and 3-Condensation mixture | <i>n</i> -Alkanals, $\text{CH}_3(\text{CH}_2)_n\text{CHO}^* \cdot \dagger$ | 2-Butanone |
| | Possible with all; ratio depends on reaction conditions | 2-Butanone and 2-pentanone |
| | Acetaldehyde | Methyl isobutyl ketone |
| 1-Condensation | All having one or no α hydrogen atoms (ArCHO , R_3CCHO , R_2CHCHO) except formaldehyde | All except 2-butanone and phenoxyacetone |

* Examples studied: $n = 0-7$, with 2-butanone only.

† 3-Methylbutanal produces 3-condensation with 2-butanone.¹⁴¹

and acetaldehyde give appreciable amounts of 3-condensation with all ketones; the lower concentration of base required resulting in higher concentration of enol would favor 3-condensation. 2-Butanone is the only ketone reported to yield substantial amounts of 3-condensation with all aldehydes (an exception is phenoxyacetone²⁶⁸). Little is known about the products of condensation of *n*-alkanals above acetaldehyde with methyl *n*-alkyl ketones, other than 2-butanone. Although acetaldehyde produces ketols derived from 3-condensation with 2-butanone²⁶⁹ and 2-pentanone²⁷⁰ under mild conditions, more vigorous conditions lead to a mixture of α,β -unsaturated ketones formed by 1- and 3-condensation.²⁷¹ Formaldehyde and acetaldehyde produce 3-condensation ketols with methyl isopropyl ketone, but chloral, 2-ethylbutanal, and various benzaldehydes and furfurals yield the α,β -unsaturated ketones derived

²⁶⁸ R. Stoermer and R. Wehln, *Ber.*, **35**, 3549 (1902).

²⁶⁹ J. E. Dubois and R. Luft, *Compt. Rend.*, **238**, 485 (1954).

²⁷⁰ J. Colonge, *Bull. Soc. Chim. France*, [4] **41**, 325 (1927).

²⁷¹ R. Heilmann, G. de Gaudemaris, and P. Arnaud, *Compt. Rend.*, **240**, 1542 (1955).

from 1-condensation;^{272, 273} butanal produces a mixture of 1- and 3-condensation ketols (principally 1-condensation) and an α,β -unsaturated ketone (1-condensation) with methyl isopropyl ketone.²⁷² Aromatic aldehydes produce α,β -unsaturated ketones formed by 1-condensation. However, when the reaction is stopped at the ketol stage, some 3-condensation products may be isolated. For example, *p*-nitrobenzaldehyde and 2-butanone lead to some 3-condensation ketol under mild conditions.^{40, 64} Isobutyraldehyde with 2-butanone produces a 55:45 ratio of 1- to 3-condensation unsaturated ketone with aqueous base, but with ethanolic sodium ethoxide the proportion is increased to 85:15;^{231, 247} with 2-heptanone, isobutyraldehyde produces 1-condensation ketol and a trace of 3-condensation isomer (ethanolic potassium hydroxide).²⁷⁴ Except as outlined above, the majority of reported examples of base-catalyzed condensations of aldehydes with methyl ketones lead to 1-condensation product, due, in part, to the favored retrogression of 3-condensation ketol to reactants.

Formation of either α,α or α,α' *bis*-condensation products seldom occurs in reactions of unsymmetrical methyl ketones, with the exception of formaldehyde condensations. 2-Butanone occasionally forms *bis*-condensation products with certain aromatic aldehydes especially in the presence of acid catalysts.²²⁶

The preceding discussion relates to aldol condensations conducted principally in protic solvents under equilibrating conditions. Use of enolates formed under kinetically controlled conditions would introduce versatility into aldol condensation syntheses, because the enolates derived from methyl ketones would be the less highly substituted isomers (14).⁴³ Few successful aldol condensations have been reported which employ enolates derived from ketones under non-equilibrating conditions.^{177, 213} No examples involving methyl ketones are known. However, what appear to be successful acylations,^{8, 43-45} alkylations,⁴³⁻⁴⁵ and carbonations²⁷⁵ of such enolates have been described. (Enol esters formed by O-acylation are believed to be precursors of C-acylation products.⁴⁵) Another apparently unexplored possibility is the use of preformed acyclic ketone enamines (which have the less substituted structure⁵²) in an aldol condensation.^{53a, 54}

α,β -Unsaturated ketones are readily obtained by heating ketols (having a hydrogen atom α to the carbonyl group) with an acid catalyst

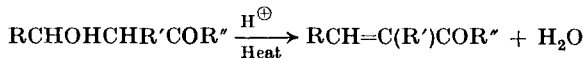
²⁷² A. T. Nielsen and E. B. W. Ovist, *J. Am. Chem. Soc.*, **76**, 5156 (1954).

²⁷³ G. B. Marcas, A. M. Municio, and S. Vega, *Anales Real Soc. Espan. Fis. Quim. (Madrid)*, *Ser. B*, **60**, 639 (1964) [*C.A.*, **63**, 1726 (1965)].

²⁷⁴ S. G. Powell and F. Hagemann, *J. Am. Chem. Soc.*, **66**, 372 (1944).

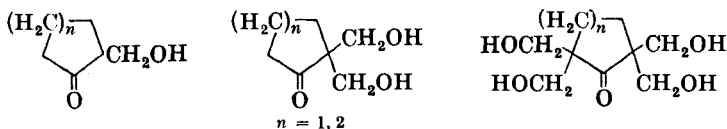
²⁷⁵ R. Levine and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1768 (1944).

such as iodine or oxalic acid;^{149, 272, 274} yields are excellent except with ketols which dissociate readily on heating (those in which R' is a large group).

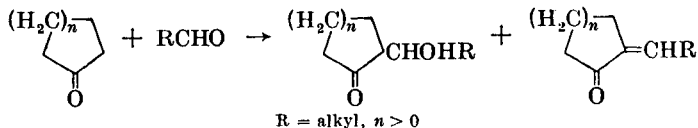


Condensation of Aldehydes with Alicyclic Ketones

Cyclopentanones and cyclohexanones condense with formaldehyde with basic catalysts to give mono-, unsymmetrical *bis*- and tetra-methylol compounds.²⁷⁶⁻²⁷⁸ Acetaldehyde behaves similarly with cyclopentanone.²⁷⁹ Paraformaldehyde in dimethyl sulfoxide containing boron



trifluoride etherate undergoes α , or vinylogously α , condensation with steroid ketones.²⁸⁰ α -Methylenecycloalkanones are conveniently prepared by pyrolysis of the Mannich base hydrochlorides.²⁸¹ *n*-Alkanals ($>C_2$) yield principally 1:1 condensation products with cycloalkanones, but the yields are low.²⁸²⁻²⁸⁶ Mild conditions (low temperature,



aqueous ethereal sodium hydroxide) are required to minimize self-condensation of the aldehyde. Chloral²⁸⁷ and 2-ethylbutanal,²⁸⁸ which do not readily undergo self-condensation, may be subjected

²⁷⁶ H. Gault and J. Skoda, *Bull. Soc. Chim. France*, [5] **13**, 308 (1946).

²⁷⁷ H. Gault and E. Steckl, *Compt. Rend.*, **207**, 475 (1938).

²⁷⁸ C. Mannich and W. Brose, *Ber.*, **56**, 833 (1923).

²⁷⁹ J. Skoda, *Bull. Soc. Chim. France*, [5] **13**, 327 (1946).

²⁸⁰ W. H. W. Lunn, *J. Org. Chem.*, **30**, 2925 (1965).

²⁸¹ M. Mühlstädt, L. Zach, and H. Becwar-Reinhardt, *J. Prakt. Chem.*, **29**, 158 (1965).

²⁸² C. E. Garland and E. E. Reid, *J. Am. Chem. Soc.*, **47**, 2333 (1925).

²⁸³ P. Lambert, G. Durr, and G. Millet, *Compt. Rend.*, **238**, 251 (1954).

²⁸⁴ I. V. Machinskaya and B. V. Tokarev, *Zh. Obshch. Khim.*, **22**, 1163 (1952) [*C.A.*, **47**, 6360 (1953)].

²⁸⁵ G. Vavon and V. M. Mitchovitch, *Bull. Soc. Chim. France*, [4] **45**, 961 (1929).

²⁸⁶ O. B. Edgar and D. H. Johnson, *J. Chem. Soc.*, 3925 (1958).

²⁸⁷ F. Caujolle, P. Couturier, and C. Dulaurans, *Bull. Soc. Chim. France*, 19 (1950).

²⁸⁸ H. A. Bruson, U.S. pat. 2,395,453 [*C.A.*, **40**, 3467 (1946)].

to more vigorous reaction conditions to yield 1:1 products. Relatively few symmetrical (α, α') *bis*-condensation products have been reported from condensations of aliphatic aldehydes with cycloalkanones.^{279, 286, 289, 290} Enamines derived from cyclopentanone condense with alkanals in boiling benzene to give α -alkylidenecyclopentanones in good yield.^{53a}

Many examples of condensations of aromatic aldehydes with alicyclic ketones are known. To obtain 1:1 products an excess of ketone is often, but not always, employed with mild conditions (dilute aqueous sodium hydroxide at room temperature or under reflux²⁹¹⁻²⁹⁷). Sodium *t*-amyloxide in toluene at temperatures below 0° is an effective catalyst for producing 1:1 condensation products.²⁹⁵ Ketols or α, β -unsaturated ketones may be obtained, relatively milder conditions favoring ketols.²⁹¹ *Ortho*-substituted aromatic aldehydes and aldehydes with electron-releasing groups such as alkyl and methoxyl more readily produce 1:1 products.^{291, 293, 298-302} For example, *o*-tolualdehyde condenses with cyclohexanone in boiling aqueous potassium hydroxide to produce 71% of 1:1 α, β -unsaturated ketone.³⁰¹ Aqueous, rather than ethanolic, alkali favors 1:1 condensation.^{291, 303} Acid catalysts favor formation of a conjugated endocyclic double bond with cyclohexanones and cyclopentanones, whereas basic catalysts favor formation of the normal arylidene derivative.³⁰⁴ A number of reported 1:1 condensation products, obtained in the presence of acid catalysts and described as arylidene cycloalkanones, may, in fact, be the isomers having an endocyclic double bond.

²⁸⁹ A. Roedig and S. Schödel, *Chem. Ber.*, **91**, 320 (1958).

²⁹⁰ R. Mayer, *Chem. Ber.*, **88**, 1853 (1955).

²⁹¹ J. D. Billimoria, *J. Chem. Soc.*, 1126 (1955).

²⁹² O. Wallach, H. Mallison, and K. von Martius, *Nachr. K. Ges., Wiss. Göttingen*, **399** (1907) [*Chem. Zentr.*, **79**, I, 637 (1908)].

²⁹³ H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).

²⁹⁴ D. Vorländer and K. Kunze, *Ber.*, **59**, 2078 (1926).

²⁹⁵ G. Vavon and J. M. Conia, *Compt. Rend.*, **234**, 526 (1952).

²⁹⁶ A. R. Poggi, A. Maccioni, and E. Marongiu, *Gazz. Chim. Ital.*, **84**, 528 (1954) [*C.A.*, **50**, 930 (1956)].

²⁹⁷ V. G. Kharchenko, *Uch. Zap. Gos. Saratovsk. Univ.*, **75**, 71 (1962) [*C.A.*, **60**, 485 (1964)].

²⁹⁸ J. Colonge and J. Sibeud, *Bull. Soc. Chim. France*, 786 (1952).

²⁹⁹ W. S. Emerson, G. H. Birum, and R. I. Longley, *J. Am. Chem. Soc.*, **75**, 1312 (1953).

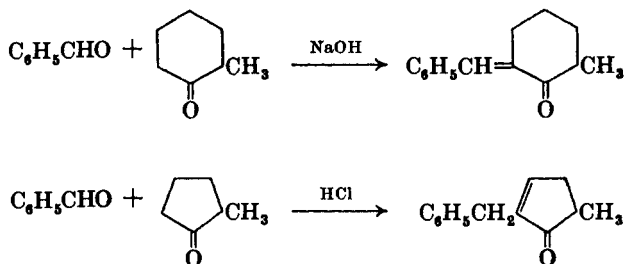
³⁰⁰ R. Poggi and M. Gottlieb, *Gazz. Chim. Ital.*, **64**, 852 (1934) [*C.A.*, **29**, 2152 (1935)].

³⁰¹ W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 636 (1940).

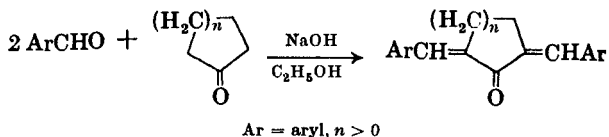
³⁰² R. Baltzly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Am. Chem. Soc.*, **77**, 624 (1955).

³⁰³ S. V. Tsukerman, L. A. Kutulya, and V. F. Lavrushin, *Zh. Obshch. Khim.*, **34**, 3597 (1964).

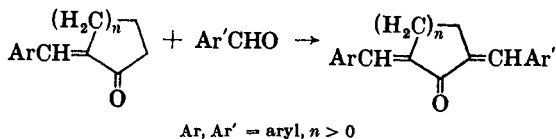
³⁰⁴ A. Hassner and T. C. Mead, *Tetrahedron*, **20**, 2201 (1964).



With 2 mole equivalents of aromatic aldehyde and ethanolic sodium hydroxide or ethoxide catalyst, good to excellent yields of *bis*-condensation products are uniformly obtained with cyclopentanone, cyclohexanone, and cycloheptanone.^{303, 305} The reactivity of the ketone appears to decrease as ring size increases. Yields with cyclooctanone^{306, 307} and higher cycloalkanones³⁰⁸ are low. Substituted cycloalkanones (exclusive of those substituted in the 2- or 3-position) behave in the same fashion as unsubstituted ones. By starting with a monoarylidene cycloalkanone,



condensation with a different aldehyde can lead to unsymmetrical *bis*-arylidene cycloalkanones³⁰³ (Table XIV).



o-Phthalaldehyde condenses with medium- and large-ring cycloalkanones to yield tricyclic *bis*-ketols which may be dehydrated to cycloheptatrienones.³⁰⁹

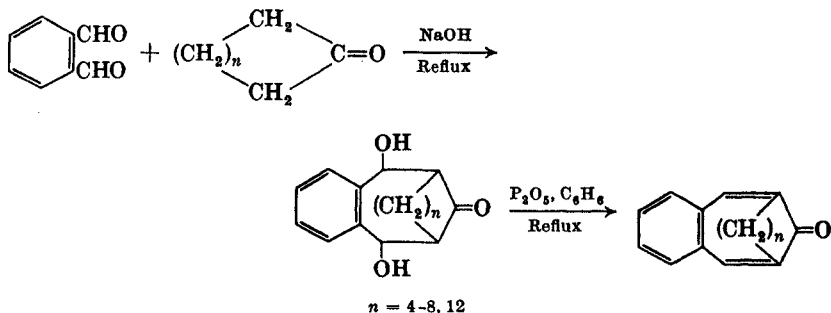
³⁰⁵ F. Mattu, *Rend. Seminario Fac. Sci. Univ. Cagliari*, **32**, 230 (1962) [*C.A.*, **63**, 17935 (1965)].

³⁰⁶ F. Mattu and M. R. Manca-Mura, *Rend. Seminario Fac. Sci. Univ. Cagliari*, **34**, 286 (1964) [*C.A.*, **63**, 13126 (1965)].

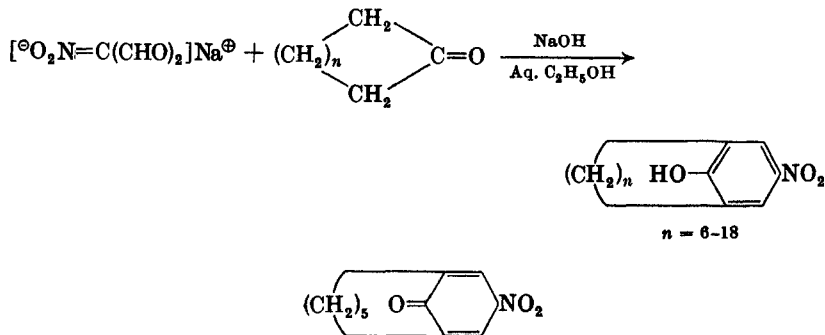
³⁰⁷ E. A. Braude, W. F. Forbes, B. F. Gofton, R. P. Houghton, and E. S. Waight, *J. Chem. Soc.*, 4711 (1957).

³⁰⁸ E. A. Braude and B. F. Gofton, *J. Chem. Soc.*, 4720 (1957).

³⁰⁹ E. Kloster-Jensen, N. Tarköy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).



Nitromalonaldehyde condenses with cycloalkanones to produce *meta*-methylene bridged bicyclic *p*-nitrophenol derivatives;³¹⁰⁻³¹² when the methylene bridge is too small ($n < 6$), a non-planar cyclohexadienone tautomer is favored.³¹¹ Although cyclobutanone has been condensed



with acetone,¹⁸⁰ no reports of its condensation with aldehydes have yet appeared.

Camphor and other bicyclic ketones produce α,β -unsaturated ketones with basic catalysts. Many aldehydes have been condensed with camphor in the presence of sodium or sodium amide in ether.³¹³⁻³¹⁵ Ethanolic hydrogen chloride-catalyzed condensation of benzaldehyde with nopinone or verbanone caused ring opening to produce a chlorinated *bis*-condensation product, whereas sodium ethoxide led to the normal 1:1 product.³¹⁵

³¹⁰ V. Prelog and K. Wiesner, *Helv. Chim. Acta*, **30**, 1465 (1947).

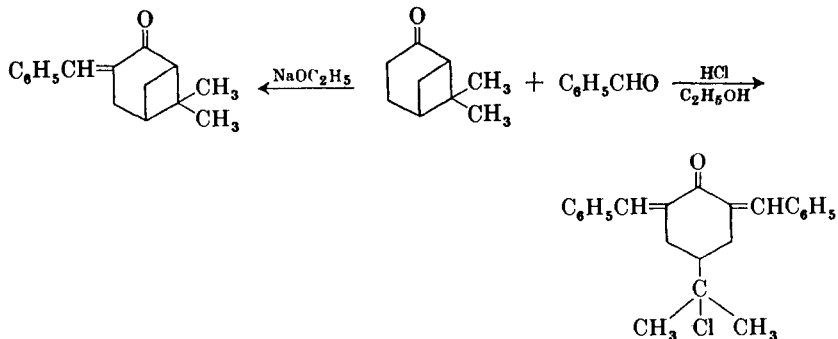
³¹¹ V. Prelog, K. Wiesner, W. Ingold, and O. Häflinger, *Helv. Chim. Acta*, **31**, 1325 (1948).

³¹² V. Prelog, K. Wiesner, and O. Häflinger, *Collection Czech. Chem. Commun.*, **15**, 900 (1951).

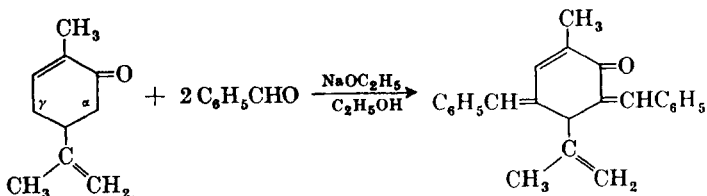
³¹³ A. Haller, *Compt. Rend.*, **113**, 22 (1891).

³¹⁴ A. Haller and E. Bauer, *Compt. Rend.*, **143**, 1490 (1909).

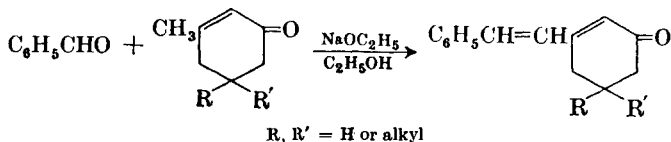
³¹⁵ O. Wallach, *Ann.*, **437**, 187 (1924).



Conjugated cycloalkenones may undergo condensation in the γ -position with basic catalysts. Carvone and menthenone condense with



2 mole equivalents of benzaldehyde.³¹⁶⁻³²⁰ 3-Methyl-2-cyclohexen-1-one,³²¹ 3,5-dimethyl-2-cyclohexen-1-one,³²¹ isophorone,^{321-322a} and piperitone³²³ condense with benzaldehyde at the 3-methyl group only (ethanolic sodium ethoxide catalyst). Evidently the most stable, non-cross-conjugated, unsaturated ketone is the favored product of these condensations.



Anhydroacetonebenzil (3,4-diphenyl-4-hydroxy-2-cyclopenten-1-one), which does not dehydrate to a stable cyclopentadienone (see page 25),

³¹⁶ R. E. Christ and R. C. Fuson, *J. Am. Chem. Soc.*, **59**, 893 (1937).

³¹⁷ A. Müller, *Ber.*, **54**, 1471 (1921).

³¹⁸ O. Wallach, *Ber.*, **29**, 1595 (1896).

³¹⁹ O. Wallach, *Ann.*, **305**, 261 (1899).

³²⁰ O. Wallach, *Ann.*, **397**, 211 (1913).

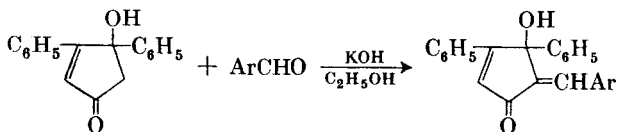
³²¹ J. M. Conia and V. O'Leary, *Compt. Rend.*, **249**, 1002 (1959).

³²² G. R. Ensor and W. Wilson, *J. Chem. Soc.*, 4068 (1956).

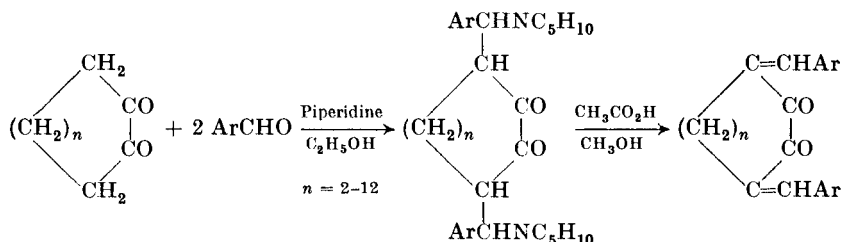
^{322a} G. Kabass, *Tetrahedron*, **22**, 1213 (1966).

³²³ J. Dewar, D. R. Morrison, and J. Read, *J. Chem. Soc.*, 1598 (1936).

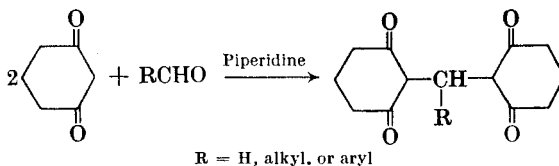
condenses with aromatic aldehydes in the 5-position³²⁴ with ethanolic potassium hydroxide.



1,2-Cycloalkanediones condense with 2 mole equivalents of aromatic aldehyde in the presence of piperidine to yield *bis*- β,β' -N-piperidyl derivatives, which form *bis*- α,β -unsaturated ketones when heated with methanolic acetic acid.³²⁵⁻³²⁷



1,3-Cyclohexanedione³²⁸ and derivatives, such as *dimedon* (5,5-dimethyl-1,3-cyclohexanedione), form 2,2'-*bis* derivatives useful for characterizing aldehydes.³²⁹⁻³³³



Few condensations of aldehydes with 1,4-cyclohexanedione have been reported.^{327, 334} *o*-phthalaldehyde (2 mole equivalents) forms a pentacene derivative in 90% yield.

³²⁴ F. R. Japp and A. Findlay, *J. Chem. Soc.*, **75**, 1017 (1899).

³²⁵ N. J. Leonard, J. C. Little, and A. J. Kresge, *J. Am. Chem. Soc.*, **79**, 6436 (1957).

³²⁶ N. J. Leonard and G. C. Robinson, *J. Am. Chem. Soc.*, **75**, 2714 (1953).

³²⁷ F. Mattu and M. R. Manca, *Chimica (Milan)*, **33**, 284 (1957) [*C.A.*, **52**, 1934 (1958)].

³²⁸ E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

³²⁹ F. E. King and D. G. I. Felton, *J. Chem. Soc.*, 1371 (1948).

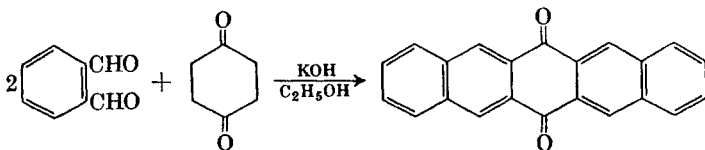
³³⁰ H. Stetter and U. Milbers, *Chem. Ber.*, **91**, 374 (1958).

³³¹ V. Kvita and J. Weichet, *Chem. Listy*, **51**, 380 (1957) [*C.A.*, **51**, 9502 (1957)].

³³² D. Vorländer and F. Kalkow, *Ann.*, **309**, 356 (1900).

³³³ D. Vorländer and O. Strauss, *Ann.*, **309**, 375 (1900).

³³⁴ F. Mattu, *Chimica (Milan)*, **38**, 3 (1962) [*C.A.*, **61**, 16025 (1964)].

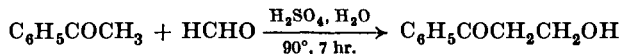


Non-aromatic heterocyclic ketones (e.g., tetrahydro- γ -pyrone, 4-piperidone) generally appear to behave like their carbocyclic analogs in condensation reactions (Table XIX).^{334a}

Condensation of Aldehydes with Alkyl Aryl Ketones

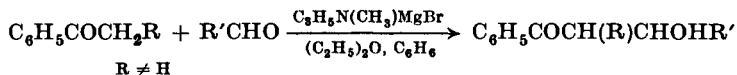
Relatively few aliphatic aldehydes other than formaldehyde have been condensed with alkyl aryl ketones.¹⁷⁷ Yields in the reactions of methyl aryl ketones with aliphatic aldehydes are uniformly poor. No general procedure has been developed for securing good yields in these reactions; the use of enamines or non-equilibrating enolates has not been explored (see p. 37). The Wittig reaction¹⁶ might be applicable.

The condensation of formaldehyde with acetophenone has been studied in some detail,^{335, 336} the best yield of the ketol, 3-hydroxy-1-phenyl-1-propanone, was 25% obtained with aqueous sulfuric acid catalyst.³³⁵



Basic ion-exchange resin Amberlite IRA 400 at 40–45° gave a 40% yield of ketol from formaldehyde and propiophenone,³³⁷ whereas potassium carbonate gave only 16–19%.³³⁶

Methylanilinumagnesium bromide, although unsuitable for aromatic methyl ketone condensations (principally because of ketone and aldehyde self-condensation) is a catalyst of general utility for condensing aliphatic and aromatic aldehydes with higher homologs of acetophenone to yield ketols.¹⁷⁷ Ketols have been obtained in the following condensations (yields in parentheses): isobutyraldehyde with propiophenone (83%), hexanal with butyrophenone (40%), and acetaldehyde with valerophenone (50%).¹⁷⁷



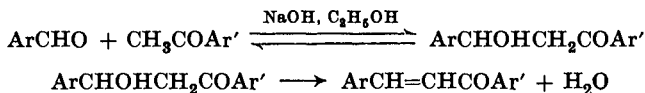
^{334a} N. Barbulescu and C. Greff, *Rev. Chim. (Bucharest)*, **17**, 202 (1966) [*C.A.*, **65**, 8869 (1966)].

³³⁵ M. G. J. Beets and L. G. Heeringa, *Rec. Trav. Chim.*, **74**, 1085 (1955).

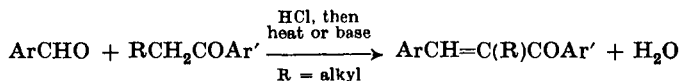
³³⁶ R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Am. Chem. Soc.*, **60**, 2935 (1938).

³³⁷ S. Yamada, I. Chibata, and H. Matsumae, *Ann. Rept. Gohei Tanabe Co., Ltd.*, **1**, 20 (1956) [*C.A.*, **51**, 6546 (1957)].

In sharp contrast to the paucity of aliphatic aldehyde condensations, a very large number of condensations of substituted benzaldehydes with acetophenone and substituted acetophenones (Table XVII) to yield chalcones are known.³³⁸⁻³⁴¹ Many heterocyclic aldehydes have been condensed with acetophenones. The initial studies of Claisen (1881-1889) were extended by v. Kostanecki (1896-1900). Ethanolic sodium hydroxide or sodium ethoxide, at room temperature or below, generally leads to chalcones in good to excellent yields, with few side reactions. Only



occasionally are ketols obtained. Acid catalysts are seldom employed and, except with certain phenols and phenol esters, appear to offer few advantages. Hydrogen chloride is useful for the condensation of aromatic aldehydes with *n*-alkyl aryl ketones to produce β -chloroketones which, on heating or treatment with base, yield α -alkyl chalcones.³⁴²⁻³⁴⁵



Substituents in the aldehyde or ketone *generally* appear to affect equilibrium yields of chalcone in the same manner for acid- or base-catalyzed reactions; electron-withdrawing substituents provide higher yields than electron-releasing ones. Rather poor yields of chalcone are sometimes realized (acid or base catalysis) with electron-releasing groups such as alkoxy, amino, and hydroxy.^{31, 338, 346-351} Side reactions may ensue with hydroxy compounds. Primary amino groups form Schiff bases, but this difficulty may be circumvented by employing the acetamido

³³³ M. Vandewalle, *Ind. Chim. Belge*, **26**, 345 (1961); a review of chalcone preparations.

³³⁸ F. M. Dean and V. Podimuang, *J. Chem. Soc.*, 3978 (1965).

³⁴⁰ P. Mahanty, S. P. Panda, B. K. Sabata, and M. K. Rout, *Indian J. Chem.*, **3**, 121 (1965).

³⁴¹ Y. S. Agasimmdin, S. D. Jolad, and S. Rajagopal, *Indian J. Chem.*, **3**, 220 (1965).

³⁴² E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).

³⁴³ L. I. Smith and L. I. Hanson, *J. Am. Chem. Soc.*, **57**, 1326 (1935).

³⁴⁴ R. D. Abell, *J. Chem. Soc.*, **79**, 928 (1901).

³⁴⁵ R. D. Abell, *J. Chem. Soc.*, 2834 (1953).

³⁴⁶ V. Balaiah, L. R. Row, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **20A**, 274 (1944) [*C.A.*, **39**, 4609 (1945)].

³⁴⁷ J. S. Buck and I. M. Heilbron, *J. Chem. Soc.*, **121**, 1095 (1922).

³⁴⁸ T. A. Geismann and R. O. Clinton, *J. Am. Chem. Soc.*, **68**, 697 (1946).

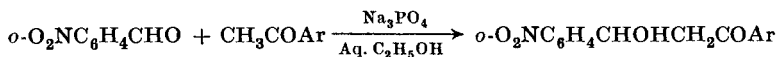
³⁴⁹ R. E. Lyle and L. P. Paradis, *J. Am. Chem. Soc.*, **77**, 6667 (1955).

³⁵⁰ W. Davey and J. R. Gwilt, *J. Chem. Soc.*, 1008 (1957).

³⁵¹ D. S. Noyce and W. A. Pryor, *J. Am. Chem. Soc.*, **81**, 618 (1959).

derivatives which can subsequently be hydrolyzed. For hydroxy-substituted benzaldehydes the best base-catalyzed procedure appears to be the use of aqueous ethanolic sodium hydroxide at 25–60° for a few hours.^{348, 352, 353} The benzoates of hydroxy compounds with hydrogen chloride in ethyl acetate at 0° gave chalcones in good yields.^{354–356}

There is a difference in the effect of substituents in benzaldehydes on rates for the condensation step (ketol formation) of acid- and base-catalyzed reactions. For the acid-catalyzed reactions the rate is *mildly* accelerated by electron-releasing substituents.^{351, 357, 358} For base-catalyzed reactions the rate is *strongly* accelerated by electron-withdrawing substituents.^{31, 349, 356–360} However, yields are determined by the various equilibria involved. The rate of cleavage of the intermediate ketol, relative to the rate of its formation and dehydration to chalcone, is a matter of importance; electron-withdrawing substituents appear to favor dehydration of ketol to chalcone, relative to retrogression in basic or acidic media.^{349, 351} Thus the effect of substituents on equilibrium yields of chalcone is roughly the same in all media. Acid catalysts favor irreversible dehydration of ketols to chalcones, and no ketols of this type have been isolated from acid media. Most of the limited number of chalcone precursor ketols that have been isolated have been obtained in alkaline medium, under mild conditions, with reactants having electron-withdrawing groups (nitro, halogen). Several ketols have been prepared from 2-nitrobenzaldehyde and various acetophenones, employing aqueous ethanolic sodium phosphate.³⁶¹ Additional quantitative work is needed in this area.



A variety of aromatic ketones, including 1-indanones, 1-tetralones,³⁶² aryl acetyl³⁶³ compounds, and benzyl aryl ketones, has been condensed with various aldehydes; yields are generally good and special conditions are not required. Heterocyclic aromatic ketones behave like

³⁵² T. A. Ellison, *J. Chem. Soc.*, 1720 (1927).

³⁵³ W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1230 (1958).

³⁵⁴ A. Russell and S. F. Clark, *J. Am. Chem. Soc.*, **61**, 2651 (1939).

³⁵⁵ A. Russell and J. Todd, *J. Chem. Soc.*, 421 (1937).

³⁵⁸ R. P. Barnes and J. L. Snead, *J. Am. Chem. Soc.*, **67**, 138 (1945).

³⁵⁷ T. Széll, A. M. Eastham, and G. Sipos, *Can. J. Chem.*, **42**, 2417 (1964); **43**, 2134 (1965).

³⁵⁸ S. M. McElvain and R. E. McMahon, *J. Am. Chem. Soc.*, **71**, 901 (1949).

³⁵⁹ M. Scholtz and L. Huber, *Ber.*, **37**, 390 (1904).

³⁶⁰ E. A. Walker and J. R. Young, *J. Chem. Soc.*, 2041 (1957).

³⁶¹ I. Tanasescu and A. Baciu, *Bull. Soc. Chim. France*, [5] **4**, 1673 (1937).

³⁶² N. P. Buu-Hoi and G. Saint-Ruf, *Bull. Soc. Chim. France*, 424 (1965).

³⁶³ J. Sam, D. W. Alwan, and K. Aparajithan, *J. Heterocyclic Chem.*, **2**, 366 (1965).

other aromatic ketones,³⁶⁴⁻³⁶⁷ except certain nitrogen-containing examples which give best yields with a piperidine catalyst in boiling ethanol.³⁶⁸ Condensations with most heterocyclic aldehydes appear to proceed normally.^{363, 366, 369-372}

Intramolecular Condensations

It is convenient to discuss the intramolecular aldol condensations of dialdehydes, diketones, and ketoaldehydes in one section. The intramolecular reaction is an important tool for synthesis of alicyclic ketones and aldehydes. The reactants may be, and often are, generated *in situ* from such intermediates as alcohols, glycols, acetals, enamines, Mannich bases and quaternary salts thereof, and vinyl chlorides. In addition, the Michael condensation is an important route to 1,5-diketones and δ -ketoaldehydes, which need not be isolated before cyclization (Robinson annelation reaction). As stated in the introduction to this volume, aldol condensations which proceed from, to, or through carbonyl precursors or derivatives have, with certain exceptions, arbitrarily been excluded from the tabular summary of this review. This restriction limits the scope of the following discussion, because carbonyl precursors are often employed in intramolecular aldol condensations and the literature coverage of these particular reactions is incomplete.

Dialdehydes. The intramolecular condensation of alkane α,ω -dialdehydes (chain length $> C_5$) generally leads to alicyclic α,β -unsaturated aldehydes under mild conditions (acid or basic catalysts). Products having rings with five,³⁷³⁻³⁷⁷ six,^{377,378} seven,³⁷⁹ fifteen,³⁸⁰ and seventeen³⁸⁰ members have been prepared by this method. More vigorous

³⁶⁴ B. Bobarevic, M. Dezelic, and V. Milovic, *Glasnik Hemicara Tehnol. Bosne Hercegovine*, **12**, 111 (1963) [*C.A.*, **63**, 18006 (1965)].

³⁶⁵ M. Vaysse and P. Pastour, *Compt. Rend.*, **259**, 2865 (1964).

³⁶⁶ S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Y. K. Yur'ev, *Zh. Org. Khim.*, **1**, 650 (1965).

³⁶⁷ Mitsubishi Chemical Industries Co., Ltd., Japan. pat. 23,907 (1965) [*C.A.*, **64**, 3499 (1966)].

³⁶⁸ P. I. Ittyerah and F. G. Mann, *J. Chem. Soc.*, 467 (1958).

³⁶⁹ J. Koo, *J. Pharm. Sci.*, **53**, 1329 (1964).

³⁷⁰ A. C. Annigeri and S. Siddappa, *Monatsh. Chem.*, **96**, 625 (1965).

³⁷¹ A. C. Annigeri and S. Siddappa, *Indian J. Chem.*, **2**, 413 (1964).

³⁷² B. S. Tanaseichuk and I. Y. Postovskii, *Zh. Org. Khim.*, **1**, 1279 (1965) [*C.A.*, **63**, 13207 (1965)].

³⁷³ E. B. Reid and J. F. Yost, *J. Am. Chem. Soc.*, **72**, 5232 (1950).

³⁷⁴ J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950).

³⁷⁵ Y. Bon and O. Yanemitsu, *Tetrahedron*, **20**, 2877 (1965).

³⁷⁶ T. P. Kutney, A. By, T. Inaba, and S. Y. Leong, *Tetrahedron Letters*, 2911 (1965).

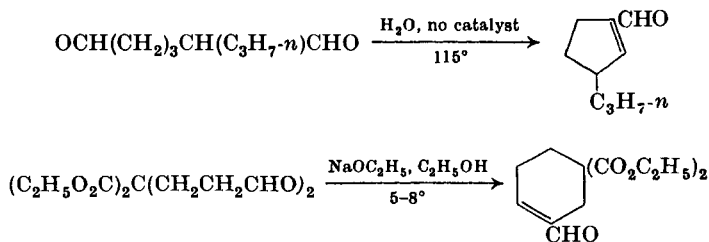
³⁷⁷ O. A. Moe, D. T. Warner, and M. I. Buckley, *J. Am. Chem. Soc.*, **73**, 1062 (1951).

³⁷⁸ J. v. Braun and E. Danziger, *Ber.*, **46**, 103 (1913).

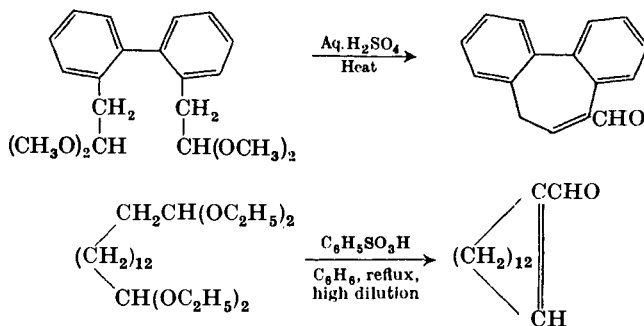
³⁷⁹ R. Weitzenböck, *Monatsh. Chem.*, **34**, 215 (1913).

³⁸⁰ M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **20**, 525 (1937).

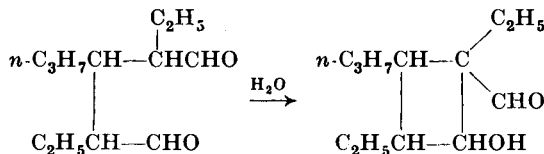
basic conditions favor formation of lactones or hydroxy acids (see p. 60). The preparation of larger rings (from the corresponding acetals) has been



achieved with acid catalysts; high-dilution conditions were employed to prepare macrocyclic compounds.³⁸⁰



A cyclobutane aldol is obtained as a major ozonolysis product of 2-hydroxy-6-propyl-1,3,5-triethyl-3-cyclohexene-1-carboxaldehyde; it is derived from the intermediate, 2,4-diethyl-3-propyl-1,5-pentanedial.³⁸¹ The buttressing effect of adjacent alkyl groups, as well as poor solvation of the intermediate enolate (or enol), may facilitate this ring closure to a four-membered ring, which is unique.

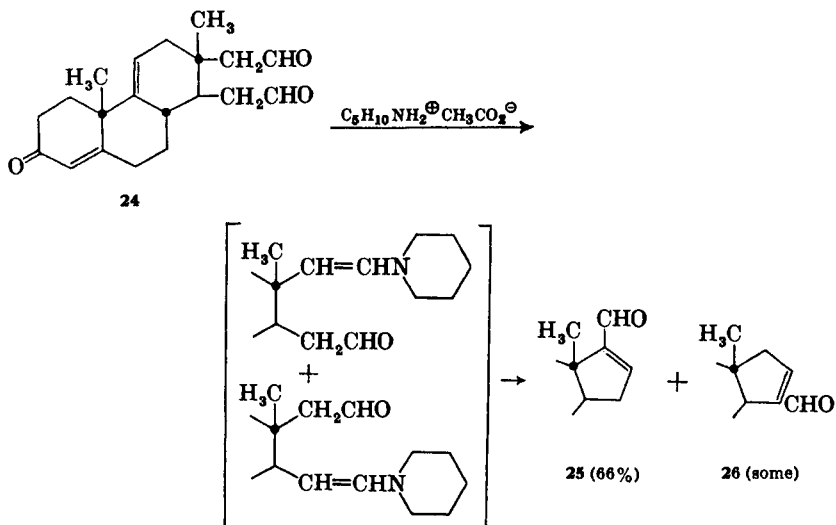


Piperidinium acetate catalyzes cyclization of the dialdehyde **24** to the tetracyclic aldehydes **25** and **26**;³⁸² the mechanism, involving an

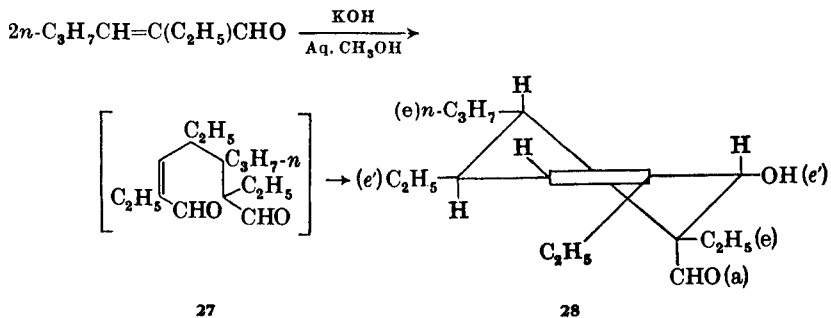
³⁸¹ A. T. Nielsen, *J. Am. Chem. Soc.*, **79**, 2518 (1957).

³⁸² R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. H. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

enamine intermediate, has been discussed.⁵² The cyclization may also be effected by heating the dialdehyde in water at 145°, whereby the relative amount of **26** in the mixture is increased.³⁸²



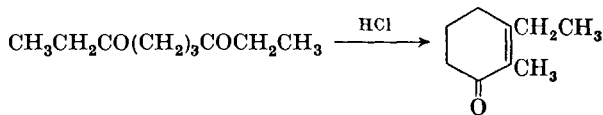
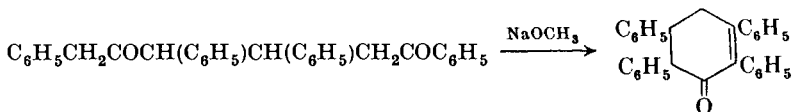
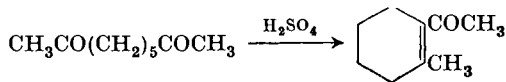
Self-condensation of 2-ethyl-2-hexenal leads, by Michael addition, to an intermediate dialdehyde (**27**, not isolated) which is cyclized to a cyclohexene aldol, **28**, existing principally (99%) in the configuration shown.^{66, 381, 383}



Diketones. The intramolecular self-condensation of α, ω -diketones is a frequently employed, useful, and important route to alicyclic β -ketols

³⁸³ A. T. Nielsen, *J. Org. Chem.*, **28**, 2115 (1963).

and α,β -unsaturated ketones. Six-membered rings are easily formed.³⁸⁴⁻³⁹¹ 1,5-Diketones yield cyclohexenones; 1,7-diketones yield acylcyclohexenes.



Although common basic and acidic catalysts (sodium ethoxide, hydrogen chloride) are quite effective in many intramolecular aldol condensations, secondary amine catalysts (pyrrolidine and piperidine) often give outstanding results³⁹² under mild conditions and also facilitate isolation of β -ketols.^{48, 68, 76, 77} The stereochemistry of the ring juncture in decalin derivatives is evidently governed by the size of the ring substituent in the 2-position of the reactant cyclohexanone;^{76, 77} sodium ethoxide at low temperature (-10°)⁶⁷ leads to the same stereochemistry in the products as does pyrrolidine^{76, 77} (see p. 13).

Five-membered^{393-397b} and seven-membered^{398, 399} rings have been

³⁸⁴ E. E. Blaise and A. Koehler, *Bull. Soc. Chim. France*, [4] **7**, 655 (1910).

³⁸⁵ E. E. Blaise, *Compt. Rend.*, **173**, 313 (1921).

³⁸⁶ P. Yates and J. E. Hyre, *J. Org. Chem.*, **27**, 4101 (1962).

³⁸⁷ E. Buchta and S. Buchholz, *Ann.*, **688**, 40 (1965).

³⁸⁸ H. Smith, *Brit. pat.* 975,594 [*C.A.*, **62**, 9068 (1965)].

³⁸⁹ G. Nomine, R. Bucourt, J. Tessier, A. Pierdet, G. Costerousse, and J. Mathieu, *Compt. Rend.*, **260**, 4545 (1965).

³⁹⁰ E. Buchta and H. Kroeger, *Naturwiss.*, **52**, 496 (1965).

³⁹¹ E. Buchta and P. Vincke, *Chem. Ber.*, **98**, 208 (1965).

³⁹² S. Ramachandran and M. S. Newman, *Org. Syntheses*, **41**, 38 (1961).

³⁹³ G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 935, 936 (1964).

³⁹⁴ R. F. Heck, *J. Org. Chem.*, **30**, 2205 (1965).

³⁹⁵ J. Kossanyi, *Bull. Soc. Chim. France*, 722 (1965).

³⁹⁶ P. Doyle, I. R. Maclean, R. D. H. Murray, W. Parker, and R. A. Raphael, *J. Chem. Soc.*, 1344 (1965).

³⁹⁷ C. P. Chiusoli and G. Bottaccio, *Chim. Ind. (Milan)*, **47**, 165 (1965) [*C.A.*, **63**, 13067 (1965)].

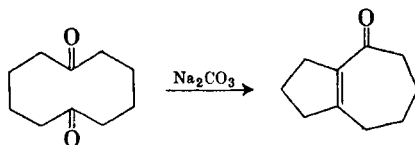
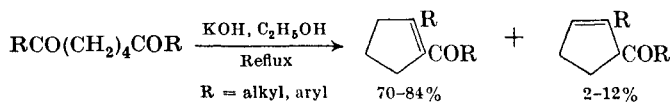
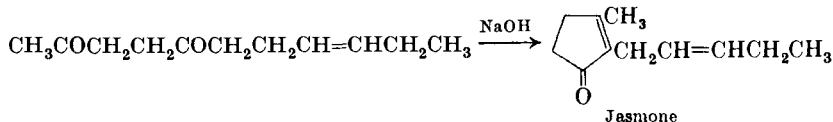
^{397a} G. Büchi and H. Wüest, *J. Org. Chem.*, **31**, 977 (1966).

^{397b} R. Breslow, W. Vitale, and K. Wendel, *Tetrahedron Letters*, 365 (1965).

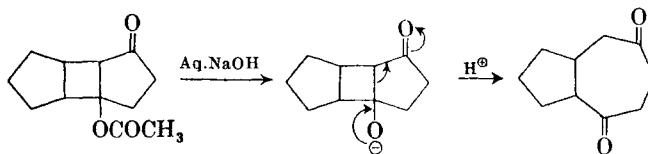
³⁹⁸ A. G. Anderson and J. A. Nelson, *J. Am. Chem. Soc.*, **73**, 232 (1951).

³⁹⁹ G. Muller and A. Poittevin, *Fr. pat.* 1,369,321 [*C.A.*, **62**, 7838 (1965)].

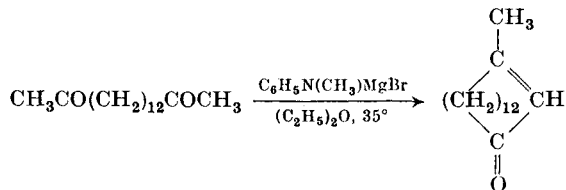
made by this intramolecular condensation but no ring closures to cyclobutane derivatives have been reported. 1,4-Diketones yield cyclopentenones; 1,6-diketones yield acylcyclopentenes or cycloheptenones.



A tricyclic β -ketol intermediate incorporating a four-membered ring was found to undergo an irreversible retroaldol condensation.⁴⁰⁰



Large rings have been prepared by employing high-dilution techniques.⁴⁰¹



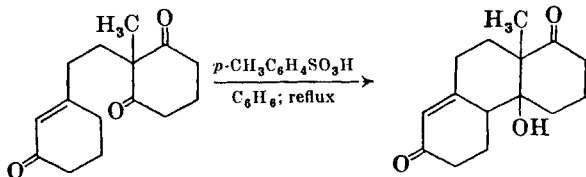
Numerous condensed ring compounds have been prepared from diketones (Table VI); an interesting example is one involving intramolecular attack at the γ position of an α,β -unsaturated ketone.^{402, 403}

⁴⁰⁰ H. Hikino and P. de Mayo, *J. Am. Chem. Soc.*, **86**, 3582 (1964).

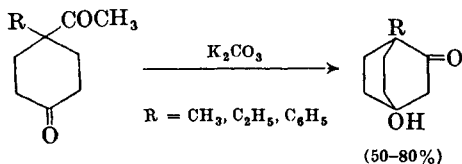
⁴⁰¹ M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **30**, 2019 (1947).

⁴⁰² N. N. Gaidamovich and I. V. Torgov, *Izv. Acad. Nauk SSSR*, 1311 (1964) [*C.A.*, **61**, 8203 (1964)].

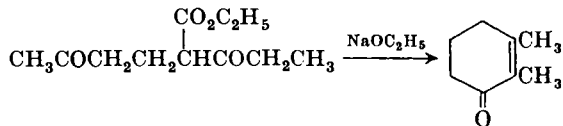
⁴⁰³ C. Sannié, J. J. Panouse, and C. Neuville, *Bull. Soc. Chim. France*, 1435 (1956).



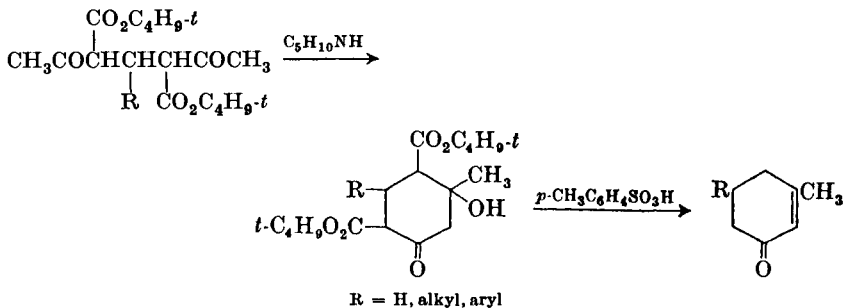
Ketols with a bridgehead hydroxyl group have been prepared.^{403a, b}



Certain readily available carboalkoxy diketones are very useful substitutes for the corresponding diketones;⁴⁰⁴ the carboalkoxy group may be lost during the condensation.⁴⁰⁵



1,5-Diketones, available by piperidine-catalyzed Knoevenagel condensation from a β -keto ester and an aldehyde, may be cyclized to yield, ultimately, α,β -unsaturated ketones.⁴⁰⁶



In some reactions, ring closure may be directed by the choice of catalyst.⁴⁰⁷ As in the dialdehyde example 24 (p. 49), kinetically controlled aldol

^{403a} J. Colonge, P. Francois, and R. Vuillemy, *Bull. Soc. Chim. France*, 1028 (1966).

^{403b} J. Colonge and R. Vuillemy, *Bull. Soc. Chim. France*, 2235 (1961).

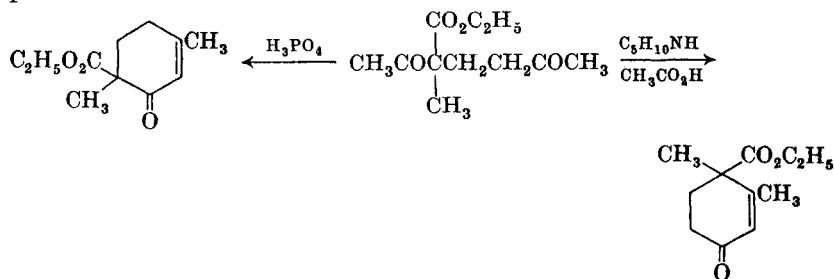
⁴⁰⁴ D. J. Goldsmith and J. A. Hartman, *J. Org. Chem.*, **29**, 3524 (1964).

⁴⁰⁵ E. Buchta and G. Satzinger, *Chem. Ber.*, **92**, 468 (1959).

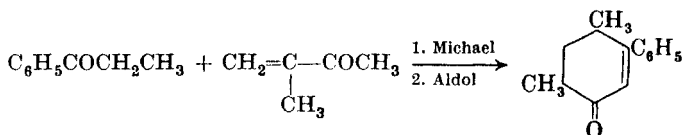
⁴⁰⁶ G. Näsland, A. Senning, and S. O. Lawesson, *Acta Chem. Scand.*, **16**, 1329 (1962).

⁴⁰⁷ H. Plieninger and T. Suchiro, *Chem. Ber.*, **89**, 2789 (1956).

condensation is favored by piperidine which evidently forms an enamine by reaction with the more reactive, less hindered carbonyl group. Other catalysts appear to favor the thermodynamically more stable condensation product.



1,5-Diketones obtained by Michael additions to α,β -unsaturated ketones may be cyclized to cyclohexenones, a reaction often referred to as the Robinson annelation reaction.^{48, 76, 408-409a} For example propiophenone adds to 3-methyl-3-buten-2-one, ultimately forming 4,6-dimethyl-3-phenyl-2-cyclohexen-1-one.⁴¹⁰ Many examples of this type of base-catalyzed reaction (Michael addition followed by aldol condensation leading to an alicyclic ketone) are known.^{51, 67, 71, 392, 408, 411-425a}



⁴⁰⁸ W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1285 (1935).

⁴⁰⁹ D. J. Baisted and J. S. Whitehurst, *J. Chem. Soc.*, 2340 (1965).

^{409a} R. Selvarajan, J. P. John, K. V. Naragan, and S. Swaminathan, *Tetrahedron*, **22**, 949 (1966).

⁴¹⁰ R. Chapurlat and J. Dreux, *Bull. Soc. Chim. France*, 349 (1962).

⁴¹¹ R. Dickinson, I. M. Heilbron, and F. Irving, *J. Chem. Soc.*, 1888 (1927).

⁴¹² E. R. H. Jones and H. P. Koch, *J. Chem. Soc.*, 393 (1942).

⁴¹³ D. Iwanov and T. Iwanow, *Ber.*, **77**, 173 (1944).

⁴¹⁴ H. Meerwein, *Ber.*, **77**, 227 (1944).

⁴¹⁵ J. Colonge and J. Dreux, *Compt. Rend.*, **231**, 1504 (1950).

⁴¹⁶ J. Colonge and J. Dreux, *Bull. Soc. Chim. France*, [5] 19, 47 (1952).

⁴¹⁷ W. A. Ayer and W. I. Taylor, *J. Chem. Soc.*, 2227 (1955).

⁴¹⁸ E. A. Braude, B. F. Gofton, G. Lowe, and E. S. Waight, *J. Chem. Soc.*, 4054 (1956).

⁴¹⁹ G. Büchi, J. H. Hansen, D. Knutson, and E. Koller, *J. Am. Chem. Soc.*, **80**, 5517 (1958).

⁴²⁰ E. D. Bergmann and P. Bracha, *J. Org. Chem.*, **26**, 4685 (1961).

⁴²¹ W. Bacon, S. Brewis, G. E. Usher, and E. S. Waight, *J. Chem. Soc.*, 2255 (1961).

⁴²² J. Wiemann and Y. Dubois, *Bull. Soc. Chim. France*, 1813 (1962).

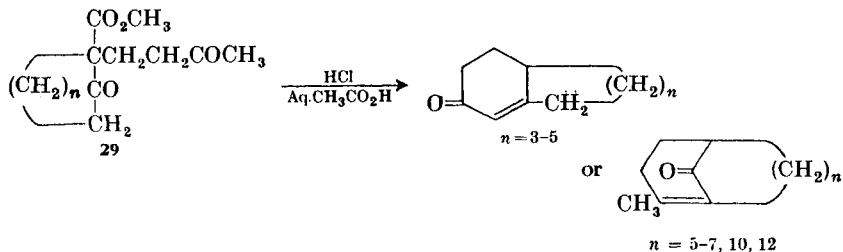
⁴²³ J. Colonge, J. Dreux, and R. Chapurlat, *Compt. Rend.*, **251**, 252 (1960).

⁴²⁴ N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).

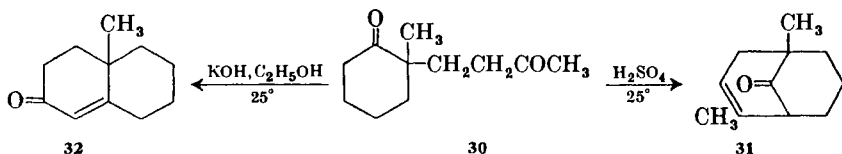
⁴²⁵ J. Wiemann, N. Ronzani, and J. J. Godfroid, *Compt. Rend.*, **256**, 4677 (1963).

^{425a} J. J. Beereboom, *J. Org. Chem.*, **31**, 2026 (1966).

The structure of the product may depend on substituents and ring size in certain condensations; in compound **29** acid-catalyzed condensation occurs on the ring methylene group if the ring is large enough; otherwise condensation occurs on the methyl group of the 3-oxobutyl side chain.^{409, 426}



Evidently this situation holds only when the group in the 2-position is or becomes hydrogen (replacement of CO_2CH_3 by H occurs during the cyclization of **29**), for when an alkyl group is initially present in the 2-position (as in **30**) condensation occurs on the ring methylene group (sulfuric acid catalyst) to yield **31**;⁴²⁷ in **31** the double bond is not at the bridgehead, however.

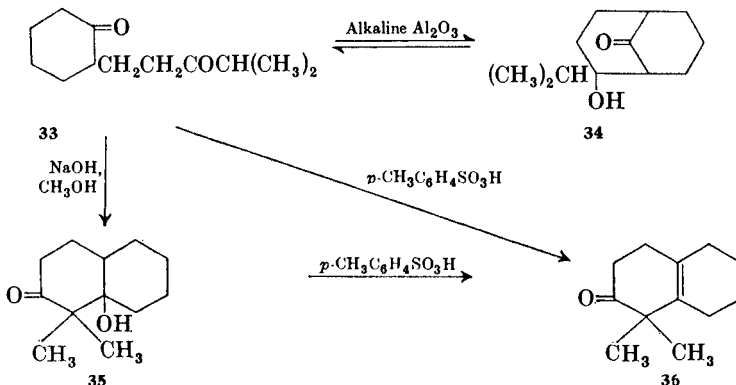


The structure of the product may depend on reaction conditions; by employing a basic catalyst, condensation of **30** occurs on the methyl group of the 3-oxobutyl side chain to yield an octalone (**32**).⁴²⁷ Maintaining reaction conditions of either kinetic or thermodynamic control may determine product composition. It has been established that in cyclization of the diketone **33** the bicyclo[3.3.1]nonane structure **34** (formed by condensation of the more rapidly formed cyclohexanone enolate with the less reactive side chain carbonyl group¹⁹⁰) is kinetically favored; prolonged reaction (equilibrium conditions) leads to the thermodynamically more stable decalone **35**.⁴⁰⁹ Acid-catalyzed cyclization of **33** leads to the octalone **36**,⁴⁰⁹ rather than to a bicyclo[3.3.1]non-2-en-9-one as with **30**. (There is no angular 2-alkyl group in **33**.)

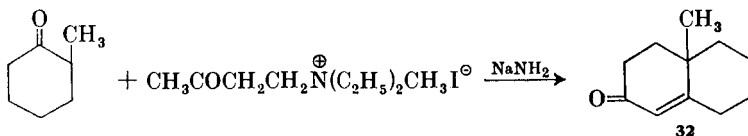
Modifications of the Robinson annelation reaction are frequently employed in practice, but are not included in the tabular summary of this

⁴²⁶ V. Prolog, L. Ruzicka, P. Barman, and L. Fronkiel, *Helv. Chim. Acta*, **31**, 92 (1948).

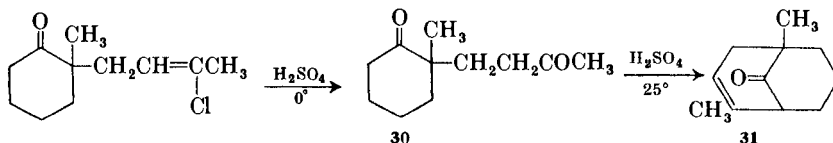
⁴²⁷ J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, **30**, 3642 (1965).



review. Three of them are mentioned now. (1) The vinyl ketone acceptor may be replaced by a Mannich base⁴⁰⁹ or its methiodide,^{428–430} thus allowing more vigorous reaction conditions which would polymerize



the vinyl ketone. (2) The Wichterle reaction^{427, 431} employs 1,3-dichloro-*cis*-2-butene as a methyl vinyl ketone surrogate to alkylate a ketone (sodium amide catalyst); the 2-(3-chloro-2-butenyl) ketone produced is treated with sulfuric acid to yield a diketone (sometimes isolable⁴²⁷) which is then cyclized. (3) Another very useful modification of the



reaction is conversion of the addend ketone into an enamine.^{52, 53, 432} This allows alkylation at the least substituted position with pyrrolidine-derived enamines^{433, 433a} (e.g., the 6-position of 2-alkylcyclohexanones) and also minimizes polymerization of the vinyl ketone.⁵²

⁴²⁸ J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949).

⁴²⁹ J. Szmuszko and H. Born, *J. Am. Chem. Soc.*, **75**, 3350 (1953).

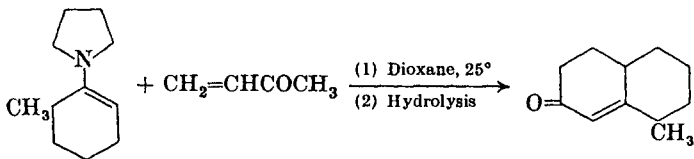
⁴³⁰ E. C. du Feu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937).

⁴³¹ O. Wichterle, J. Prochazka and J. Hofmann, *Collection Czech. Chem. Commun.* **13**, 300 (1948).

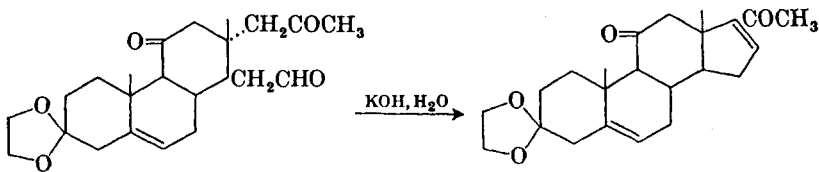
⁴³² R. L. Augustine and J. A. Caputo, *Org. Syntheses*, **45**, 80 (1965).

⁴³³ S. K. Malhotra and F. Johnson, *Tetrahedron Letters*, 4027 (1965).

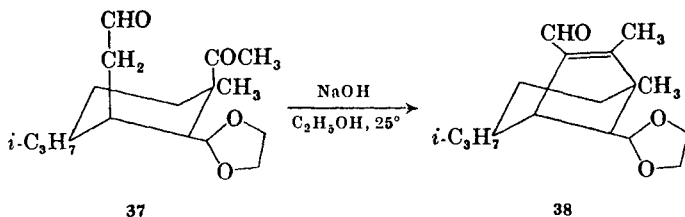
^{433a} W. D. Gurowitz and M. A. Joseph, *Tetrahedron Letters*, 4433 (1965).



Ketoaldehydes. Ketoaldehydes (sometimes generated *in situ*) have been condensed intramolecularly to form five- or six-membered rings (Table XX).^{75b} One example of formation of a seven-membered ring has been reported.⁷⁰ The reaction has been employed in steroid syntheses.⁴³⁴



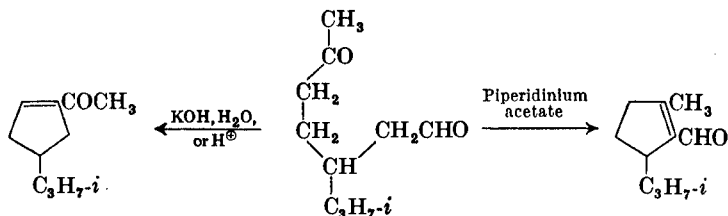
It is interesting that condensation of the ketonic carbonyl group occurs on the α carbon atom of the aldehyde in some of these examples producing a cyclopentene-1-carboxaldehyde or the related aldol.⁴³⁵⁻⁴⁴³ Cyclization of the ketoaldehyde **37** catalyzed by ethanolic sodium hydroxide led to the five-membered ring aldehyde **38** rather than a seven-membered ring ketone;⁴⁴³ the result illustrates the dominant



- ⁴³⁴ G. I. Poos, W. F. Johns, and L. H. Sarett, *J. Am. Chem. Soc.*, **77**, 1026 (1955).
⁴³⁵ B. Berkoz, E. Denot, and A. Bowers, *Steroids* **1**, 251 (1963) [*C.A.*, **59**, 7588 (1963)].
⁴³⁶ R. Lalande, J. Moulines, and J. Duboudin, *Compt. Rend.*, **254**, 1087 (1962).
⁴³⁷ H. E. Eschinazi, U.S. pat. 2,946,823 [*C.A.*, **55**, 1480 (1961)].
⁴³⁸ N. L. Wendler and H. L. Slates, *J. Am. Chem. Soc.*, **80**, 3937 (1958).
⁴³⁹ E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **85**, 3527 (1963).
⁴⁴⁰ G. H. Whitman and J. A. F. Wickramasinghe, *J. Chem. Soc.*, 1655 (1964).
⁴⁴¹ K. Tanabe and Y. Morisawa, *Chem. Pharm. Bull. (Tokyo)*, **11**, 536 (1963) [*C.A.*, **59**, 7600 (1963)].
⁴⁴² K. Tanabe, R. Hayashi, and R. Takasaki, *Chem. Pharm. Bull. (Tokyo)*, **9**, 1 (1961) [*C.A.*, **60**, 9331 (1964)].
⁴⁴³ E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **87**, 5728 (1965).

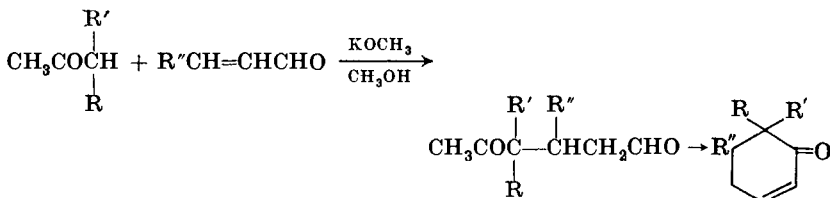
influence of strain and ring size rather than the relative reactivities of aldehyde and ketone carbonyl groups on the structure of the product.⁴⁹⁰

The composition of the product has been shown to depend on the catalyst with 6-oxo-3-isopropylheptanal, piperidinium acetate leading solely to 2-methyl-5-isopropyl-1-cyclopentene-1-carboxaldehyde⁴³⁶ and aqueous potassium hydroxide or an acid catalyst to 1-acetyl-4-isopropyl-1-cyclopentene as the major product;^{436, 437} 6-oxo-3-isopropenylheptanal behaves

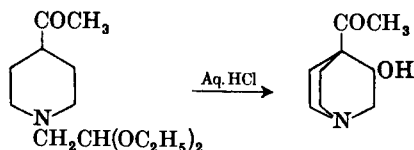


similarly.⁴⁴⁴⁻⁴⁴⁶ This result may be explained by attack of ketone carbonyl on the more rapidly formed aldehyde enamine (kinetic control) with piperidine catalyst and the more reactive aldehyde carbonyl attacking the ketone enolate (thermodynamic control) with hydroxide-ion catalysis.

Michael addition of ketones to α,β -unsaturated aldehydes leads to δ -ketoaldehydes which can be cyclized to cyclohexenones.^{447, 448}



Bicyclic bridged ketols (which cannot readily dehydrate) have been prepared from acetals with acid catalysts;^{449, 450} more vigorous conditions lead to β,γ -unsaturated ketones.⁴⁵¹



⁴⁴⁴ J. Wolinsky and W. Barker, *J. Am. Chem. Soc.*, **82**, 636 (1960).

⁴⁴⁵ J. Wolinsky, M. R. Slabaugh, and T. Gibson, *J. Org. Chem.*, **29**, 3740 (1964).

⁴⁴⁶ J. M. Conia and C. Faget, *Bull. Soc. Chim. France*, 1963 (1964).

⁴⁴⁷ J. Colonge, J. Dreux, and M. Thiers, *Compt. Rend.*, **243**, 1425 (1956).

⁴⁴⁸ J. Colonge, J. Dreux, and M. Thiers, *Compt. Rend.*, **244**, 89 (1957).

⁴⁴⁹ R. W. Guthrie, A. Philipp, Z. Valenta, and K. Wiesner, *Tetrahedron Letters*, 2945 (1965).

⁴⁵⁰ A. T. Nielsen, *J. Org. Chem.*, **31**, 1053 (1966).

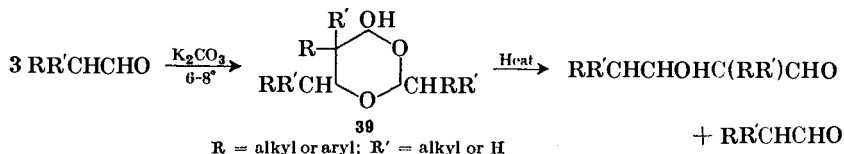
⁴⁵¹ E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965).

It would be desirable to have rules predicting the course of intramolecular aldol condensations. Potentially two or more routes may be available and may lead to different ring systems or to different arrangements of substituents. It appears that the factors which determine the equilibrium course of intermolecular condensations apply also to intramolecular condensations, with the important restriction that ring size and ring strain in the product are quite crucial. In general, the order of favored ring size formation is: $6 > 5 > 7 \gg 4$. Substitution of endocyclic double bonds by alkyl, aryl, or acyl groups will stabilize the product.

SIDE REACTIONS

Because of the great reactivity of aldehydes and ketones and their derived condensation products, aldol condensation side reactions are ubiquitous. In the following summary some of these reactions (acetal formation, hydride transfer, and additions to α,β -unsaturated ketones) are briefly discussed. Most discussion of mechanism has been omitted.

It is an interesting fact, perhaps not generally recognized, that cyclic acetal formation can occur in basic as well as acidic media when certain reaction conditions and structural requirements combine. The relatively unstable aldehyde trimers, 4-hydroxy-1,3-dioxanes (aldoxans, **39**), are produced from aliphatic aldehydes by mild basic catalysts. For example, propanal with aqueous potassium carbonate at $6-8^\circ$ leads to **39** ($R' = H$, $R = CH_3$; yield, 94%).⁴⁵² The aldoxans readily dissociate into the



parent aldol and aldehyde (1 mole of each) when strongly heated; for this reason, yields of aldols rarely exceed 66.7%. The reaction has been reported for acetaldehyde, butanal, isobutyraldehyde, and phenylacetaldehyde.⁴⁵²⁻⁴⁵⁸ The reaction is also catalyzed by acids.⁴⁵⁹ The

⁴⁵² E. Späth, R. Lorenz, and E. Freund, *Ber.*, **76**, 1196 (1943).

⁴⁵³ F. J. Villani and F. F. Nord, *J. Am. Chem. Soc.*, **68**, 1674 (1946).

⁴⁵⁴ F. Urech, *Ber.*, **12**, 191 (1879); **13**, 483 (1880).

⁴⁵⁵ J. L. E. Erickson and G. N. Grammer, *J. Am. Chem. Soc.*, **80**, 5466 (1958).

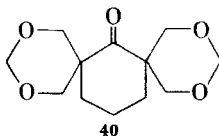
⁴⁵⁶ E. R. Alexander and E. N. Marvell, *J. Am. Chem. Soc.*, **72**, 1396 (1950).

⁴⁵⁷ R. H. Saunders, M. J. Murray, F. F. Cleveland, and V. T. Komarewsky, *J. Am. Chem. Soc.*, **65**, 1309, 1714 (1943).

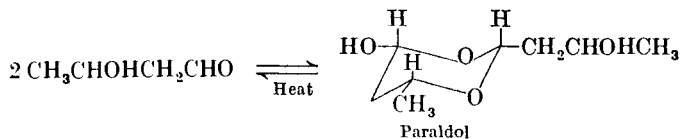
⁴⁵⁸ R. H. Saunders and M. J. Murray, *J. Am. Chem. Soc.*, **66**, 206 (1944).

⁴⁵⁹ J. C. Bevington, *Quart. Rev. (London)*, **6**, 141 (1952).

bis-1,3-dioxane **40** was obtained in 30% yield from cyclohexanone and formaldehyde with sulfuric acid in acetic acid.⁴⁶⁰ The formation of acetals from aldols has been reviewed.⁴⁶¹

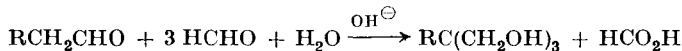


Aldols dimerize on standing, often rapidly; acetaldehyde forms paraldehyde.^{461, 462} The stereochemistry of paraldehyde has been examined.^{462a} Aldol dimerization can be reversed by heat. Distillation of aldols immediately before use is recommended; traces of accumulated acidic impurities



should be removed prior to this operation to avoid dehydration of the aldol.

Hydride transfer reactions such as the Cannizzaro reaction are encountered with a few reactive aldehydes, notably formaldehyde, under basic conditions.^{123, 123a} However, aldol condensation reaction conditions are usually sufficiently mild to obviate extensive hydride transfer as a competing reaction. A molar excess of formaldehyde with basic catalysts, such as aqueous calcium hydroxide, at 25–100°, will produce diols or triols from aliphatic aldehydes;^{121, 463–468} acetaldehyde yields pentaerythritol.^{469–470b} The reduction of aldols of higher molecular weight is less



⁴⁶⁰ S. Olsen, *Acta Chem. Scand.*, **7**, 1364 (1953).

⁴⁶¹ L. N. Owen, *Ann. Rept. Progr. Chem. (Chem. Soc. London)*, **41**, 139–148 (1945).

⁴⁶² E. Späth and H. Schmid, *Ber.*, **74**, 859 (1941).

^{462a} M. Vogel and D. Rhum, *J. Org. Chem.*, **31**, 1775 (1966).

⁴⁶³ J. A. Wyler, U.S. pat. 2,468,718 [*C.A.*, **43**, 7505 (1949)].

⁴⁶⁴ G. Dupont, R. Doulou, and A. Duplessis-Kergomard, *Bull. Soc. Chim. France*, [5] **17**, 314 (1949).

⁴⁶⁵ O. C. Dermer and P. W. Solomon, *J. Am. Chem. Soc.*, **76**, 1697 (1954).

⁴⁶⁶ C. M. van Marle and B. Tollens, *Ber.*, **36**, 1341, 1347 (1903).

⁴⁶⁷ W. Hensinger, Fr. pat. 1,103,113 [*C.A.*, **52**, 19953 (1958)].

⁴⁶⁸ A. Just, *Monatsh. Chem.*, **17**, 76 (1896).

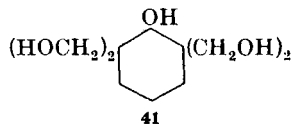
⁴⁶⁹ S. F. Marrian, *Chem. Rev.*, **43**, 149 (1948).

⁴⁷⁰ H. B. J. Schurink, *Org. Syntheses, Coll. Vol.*, **1**, 425 (1941).

^{470a} H. C. Da Silva and L. M. Chaves, *Tecnica (Lisbon)*, **40**, 649 (1965) [*C.A.*, **64**, 17406 (1966)].

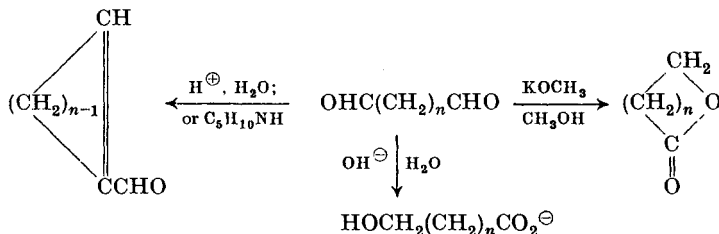
^{470b} H. Guenther and H. Mirbach, Ger. pat. 1,220,842 [*C.A.*, **65**, 12108 (1966)].

efficient; nonanal⁴⁷¹ and 2-methylheptanal⁴⁷¹ undergo normal aldol condensation with formaldehyde under conditions whereby lower aldol homologs are reduced. Reduction of ketols by excess formaldehyde can also occur. Although cyclohexanone condenses with 4 mole equivalents of formaldehyde (aqueous calcium hydroxide catalyst) to produce the tetramethylol derivative (40% yield), use of 5.5 mole equivalents of formaldehyde leads to the pentahydroxy compound **41** (73–85%).⁴⁷² Some



examples of reductions of aldols or ketols involving aldehydes other than formaldehyde have been reported (e.g., benzaldehyde, 2-methylpropanal, furfural, 2-methylbutanal, acetaldehyde, and 2-nitrobenzaldehyde).^{473–476}

Although alkane α,ω -dicarboxaldehydes produce cycloalkene carboxaldehydes by intramolecular aldol condensation under acidic or mild basic conditions,^{373, 374, 377–381} somewhat more vigorous basic conditions employing alcohol solvents (e.g., warm methanolic potassium methoxide) lead to lactones.^{477, 478} Warm aqueous alkali leads to hydroxy acids.⁴⁷⁷ Similarly, ω -ketoaldehydes may form lactones, hydroxy acids,⁴⁷⁷ cycloalkenones, or cycloalkene carboxaldehydes,^{434–442} depending on reaction



conditions. High concentrations of hydroxide or alkoxide ion favor conversion of the aldehyde carbonyl function into hydroxy or alkoxy alkoxide Cannizzaro intermediates,¹²³ which undergo facile cyclization

⁴⁷¹ E. Fourneau, G. Benoit, and R. Firmenich, *Bull. Soc. Chim. France*, [4] **47**, 858 (1930).

⁴⁷² H. Wittcoff, *Org. Syntheses, Coll. Vol.*, **4**, 907 (1963).

⁴⁷³ R. Cornubert and H. Le Bihan, *Bull. Soc. Chim. France*, [4] **41**, 1077 (1927).

⁴⁷⁴ G. Lindauer, *Monatsh. Chem.*, **21**, 72 (1900).

⁴⁷⁵ A. Franke and R. Stern, *Monatsh. Chem.*, **49**, 21 (1928).

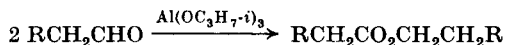
⁴⁷⁶ A. Baeyer and V. Drewsen, *Ber.*, **15**, 2856 (1882).

⁴⁷⁷ A. Meerwein, *Ber.*, **53**, 1829 (1920).

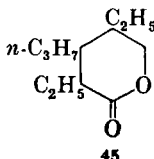
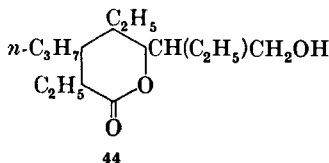
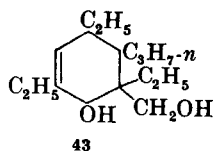
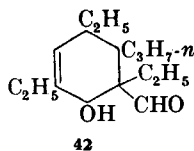
⁴⁷⁸ R. H. Hall, *J. Chem. Soc.*, 4303 (1954).

to lactones (ring opening occurs in aqueous base). Enamine intermediates and acid catalysts lead to aldol condensation products.

The condensation of aliphatic aldehydes to esters (Tischenko condensation) is most readily effected by aluminum alkoxides at room temperature.^{104, 479} Alkoxides such as $Mg[Al(OC_2H_5)_4]_2$ and calcium ethoxide cause formation of glycol esters.^{104, 453}



When aliphatic aldehydes are subjected to vigorous, base-catalyzed reaction conditions (relatively high temperatures, high catalyst concentration), numerous reactions (including Cannizzaro reaction) other than aldol condensation may ensue and some of these have been studied. Resin-like polymers result from very reactive aldehydes such as acetaldehyde and certain α,β -unsaturated aldehydes.^{457, 480-482} Butanal undergoes self-condensation with concentrated aqueous alcoholic potassium or sodium hydroxide (25-110°) to produce several products including butanol, 2-ethyl-2-hexen-1-ol, butyric acid, 2-ethyl-2-hexenoic acid, the aldol **42**, the glycol **43**, and the lactones **44** and **45**, some of these (**42-44**) in yields up to 40-50% depending on reaction conditions.^{66, 391, 393, 483-485} Products **43-45** are derived from **42** and butanal or 2-ethyl-2-hexenal by



⁴⁷⁹ I. Lin and A. R. Day, *J. Am. Chem. Soc.*, **74**, 5133 (1952).

⁴⁸⁰ A. Michael and A. Kopp *Am. Chem. J.*, **5**, 182 (1883).

⁴⁸¹ J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, pp. 43-123, Interscience, New York, 1963.

⁴⁸² E. E. Degering and T. Stoudt, *J. Polymer Sci.*, **7**, 653 (1951).

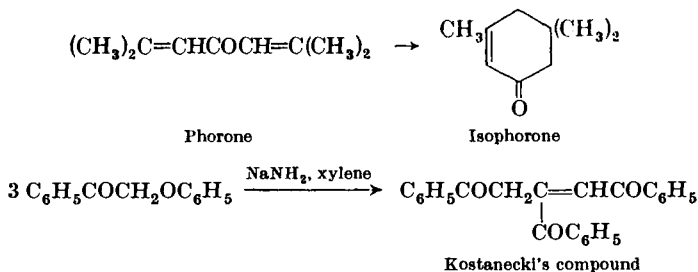
⁴⁸³ M. Häusermann, *Helv. Chim. Acta*, **34**, 1482 (1951).

⁴⁸⁴ P. Y. Blanc, A. Perret, and F. Teppa, *Helv. Chim. Acta*, **47**, 567, 725 (1964).

⁴⁸⁵ R. H. Hall and K. H. W. Tuerck, Brit. pat. 608,985 [*C.A.*, **44**, 4493 (1950)].

reactions which include hydride transfer.^{381, 383} Compounds of undetermined structure, composed of four aldehyde units, have been reported to form with strong base from other aliphatic aldehydes including propanal,^{383, 485-487} pentanal,⁴⁸⁸⁻⁴⁹¹ 2-hexenal,⁴⁹² hexanal,⁴⁹² and heptanal.^{483, 487-496} It is likely that some of these products are homologs of 42-45.

The self-condensation of ketones can lead to various side reactions.⁴⁹⁷⁻⁵⁰⁶ Isophorone is produced from phorone (from acetone) with basic catalysts by an intramolecular Michael addition;⁵⁰² homoisophorones are formed similarly from 2-butanone.⁵⁰³ Homoisophorone formation is also acid-catalyzed.⁵⁰⁴ "Kostanecki's compound,"⁴⁹⁷ formed by self-condensation of phenoxyacetophenone with sodium or sodium amide in xylene, has been shown to be 1,2,3-tribenzoylpropene.⁴⁹⁸⁻⁵⁰¹



1,3,5-Trisubstituted benzenes are obtained from methyl ketones, particularly with acid catalysts. Acetone yields mesitylene,⁵⁰⁵ and

⁴⁸⁵ J. Dueasse, *Bull. Soc. Chim. France*, [5] 11, 333 (1944).

⁴⁸⁷ A. v. Lenz, *Monatsh. Chem.*, 24, 155 (1903).

⁴⁸⁸ F. Gäss and C. Hell, *Ber.*, 8, 369 (1875).

⁴⁸⁹ G. Bruylants, *Ber.*, 8, 414 (1875).

⁴⁹⁰ A. Borodin, *Ber.*, 5, 480 (1872).

⁴⁹¹ A. Borodin, *Ber.*, 6, 982 (1873).

⁴⁹² H. Anselm and E. Nickl, Ger. pat. 752,482 [*C.A.*, 50, 2658 (1956)].

⁴⁹³ W. H. Perkin, Jr., *J. Chem. Soc.*, 43, 45 (1883).

⁴⁹⁴ W. H. Perkin, Jr., *J. Chem. Soc.*, 43, 79 (1883).

⁴⁹⁵ W. H. Perkin, Jr., *Ber.*, 15, 2802 (1882).

⁴⁹⁶ H. G. Kuivila, S. C. Slack, and P. K. Siiteri, *J. Am. Chem. Soc.*, 73, 123 (1951).

⁴⁹⁷ S. v. Kostanecki and J. Tambor, *Ber.*, 35, 1679 (1902).

⁴⁹⁸ R. E. Lutz and F. S. Palmer, *J. Am. Chem. Soc.*, 57, 1947 (1935).

⁴⁹⁹ P. Yates, D. G. Farnum, and G. H. Stout, *Chem. Ind. (London)*, 821 (1956).

⁵⁰⁰ P. F. Devitt, E. M. Philbin, and T. S. Wheeler, *Chem. Ind. (London)*, 822 (1956).

⁵⁰¹ P. F. Devitt, E. M. Philbin, and T. S. Wheeler, *J. Chem. Soc.*, 510 (1958).

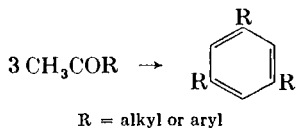
⁵⁰² K. Hess and K. Munderloh, *Ber.*, 51, 377 (1918).

⁵⁰³ C. Porlezza and V. Gatti, *Gazz. Chim. Ital.*, 55, 224 (1925).

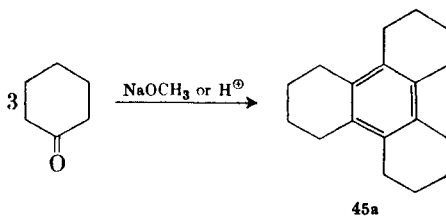
⁵⁰⁴ F. B. Ekeley and W. W. Howe, *J. Am. Chem. Soc.*, 45, 1917 (1923).

⁵⁰⁵ R. Adams and R. W. Hufferd, *Org. Syntheses, Coll. Vol.*, 1, 341 (1941).

⁵⁰⁶ A. F. Odell and C. W. Hines, *J. Am. Chem. Soc.*, 35, 81 (1913).



acetophenone yields 1,3,5-triphenylbenzene.⁵⁰⁶ Such reactions may also be catalyzed by bases⁵⁰⁷ and can occur with cycloalkanones. Cyclohexanone with sodium methoxide or acid catalysts forms the dodecahydrotriphenylene **45a**; cyclopentanone and 1-indanone behave analogously.^{160, 508, 509}



Side reactions involving the aldehyde are encountered in aldehyde-ketone condensations. An important side reaction is self-condensation of aliphatic aldehydes (particularly those having an α -methylene group) to aldols, since this reaction may proceed more rapidly than condensation with the ketone. Slow addition of the aldehyde to a large molar excess of ketone containing the catalyst may circumvent this difficulty; or, for ketones which do not undergo self-condensation readily (diisopropyl ketone), the ketone anion may be formed irreversibly with a strong base before adding the aldehyde.¹⁷⁷ Only occasionally does the separation of aldehyde self-condensation by-products create difficulty (butanal-acetone condensation, for example).⁵¹⁰⁻⁵¹² Side reactions of ketone self-condensation are important only with acetone (to yield mesityl oxide) in condensation with unreactive aldehydes such as pivaldehyde which do not undergo self-condensation.⁵¹¹

Retrograde aldol condensation may present difficulties. An attempt to condense propanal with a large excess of 3-methyl-2-butanone led only to propionaldol and 2-methyl-2-pentenal; no aldehyde-ketone condensation products could be isolated under conditions whereby acetaldehyde and

⁵⁰⁷ P. D. Bartlett, M. Roha, and M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

⁵⁰⁸ J. Hausmann, *Ber.*, **22**, 2019 (1889).

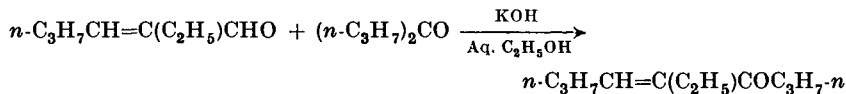
⁵⁰⁹ H. Stobbe and F. Zschoch, *Ber.*, **60**, 457 (1927).

⁵¹⁰ E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 905 (1930).

⁵¹¹ R. Heilmann, G. de Gaudemaris, P. Arnaud, and G. Scheuerbrandt, *Bull. Soc. Chim. France*, 112 (1957).

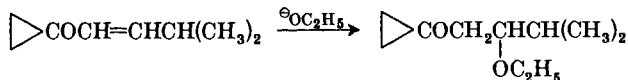
⁵¹² G. de Gaudemaris and P. Arnaud, *Compt. Rend.*, **241**, 1311 (1955).

butanal readily produce good yields of ketols with this ketone.²⁷² An attempt to condense 3-(3,4-methylenedioxyphenyl)-2-propenal with 3,3-dimethyl-2-butanone led to a piperonal condensation product (73% yield) due to cleavage of the propenal.⁵¹³ An attempt to condense 2-ethyl-2-hexenal with 4-heptanone (aqueous ethanolic potassium hydroxide catalyst) led to 5-ethyl-5-nonen-4-one derived from butanal and the ketone.^{222, 514} The formation of *bis*-styryl ketones from styryl alkyl ketones with basic catalysts is a similar reaction.⁵¹⁵



The position of the double bond in unsaturated carbonyl compounds obtained as condensation products is pertinent. α,β -Unsaturation predominates in the reaction equilibria in most examples. β,γ -Unsaturation is favored by alkyl substituents in the α position and, to a greater extent, in the γ position.^{80, 142, 274, 516-518} Acid catalysts favor formation of α,β -unsaturated ketones with endocyclic double bonds in condensations of benzaldehyde with cyclohexanones and cyclopentanones; with basic catalysts the product has an exocyclic double bond.³⁰⁴ The mechanism of the base-catalyzed $\alpha, \beta \rightleftharpoons \beta, \gamma$ interconversion has been studied.⁹⁴

α,β -Unsaturation undergo many additions to the olefinic double bond which account for side reactions. Addition of alkoxide ion may lead to ethers when alcoholic or aqueous alcoholic base is employed.^{513, 519} The presence of these products can complicate the separation of liquid ketols by distillation, as the mixture of 1-cyclopropyl-3-ethoxy-4-methyl-1-pentanone and the related ketol.⁵²⁰ Secondary amine catalysts may undergo a similar addition reaction leading to β -aminoketones.^{325, 327, 521}



⁵¹³ S. G. Powell and W. J. Wasserman, *J. Am. Chem. Soc.*, **79**, 1934 (1957).

⁵¹⁴ E. G. Fischer and K. Löwenberg, *Ann.*, **494**, 263 (1932).

⁵¹⁵ I. M. Heilbron and J. S. Buck, *J. Chem. Soc.*, **119**, 1500 (1921).

⁵¹⁶ S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1538 (1963).

⁵¹⁷ P. Maroni and J. E. Dubois, *Bull. Soc. Chim. France*, 126 (1955).

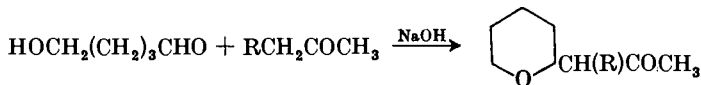
⁵¹⁸ K. G. Lewis and G. J. Williams, *Tetrahedron Letters*, 4573 (1965).

⁵¹⁹ R. C. Fuson and C. H. McKeever, *J. Am. Chem. Soc.*, **62**, 999 (1940).

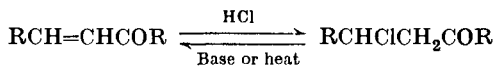
⁵²⁰ A. T. Nielsen, D. W. Moore, and K. Highberg, *J. Org. Chem.*, **26**, 3691 (1961).

⁵²¹ W. Dilthey and N. Nagel, *J. Prakt. Chem.*, [2] **130**, 147 (1931).

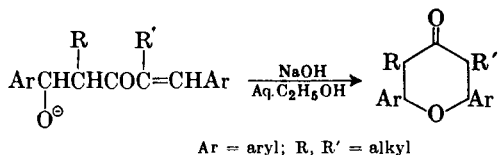
1-Alkyl-1-(2-tetrahydropyranyl)-2-propanones are reported to result from the condensation of 5-hydroxypentanal with methyl ketones.⁵²² Hydrogen chloride adds to α,β -unsaturated ketones forming β -chloroketones;



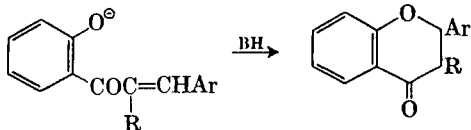
however, these products are ordinarily quite easily reconverted to α,β -unsaturated ketones by heating or treatment with bases such as quinoline, potassium carbonate, potassium hydroxide, or sodium ethoxide (ethanol or water solvent).



The formation of γ -pyrones, frequently encountered in base-catalyzed condensations of benzaldehyde (2 mole equivalents) with certain aliphatic ketones (2-butanone, 3-pentanone) is a result of intramolecular alkoxide addition in a *bis*-condensation product.^{523, 524}



The base-catalyzed formation of chromanones (flavanones) from 2-hydroxyphenyl styryl ketones is another example of this type of reaction.⁵²⁵⁻⁻⁵²⁹ γ -Pyrone formation may be acid-catalyzed as in the



condensation of benzaldehyde with 2,6-dialkylcyclohexanones; **46** (R = CH₃, Ar = C₆H₅) was formed in 88% yield (hydrogen chloride

⁵²² J. Colonge and P. Corbet, *Bull. Soc. Chim. France*, 283 (1960).

⁵²³ F. R. Japp and W. Maitland, *J. Chem. Soc.*, **85**, 1488 (1904).

⁵²⁴ D. Vorländer and F. Kalkow, *Ber.*, **30**, 2268 (1897).

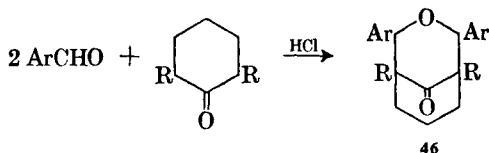
⁵²⁵ S. v. Kostanecki, R. Levi, and J. Tambor, *Ber.*, **32**, 326 (1899).

⁵²⁶ S. v. Kostanecki and S. Oderfeld, *Ber.*, **32**, 1926 (1899).

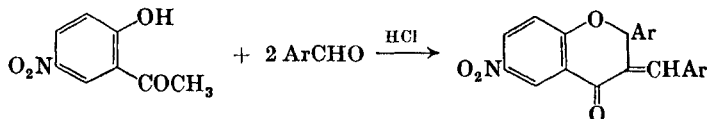
⁵²⁷ L. Reichel, W. Burkhart, and K. Müller, *Ann.*, **550**, 146 (1942).

⁵²⁸ C. C. Patel and N. M. Shah, *J. Indian Chem. Soc.*, **31**, 867 (1954).

⁵²⁹ R. Neu, *Arch. Pharm.*, **295**, 1 (1962) [*C.A.*, **57**, 7153 (1962)].



catalyst).⁵³⁰⁻⁵³² The hydrogen chloride-catalyzed condensation of nitro-2-hydroxyacetophenones with an excess of aromatic aldehyde leads to 3-arylideneflavanones.^{533, 534}



Michael additions to α,β -unsaturated ketones are the basis for many side reactions. 1,5-Diketones result from the addition of ketones, a reaction favored by use of more concentrated base and excess ketone. The diketones (47) frequently are formed from aromatic ketones and aromatic aldehydes,^{526, 532, 535-549} less frequently (except formaldehyde) from aliphatic aldehydes.⁵⁴⁷ Substitution in the acetophenone inhibits this side reaction.⁵⁴⁹ Benzaldehyde and desoxybenzoin may yield benzamaron (47, Ar, Ar', Ar'', R = C₆H₅).^{546, 548} Cycloalkanones also form 1,5-diketones (48),^{550-551a} which may undergo intramolecular aldol

⁵³⁰ A. Haller and R. Cornubert, *Bull. Soc. Chim. France*, [4] **39**, 1621 (1926).

⁵³¹ A. Haller and R. Cornubert, *Bull. Soc. Chim. France*, [4] **41**, 367 (1927).

⁵³² R. Cornubert and C. Borrel, *Compt. Rend.*, **183**, 294 (1926).

⁵³³ T. Széll and R. E. M. Unyi, *J. Org. Chem.*, **28**, 1146 (1963).

⁵³⁴ A. C. Annigeri and S. Siddappa, *Indian J. Chem.*, **1**, 484 (1963).

⁵³⁵ M. N. Tilichenko and V. G. Kharchenko, *Zh. Obshch. Khim.*, **32**, 1192 (1962) [*C.A.* **58**, 1414 (1963)].

⁵³⁶ W. Feuerstein and S. v. Kostanecki, *Ber.*, **32**, 315 (1899).

⁵³⁷ S. v. Kostanecki and L. Podrajansky, *Ber.*, **29**, 2248 (1896).

⁵³⁸ S. v. Kostanecki and G. Rossbach, *Ber.*, **29**, 2245 (1896).

⁵³⁹ J. Blumstein and S. v. Kostanecki, *Ber.*, **33**, 1478 (1900).

⁵⁴⁰ W. Dilthey, *J. Prakt. Chem.*, [2] **101**, 177 (1921).

⁵⁴¹ W. Dilthey and R. Taucher, *Ber.*, **53**, 252 (1920).

⁵⁴² A. Cornelson and S. v. Kostanecki, *Ber.*, **29**, 240 (1896).

⁵⁴³ W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955).

⁵⁴⁴ H. v. Lendenfeld, *Monatsh. Chem.*, **27**, 969 (1906).

⁵⁴⁵ C. S. Marvel, L. E. Coleman, and G. P. Scott, *J. Org. Chem.*, **20**, 1785 (1955).

⁵⁴⁶ F. Klingemann, *Ann.*, **275**, 50 (1893).

⁵⁴⁷ M. N. Tilichenko, *Zh. Obshch. Khim.*, **25**, 2503 (1955) [*C.A.*, **50**, 9327 (1956)].

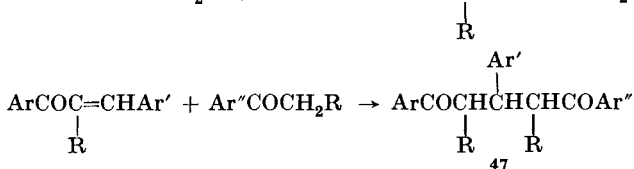
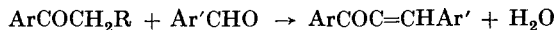
⁵⁴⁸ F. Klingemann, *Ber.*, **26**, 818 (1893).

⁵⁴⁹ L. C. Raiford and L. K. Tanzer, *J. Org. Chem.*, **6**, 722 (1941).

⁵⁵⁰ J. Colonge, J. Dreux, and H. Delplace, *Bull. Soc. Chim. France*, 1635 (1956).

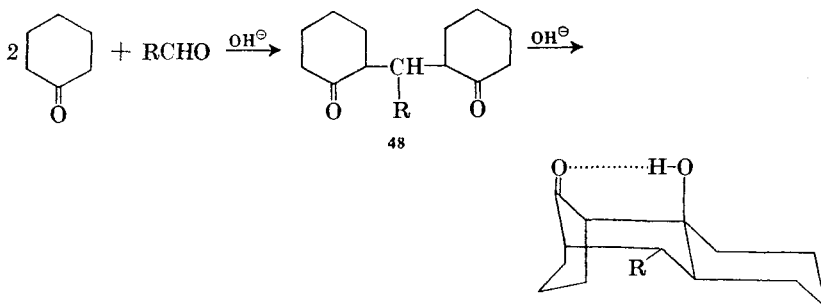
⁵⁵¹ M. N. Tilichenko, *Zh. Obshch. Khim.*, **10**, 718 (1940) [*C.A.*, **35**, 2471 (1940)].

^{551a} A. Polsky, J. Huet, and J. Dreux, *Compt. Rend., Ser. C*, **262**, 1543 (1966).



Ar, Ar', Ar'' = aryl
R = aryl, alkyl, or H

condensation to yield tricyclic ketols, **49**.^{552-555a} The latter have also been obtained from cyclohexanone and a primary alcohol, RCH₂OH.⁵⁵⁶ 1,3-Diketones³²⁸⁻³³² and desoxybenzoins⁵⁵⁷ readily form 1,5-diketones, especially with formaldehyde.⁵⁵⁸



R = aryl, alkyl, or H

The base-catalyzed self-condensation of α,β -unsaturated ketones proceeds initially as a Michael condensation to form as the primary product an acyclic monoolefinic 1,5- or 1,7-diketone. As the final product there results either (A) the acyclic monoolefinic diketone, (B) a cyclic saturated diketone, (C) a cyclic monoolefinic ketol, or (D) a cyclic diolefinic mono-ketone; products B-D arise from A by Michael or aldol condensations. Numerous examples of these various possibilities are known,^{322a, 520, 559-560b}

⁵⁵² M. N. Tilichenko, *Uch. Zap. Saratovsk. Gos. Univ.*, **75**, 60 (1962) [*C.A.*, **60**, 419 (1964)].

⁵⁵³ N. Barbulescu, *Rev. Chim. (Bucharest)*, **7**, 45 (1958) [*C.A.*, **51**, 3470 (1957)].

⁵⁵⁴ J. Pithia, M. N. Tilichenko, and V. G. Kharchenko, *Zh. Obshch. Khim.*, **34**, 1936 (1964) [*C.A.*, **61**, 8163 (1964)].

⁵⁵⁵ J. Pithia, J. Plesek, and M. Horak, *Collection Czech. Chem. Commun.* **26**, 1209 (1961).

^{555a} L. Ivan and N. Barbulescu, *Analele Univ. Bucuresti Ser. Stiint. Nat.*, **12**, 155 (1963) [*C.A.* **65**, 2145 (1966)].

⁵⁵⁶ P. Munk and J. Plesek, *Chem. Listy*, **51**, 633 (1957) [*C.A.*, **51**, 11261 (1957)].

⁵⁵⁷ L. Mehr, E. I. Becker, and P. E. Spoerri, *J. Am. Chem. Soc.*, **77**, 984 (1955).

⁵⁵⁸ M. Scholtz, *Ber.*, **35**, 2295 (1897).

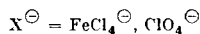
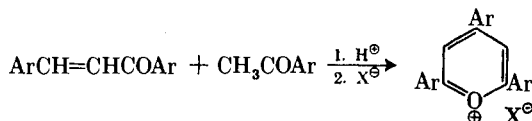
⁵⁵⁹ J. Wiemann and J. Dupayrat, *Bull. Soc. Chim. France*, 209 (1961).

⁵⁶⁰ B. Furth and J. Wiemann, *Bull. Soc. Chim. France*, 1819 (1965).

^{560a} G. Kabas and H. C. Rutz, *Tetrahedron*, **22**, 1219 (1966).

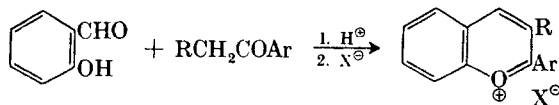
^{560b} O. Samuel and R. Setton, *Bull. Soc. Chim. France*, 1201 (1966).

chalcones is favored by the presence of electron-releasing groups such as methoxy or dimethylamino.⁵⁶⁵⁻⁵⁶⁷ The reaction may result by using 2 mole equivalents of the ketone and 1 of the aldehyde with acid catalysts (with basic catalysts an intermediate 1,5-diketone is formed which may subsequently be cyclized by acid catalysts). The pyrylium cations may be isolated as their chloroferrates or perchlorates.

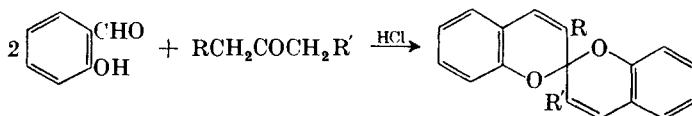


Ar = aryl with electron-releasing substituents

Benzopyrylium salts result from 2-hydroxy aromatic aldehydes and aromatic ketones.⁵⁶⁸⁻⁵⁷³ Spiro compounds are obtained from 2-hydroxy



aromatic aldehydes (2 mole equivalents) and alkyl ketones (including dibenzyl ketone) with hydrogen chloride catalyst.^{239, 574, 575}



R, R' = alkyl or aryl

EXPERIMENTAL CONDITIONS

Reaction conditions are extremely important. A great variety of experimental procedures has been employed and it is quite difficult to make generalizations of broad applicability. In a series of papers Dubois

⁵⁶⁵ W. Dilthey, *J. Prakt. Chem.*, [2] **95**, 107 (1917).

⁵⁶⁶ W. Dilthey, C. Berres, E. Holterhoff, and H. Wübken, *J. Prakt. Chem.*, [2] **114**, 179 (1926).

⁵⁶⁷ R. Wizinger, S. Losinger, and P. Ulrich, *Helv. Chim. Acta*, **39**, 5 (1956).

⁵⁶⁸ H. Decker and T. von Fellenberg, *Ber.*, **40**, 3815 (1907).

⁵⁶⁹ H. Decker and T. von Fellenberg, *Ann.*, **364**, 1 (1909).

⁵⁷⁰ J. W. Gramshaw, A. W. Johnson, and T. J. King, *J. Chem. Soc.*, 4040 (1958).

⁵⁷¹ W. H. Perkin, Jr., R. Robinson, and M. R. Turner, *J. Chem. Soc.*, **93**, 1085 (1908).

⁵⁷² S. G. Sastry and B. N. Ghosh, *J. Chem. Soc.*, **107**, 1442 (1915).

⁵⁷³ A. Robertson and R. Robinson, *J. Chem. Soc.*, 1951 (1926).

⁵⁷⁴ W. Dilthey and H. Wübken, *Ber.*, **61**, 963 (1928).

⁵⁷⁵ R. Dickinson and I. M. Heilbron, *J. Chem. Soc.*, 1699 (1927).

reported a detailed study of experimental conditions influencing the aldol condensation.^{269, 576-581} Condensations of aldehydes with 2-butanone^{582, 583} and chalcone formation³³⁸ have been reviewed. The reaction conditions (catalyst, solvent, temperature, reaction time, and ratio of reactants) are summarized in the following discussion, which applies principally to conditions such that the reaction course is determined by thermodynamic considerations.

Catalyst. The choice of catalyst and its concentration are extremely important factors in determining a successful condensation. The matter of catalyst concentration has often been overlooked. Dubois' experiments clearly demonstrate the signal importance of this factor, particularly in base-catalyzed reactions of simple aliphatic aldehydes and ketones.^{269, 576-581} For example, in the condensation of acetaldehyde with acetone to yield the ketol, 4-hydroxy-2-pentanone, a maximum yield of 87% could be obtained under appropriate conditions at a particular concentration of potassium hydroxide in ethanol; a very slight increase or decrease of catalyst concentration from the optimum value produced an abrupt decrease in yield of ketol.⁵⁷⁷ The rates of the forward and reverse reactions and their relative magnitudes are important in determining the required catalyst concentration for a particular condensation. Excess base favors the retrograde process of cleaving aldols to reactants, but if the base concentration is too low the forward rate is too slow. Fortunately, most aldol condensations are not extremely sensitive to catalyst concentration. Often the reverse process is not rapid, as when an α,β -unsaturated carbonyl compound, rather than an aldol, is the product and only a small amount of catalyst is needed to secure maximum yield. Excess base favors dehydration and is to be avoided if aldols are desired. In certain procedures, salts of weak acids such as sodium carbonate, sodium phosphate, or potassium cyanide serve to provide a buffered control of pH and optimum conditions. Acid-catalyzed condensations are generally not so sensitive to catalyst concentration because these reactions are largely irreversible and, with few exceptions, lead to α,β -unsaturated carbonyl compounds.

Although a wide variety of materials have been employed as catalysts in the aldol condensation, frequent use is limited to a few. In the following

⁵⁷⁶ J. E. Dubois, *Bull. Soc. Chim. France*, [5] **16**, 66 (1949).

⁵⁷⁷ J. E. Dubois, *Ann. Chim. (Paris)*, [12] **6**, 406 (1951).

⁵⁷⁸ J. E. Dubois, *Compt. Rend.*, **235**, 296 (1952).

⁵⁷⁹ J. E. Dubois and R. Luft, *Bull. Soc. Chim. France*, 1148 (1954).

⁵⁸⁰ J. E. Dubois and R. Luft, *Bull. Soc. Chim. France*, 1153 (1954).

⁵⁸¹ J. E. Dubois, *Bull. Soc. Chim. France*, 272 (1955).

⁵⁸² M. G. J. Beets and H. van Essen, *Rec. Trav. Chim.*, **77**, 1138 (1958).

⁵⁸³ H. Haeussler and C. Brugger, *Ber.*, **77**, 152 (1944).

discussion, catalysts have been classified by chemical type and approximate base strength.

Primary and secondary, but not tertiary, amines are of value as catalysts for reactions with very reactive aldehydes that are sensitive to stronger bases, and for reactions with ketones of high enol content such as 1,3-diketones. The amines can react to form imine or enamine intermediates. Pyrrolidine and piperidine are quite effective for intramolecular condensations.^{48, 68, 76, 382, 406, 436} Added acid, usually acetic, often facilitates the condensation (cf. p. 8). Pyrrolidinium and piperidinium acetates have been employed in self-condensation or mixed condensation reactions of α,β -unsaturated aldehydes leading to polyenals,^{105-111, 115, 514, 584-587} and in condensation of aldehydes with 1,3-diketones.^{216, 217, 328-332, 588-596} These catalysts have also been employed in condensations of aldehydes with 1,2-diketones,³²⁵ desoxybenzoins,^{597, 598} and tetrahydro- γ -pyrone.⁵⁹⁹ In the condensation of 4-dimethylaminobenzaldehyde with certain 1,2,3,4-tetrahydro-1-methyl-4-oxoquinolines, piperidine was effective where sodium hydroxide failed, although the situation was reversed in the condensation of benzaldehyde with these ketones; i.e., sodium hydroxide was the most effective catalyst.³⁶⁸ In the condensation of aromatic aldehydes with phenylacetone, piperidine caused condensation at the methylene group,²⁶⁵⁻²⁶⁷ whereas sodium hydroxide produced condensation at the methyl group (see discussion p. 35).²⁶⁴ Piperidine was effective at high temperature (175-200°) for the rapid condensation of indole-3-carboxaldehydes with acetophenone.⁶⁰⁰ Diethylamine effected condensation of *o*-phthalaldehyde with phenylacetone and with 2,4-pentanedione to yield the corresponding *bis*-ketols in excellent yields; potassium hydroxide was ineffective for this purpose.⁶⁰¹ Other amines have found

⁵⁸⁴ G. W. Seymour and V. S. Salvin, U.S. pat. 2,408,127 [*C.A.*, **41**, 772 (1947)].

⁵⁸⁵ E. Barraclough, J. W. Batty, I. M. Heilbron, and W. E. Jones, *J. Chem. Soc.*, 1549 (1939).

⁵⁸⁶ R. Kuhn and C. J. O. Morris, *Ber.*, **70**, 853 (1937).

⁵⁸⁷ P. Karrer and A. Rügger, *Helv. Chim. Acta*, **23**, 284 (1940).

⁵⁸⁸ E. Knoevenagel, *Ber.*, **37**, 4461 (1904).

⁵⁸⁹ E. Hase and G. Stjernvall, *Suomen Kemistilehti*, **21B**, 42 (1948) [*C.A.*, **42**, 8176 (1948)].

⁵⁹⁰ H. Midorikawa, *Bull. Chem. Soc. Japan*, **27**, 149 (1954).

⁵⁹¹ P. T. Mora and T. Széki, *J. Am. Chem. Soc.*, **72**, 3009 (1950).

⁵⁹² H. Schlenk, *Chem. Ber.*, **81**, 175 (1948).

⁵⁹³ H. Schlenk, *Chem. Ber.*, **85**, 901 (1952).

⁵⁹⁴ N. A. Sørensen, E. Samuelsen, and F. R. Oxaal, *Acta Chem. Scand.*, **1**, 458 (1947).

⁵⁹⁵ R. H. Wiley, C. H. Jarboe, and H. G. Ellert, *J. Am. Chem. Soc.*, **77**, 5102 (1955).

⁵⁹⁶ P. Delest and R. Pallaud, *Compt. Rend.*, **245**, 2056 (1957).

⁵⁹⁷ A. Dornow and F. Boberg, *Ann.*, **578**, 122 (1952).

⁵⁹⁸ K. Matsumura, *J. Am. Chem. Soc.*, **57**, 496 (1935).

⁵⁹⁹ N. J. Leonard and D. Choudhury, *J. Am. Chem. Soc.*, **79**, 156 (1957).

⁶⁰⁰ R. B. Van Order and H. G. Lindwall, *J. Org. Chem.*, **10**, 128 (1945).

⁶⁰¹ W. Davey and H. Gottfried, *J. Org. Chem.*, **26**, 3699 (1961).

limited use as catalysts for the aldol condensation (dimethylamine, morpholine, pyridine,⁵⁰ triethylamine⁴⁸²) and generally are less effective than piperidine and pyrrolidine.

Alkali and alkaline earth metal hydroxides in dilute solution are very effective catalysts for the aldol condensation and have found the widest use. A study has been made of the effect of the nature of the cation on catalytic activity of hydroxides.⁵⁸² Sodium hydroxide in aqueous or aqueous ethanolic solution is the catalyst most frequently employed; potassium hydroxide is equally effective. By selecting a suitable catalyst concentration and solvent, excellent yields of condensation product may often be obtained. For condensations involving very reactive or base-sensitive aldehydes such as formaldehyde or α,β -unsaturated aldehydes the alkaline earth hydroxides, calcium or barium hydroxide, are valuable catalysts.^{278, 514, 602} Barium oxide is effective for preparing diacetone alcohol from acetone (Soxhlet apparatus, 75% yield),¹⁴⁷ but 2-butanone under the same conditions affords the homologous ketol in only 11% yield.¹⁴⁶ Quaternary ammonium hydroxides such as Triton-B have found only limited use as aldol condensation catalysts.⁵⁸²

Alkoxides of the alkali and alkaline earth metals and of magnesium and aluminum are frequently employed as catalysts. These strong bases are often effective when sodium hydroxide fails. Sodium ethoxide in ethanol has been widely employed and is very efficient, especially for preparation of most chalcones; sodium methoxide, potassium methoxide, and lithium ethoxide⁵⁸² have been used effectively, but less frequently. Other alkoxides have been employed, principally in aprotic solvents such as ether, benzene, or toluene. Excellent solvents less commonly employed are tetrahydrofuran, 1,2-dimethoxyethane, and dimethylformamide.⁶⁰³ Sodium *t*-amyloxide (soluble in benzene or toluene) rapidly condenses aromatic aldehydes with cycloalkanones at 0°,²⁹⁵ and sodium pentoxide has been employed for self-condensation of 3-methylbutanal at 75°.⁶⁰⁴ Potassium *t*-butoxide in boiling benzene has been employed for self-condensation of cycloalkanones to α,β -unsaturated ketones⁶⁰⁵ and for the cyclization of certain diketones.⁶⁰⁶ Solvent-free potassium *t*-butoxide is less soluble in benzene than is sodium *t*-amyloxide; it is soluble in 1,2-dimethoxyethane, whereas the solvated material is not. Although aluminum alkoxides

⁶⁰² A. Kuzin, *Zh. Obshch. Khim.*, **8**, 592 (1938) [*C.A.*, **33**, 1271 (1939)].

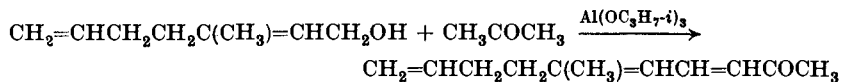
⁶⁰³ A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962); A. J. Parker, *Advan. Org. Chem.*, **5**, 1-46 (1965).

⁶⁰⁴ V. I. Lyubomilov, *Zh. Obshch. Khim.*, **26**, 2738 (1956) [*C.A.*, **51**, 7293 (1957)].

⁶⁰⁵ W. Rosenfelder and D. Ginsburg, *J. Chem. Soc.*, 2955 (1954).

⁶⁰⁶ P. Wieland, K. Heusler, H. Ueberwasser, and A. Wettstein, *Helv. Chim. Acta*, **41**, 74 (1958).

(particularly isopropoxide) generally produce Tischenko reactions (ester formation) with aldehydes,^{104, 479} aluminum *t*-butoxide in boiling benzene has been found effective for condensation of high-molecular-weight polyenals with ketones^{607, 608} or for the self-condensation of certain ketones.^{151, 609} In a novel procedure an allylic alcohol is oxidized to the corresponding aldehyde with aluminum isopropoxide in the presence of acetone; an aldol condensation follows to yield an α,β -unsaturated ketone.⁶¹⁰ Sodium phenoxide, employed as a catalyst in only one instance, was claimed to be



very effective in condensing citral with acetone (81% yield of unsaturated ketone).^{611, 612} Butoxymagnesium bromide and iodide have been employed for aldehyde self-condensations but are not too effective.⁶¹³ Alkali metal alkoxyborohydrides, with some exceptions, are ineffective catalysts.⁶¹⁴ Sodium metal was employed in condensations of aldehydes with camphor in the early work of Haller,³¹³ but its use is now generally avoided because of the competing reductions.

Alkali metal salts of weak acids have been employed effectively as catalysts. They provide the constant pH needed for condensations sensitive to hydroxide-ion concentration. Potassium and sodium carbonate are useful as mild catalysts for many aldehyde-aldehyde and aldehyde-ketone condensations for which a stronger base is undesirable; i.e., with formaldehyde, acetaldehyde, and α,β -unsaturated aldehydes. Sodium phosphate was found suitable for condensation of nitrobenzaldehydes with acetophenones to produce ketols.³⁶¹ Although potassium cyanide has been employed effectively for some condensations (the preparation of aldol itself⁶ and the condensation of acetaldehyde with methyl isopropyl ketone⁶¹⁵), it is seldom used; its catalytic effect appears to resemble that of sodium hydroxide very closely.⁵⁸² Potassium cyanide condenses aromatic aldehydes with acetophenones to yield complex cyano compounds⁶¹⁶ and causes self-condensation of aromatic aldehydes to

⁶⁰⁷ C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3972 (1958).

⁶⁰⁸ C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3986 (1958).

⁶⁰⁹ K. Billig, Ger. pat. 639,291 [*C.A.*, **31**, 1431 (1939)].

⁶¹⁰ R. Helg, F. Zobrist, A. Lauchenauer, K. Brack, A. Caliezi, D. Stauffacher, E. Zweifel, and H. Schinz, *Helv. Chim. Acta*, **39**, 1269 (1956).

⁶¹¹ Z. Arnold and K. Hejno, Czech. pat. 85,207 [*C.A.*, **50**, 10781 (1956)].

⁶¹² E. I. Kozlov, M. T. Yanotovskii, and G. I. Samokhvalov, *Zh. Obshch. Khim.*, **34**, 2748 (1964) [*C.A.*, **61**, 14716 (1964)].

⁶¹³ V. Grignard and M. Fluchaire, *Ann. Chim. (Paris)*, [10] **9**, 1 (1928).

⁶¹⁴ G. Hesse and M. Maurer, *Ann.*, **658**, 21 (1962).

⁶¹⁵ J. Salkind, *J. Russ. Phys. Chem. Soc.*, **37**, 484 (1905); [*Chem. Zentr.*, **76**, II, 752 (1905)].

⁶¹⁶ R. B. Davis, *J. Org. Chem.*, **24**, 880 (1959).

benzoins (the benzoin condensation).⁶¹⁷ The bases, sodium amide, sodium hydride, and calcium hydride, have been used occasionally and have value for condensations involving hindered aldehydes which do not readily undergo self-condensation.^{143, 314, 514, 618-622} They are polymeric solids insoluble in solvents with which they do not react. They are useful for preparing certain enolates in aprotic solvents; the reaction may be followed by measuring the hydrogen evolved. Enolates of methyl ketones usually cannot be prepared without concomitant aldol condensation.²⁴⁷ Certain soaps have been used effectively for self-condensation of aliphatic aldehydes.⁶²³⁻⁶²⁶ Sodium sulfite condensed 3,5-dimethyl-2,6-octadienal with acetone to 6,8-dimethyl-3,5,9-undecatrien-2-one in 67% yield.⁶²⁷ Alumina at room temperature has been used.^{404, 441} Barium nitride is reported to be a powerful catalyst for effecting self-condensation of ketones.^{627a} Several other salts have been employed at times as aldol condensation catalysts, but none appears to offer distinct advantages.

Aminomagnesium halides and some Grignard reagents are very effective aldol condensation agents in certain cases. Methylanilinomagnesium bromide provides high yields of ketols by self-condensation of most ketones.^{150, 159} Certain hindered ketones (non-methyl) for which this reagent cannot effect self-condensation are converted to their enolate anions, which may be treated with a different ketone or aldehyde to prepare a wide variety of ketols in good yield.^{177, 198} Certain Grignard reagents such as isopropyl- and *t*-butyl-magnesium bromide have been employed for self-condensation of hindered ketones to ketols,¹⁵⁷ but in general these catalysts appear to be less effective than methylanilinomagnesium bromide. Diethylzinc is an ineffective catalyst.⁶²⁸ Lithium amides [e.g., $(C_2H_5)_2NLi$]^{221, 629} are very strong bases and appear to be of potential value as aldol condensation catalysts.

Use of ion-exchange resins (basic types most frequently) as aldol

⁶¹⁷ W. S. Ide and J. S. Buck, *Org. Reactions*, **4**, 269-304 (1948).

⁶¹⁸ N. Wolff, *Ann. Chim. (Paris)*, [9] **20**, 82 (1923).

⁶¹⁹ C. Daesslé and H. Schinz, *Helv. Chim. Acta*, **40**, 2270 (1957).

⁶²⁰ H. Favre and H. Schinz, *Helv. Chim. Acta*, **41**, 1368 (1958).

⁶²¹ L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, **23**, 959 (1940).

⁶²² I. M. Heilbron, W. E. Jones, and J. W. Batty, *Brit. pat.* 510,540 [*C.A.*, **34**, 5092 (1940)].

⁶²³ R. A. Reek and R. P. Arthur, *U.S. pat.* 2,982,784 [*C.A.*, **55**, 20962 (1961)].

⁶²⁴ R. M. Cole, *U. S. pat.* 2,545,261 [*C.A.*, **45**, 6654 (1951)].

⁶²⁵ F. A. Biribauer, C. S. Carlson, and C. E. Morrell, *U.S. pat.* 2,684,385 [*C.A.*, **49**, 11002 (1955)].

⁶²⁶ J. Kollar and J. G. Schulz, *U.S. pat.* 3,060,236 [*C.A.*, **58**, 5517 (1963)].

⁶²⁷ A. A. Petrov, N. A. Razumova, and M. L. Genusov, *Zh. Obshch. Khim.*, **28**, 1128 (1958) [*C.A.*, **52**, 20027 (1958)].

^{627a} Y. Okamoto and J. C. Goswami, *Bull. Chem. Soc. Japan*, **39**, 2778 (1966).

⁶²⁸ R. Rieth and F. Beilstein, *Ann.*, **126**, 241 (1863).

⁶²⁹ G. Wittig and H. D. Frommelt, *Chem. Ber.*, **97**, 3541 (1964).

condensation catalysts has been studied often for self-condensation of aldehydes,^{100, 101, 630-632} but seldom for ketone-ketone or aldehyde-ketone condensations.^{337, 633, 634} Acetone provides a 79% yield of mesityl oxide when heated under reflux with Dowex 50H; good yields of aldols may be obtained from aliphatic aldehydes with ion-exchange catalysts when other catalysts fail.¹⁰⁰ In many other reactions, however, yields obtained with ion-exchange catalysts are somewhat inferior to those obtained with more conventional catalysts. In use, resin catalysts are often deactivated rapidly and cannot be reused.¹⁰⁰

Acid catalysts are less frequently employed for aldol condensations. Ordinarily α,β -unsaturated carbonyl products rather than aldols, are formed. A remarkable exception is phosphorus oxychloride which is reported to produce aldols from alkanals.^{102, 103} In general, yields are lower with acid catalysts and the products are more difficult to purify. With aldehyde-aldehyde condensations, acid catalysts usually lead to resin formation or other side reactions, and, except for intramolecular condensation of some α,ω -dialdehydes³⁷³⁻³⁸¹ and ketoaldehydes^{449, 450} (formed *in situ* from acetal precursors), have found little practical use. In the self-condensation of 2-butanone, and in condensations of aldehydes with methyl ketones, acid catalysts permit condensation at the methylene carbon, whereas basic catalysts cause condensation at the methyl group. Hydrogen chloride is the acid catalyst most often employed, although hydrogen bromide and hydrogen iodide appear to be more effective,^{152, 156} about two-thirds of 1 mole equivalent of hydrogen halide is needed to attain maximum yields.¹⁵² Frequently β -halo ketones result. They can be dehydrohalogenated to α,β -unsaturated ketones by treatment with ethanolic sodium hydroxide, but this treatment may cause some polymerization of the product. However, milder base treatment (pyridine, quinoline or potassium carbonate) in water or ethanol is often sufficient to effect dehydrohalogenation. Perchloro aldehydes such as chloral and trichloropropenal undergo condensations with ketones to yield ketols or α,β -unsaturated ketones in excellent yields with acid catalysts such as acetic or sulfuric acid.^{289, 635-639}

⁶³⁰ G. Durr, *Compt. Rend.*, **235**, 1314 (1952).

⁶³¹ I. G. Farbeniud. A.-G., Brit. pat. 349,556 [*C.A.*, **26**, 5430 (1932)].

⁶³² G. Durr and R. L. Farhi, *Compt. Rend.*, **245**, 75 (1957)].

⁶³³ B. Tomek and J. Cvrtnik, Czech. pat. 100,648 [*C.A.*, **58**, 4429 (1963)].

⁶³⁴ Rheinpreussen A.-G. für Bergbau und Chemie, Fr. pat. 1,383,548 [*C.A.*, **62**, 9013 (1965)].

⁶³⁵ F. L. Breusch and H. Keskin, *Arch. Biochem.*, **18**, 305 (1948).

⁶³⁶ W. Koenigs, *Ber.*, **25**, 792 (1892).

⁶³⁷ L. K. Zakharkin and L. P. Sorokina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1445 (1958) [*C.A.*, **53**, 8130 (1959)].

⁶³⁸ L. K. Zakharkin and L. P. Sorokina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 287 (1962) [*C.A.*, **57**, 12417 (1962)].

⁶³⁹ A. Roedig, R. Manger, and S. Schödel, *Chem. Ber.*, **93**, 2294 (1960).

Acid catalysts are of value for preparing certain hydroxy-substituted chalcones.^{640, 641} Condensation of 2-nitrobenzaldehyde with tetralones gives excellent yields of α,β -unsaturated ketones with sulfuric acid catalysis.⁶⁴²⁻⁶⁴⁴ In the reaction of 5-chloro- and 4-chloro-2-nitrobenzaldehyde with 4,4-dimethyl-1-tetralone, aqueous acetic acid and iron powder produced 90-94% yields of the corresponding amino α,β -unsaturated ketones by aldol condensation and reduction of the nitro group.⁶⁴⁵ This procedure may be of general value in preparing condensation products containing primary amino groups since condensations involving aminobenzaldehydes often give very poor yields³⁵⁰ and condensations with primary amino ketones may lead to Schiff bases.^{352, 359} Nitrofurans, carboxaldehydes and, to a lesser extent, nitrothiophene carboxaldehydes and ketones undergo resinification with base, and sulfuric acid in acetic acid has been advantageously employed in aldol condensations involving these substances.^{646, 647} Sulfuric acid has occasionally been used for cyclization of α,ω -diketones,^{384, 648} as has *p*-toluenesulfonic acid,⁴⁰³ but other catalysts, such as sodium carbonate and sodium methoxide, are often better. Seldom used, and generally less effective acid catalysts, are nitric acid, boron trifluoride, phosphorus oxychloride, phosphorus pentoxide, zinc chloride, ferric chloride, aluminum chloride, and acetic anhydride. Acetic acid is often used as a solvent when acid catalysts are employed.

Solvent. The choice of solvent generally depends on solubility of reactants and catalyst. Ethanol, aqueous ethanol, or water is most commonly employed; sodium ethoxide is used in ethanol. The heterogeneous mixture, aqueous sodium hydroxide-ether, has been found excellent for condensation reactions of reactive aliphatic aldehydes.⁶⁴⁹ Strong bases generally require aprotic solvents;⁶⁰⁹ methylanilinomagnesium bromide is employed in ether-benzene, and sodium amide is used as a suspension in ether, benzene, or toluene. Solvents less often exploited, such as tetrahydrofuran, 1,2-dimethoxyethane, dimethylformamide, and dimethyl sulfoxide^{649a} might offer advantages in some reactions. Hydrogen

⁶⁴⁰ J. F. Miguel, *Bull. Soc. Chim. France*, 1369 (1961).

⁶⁴¹ T. Széll, *Chem. Ber.*, **92**, 1672 (1959).

⁶⁴² V. L. Bell and N. H. Cromwell, *J. Org. Chem.*, **23**, 789 (1958).

⁶⁴³ A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

⁶⁴⁴ J. L. Adelfang and N. H. Cromwell, *J. Org. Chem.*, **26**, 2368 (1961).

⁶⁴⁵ N. H. Cromwell and V. L. Bell, *J. Org. Chem.*, **24**, 1077 (1959).

⁶⁴⁶ V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, *Zh. Obshch. Khim.*, **32**, 1324, 1329 (1962) [*C.A.*, **58**, 1422, 5603 (1963)].

⁶⁴⁷ S. V. Tsukerman, V. M. Nikitchenko, and V. F. Lavrushin, *Zh. Obshch. Khim.*, **32**, 2324 (1962) [*C.A.*, **58**, 7896 (1963)].

⁶⁴⁸ W. G. Dauben and J. W. McFarland, *J. Am. Chem. Soc.*, **82**, 4245 (1960).

⁶⁴⁹ V. Grignard and M. Dubien, *Ann. Chim. (Paris)*, [10] **2**, 282 (1924).

^{649a} B. Wesslen, *Acta. Chem. Scand.*, **21**, 713 (1967).

chloride is often used in the absence of a solvent and less frequently with methanol, ethanol, ethyl acetate, ether, or benzene. Ether or benzene, rather than an alcohol, would be preferred to avoid side reactions such as acetal formation. Acetic acid has been used as solvent for sulfuric acid and hydrogen chloride catalysis. The effect of solvent on the kinetics of the base-catalyzed cleavage of tertiary β -ketols has been studied.^{650, 651} The selection of solvent may be exploited to determine the ratio of 1-condensation to 3-condensation products derived from condensation reactions of methyl ketones.^{231, 248}

Temperature and Reaction Time. The aldol condensation is reversible and slightly exothermic, and best yields are generally obtained at 5–25° (however, low temperatures also favor aldehyde trimer formation; see p. 58). Rates are sufficiently rapid at room temperature that maximum yields are usually reached within 12 to 24 hours. For reactions which are more rapid or produce an unstable product, temperatures between 0 and 5°, or a short reaction time at room temperature, may be employed. Acid-catalyzed reactions usually require a low temperature; hydrogen chloride-catalyzed reactions are often conducted at 0–5°. For base-catalyzed reactions, reflux temperatures of solvents such as ethanol, ether, or benzene may be used to reduce the reaction time. Condensations of indole-3-carboxaldehydes with acetophenones have been accomplished at 175–200° (in the absence of added catalyst) within 5 minutes, giving good yields of α,β -unsaturated ketones.⁶⁰⁰ If the reaction is essentially irreversible, as is chalcone formation, and the product is stable, the higher temperature does not result in appreciably lower yields. Excessively high temperatures are generally unnecessary and are avoided, because side reactions are more likely to result. High temperatures favor the formation of α,β -unsaturated carbonyl compounds rather than aldols or ketols and favor 1-condensation over 3-condensation in reactions of aldehydes with methyl alkyl ketones.

Ratio of Reactants. In mixed condensations the ratio of reactants may determine products. Generally, stoichiometric quantities are employed. An important exception involves condensations of certain reactive aliphatic aldehydes with ketones where a large molar excess of ketone is often used to minimize self-condensation of the aldehyde and to secure best yields of 1:1 condensation products; the excess ketone does not undergo self-condensation under the reaction conditions and is recovered. Self-condensation of the aldehyde may also be minimized by very slow addition of the aldehyde to an excess of ketone containing the catalyst. In condensations of alicyclic ketones with aldehydes an excess

⁶⁵⁰ J. Barthel and J. E. Dubois, *Z. Phys. Chem.*, **32**, 296 (1962).

⁶⁵¹ J. Barthel and J. E. Dubois, *Compt. Rend.*, **248**, 1649 (1959).

of ketone may be required to minimize formation of *bis*-condensation products;²⁹⁷ with other ketones (except acetone) it is usually difficult to obtain other than 1:1 products.

An excess of aldehyde may be of value in condensations with unreactive ketones if the aldehyde does not readily condense with itself (e.g., aromatic aldehydes). Because formaldehyde does not readily undergo self-condensation and is very reactive, polymethylol compounds are easily produced with most active methylene compounds; however, an excess of formaldehyde can lead to reduction of carbonyl groups.

EXPERIMENTAL PROCEDURES

The best yields in aldol condensations are obtained when all reactants and solvents are carefully purified immediately before use. Although traces of peroxides do not inhibit the aldol condensation, larger amounts may cause lower yields.³⁸¹ Liquid aldehydes readily accumulate carboxylic and peroxidic impurities on storage; the impurities may be removed by careful washing with dilute aqueous sodium hydroxide or carbonate, followed by drying and distillation in a nitrogen atmosphere. Although liquid ketones are much less susceptible to oxidation than aldehydes, these reactants, too, should be carefully distilled before use. Melting points of solids should be checked as an indication of purity and samples recrystallized if necessary. Use of a nitrogen atmosphere during the reaction is of value, particularly in reactions of strongly basic enolates (prepared in aprotic solvents) since these intermediates react with oxygen and carbon dioxide; the inert atmosphere is also of value when oxidizable reactants or products are involved (α,β -unsaturated aldehydes or ketones, dialdehydes), and when reaction time is prolonged. However, there are routine condensations (many chalcone preparations, for example) which do not require an inert atmosphere.

In working up reaction mixtures conventional procedures are followed, but special care should be taken if products are to be distilled. Because many aldols and ketols readily dissociate to reactants when heated, isolation of these substances by distillation at a low temperature under reduced pressure in a nitrogen atmosphere is recommended. Complete removal of acidic or basic substances (including those in solvents used) prior to distillation is necessary for efficient recovery of liquid aldols or ketols because these impurities catalyze dissociation or dehydration. Thorough washing of the product (conveniently in purified ether solution) with saturated aqueous sodium bicarbonate will remove most undesirable impurities. α,β -Unsaturated aldehydes and ketones are readily oxidized, especially when heated in air, and should be distilled immediately after

work-up, under reduced pressure, preferably in a nitrogen atmosphere. Aldols dimerize on storage and should be redistilled before use. Redistillation of stored products may result in their decomposition (dealdolization, dehydration, or polymerization) unless accumulated acidic or peroxidic impurities are removed by washing with dilute aqueous alkali.

A few special procedures have been developed for certain reactions to avoid reversal of the condensation and to secure higher yields of product. One example is use of a column reactor in which formaldehyde and sodium hydroxide are added simultaneously to the vapor of refluxing ketone in a tube; a non-volatile acid is contained in the liquid ketone to neutralize the basic catalyst.⁶⁵² The use of barium oxide in a Soxhlet extractor leads to diacetone alcohol in good yield from acetone.^{146, 147} A cation-exchange resin has been employed for continuous removal of sodium hydroxide catalyst after condensation of acetone to diacetone alcohol.⁶⁵³

Several aldol condensation procedures are to be found in volumes of *Organic Syntheses*. Aldehydes condensed with acetone to yield α,β -unsaturated methyl ketones, $RCH=CHCOCH_3$, are as follows (yields in parentheses): citral (45–49),⁶⁵⁴ benzaldehyde (65–78),⁶⁵⁵ 4-methoxybenzaldehyde (83),⁶⁵⁵ and furfural (60–66).⁶⁵⁶ Dibenzalacetone (90–94%) has been prepared from benzaldehyde and acetone.⁶⁵⁷ Benzaldehyde has also been condensed with acetophenone to form chalcone (85%)⁶⁵⁸ and with pinacolone to form benzalpinacolone (88–93%).⁶⁵⁹

Also described in *Organic Syntheses* are procedures for the self-condensation of acetone to diacetone alcohol (71%)¹⁴⁷ employing a Soxhlet apparatus; the dehydration of this ketol to mesityl oxide;¹⁴⁹ the sulfuric acid-catalyzed condensation of acetone to mesitylene (13–17%);⁵⁰⁵ the preparation of dypnone in 77–82% yield from acetophenone;⁶⁶⁰ and the preparation of tetraphenylcyclopentadiene (tetracyclone) from dibenzyl ketone and benzil (91–96%).²⁰⁴

Three procedures for intramolecular condensation of diketones are described in *Organic Syntheses*. 4-Carboethoxy-3,5-dimethyl-2-cyclohexen-1-one has been prepared by cyclization (sulfuric acid-acetic acid) of

⁶⁵² J. T. Hays, G. F. Hager, H. M. Engelmann, and H. M. Spurlin, *J. Am. Chem. Soc.*, **73**, 5369 (1951).

⁶⁵³ D. C. Buttle, *Brit. pat.* 917,782 [*C.A.*, **59**, 1491 (1963)].

⁶⁵⁴ A. Russell and R. L. Kenyon, *Org. Syntheses, Coll. Vol.*, **3**, 747 (1955).

⁶⁵⁵ N. L. Drake and P. Allen, *Org. Syntheses, Coll. Vol.*, **1**, 77 (1941).

⁶⁵⁶ C. J. Leuck and L. Cejka, *Org. Syntheses, Coll. Vol.*, **1**, 283 (1941).

⁶⁵⁷ C. R. Conard and M. A. Dolliver, *Org. Syntheses, Coll. Vol.*, **2**, 167 (1943).

⁶⁵⁸ E. P. Kohler and H. M. Chadwell, *Org. Syntheses, Coll. Vol.*, **1**, 78 (1941).

⁶⁵⁹ G. A. Hill and G. M. Bramann, *Org. Syntheses, Coll. Vol.*, **1**, 81 (1941).

⁶⁶⁰ W. Wayne and H. Adkins, *Org. Syntheses, Coll. Vol.*, **3**, 367 (1955).

ethylidene *bis*-acetoacetic ester (prepared from acetaldehyde and acetoacetic ester); the overall yield of cyclized product based on acetaldehyde is 47–50%.⁶⁶¹ Cyclization of 2-(3-oxobutyl)-2-methyl-1,3-cyclohexanedione to 1,6-dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene occurs in 75% yield with pyrrolidine catalyst.³⁹² $\Delta^{1(9)}$ -2-Octalone has been prepared by reaction of 1-morpholino-1-cyclohexene with methyl vinyl ketone to generate the diketone enamine *in situ*, followed by ring closure.⁴³²

Aldol condensation followed by Canizzaro reaction is illustrated by the condensation of formaldehyde with acetaldehyde (to yield pentaerythritol, 55–57%)⁴⁷⁰ and with cyclohexanone (to yield 2,2,6,6-tetramethylcyclohexanol, 73–85%).⁴⁷²

Following are representative aldol condensation procedures not found in *Organic Syntheses*.

Aldol (Self-Condensation of Acetaldehyde).⁶⁶² Acetaldehyde (1 kg., 22.7 moles) contained in a 2-l. flask is cooled below 5°. Over a 20-minute period 25 ml. of 10% aqueous sodium hydroxide is added dropwise with vigorous stirring while the temperature of the reaction mixture is maintained at 4–5°. After the mixture has been stirred for 1 hour at 4–5°, it is made slightly acidic with tartaric acid. The mixture is filtered to remove sodium tartrate (addition of diethyl ether facilitates the filtration). The filtrate is distilled under reduced pressure from an oil bath by raising the temperature slowly. Acetaldehyde and aldol slowly distil together as the aldolan dissociates (see p. 58). Redistillation of the aldol fraction yields about 500 g. (50%) of aldol, b.p. 72°/12 mm. Aldol should be distilled immediately before use since it dimerizes to paraldehyde on standing.^{461, 462}

2-Ethyl-2-hexenal (Self-Condensation of Butanal).⁴⁸³ To 750 ml. of aqueous 1 *M* sodium hydroxide at 80° is added, dropwise and with vigorous stirring during 1.5 hours, 2520 g. (35 moles) of freshly distilled *n*-butanal. A large efficient reflux condenser is required for rapid addition of the aldehyde; the solution temperature rises to 93°. After the addition of aldehyde is complete, the mixture is heated under reflux for 1 hour. It is then cooled to room temperature, the organic layer is separated and, without further treatment, distilled through a 150-cm. Vigreux column to yield 1880 g. (86%) of pure 2-ethyl-2-hexenal, b.p. 59.5–60°/10 mm.; n_D^{18} 1.4556.*

⁶⁶¹ E. C. Horning, M. O. Denekas, and R. E. Field, *Org. Syntheses, Coll. Vol.*, **3**, 317 (1955).

⁶⁶² L. P. Kyriakides, *J. Am. Chem. Soc.*, **36**, 530 (1914).

* The following measurements were made on the 2-ethyl-2-hexenal. Gas-liquid chromatograph of the product (10 ft. \times $\frac{1}{4}$ in. column, 20% Apiezon L on Chromosorb W, 150°, flow rate 60 cc./minute) indicated a purity of 97–99% (single major peak with retention time of about 8 minutes). A single isomer is also indicated by the n.m.r. spectrum; vinyl

2-Cyclohexylidenecyclohexanone (Self-Condensation of Cyclohexanone).^{163, 164} *A.* 2-(1-Chlorocyclohexyl)cyclohexanone.^{162, 164} Dry hydrogen chloride is bubbled through pure cyclohexanone (40 g.) contained in a flask cooled by a water bath. After 15 hours the gas flow is stopped and the crystalline 2-(1-chlorocyclohexyl)cyclohexanone (32 g., 71%) is collected by filtration. Wallach reports m.p. 41–43°.¹⁶²

B. 2-Cyclohexylidenecyclohexanone.^{163, 164} To 2-(1-chlorocyclohexyl)cyclohexanone (70 g., 0.326 mole) in 100 ml. of diethyl ether is added, dropwise and with vigorous stirring, a cooled solution of 7.5 g. (0.326 g.-atom) of sodium in 150 g. of methanol while the temperature is kept below 10°. After the reaction is complete, water is added and the ether solution separated and washed until it is neutral. Evaporation of the ethereal solution under reduced pressure leaves a crystalline residue which is crystallized from methanol-water (4:1) to furnish 51.0 g. (88%) of 2-cyclohexylidenecyclohexanone, m.p. 56–57°.

Dehydrochlorination with aqueous sodium hydroxide at 25° yields principally 2-(1-cyclohexenyl)cyclohexanone.¹⁶⁴

3-Methyl-4-phenyl-trans-3-buten-2-one (Condensation of Benzaldehyde with 2-Butanone).^{233–235} A mixture of 2-butanone (25 g., 0.35 mole) and benzaldehyde (35 g., 0.33 mole) is saturated with dry hydrogen chloride with cooling. After it has stood for 2 hours, the brown reaction mixture, is shaken with dilute aqueous sodium hydroxide, washed with water, and extracted with diethyl ether. After the ether solution has been dried and concentrated under reduced pressure, the crude product is crystallized from petroleum ether (b.p. 60–80°) to yield 45 g. (85%) of 3-methyl-4-phenyl-trans-3-buten-2-one, m.p. 37–38°. Harries and Müller report m.p. 38° after distilling the crude product at b.p. 127–130°/12 mm. and recrystallizing the distillate from petroleum ether.²³²

2-Furfurylidenecyclopentanone (Condensation of Furfural with Cyclopentanone).²⁹⁷ A mixture of freshly distilled furfural (32 g., 0.33 mole), cyclopentanone (28.0 g., 0.33 mole), diethyl ether (150 ml.) and 0.1 *N* sodium hydroxide solution (300 ml.) is stirred with external cooling to moderate the exothermic reaction. After about 30 minutes, yellow crystalline material (presumably 2,5-difurfurylidenecyclopentanone) begins to separate in rapidly increasing amounts. After the mixture has been stirred for a total of 45 minutes it is filtered with suction. The solid on the funnel and the aqueous layer from the filtrate are extracted

triplet ($J = 7$ c.p.s.) centered at τ 4.42 (Varian A-60 instrument; measurement in carbon tetrachloride); infrared bands (liquid film) at 1685 (C=O) and 1643 (C=C) cm^{-1} (Perkin Elmer Model 621 grating spectrophotometer). These results suggest that the β -propyl and carboxaldehyde groups are *trans* (cf. tiglaldehyde⁸⁷).^{88, 89}

with ether. The combined ethereal solutions are washed twice with water and concentrated on the steam bath. The residue is distilled under reduced pressure. After a fore-run of starting material, the product is collected as a yellow oil, b.p. 154°/15 mm., which readily crystallizes (55 g., 60% yield). Recrystallization from diisopropyl ether furnishes 2-furfurylidencyclopentanone melting at 59–60°.

2,4-Dimethyl-3-hydroxy-1-phenyl-1-pentanone (Condensation of 2-Methylpropanal with Propiophenone).¹⁷⁷ Methylanilinomagnesium bromide is prepared by adding, with cooling and stirring, a solution of 33.8 g. (0.315 mole) of freshly distilled N-methylaniline in 100 ml. of dry benzene to an ether solution of ethylmagnesium bromide [prepared from 8.0 g. (0.33 mole) of magnesium turnings, 40 g. (0.364 mole) of ethyl bromide, and 80 ml. of diethyl ether under a nitrogen atmosphere].

To the freshly prepared solution of methylanilinomagnesium bromide is added, during 30 minutes, a solution of 48.8 g. (0.364 mole) of dry propiophenone in 100 ml. of dry benzene while the temperature is kept at 15–20°. The resulting mixture is allowed to stand at 25° for 2 hours and a solution of 15.8 g. (0.291 mole) of freshly distilled 2-methylpropanal in 20 ml. of dry benzene is then added during 15 minutes keeping the temperature at –10°. After the reaction mixture has stood for 2½ hours at –10° to 0°, 300 ml. of aqueous 3 *M* hydrochloric acid is added and the organic layer separated, washed with five portions of 6 *M* hydrochloric acid and finally with water. The organic solution is dried with anhydrous sodium sulfate and the solvents are removed by distillation at 15–30 mm. from a hot-water bath (60–70°). The residue is distilled to separate, after a fore-run of recovered propiophenone, 37.5 g. (83%) of 2,4-dimethyl-3-hydroxy-1-phenyl-1-pentanone, b.p. 101–107/0.4 mm.

3-Ferrocenyl-1-phenyl-2-propen-1-one (Condensation of Ferrocene Carboxaldehyde with Acetophenone).⁶⁶³ To a stirred solution of 2.56 g. (0.064 mole) of sodium hydroxide in 20 ml. of water (cooled to 15°) are added, successively, solutions of 6.0 g. (0.05 mole) of acetophenone in 10 ml. of 95% ethanol and 10.8 g. (0.05 mole) of ferrocene carboxaldehyde in 30 ml. of 95% ethanol. The mixture is stirred at room temperature for 3 hours and allowed to stand overnight. The thick purple suspension is filtered and the collected solid washed thoroughly with water, followed by a small portion of ice-cold 95% ethanol. After drying, 14.5 g. (92%) of 3-ferrocenyl-1-phenyl-2-propen-1-one (purple solid), m.p. 123–126°, is obtained. Recrystallization from 95% ethanol gives the pure unsaturated ketone; deep purple needles, m.p. 126–128°.

4-Keto-1,2,3,4,5,6,7,8-octahydroazulene (Intramolecular Self-Condensation of 1,6-Cyclodecanedione).³⁹⁸ 1,6-Cyclodecanedione (50

⁶⁶³ C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).

g., 0.3 mole) is heated under reflux in 500 ml. of aqueous 5% sodium carbonate for 1 hour. The product is then steam-distilled and the distillate simultaneously extracted with chloroform in an apparatus described by Vogel.⁶⁶⁴ The chloroform is removed and the residue distilled. The fraction (43 g., 96%) boiling at 126–128°/15 mm. is collected.

cis-9-Acetoxy-10-hydroxy-5-methyldecalin-1,6-dione [Intramolecular Condensation of 2-Acetoxy-2-(3-oxopentyl)cyclohexane-1,3-dione].⁶⁶⁵ To a stirred solution of 42.3 g. (0.167 mole) of 2-acetoxy-2-(3-oxopentyl)cyclohexane-1,3-dione⁶⁶⁵ in 850 ml. of dry benzene is added 33.3 ml. (0.40 mole) of pyrrolidine, and then 25 ml. (0.44 mole) of glacial acetic acid is added dropwise (noticeable heating occurs). The yellow solution is stirred at room temperature for 72 hours. The entire reaction mixture is poured onto a column packed with 900 g. of acid-washed alumina. Elution with a 2:3 acetone-hexane mixture affords 28.42 g. (67%) of nearly pure ketol, m.p. 216–218°, after the crude fractions have been washed with ether. Recrystallization from acetone and from an acetone-hexane mixture affords the pure product, m.p. 217–217.5°.

β-Phenylcinnamaldehyde (Condensation of Benzophenone with Acetaldehyde).²²¹ *A. Ethylidenecyclohexylamine.* Acetaldehyde (44.1 g., 1 mole) is slowly added dropwise, with vigorous stirring, to 99.2 g. (1 mole) of cyclohexylamine, keeping the temperature at –20°. After the mixture has stood for 1 hour at –20°, it is treated with 5 g. of sodium sulfate. The organic layer is separated at room temperature and treated with anhydrous sodium carbonate. The dried product is rapidly distilled under reduced pressure through a fractionating column. The ethylidenecyclohexylamine fraction is redistilled just before use; b.p. 47–48°/12 mm. Tiollais reports b.p. 54°/18 mm., n_D^{15} 1.4647, and 76% yield by a similar procedure.⁶⁶⁶

B. 3,3-Diphenyl-3-hydroxypropylidenecyclohexylamine. A nitrogen atmosphere is employed throughout this procedure. Ethylidenecyclohexylamine (3.0 g., 0.025 mole) in 20 ml. of absolute diethyl ether is added to a cold (0°) ether solution of lithium diisopropylamide (0.025 mole) prepared from 2.53 g. (0.025 mole) of diisopropylamine in 25 ml. of ether at room temperature by addition of 0.025 mole of methyl-lithium⁶⁶⁷ in 24 ml. of ether.^{221, 629} The solution is left for 10 minutes at 0°, cooled to –70°, and treated, dropwise, with a solution of 4.55 g.

⁶⁶⁴ A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 3rd ed., p. 224, Longmans, Green, New York, 1956.

⁶⁶⁵ T. A. Spencer, K. K. Schmiegel, and W. W. Schmiegel, *J. Org. Chem.*, **30**, 1626 (1965).

⁶⁶⁶ R. Tiollais, *Bull. Soc. Chim. France* [5] **14**, 708 (1947).

⁶⁶⁷ A solution of methylolithium in diethyl ether (0.5 M) is available from Foote Mineral Co., Exton, Pennsylvania, U.S.A.

(0.025 mole) of benzophenone in 25 ml. of ether. The mixture is allowed to stand for 24 hours at room temperature, cooled to 0°, and then treated with water. From the ether solution is isolated 7.05 g. (92%) of 3,3-diphenyl-3-hydroxypropylidenecyclohexylamine, m.p. 127–128°.

C. β -Phenylcinnamaldehyde. 3,3-Diphenyl-3-hydroxypropylidenecyclohexylamine (1.54 g., 0.005 mole) and oxalic acid (10.0 g.) are added to water and the mixture is steam-distilled. From the distillate is isolated 1.03 g. (99%) of slightly impure β -phenylcinnamaldehyde, m.p. 42–44°. Recrystallization from petroleum ether (b.p. 40°) furnishes 0.89 g. (85%) of pure product, m.p. 46–47°.

TABULAR SURVEY

The following tables summarize data in the literature through August 1966. The general arrangement is explained by the titles of the tables which are grouped: II–V, condensations of aldehydes only; VI and VII, condensations of ketones only; VIII–XX, condensations of aldehydes with ketones. Procedures leading to no aldol condensation and/or side reactions have for the most part been omitted. Aldol condensations which proceeded from, to, or through carbonyl precursors or derivatives, with certain exceptions, have been excluded.

Reactants. Entries in each table are arranged by molecular formula. Radical prefixes in names appear in alphabetical order; in abbreviated structural formulas they appear in numerical order. The sequence for substances having the same molecular formula follows Beilstein; acyclic (unbranched, branched), alicyclic by ring size, etc. An aldehyde or ketone is designated aromatic if the carbonyl group is attached directly to the aromatic ring. A heterocyclic ketone has a carbonyl group attached directly to the heterocyclic ring system or has a keto group within the heterocyclic ring.

In mixed condensations of aldehydes with aldehydes (Tables III–V) and ketones with ketones (VII), entries are found under the reactant having the lowest carbon content, except in Table IV where entries are in order of molecular formula of the aliphatic aldehyde. The aldehyde-ketone condensations (Tables VII–XIX) are arranged by ketone.

Catalyst. The catalyst(s) listed give(s) the product indicated in the yield stated. Where more than one catalyst is listed for a particular condensation the order of arrangement is as follows (incomplete list): (1) bases–metals, alkali hydroxides, alkaline earth hydroxides, alkali metal alkoxides, salts, alkoxides of metals other than alkali, amino-magnesium halides, amines; (2) ion-exchange resins (basic, acidic);

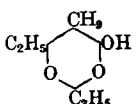
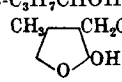
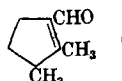
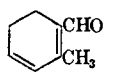
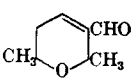
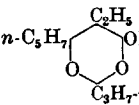
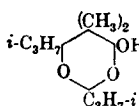
and (3) acids: acidic salts, acid anhydrides, acid halides, acids. Occasionally, after the catalyst leading to the product cited, other catalysts are listed which yield the same product in lower or unstated yield. When different reaction conditions (solvent, temperature, reaction time) produce different products with the same catalyst, the conditions are given with the appropriate product.

Product. The product indicated by name or structural formula is obtained with the catalyst(s) and reaction conditions cited. Products designated by a molecular formula are of unknown or unassigned structure. In the aldehyde-ketone tables the condensation product formula is abbreviated, R being employed to indicate the carboxaldehyde substituent in RCHO.

Yield. The yield is listed in parentheses after the product and refers to product formed with the catalyst and conditions cited, and in most instances is the highest value reported. When several catalysts giving the same product are listed, a range of yields may be reported. A dash indicates yield not stated or unavailable from data in reference cited.

References. The first reference cited refers to the catalyst and conditions listed leading to the highest yield stated. The remaining references are listed in numerical order and refer to other preparations of the same product by aldol condensation, possibly under quite different conditions, but in lower or unstated yield.

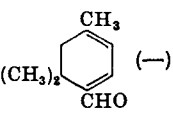
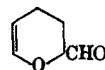
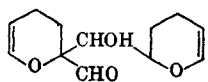
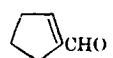
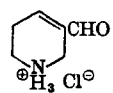
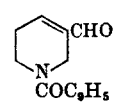
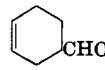
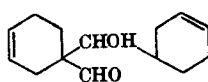
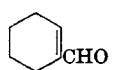
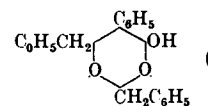
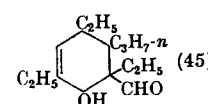
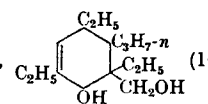
TABLE II. SELF-CONDENSATION OF ALIPHATIC ALDEHYDES

| Aldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|--|
| CH ₃ CHO* | NaOH; Na ₂ B ₄ O ₇ POCl ₃ | CH ₃ CHOHCH ₂ CHO (50-75) CH ₃ CHOHCH ₂ CHO (27) | 662, 668 103 |
| C ₂ H ₅ CHO | SOCl ₂ ; H ₂ SO ₄ KOH | CH ₃ CH=CHCHO (43-61) C ₂ H ₅ CHOHCH(CH ₃)CHO (—), C ₂ H ₅ CH=C(CH ₃)CHO (—) | 103, 669-671 738, 137, 696, 739 |
| | NaOCH ₃ , CH ₃ CO ₂ Na, soap, or K[B(OCH ₃) ₄] | C ₂ H ₅ CH=C(CH ₃)CHO (59-83) | 614, 483, 624, 716, 740, 741 |
| | K ₂ CO ₃ |  (94) | 452 |
| | Al(OC ₃ H ₇ - <i>n</i>) ₃ | C ₂ H ₅ CO ₂ C ₂ H ₅ - <i>n</i> (—), C ₂ H ₅ CHOHCH(CH ₃)CO ₂ C ₂ H ₅ - <i>n</i> (—) | 742 |
| | Ion-exchange resin POCl ₃ | C ₂ H ₅ CH=C(CH ₃)CHO (—) C ₂ H ₅ CHOHCH(CH ₃)CHO (31), C ₂ H ₅ CH=C(CH ₃)CHO (—) | 732 103, 102 |
| CH ₃ OCH ₂ CHO HOCH ₂ CHOHCHO CH ₃ CH=CHCHO | K ₂ CO ₃ NaOH NaHg | CH ₃ OCH ₂ CHOHCH(OCH ₃)CHO (10) Fructose (41), sorbose (40) <i>n</i> -C ₃ H ₇ CHOHCH(CH ₃)CH ₂ CH ₂ OH (50),  (40),  (Low) | 743 35, 744-746 747 |
| | K ₂ CO ₃ | CH ₃ CH=CHCHOHCH ₂ CH=CHCHO (—) | 748, 722, 749 |
| | C ₂ H ₅ OMgCl |  (—) | 750 |
| | (CH ₂) ₅ NH or morpholine, CH ₃ CO ₂ H | CH ₃ (CH=CH) ₃ CHO (—), CH ₃ (CH=CH) ₅ CHO (—) | 751, 752, 109, 110, 482, 729, 753- 759 |
| | HCl |  (—) | 760-762 |
| <i>n</i> -C ₃ H ₇ CHO | NaOH; also KOH, NaOC ₂ H ₅ , (CH ₃) ₂ C ₆ H ₅ SO ₃ Na | <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (65-97), <i>n</i> -C ₃ H ₇ CHOHCH(C ₂ H ₅)CHO (—) | 483, 104, 138, 139, 222, 635, 680, 696, 731, 763-771 |
| | KOH, H ₂ O, (C ₂ H ₅) ₂ O; also Ca(OH) ₂ , <i>n</i> -C ₄ H ₉ OMgI | <i>n</i> -C ₃ H ₇ CHOHCH(C ₂ H ₅)CHO (75) | 772, 613, 773 |
| | K ₂ CO ₃ , H ₂ O, 10° |  (73) | 452-454 |
| | Ion-exchange resin, Wolfatit L 150 | <i>n</i> -C ₃ H ₇ CHOHCH(C ₂ H ₅)CHO (58-79) | 774, 100, 631, 775 |
| | Ion-exchange resin, Amberlite IR-4B | <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (14-54) | 630, 101, 632, 776 |
| | POCl ₃ ; also SOCl ₂ , H ₂ SO ₄ | <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (53) | 103, 102, 777- 779 |
| <i>i</i> -C ₃ H ₇ CHO | NaOH; also KOH, Mg[Al(OC ₄ H ₉ - <i>n</i>) ₃] ₂ , POCl ₃ | (CH ₃) ₂ CHCHOHCH(CH ₃) ₂ CHO (85) | 780, 102, 103, 457, 767, 781-794 |
| | K ₂ CO ₃ , H ₂ O, 20° |  (75) | 452 |
| CH ₃ CHOHCH ₂ CHO | NaCN CaO; also NaOH, K ₂ CO ₃ | <i>i</i> -C ₃ H ₇ CHOHCH(CH ₃) ₂ CHOHCN (—) CH ₃ (CHOHCH ₂) _{<i>n</i>} CHO (—) | 791 795, 684, 722, 729, 796 |

Note: References 668-2359 are on pp. 403-438.

* Acetaldehyde is also converted to aldol and/or 2-butenal in mostly unspecified yield by the following catalysts. The numbers following each catalyst are the pertinent references. MgHg, 672; NaOH or KOH, 480, 631, 673-711; Ba(OH)₂, 712, 713; MgO, 714-716; NaOC₂H₅, 700-702; K₂CO₃, 480, 717-722; KCN, 6; HCO₂K, 480; CH₃CO₂Na, 480, 723, 724; Na₂SO₃, 691, 725; ROMgI (R = alkyl), 613; morpholine, 726; amino acids, amines, 482, 609, 727-729; ZnCl₂, 480, 724, 730; ion-exchange resin Amberlite, 101, 630, 632, 731-734; silica gel, 735; HCl, 1, 736, 737.

TABLE II. SELF-CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

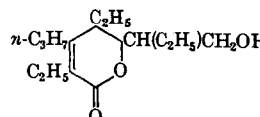
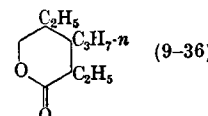
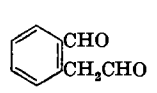
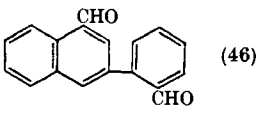
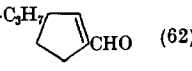
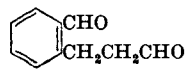
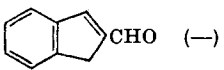
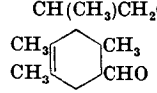
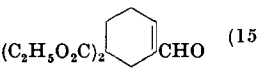
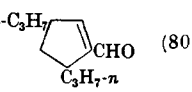
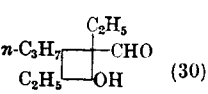
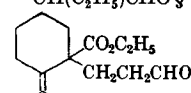
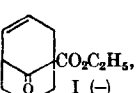
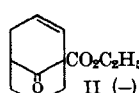
| Aldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|--|
| $(\text{CH}_3)_2\text{C}=\text{CHCHO}$ | NaOH; also $\text{Ba}(\text{OH})_2$ | $(\text{CH}_3)_2\text{C}=\text{CHCH}=\text{CHC}(\text{CH}_3)=\text{CHCHO}$ (—), 3,7,11-trimethyl-2,4,6,8,10-dodecapentaenal (—), $\text{C}_{15}\text{H}_{20}\text{O}$ (—) | 105, 106 |
| | NaNH_2 |  (—) | 105 |
| $n\text{-C}_4\text{H}_9\text{CHO}$ | $(\text{CH}_3)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ KOH K_2CO_3 ; also $\text{Ca}(\text{OH})_2$, $\text{Zn}(\text{C}_2\text{H}_5)_2$, HCl | $(\text{CH}_3)_2\text{C}=\text{CHCH}=\text{CHC}(\text{CH}_3)=\text{CHCHO}$ (14.5) $\text{C}_{20}\text{H}_{38}\text{O}_3$ (—) $n\text{-C}_4\text{H}_9\text{CH}=\text{C}(\text{C}_3\text{H}_7\cdot n)\text{CHO}$ (—), $\text{C}_{15}\text{H}_{28}\text{O}$ (—), $\text{C}_{20}\text{H}_{30}\text{O}$ (—) | 115 489-491 488, 290, 628, 767, 797- 800 |
| $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CHO}$ $i\text{-C}_3\text{H}_7\text{CH}_2\text{CHO}$ | K_2CO_3 NaOC_2H_5 ; also NaOH, MgI_2 , leucine KOH; also $\text{Ba}(\text{OH})_2$ | $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CHOHC}(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHO}$ (—) $i\text{-C}_3\text{H}_7\text{CH}_2\text{CH}=\text{C}(\text{C}_3\text{H}_7\cdot i)\text{CHO}$ (66) | 801 604, 802-804 |
| $\text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{CHO}$ | K_2CO_3 | $i\text{-C}_3\text{H}_7\text{CH}_2\text{CH}=\text{C}(\text{C}_3\text{H}_7\cdot i)\text{CHO}$ (17), $i\text{-C}_3\text{H}_7\text{CH}_2\text{CHOHC}(\text{C}_3\text{H}_7\cdot i)\text{CHO}$ (—) $\text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{CHOHC}(\text{CHO})=\text{CHCH}_3$ (30) | 805, 797, 806-812 813 |
|  | NaOH or $(\text{C}_6\text{H}_5\text{CO}_2)_2\text{Cu}$ |  (59-76) | 814-816 |
| $n\text{-C}_7\text{H}_{13}\text{CH}=\text{CHCHO}$ $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CHO}^\dagger$ | NaOH $\text{KOC}_4\text{H}_9\cdot t$ | High-mol.-wt. acid, alcohol, lactone (—) $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}=\text{C}(\text{CHO})\text{CH}_2\text{CH}_2\cdot$ $\text{CH}=\text{CH}_2$ (—) | 492 817 |
| $\text{OHC}(\text{CH}_2)_4\text{CHO}$ | KOH; also $\text{CH}_3\text{CO}_2\text{H}$, H_3PO_4 |  (58-62) | 374, 818-820 |
| $\text{HN}[(\text{CH}_2)_2\text{CHO}]_2$ | HCl |  (75) | 821 |
| | HCl, $\text{C}_6\text{H}_5\text{COCl}$, $\text{C}_6\text{H}_5\text{N}$ |  (100) | 821 |
| $n\text{-C}_5\text{H}_{11}\text{CHO}$ | Ion-exchange resin, Amberlite IR-4B Ion-exchange resins | $n\text{-C}_5\text{H}_{11}\text{CH}=\text{C}(\text{C}_4\text{H}_9\cdot n)\text{CHO}$ (16-60) $n\text{-C}_5\text{H}_{11}\text{CHOHC}(\text{C}_4\text{H}_9\cdot n)\text{CHO}$ (50-66) | 101, 630 100 |
|  | NaOH |  (—) | 822 |
| $\text{OHC}(\text{CH}_2)_5\text{CHO}$ | H_2SO_4 |  (—) | 378 |
| $n\text{-C}_6\text{H}_{13}\text{CHO}$ | KOH; also K_2CO_3 , $(i\text{-C}_3\text{H}_7\text{O})_2\text{B}$, $\text{Zn}(\text{C}_2\text{H}_5)_2$, ZnCl_2 , HCONH_2 Ion-exchange resin, Amberlite POCl_3 ; also SOCl_2 , HNO_3 | $n\text{-C}_6\text{H}_{13}\text{CH}=\text{C}(\text{C}_5\text{H}_{11}\cdot n)\text{CHO}$ (80), $\text{C}_{28}\text{H}_{50}\text{O}$ (—), $\text{C}_{28}\text{H}_{54}\text{O}_2$ (—) $n\text{-C}_6\text{H}_{13}\text{CH}=\text{C}(\text{C}_5\text{H}_{11}\cdot n)\text{CHO}$ (16-57) | 493, 489-496, 628, 823, 824 101, 632, 825 |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ | $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ | $n\text{-C}_6\text{H}_{12}\text{CHOHC}(\text{C}_5\text{H}_{11}\cdot n)\text{CHO}$ (41-46), $n\text{-C}_6\text{H}_{13}\text{CH}=\text{C}(\text{C}_5\text{H}_{11}\cdot n)\text{CHO}$ (—) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CHO}$ (35) | 103, 102, 792, 793, 826 827 |
| | KOH |  (27.5) | 455 |
| $n\text{-C}_3\text{H}_7\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$ | NaOH |  (45),  (16-25) | 381, 66, 383, 483-485, 492 |

(See also p.90)

Note: References 668-2359 are on pp. 403-438.

† Formed *in situ* from cyclohexane-*cis*-(or *trans*)-1,3-diol mono-4-bromobenzenesulfonate.

TABLE II. SELF-CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

| Aldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|-------------------------------|
| $n\text{-C}_3\text{H}_7\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$ (<i>conid.</i>) | NaOH (<i>contd.</i>) |  (30-56),  (9-36), $n\text{-C}_3\text{H}_7\text{CO}_2\text{H}$ (5), $n\text{-C}_3\text{H}_7\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CO}_2\text{H}$ (1.5) $n\text{-C}_7\text{H}_{15}\text{CH}=\text{C}(\text{C}_6\text{H}_{13}\text{-}n)\text{CHO}$ (36-79) | 381, 66, 383, 483-485, 492 |
| $n\text{-C}_7\text{H}_{15}\text{CHO}$ | NaOC_2H_5 ; also fatty acid metal salt, MgI_2 , ion- exchange resin, Amberlite, IR-4B | $n\text{-C}_7\text{H}_{15}\text{CO}_2\text{H}$ (5), $n\text{-C}_3\text{H}_7\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CO}_2\text{H}$ (1.5) $n\text{-C}_7\text{H}_{15}\text{CH}=\text{C}(\text{C}_6\text{H}_{13}\text{-}n)\text{CHO}$ (36-79) | 104, 101, 623, 803, 2349 |
| $i\text{-C}_3\text{H}_7(\text{CH}_2)_4\text{CHO}$ | NaNH_2 $[i\text{-C}_3\text{H}_7(\text{CH}_2)_4\text{CO}_2]_2\text{Mg}$ | C_{16} alcohol (—), C_{16} diol (—) $i\text{-C}_3\text{H}_7(\text{CH}_2)_4\text{CH}=\text{C}(\text{CHO})(\text{CH}_2)_3\text{C}_3\text{H}_7\text{-}i$ (98) | 828 626, 2349 |
|  | NaOH |  (46) | 829, 830 |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$ | K_2CO_3 | $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CHO})\text{CH}_2\text{C}_6\text{H}_5$ (26) | 831 |
| $\text{OHC}(\text{CH}_2)_3\text{CH}(\text{C}_3\text{H}_7\text{-}n)\text{CHO}$ | None, H_2O , 115° | $n\text{-C}_3\text{H}_7$  (62) | 818 |
|  | H_2SO_4 |  (—) | 832 |
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{-}$ $\text{C}(\text{CH}_3)=\text{CHCHO}$, citral | $(\text{CH}_2)_5\text{NH}$ | $\text{C}_{20}\text{H}_{30}\text{O}$ (—) | 833 |
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$, citronellal | KOH | $\text{C}_{20}\text{H}_{32}\text{O}_2$ (64) | 834 |
|  | " | Polymer (—) | 835 |
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}[\text{C}(\text{CH}_3)=\text{CH}_2]\text{-}$ CH_2CHO | $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ |  (59) | 836 |
| $n\text{-C}_9\text{H}_{19}\text{CHO}$ | Fatty acid metal salt | $n\text{-C}_9\text{H}_{19}\text{CH}=\text{C}(\text{CHO})\text{C}_8\text{H}_{17}\text{-}n$ (70) | 623 |
| $\text{OHC}(\text{CH}_2)_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{-}$ $(\text{CH}_2)_2\text{CHO}$ | NaOC_2H_5 | $(\text{C}_2\text{H}_5\text{O}_2\text{C})_2$  (15) | 377 |
| $\text{OHCCH}(\text{C}_3\text{H}_7\text{-}n)\text{CH}_2\text{-}$ $\text{CH}(\text{C}_3\text{H}_7\text{-}n)\text{CH}_2\text{CHO}^\ddagger$ | None, heat | $n\text{-C}_3\text{H}_7$  (80) | 818 |
| $\text{OHCCH}(\text{C}_2\text{H}_5)\text{CH}(\text{C}_3\text{H}_7\text{-}n)\text{-}$ $\text{CH}(\text{C}_2\text{H}_5)\text{CHO}^\S$ | " | $n\text{-C}_3\text{H}_7$  (30) | 381 |
|  | H_2SO_4 |  I (—)  II (—) I:II=4.7:1 | 451 |

Note: References 668-2359 are on pp. 403-438.

† Formed *in situ* by lead tetracetate oxidation of 3,5-di-*n*-propylcyclohexane-1,2-diol.

§ Formed *in situ* as an ozonolysis product of

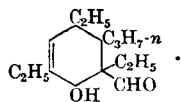
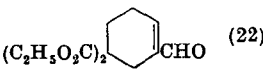
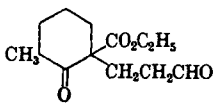
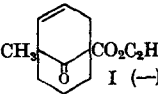
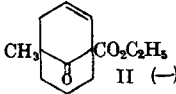
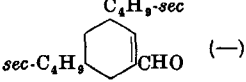
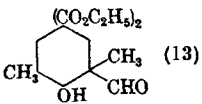
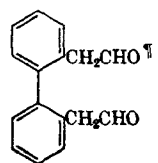
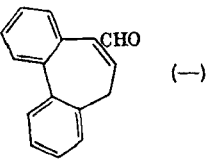
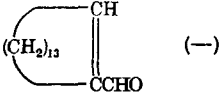
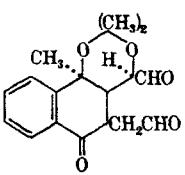
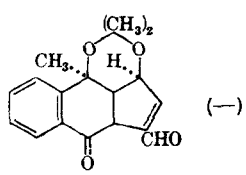
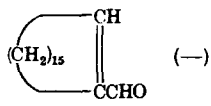
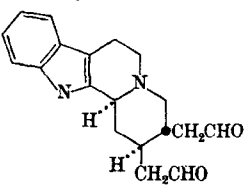
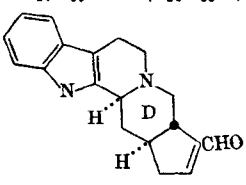
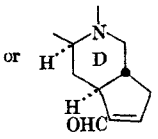
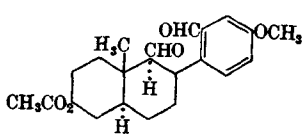
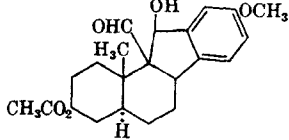


TABLE II. SELF-CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

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| Aldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|-----------------|
| $\text{OHC}(\text{CH}_2)_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{-(CH}_2)_2\text{CHO}$ | NaOC_2H_5 |  (22) | 377 |
|  | H_2SO_4 |  I (—)  II (—) I:II = 2.8:1 | 451, 2318, 2358 |
| $\text{OHCCH}_2\text{CH}(\text{C}_4\text{H}_9\text{-}sec)\text{CH}_2\text{-CH}(\text{C}_4\text{H}_9\text{-}sec)\text{CHO}$ | None | $\text{C}_4\text{H}_9\text{-}sec$  (—) | 373 |
| $\text{OHCCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{-CH}_2\text{CH}(\text{CH}_3)\text{CHO}$ | NaOC_2H_5 |  (13) | 377 |
|  | H_2SO_4 |  (—) | 379 |
| $\text{OHC}(\text{CH}_2)_{14}\text{CHO}$ | $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ |  (—) | 380 |
|  | $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 837, 838 |
| $\text{OHC}(\text{CH}_2)_{16}\text{CHO}$ | $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ |  (—) | 380 |
| $n\text{-C}_{17}\text{H}_{35}\text{CHO}$ | $(n\text{-C}_{17}\text{H}_{35}\text{CO}_2)\text{Co}$ | $n\text{-C}_{17}\text{H}_{35}\text{CH}=\text{C}(\text{C}_{16}\text{H}_{33}\text{-}n)\text{CHO}$ (81) | 623 |
|  | None |  or  (—) | 375 |
|  | NaOH |  (—) | 376 |

Note: References 668–2359 are on pp. 403–438.

|| Formed *in situ* by lead tetracetate oxidation of 3,5-di-*sec*-butylcyclohexane-1,2-diol.

¶ Formed *in situ* from the tetramethyl acetal.

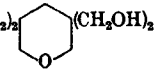
ORGANIC REACTIONS

THE ALDOL CONDENSATION

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TABLE III. MIXED CONDENSATION OF ALIPHATIC ALDEHYDES

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| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|--|
| CH ₃ O and CH ₃ CHO | Ca(OH) ₂ ; also NaOH, KOH, H ₂ SO ₄ | C(CH ₂ OH) ₄ (79-80), HC(CH ₂ OH) ₃ (70) | 839, 117, 118, 722, 840-863 |
| | MgO K ₂ CO ₃ | C(CH ₂ OH) ₄ (90) HOCH ₂ CH ₂ CHO (-), CH ₃ CHOHCH ₂ CHO (-) | 864 865-867 |
| HOCH ₂ CHO C ₂ H ₅ CHO | CsOH; also Al ₂ O ₃ , SiO ₂ , or MnO ₂ , 300° | CH ₂ =CHCHO (62) | 125, 126, 868-884 |
| | Ca(OH) ₂ NaOH; also Ca(OH) ₂ | HOCH ₂ CHOHCHO (75) CH ₃ C(CH ₂ OH) ₃ (94) | 602 885, 463, 886-894 |
| | KOH | HOCH ₂ CH(CH ₃)CHO (-), CH ₂ =C(CH ₃)CHO (-), C ₂ H ₅ CHOHC(CH ₃)(CH ₂ OH)CHO (-) | 895 |
| | K ₂ CO ₃ | CH ₃ C(CH ₂ OH) ₃ (-), CH ₃ C(CHO)(CH ₂ OH) ₂ (-) | 895 |
| CH ₃ OCH ₂ CHO HOCH ₂ CH ₂ CHO CH ₂ CH=CHCHO | Na ₂ O, SiO ₂ , 275° BF ₃ | CH ₂ =C(CH ₃)CHO (46) CH ₂ =C(CH ₃)CHO (-), C ₂ H ₅ CH=C(CH ₃)CHO (-) | 125, 126, 880 896 |
| | H ₂ SO ₄ ; also H ₂ SO ₄ , CH ₃ CO ₂ H | CH ₂ =C(CH ₃)CHO (60), C ₂ H ₅ CH=C(CH ₃)CHO (-), CH ₃ C(CH ₂ OH) ₃ (-) | 897, 460, 898 |
| | CaO Ca(OH) ₂ | CH ₃ OC(CH ₂ OH) ₃ (15) C(CH ₂ OH) ₄ (63) | 465 899, 722 |
| | K ₂ CO ₃ | Polymer (-) | 900-902 |
| | NaO ₂ CCH ₃ | $\begin{array}{c} \text{CH}_2=\text{CH}-\text{CHO} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CHO} \end{array}$ (-) | 900 |
| | C ₅ H ₅ N H ₂ SO ₄ | C ₁₀ H ₁₂ O ₂ (-) CH ₃ (CH=CH) ₂ CHO (-) | 903 501 |
| <i>n</i> -C ₂ H ₅ CHO | NaOH or Ca(OH) ₂ | C ₄ H ₉ C(CH ₂ OH) ₂ (80-90) | 887, 463, 886, 888, 894, 905-908 |
| | K ₂ CO ₃ Na ₂ O, silica gel | C ₂ H ₅ C(CH ₂ OH) ₂ CHO (90) CH ₂ =C(C ₂ H ₅)CHO (49) | 122 125, 120, 880, 909 |
| <i>i</i> -C ₂ H ₅ CHO | H ₂ SO ₄ Ca(OH) ₂ ; also NaOH, KOH | CH ₂ =C(C ₂ H ₅)CHO (40) HOCH ₂ C(CH ₃) ₂ CH ₂ OH (90) | 898 463, 468, 471, 890, 894, 910-917, 925 |
| | K ₂ CO ₃ | HOCH ₂ C(CH ₃) ₂ CHO (40) | 918, 471, 919-924 |
| C ₂ H ₅ OCH ₂ CHO | CaO | C ₂ H ₅ OC(CH ₂ OH) ₂ (24) | 465 |
| CH ₃ CHOHCH ₂ CHO | (C ₂ H ₅) ₂ NH·HCl Ca(OH) ₂ or Pb(OH) ₂ | CH ₂ =C(OC ₂ H ₅)CHO (67) C(CH ₂ OH) ₄ (-) | 904 926 |
| CH ₂ =CH(CH ₃)CHO | Na ₂ CO ₃ NaOH | CH ₃ CHOHC(CH ₂ OH) ₂ CHO (91) CH ₂ =CHCH ₂ C(CH ₂ OH) ₃ (73) | 927 928 |
| OHC(CH ₂) ₄ CHO | .. | (HOCH ₂) ₂  (CH ₂ OH) ₂ (33) | 929 |
| <i>n</i> -C ₂ H ₅ CHO C ₂ H ₅ CH(CH ₃)CHO | None, H ₂ O, 100° KOH .. | <i>n</i> -C ₂ H ₅ C(CHO)=CH ₂ (65) C ₂ H ₅ C(CH ₃)(CH ₂ OH)CHO (60) C ₂ H ₅ C(CH ₃)(CH ₂ OH) ₂ (55-87) | 127, 125, 880 930 931, 471, 932, 933 |
| | <i>i</i> -C ₂ H ₅ CHO | <i>i</i> -C ₂ H ₅ C(CH ₂ OH) ₂ (63) | 934, 466, 935 |
| <i>n</i> -C ₂ H ₇ OCH ₂ CHO CH ₃ CH(OCH ₂) ₂ CHO | NaOH K ₂ CO ₃ CaO K ₂ CO ₃ | <i>i</i> -C ₂ H ₅ CH(CH ₂ OH)CHO (52) <i>n</i> -C ₂ H ₇ OC(CH ₂ OH) ₃ (10) CH ₃ CH=C(CH ₂ OH)CHO (15) | 120 465 813, 900 |
| | C ₄ H ₅ N | $\begin{array}{c} \text{CH}_2=\text{CH}-\text{CHO} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CHO} \end{array}$ (-), CH ₃ CH=C(CH ₂ OH)CHO (-) | 900 |

ORGANIC REACTIONS




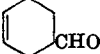

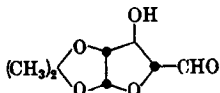
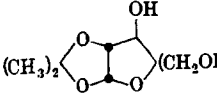
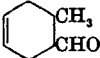

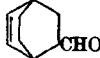

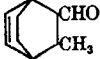

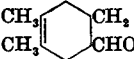
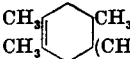
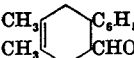
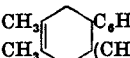
THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE III. MIXED CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

96

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|------------------------------|
| CH_3O (contd.) and $\text{HOCH}_2(\text{CH}_2)_2\text{CHO}$ | NaOH | $\text{HOCH}_2(\text{CH}_2)_2\text{C}(\text{CH}_2\text{OH})_2$ (75) | 936, 937 |
| | .. |  (—) | 937 |
|  | KOH |  (65) | 938 |
| $n\text{-C}_6\text{H}_{11}\text{CHO}$ | NaOH K_2CO_3 None, H_2O , 100° | $n\text{-C}_4\text{H}_9\text{C}(\text{CH}_2\text{OH})_2$ (70) $n\text{-C}_4\text{H}_9\text{C}(\text{CH}_2\text{OH})_2\text{CHO}$ (70) $n\text{-C}_3\text{H}_7\text{C}(\text{CHO})=\text{CH}_2$ (65) | 934, 465, 939 122 127 |
| $n\text{-C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{CHO}$ | KOH | $n\text{-C}_3\text{H}_7\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (—) | 940 |
| $i\text{-C}_7\text{H}_{15}\text{CH}(\text{CH}_3)\text{CHO}$ | .. | $i\text{-C}_3\text{H}_7\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (46) | 931 |
| $(\text{C}_2\text{H}_5)_2\text{CHCHO}$ | .. | $(\text{C}_2\text{H}_5)_2\text{C}(\text{CH}_2\text{OH})_2$ (90) | 913 |
|  | .. |  (91) | 941, 835 |
| $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CHO}$ | K_2CO_3 | $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (—) | 471 |
|  | NaOH |  (90) | 942 |
| $n\text{-C}_9\text{H}_{19}\text{CHO}$ | KOH $\text{Ca}(\text{OH})_2$ | $n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_2\text{OH})_2\text{CHO}$ (—) $n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_2\text{OH})_2$ (60) | 121 464, 466, 939, 943 |
| $sec\text{-C}_8\text{H}_{17}\text{CH}(\text{CH}_3)\text{CHO}$ | NaOH | $sec\text{-C}_4\text{H}_9\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (41) | 944, 945 |
|  | KOH |  (50-60) | 835 |
| $n\text{-C}_7\text{H}_{13}\text{CH}=\text{C}(\text{C}_2\text{H}_5)\text{CHO}$ | .. | $n\text{-C}_7\text{H}_{13}\text{CH}=\text{C}(\text{CH}_2\text{OH})\text{C}_2\text{H}_5$ (48) | 946 |
| $\text{C}_7\text{H}_5\text{O}_2\text{C}(\text{CH}_2)_2\text{CHO}$ | CaO | $(\text{HOCH}_2)_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$ (17) | 947 |
| $n\text{-C}_8\text{H}_{17}\text{CHO}$ | .. | $n\text{-C}_6\text{H}_{13}\text{C}(\text{CH}_2\text{OH})_2$ (—) | 465 |
| $n\text{-C}_8\text{H}_{17}\text{CH}(\text{CH}_3)\text{CHO}$ | K_2CO_3 | $n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})\text{CHO}$ (80) | 471 |
| $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CHO}$ | KOH; also K_2CO_3 | $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (85) | 948, 932 |
| | K_2CO_3 | $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})\text{CHO}$ (—) | 471 |
|  | $\text{Ca}(\text{OH})_2$ |  (—) | 948 |
| $n\text{-C}_8\text{H}_{17}\text{CHO}$ | KOH | $n\text{-C}_7\text{H}_{15}\text{C}(\text{CH}_2\text{OH})_2\text{CHO}$ (—) | 121 |
| | .. | $n\text{-C}_7\text{H}_{15}\text{C}(\text{CH}_2\text{OH})_2$ (65) | 939 |
| $i\text{-C}_8\text{H}_{17}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CHO}$ | K_2CO_3 | $i\text{-C}_3\text{H}_7(\text{CH}_2)_3\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (80-90) | 471 |
|  | NaOH |  (—) | 948 |
|  | KOH |  (50-60) | 835 |
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$ | .. | $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_2$ (5) | 465 |
| $n\text{-C}_9\text{H}_{19}\text{CHO}$ | .. | $n\text{-C}_8\text{H}_{17}\text{C}(\text{CH}_2\text{OH})_2$ (47) | 939, 465 |
| $n\text{-C}_{10}\text{H}_{21}\text{CHO}$ | .. | $n\text{-C}_8\text{H}_{17}\text{C}(\text{CH}_2\text{OH})_2$ (—) | 939 |
| $n\text{-C}_8\text{H}_{17}\text{CH}(\text{CH}_3)\text{CHO}$ | K_2CO_3 | $n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (80-90) | 471 |
| $n\text{-C}_8\text{H}_{17}\text{CH}(\text{CH}_3)\text{CHO}$ | .. | $n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ (80-90) | 471 |
| $n\text{-C}_{12}\text{H}_{25}\text{CHO}$ | KOH | $n\text{-C}_{11}\text{H}_{23}\text{C}(\text{CH}_2\text{OH})_2$ (—) | 939 |
| $(\text{C}_2\text{H}_5)_2\text{CHCHO}$ | NaOH | $(\text{C}_2\text{H}_5)_2\text{C}(\text{CH}_2\text{OH})_2$ (25) | 949 |
| $\text{C}_6\text{H}_5\text{COCH}(\text{C}_6\text{H}_5)\text{CHO}$ | KOH | $\text{C}_6\text{H}_5\text{COC}(\text{C}_6\text{H}_5)(\text{CH}_2\text{OH})_2$ (60) | 949 |
|  | .. |  (50-60) | 835 |

ORGANIC REACTIONS

THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE III. MIXED CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

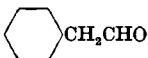
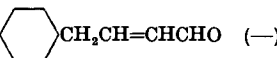






| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|-----------------------------|
| CH ₂ O (contd.) and | | | |
| | H ₂ SO ₄ | (58) | 124 |
| | HCON(CH ₃) ₂ | (20) | 124 |
| | | (8) | |
| | | (60) | |
| | CaO, HCON(CH ₃) ₂ | (—) | 950 |
| | KOH | (—) | 951, 124 |
| | | (—) | 952 |
| (CHO) ₂ and CH ₃ CHO | HCl or (CH ₂) ₆ NH, CH ₃ CO ₂ H | Polymer (—) | 953 |
| <i>i</i> -C ₃ H ₇ CHO | KOH | OHCC(CH ₃) ₂ CHOHC(OH)C(CH ₃) ₂ CHO (—), OHCCHOHC(CH ₃) ₂ CHOHC(CH ₃) ₂ CHO (—) | 954 |
| CCl ₃ CHO and CH ₃ CHO | CH ₃ CO ₂ H | C ₆ H ₅ Cl ₂ O ₂ (—), C ₆ H ₅ Cl ₃ O ₂ (—) | 636 |
| CH ₃ CHO and C ₃ H ₇ CHO | NaOH KOH H ₂ SO ₄ , CH ₃ CO ₂ H | CH ₃ CH=C(CH ₃)CHO (53) CH ₃ CHOHC(CH ₃)CHO (—) CH ₃ CHOHC(CH ₃)(CH ₂ OH)CHOHCH ₃ (—) | 138, 139 137, 955 460 |
| CH ₃ CHClCCl ₂ CHO | CH ₃ CO ₂ H | CH ₃ CHClCCl ₂ CHOHC(CH ₃)CHOHCH ₃ (—) | 636 |

Note: References 668-2359 are on pp. 403-438.

* This compound was formed *in situ* from its dimethyl acetal.

TABLE III. MIXED CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

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| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|---|
| CH ₃ CHO (<i>contd.</i>) and CH ₃ CH=CHCHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H .. | CH ₃ (CH=CH) ₂ CHO (—) CH ₃ (CH=CH) ₂ CHO (—), CH ₃ (CH=CH) ₃ - CHO (—) | 751, 956, 957 958, 107, 956, 957, 959-963 138, 776 |
| <i>n</i> -C ₃ H ₇ CHO | NaOH; also ion- exchange resin KOH Ni ₃ (PO ₄) ₂ or Cd ₃ (PO ₄) ₂ on silica gel at 275°; also K ₂ CO ₃ | CH ₃ CH=C(C ₂ H ₅)CHO (41) CH ₃ CHOHCH(C ₂ H ₅)CHO (61) CH ₃ CH=CHCHO (—), CH ₃ =CHCH ₂ CHO (—), CH ₃ CH=C(C ₂ H ₅)CHO (—), CH ₃ (CH ₂) ₂ CH=CHCHO (—), <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (—) | 662 691, 963 |
| <i>i</i> -C ₂ H ₅ CHO C ₂ H ₅ OCH ₂ CHO <i>i</i> -C ₄ H ₉ CHO C ₂ H ₅ CH ₂ CHO CH ₃ (CH=CH) ₂ CHO | KOH K ₂ CO ₃ CH ₃ CO ₂ Na .. (CH ₂) ₅ NH, CH ₃ CO ₂ H | CH ₃ CHOHC(CH ₃) ₂ CHO (40) C ₂ H ₅ OCH ₂ CHOHC(CH ₃) ₂ CHO (—) Unsaturated aldehydes (—) CH ₃ CH=C(C ₂ H ₅)CHO (44) CH ₃ (CH=CH) ₄ CHO (—) | 964, 918 965 966 967 958 |
|  CH ₂ CHO | NaOC ₂ H ₅ |  (—) | 968 |
| 2-O ₂ NC ₆ H ₄ CH=CHCHO C ₆ H ₅ CH=CHCHO 4-O ₂ NC ₆ H ₄ CH=C(CH ₃)CHO C ₆ H ₅ CH=C(CH ₃)CHO | NaOH NaOH; also NaNH ₂ NaOH .. | 2-O ₂ NC ₆ H ₄ (CH=CH) ₂ CHO (—) C ₆ H ₅ (CH=CH) ₂ CHO (20) 4-O ₂ NC ₆ H ₄ CH=C(CH ₃)CH=CHCHO (—) C ₆ H ₅ CH=C(CH ₃)CH=CHCHO (21) | 969 970, 585 971 972 |
| CH ₂ =C(CH ₃)  CHO | .. | CH ₂ =C(CH ₃)  CH=CHCHO (—) | 973 |
| Citral | NaNH ₂ (CH ₂) ₅ NH, CH ₃ CO ₂ H | Citrylideneacetaldehyde (9) Citrylideneacetaldehyde (—), α- and β-citrylideneacetaldehyde (—) | 585, 622 585, 958 |
| C ₆ H ₅ (CH=CH) ₂ CHO | NaOH | C ₆ H ₅ (CH=CH) ₃ CHO (—) | 970 |
| CH ₃  CH(CH ₃)CH ₂ CHO | KOH | CH ₃  CH(CH ₃)CH ₂ CH=CHCHO (—) | 144 |
| <i>n</i> -C ₁₀ H ₂₁ CHO | NaNH ₂ | <i>n</i> -C ₁₀ H ₂₁ CHOHCH ₂ CHO (41), <i>n</i> -C ₉ H ₁₉ CH(CHOHCH ₃)CHO (19) | 143 |
| HOCH ₂ CHO and HOCH ₂ CHOHCHO | Ca(OH) ₂ | Ribose, arabinose, xylose (—) | 129, 974, 975 |
| C ₂ H ₅ CHO and <i>n</i> -C ₃ H ₇ CHO <i>i</i> -C ₃ H ₇ CHO C ₅ H ₅ CH=CHCHO | NaOH KOH NaOH | C ₂ H ₅ CH=C(C ₂ H ₅)CHO (42) C ₂ H ₅ CHOHC(CH ₃) ₂ CHO (—) C ₅ H ₅ CH=CHCH=C(CH ₃)CHO (60) | 138 133 972, 976 |
|  CH ₂ CH ₂ CH=C(CH ₃) ₂ | KOH | (CH ₃) ₂ C=CHCH ₂ CH ₂  CH=C(CH ₃)CHO (—) | 977 |
| CH ₃ CH=CHCHO and <i>i</i> -C ₄ H ₉ CHO CH ₃ (CH=CH) ₂ CHO | — (CH ₂) ₅ NH, CH ₃ CO ₂ H .. | Liquid, b.p. 85-120°/12 mm. (8) CH ₃ (CH=CH) ₆ CHO (—), CH ₃ (CH=CH) ₄ CHO (—) | 978 753 |
| CH ₃ (CH=CH) ₃ CHO C ₆ H ₅ CH=CHCHO | | CH ₃ (CH=CH) ₅ CHO (7) C ₆ H ₅ (CH=CH) ₆ CHO (—), C ₆ H ₅ (CH=CH) ₇ CHO (—) | 754 979 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO, citral C ₆ H ₅ (CH=CH) ₂ CHO | NaNH ₂ (CH ₂) ₅ NH, CH ₃ CO ₂ H .. | α-Citrylideneacetaldehyde (—) α- and β-Citrylideneacetaldehyde (12-19) C ₆ H ₅ (CH=CH) ₄ CHO (—), C ₆ H ₅ (CH=CH) ₆ CHO (—) | 585, 622 585, 980 116 |
| <i>n</i> -C ₁₀ H ₂₁ CHO | .. | CH ₃ CH=C(C ₂ H ₅ - <i>n</i>)CHO (—), <i>n</i> -C ₁₀ H ₂₁ (CH=CH) ₄ CHO (—) | 143 |
| CH ₃ (CH=CH) ₃ CHO C ₆ H ₅ (CH=CH) ₅ CHO | | CH ₃ (CH=CH) ₇ CHO (—) C ₆ H ₅ (CH=CH) ₇ CHO (—) | 753 116 |
| <i>n</i> -C ₃ H ₇ CHO and <i>i</i> -C ₃ H ₇ CHO | NaOH | <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO, <i>i</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (Total, 88) | 767, 136, 731 |
| C ₂ H ₅ CH=CHCHO CH ₃ C(OH)(CO ₂ C ₂ H ₅)- CH(C ₂ H ₅)CHO | .. (C ₂ H ₅) ₂ NH | C ₂ H ₅ CH=CHCH=C(C ₂ H ₅)CHO (55) CH ₃ C(OH)(CO ₂ C ₂ H ₅)CH(C ₂ H ₅)CH=C(C ₂ H ₅)CHO (20-30) | 976, 972 981 |


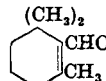

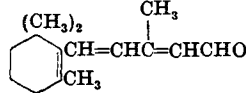
ORGANIC REACTIONS

THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE III. MIXED CONDENSATION OF ALIPHATIC ALDEHYDES (Continued)

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|------------------------|
| <i>i</i> -C ₃ H ₇ CHO and <i>i</i> -C ₄ H ₉ CHO C ₂ H ₅ CH=C(CH ₃)CHO C ₆ H ₅ CH=CHCHO | KOH " " | <i>i</i> -C ₄ H ₉ CHOHC(CH ₃) ₂ CHO (-) C ₂ H ₅ CH=C(CH ₃)CHOHC(CH ₃) ₂ CHO (-) C ₁₃ H ₁₆ O ₂ (-) | 134, 135 982 983 |
| (CH ₃) ₂ C=CHCHO and (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO, citral | NaNH ₂ | (CH ₃) ₂  CH=CHC(CH ₃)=CHCHO (-) | 585, 622 |
|  | (CH ₂) ₅ NH, CH ₃ CO ₂ H | (CH ₃) ₂  CH=CHC(CH ₃)=CHCHO (-) | 984 |
|  | " | Vitamin A aldehyde (-) | 586, 984 |
| <i>n</i> -C ₄ H ₉ CHO and <i>i</i> -C ₃ H ₇ CHO | NaOH | <i>n</i> -C ₄ H ₉ CH=C(C ₃ H ₇ - <i>n</i>)CHO, <i>i</i> -C ₃ H ₇ CH=C(C ₃ H ₇ - <i>n</i>)CHO (Total, 90) | 767 |
| <i>n</i> -C ₇ H ₁₅ CHO and C ₆ H ₅ CH=CHCHO <i>n</i> -C ₁₁ H ₂₃ CHO | " (C ₁₇ H ₃₅ CO ₂) ₄ Fe | C ₆ H ₅ CH=CHCH=C(C ₆ H ₁₃ - <i>n</i>)CHO (54) <i>n</i> -C ₇ H ₁₅ CH=C(C ₆ H ₁₃ - <i>n</i>)CHO (-), <i>n</i> -C ₁₁ H ₂₃ CH=C(C ₆ H ₁₃ - <i>n</i>)CHO (-), <i>n</i> -C ₇ H ₁₅ CH=C(C ₁₀ H ₂₁ - <i>n</i>)CHO (-), <i>n</i> -C ₁₁ H ₂₃ CH=C(C ₁₀ H ₂₁ - <i>n</i>)CHO (-) | 972 623 |

Note: References 668-2359 are on pp. 403-438.

TABLE IV. CONDENSATION OF CARBOCYCLIC AROMATIC ALDEHYDES WITH ALDEHYDES

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|---------------------------|
| CH ₂ ClCHO and 4-O ₂ NC ₆ H ₄ CHO | KOH | 4-O ₂ NC ₆ H ₄ CH=CClCHO (—) | 985 |
| CH ₃ CHO and | | | |
| 2-ClC ₆ H ₄ CHO | .. | 2-ClC ₆ H ₄ CH=CHCHO (—) | 986 |
| 2-O ₂ NC ₆ H ₄ CHO | NaOH | 2-O ₂ NC ₆ H ₄ CH=CHCHO (—) | 987 |
| | Ba(OH) ₂ | 2-O ₂ NC ₆ H ₄ CHOHCH ₂ CH ₂ OH (—) | 476 |
| 3-O ₂ NC ₆ H ₄ CHO | NaOH, 5 min. | 3-O ₂ NC ₆ H ₄ CHOHCH ₂ CHO (—) | 988 |
| | NaOH, 12 hr. | 3-O ₂ NC ₆ H ₄ CH=CHCHO (50) | 989 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH, H ₂ O | 4-O ₂ NC ₆ H ₄ CHOHCH ₂ CHO (—) | 990 |
| | KOH, CH ₃ OH | 4-O ₂ NC ₆ H ₄ CH=CHCHO (70) | 991 |
| C ₆ H ₅ CHO | NaOH, POCl ₃ , or HCl | C ₆ H ₅ CH=CHCHO (42-90) | 992, 103, 779, 993-998 |
| | NaOH | C ₆ H ₅ (CH=CH) ₂ CHO (15), C ₆ H ₅ (CH=CH) ₃ CHO (—) | 999, 1000 |
| | Ion-exchange resins IR-4B and IR-120 | CH ₃ CH=CHCHO (9-13) | 101 |
| 2-H ₂ NC ₆ H ₄ CHO | NaOH | Quinoline (—) | 1001 |
| C ₆ H ₄ (CHO) ₂ -1,4 | KOH | C ₆ H ₄ (CH=CHCHO) ₂ -1,4 | 1002, 1003 |
| 3,4-(OCH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | 3,4-(OCH ₂ O) ₂ C ₆ H ₃ CH=CHCHO (—) | 1004 |
| 2-CH ₃ C ₆ H ₄ CHO | .. | 2-CH ₃ C ₆ H ₄ CH=CHCHO (—) | 1005 |
| 4-CH ₃ C ₆ H ₄ CHO | .. | 4-CH ₃ C ₆ H ₄ CH=CHCHO (25-30) | 1006 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | 4-CH ₃ OC ₆ H ₄ CH=CHCHO (—) | 1006 |
| 2-C ₂ H ₅ C ₆ H ₄ CHO | .. | 2-C ₂ H ₅ C ₆ H ₄ CH=CHCHO (—) | 1005 |
| 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | 2,3-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO (33) | 1007 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO (77) | 1008 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO (22) | 1007 |
| 4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CHO | .. | 4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CH=CHCHO (37) | 1009 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ | 4-(CH ₃) ₂ NC ₆ H ₄ CH=CHCHO (—), 4-(CH ₃) ₂ NC ₆ H ₄ (CH=CH) ₂ CHO (—), 4-(CH ₃) ₂ NC ₆ H ₄ (CH=CH) ₃ CHO (6), 4-(CH ₃) ₂ NC ₆ H ₄ (CH=CH) ₂ CHO (—) | 1010 |
| 2-CH ₃ OCH ₂ O-3-CH ₃ OC ₆ H ₃ CHO | KOH | 2-CH ₃ OCH ₂ O-3-CH ₃ OC ₆ H ₃ CH=CHCHO (49) | 1009 |
| 3-CH ₃ O-4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CHO | .. | 3-CH ₃ O-4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CH=CHCHO (26-45) | 1009 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

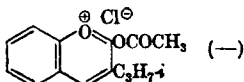

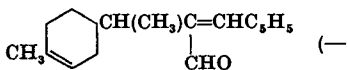
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TABLE IV. CONDENSATION OF CARBOCYCLIC AROMATIC ALDEHYDES WITH ALDEHYDES (Continued)

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|--|
| CH ₃ CHO (contd.) and | | | |
| 4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | 4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₃ CH=CHCHO (—) | 1011 |
| 3,5-(CH ₃ O) ₂ -4-(CH ₃ OCH ₂ O)- C ₆ H ₃ CHO | KOH | 3,5-(CH ₃ O) ₂ -4-(CH ₃ OCH ₂ O) ₂ C ₆ H ₂ - CH=CHCHO (25-28) | 1012 |
| C ₂ H ₅ CHO and C ₆ H ₅ CHO | NaOH | C ₆ H ₅ CH=C(CH ₃)CHO (—), C ₁₀ H ₁₂ O ₂ (—) | 1013, 967, 976, 1011, 1014, 2330 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH=C(CH ₃)CHO (75) | 1015 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | NaOH | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CH=C(CH ₃)CHO (80) | 1016 |
| CH ₃ CH=CHCHO and C ₆ H ₅ CHO | .. | C ₆ H ₅ (CH=CH) ₂ CHO (11) | 1017 |
| | (CH ₂) ₅ NH, CH ₃ CO ₂ H | C ₆ H ₅ (CH=CH) ₂ CHO (—), C ₆ H ₅ (CH=CH) ₃ CHO (—), C ₆ H ₅ (CH=CH) ₂ CHO (—) | 116 |
| <i>n</i> -C ₃ H ₇ CHO and C ₆ H ₅ CHO | KOH | C ₆ H ₅ CH=C(C ₂ H ₅)CHO (58) | 1018, 976 |
| | NaOH | C ₆ H ₅ CH=C(C ₂ H ₅)CHO (27-53), <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (43-57) | 998, 993 |
| | Ion-exchange resins IR-4B and IR-120 | C ₆ H ₅ CH=C(C ₂ H ₅)CHO (5-16), <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (34-52) | 101 |
| <i>i</i> -C ₃ H ₇ CHO and C ₆ H ₅ CHO | KOH | C ₆ H ₅ CHOHC(CH ₃) ₂ CHOHC(CH ₃) ₂ CHO (—) | 1019 |
| 4-HOC ₆ H ₄ CHO | .. | <i>i</i> -C ₃ H ₇ CHOHC(CH ₃) ₂ CHO (—) | 1020 |
| 3-C ₂ H ₅ OC ₆ H ₄ CHO | .. | 3-C ₂ H ₅ OC ₆ H ₄ CHOHC(CH ₃) ₂ CHO (—) | 1021 |
| 4-C ₂ H ₅ OC ₆ H ₄ CHO | .. | 4-C ₂ H ₅ OC ₆ H ₄ CHOHC(CH ₃) ₂ CHO (—) | 1020 |
| C ₂ H ₅ CH(CH ₃)CHO and C ₆ H ₅ CHO | .. | C ₆ H ₅ CHOHC(CH ₃)(C ₂ H ₅)CH ₂ OH (—) | 475 |
| <i>i</i> -C ₄ H ₉ CHO and C ₆ H ₅ CHO | .. | C ₆ H ₅ CH=C(C ₃ H ₇ - <i>i</i>)CHO (—) | 976 |

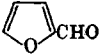
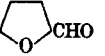
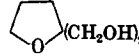
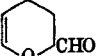
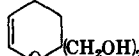
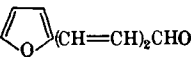

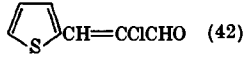
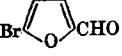
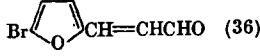
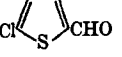
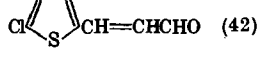
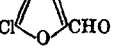
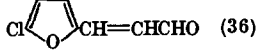
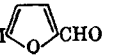
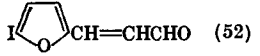
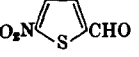
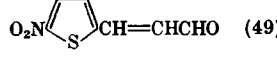
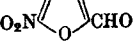
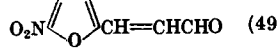
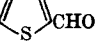
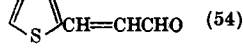
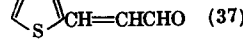
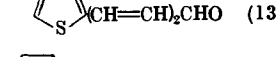
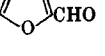
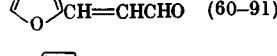
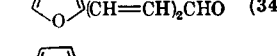
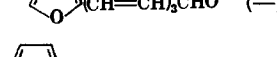
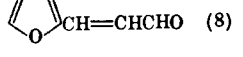
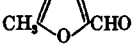
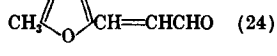
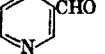
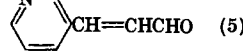
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ORGANIC REACTIONS

| | | | |
|---|---|--|------------------------------|
| 2-HOC ₆ H ₄ CHO | HCl |  (—) | 772 |
| <i>n</i> -C ₆ H ₁₃ CHO and C ₆ H ₅ CHO | NaOH Ion-exchange resins IR-4B and IR-120 NaOH | C ₆ H ₅ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (—) C ₆ H ₅ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (2-13), <i>n</i> -C ₆ H ₁₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (27-49) C ₆ H ₅ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO, <i>n</i> -C ₆ H ₁₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (Total, 14-28) | 1022, 901 101 998, 993 |
| 2-HOC ₆ H ₄ CHO | POCl ₃ | C ₆ H ₅ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (73) | 103, 779 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | <i>n</i> -C ₆ H ₁₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (—) | 1023 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (17) | 1023 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | (CH ₃) ₅ NH KOH | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (—) | 1024 |
| 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | 4-CH ₃ OC ₆ H ₄ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (14) | 1023, 976 |
| C ₆ H ₅ CH ₂ CHO and C ₆ H ₅ CHO | (CH ₂) ₅ NH KOH | <i>n</i> -C ₆ H ₁₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (60) | 1023 |
| <i>n</i> -C ₇ H ₁₅ CHO and C ₆ H ₅ CHO | KOH | 2,3-(CH ₃ O) ₂ C ₆ H ₃ CH=C(C ₆ H ₁₁ - <i>n</i>)CHO (—) | 1024 |
|  CH(CH ₃)CH ₂ CHO and C ₆ H ₅ CHO | NaOH | C ₆ H ₅ CH=C(C ₆ H ₅)CHO (69) | 967, 88 |
| | KOH | C ₆ H ₅ CH=C(C ₆ H ₁₃ - <i>n</i>)CHO (—) | 1026 |
| | |  (—) | 144 |

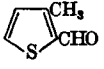
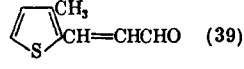
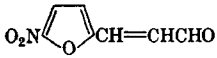
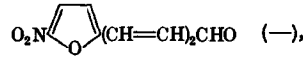
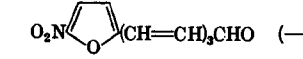
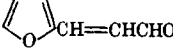
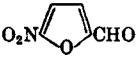
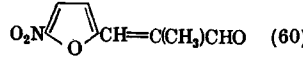
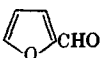
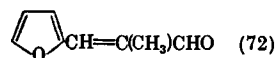
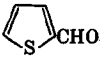
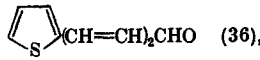
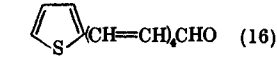
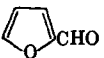
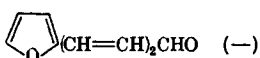
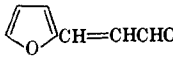
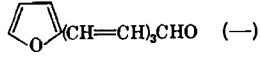
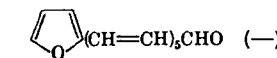
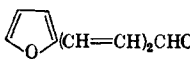

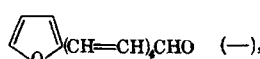
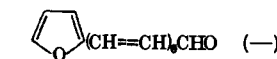
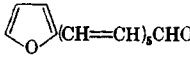
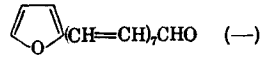
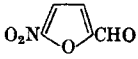
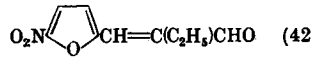
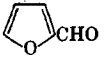
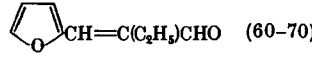
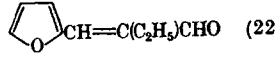
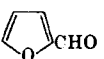
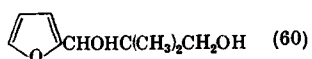
Note: References 668-2359 are on pp. 403-438.

TABLE V. CONDENSATION OF HETEROCYCLIC ALDEHYDES WITH ALDEHYDES

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|---------------------------------------|
| CH₂O and | | | |
|  | NaOH | Resin (—) | 1028, 1029 |
|  | .. |  (90) | 1025, 1027 |
|  | .. |  (83) | 1027 |
|  | .. | Resin (—) | 1028 |
| CH₂ClCHO and  | .. |  (42) | 1030 |
| CH₂CHO and | | | |
|  | .. |  (36) | 1031 |
|  | .. |  (42) | 1030, 1032 |
|  | .. |  (36) | 1031 |
|  | KOH |  (52) | 1031 |
|  | .. |  (49) | 1033, 1032 |
|  | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (49) | 1034 |
|  | NaOH |  (54) | 1035 |
| | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (37),  (13) | 1036 |
|  | NaOH; also Na ₂ CO ₃ , NaNO ₃ |  (60-91),  (34),  (—) | 1037, 978, 996, 1028, 1035-1047 |
| | Ion-exchange resin Amberlite IRA-400 |  (8) | 1048, 101 |
|  | NaOH |  (24) | 2329 |
|  | NaOH; also H ₂ SO ₄ |  (5) | 1121 |

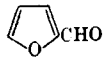
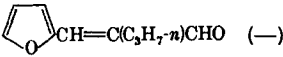
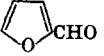
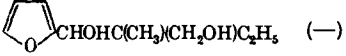
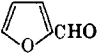
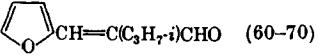
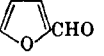
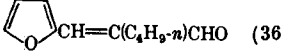
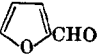
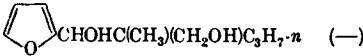
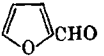
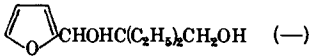
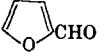
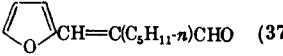
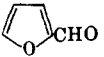
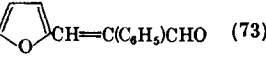
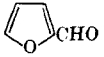
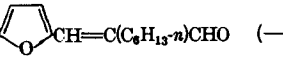
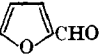
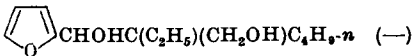
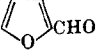
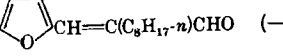
Note: References 668-2359 are on pp. 403-438.

TABLE V. CONDENSATION OF HETEROCYCLIC ALDEHYDES WITH ALDEHYDES (Continued)

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|---------------------------------|
| CH₃CHO (contd.) and | | | |
|  | NaOH |  (39) | 1030 |
|  | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (-),  (-) | 1049 |
|  | FeCl ₃ | Resin (-) | 1050 |
| C₂H₅CHO and | | | |
|  | KOH |  (60) | 1033 |
|  | NaOH; also ion-exchange resin Amberlite IRA-400 |  (72) | 1043, 625, 632, 972, 1045, 1051 |
| CH₃CH=CHCHO and | | | |
|  | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (36),  (16) | 1036 |
|  | NaOH |  (-) | 978, 1028 |
|  | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (-),  (-) | 116 |
|  | NaOH | Resin (-) | 1028 |
|  | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (-),  (-) | 116 |
|  | " |  (-) | 116 |
| n-C₂H₇CHO and | | | |
|  | KOH |  (42) | 1033 |
|  | NaOH; also Na ₂ CO ₃ , NaNO ₃ , n-C ₄ H ₉ OMgBr |  (60-70) | 1045, 613, 1040, 1043, 1047 |
| | Ion-exchange resin Amberlite IRA-400 |  (22) | 101 |
| <i>i</i> -C ₃ H ₇ CHO and  | KOH |  (60) | 474, 1052 |

Note: References 668-2359 are on pp. 403-438.

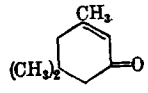
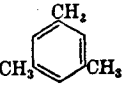
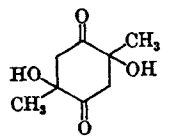
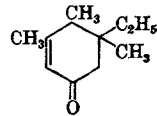
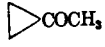
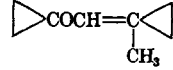
TABLE V. CONDENSATION OF HETEROCYCLIC ALDEHYDES WITH ALDEHYDES (Continued)

| Reactants | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|--------------------------|
| $n\text{-C}_4\text{H}_9\text{CHO}$ and  | NaOH |  (—) | 1043, 1047 |
| $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CHO}$ and  | .. |  (—) | 1052 |
| $i\text{-C}_3\text{H}_7\text{CH}_2\text{CHO}$ and  | .. |  (60-70) | 1045, 978 |
| $n\text{-C}_5\text{H}_{11}\text{CHO}$ and  | Ion exchange resin Amberlite IRA-400 |  (36) | 1053, 101, 1048 |
| $n\text{-C}_3\text{H}_7\text{CH}(\text{CH}_3)\text{CHO}$ and  | NaOH |  (—) | 1052 |
| $(\text{C}_2\text{H}_5)_2\text{CHCHO}$ and  | .. |  (—) | 1052 |
| $n\text{-C}_6\text{H}_{13}\text{CHO}$ and  | Ion-exchange resin Amberlite IRA-400; also Na_2CO_3 |  (37) | 1048, 101, 1043, 1047 |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ and  | NaOH |  (73) | 972 |
| $n\text{-C}_7\text{H}_{15}\text{CHO}$ and  | Ion-exchange resin Amberlite IRA-400 |  (—) | 1048, 101 |
| $n\text{-C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$ and  | NaOH |  (—) | 1052 |
| $n\text{-C}_8\text{H}_{17}\text{CHO}$ and  | Ion-exchange resin Amberlite IRA-400 |  (—) | 1048, 101 |

Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES

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| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|---|
| $\text{CH}_3\text{COCH}_3^*$ | BaO or CaO ; Al_2O_3 , Fe_2O_3 , various temps. | $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3$ (75), $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ (—), $(\text{CH}_3)_2\text{C}=\text{CHCOCH}=\text{C}(\text{CH}_3)_2$ (—),  (62),  (—) | 146, 145, 1054-1067 |
| | $\text{Al}(\text{OC}_4\text{H}_9)_3$; also $\text{C}_2\text{H}_5\text{OMgBr}$, $i\text{-C}_3\text{H}_7\text{OMgBr}$ CaC_2 | $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ (37), $(\text{CH}_3)_2\text{C}=\text{CHCOCH}=\text{C}(\text{CH}_3)_2$ (19) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ (48) | 151, 1068, 1069 1070, 502, 1067, 1071, 1072 |
| | Ion-exchange resin Dowex 50HH H_2SO_4 | $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ (79) Mesitylene, durene, isodurene, penta- methylbenzene, $\text{C}_{14}\text{H}_{20}$, $\text{C}_{15}\text{H}_{18}$, $\text{C}_{16}\text{H}_{20}$ (—) | 148, 1073 1074-1079, 2, 1072 |
| $\text{CH}_2\text{COCOCH}_3$ | KOH |  (—) | 168, 169 |
| $\text{CH}_3\text{COC}_2\text{H}_5$ | NaOH NaOCH_3 ; also NaOH , KOH , or BaO $\text{Al}(\text{OC}_4\text{H}_9)_3$ | $\text{CH}_3\text{COC}(\text{OH})(\text{CH}_2)\text{CH}_2\text{COCOCH}_3$ (—) $\text{C}_2\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (29), $\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_2)\text{C}_2\text{H}_5$ (2-11) $\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{C}_2\text{H}_5$ (72) | 170, 171 146, 156, 504, 1094, 1122-1125 151, 146, 157, 613, 1126, 1127 |
| | $\text{C}_2\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ Alkali and alkaline earth metals and their hydrides, carbides, and amides; also Al_2O_3 | $\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{C}_2\text{H}_5$ (60-67) $\text{C}_2\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (13),  (—), $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{CHCOC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (—), $\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_2)\text{C}_2\text{H}_5$ (—), $1,3,5\text{-}(\text{C}_2\text{H}_5)_3\text{C}_6\text{H}_3$ (—) | 150, 1128, 1129 1130, 154, 503, 1058, 1060, 1119, 1131-1136, 2325 |
| | Ion-exchange resin, Dowex-50 HCl or HBr | $\text{C}_2\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{C}_2\text{H}_5$ (—) $\text{CH}_3\text{COC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (46-67) | 148 152, 154, 156, 1058, 1122, 1138 |
| | H_2SO_4 | $\text{CH}_3\text{COC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (12), $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{CHCOC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (13), $1,3,5\text{-}(\text{C}_2\text{H}_5)_3\text{C}_6\text{H}_3$ (—) | 504, 154, 1139 |
| $\text{CH}_3\text{COCH}=\text{CHCH}_3$ | POCl_3 or ZnCl_2 $n\text{-C}_4\text{H}_9\text{OMgBr}$ | $\text{C}_2\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ (48) $\text{CH}_2\text{CH}=\text{CHCOCH}=\text{C}(\text{CH}_3)\text{CH}=\text{CHCH}_3$ (—) | 153 613 |
|  | KOH |  (14), $\text{C}_{15}\text{H}_{22}\text{O}_2$ (—) | 1140 |

Note: References 668-2359 are on pp. 403-438.


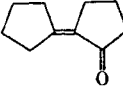
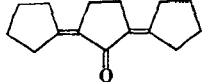
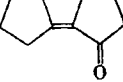
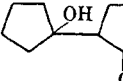
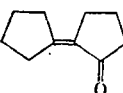
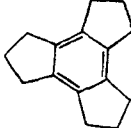
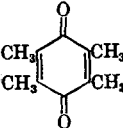
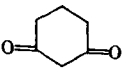
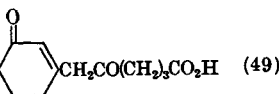

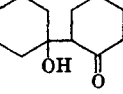
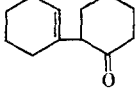
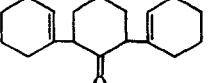
* Self-condensation of acetone is also brought about by the following catalysts. The numbers following each catalyst are the pertinent references. Alkali or alkaline earth metals or amalgams, 1030-1086, 2324; NaOH or KOH , 653, 694, 1072, 1087-1096; $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, 662, 694, 1097-1099; Fe_2O_3 , ThO_2 , ZnO , or PbO , 1055-1061, 1117-1120; NaOC_2H_5 , 1062, 1100-1102; $\text{C}_2\text{H}_5\text{OMgI}$, 613, 649, 1103-1105; ZnCl_2 , AlCl_3 , BF_3 , or HCl , 156, 1057, 1072, 1105-1116.

ORGANIC REACTIONS

THE ALDOL CONDENSATION


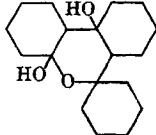
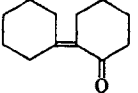
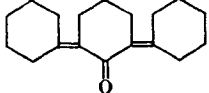
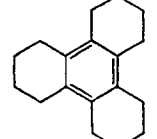
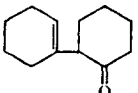
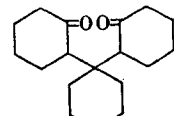
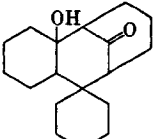
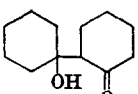
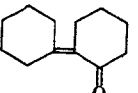
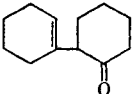
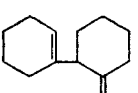
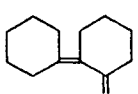
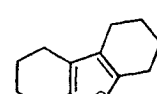
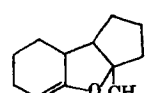
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TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|---|
|  | KOH; also NaOH, NaOC ₂ H ₅ |  (12-50),  (12-81), C ₂₀ H ₂₂ O (2) | 160, 165, 167, 181, 605, 1073, 1141-1150, 2323, 2348 |
| | CaH ₂ or CaC ₂ ; also Al ₂ O ₃ |  (—), C ₁₅ H ₂₀ O (—) | 1151, 1152 |
| | <i>sec</i> -C ₄ H ₉ MgBr; also C ₆ H ₅ NHMgBr, <i>i</i> -C ₄ H ₉ MgCl |  (42) | 1153, 159, 1128, 1154, 1155 |
| | HCl; also P ₂ O ₅ , AlCl ₃ , or H ₂ SO ₄ |  (54),  (8) | 825, 160, 826, 1109, 1146, 1156, 1157 |
| CH ₃ COCOC ₂ H ₅ | NaOH |  (10) | 171 |
| CH ₃ COCH ₂ COCH ₃ | KOH | No condensation | 174 |
| CH ₃ COC ₂ H _{7-n} | NaOH, <i>n</i> -C ₄ H ₉ OMgBr, or BaO | <i>n</i> -C ₃ H ₇ COCH ₂ C(OH)(CH ₃)C ₃ H _{7-n} (3-57) | 1124, 146, 157, 613 |
| (C ₂ H ₅) ₂ CO | HCl, HBr, or HI NaOC ₂ H ₅ , or Al(OC ₂ H ₅) ₃ | <i>n</i> -C ₃ H ₇ COCH=C(CH ₃)C ₃ H _{7-n} (27-74) C ₂ H ₅ COC(CH ₃)=C(C ₂ H ₅) ₂ (21-40) | 152, 156 1158, 151, 503, 1124, 1159 |
| | C ₆ H ₅ N(CH ₃)MgBr; also <i>i</i> -C ₄ H ₉ MgCl, <i>n</i> -C ₄ H ₉ OMgBr | C ₂ H ₅ COCH(CH ₃)C(OH)(C ₂ H ₅) ₂ (60) | 1128, 150, 157, 613, 1126, 1161 |
| | Ion-exchange resin Dowex-50 | C ₃ H ₇ COC(CH ₃)=C(C ₂ H ₅) ₂ (10) | 148 |
| | HBr, HCl, POCl ₃ , ZnCl ₂ , or AlCl ₃ | C ₂ H ₅ COC(CH ₃)=C(C ₂ H ₅) ₂ (12-52) | 833, 153, 156, 830, 1160, 1162, 1163 |
| CH ₃ COC ₃ H _{7-i} | <i>i</i> -C ₄ H ₉ MgCl; also NH ₄ Cl, C ₆ H ₅ N- (CH ₃)MgBr, or Al(OC ₂ H ₅) ₃ | <i>i</i> -C ₃ H ₇ COCH ₂ C(OH)(CH ₃)C ₃ H _{7-i} (70) | 1153, 150, 151, 157, 1164, 1165 |
| | <i>t</i> -C ₄ H ₉ MgCl, or Zn(CH ₃) ₂ | <i>i</i> -C ₃ H ₇ COCH=C(CH ₃)C ₃ H _{7-i} (36) | 1164, 1069 |
| CH ₃ COC(OH)(CH ₃) ₂ | KOH; K ₂ CO ₃ | (CH ₃) ₂ C(OH)C(CH ₃)=CH- COC(OH)(CH ₃) ₂ (52) | 1166, 1085, 1167 |
|  | NaHCO ₃ , pH 6 |  (49) | 1168, 1169 |
|  | KOH; also C ₆ H ₅ - N(CH ₃)MgBr |  (22),  (12),  (22) | 165, 166, 557, 716, 1129, 1141, 1151, 1171-1176, 2353 |


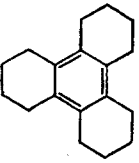
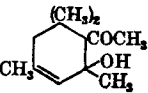
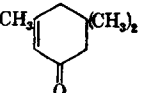
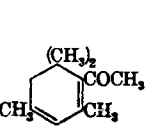
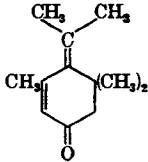

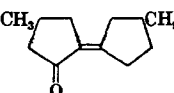

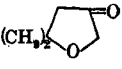
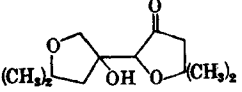
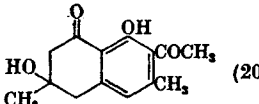
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|------------------------------|
|  (<i>contd.</i>) | NaOH |  (40) | 1177, 1137 |
| | NaOCH ₃ |  (—),  (—), | 1178, 1146 |
| | |  (—) | |
| | |  (—),  (—) | 1179 |
| | |  (40) | 1180 |
| | Al(OC ₄ H ₉ - <i>t</i>) ₃ ; also <i>i</i> -C ₈ H ₁₇ MgCl, C ₆ H ₅ N(CH ₃)- MgBr |  (78) | 151, 159, 1153 |
| | C ₆ H ₅ N, C ₆ H ₅ COCl; also aliphatic amines, ion- exchange resin Amberlite IR-120 |  (20-77) | 1177, 1098, 1181 |
| | Ion-exchange resin Dowex-50 |  (54) | 148, 181, 1182 |
| | ZnCl ₂ ; also BF ₃ , AlCl ₃ -C ₆ H ₅ - N(CH ₃) ₂ , Al ₂ O ₃ | 2-Cyclohexylidene-cyclohexanone (19), 2,6-dicyclohexylidene-cyclohexanone (30), dodecahydrotriphenylene (7) | 1183, 1109, 1178 |
| | HCl |  (63) | 1184, 162-164, 1176, 1185 |
| H ₂ SO ₄ , 30° |  (83-93),  (6), | 1186-1188, 1175, 1177 | |
| |  (3) | | |

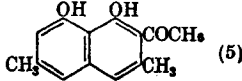

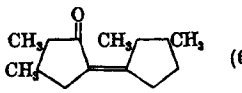

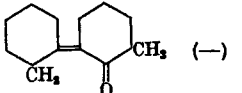

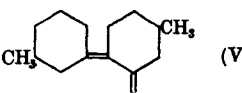
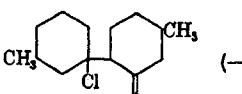

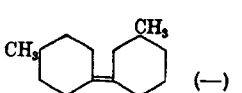

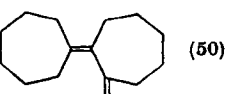

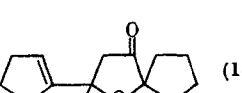
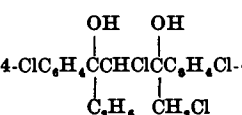
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|--|
|  (contd.) | H ₂ SO ₄ , rfx. |  (9) | 1189, 624, 1175, 1178 |
| CH ₃ COCH=C(CH ₃) ₂ | Li |  (—) | 1190, 418, 1191 |
| | Ba(OH) ₂ or ion-exchange resins |  (—), xylitones (—) | 1192–1194 |
| | NaOC ₂ H _{11-t} , BaO, MgO, ion-exchange resins, or CaC ₂ |  (—),  (—), xylitones (—), iaoxylitones (—) | 1190, 1131, 1132, 1193, 1195–1197 |
| | C ₆ H ₅ N(CH ₃)MgBr | (CH ₃) ₂ C=CHC(OH)(CH ₃)CH ₂ CO-CH=C(CH ₃) ₂ (67) | 198 |
|  | CaH ₂ or HCl |  (—) | 1151, 1146 |
| CH ₃ COCH ₂ CH ₂ COCH ₃ | NaOH |  (42) | 1198, 174 |
|  | K |  (50) | 1199 |
| CH ₃ COC ₄ H _{9-n} | Al(OC ₄ H _{9-t}) ₃ ; also n-C ₄ H ₉ OMgBr | n-C ₄ H ₉ COCH ₂ C(OH)(CH ₃)C ₄ H _{9-n} (73) | 151, 613 |
| CH ₃ COC ₄ H _{9-sec} | HCl | n-C ₄ H ₉ COCH=C(CH ₃)C ₄ H _{9-n} (22) | 156 |
| | C ₆ H ₅ N(CH ₃)MgBr | sec-C ₄ H ₉ COCH ₂ C(OH)(CH ₃)C ₄ H _{9-sec} (55) | 1200, 1128 |
| | HBr | sec-C ₄ H ₉ COCH=C(CH ₃)C ₄ H _{9-sec} (35–40) | 152, 156 |
| CH ₃ COC ₄ H _{9-i} | C ₆ H ₅ N(R)MgBr (R=H or alkyl); also Al(OC ₄ H _{9-t}) ₃ or i-C ₄ H ₉ MgCl | i-C ₄ H ₉ COCH ₂ C(OH)(CH ₃)C ₄ H _{9-i} (61–77) | 1200, 151, 157, 1128, 1201 |
| | HCl or CaC ₂ | i-C ₄ H ₉ COCH=C(CH ₃)C ₄ H _{9-i} (20) | 156, 1131, 1132 |
| | i-C ₄ H ₉ MgCl | i-C ₄ H ₉ COCH(CH ₃)C(OH)(C ₂ H ₅)C ₄ H _{9-i} (60) | 157, 1126 |
| C ₂ H ₅ COC ₄ H _{9-i} | C ₆ H ₅ N(R)MgBr (R = CH ₃ , C ₂ H ₅ , C ₃ H ₇); also CH ₃ MgI, i-C ₄ H ₉ MgCl, i-C ₄ H ₉ MgCl, or Al(OC ₄ H _{9-t}) ₃ | i-C ₄ H ₉ COCH ₂ C(OH)(CH ₃)C ₄ H _{9-t} (60–70) | 150, 151, 157, 1126, 1128, 1153, 1161, 1200, 1202–1204 |
| | KOC ₄ H _{9-t} | i-C ₄ H ₉ COCH=C(CH ₃)C ₄ H _{9-t} (70) | 507 |
| CH ₃ COC(OH)(CH ₃)C ₂ H ₅ | HCl, HBr, or HI | No condensation | 152, 156 |
| | KOH | C ₂ H ₅ C(OH)(CH ₃)COCH=C(CH ₃)-C(OH)(CH ₃)C ₂ H ₅ (30) | 1205 |
| CH ₃ COCH ₂ COCH ₂ COCH ₃ | NaOH, KH ₂ PO ₄ , pH 7.1–7.2 |  (20) | 173 |

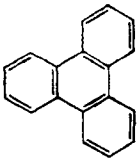
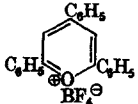
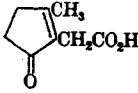
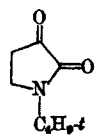
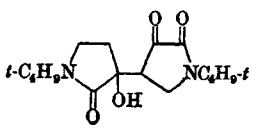
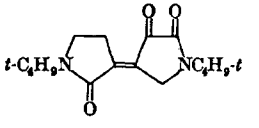

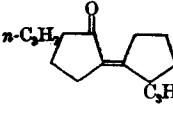
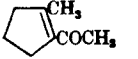
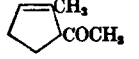
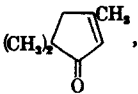
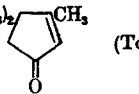
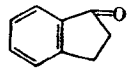
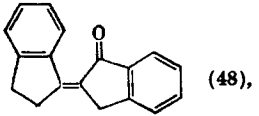
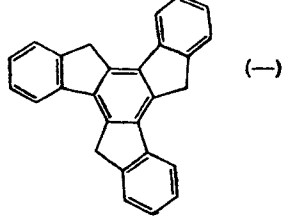
Note: References 668–2359 are on pp. 403–438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|---|
| $\text{CH}_3\text{COCH}_2\text{COCH}_2\text{COCH}_3$ (contd.) | NaOH , KH_2PO_4 , $\text{pH } 8.2$ |  (5) | 173 |
|  | KOH |  (60) | 1206 |
|  | CaH_2 |  (—) | 1207, 530, 1173, 1208 |
|  | .. |  (Very good) | 1151, 1146, 1173 |
| | HCl |  (—) | 1209, 1146 |
|  | CaH_2 |  (—) | 1207, 1173 |
|  | KOC_2H_5 ; also CaH_2 , AlCl_3 , or BF_3 |  (50) | 605, 1109, 1210 |
|  | KOH |  (14) | 1211 |
| $\text{CH}_3\text{COC}_8\text{H}_{11-n}$ | $i\text{-C}_3\text{H}_7\text{MgCl}$ HCl | $n\text{-C}_8\text{H}_{11}\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{C}_8\text{H}_{11-n}$ (50) $\text{C}_8\text{H}_{11}\text{O}$ (14) | 157, 1126 156 |
| $n\text{-C}_7\text{H}_7\text{COC}_3\text{H}_7-n$ | $\text{Al}(\text{OC}_2\text{H}_5)_3$ $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ HBr or HCl | No condensation $n\text{-C}_7\text{H}_7\text{COCH}(\text{C}_6\text{H}_5)\text{C}(\text{OH})(\text{C}_3\text{H}_7-n)_2$ (45) | 151 150, 1128, 1200 |
| $i\text{-C}_3\text{H}_7\text{COC}_3\text{H}_7-i$ | $\text{Al}(\text{OC}_2\text{H}_5)_3$ or $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ | $n\text{-C}_3\text{H}_7\text{COC}(\text{C}_6\text{H}_5)=\text{C}(\text{C}_3\text{H}_7-n)_2$ (30) No condensation | 156 151, 177 |
| $4\text{-ClC}_6\text{H}_4\text{COCH}_2\text{Cl}$ | $\text{C}_6\text{H}_5\text{MgCl}$ |  (—) | 1212 |
| $\text{C}_6\text{H}_5\text{COCH}_3$ | NaOC_2H_5 , $\text{C}_2\text{H}_5\text{OH}$, $130\text{--}140^\circ$ $\text{Al}(\text{OC}_2\text{H}_5)_3$; also ion exchange resins, AlCl_3 , PCl_5 , CaH_2 , ZnCl_2 , HBr $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ $\text{K}_2\text{S}_2\text{O}_7$, H_2SO_4 ; also ZnCl_2 , BF_3 , ArSO_3H | $3,5\text{-}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_2\text{CH}_2$ (—), $2\text{-CH}_2\text{-}4,6(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_2\text{COC}_6\text{H}_5$ (—) $\text{C}_6\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ (82) | 1213–1215 151, 148, 152, 1093, 1216–1219 |
| | | $\text{C}_6\text{H}_5\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{C}_6\text{H}_5$ (25) $1,3,5\text{-}(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2$ (68–85) | 1128, 159 506, 1119, 1215, 1220–1224 |

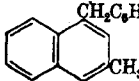
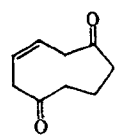
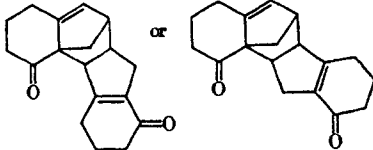
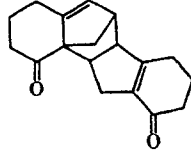
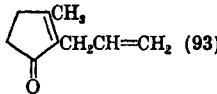
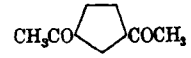
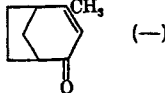
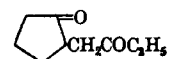
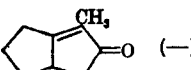
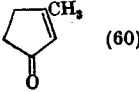
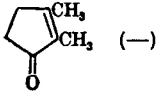
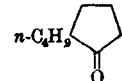
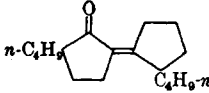
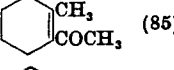
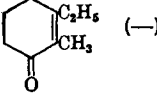
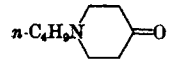
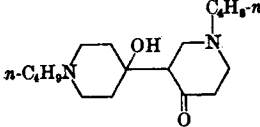
Note: References 668–2359 are on pp. 403–438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|---|
| $C_6H_5COCH_3$ (contd.) | $AlCl_3$ |  (50) | 1109 |
| | BF_3 |  (22) | 1225 |
| | HCl ; also SiO_2 or Al_2O_3 | $C_6H_5COCH=C(CH_3)C_6H_5$ (21-45), $1,3,5-(C_6H_5)_3C_6H_2$ (60) | 1226, 156, 1113, 1119, 1215, 1223, 1227-1231 |
| $CH_2CO(CH_2)_4CO(CH_2)_4CO_2H$ | KOH |  (97) | 1232 |
|  | None, heat |  (Quant.) | 1233 |
| | C_6H_5N |  (96) | 1233 |
|  | KOH |  (83) | 1206 |
| $CH_2CO(CH_2)_4COCH_3$ | KOH |  (83),  (8) | 395 |
| $CH_2COCH_2C(CH_3)_2COCH_3$ | $NaOH$ |  (CH ₃) ₂ ,  (CH ₃) ₂ (Total, 70) | 1234 |
|  | $Al(OC_4H_9-t)_3$; also H_2SO_4 , ion-exchange resins, $AlCl_3$, HCl |  (48),  (-) | 151, 508, 509, 1109, 1235, 1236 |
| $C_6H_5COC_2H_5$ | $Al(OC_4H_9-t)_3$; also HBr | $C_6H_5COC(CH_3)=C(C_6H_5)C_2H_5$ (22) | 151, 152, 156 |
| $4-CH_2C_2H_4COCH_3$ | $C_2H_5N(CH_3)MgBr$ | $4-CH_2C_2H_4COCH=C(CH_3)C_6H_4CH_3-4$ (53) | 1237 |

Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

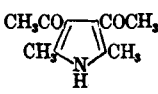
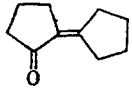
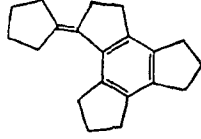
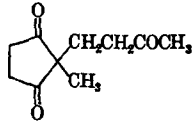
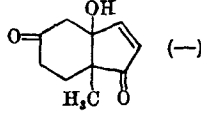
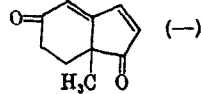
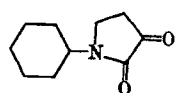
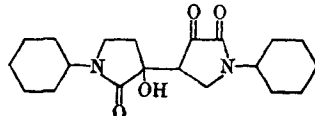
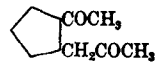
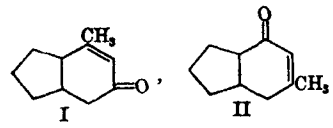
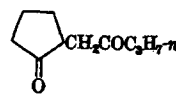
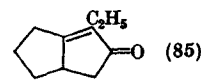
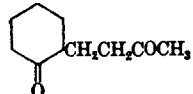
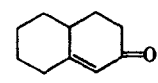
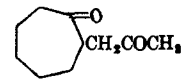
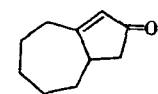
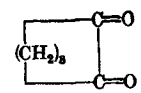
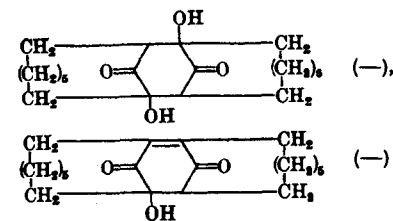
| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|----------------------|---|-----------------|
| $C_8H_8CH_2COCH_3$ | HCl | $C_{16}H_{16}CH_2C(CH_3)=CHCOCH_2C_8H_8$ (50)† | 156 |
| | 70% H_2SO_4 , rfx. |  (18) | 1238 |
| $4-CH_3OC_6H_4COCH_3$ | BF_3 | $4-CH_3OC_6H_4C(=O)C_6H_4OCH_3-4$ (10) BF_4^- | 1225 |
|  | CH_3CO_2Na |  or  (—) | 1239 |
| $(CH_3)_2C=CHCOCH=C(CH_3)_2$ | $Al(OC_2H_5)_3$ | $C_{18}H_{28}O$ (21) | 151 |
| $CH_3CO(CH_2)_2CO(CH_2)_2CH=CH_2$ | — |  (93) | 393 |
|  | $NaOC_2H_5$ |  (—) | 1240, 1241 |
|  | KOH |  (—) | 1242 |
| $CH_3COCH_2CH(CO_2C_2H_5)COCH_3$ | NaOH |  (60) | 1198 |
| $CH_3COCH_2CH(CO_2CH_3)COC_2H_5$ | $NaOCH_3$ |  (—) | 1243 |
| $n-C_4H_9$  | KOH | $n-C_4H_9$  (78) | 1206 |
| $CH_3CO(CH_2)_4COCH_3$ | H_2SO_4 |  (85) | 384, 1244, 1245 |
| $C_2H_5CO(CH_2)_4COC_2H_5$ | HCl |  (—) | 385 |
| $n-C_4H_9N$  | $C_6H_{11}MgCl$ | $n-C_4H_9N$  (60) | 1246 |

Note: References 668–2359 are on pp. 403–438.

† The structure of this product was not established.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

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| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|-----------------|
| $\text{CH}_3\text{COC}_7\text{H}_{15-n}$ $i\text{-C}_4\text{H}_9\text{COC}_4\text{H}_9-i$ | HCl $\text{Al}(\text{OC}_2\text{H}_5-t)_3$ or $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ | $n\text{-C}_7\text{H}_{15}\text{C}(\text{CH}_3)=\text{CHCOC}_7\text{H}_{15-n}$ (—) No condensation | 155 151, 177 |
|  | NaH, NaOH, or $\text{NaOC}_4\text{H}_9-i$ | No condensation | 1247 |
|  | $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  (—) | 160 |
|  | $(\text{CH}_2)_6\text{NH}_2$, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 1248, 1249 |
| | $(\text{CO}_2\text{H})_2$; also H_3BO_3 |  (—) | 1248, 1249 |
|  | $\text{C}_6\text{H}_5\text{N}$ |  (96) | 1233 |
|  | NaOH |  I:II = 3:2 | 1250 |
|  | KOH |  (85) | 1242 |
|  | $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  (90) | 1251, 1249 |
|  | KOH |  (72) | 1252 |
|  | NaOCH_3 |  (—), (—) | 172 |

ORGANIC REACTIONS

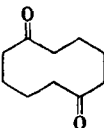
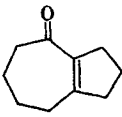
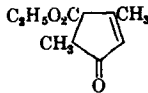
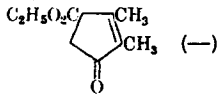
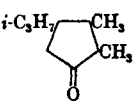

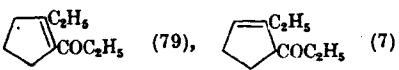
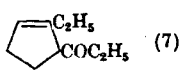
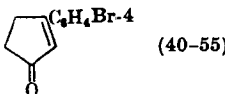
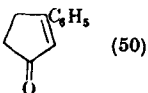
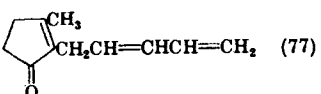
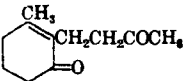
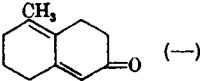
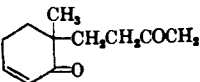
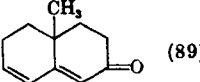
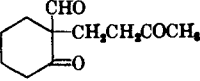
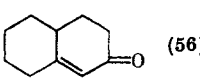
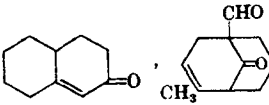
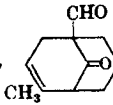
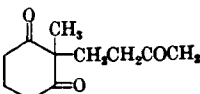
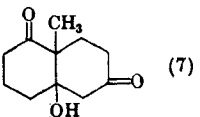
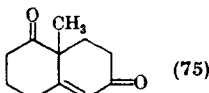
THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

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| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|-----------------|
|  | Na_2CO_3 ; also H_2SO_4 |  (96) | 398, 1253-1255 |
| $\text{CH}_3\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}(\text{CH}_3)\text{COCH}_3$ | None |  (—) | 1256 |
| $\text{CH}_3\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{COC}_2\text{H}_5$ | NaOC_2H_5 |  (—) | 1257 |
|  | CaH_2 |  (—) | 1258 |
| $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_4\text{COC}_2\text{H}_5$ | KOH |  (79),  (7) | 395 |
| $4\text{-BrC}_6\text{H}_4\text{CO}(\text{CH}_2)_4\text{COCH}_3$ | NaOH |  (40-55) | 394 |
| $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_4\text{COCH}_3$ | .. |  (50) | 1259, 174 |
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}(\text{CH}_2)_2\text{CH}=\text{CHCH}=\text{CH}_2$ | .. |  (77) | 397a, 393, 1260 |
|  | NaOCH_3 |  (—) | 1261 |
|  | KOH |  (89) | 427 |
|  | KOH; also $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  (56) | 1251 |
| | $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  ,  (Total, 61) | 1251 |
|  | $\text{Al}(\text{OC}_2\text{H}_5)_3$ |  (7) | 1147, 1262 |
| | $(\text{CH}_2)_4\text{NH}$ |  (75) | 76 |


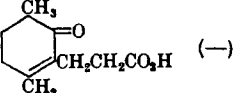
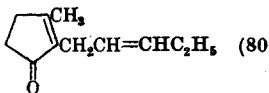
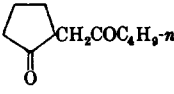
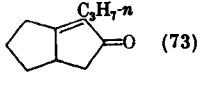
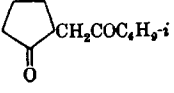
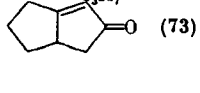
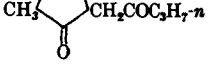
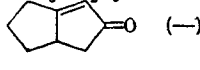
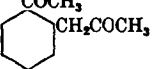
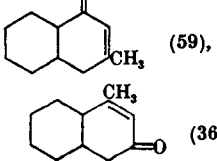
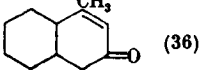
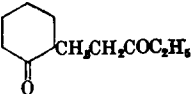
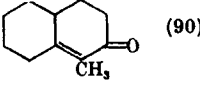
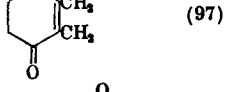
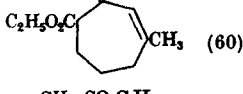
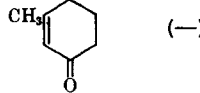
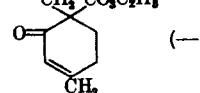
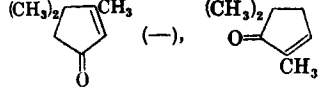
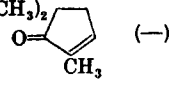
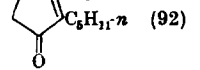
Note: References 668-2359 are on pp. 403-438.

ORGANIC REACTIONS

THE ALDOL CONDENSATION

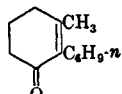
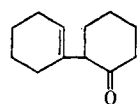
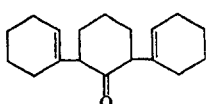
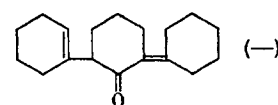
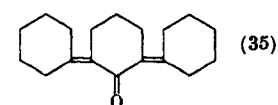
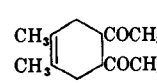
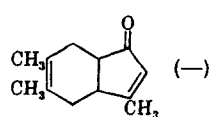
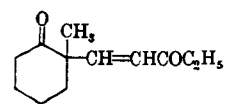
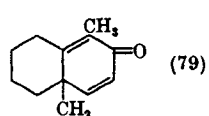
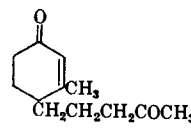
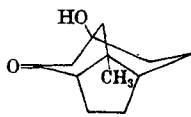
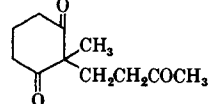
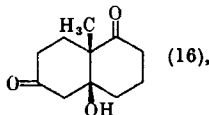
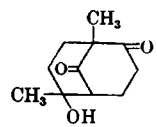
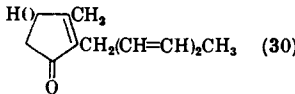
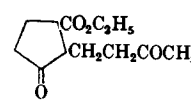
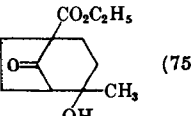
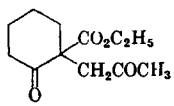
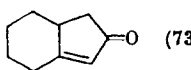
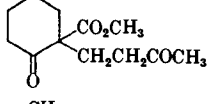
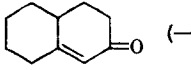
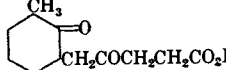
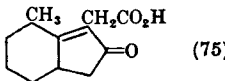
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TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|-----------------|
|  | NaOH |  (—) | 1262 |
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}(\text{CH}_2)_2\text{CH}=\text{CHC}_2\text{H}_5$ | .. |  (80) | 393, 1260, 1263 |
|  | KOH |  (73) | 1242 |
|  | .. |  (73) | 1242 |
|  | NaOH |  (—) | 397 |
|  | HCl |  (59),  (36) | 1250, 1264 |
|  | KOH |  (90) | 1265 |
| $\text{CH}_2\text{CO}(\text{CH}_2)_2\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ | NaOC_2H_5 |  (97) | 405 |
| $\text{CH}_2\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)(\text{CH}_2)_2\text{COCH}_2$ | HCl |  (60) | 1266 |
| $\text{CH}_2\text{COC}(\text{CO}_2\text{C}_2\text{H}_5)(\text{CH}_2)(\text{CH}_2)_2\text{COCH}_2$ | $(\text{CH}_3)_4\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 407 |
| | H_3PO_4 |  (—) | 407 |
| $\text{CH}_2\text{COC}(\text{CH}_3)_2\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\text{COCH}_2$ | KOH |  (—),  (—) | 1267 |
| $\text{CH}_2\text{CO}(\text{CH}_2)_2\text{COC}_6\text{H}_{11-n}$ | NaOH |  (92) | 1232, 1268, 393 |

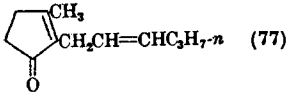
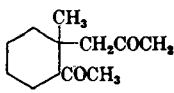
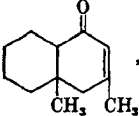
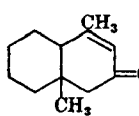
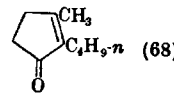
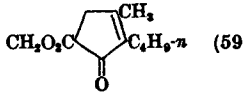
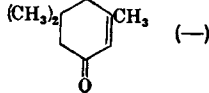
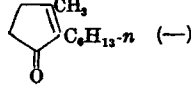
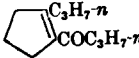
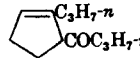
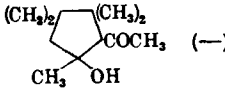
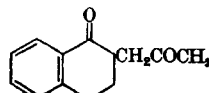
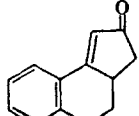
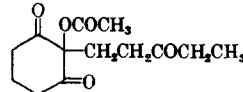
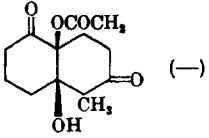
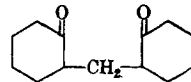
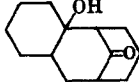
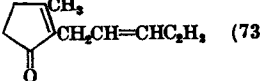
Note: References 668–2359 are on pp. 403–438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|-----------|
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COC}_8\text{H}_{11-n}$ | NaOH |  (—) | 393 |
| $\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_2\text{COC}_2\text{H}_5$ | H_2SO_4 | No condensation | 384 |
|  | KOH |  (45), | 166 |
| | |  (—), | |
| | |  (35) | |
|  | NaOCH_3 |  (—) | 1256 |
|  | NaOC_2H_5 ; also H_2SO_4 |  (79) | 2336 |
|  | KOC_4H_9-t |  (78) | 1269 |
|  | $(\text{CH}_2)_4\text{NH}$ |  (16),  (16) | 48 |
| $\text{CH}_3\text{COCHOHCH}_2\text{CO}(\text{CH}_2)_2(\text{CH}=\text{CH})_2\text{CH}_3$ | NaOH |  (30) | 1270 |
|  | H_2SO_4 |  (75) | 648 |
|  | KOH |  (73) | 1271 |
|  | HCl, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 426, 2311 |
|  | KOH |  (75) | 1272 |

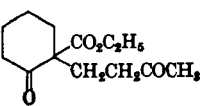
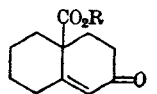
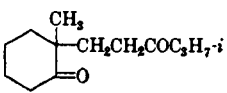
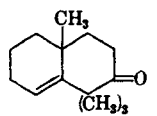
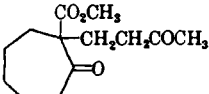
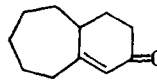
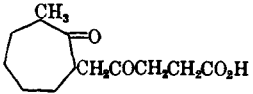
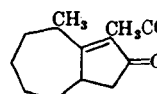
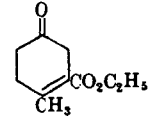
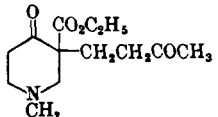
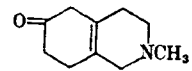
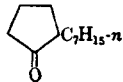
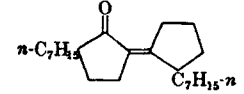
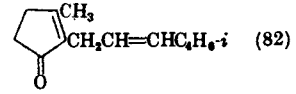
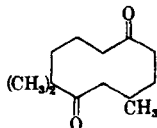
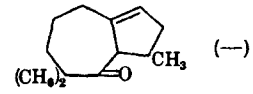
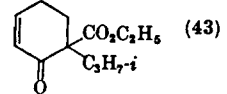
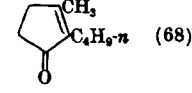
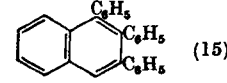
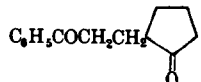
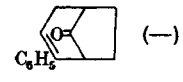
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|-----------|
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}(\text{CH}_2)_2\text{CH}=\text{CHC}_3\text{H}_7-n$ | NaOH |  (77) | 1260 |
|  | .. |  I  II (I:II = 4:1) | 1250 |
| $\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{COC}_6\text{H}_{11}-n$ | .. |  (68) | 1232 |
| | NaOCH ₃ |  (59) | |
| $\text{CH}_3\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$ | NaOC ₂ H ₅ |  (—) | 1273 |
| $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{COC}_6\text{H}_{13}-n$ | Na ₂ B ₄ O ₇ |  (—) | 1232 |
| $n\text{-C}_3\text{H}_7\text{CO}(\text{CH}_2)_4\text{COC}_3\text{H}_7-n$ | KOH |  (80),  (8) | 395 |
| $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$ | None |  (—) | 69 |
|  | KOH |  (80) | 1274 |
|  | $(\text{CH}_2)_4\text{NH}_2$, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 665 |
|  | KOH |  (22) | 555 |
| $\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{CO}-$ $(\text{CH}_2)_4\text{CH}=\text{CHC}_2\text{H}_5$ | NaOH |  (73) | 393, 1263 |



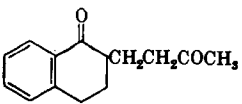
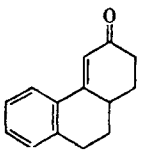
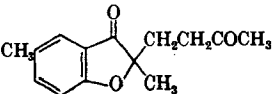
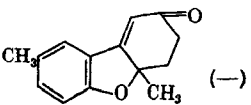

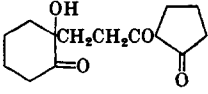
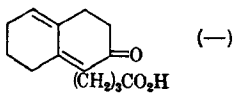
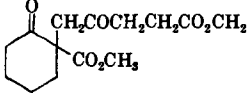
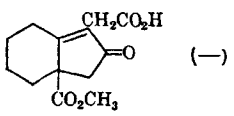
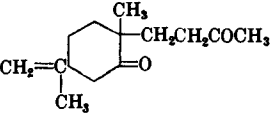
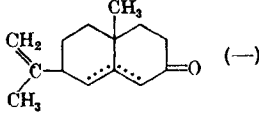
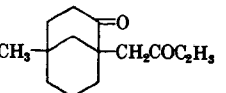
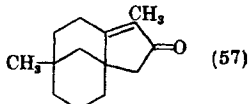
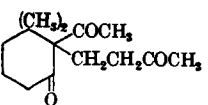
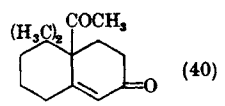
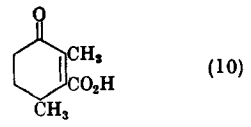
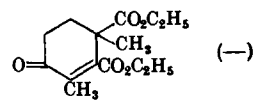
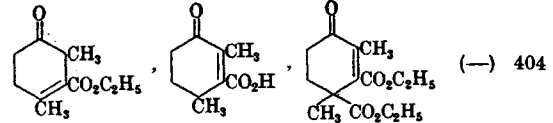
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|------------------------------|---|-------|
|  | NaOC2H5 |  R = H (15), R = C2H5 (66) | 1276 |
|  | NaOCH3 |  (—) | 1277 |
|  | HCl, CH3CO2H |  (—) | 426 |
|  | KOH |  (80) | 1272 |
| CH3COCH2CH2C(CO2C2H5)(CH3)COCO2C2H5 | HCl |  (—) | 404 |
|  | KOH |  (20) | 1278 |
|  | " |  (50) | 1206 |
| CH3CO(CH2)2CO(CH2)2CH=CHC4H9-i | NaOH |  (82) | 1260 |
|  | " |  (—) | 1279 |
| CH3COC(CO2C2H5)(C2H5-i)(CH3)COCH3 | C6H5N(C2H5)2, 140° |  (43) | 1280 |
| CH3COCH2CH(CO2C2H5)COC5H11-n | NaOH |  (68) | 1232 |
| C6H5CH2COC6H5 | Polyphosphoric acid, 150° |  (15) | 1281 |
|  | 4-CH3C6H4SO3H |  (—) | 1282 |

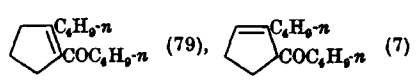
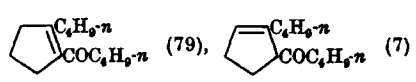
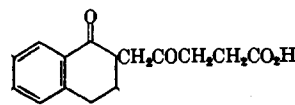
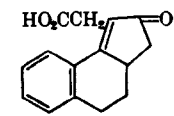
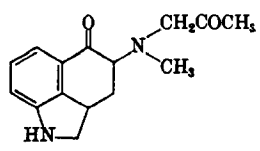
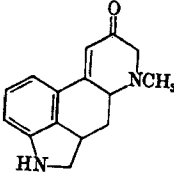

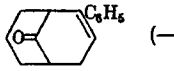
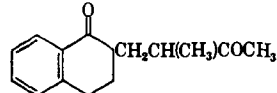
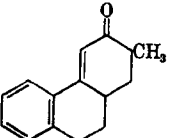
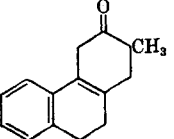
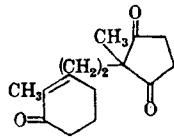
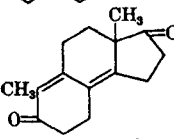
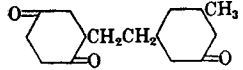
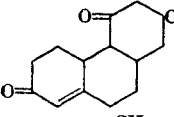
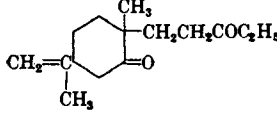
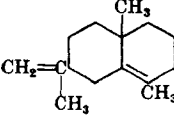
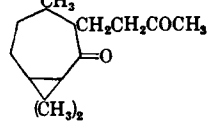
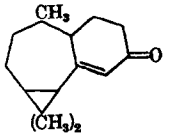
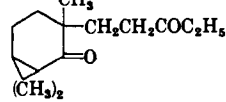
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|------------------|--|-------|
| $C_6H_5COCH_2CH_2$  (contd.) | HCl, CH_3CO_2H | C_6H_5  CO_2H (—) | 1282 |
|  | KOC_2H_5 |  (73) | 1142 |
|  | KOH |  (—) | 1283 |
| $C_6H_5COCH_2CH(COCH_3)CO_2C_2H_5$ | NaOH |  (—) | 1284 |
|  | KOH |  (—) | 1285 |
|  | KOC_4H_9-t |  (—) | 1286 |
|  | $NaOC_2H_5$ |  (—) | 1288 |
|  | KOH |  (57) | 1275 |
|  | .. |  (40) | 1289 |
| $C_6H_5COCH_2CH_2C(CH_3)(CO_2C_2H_5)CO_2C_2H_5$ | .. |  (10) | 404 |
| | $NaOCH_3$ |  (—) | 404 |
| | HCl |  (—) | 404 |

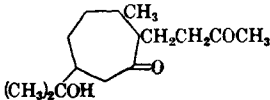
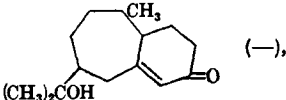
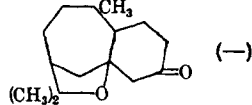
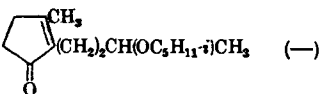
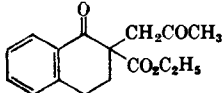
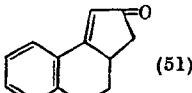
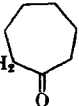
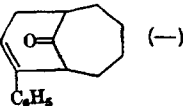
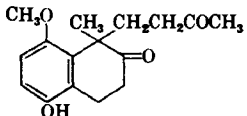
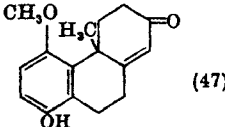
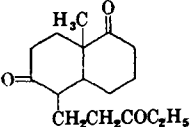
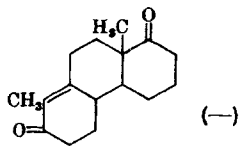
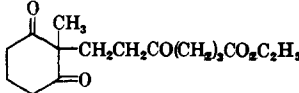
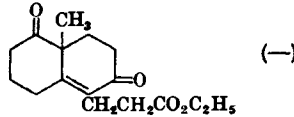
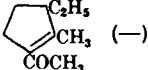
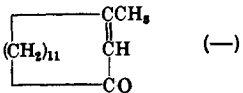
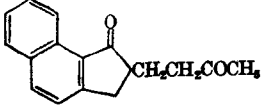
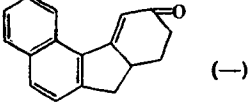
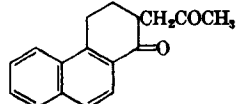
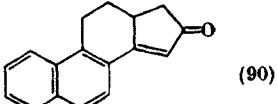
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|-------|
| $n\text{-C}_4\text{H}_9\text{CO}(\text{CH}_2)_4\text{COC}_4\text{H}_9\text{-}n$ | KOH |  (79),  (7) | 395 |
|  | $\text{KOC}_4\text{H}_9\text{-}t$ |  (51) | 1290 |
|  | NaOCH_3 |  (69) | 1291 |
| $(\text{C}_6\text{H}_5)_3\text{CHCOCH}_3$ | $\text{C}_6\text{H}_5\text{MgBr}$ or $(\text{CH}_2)_3\text{CHMgBr}$ | $(\text{C}_6\text{H}_5)_3\text{CHC}(\text{CH}_3)=\text{CHCOCH}(\text{C}_6\text{H}_5)_2$ (30) | 1292 |
| $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2$  | - |  (-) | 1293 |
|  | KOH |  (-) | 1294 |
| | H_3PO_4 |  (-) | 1294 |
|  | $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  (76) | 403 |
|  | HCl |  (70) | 1295 |
|  | NaOC_2H_5 or H_2SO_4 |  (-) | 1288 |
|  | KOH |  (-) | 1296 |
|  | Various catalysts | No condensation | 1297 |

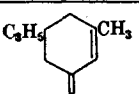
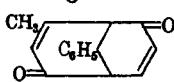
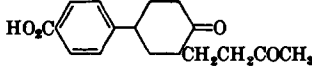
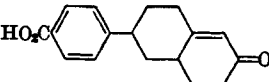
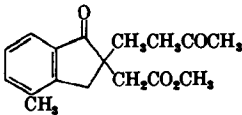

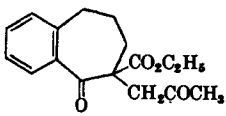
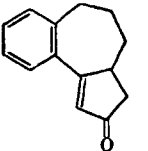
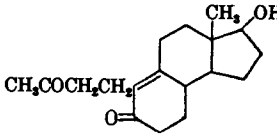
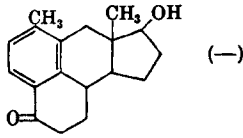
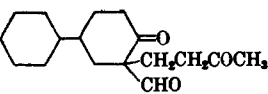
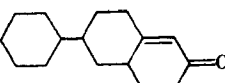
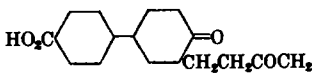
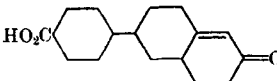

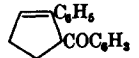
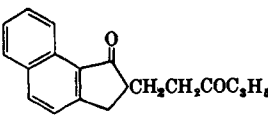
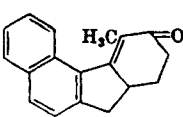
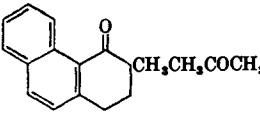
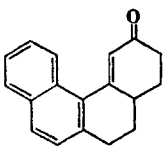
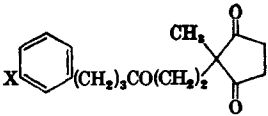
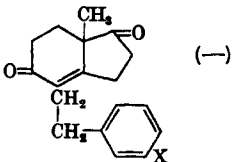
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|------------|
|  | KOH |  (—),  (—) | 1296, 1298 |
| $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CO}(\text{CH}_2)_3\text{CH}(\text{OC}_2\text{H}_5)_2\text{CH}_3$ | HBr |  (—) | 1232 |
|  | KOH |  (51) | 1274 |
| $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2$  | $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ |  (—) | 1282 |
|  | HCl |  (47) | 1299 |
|  | .. |  (—) | 1300 |
|  | $(\text{C}_2\text{H}_5)_2\text{N},$ $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ |  (—) | 1300 |
| $\text{CH}_3\text{COC}(\text{C}_2\text{H}_5)(\text{CO}_2\text{C}_2\text{H}_5)(\text{CH}_2)_2\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)\text{COCH}_3$ | KOH |  (—) | 1301 |
| $\text{CH}_2\text{CO}(\text{CH}_2)_{11}\text{COCH}_3$ | $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ |  (—) | 1302 |
|  | HCl |  (—) | 1303 |
|  | KOH |  (90) | 1304 |

Note: References 668–2359 are on pp. 403–438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|-------|
| $\text{CH}_3\text{COCH}(\text{COCH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{COCH}_3)\text{COCH}_3$ | KOH |  (—) | 46 |
| | HCl |  (—) | 46 |
|  | NaOH |  (72) | 1305 |
|  | NaOCH_3 |  (33) | 1306 |
|  | KOH |  (61) | 1307 |
|  | HCl |  (—) | 1308 |
|  | HCl; also KOH |  (82) | 1309 |
|  | NaOH |  (83-90) | 1305 |
| $\text{C}_6\text{H}_5\text{CO}(\text{CH}_3)_2\text{COC}_6\text{H}_5$ | KOH |  (79),  (12) | 395 |
|  | HCl |  (—) | 1303 |
|  | KOH |  (91) | 1310 |
|  X = H, O ₂ N, CH ₃ O | $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$, or $\text{Al}(\text{OC}_2\text{H}_5)_3$ |  (—) | 388 |
| | | X = H, NO ₂ , OCH ₃ | |

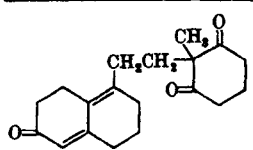
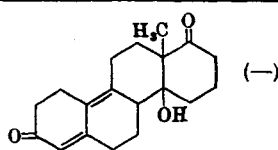
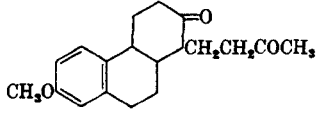
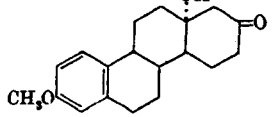
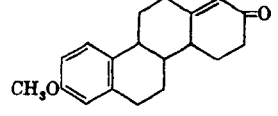
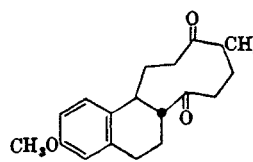
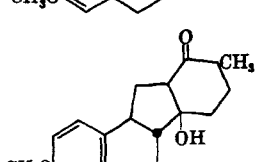
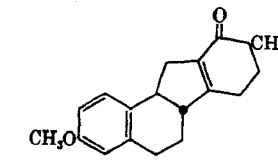
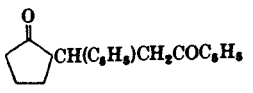
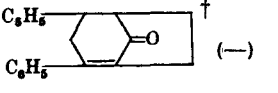
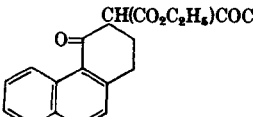
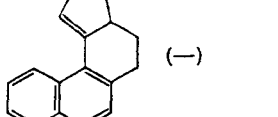
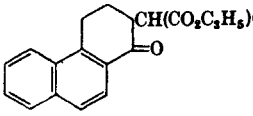
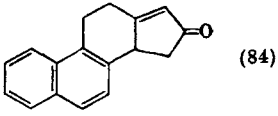
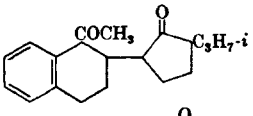
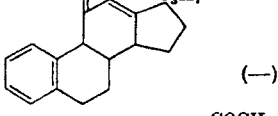
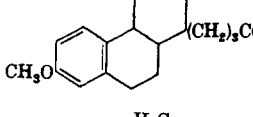
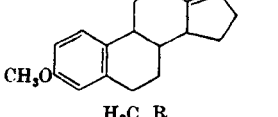
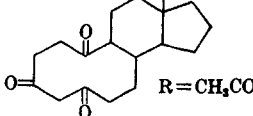
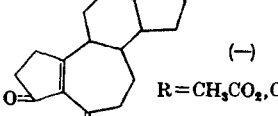
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--------|--|--|--------------|
| | KOH | (50) | 1305 |
| | NaOH | (—) | 1311 |
| | KOC ₄ H _{9-t} | (—) | 606 |
| | HCl or NaOCH ₃ | (—) | 1312 |
| | KOH | (48) | 1309 |
| | NaOCH ₃ | (17) | 1309 |
| | KOH | (37-40) | 1313 |
| | CH ₃ CO ₂ Na, (CH ₃ CO) ₂ O | (70) | 1314 |
| | H ₂ SO ₄ , P ₂ O ₅ | No condensation C ₁₉ H ₁₈ O (—) | 1244 1244 |
| | NaOCH ₃ | (—) or | 1315 |
| | | (—) | |
| | NaOC ₂ H ₅ | (—) or | 1315 |
| | | (—) | |
| | | (—) | |

Note: References 668-2359 are on pp. 403-438.

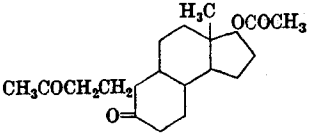
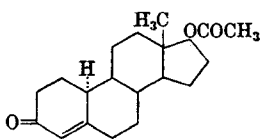
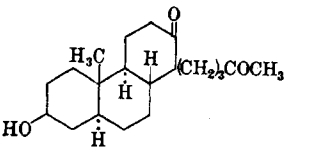
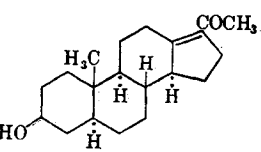
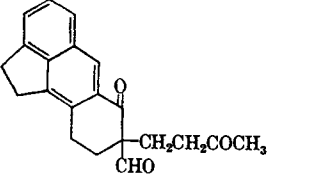
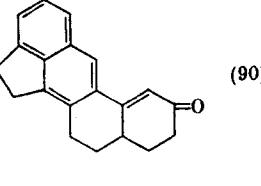
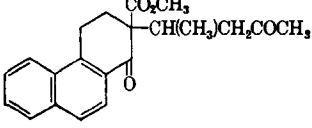
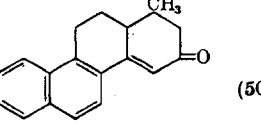
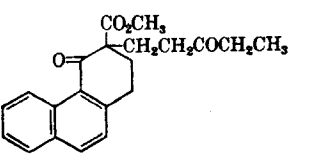
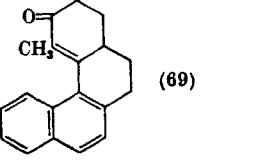
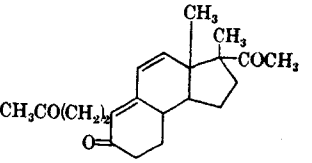
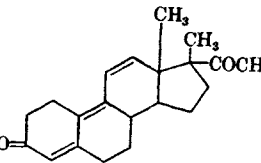
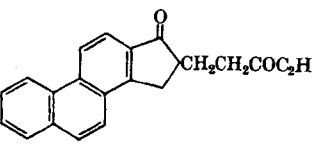
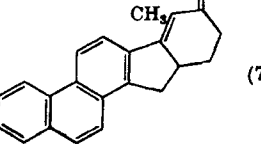
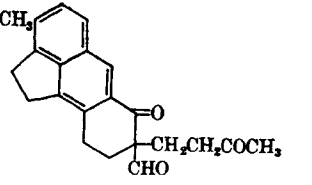
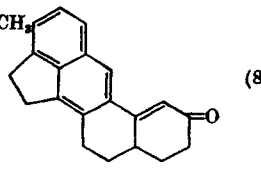
TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|-----------------|
|  | 4-CH ₃ C ₆ H ₄ SO ₃ H |  (—) | 402 |
|  | KOH, 25° |  (88) | 1316 |
| | KOH, heat |  (—) | 1316 |
|  | KOH |  (29), | 1316 |
| | |  (32) | |
|  | HCl |  † (—) | 1317 |
|  | KOH |  (—) | 1318 |
|  | .. |  (84) | 1304 |
|  | NaOC ₂ H ₅ |  (—) | 1319 |
|  | NaOCH ₃ |  (—) | 1320 |
|  | CH ₃ CO ₂ H |  (—) | 1321, 399, 1322 |

Note: References 668–2359 are on pp. 403–438.

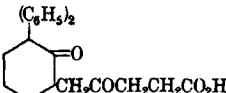
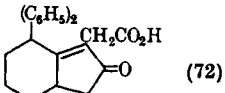
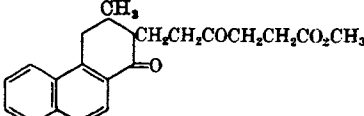
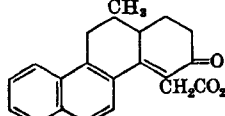
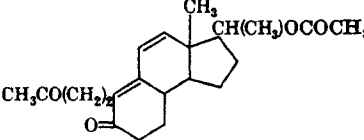
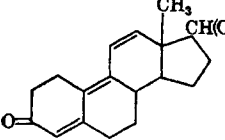
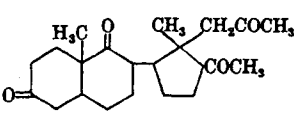
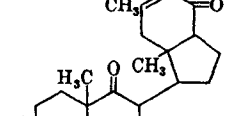
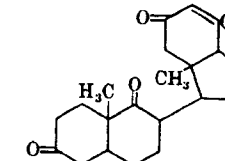
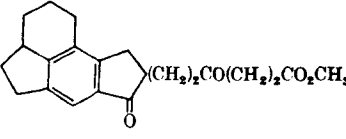
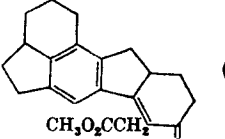
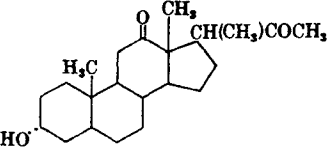
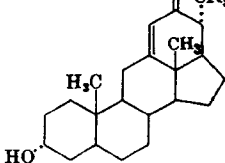
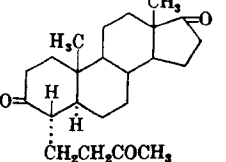
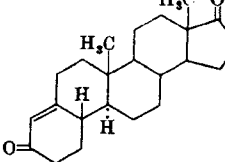
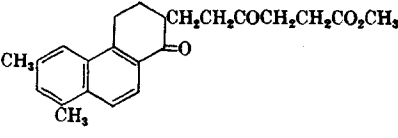
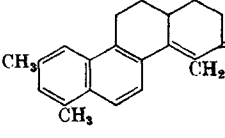
† The structure of this product was not established.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--------------------------------|---|------------|
|  | KOH |  (—) | 1323 |
|  | NaOH |  (—) | 1324, 1325 |
| $(C_6H_5)_3CCOCH_3$ | $(C_6H_5)_3CNa$ | $(C_6H_5)_3CCOCH_2COCH_3$ (92) | 1326 |
|  | KOH |  (90) | 1327 |
|  | .. |  (50) | 131, 1328 |
|  | HCl, CH_3CO_2H ; also KOH |  (69) | 1310 |
|  | $NaOC_6H_{11}t$ |  (—) | 389 |
|  | KOH |  (72) | 1329 |
|  | .. |  (88) | 1327 |

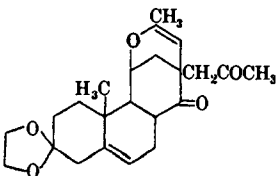
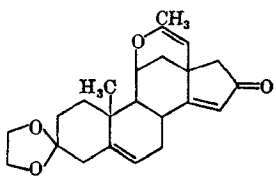
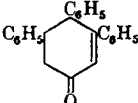
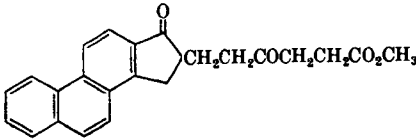
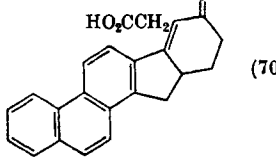
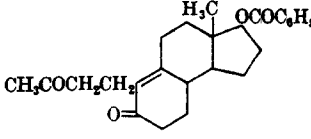
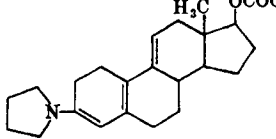
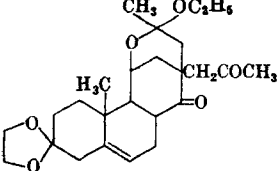
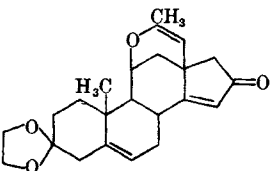
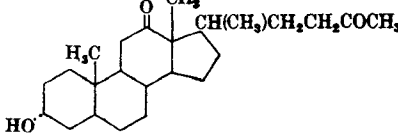
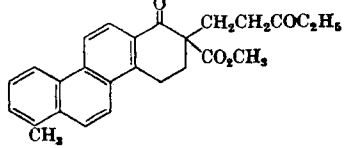
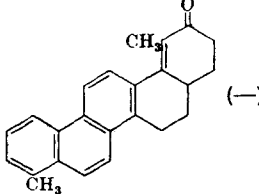
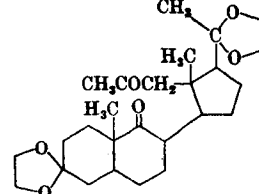
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|-------|
|  | KOH |  (72) | 1272 |
|  | NaOCH ₃ |  (88) | 387 |
|  | NaOC ₂ H ₁₁ -t |  (—) | 389 |
|  | NaOCH ₃ |  | 1330 |
| | |  (Total, 35) | |
|  | NaOCH ₃ , C ₆ H ₅ N |  (—) | 390 |
|  | NaH |  (54) | 1331 |
|  | H ₂ SO ₄ |  (—) | 1332 |
|  | NaOCH ₃ |  (96) | 387 |

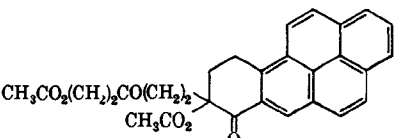
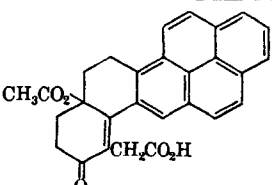
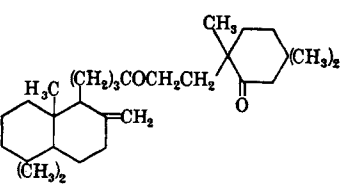
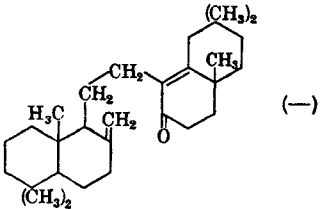
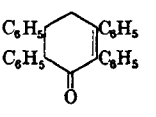
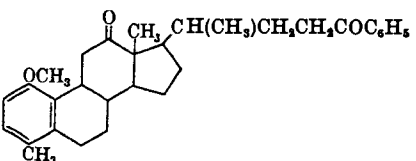
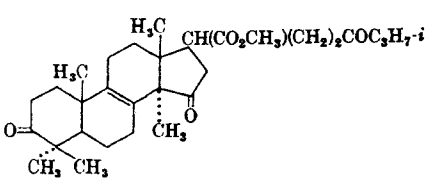
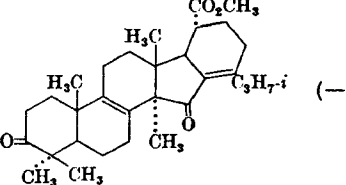
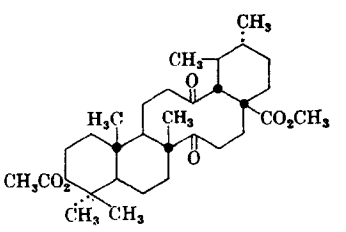
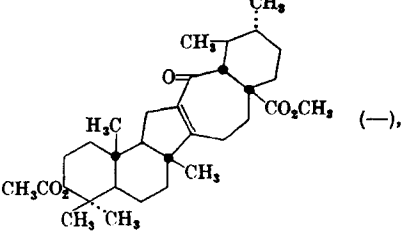

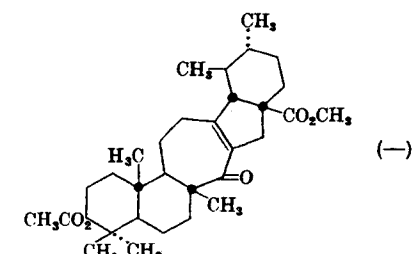
Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---------------------------------------|--|------------|
|  | KOC_4H_9-t |  (—) | 606 |
| $\text{C}_6\text{H}_5\text{COCH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCH}_3$ | HCl |  (50) | 1220 |
|  | KOH |  (70) | 1333 |
|  | $(\text{CH}_2)_4\text{NH}$ |  (—) | 1334, 1335 |
|  | KOC_4H_9-t |  (—) | 606 |
|  | .. | No condensation | 1331 |
|  | HCl, $\text{CH}_3\text{CO}_2\text{H}$ |  (—) | 1336 |
|  | NaOCH_3 | No condensation | 1330 |

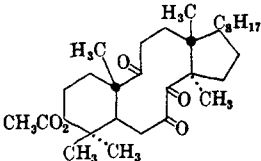
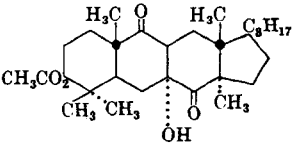
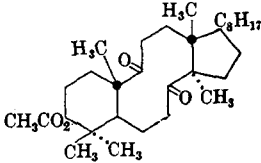
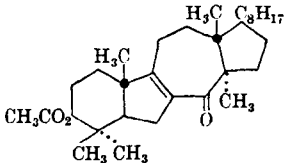
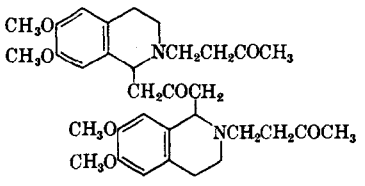
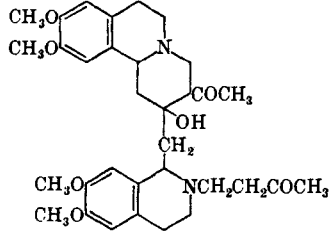
Note: References 668–2359 are on pp. 403–438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|----------------|
|  | NaOCH ₃ |  | (—) 391 |
|  | KOC ₄ H ₉ -t |  | (—) 1337 |
| <p>C₆H₅COCH₂CH(C₆H₅)CH(C₆H₅)COCH₂C₆H₅</p> | NaOCH ₃ |  | (75) 386, 1338 |
|  | NaOCH ₃ , NaNH ₂ , or NaH | No condensation | 1331 |
|  | KOC ₄ H ₉ -t |  | (—) 1339 |
|  | HCl, CH ₃ CO ₂ H |  | (—), 1340 |
|  | |  | (—) |







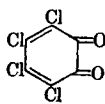
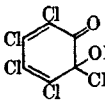
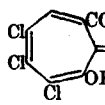


Note: References 668-2359 are on pp. 403-438.

TABLE VI. SELF-CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|-------|
|  | HCl, CH ₃ CO ₂ H |  (—) | 1340 |
|  | .. |  (—) | 1340 |
|  | NaOCH ₃ |  (—) | 1312 |
| $C_6H_5COC(C_6H_5)=C(C_6H_5)-$ $C(C_6H_5)=C(C_6H_5)CH_2C_6H_5$ | Na | Hexaphenylbenzene (72) | 1341 |

Note: References 668-2359 are on pp. 403-438.

TABLE VII. MIXED CONDENSATION OF KETONES







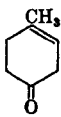

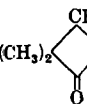


| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|----------------|
| CH ₃ COCO ₂ H and CH ₃ COCH ₃ | KOH (CH ₂) ₆ NH | CH ₃ COCH ₂ C(OH)(CH ₃)CO ₂ H (14-19) CH ₃ COCH=C(CH ₃)CO ₂ H (28) | 1342 1343 |
| CH ₃ COC ₂ H ₅ C ₂ H ₅ COCH ₃ CH ₃ COCH ₃ and | KOH .. | CH ₃ COCH(CH ₃)C(OH)(CH ₃)CO ₂ H (-) C ₂ H ₅ COCH ₂ C(OH)(CH ₃)CO ₂ H (-) | 1342 1344 |
|  | NaOH |  (20),  (20) 180 | |
| CH ₃ COC ₂ H ₅ | Metal oxides; also Ba(OH) ₂ , HCl | 3-Methyl- and 3-ethyl-2-cyclohexen-1-one (-) | 175, 1345-1347 |
|  | NaOCH ₃ |  (39),  (-) 1348, 181, 182, 2344 | |
|  | HCl, -30° |  (-) | 1349 |
| | HCl, 25° |  (-) | 1349 |
|  | NaOC ₂ H ₅ |  (-) | 182 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION


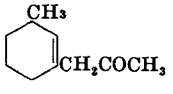
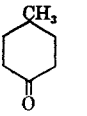
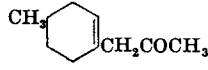
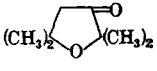
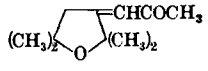
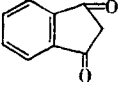
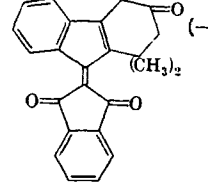
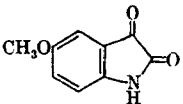
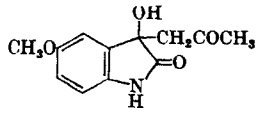
159

TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|-------|
| CH ₃ COCH ₃ (contd.) and | | | |
|  | NaOC ₂ H ₅ |  (-) | 182 |
|  | .. |  (23) | 182 |
| CH ₃ N  | Ion-exchange resin Amberlite IRA 400 |  (-) | 1350 |
|  | NaOC ₂ H ₅ | Solid, m.p. 73° (-) | 1351 |
| (+)-(CH ₃) ₂  | NaOH |  (-) | 1352 |
|  | NaOC ₂ H ₅ |  (-) | 182 |

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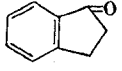
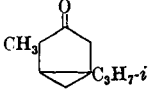
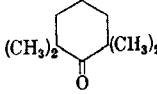
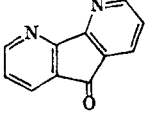
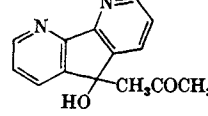
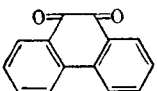
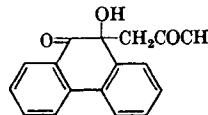
ORGANIC REACTIONS

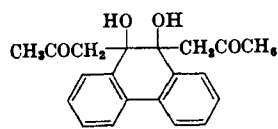
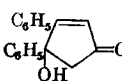
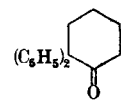
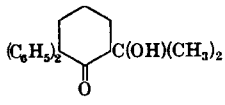
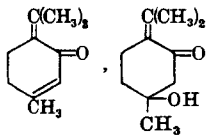
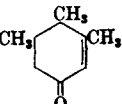
| | | | |
|---|------------------------------------|--|--------------------------|
|  | .. |  (—), (CH ₃) ₂ C=CHCOCH ₃ (—), (CH ₃) ₂ C=CHCOCH=C(CH ₃) ₂ (—), C ₁₃ H ₂₀ O (—) | 1353, 182, 1146, 1354 |
|  | .. |  (17) | 182 |
|  | NaOCH ₃ |  (—) | 1355, 1356 |
|  | (CH ₃) ₂ NH |  (—) | 1357 |
|  | .. |  (—) | 1371 |

Note: References 668–2359 are on pp. 403–438.

* The optical activity was preserved in the product.

TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

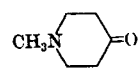
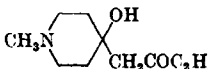


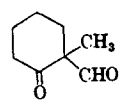
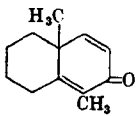
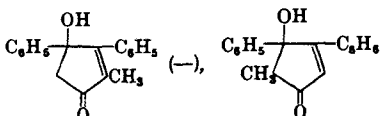

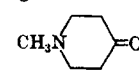
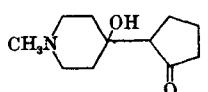
| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|-------------|
| CH ₃ COCH ₃ (contd.) and | | | |
|  | KOH | C ₁₂ H ₁₂ O (—) | 1235, 2344 |
| C ₆ H ₅ CH ₂ COCO ₂ H <i>i</i> -C ₃ H ₇ CH ₂ COCH ₂ C ₃ H ₇ - <i>i</i> | .. <i>i</i> -C ₃ H ₇ MgCl | CH ₃ COCH ₂ C(OH)(CH ₂ C ₆ H ₅)CO ₂ H (—) (CH ₃) ₂ C(OH)CH(C ₃ H ₇ - <i>i</i>)COCH ₂ C ₃ H ₇ - <i>i</i> (—) | 1358 176 |
|  | NaOCH ₃ | Solid, m.p. 78.5° (8) | 1359 |
|  | C ₆ H ₅ N(CH ₃)MgCl | No condensation | 1360 |
|  | Al ₂ O ₃ |  (75) | 1361 |
|  | KOH |  (—), | 1362 |

| | | | | |
|---|--------------------------------|--|---|------------|
| | |  | (—) | |
| $C_6H_5COCOC_6H_5$ | .. |  | (60), $C_{17}H_{16}O_3$ (—), $C_{31}H_{24}O_4$ (—) | 1362-1364 |
|  | C_6H_5MgX (X = Cl, Br, I) |  | (58) | 1365 |
| $CH_3COCH=CH_2$ and $(CH_3)_2C=CHCOCH_3$ | BaO, MgO, or CaO |  | (Total, 15) | 1366, 1196 |
| CH_3COCH_2CHO and $(C_6H_5)_2CO$ | KNH_2 | $(C_6H_5)_2C(OH)CH_2COCH_2CHO$ † | (67) | 212 |
| $C_6H_5COCO_2H$ and $C_6H_5COCH_3$ | KOH | $C_6H_5COCH_2C(OH)(C_6H_5)CO_2H$ | (—) | 1344 |
| $CH_3COC_2H_5$ and $CH_3COCH(CH_3)CH_2OH$ | .. |  | (52) | 1367 |

Note: References 668-2359 are on pp. 403-438.

† This compound was isolated as its copper enolate.

TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|--------------------------|
| $CH_3COC_2H_5$ (contd.) and  | Ion-exchange resin Amberlite IRA 400 |  | (—) 1350 |
|  | NaOH |  | (—) 178 |
| $C_6H_5COCH_3$ | $C_6H_5(R)NMgX$, (R = H, CH_3 , C_2H_5 , C_6H_5) | $C_6H_5COCH=C(C_6H_5)CH_3$ (28), $C_6H_5COCH_2C(OH)(CH_3)C_2H_5$ (34) | 198 |
|  | $(CH_3)_3NH$, CH_3CO_2H |  | (2) 1368 |
| $C_6H_5COCOC_6H_5$ | NaOH |  | (—), (—) 1369, 199, 1370 |
|  and  | Ion-exchange resin Amberlite IRA 400 |  | (—) 1360 |

| | | | | |
|---|--|---|---------|------|
| | NaNH ₂ | | (—) | 1143 |
| C ₆ H ₅ CH ₂ COCO ₂ H | NaOH; KOH | | (4-39), | 184 |
| | | HO ₂ C(C ₆ H ₅ CH ₂)(HO)C | | |
| | HCl | | (55) | 1157 |
| CH ₃ COCH ₂ CH ₂ CO ₂ H and C ₆ H ₅ COCOC ₆ H ₅ | KOH | | (40) | 200 |
| CH ₃ COC ₃ H _{7-n} and | Ion-exchange resin Amberlite IRA 400 | | (—) | 1350 |
| C ₆ H ₅ COCH ₃ | C ₆ H ₅ (R)NMgX, (R = H, CH ₃ , C ₂ H ₅ , C ₆ H ₅) | C ₆ H ₅ COCH=C(CH ₃)C ₃ H _{7-n} | (32) | 198 |
| C ₆ H ₅ COCOC ₆ H ₅ | KOH | C ₁₉ H ₁₅ O ₆ | (—) | 199 |

Note: References 668-2359 are on pp. 403-438.

TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|-----------------|
| CH ₃ COC ₃ H _{7-i} and | Ion-exchange resin Amberlite IRA 400 | | (—) 1350 |
| | (C ₂ H ₅) ₂ NH | | (—) 1371 |
| (C ₂ H ₅) ₂ CO and C ₆ H ₅ COCOC ₆ H ₅ | KOH | | (88) 201, 199 |
| CH ₃ COCH=C(CH ₃) ₂ and C ₆ H ₅ COCH ₃ | C ₆ H ₅ N(CH ₃)MgBr | C ₆ H ₅ COCH ₂ C(OH)(CH ₃)CH=C(CH ₃) ₂ (31), C ₆ H ₅ C(OH)(CH ₃)CH ₂ COCH=C(CH ₃) ₂ (33) | 198 |
| and | Ion-exchange resin Amberlite IRA 400 | | (—) 1350 |
| | KOC ₄ H _{9-t} , C ₅ H ₅ N | | (Total, 56) 179 |
| C ₆ H ₅ CH ₂ CH ₂ COCO ₂ H | KOH or NaOH | | (15-40), 1372 |

| | | | | |
|---|---|-------------------|------------|------|
| | HCl | (-) | (29) | 1157 |
| | Primary aliphatic or cycloaliphatic amines | (-) | (-) | 1181 |
| | H ₂ SO ₄ | (30), (30) | (30), (30) | 1178 |
| | C ₆ H ₅ N(CH ₃)MgBr | No condensation | | 1373 |
| C ₆ H ₅ COCOC ₆ H ₅ | KOH | (70-90) | (70-90) | 207 |

Note: References 668-2359 are on pp. 403-438.

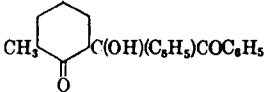
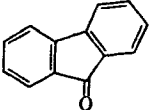
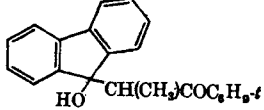
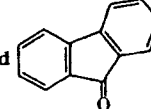
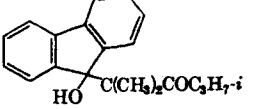
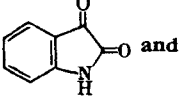
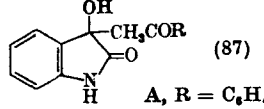
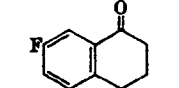
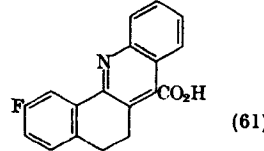
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TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|------------------------------|
| CH ₃ COC ₆ H ₄ - <i>t</i> and C ₆ H ₅ COCH ₃ 4-CH ₃ C ₆ H ₄ COCH ₃ 4-C ₂ H ₅ C ₆ H ₄ COCH ₃ 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ COCH ₃ | C ₆ H ₅ N(CH ₃)MgI " " " | C ₆ H ₅ COCH ₂ C(OH)(CH ₃)C ₆ H ₄ - <i>t</i> (48) 4-CH ₃ C ₆ H ₄ COCH ₂ C(OH)(CH ₃)C ₆ H ₄ - <i>t</i> (31) 4-C ₂ H ₅ C ₆ H ₄ COCH ₂ C(OH)(CH ₃)C ₆ H ₄ - <i>t</i> (33) 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ COCH ₂ C(OH)(CH ₃)C ₆ H ₄ - <i>t</i> (21) | 1374 1374 1374 1374 |
| | (C ₆ H ₅) ₂ NH | (-) | 2078 |
| | C ₆ H ₅ N(CH ₃)MgBr | HO CH ₂ COC ₆ H ₄ - <i>t</i> (70) | 1033 |
| C ₆ H ₅ COC ₆ H ₅ | " | (C ₆ H ₅) ₂ C(OH)CH ₂ COC ₆ H ₅ - <i>t</i> (35) | 1033, 159 |
| | " | HO CH ₂ COC ₆ H ₄ - <i>t</i> (90) | 1373 |

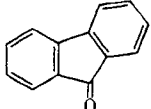
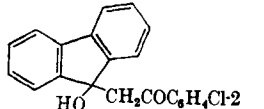
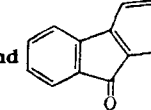
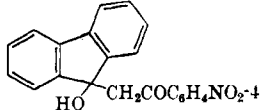
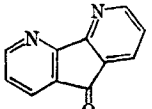
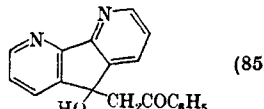
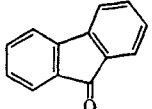
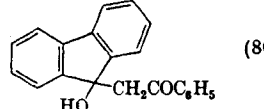
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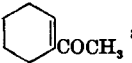
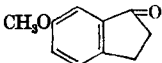
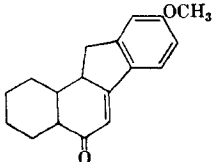
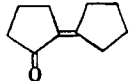
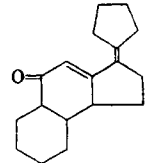
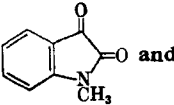
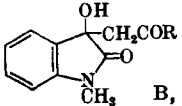
ORGANIC REACTIONS

| | | | | |
|---|---------------------|--|---------|------|
| $C_6H_5COCOC_6H_5$ | KOH |  | (70-90) | 207 |
| $C_6H_5COC_6H_4H_t$ and  | $C_6H_5N(CH_3)MgBr$ |  | (60) | 1033 |
| $i-C_6H_7COC_6H_7-i$ and  | .. |  | (60) | 1033 |
|  and $4-BrC_6H_4COCH_3$ | $(C_6H_5)_2NH$ |  | (87) | 1375 |
| $4-ClC_6H_4COCH_3$ | .. | A, R = C_6H_4Br-4 | | 1375 |
| $3-O_2NC_6H_4COCH_3$ | .. | A, R = C_6H_4Cl-4 (87) | | 1376 |
| $C_6H_5COCH_3$ | .. | A, R = $C_6H_4NO_2-3$ (66) | | 1375 |
| $4-CH_3C_6H_4COCH_3$ | .. | A, R = C_6H_5 (63) | | 1375 |
| $4-CH_3OC_6H_4COCH_3$ | .. | A, R = $C_6H_4CH_3-4$ (86) | | 1375 |
| | .. | A, R = $C_6H_4OCH_3-4$ (85) | | 1375 |
|  | KOH |  | (61) | 1377 |

Note: References 668-2359 are on pp. 403-438.

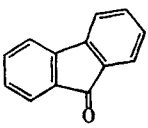
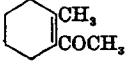
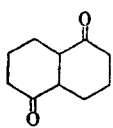
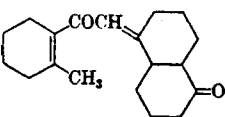
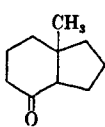
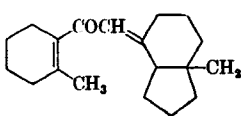
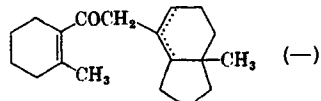
TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

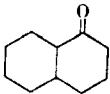
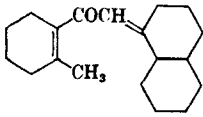
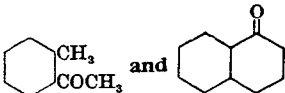
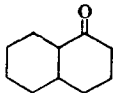
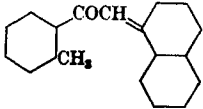
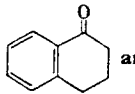
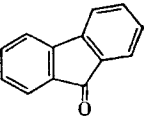
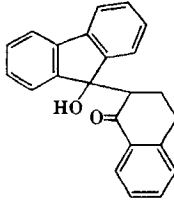
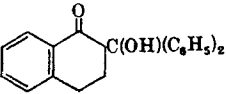
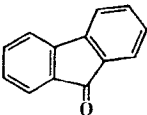
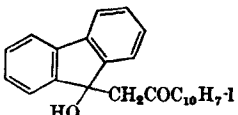
| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|--------------------------|
| $2-ClC_6H_4COCH_3$ and  | $C_6H_5N(CH_3)MgBr$ |  | (45) 1373 |
| $4-O_2NC_6H_4COCH_3$ and  | .. |  | (45) 1373 |
| $C_6H_5COCH_3$ and $C_6H_5CH_2COCO_2H$ $3,4-(CH_2O)_2C_6H_3CH_2COCO_2H$ | KOH .. | $C_6H_5COCH_2C(OH)(CH_2C_6H_5)CO_2H$ (—) $3,4-(CH_2O)_2C_6H_3CH_2C(OH)-$ $(CH_2COC_6H_5)CO_2H$ (62) | 1378 1379 |
|  | Al_2O_3 |  | (85) 1361 |
| $C_6H_5COCH_2C_6H_5$ | $NaOCH_3$ | $C_6H_5COC(C_6H_5)=C(CH_3)C_6H_5$ (80-85) | 1380 |
|  | $C_6H_5N(CH_3)MgBr$ |  | (80-85) 1373, 1033 |
| $C_6H_5COCOC_6H_5$ | KOH; $NaOCH_3$ or $C_6H_5N(CH_3)MgBr$ | $C_6H_5COC(C_6H_5)=CHCOC_6H_5$ (80), $C_{22}H_{18}O_3$ (—) | 1381, 208, 1362, 1373 |

| | | | | |
|---|-----|--|--|---|
|  | and | | | |
|  | | KOC ₄ H ₉ - <i>t</i> |  | (25) 1382 |
|  | | NaNH ₂ |  | (—) 1143 |
| CH ₃ COCH ₂ H _{13-n} and C ₆ H ₅ COCOC ₆ H ₅ | | KOH | C ₂₂ H ₂₄ O ₂ (—) | 199 |
|  | and | | | |
| 4-BrC ₆ H ₄ COCH ₃ | | (C ₂ H ₅) ₂ NH |  | B, R = C ₆ H ₄ Br-4 (54) 1376 |
| 4-ClC ₆ H ₄ COCH ₃ | | .. | B, R = C ₆ H ₄ Cl-4 (67) | 1376 |
| 3-O ₂ NC ₆ H ₄ COCH ₃ | | .. | B, R = C ₆ H ₄ NO ₂ -3 (75) | 1376 |
| C ₆ H ₅ COCH ₃ | | .. | B, R = C ₆ H ₅ (72) | 1375 |
| 4-CH ₃ OC ₆ H ₄ COCH ₃ | | .. | B, R = C ₆ H ₄ OCH ₃ -4 (60) | 1376 |

Note: References 668-2359 are on pp. 403-438.

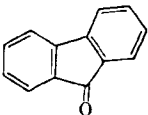
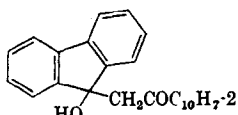
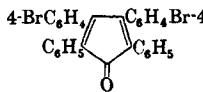
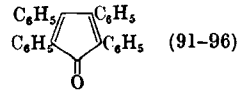
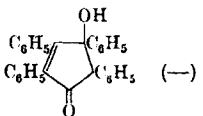
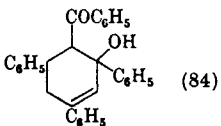
TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

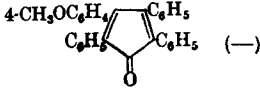
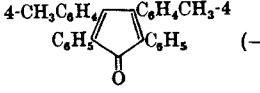
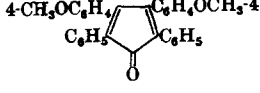
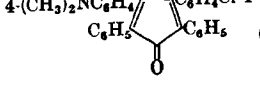
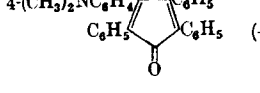
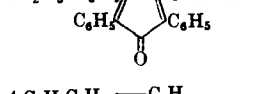
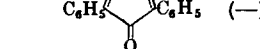
| Ketone | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|--|--|-----------|
| C ₆ H ₅ CH ₂ COCO ₂ H and C ₆ H ₅ (CH ₂) ₄ COCH ₃ | NaOH | C ₆ H ₅ (CH ₂) ₂ COCH ₂ C(OH)(CH ₂ C ₆ H ₅)CO ₂ H (40) | 1383, 1384 | |
| 4-CH ₃ OC ₆ H ₄ (CH ₂) ₂ COCH ₃ | .. | 4-CH ₃ OC ₆ H ₄ (CH ₂) ₂ COCH ₂ - C(OH)(CH ₂ C ₆ H ₅)CO ₂ H (—) | 1384 | |
| C ₆ H ₅ COC ₆ H ₅ and  | C ₆ H ₅ N(CH ₃)MgBr | No condensation | 1373 | |
|  | and | | | |
|  | | KOC ₄ H ₉ - <i>t</i> or Al(OC ₄ H ₉ - <i>t</i>) ₃ |  | (61) 1385 |
|  | | KOC ₄ H ₉ - <i>t</i> |  | (—) 1386 |
| | | |  | (—) |

| | | | | |
|---|--|--|------|------|
|  | .. |  | (37) | 1385 |
|  and  | $\text{Al}(\text{OC}_2\text{H}_5)_3$ |  | (32) | 1385 |
|  and  | $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ |  | (84) | 1373 |
| $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ | .. |  | (21) | 1373 |
| $1\text{-C}_{10}\text{H}_7\text{COCH}_3$ and  | .. |  | (60) | 1373 |

Note: References 668-2359 are on pp. 403-438.

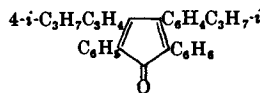
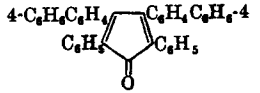
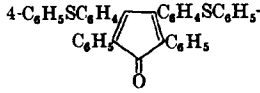
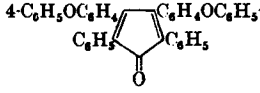
TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|----------------|
| $2\text{-C}_{10}\text{H}_7\text{COCH}_3$ and  | $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{MgBr}$ |  (45) | 1373 |
| $(\text{C}_6\text{H}_5)_2\text{CO}$ | .. | $2\text{-C}_{10}\text{H}_7\text{COCH}_2\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2$ (57) | 1373 |
| $\text{C}_6\text{H}_5(\text{COCH}_2)_2\text{COCH}_3$ and $(\text{C}_6\text{H}_5)_2\text{CO}$ | NaNH_2 | $\text{C}_6\text{H}_5(\text{COCH}_2)_3\text{C}(\text{C}_6\text{H}_5)_2\text{OH}$ (—) | 213 |
| $(4\text{-BrC}_6\text{H}_4\text{CO})_2$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CO}$ | NaOCH_3 |  (—) | 203 |
| $(\text{C}_6\text{H}_5\text{CO})_2$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{CO}$ | KOH |  (91-96) | 204, 202, 1387 |
| | $\text{KOH}, \text{C}_2\text{H}_5\text{OH},$ 3-5 min. |  (—) | 1387 |
| $\text{C}_6\text{H}_5\text{COCH}=\text{CHC}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{COCH}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$ | NaOC_2H_5 |  (84) | 1388 |

| | | | | |
|---|--------------------|--|-----|-----|
| 4-CH ₃ OC ₆ H ₄ COCOC ₆ H ₅ and (C ₆ H ₅ CH ₂) ₂ CO | NaOCH ₃ |  | (—) | 203 |
| (C ₆ H ₅ CH ₂) ₂ CO and | | | | |
| (4-CH ₃ C ₆ H ₄ CO) ₂ | .. |  | (—) | 203 |
| (4-CH ₃ OC ₆ H ₄ CO) ₂ | .. |  | (—) | 203 |
| 4-(CH ₃) ₂ NC ₆ H ₄ COCOC ₆ H ₄ Cl-4 | .. |  | (—) | 203 |
| 4-(CH ₃) ₂ NC ₆ H ₄ COCOC ₆ H ₅ | .. |  | (—) | 203 |
| (4-C ₆ H ₅ OC ₆ H ₄ CO) ₂ | .. |  | (—) | 203 |
| 4-C ₆ H ₅ C ₆ H ₄ COCOC ₆ H ₅ | .. |  | (—) | 203 |

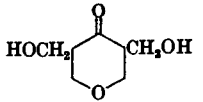

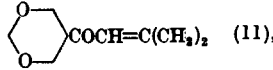
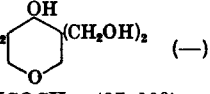
Note: References 668-2359 are on pp. 403-438.

TABLE VII. MIXED CONDENSATION OF KETONES (Continued)

| Ketone | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--------------------|--|------------|
| (C ₆ H ₅ CH ₂) ₂ CO (<i>constd.</i>) and (4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CO) ₂ | NaOCH ₃ |  | (—) 203 |
| (4-C ₆ H ₅ C ₆ H ₄ CO) ₂ | .. |  | (—) 203 |
| (4-C ₆ H ₅ SC ₆ H ₄ CO) ₂ | .. |  | (—) 203 |
| (4-C ₆ H ₅ OC ₆ H ₄ CO) ₂ | .. |  | (—) 203 |

Note: References 668-2359 are on pp. 403-438.

TABLE VIII. CONDENSATION OF ALIPHATIC ALDEHYDES WITH ACETONE
(R in the product is the group R in the aldehyde RCHO.)

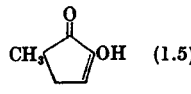
| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|----------------------|--|--|--|
| CH ₃ O | LiOH | (HOCH ₂) ₂ CHCOCH ₃ (80) | 1389-1392 |
| | NaOH | HOCH ₂ CH ₂ COCH ₃ (84) | 652, 577, 1123, 1389, 1393- 1405 |
| | .. | HOCH ₂ CH ₂ COCH ₃ (2.4), | 1406 |
| | .. |  (1.5) | |
| | KOH or K ₂ CO ₃ | (C ₄ H ₈ O) _n (80) HOCH ₂ CH ₂ COCH ₃ (25-29), CH ₂ =C(CH ₂ OH)COCH ₃ (5-10), | 1407, 1408 1409-1413 |
| | .. |  (4), | |
| | .. |  (11), | |
| | .. | (CH ₃) ₂ C(OH)CH ₂ COCH ₃ (5) | |
| | Ca(OH) ₂ |  (—) | 911, 910, 1389, 1414, 1415 |
| | Ca ₃ (PO ₄) ₂ , 450° | CH ₂ =CHCOCH ₃ (97-100) | 1416, 125, 126, 1417 |
| CCl ₃ CHO | CH ₂ CO ₂ Na, (CH ₃ CO) ₂ O | RCHOHCH ₂ COCH ₃ (60) | 273, 287, 635, 636, 1418, 1419 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

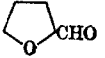
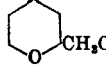

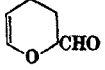
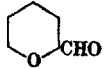
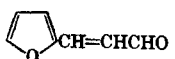
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TABLE VIII. CONDENSATION OF ALIPHATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|--|
| CH ₃ CHO | KOH | RCHOHCH ₂ COCH ₃ (87) | 576, 6, 229, 577, 1393, 1420- 1425 |
| | NaOH; (CO ₂ H) ₂ | RCH=CHCOCH ₃ (45) | 613, 577, 1393, 1421-1423, 1425-1429 |
| | Ca ₃ (PO ₄) ₂ | (CH ₃) ₂ C=CHCH=CHCOCH ₃ (—) | 2326 |
| C(Cl ₂)=CClCHO | H ₂ SO ₄ | (RCH=CH) ₂ CO (65) | 289 |
| | .. | (RCH=CH) ₂ CO (40) | 638 |
| O ₂ NCH(CHO) ₂ CH ₂ =CHCHO | NaOH | RCH=CHCOCH ₃ (57) | 1430 |
| | .. | HOC ₂ H ₄ NO ₂ -4 (65) | 1431, 1432 |
| | KCN | Polymers (—) | 1423 |
| | HCl | (CH ₃) ₂ C=CHCOCH ₃ (—) | 1423 |
| HOCH(CHO) ₂ | NaOH |  (1.5) | 1433, 1434 |
| C ₂ H ₅ CHO | .. | RCHOHCH ₂ COCH ₃ (60) | 1435, 577 |
| | NaOH; (CO ₂ H) ₂ | RCH=CHCOCH ₃ (50) | 1436, 613, 1428, 1435, 1437 |
| CH ₃ CH=CHCHO | NaOH | (RCH=CH) ₂ CO (31), RCH=CHCOCH ₃ (24) | 1438-1440, 1399, 2359 |
| | KOH | RCH=CHCOCH ₃ (38) | 301, 1399, 1425, 1438-1441 |
| <i>n</i> -C ₃ H ₇ CHO | NaOH, H ₂ O, (C ₂ H ₅) ₂ O, 15° | RCHOHCH ₂ COCH ₃ (84) | 511, 510, 649, 1442 |
| | NaOH; (CO ₂ H) ₂ | RCH=CHCOCH ₃ (60) | 613, 1442, 1443 |
| | Na ₂ CO ₃ | RCH=CHCOCH ₃ (8), <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (18) | 510-512, 763, 1442-1445 |
| <i>i</i> -C ₃ H ₇ CHO | NaOH | RCHOHCH ₂ COCH ₃ (50) | 511, 510, 577, 1446, 1447 |
| | NaOH; I ₂ | RCH=CHCOCH ₃ (37) | 511, 1446 |
| | NaOH | RCH=CHCOCH ₃ (—), (CH ₃) ₂ C=CHCH ₂ COCH ₃ (—) | 511, 510, 577, 1436, 1437, 1448-1450 |

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ORGANIC REACTIONS


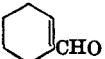
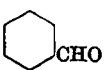
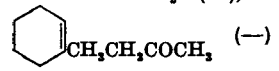
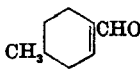
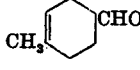
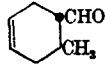
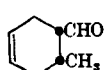
| | | | |
|--|---|--|---|
| $C(Cl_2)=CHCH=CHCHO$ $CH_2CH=C(CH_3)CHO$ $(CH_3)_2C=CHCHO$ | HCl NaOC ₂ H ₅ NaOH | $(RCH=CH)_2CO$ (58) $RCH=CHCOCH_3$ (44) $RCH=CHCOCH_3$ (—) | 1451 105, 1452 1453 |
|  | " | $RCHOHCH_2COCH_3$ (41) | 1454, 1455 |
| <i>n</i> -C ₄ H ₉ CHO <i>i</i> -C ₄ H ₉ CHO | " NaOH; I ₂ | $RCHOHCH_2COCH_3$ (—) $RCHOHCH_2COCH_3$ (76) $RCH=CHCOCH_3$ (68) | 1456 511, 1435 511, 1422, 1435, 1444, 1450, 1457-1463 |
| <i>t</i> -C ₄ H ₉ CHO | NaOC ₂ H ₅ ; I ₂ | $RCH=CHCOCH_3$ (30), $(CH_3)_2C=CHCOCH_3$ (12) | 511 |
| HO(CH ₂) ₄ CHO | NaOH |  (54) | 1464, 522 |
| CH ₂ (CH=CH) ₂ CHO | NaOH | $RCH=CHCOCH_3$ (—) | 1465 |
|  | " | $RCH=CHCOCH_3$ (51) | 1466 |
|  | " | $RCH=CHCOCH_3$ (65) | 1467 |
| <i>n</i> -C ₂ H ₅ O ₂ CCHO C ₂ H ₅ CH=C(CH ₃)CHO | Heat NaOH | $RCHOHCH_2COCH_3$ (47) $RCH=CHCOCH_3$ (—) | 1468 1437, 1469 |
|  | " | $RCHOHCH_2COCH_3$ (41) | 1467 |
| <i>n</i> -C ₂ H ₅ CH(CH ₃)CHO (C ₂ H ₅) ₂ CHCHO | Ba(OH) ₂ " | $RCH=CHCOCH_3$ (—) $RCH=CHCOCH_3$ (—) | 1469 288, 1470 |
|  | NaOH | $RCH=CHCOCH_3$ (71) | 1471, 1039, 1438 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

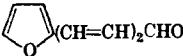

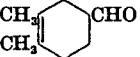
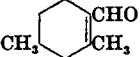




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TABLE VIII. CONDENSATION OF ALIPHATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|---|
|  (contd.) | NaOH | $(RCH=CH)_2CO$ (97) | 1471, 1399, 1535 |
|  | " | $RCH=CHCOCH_3$ (38) | 1472 |
|  | " | $RCHOHCH_2COCH_3$ (21), $RCH=CHCOCH_3$ (33),  (—) | 178, 1473 |
| <i>n</i> -C ₂ H ₅ CHO | " NaOH; (CO ₂ H) ₂ | $RCHOHCH_2COCH_3$ (37), $RCH=CHCOCH_3$ (41) $RCH=CHCOCH_3$ (70) | 90, 1436, 1456, 1474-1477 613, 90, 1422, 1437, 1444, 1474-1478 1477, 1474-1476 |
| (CH ₃) ₂ C[CH ₂ N(CH ₃) ₂] ₂ CHO CH ₂ (CH=CH) ₂ CHO | NaOC ₂ H ₅ " | $C_{17}H_{34}O_2$ (5) $RCH=CHCOCH_3$ (24) $RCH=CHCOCH_3$ (17) | 1479 1480, 1465 |
|  | NaOH | $RCH=CHCOCH_3$ (60) | 1481 |
|  | " | $RCH=CHCOCH_3$ (70) | 1481, 1484 |
|  | " | $RCHOHCH_2COCH_3$ (44) | 1482, 1483 |
|  | " | $RCH=CHCOCH_3$ (68) | 1482-1485 |
| <i>n</i> -C ₇ H ₁₅ CHO | " | $RCHOHCH_2COCH_3$ (22) | 1474 |


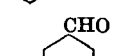

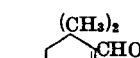
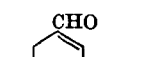

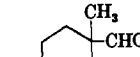
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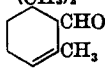
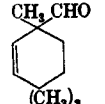
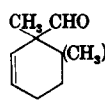
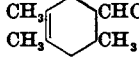
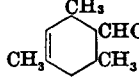
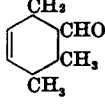
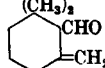
ORGANIC REACTIONS

| | | | |
|---|---|---|---------------------|
| $n\text{-C}_4\text{H}_9\text{CH}(\text{C}_3\text{H}_7)\text{CHO}$ | $\text{Ba}(\text{OH})_2$ | $\text{RCHOHCH}_2\text{COCH}_3$ (—) | 288 |
|  | NaOH | $(\text{RCH}=\text{CH})_2\text{CO}$ (100) | 1486 |
|  | NaOC_2H_5 | $\text{RCH}=\text{CHCOCH}_3$ (70) | 1487 |
|  | NaOCH_3 | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1484 |
|  | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (60) | 1481 |
|  | .. | $\text{RCH}=\text{CHCOCH}_3$ (60) | 1481 |
|  | .. | $\text{RCH}=\text{CHCOCH}_3$ (70) | 1481, 1484 |
|  | NaOCH_3 | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1484 |
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{SC}(\text{CH}_3)=\text{CHCHO}$ $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CHO}$ $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CHCHO}$ | NaOH $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ NaOH | $\text{RCH}=\text{CHCOCH}_3$ (50) $\text{RCH}=\text{CHCOCH}_3$ (14) $\text{RCH}=\text{CHCOCH}_3$ (55) | 1488 218 1472 |
|  | KOH | $\text{RCH}=\text{CHCOCH}_3$ (53) | 1489 |

Note: References 668-2359 are on pp. 403-438.

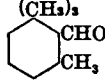
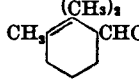
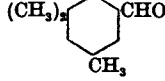
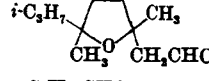
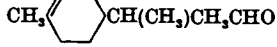
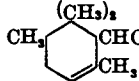
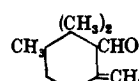
TABLE VIII. CONDENSATION OF ALIPHATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|---------------------|
|  | NaOC_2H_5 | $\text{RCHOHCH}_2\text{COCH}_3$ (13), $\text{RCH}=\text{CHCOCH}_3$ (56) | 1490 |
|  | .. | $\text{RCH}=\text{CHCOCH}_3$ (21) | 1490 |
| $n\text{-C}_8\text{H}_{17}\text{CHO}$ $4\text{-O}_2\text{NC}_6\text{H}_4\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$ $(\text{CH}_2)_2\text{C}=\text{CHCH}=\text{CHC}(\text{CH}_3)=\text{CHCHO}$ | NaOH .. NaOC_2H_5 | $\text{RCHOHCH}_2\text{COCH}_3$ (15) $\text{RCH}=\text{CHCOCH}_3$ (30) $\text{RCH}=\text{CHCOCH}_3$ (62) | 1474 971 1480 |
|  | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (—) | 836 |
|  | NaNH_2 | $\text{RCH}=\text{CHCOCH}_3$ (46) | 105 |
|  | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (—), $(\text{RCH}=\text{CH})_2\text{CO}$ (—) | 973 |
|  | NaOCH_3 | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1485, 1484 |
|  | $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1313 |

| | | | |
|--|---------------------------|---|-----------------------------|
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$, citral | NaOC_2H_5 | $\text{RCH}=\text{CHCOCH}_3$ (81) | 611, 612, 654, 1492-1501 |
| $\text{CH}_3\text{CH}=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ | Na_2SO_3 | $\text{RCH}=\text{CHCOCH}_3$ (68) | 627 |
|  | NaOC_2H_5 | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1502 |
|  | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (40) | 1503 |
|  | " | $\text{RCH}=\text{CHCOCH}_3$ (37) | 619 |
|  | NaOCH_3 | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1484 |
|  | " | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1485, 2352 |
|  | " | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1484 |
|  | NaH | $\text{RCH}=\text{CHCOCH}_3$ (11), β -ionone (66) | 1504 |

Note: References 668-2359 are on pp. 403-438.

TABLE VIII. CONDENSATION OF ALIPHATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|---------------------------|
| $(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$ | $\text{KOH}; (\text{CH}_3\text{CO})_2\text{O}$ | $\text{RCH}=\text{CHCOCH}_3$ (42) | 1505, 1496, 1506, 1507 |
| $i\text{-C}_3\text{H}_7\text{CH}_2\text{CH}=\text{C}(\text{C}_2\text{H}_5)_2\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1437 |
|  | KOH | $\text{RCH}=\text{CHCOCH}_3$ (55-58) | 225 |
|  | NaOC_2H_5 | $\text{RCH}=\text{CHCOCH}_3$ (9) | 1490 |
|  | KOH | $\text{RCH}=\text{CHCOCH}_3$ (—) | 225 |
|  | NaOH | $\text{RCH}=\text{CHCOCH}_3$ (—) | 1508 |
| $n\text{-C}_7\text{H}_{15}\text{CHO}$ | " | $\text{RCHOHCH}_2\text{COCH}_3$ (15) | 1474 |
| $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOCH}_3$ (71), $(\text{RCH}=\text{CH})_2\text{CO}$ (—) | 1496 |
| $\text{C}_2\text{H}_5(\text{CH}=\text{CH})_2\text{CHO}$ | NaOH | $(\text{RCH}=\text{CH})_2\text{CO}$ (56) | 1000 |
| $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCHO}$ | " | $\text{RCH}=\text{CHCOCH}_3$ (65) | 1509, 1510 |
|  | KOH | $\text{RCH}=\text{CHCOCH}_3$ (—) | 144 |
|  | NaNH_2 | $\text{RCH}=\text{CHCOCH}_3$ (28) | 621 |
|  | NaH | $\text{RCH}=\text{CHCOCH}_3$ (28), 6-Methyl- β -ionone (26) | 620 |

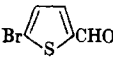
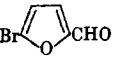
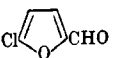
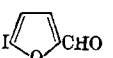

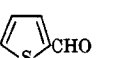
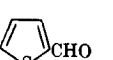
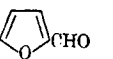
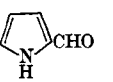
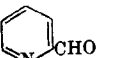
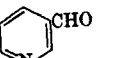
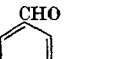
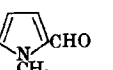
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|--|--|---|------|
| | NaNH ₂ | RCH=CHCOCH ₃ (—) | 1511 |
| | KOH | RCH=CHCOCH ₃ (—) | 144 |
| 2,9-Dimethyl-2,8-decadien-4,6-diyne-1,10-dial | Al(OC ₄ H ₉ -t) ₃ | 5,12-Dimethyl-3,5,11,13-hexadecatetraene-7,9-diyne-2,15-dione (28) | 607 |
| 4-O ₂ NC ₈ H ₄ CH=C(CH ₃)CH=CHCHO | NaOH | RCH=CHCOCH ₃ (—) | 971 |
| 2,9-Dimethyl-2,4,6,8-decatetraene-1,10-dial | KOH | 5,12-Dimethyl-3,5,7,9,11,13-hexadecaheptasene-2,15-dione (34) | 607 |
| | NaOH | RCH=CHCOCH ₃ (—) | 1512 |
| <i>n</i> -C ₁₁ H ₂₃ CHO | .. | RCHOHCH ₂ COCH ₃ (10) | 1474 |
| | .. | RCH=CHCOCH ₃ (—) | 1512 |
| | .. | RCH=CHCOCH ₃ (—) | 1513 |
| | .. | RCH=CHCOCH ₃ (—) | 1512 |
| 3,7,11-Trimethyl-2,4,6,10-dodecatetraenal | NaOC ₂ H ₅ | RCH=CHCOCH ₃ (28) | 1480 |
| | NaOH | RCH=CHCOCH ₃ (98) | 1514 |
| Crocin dialdehyde | KOH | 5,9,14,18-Tetramethyl-3,5,7,9,11,13,15,17,19-docosanonasene-2,21-dione (52) | 607 |

Note: References 668–2359 are on pp. 403–438.

TABLE IX. CONDENSATION OF AROMATIC ALDEHYDES WITH ACETONE
(R in the product is the group R in the aldehyde RCHO.)

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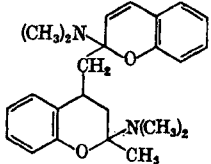
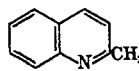
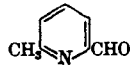
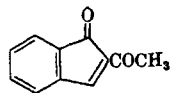
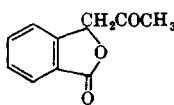
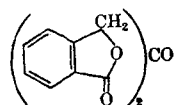
| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--------------------------------|--|--------------------------------|
|  | NaOH | RCH=CHCOCH ₃ (—) | 1515 |
|  | KOH | (RCH=CH) ₂ CO (91) | 1516 |
|  | .. | (RCH=CH) ₂ CO (91) | 1516 |
|  | .. | (RCH=CH) ₂ CO (91) | 1516 |
|  | H ₃ PO ₄ | (RCH=CH) ₂ CO (52) | 1519, 1516-1518 |
|  | NaOH | RCH=CHCOCH ₃ (69) | 1520, 1035, 1521 |
| | .. | (RCH=CH) ₂ CO (58-90) | 1030, 1521, 2334, 2335 |
|  | .. | RCH=CHCOCH ₃ (71) | 1522 |
|  | .. | RCH=CHCOCH ₃ (74) | 1471, 3, 1051, 1393, 1523-1538 |
| | .. | (RCH=CH) ₂ CO (90) | 1525-1537, 3 |
|  | Ca(OH) ₂ | RCHOHCH ₂ COCH ₃ (—) | 1523 |
| | KOH | RCH=CHCOCH ₃ (75), (RCH=CH) ₂ CO (4) | 1540, 1541 |
|  | NaOH | RCHOHCH ₂ COCH ₃ (41) | 1542 |
|  | .. | RCHOHCH ₂ COCH ₃ (14), RCH=CHCOCH ₃ (14), (RCH=CH) ₂ CO (1.4) | 1542, 1543 |
|  | .. | RCH=CHCOCH ₃ (21) | 1542, 1543 |
|  | .. | (RCH=CH) ₂ CO (45) | 1541 |
| 3,5-Br ₂ -4-HOC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (48) | 1544 |
| 4-BrC ₆ H ₄ CHO | .. | (RCH=CH) ₂ CO (50) | 1545 |
| 2-HO-3-BrC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (56) | 1544 |
| 2-HO-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (100) | 1547, 1546, 1549 |
| 2-ClC ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (58) | 1548 |
| 3-ClC ₆ H ₄ CHO | .. | (RCH=CH) ₂ CO (—) | 1550 |
| 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (—) | 1551 |
| 2-O ₂ NC ₆ H ₄ CHO | .. | RCHOHCH ₂ COCH ₃ (100) | 476, 1552 |
| | .. | (RCH=CH) ₂ CO (—) | 1550 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (—), (RCH=CH) ₂ CO (—) | 1553 |
| | Ba(OH) ₂ | RCHOHCH ₂ COCH ₃ (—) | 1554, 1548 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCHOHCH ₂ COCH ₃ (—) | 1555, 61, 1556 |
| | .. | (RCH=CH) ₂ CO (—) | 1550 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

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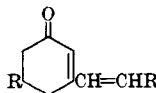
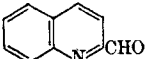
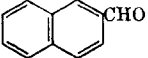
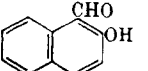
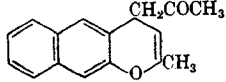
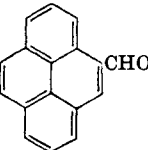
TABLE IX. CONDENSATION OF AROMATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|-------------------------------------|--|--|
| 2-HO-5-O ₂ NC ₆ H ₃ CHO C ₈ H ₇ CHO | NaOH .. | RCH=CHCOCH ₃ (-) <i>trans</i> -RCH=CHCOCH ₃ (78) | 1547 655, 6, 83, 89, 236, 613, 1523, 1525, 1539, 1548, 1557- 1561 |
| | .. | (RCH=CH) ₂ CO (94) | 657, 4, 613, 1525, 1528, 1558-1562 |
| 2-HOC ₆ H ₄ CHO | Ca(OH) ₂ NaOH .. | RCHOHCH ₂ COCH ₃ (-) RCH=CHCOCH ₃ (65) (RCH=CH) ₂ CO (98) | 1523, 61 1544, 1546, 1564, 1565 591, 1565-1568 |
| | (CH ₃) ₂ NH |  (25) | 1569 |
| 4-HOC ₆ H ₄ CHO | NaOH .. HCl | RCH=CHCOCH ₃ (66) (RCH=CH) ₂ CO (100) (RCH=CH) ₂ CO (52), RCH=CHCOCH ₃ (-) | 1544, 1570, 1571 347, 1570, 1572 1571, 1570, 1572 |
| 2,6-(HO) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₃ (-) | 1568 |
| 2-H ₂ NC ₆ H ₄ CHO | — |  (-) | 1573 |
|  | KOH | RCH=CHCOCH ₃ (-) | 1543 |
| C ₈ H ₄ (CHO) ₂ -1,2 | .. |  (-) | 1574 |
| C ₆ H ₄ (CHO) ₂ -1,4 | NaOH | C ₆ H ₄ (CH=CHCOCH ₃) ₂ -1,4 (75) | 1575, 1576 |
| 2-HO ₂ CC ₆ H ₄ CHO | .. |  (-),  (-) | 1577 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₃ (90) | 1578-1581, 1546 |
| 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | .. | (RCH=CH) ₂ CO (-) | 1581 |
| 3-O ₂ N-4-CH ₃ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (-) | 1582 |
| 4-CH ₃ C ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (90) | 1583 |
| 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (-) | 1583 |
| | .. | RCH=CHCOCH ₃ (-) | 1580, 515, 1441, 1546 |
| | .. | (RCH=CH) ₂ CO (-) | 1584 |
| | .. | (RCH=CH) ₂ CO (-) | 1584 |
| | .. | RCH=CHCOCH ₃ (83), (RCH=CH) ₂ CO (3) | 1585, 1580, 1586 |
| | .. | RCHOHCH ₂ COCH ₃ (-) | 61 |
| | Ion-exchange resin Amberlite 400 | (RCH=CH) ₂ CO (-) | 1563 |
| 2-HO-3-CH ₃ OC ₆ H ₃ CHO | NaOH | RCHOHCH ₂ COCH ₃ (-) | 1547 |
| 2-HO-4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (-) | 1547, 1587 |
| 2-HO-5-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (-) | 1547 |
| 3-HO-4-CH ₃ OC ₆ H ₃ CHO | HCl | RCH=CHCOCH ₃ (-) | 1588 |
| 2-CH ₃ O-4-HOC ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₃ (-) | 1587 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (88) | 1579, 1546, 1580, 1582, 1589- 1591 |
| 2-O ₂ NC ₆ H ₃ CH=CHCHO | HCl | (RCH=CH) ₂ CO (55) | 1591, 1593 |
| C ₆ H ₃ CH=CHCHO | NaOH | RCH=CHCOCH ₃ (-) | 1594 |
| | .. | RCH=CHCOCH ₃ (-), (RCH=CH) ₂ CO (-) | 1595, 1561 |
| | NaOC ₂ H ₅ | (RCH=CH) ₂ CO (-) | 1596, 1561, 1563, 1595, 1597 |

Note: References 668-2359 are on pp. 403-438.

TABLE IX. CONDENSATION OF AROMATIC ALDEHYDES WITH ACETONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|----------------------------------|---|---|
| 2-C ₂ H ₅ OC ₆ H ₄ CHO | NaOH | (RCH=CH) ₂ CO (—) | 1598 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1587, 1008 |
| 2,6-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1568 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (97) | 1578, 411, 1580, 1589, 1598, 1599 |
| | .. |  (20) | 411, 1578, 1589 |
| 2-HO-3-C ₂ H ₅ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1590 |
| 3,5-(OCH ₃) ₂ -4-HOC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (50) | 1600 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (—) | 1601, 1602 |
|  | KOH | RCH=CHCOCH ₃ (—) | 1543 |
| 4-CH ₃ OC ₆ H ₄ CH=CHCHO | NaOH | RCH=CHCOCH ₃ (—) | 1603 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (—) | 1525 |
| | .. | (RCH=CH) ₂ CO (90) | 1525 |
| 2,3,6-(CH ₃) ₃ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (60), (RCH=CH) ₂ CO (5) | 1604, 1605 |
| 2,4,5-(CH ₃) ₃ C ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOCH ₃ (59) | 1606, 1604 |
| | NaOH | RCHOHCH ₂ COCH ₃ (—), RCH=CHCOCH ₃ (—) | 1606 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₃ CHO | — | RCH=CHCOCH ₃ (—) | 1607 |
| 3-CH ₃ O-4-C ₂ H ₅ OC ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₃ (83), (RCH=CH) ₂ CO (50) | 411 |
| 2,4,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1608 |
| 2,4,6-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (Very good) | 1008 |
| 3,4,5-(CH ₃ O) ₃ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (40) | 1600 |
| 2-(CH ₃) ₂ N-5-CH ₃ C ₆ H ₃ CHO | Various conditions | No condensation | 1573 |
|  | NaOH | RCH=CHCOCH ₃ (—) | 1610 |
| | NaOCH ₃ | (RCH=CH) ₂ CO (—) | 1610 |
|  | KOH |  (Poor) | 1611 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO | NaOH | RCH=CHCOCH ₃ (80) | 1008 |
| 3-(CH ₃) ₂ NC ₆ H ₄ CH=CHCHO | .. | RCH=CHCOCH ₃ (—) | 1602 |
| 4- <i>i</i> -C ₄ H ₉ C ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (80) | 1612 |
| 2- <i>n</i> -C ₃ H ₇ O-3-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1590 |
| 3-CH ₃ O-4- <i>n</i> -C ₃ H ₇ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 411 |
| 3-CH ₃ O-4- <i>i</i> -C ₃ H ₇ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 411 |
| 2,4,6-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO | .. | RCH=CHCOCH ₃ (—) | 1008 |
| 2- <i>n</i> -C ₄ H ₉ O-3-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1590 |
| 2- <i>n</i> -C ₃ H ₇ O-3-C ₂ H ₅ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1590 |
| 2- <i>n</i> -C ₃ H ₇ O-3-C ₂ H ₅ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (—) | 1590 |
| 4-C ₆ H ₅ CH ₂ C ₆ H ₄ CHO | .. | RCH=CHCOCH ₃ (25), (RCH=CH) ₂ CO (48) | 1613 |
| 2-HO-4-C ₆ H ₃ CH ₂ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (50) | 1587 |
| 2,6-(CH ₃ O) ₂ -4- <i>n</i> -C ₃ H ₇ C ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (85) | 1614 |
| 3-CH ₃ O-4-C ₆ H ₃ CH ₂ OC ₆ H ₃ CHO | .. | RCH=CHCOCH ₃ (80) | 411 |
|  | .. | RCH=CHCOCH ₃ (100) | 1615 |

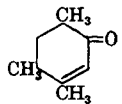
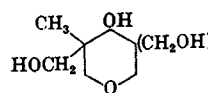
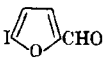
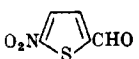
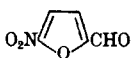

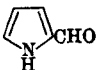
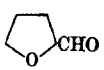
Note: References 668-2359 are on pp. 403-438.

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THE ALDOL CONDENSATION

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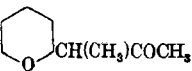

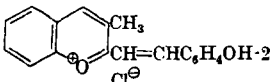
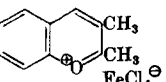
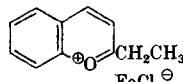
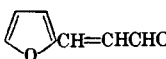
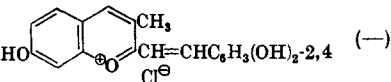
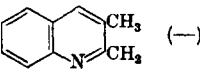

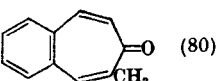
TABLE X. CONDENSATION OF ALDEHYDES WITH 2-BUTANONE
(R in the product is the group R in the aldehyde RCHO.)

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|--|
| CH ₃ O | LiOH or NaOH | CH ₃ C(CH ₂ OH) ₂ COCH ₃ (85) | 1389, 551, 577, 927, 1392, 1406, 1616-1619 |
| | KOH | CH ₃ CH(CH ₂ OH)COCH ₃ (97) | 1620, 119, 126, 337, 577, 652, 1389, 1394, 1396, 1400, 1405, 1406, 1621-1629 |
| | KOH, or ion-exchange resin Dowex-50-X8 | CH ₂ =C(CH ₃)COCH ₃ (82-90) | 1630, 125, 634 |
| | KOCH ₃ |  (49) | 1367, 1624 |
| | Ca(OH) ₂ , H ₂ O, 50-55°, 2 hr. |  (—) | 1415, 1389 |
| | Ca(OH) ₂ , H ₂ O, 5-50°, 10 hr. PbO, MgSiO ₃ | CH ₃ C(CH ₂ OH) ₂ CHOHCH(CH ₂ OH) ₂ (70) CH ₂ =CHCOC ₂ H ₅ (—), CH ₂ =C(CH ₃)COCH ₃ (—) | 1631 1632, 1620, 1626, 1633 |
| CCl ₂ CHO CH ₃ CHO | CH ₃ CO ₂ K, (CH ₃ CO) ₂ O KOH | RCHOHCH(CH ₃)COCH ₃ (55) | 287, 273, 635 |
| | | RCHOHCH(CH ₃)COCH ₃ (87) | 269, 271, 576, 577, 615, 1634-1637 |
| C(Cl ₂)=CHCHO | NaOH; HBr HCl | RCH=C(CH ₃)COCH ₃ (77) | 1636, 1638, 1639 |
| | | RCH=C(CH ₃)COCH ₃ (30) | 637 |
| O ₂ NCH(CHO) ₂ C ₂ H ₅ CHO CH ₃ CH=CHCHO | NaOH | 2-CH ₃ -4-NO ₂ -C ₆ H ₄ OH (100) | 1640 |
| | KOH | RCHOHCH(CH ₃)COCH ₃ (61) | 1641 |
| | NaOH | RCH=C(CH ₃)COCH ₃ (24), RCH=CHCOC(CH ₃)=CHR (16) | 1438, 583, 1399, 1439 |
| <i>n</i> -C ₃ H ₇ CHO | .. | RCHOHCH(CH ₃)COCH ₃ (82) | 1636, 1642 |
| | .. | RCH=C(CH ₃)COCH ₃ (30), <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO (31) | 1445, 1444 |
| <i>i</i> -C ₃ H ₇ CHO | .. | RCH=CHCOC ₂ H ₅ (21), RCH=C(CH ₃)COCH ₃ (17) | 231, 1643 |
| | NaOC ₂ H ₅ | RCH=CHCOC ₂ H ₅ (85%), RCH=C(CH ₃)COCH ₃ (15%) (—) | 231 |
| | HCl | RCH=C(CH ₃)COCH ₃ (28) | 231 |
|  | NaOH | RCH=CHCOC ₂ H ₅ , RCH=C(CH ₃)COCH ₃ (—) | 1644 |
|  | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CHCOC(CH ₃)=CHR (—) | 226 |
|  | HCl | RCH=C(CH ₃)COCH ₃ (90) | 1645, 226 |
|  | NaOH | RCH=CHCOC ₂ H ₅ , RCH=C(CH ₃)COCH ₃ , RCH=CHCOC(CH ₃)=CHR (—) | 1646, 590, 1523, 1526, 1530, 1535, 1647-1649 |
|  | KOH | RCH=CHCOC ₂ H ₅ (90) | 1541, 1540 |
|  | NaOH | RCHOHCH(CH ₃)COCH ₃ (67) | 1454 |

Note: References 668-2359 are on pp. 403-438.

TABLE X. CONDENSATION OF ALDEHYDES WITH 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|--|
| <i>n</i> -C ₄ H ₉ CHO | KOH | RCHOHCH(CH ₃)COCH ₃ (35) | 1641 |
| <i>sec</i> -C ₄ H ₉ CHO | " | RCHOHCH ₂ COC ₂ H ₅ (-) | 1650 |
| <i>i</i> -C ₄ H ₉ CHO | " | RCHOHCH(CH ₃)COCH ₃ (34) | 1651, 141 |
| HOCH ₂ (CH ₂) ₃ CHO | NaOH |  (37) | 1464, 522 |
|  | KOH | RCH=CHCOC ₂ H ₅ (43) | 1541 |
| (C ₂ H ₅) ₂ CHCHO | " | RCHOHCH ₂ COC ₂ H ₅ (-) | 1650, 1652 |
| 2-O ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ | RCH=C(CH ₃)COCH ₃ (-) | 1653 |
| 3-O ₂ NC ₆ H ₄ CHO | " | RCH=C(CH ₃)COCH ₃ (-) | 1653, 1654 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCHOHCH ₂ COC ₂ H ₅ , RCHOHCH(CH ₃)COCH ₃ (-) | 40 |
| C ₆ H ₅ CHO | H ₂ SO ₄ | RCH=C(CH ₃)COCH ₃ (-) | 1653 |
| | NaOH, H ₂ O, 3-5°, 6 hr. | RCHOHCH ₂ COC ₂ H ₅ , RCHOHCH(CH ₃)COCH ₃ (Total, 83) | 1656 |
| | NaOH, H ₂ O, 8 days | RCH=CHCOC ₂ H ₅ (95), C ₁₈ H ₁₈ O ₂ (-) | 232, 240, 523, 582, 1524, 1656-1658, 1663, 1664 |
| | HCl | RCH=C(CH ₃)COCH ₃ (42-85), RCH=CHCOC(CH ₃)=CHR (22) | 233, 232, 234- 236, 240, 1444, 1656-1661 |
| 2-HOC ₆ H ₄ CHO | HBr | RCH=CHCOC(CH ₃)=CHR (-), C ₂₅ H ₂₀ O (-) | 1659, 1664, 1665 |
| | NaOH | RCH=CHCOC ₂ H ₅ (-) | 1524, 569, 1666, 1667 |
| | HCl |  (-) | 1668 |
| | HCl, FeCl ₃ |  (15),  (-) | 569, 568 |
| 3-HOC ₆ H ₄ CHO | HCl | RCH=CHCOC(CH ₃)=CHR (-) | 1669 |
| 4-HOC ₆ H ₄ CHO | " | RCH=C(CH ₃)COCH ₃ (-) | 1669, 1666 |
|  | NaOH | RCH=C(CH ₃)COCH ₃ (24), RCH=CHCOC(CH ₃)=CHR (-) | 1438, 1399 |
| 2,4-(HO) ₂ C ₆ H ₃ CHO | HCl |  (-) | 1668 |
| 3,4-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC(CH ₃)=CHR (-) | 1669 |
| 2-H ₂ NC ₆ H ₄ CHO | NaOH |  (-) | 1670 |
|  | " | RCH=CHCOC ₂ H ₅ (-) | 1671 |
| | NaOC ₂ H ₅ | RCH=CHCOC ₂ H ₅ (-), RCH=C(CH ₃)COCH ₃ (-) | 1671 |
| <i>n</i> -C ₆ H ₁₃ CHO | KOH | RCHOHCH(CH ₃)COCH ₃ (50) | 1641 |
| C ₆ H ₄ (CHO) ₂ -1,2 | NaOH |  (80) | 1672, 223 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₂ H ₅ (-) | 1666, 1669, 1673 |
| | HCl, -3° | RCH=C(CH ₃)COCH ₃ (-) | 1666 |
| | HCl, C ₂ H ₅ OH | C ₂₈ H ₂₀ O ₇ (-) | 1664 |
| 2-CH ₃ C ₆ H ₄ CHO | NaOH | RCH=CHCOC ₂ H ₅ (21) | 1674 |

Note: References 668-2359 are on pp. 403-438.

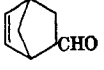
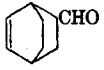
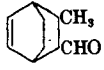
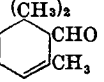
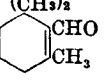
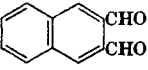
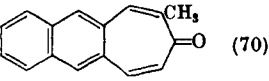
ORGANIC REACTIONS

THE ALDOL CONDENSATION

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TABLE X. CONDENSATION OF ALDEHYDES WITH 2-BUTANONE (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

196

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|----------------------------------|---|----------------------------------|
|  | NaOC ₂ H ₅ | RCH=C(CH ₃)COCH ₃ or RCH=CHCOC ₂ H ₅ * (60) | 1487 |
| 2-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₂ H ₅ (—) | 1666 |
| | HCl | RCH=C(CH ₃)COCH ₃ (81) | 1661, 1666 |
| 3-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOC(CH ₃)=CHR (—) | 1669 |
| | .. | RCH=C(CH ₃)COCH ₃ (61) | 1661 |
| 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₂ H ₅ (—) | 1673, 240, 1669 |
| | HCl | RCH=C(CH ₃)COCH ₃ (84) | 1661, 240, 1669 |
| 2-HO-3-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOC ₂ H ₅ (—) | 1570 |
| 2-HO-4-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOC ₂ H ₅ (—) | 1570 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOC ₂ H ₅ (—) | 1675, 1667 |
| | HCl | RCH=C(CH ₃)COCH ₃ (—) | 1675 |
| n-C ₄ H ₉ CH(C ₂ H ₅)CHO | KOH | RCHOHCH ₂ COC ₂ H ₅ (—) | 1650 |
| C ₆ H ₅ CH=CHCHO | NaOH | RCH=C(CH ₃)COCH ₃ (44) | 583, 1662, 1676, 1677 |
| | HCl | RCH=C(CH ₃)COCH ₃ * (63) | 583 |
| C ₆ H ₅ CH(CH ₃)CHO | NaOH | RCH=C(CH ₃)COCH ₃ (62) | 231 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | HCl | RCH=CHCOC(CH ₃)=CHR (—) | 1669 |
|  | NaOCH ₃ | RCH=CHCOC ₂ H ₅ or RCH=C(CH ₃)COCH ₃ * (—) | 1678, 1474 |
| 4-CH ₃ OC ₆ H ₄ CH=CHCHO | NaOH | RCH=C(CH ₃)COCH ₃ (25) | 583 |
| | HCl | RCH=C(CH ₃)COCH ₃ (67) | 583 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | NaOH | RCH=CHCOC ₂ H ₅ (68) | 1666, 1679, 1787 |
| | HCl | RCH=C(CH ₃)COCH ₃ (45) | 1679, 1680, 1787 |
|  | NaOCH ₃ | RCH=CHCOC ₂ H ₅ (—) | 1484 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO | LiOC ₂ H ₅ | RCH=CHCOC ₂ H ₅ (53), RCH=C(CH ₃)COCH ₃ (12) | 582, 1491, 1506, 1592, 1681-1688 |
| | Triton B | RCH=CHCOC ₂ H ₅ (25), RCH=C(CH ₃)COCH ₃ (35) | 582 |
|  | NaOC ₂ H ₅ | RCH=CHCOC ₂ H ₅ (52) | 1685, 1689 |
|  | .. | RCH=CHCOC ₂ H ₅ (63) | 1685, 1689 |
|  | NaOH |  (70) | 1690 |

Notes: References 668-2359 are on pp. 403-438.

* The structure of the product was not proved.

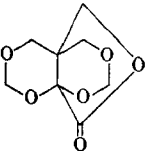
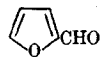
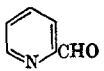
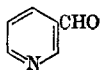
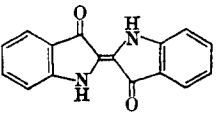
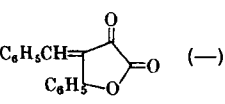
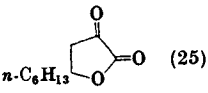
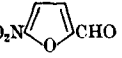
ORGANIC REACTIONS

THE ALDOL CONDENSATION

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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|------------------------|
| $\text{Cl}_2\text{CHCOCH}_3$ and CH_2O | Na_2CO_3 | $\text{Cl}_2\text{CHCOCH}_2\text{CH}_2\text{OH}$ (75) | 1691 |
| $2\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOCHCl}_2$ (—) | 1653 |
| $3\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCHCl}_2$ (—) | 1653 |
| $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCHCl}_2$ (30) | 1653 |
| $\text{CH}_3\text{COCO}_2\text{H}$ and CH_2O | $\text{H}_2\text{SO}_4, \text{CH}_3\text{CO}_2\text{H}$ |  (40) | 1692 |
| $\text{C}(\text{Cl}_2)=\text{CHCHO}$ | HCl | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (66) | 1693 |
| $n\text{-C}_7\text{H}_7\text{CHO}$ | $(\text{C}_2\text{H}_5)_2\text{NH}$ | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (4) | 219 |
|  | NaOH | $\text{RCH}=\text{CHCOCO}_2\text{H}^*$ (Excellent) | 1694, 1695 |
|  | KOH | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (16) | 1696 |
|  | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (51) | 1696 |
| $2\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " |  (—) | 1695 |
| $3\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $\text{C}_6\text{H}_5\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}^*$ (30) | 1694, 1695, 1697, 1698 |
| | HCl |  (—) | 1700 |
| $2\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $4\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $2,4\text{-(HO)}_2\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $n\text{-C}_8\text{H}_{17}\text{CHO}$ | H_2SO_4 |  (25) | 219 |
| $3,4\text{-(CH}_2\text{O)}_2\text{C}_6\text{H}_3\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (67) | 1699, 1695 |
| $4\text{-CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695, 1697 |
| $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $2,5\text{-(CH}_3)_2\text{-4-CH}_2\text{OC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (90) | 1701 |
| $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{-C}(\text{CH}_3)=\text{CHCHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1695 |
| $2,5\text{-(CH}_3)_2\text{-4-C}_6\text{H}_3\text{CH}_2\text{OC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOCO}_2\text{H}$ (—) | 1701 |
| $\text{CH}_3\text{COCH}_2\text{Br}$ and  | $\text{H}_2\text{SO}_4, \text{CH}_3\text{CO}_2\text{H}$ | $\text{RCH}=\text{C}(\text{Br})\text{COCH}=\text{CHR}$ (—) | 1702 |

ORGANIC REACTIONS

THE ALDOL CONDENSATION

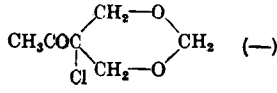
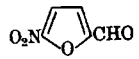
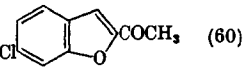

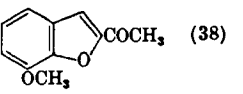

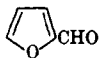
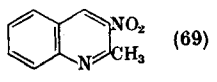
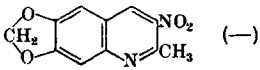
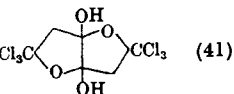
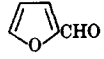
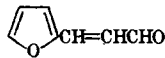
Note: References 668-2359 are on pp. 403-438.

* This compound was isolated as the sodium or potassium salt.

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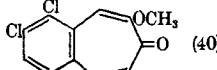
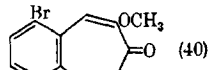
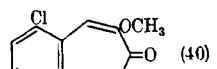
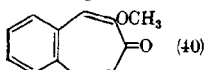


TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES OTHER THAN ACETONE AND 2-BUTANONE (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|----------------|
| CH ₃ COCH ₂ Cl and CH ₂ O | NaOH | CH ₃ COC(Cl)(CH ₂ OH) ₂ (33),  (—) | 1691 |
|  | .. | CH ₃ COC(OH)(CH ₂ OH) ₂ (36) | 1691 |
| 2-HO-4-ClC ₆ H ₃ CHO | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CClCOCH=CHR (—) | 1702 |
| 2-HO-4-ClC ₆ H ₃ CHO | KOH |  (60) | 1703 |
| 2-HOC ₆ H ₄ CHO | .. |  (80) | 1704, 1703 |
| 2-HO-3-CH ₃ OC ₆ H ₃ CHO | .. |  (38) | 1703 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | HCl, CH ₃ CO ₂ H | RCH=CClCOCH ₃ (—) | 1705 |
| CH ₃ COCH ₂ I and  | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CICOCH=CHR (—) | 1702 |
| CH ₃ COCH=NOH and 3-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOCH=NOH (100) | 1706 |
| C ₆ H ₅ CHO | .. | RCH=CHCOCH=NOH (90) | 1706 |
| 4-i-C ₂ H ₅ C ₆ H ₄ CHO | .. | RCH=CHCOCH=NOH (—) | 1706 |
| CH ₃ COCH ₂ NO ₂ and  | .. | RCH=CHCOCH ₂ NO ₂ (90) | 1707 |
| 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOCH ₂ NO ₂ (49) | 1707 |
| C ₆ H ₅ CHO | .. | RCH=CHCOCH ₂ NO ₂ (90) | 1707 |
| 2-H ₂ NC ₆ H ₄ CHO | None |  (69) | 1707 |
| 2-H ₂ N-4,5-(CH ₂ O) ₂ C ₆ H ₃ CHO | CH ₃ CO ₂ H |  (—) | 1707 |
| 4-CH ₃ C ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ NO ₂ (66) | 1707 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOCH ₂ NO ₂ (81) | 1707 |
| CH ₃ COCOCH ₃ and Cl ₃ CCHO | (CH ₂) ₃ NH, CH ₃ CO ₂ H |  (41) | 1708, 593 |
|  | .. | RCH=CHCOCOCH=CHR (22) | 592, 1486 |
| 4-BrC ₆ H ₄ CHO | KOH | C ₂₃ H ₂₂ O ₃ (—) | 1709 |
| 4-ClC ₆ H ₄ CHO | (CH ₂) ₃ NH, CH ₃ CO ₂ H | RCH=CHCOCOCH=CHR (5-21) | 593 |
| C ₆ H ₅ CHO | .. | RCH=CHCOCOCH=CHR (5-21) | 593 |
| | .. | RCH=CHCOCOCH=CHR (10) | 594, 592, 1710 |
| | KOH | C ₂₃ H ₂₂ O ₃ (45) | 1709 |
|  CH=CHCHO | (CH ₂) ₃ NH | RCH=CHCOCOCH=CHR (—) | 1486 |

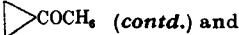

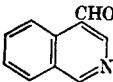



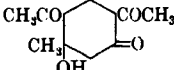
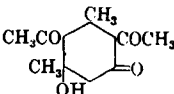


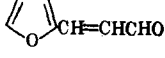
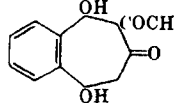
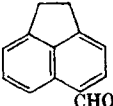
Note: References 668-2359 are on pp. 403-438.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|-----------------|
| CH ₃ COCOCH ₃ (contd.) and | | | |
| 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | (CH ₂) ₃ NH, CH ₃ CO ₂ H | RCH=CHCOCOCH=CHR (5-21) | 593 |
| 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCOCH=CHR (5-21) | 593 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCOCH=CHR (5-21) | 593 |
| CH ₃ (CH=CH) ₃ CHO | KOH | C ₂ H ₅ O ₂ (-) | 1709 |
| | (CH ₂) ₃ NH | RCH=CHCOCOCH ₃ (4), RCH=CHCOCOCH=CHR (-) | 1711 |
| C ₆ H ₅ CH=CHCHO | (CH ₂) ₃ NH, CH ₃ CO ₂ H | RCH=CHCOCOCH=CHR (57) | 594, 592, 1712 |
|  (CH=CH) ₂ CHO | (CH ₂) ₃ NH | RCH=CHCOCOCH=CHR (-) | 1486 |
| 2-C ₂ H ₅ OC ₆ H ₄ CHO | (CH ₂) ₃ NH, CH ₃ CO ₂ H | RCH=CHCOCOCH=CHR (5-21) | 593 |
| C ₆ H ₅ (CH=CH) ₂ CHO | " | RCH=CHCOCOCH=CHR (32) | 592, 594, 1712 |
| C ₆ H ₅ (CH=CH) ₃ CHO | " | RCH=CHCOCOCH ₃ (9), RCH=CHCOCOCH=CHR (18) | 592, 1712 |
| C ₆ H ₅ (CH=CH) ₃ CHO | " | RCH=CHCOCOCH ₃ (-) | 592 |
| CH ₃ COCH ₂ OCH ₃ and | | | |
| 3,4-Cl ₂ C ₆ H ₃ (CHO) _{1,1,2} | NaOH |  (40) | 1713 |
| 3-BrC ₆ H ₃ (CHO) _{1,1,2} | " |  (40) | 1713 |
| 3-ClC ₆ H ₃ (CHO) _{1,1,2} | " |  (40) | 1713 |
| C ₆ H ₄ (CHO) _{1,1,2} | " |  (40) | 1713 |
| CH ₃ COCHOHCH ₃ and CH ₂ O CH ₃ CHO | KOH | CH ₃ COC(OH)(CH ₂ OH)CH ₃ (60) | 230 |
| | " | CH ₃ COC(OH)(CH ₂)CHOHCH ₃ (60) | 230 |
| CH ₃ COC(CH ₃)=CH ₂ and CH ₂ O | " | HOCH ₂ CH ₂ COC(CH ₃)=CH ₂ (20) | 1714 |
| | K ₂ CO ₃ | CH ₃ COCH(CH ₃)CH ₂ OCH ₃ (20), CH ₃ COC(CH ₃)(CH ₂ OH)CH ₂ OCH ₃ (47) | 1714 |
|  and | | | |
| CH ₂ O | KOH | HOCH ₂ CH ₂ CO (-), CH ₂ =CHCO (-) | 1717 |
| CCl ₃ CHO | " | RCHOHCH ₂ CO (Low) | 1717 |
| CH ₃ CHO | " | RCHOHCH ₂ CO (-), RCH=CHCO (-) | 1717 |
| n-C ₃ H ₇ CHO | " | RCHOHCH ₂ CO (28), n-C ₃ H ₇ CH=C(C ₂ H ₅)CHO (18) | 1717 |
| i-C ₃ H ₇ CHO | " | RCHOHCH ₂ CO (26), RCH=CHCO (29) | 1715, 520, 1717 |
|  CHO | " | RCH=CHCO (95) | 1716 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCO (33) | 1717 |
| C ₆ H ₅ CHO | " | RCH=CHCO (72) | 1717 |
| 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCO (62) | 1717 |
| C ₆ H ₅ CH=CHCHO | " | RCH=CHCO (66) | 1717, 1718 |

Note: References 668-2359 are on pp. 403-438.

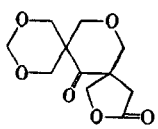

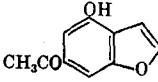
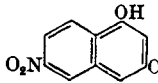
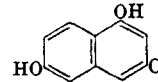
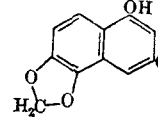
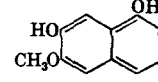
TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|-------------------------------------|--|------------|
|  COCH_3 (contd.) and | | | |
| $2\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCO}$  (74) | 1717 |
|  | .. | $\text{RCH}=\text{CHCO}$  (65) | 1717 |
| $1\text{-C}_{10}\text{H}_7\text{CHO}$ | .. | $\text{RCH}=\text{CHCO}$  (48) | 1717 |
| $3,4\text{-(C}_2\text{H}_5\text{O)}_2\text{C}_6\text{H}_2\text{CHO}$ | .. | $\text{RCH}=\text{CHCO}$  (78) | 1717 |
| $\text{CH}_3\text{COCH}_2\text{COCH}_3$ and | | | |
| CH_2O | $(\text{C}_2\text{H}_5)_3\text{N}$ |  (70) | 220 |
| CH_3CHO | .. |  (89) | 220, 1719 |
| $\text{Cl}_2\text{C}=\text{CClCHO}$ | HCl | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (44) | 216, 1719 |
| $\text{C}_2\text{H}_5\text{CHO}$ | H_2SO_4 | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (50) | 289 |
| $n\text{-C}_3\text{H}_7\text{CHO}$ | $(\text{C}_2\text{H}_5)_2\text{NH}$ | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (43) | 220, 216 |
| | $(\text{CH}_2)_5\text{NH}$ | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (85) | 220, 217 |
|  | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
|  | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (80) | 590, 1721 |
| $\text{C}_6\text{H}_5\text{CHO}$ | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (66) | 216, 1722 |
| $2\text{-HOC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 591, 1720 |
| | .. | $\text{RCH}=\text{CHCOCH}=\text{CHR}$ (—) | 591 |
|  | Ion-exchange resin, Amberlite | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
| $\text{C}_6\text{H}_4(\text{CHO})_2\text{-1,2}$ | $(\text{C}_2\text{H}_5)_2\text{NH}$ |  (85) | 601 |
| $4\text{-CH}_2\text{C}_6\text{H}_4\text{CHO}$ | $(\text{CH}_2)_5\text{NH}$ | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (48) | 589 |
| $3\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$ | Ion-exchange resin, Amberlite | $\text{RCH}(\text{OH})\text{CH}(\text{COCH}_3)_2$ (—) | 1720 |
| $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ | $(\text{CH}_2)_5\text{NH}$ | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1723, 1720 |
| $3,4\text{-(CH}_2\text{O)}_2\text{C}_6\text{H}_3\text{CHO}$ | Ion-exchange resin, Amberlite | $\text{RCH}(\text{OH})\text{CH}(\text{COCH}_3)_2$ (—) | 1720 |
| $3\text{-HO-5-C}_2\text{H}_5\text{OC}_6\text{H}_3\text{CHO}$ | NaNH_2 | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
| $4\text{-i-C}_3\text{H}_7\text{C}_6\text{H}_4\text{CHO}$ | $(\text{CH}_2)_5\text{NH}$ | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
| | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
|  | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
| $4\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}=\text{CHCHO}$ | .. | $\text{RCH}=\text{C}(\text{COCH}_3)_2$ (—) | 1720 |
| $\text{CH}_3\text{COCO}_2\text{C}_2\text{H}_5$ and | | | |
| $\text{C}_2\text{H}_5\text{CHO}$ | $(\text{C}_2\text{H}_5)_2\text{NH}$ | $\text{CH}_2\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (45) | 215 |
| $n\text{-C}_3\text{H}_7\text{CHO}$ | .. | $\text{C}_2\text{H}_5\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (45-50) | 214, 215 |
| $n\text{-C}_4\text{H}_9\text{CHO}$ | .. | $n\text{-C}_3\text{H}_7\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (37-48) | 214, 215 |
| $n\text{-C}_5\text{H}_{11}\text{CHO}$ | .. | $n\text{-C}_4\text{H}_9\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (37-57) | 214, 215 |
| $n\text{-C}_6\text{H}_{13}\text{CHO}$ | .. | $n\text{-C}_5\text{H}_{11}\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (57) | 214, 215 |
| $n\text{-C}_7\text{H}_{15}\text{CHO}$ | .. | $n\text{-C}_6\text{H}_{13}\text{CH}(\text{CHO})\text{C}(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$ (56) | 214 |

Note: References 668-2359 are on pp. 403-438.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)

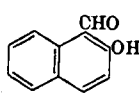
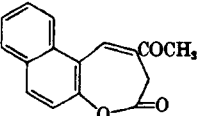
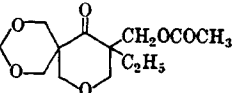
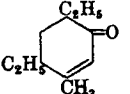
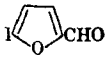
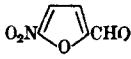
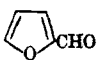
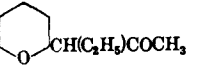
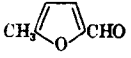
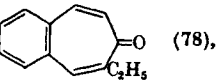
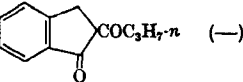
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|---------------------------|
| CH₃COCH₂CH₂CO₂H and | | | |
| CH ₂ O | H ₂ SO ₄ , CH ₃ CO ₂ H |  (—) | 1724–1727 |
| <i>i</i> -C ₃ H ₇ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (—) | 1728 |
|  CHO | " | RCH=CHCOCH ₂ CH ₂ CO ₂ H (—) | 1729 |
| | CH ₃ CO ₂ Na | RCH=C(COCH ₃)CH ₂ CO ₂ H (—) | 1730 |
| | HCl |  (70) | 1731 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (40) | 1732 |
| 2-ClC ₆ H ₄ CHO | " | RCH=CHCOCH ₂ CH ₂ CO ₂ H (—) | 1732 |
| 3-ClC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (—) | 1733 |
| 4-ClC ₆ H ₄ CHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (50) | 1732 |
| 2-O ₂ NC ₆ H ₄ CHO | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (60) | 1731 |
| 3-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (40) | 1731 |
| | HCl |  (95) | 1731 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (30) | 1731 |
| | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (50) | 1731, 2331 |
| C₆H₅CHO | | | |
| | NaOH or (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (50–60) | 1731, 1732, 1734, 2331 |
| | CH ₃ CO ₂ Na or ion- exchange resin, Amberlite IR-120 | RCH=C(COCH ₃)CH ₂ CO ₂ H (12–48) | 1735–1737 |
| 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (55) | 1732, 1731 |
| 3-HOC ₆ H ₄ CHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (50) | 1732, 1731 |
| | HCl |  (50) | 1731 |
| 4-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (25) | 1731, 1738 |
| | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (55) | 1732 |
| | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (60) | 1731 |
| 2,4-(HO) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (40) | 1731 |
| | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (80) | 1731 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (43) | 1732 |
| | HCl |  (50) | 1731 |
| 2-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (55) | 1732 |
| 3-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCH ₂ CH ₂ CO ₂ H (50) | 1732 |
| 4-CH ₃ OC ₆ H ₄ CHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOCH ₂ CH ₂ CO ₂ H (67) | 1732, 1739 |
| | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (60) | 1731 |
| 3-CH ₂ O-4-HOC ₆ H ₃ CHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (30) | 1731, 1732 |
| | HCl |  (60) | 1731 |
| C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOCH ₂ CH ₂ CO ₂ H (60) | 1731 |
| | HCl | RCH=C(COCH ₃)CH ₂ CO ₂ H (80) | 1731 |

Note: References 668–2359 are on pp. 403–438.

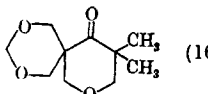
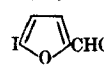
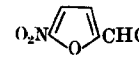
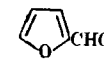
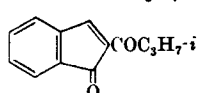
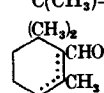
TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|--|
| CH ₃ COCH ₂ CH ₂ CO ₂ H (contd.) and 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 2-C ₂ H ₅ OC ₆ H ₄ CHO 4-C ₂ H ₅ OC ₆ H ₄ CHO 4-(CH ₃) ₂ NC ₆ H ₄ CHO (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO | NaOH " " " " " HCl | RCH=CHCOCH ₂ CH ₂ CO ₂ H (63) RCH=CHCOCH ₂ CH ₂ CO ₂ H (40) RCH=CHCOCH ₂ CH ₂ CO ₂ H (50) RCH=CHCOCH ₂ CH ₂ CO ₂ H (54) RCH=CHCOCH ₂ CH ₂ CO ₂ H (66) RCH=C(COCH ₃)CH ₂ CO ₂ H (25) | 1731 1731 1731 1731 1731 1731 |
|  | " |  (40) | 1731 |
| CH ₃ COC ₂ H _{7-n} and CH ₃ O | H ₂ SO ₄ ; CH ₃ CO ₂ H |  (—) | 1740 |
| | KOCH ₃ |  (20) | 1624 |
| CCl ₃ CHO CH ₃ CHO | NaOH NaOH, SiO ₂ , 260° CH ₃ CO ₂ H KOCH ₃ — | RCHOHCH(C ₂ H ₅)COCH ₃ (54) RCH=C(C ₂ H ₅)COCH ₃ (23) RCHOHCH ₂ COC ₂ H _{7-n} (14) RCHOHCH(C ₂ H ₅)COCH ₃ (55) RCH=CHCOC ₂ H _{7-n} (60%), RCH=C(C ₂ H ₅)COCH ₃ (40%) (—) | 1622, 1624 125 635 270 271 |
| C ₂ H ₅ CHO | NaOH | RCH=CHCOC ₂ H _{7-n} and/or RCH=C(C ₂ H ₅)COCH ₃ (—) | 1436 |
| n-C ₃ H ₇ CHO | — | RCH=CHCOC ₂ H _{7-n} (—), RCH=C(C ₂ H ₅)COCH ₃ (—) | 1444 |
| i-C ₃ H ₇ CHO | KOH NaOH | RCHOHCH ₂ COC ₂ H _{7-n} (—) RCH=CHCOC ₂ H _{7-n} (30) | 274 1643 |
|  | " | RCH=CHCOC ₂ H _{7-n} and/or RCH=C(C ₂ H ₅)COCH ₃ (—) | 1644 |
|  | HCl | RCH=C(C ₂ H ₅)COCH ₃ (—) | 1645 |
|  | NaOH | RCH=CHCOC ₂ H _{7-n} (60), RCH=C(C ₂ H ₅)COCH ₃ (—) | 1655, 1649 |
| HOCH ₂ (CH ₂) ₂ CHO | " |  (21) | 522 |
|  | " | RCH=CHCOC ₂ H _{7-n} (75) | 1741 |
| 3-O ₂ NC ₆ H ₄ CHO | POCl ₃ | RCH=CHCOC ₂ H _{7-n} and/or RCH=C(C ₂ H ₅)COCH ₃ (—) | 1654 |
| C ₂ H ₅ CHO | NaOH HCl | RCH=CHCOC ₂ H _{7-n} (100) RCH=C(C ₂ H ₅)COCH ₃ (90) | 1742, 1743 236, 1742 |
| 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₂ H _{7-n} (52) | 1667 |
| 3-HOC ₆ H ₄ CHO | HCl | RCH=CHCOC(C ₂ H ₅)=CHR (—) | 237 |
| 4-HOC ₆ H ₄ CHO | " NaOH | RCH=C(C ₂ H ₅)COCH ₃ (76) RCH=CHCOC ₂ H _{7-n} (—) | 237 1570 |
| C ₆ H ₄ (CHO) ₂ -1,2 | " |  (78),  (—) | 1672, 223 |

Note: References 668-2359 are on pp. 403-438.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|---------------------------------|
| CH ₃ COC ₃ H _{7-n} (<i>contd.</i>) and 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOC ₃ H _{7-n} (53) | 1666 |
| 3-CH ₂ OC ₆ H ₄ CHO | HCl | RCH=CHCOC(C ₂ H ₅)=CHR (—) | 237 |
| 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=C(C ₂ H ₅)COCH ₃ (48) | 1666, 237 |
| 2-HO-3-CH ₂ OC ₆ H ₃ CHO | NaOH | RCH=CHCOC ₃ H _{7-n} (46) | 1666 |
| 2-HO-4-CH ₂ OC ₆ H ₃ CHO | " | RCH=CHCOC ₃ H _{7-n} (—) | 1570 |
| 3-CH ₂ O-4-HOC ₆ H ₃ CHO | KOH | RCH=CHCOC ₃ H _{7-n} (—) | 1570 |
| C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOC ₃ H _{7-n} (—) | 1667, 1593 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | " | RCH=CHCOC ₃ H _{7-n} (60) | 1718 |
| | " | RCH=CHCOC ₃ H _{7-n} (96) | 1679, 1666 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO | HCl | RCH=C(C ₂ H ₅)COCH ₃ (69) | 1679 |
| | NaOC ₂ H ₅ | RCH=CHCOC ₃ H _{7-n} and/or RCH=C(C ₂ H ₅)COCH ₃ (Total, 70) | 1492 |
| | NaOH | RCH=CHCOC ₃ H _{7-n} (28), RCH=C(C ₂ H ₅)COCH ₃ (8) | 1687, 1682 |
| 1-C ₁₀ H ₇ CHO | " | RCH=CHCOC ₃ H _{7-n} (—) | 1744 |
| CH ₃ COC ₃ H _{7-i} and CH ₂ O | K ₂ CO ₃ | CH ₃ COC(CH ₂) ₂ CH ₂ OH (40), HOCH ₂ CH ₂ COC(CH ₃) ₂ CH ₂ OH (—) | 577, 1618 |
| | H ₂ SO ₄ |  (16) | 1740 |
| CCl ₃ CHO | CH ₃ CO ₂ Na, (CH ₃ CO) ₂ O | RCHOHCH ₂ COC ₃ H _{7-i} (—) | 273 |
| CH ₃ CHO | KOH | RCHOHC(CH ₃) ₂ COCH ₃ (70) | 269, 272, 577, 615, 1745 |
| C ₂ H ₅ CHO | " | C ₂ H ₅ CH=C(CH ₃)CHO (34), C ₂ H ₅ CHOHCH(CH ₃)CHO (11) | 272 |
| <i>n</i> -C ₃ H ₇ CHO | " | RCHOHC(CH ₃) ₂ COCH ₃ and RCHOHCH ₂ COC ₃ H _{7-i} (Total 28), RCH=CHCOC ₃ H _{7-i} (12) | 272 |
| <i>i</i> -C ₃ H ₇ CHO | NaOH | RCH=CHCOC ₃ H _{7-i} (35) | 1643 |
|  | " | RCH=CHCOC ₃ H _{7-i} † (—) | 1644 |
|  | KOH | RCH=CHCOC ₃ H _{7-i} (33) | 273 |
|  | NaOH | RCH=CHCOC ₃ H _{7-i} (60) | 1655 |
| (C ₂ H ₅) ₂ CHCHO | KOH | RCHOHCH ₂ COC ₃ H _{7-i} (6), RCH=CHCOC ₃ H _{7-i} (47) | 272 |
| C ₆ H ₅ CHO | NaOH | RCH=CHCOC ₃ H _{7-i} (—) | 1663, 1524, 1666, 1743, 1746 |
| 2-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₃ H _{7-i} (—) | 1570 |
| 4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₃ H _{7-i} (57) | 1747 |
| C ₆ H ₄ (CHO) ₂ -1,2 | KOCH ₃ |  (17) | 1672 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOC ₃ H _{7-i} (—) | 1666 |
| 2-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOC ₃ H _{7-i} (65) | 1666 |
| 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOC ₃ H _{7-i} (72) | 1548 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO | " | RCH=CHCOC ₃ H _{7-i} (—) | 1683 |
|  | NaOC ₂ H ₅ | RCH=CHCOC ₃ H _{7-i} (—) | 1689 |
| C ₂₆ H ₂₄ O ₂ , crocetin dialdehyde | KOH | R(CH=CHCOC ₃ H _{7-i}) ₂ (75) | 607 |


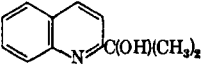
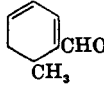



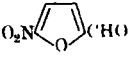

Note: References 668-2359 are on pp. 403-438.

† The structure of this compound was not established.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|------------------|
| $\text{CH}_3\text{COC(OH)(CH}_3)_2$ and | | | |
|  | NaOH | $\text{RCH=CHCOC(OH)(CH}_3)_2$ (91) | 1748 |
| $\text{C}_6\text{H}_5\text{CHO}$ | NaOCH_3 | $\text{RCH=CHCOC(OH)(CH}_3)_2$ (89) | 1749, 1167, 1748 |
| $2\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOH |  (52) | 1748 |
| $3,4\text{-(CH}_2\text{O)}_2\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH=CHCOC(OH)(CH}_3)_2$ (89) | 1748 |
| $\text{C}_6\text{H}_5\text{CH=CHCHO}$ | .. | $\text{RCH=CHCOC(OH)(CH}_3)_2$ (95) | 1748 |
| $\text{CH}_3\text{CO(CH}_2)_2\text{CH=CH}_2$ and $(\text{CH}_3)_2\text{C=CHCH}_2\text{CH}_2\text{-}$ $\text{C(CH}_3)_2\text{=CHCHO}$ | NaOCH_3 | $\text{RCH=CHCO(CH}_2)_2\text{CH=CH}_2$ (64) | 1750, 1751 |
| $\text{CH}_3\text{COCH=C(CH}_3)_2$ and CH_2O | MgO | $\text{HOCH}_2\text{CH}_2\text{COCH=C(CH}_3)_2$ (25), $\text{CH}_3\text{COCH(CH}_2\text{OH)C(CH}_3)_2\text{=CH}_2$ (20) | 1752, 1753 |
| CCl_3CHO | $\text{CH}_3\text{CO}_2\text{H}$ | $\text{RCHOHCH}_2\text{COCH=C(CH}_3)_2$ (10) | 635 |
| $\text{CH}_2=\text{CHCHO}$ | Mg, 200° | $\text{RCHOHCH}_2\text{COCH=C(CH}_3)_2$ (5) | 1754 |
| $\text{C}_2\text{H}_5\text{CHO}$ | Mg, 300° | $\text{RCH=CHCOCH=C(CH}_3)_2$ (2) | 1754 |
| $\text{CH}_3\text{CH=CHCHO}$ | BaO | $\text{RCH=CHCOCH=C(CH}_3)_2$ (5),  (12) | 559, 1755 |
| $n\text{-C}_7\text{H}_7\text{CHO}$ | KOH | $\text{RCH=CHCOCH=C(CH}_3)_2$ (22), $n\text{-C}_7\text{H}_7\text{CH=C(C}_2\text{H}_5)_2\text{CHO}$ (14) | 513, 559, 1755 |
|  | NaOH | $\text{RCH=CHCOCH=C(CH}_3)_2$ (17) | 1530, 1529 |
| $\text{C}_6\text{H}_5\text{CHO}$ | $(\text{CH}_2)_5\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ | $\text{RCH=CHCOCH=C(CH}_3)_2$ (—) | 1560, 4 |
| $2\text{-HOC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH=CHCOCH=C(CH}_3)_2$ (Small) | 1570 |
| $(\text{CH}_3)_2\text{C=CHCH}_2\text{CH}_2\text{-}$ $\text{C(CH}_3)_2\text{=CHCHO}$ | .. | $\text{RCH=CHCOCH=C(CH}_3)_2$ (—) | 1756 |
|  | NaOC_2H_5 | $\text{RCH=CHCOCH=C(CH}_3)_2$ (—) | 1689 |
| $\text{CH}_3\text{CO(CH}_2)_2\text{CO}_2\text{H}$ and $4\text{-HOC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH=CHCO(CH}_2)_2\text{CO}_2\text{H}$ (40) | 1738 |
| $\text{CH}_3\text{COC}_4\text{H}_9\text{-}n$ and CH_2O | — | $\text{RCH=C(C}_2\text{H}_5\text{-}n\text{)COCH}_3$ (—) | 125 |
| Cl_3CCHO | $\text{CH}_3\text{CO}_2\text{H}$ | $\text{RCHOHCH}_2\text{COC}_4\text{H}_9\text{-}n$ (15) | 635 |
| CH_3CHO | $i\text{-C}_2\text{H}_7\text{MgCl}$ | $\text{RCHOHCH}_2\text{COC}_4\text{H}_9\text{-}n$ (25) | 1757 |
| $i\text{-C}_3\text{H}_7\text{CHO}$ | KOH | $\text{RCHOHCH}_2\text{COC}_4\text{H}_9\text{-}n$ (—) | 274 |
|  | NaOH | $\text{RCH=CHCOC}_4\text{H}_9\text{-}n$ † (—) | 1644 |
|  | HCl | $\text{RCH=C(C}_2\text{H}_5\text{-}n\text{)COCH}_3$ (—) | 1645 |
|  | NaOH | $\text{RCH=CHCOC}_4\text{H}_9\text{-}n$ (—) | 1649 |
| $\text{C}_6\text{H}_5\text{CHO}$ | .. | $\text{RCH=CHCOC}_4\text{H}_9\text{-}n$ (—) | 1663, 1524 |
| | HCl | $\text{RCH=C(C}_2\text{H}_5\text{-}n\text{)COCH}_3$ (90) | 236, 1663 |
| $3\text{-HOC}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH=C(C}_2\text{H}_5\text{-}n\text{)COCH}_3$ (—) | 237 |
| $4\text{-HOC}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH=C(C}_2\text{H}_5\text{-}n\text{)COCH}_3$ (—) | 237 |

Note: References 668–2359 are on pp. 403–438.

† The structure of this compound was not established.

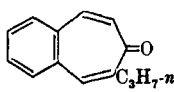
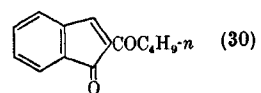
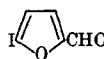
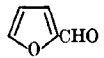
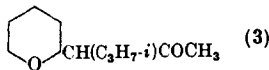
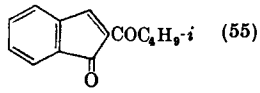
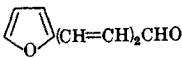
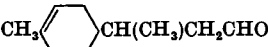
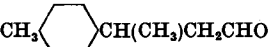
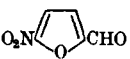
THE ALDOL CONDENSATION

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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|--------------------------------|
| CH₃COC₄H₉-<i>n</i> (contd.) and | | | |
| C ₆ H ₄ (CHO) ₂ -1,2 | NaOH |  (60),  (30) | 1672, 223 |
| 3-CH ₃ OC ₆ H ₄ CHO | HCl | RCH=C(C ₂ H ₅ - <i>n</i>)COCH=CHR (—) | 237 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=C(C ₂ H ₅ - <i>n</i>)COCH ₃ (—) | 237 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>n</i> (—) | 1593 |
| CH ₃ COC ₄ H ₉ - <i>i</i> and CH ₂ O | " | CH ₃ COCH(CH ₂ OH)C ₃ H ₇ - <i>i</i> (54) | 1622, 1740 |
| Cl ₂ CCO | CH ₃ CO ₂ H | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (32) | 635, 1287 |
| CH ₃ CHO | KOH | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (—) | 1758, 1745 |
| | <i>i</i> -C ₂ H ₅ MgCl | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (38) | 141 |
| C ₂ H ₅ CHO | KOH | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (24) | 579 |
| <i>n</i> -C ₃ H ₇ CHO | " | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (38) | 579, 1652 |
| <i>i</i> -C ₃ H ₇ CHO | " | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (—) | 274 |
|  CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>i</i> † (—) | 1644 |
|  CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (80) | 1530, 590, 1648, 1759, 1760 |
| HOCH ₂ (CH ₂) ₂ CHO | " |  (3) | 522 |
| (C ₂ H ₅) ₂ CHCHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 1470 |
| C ₆ H ₅ CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (64) | 243, 238, 239, 1743 |
| 2-HOC ₆ H ₄ CHO | HCl NaOH HCl | RCH=CHCOC ₄ H ₉ - <i>i</i> (38) RCH=CHCOC ₄ H ₉ - <i>i</i> (—) RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 238, 239 239 239 |
| C ₆ H ₄ (CHO) ₂ -1,2 | KOCH ₃ |  (55) | 1672 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 1743 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (89) | 1762, 240 |
| | HCl | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 240 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 1763 |
| <i>n</i> -C ₃ H ₇ CH=C(C ₂ H ₅)CHO | (—) | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (—) | 1764 |
| <i>n</i> -C ₃ H ₇ CH(C ₂ H ₅)CHO | (—) | RCHOHCH ₂ COC ₄ H ₉ - <i>i</i> (—) | 1764 |
| C ₆ H ₅ CH=CHCHO | NaOC ₂ H ₅ | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 1765 |
|  CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>i</i> (71) | 1766 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (50) | 1666, 1743 |
| 1-C ₁₀ H ₇ CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 1744 |
| CH ₃  CH(CH ₃)CH ₂ CHO | KOH | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 144 |
| CH ₃  CH(CH ₃)CH ₂ CHO | " | RCH=CHCOC ₄ H ₉ - <i>i</i> (—) | 144 |
| CH₃COC₄H₉-<i>t</i> and | | | |
| CH ₂ O | NaOH | HOCH ₂ CH ₂ COC ₄ H ₉ - <i>t</i> (—), (HOCH ₂) ₂ CHCOC ₄ H ₉ - <i>t</i> (10) | 577, 2339 |
| CCl ₃ CHO | CH ₃ CO ₂ Na, (CH ₃ CO) ₂ O | RCHOHCH ₂ COC ₄ H ₉ - <i>t</i> (—) | 273 |
| CH ₃ CHO | <i>i</i> -C ₂ H ₅ MgCl | RCHOHCH ₂ COC ₄ H ₉ - <i>t</i> (—) | 1757, 513 |
| O ₂ N  CHO | KOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (45) | 273 |

Note: References 668-2359 are on pp. 403-438.



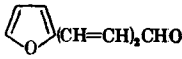

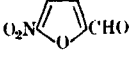

† The structure of this compound was not established.

THE ALDOL CONDENSATION

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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|--------------------------|
| CH₃COC₄H₉-<i>t</i> (contd.) and | | | |
|  | NaOCH ₃ | RCH=CHCOC ₄ H ₉ - <i>t</i> (68) | 1532, 1526, 1655 |
|  | NaOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (43) | 1542 |
| C ₆ H ₅ CHO | " | RCH=CHCOC ₄ H ₉ - <i>t</i> (93) | 1768, 524, 1524, 1663 |
| 2-HOC ₂ H ₄ CHO | " | RCH=CHCOC ₄ H ₉ - <i>t</i> (—) | 1570 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | NaOC ₂ H ₅ | RCH=CHCOC ₄ H ₉ - <i>t</i> (95) | 513, 1769 |
| 4-CH ₂ OC ₂ H ₄ CHO | NaOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (65) | 1771 |
| 3-CH ₂ O-4-HOC ₂ H ₄ CHO | KOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (—) | 1579, 1593 |
| C ₆ H ₅ CH=CHCHO | NaOC ₂ H ₅ | RCH=CHCOC ₄ H ₉ - <i>t</i> (38) | 513 |
|  | NaOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (51) | 1766 |
| 3,5-(CH ₂) ₂ -4-HOC ₂ H ₄ CHO | " | RCH=CHCOC ₄ H ₉ - <i>t</i> (43) | 2337 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₄ CH=CHCHO | NaOC ₂ H ₅ | RCH=CHCOC ₄ H ₉ - <i>t</i> (73) | 513 |
| 2,7-Dimethyl-2,6-octadien-4-yne-1,8-dial | Al(OC ₄ H ₉ - <i>t</i>) ₃ | R(CH=CHCOC ₄ H ₉ - <i>t</i>) ₂ (30) | 1772 |
| 2,7-Dimethyl-2,4,6-octatriene-1,8-dial | " | R(CH=CHCOC ₄ H ₉ - <i>t</i>) ₂ (35) | 1772 |
| (CH ₂) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CH-CHO, citral | NaOH | RCH=CHCOC ₄ H ₉ - <i>t</i> (68) | 1773 |
| 2,9-Dimethyl-2,8-decadiene-4,6-diyne-1,10-dial | Al(OC ₄ H ₉ - <i>t</i>) ₃ | R(CH=CHCOC ₄ H ₉ - <i>t</i>) ₂ (46) | 607 |
| 2,9-Dimethyl-2,4,6,8-decatriene-1,10-dial | " | R(CH=CHCOC ₄ H ₉ - <i>t</i>) ₂ (79) | 607 |
| Pyrene-3-carboxaldehyde | NaOC ₂ H ₅ | RCH=CHCOC ₄ H ₉ - <i>t</i> (80) | 1615 |
| C ₂₀ H ₁₂ O ₂ , crocetin dialdehyde | KOH | R(CH=CHCOC ₄ H ₉ - <i>t</i>) ₂ (49) | 607 |
| CH ₃ COCH=CHC ₂ H ₅ - <i>n</i> and <i>n</i> -C ₄ H ₉ CH(C ₂ H ₅)CHO | NaOH | RCHOHCH ₂ COCH=CHC ₂ H ₅ - <i>n</i> (—) | 1652 |
| CH₃COCOC₄H₉-<i>t</i> and C₆H₅CHO | | | |
| (CH ₂) ₂ NH | | RCH=CHCOCOC ₄ H ₉ - <i>t</i> (34) | 325 |
| CH₃CO(CH₂)₄CO₂H and 4-HOC₂H₄CHO | | | |
| NaOH | | RCH=CHCO(CH ₂) ₄ CO ₂ H (24) | 1738 |
| CH₃COC₅H₁₁-<i>n</i> and CH₃O | | | |
| CCL ₂ CHO | K ₂ CO ₃ | CH ₃ COCH(CH ₂ OH)C ₄ H ₉ - <i>n</i> † (42) | 577 |
| <i>n</i> -C ₂ H ₅ CHO | CH ₃ CO ₂ H | RCHOHCH ₂ COC ₅ H ₁₁ - <i>n</i> (20) | 635 |
| <i>i</i> -C ₃ H ₇ CHO | NaOH | RCHOHCH ₂ COC ₅ H ₁₁ - <i>n</i> † (—) | 1652 |
| | KOH | RCHOHCH ₂ COC ₅ H ₁₁ - <i>n</i> (—), RCHOHCH(C ₄ H ₉ - <i>n</i>)COCH ₃ (Trace) | 274 |
|  | NaOH | RCH=CHCOC ₅ H ₁₁ - <i>n</i> † (—) | 1644 |
|  | HCl | RCH=C(C ₄ H ₉ - <i>n</i>)COCH ₃ (—) | 1645 |
|  | NaOH | RCH=CHCOC ₅ H ₁₁ - <i>n</i> (—) | 1649 |
| (C ₂ H ₅) ₂ CHCHO | " | RCH=CHCOC ₅ H ₁₁ - <i>n</i> † (—) | 1470 |
| C ₆ H ₅ CHO | " | RCH=CHCOC ₅ H ₁₁ - <i>n</i> (45) | 243 |
| | HCl | RCH=C(C ₄ H ₉ - <i>n</i>)COCH ₃ (23), RCH=CHCOC ₅ H ₁₁ - <i>n</i> (2) | 243, 236 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | NaOH | RCH=CHCOC ₅ H ₁₁ - <i>n</i> † (—) | 1761 |
| 3-CH ₂ O-4-HOC ₂ H ₄ CHO | " | RCH=CHCOC ₅ H ₁₁ - <i>n</i> (40) | 1774 |
| <i>n</i> -C ₄ H ₉ CH(C ₂ H ₅)CHO | " | RCHOHCH ₂ COC ₅ H ₁₁ - <i>n</i> † (—) | 1652 |
| CH₃COCH₂C₄H₉-<i>i</i> and CCL₂CHO | | | |
| CH ₃ CO ₂ H | | RCHOHCH ₂ COCH ₂ C ₄ H ₉ - <i>i</i> (15) | 635 |
| CH₃COCH₂C₄H₉-<i>t</i> and CH₃CHO | | | |
| KOH, CH ₃ OH | | RCHOHCH ₂ COCH ₂ C ₄ H ₉ - <i>t</i> (40), RCH=CHCOCH ₂ C ₄ H ₉ - <i>t</i> (10), CH ₂ CH(OCH ₃)CH ₂ COCH ₂ C ₄ H ₉ - <i>t</i> (10) | 1775, 1757, 1758 |
| KOH, C ₂ H ₅ OH | | RCH=CHCOCH ₂ C ₄ H ₉ - <i>t</i> (35), CH ₂ CH(OCH ₃)CH ₂ COCH ₂ C ₄ H ₉ - <i>t</i> (30) | 1775-1777 |
| CH₃COCH(CH₃)CH(OCH₃)₂ and 9-(2,6,6-Trimethylcyclohexen-1-yl)-3,7-dimethyl-2,4,6,8-nonatetraen-1-al | | | |
| NaOCH ₃ | | RCH=CHCOCH(CH ₃)CH(OCH ₃) ₂ (65) | 1778 |

ORGANIC REACTIONS
















THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

† The structure of this compound was not established.

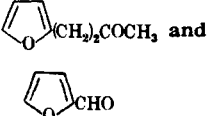
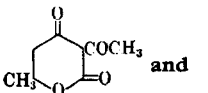
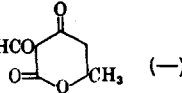
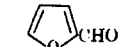
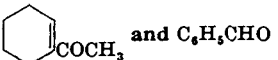

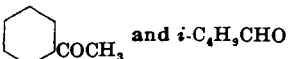

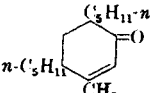
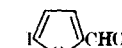

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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|---|
| $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}(\text{OCH}_3)_2$ (contd.) and 13-(2,6,6-Trimethylcyclohexen-1-yl)-2,7,11-trimethyl-2,4,6-8,10,12-tridecahexaen-1-al | NaOCH_3 | $\text{RCH}=\text{CHCOCH}(\text{CH}_3)\text{CH}(\text{OCH}_3)_2$ (—) | 1778 |
|  $\text{CH}=\text{CHCOCH}_3$ and 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$ 2,4-(CH_3O) $_2\text{C}_6\text{H}_3\text{CHO}$ | $\text{H}_2\text{SO}_4, \text{CH}_3\text{CO}_2\text{H}$ | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})\text{NO}_2$ -5 (35) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})\text{NO}_2$ -5 (40) | 646 646 |
|  $\text{CH}=\text{CHCOCH}_3$ and  CHO | NaOH | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{S})$ (52) | 1030 |
|  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{S})$ (87) | 1779 |
| 4- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_3\text{S})$ (52) | 647 |
|  $\text{CH}=\text{CHCHO}$ | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{S})$ (79) | 1779 |
| 2,4-(CH_3O) $_2\text{C}_6\text{H}_3\text{CHO}$ 2,4,6-(CH_3O) $_3\text{C}_6\text{H}_2\text{CHO}$ | " " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_3\text{S})$ (69) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_2\text{S})$ (85) | 1008 1008 |
|  $\text{CH}=\text{CHCOCH}_3$ and  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{Se})$ (52) | 1522 |
|  $\text{CH}=\text{CHCOCH}_3$ and Br-  CHO | KOH | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (88) | 1516 |
| Cl-  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (91) | 1516 |
| I-  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (84) | 1516 |
|  CHO | NaOH | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (87) | 1779 |
|  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (64) | 1522 |
|  CHO | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (95) | 1780 |
| 2- $\text{ClC}_6\text{H}_4\text{CHO}$ 2- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ 3- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ 4- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ $\text{C}_6\text{H}_5\text{CHO}$ | " " " " $\text{H}_2\text{SO}_4, \text{CH}_3\text{CO}_2\text{H}$ NaOH | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (—) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (29) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (33) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (86) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_5\text{O})$ (—) | 1781 1781 1781 646, 1781 1525 |
|  $\text{CH}=\text{CHCHO}$ | " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_4\text{H}_3\text{O})$ (49) | 1779 |
| 3,4-(CH_2O) $_2\text{C}_6\text{H}_3\text{CHO}$ 4- $\text{CH}_2\text{C}_6\text{H}_4\text{CHO}$ 4- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ 4-(CH_3) $_2\text{NC}_6\text{H}_4\text{CHO}$ | " " " " | 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_3\text{O})$ (—) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (50) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_4\text{O})$ (—) 2- $\text{RCH}=\text{CHCOCH}=\text{CH}(\text{C}_6\text{H}_3\text{O})$ (33) | 1780 1781 1780 1780 |

Note: References 668-2359 are on pp. 403-438.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|--------------|
|  | NaOH | 2-RCH=CHCO(CH ₂) ₂ (C ₄ H ₈ O) (54) | 1533 |
|  | (CH ₂) ₅ NH | RCH=CHCO  (—) A, R = 2-C ₄ H ₈ S | 595 |
|  | .. | A, R = 2-C ₄ H ₈ O (85) | 595 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | .. | A, R = 3,4-Cl ₂ C ₆ H ₃ (46) | 595 |
| 2-O ₂ NC ₆ H ₄ CHO | .. | A, R = 2-O ₂ NC ₆ H ₄ (65) | 595 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | A, R = 3-O ₂ NC ₆ H ₄ (60) | 595 |
| C ₆ H ₅ CHO | .. | A, R = C ₆ H ₅ (55) | 595, 1782 |
| C ₆ H ₅ CH=CHCHO | .. | A, R = C ₆ H ₅ CH=CH (57) | 595 |
| 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | A, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (47) | 595 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | A, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (46) | 595 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | A, R = 4-(CH ₃) ₂ NC ₆ H ₄ (63) | 595 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | .. | A, R = <i>i</i> -C ₃ H ₇ C ₆ H ₄ (65) | 595 |
| 1-C ₁₀ H ₇ CHO | .. | A, R = 1-C ₁₀ H ₇ (62) | 595 |
| 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | .. | A, R = (C ₂ H ₅ O) ₂ C ₆ H ₃ (43) | 595 |
| 4-(C ₂ H ₅) ₂ NC ₆ H ₄ CHO | .. | A, R = (C ₂ H ₅) ₂ NC ₆ H ₄ (58) | 595 |
|  | NaOC ₂ H ₅ | RCH=CHCO  (40) | 316 |
| CH ₃ COC(CH ₃)=CHC ₆ H ₄ - <i>n</i> and <i>n</i> -C ₆ H ₄ CH=C(C ₂ H ₅)CHO | NaOH | RCHOHCH ₂ COC(CH ₃)=CHC ₆ H ₄ - <i>n</i> (—) | 1652 |
| CH ₃ COCH ₂ CH ₂ CH=C(CH ₃) ₂ and CH ₂ O | NaNH ₂ CH ₃ CO ₂ Na | CH ₂ =C(COCH ₃)CH ₂ CH=C(CH ₃) ₂ (15) HOCH ₂ CH(COCH ₃)CH ₂ CH=C(CH ₃) ₂ (10) | 1783 1783 |
|  | NaOH | RCH=CHCO  (13) | 1459 |
| CH ₃ CO(CH ₂) ₂ CO ₂ H and 4-HOC ₆ H ₄ CHO | .. | RCH=CHCO(CH ₂) ₂ CO ₂ H (42) | 1738 |
| CH ₃ COC ₆ H ₁₃ - <i>n</i> and CH ₂ O | K ₂ CO ₃ | CH ₃ COCH(CH ₂ OH)C ₆ H ₁₁ - <i>n</i> † (46) | 577 |
| | KOCH ₃ |  (32) | 1624 |
| CCl ₃ CHO <i>i</i> -C ₆ H ₇ CHO | CH ₃ CO ₂ H KOH | RCHOHCH ₂ COC ₆ H ₁₃ - <i>n</i> (15) RCHOHCH ₂ COC ₆ H ₁₃ - <i>n</i> (—) | 635 274 |
|  | NaOH | RCH=CHCOC ₆ H ₁₃ - <i>n</i> † (—) | 1644 |
|  | HCl | RCH=C(C ₆ H ₁₁ - <i>n</i>)COCH ₃ (—) | 1645 |
| C ₆ H ₅ CHO | KOH | RCH=CHCOC ₆ H ₁₃ - <i>n</i> (—) | 1743 |
| 2-HOC ₆ H ₄ CHO | HCl | RCH=C(C ₆ H ₁₁ - <i>n</i>)COCH ₃ (90) | 236 |
| | NaOH | RCH=CHCOC ₆ H ₁₃ - <i>n</i> (—) | 1667 |

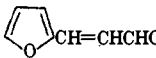
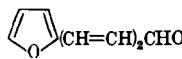
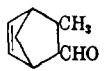
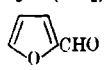
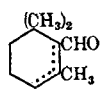
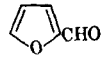
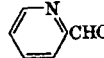
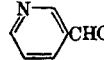
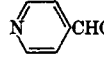
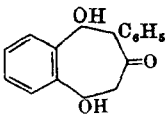
Note: References 668–2359 are on pp. 403–438.

† The structure of this compound was not established.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|--------------|
| CH₃COC₆H_{13-n} (contd.) and | | | |
|  | NaOH | RCH=CHCOC ₆ H _{13-n} (44) | 1766 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H _{13-n} † (87) | 1761 |
| 4-CH ₂ OC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H _{13-n} (-) | 1743 |
| C ₆ H ₅ CH=CHCHO | NaOC ₂ H ₅ | RCH=CHCOC ₆ H _{13-n} (-) | 1784 |
|  | NaOH | RCH=CHCOC ₆ H _{13-n} (92) | 1766 |
|  | NaOC ₂ H ₅ | RCH=CHCOC ₆ H _{13-n} † (35) | 1487 |
| CH ₃ COCH(CH ₃)C ₄ H _{9-n} and n-C ₃ H ₇ CH=C(C ₂ H ₅)CHO | NaOH | RCHOHCH ₂ COCH(CH ₃)C ₄ H _{9-n} (-) | 1652 |
| CH ₃ CO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ -(d,l) and C ₆ H ₅ CHO | .. | RCH=CHCO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ (-) | 1785 |
| 4-CH ₂ OC ₆ H ₄ CHO | .. | RCH=CHCO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ (-) | 1785 |
| CH ₃ CO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ -(+) and C ₆ H ₅ CHO | .. | RCH=CHCO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ (-) | 1785 |
| 4-CH ₂ OC ₆ H ₄ CHO | .. | RCH=CHCO(CH ₂) ₂ CH(CH ₃)C ₂ H ₅ (-) | 1785 |
| CH ₃ CO(CH ₂) ₂ C ₃ H _{7-i} and  | .. | RCH=CHCO(CH ₂) ₂ C ₃ H _{7-i} (-) | 1649 |
|  | NaOC ₂ H ₅ | RCH=CHCO(CH ₂) ₂ C ₃ H _{7-i} † (-) | 1689 |
| C₆H₅CH₂COCH₃ and | | | |
|  | NaOH | RCH=CHCOCH ₂ C ₆ H ₅ (73) | 590, 1759 |
|  | HBr, CH ₃ CO ₂ H | RCH=C(C ₆ H ₅)COCH ₃ (72) | 1786 |
|  | .. | RCH=C(C ₆ H ₅)COCH ₃ (72) | 1786 |
|  | .. | RCH=C(C ₆ H ₅)COCH ₃ (70) | 1786 |
| 2-O ₂ NC ₆ H ₄ CHO | (CH ₂) ₂ NH, n-C ₆ H ₁₃ CO ₂ H | RCH=C(C ₆ H ₅)COCH ₃ (22) | 84 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | RCH=C(C ₆ H ₅)COCH ₃ (57) | 84 |
| C ₆ H ₅ CHO | KOH | RCH=CHCOCH ₂ C ₆ H ₅ (48) | 264, 2327 |
| | (CH ₂) ₂ NH | RCH=C(C ₆ H ₅)COCH ₃ (80) | 265, 84, 597 |
| | HCl | RCH=C(C ₆ H ₅)COCH ₃ (-) | 264, 1788 |
| | H ₂ SO ₄ | trans-C ₆ H ₅ CH=CHC ₆ H ₅ (-) | 264, 1788 |
| 2-HOC ₆ H ₄ CHO | (CH ₂) ₂ NH | RCH=CHCOCH ₂ C ₆ H ₅ (50) | 266, 239 |
| C ₆ H ₄ (CHO) _{2-1,2} | .. |  (73) | 601 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOCH ₂ C ₆ H ₅ (64) | 1789 |
| 4-CH ₂ C ₆ H ₄ CHO | .. | RCH=CHCOCH ₂ C ₆ H ₅ (-) | 1789 |
| 2-CH ₃ OC ₆ H ₄ CHO | HCl | RCH=C(C ₆ H ₅)COCH ₃ (37), RCH=C(C ₆ H ₅)COCH=CHR (-) | 266, 239 |
| 4-CH ₂ OC ₆ H ₄ CHO | KOH | RCH=CHCOCH ₂ C ₆ H ₅ (-) | 1789 |
| | HCl | RCH=C(C ₆ H ₅)COCH ₃ (27) | 1790 |
| C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOCH ₂ C ₆ H ₅ (-) | 1791 |

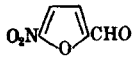
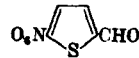
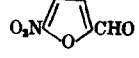
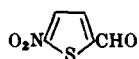
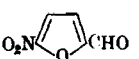
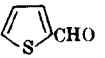
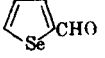
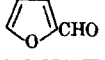
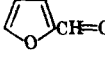
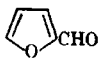
Note. References 668-2359 are on pp. 403-438.

† The structure of this compound was not established.

THE ALDOL CONDENSATION


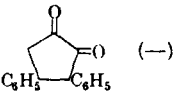
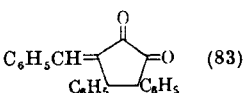
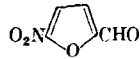
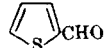
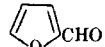
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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|--|
| $C_6H_5OCH_2COCH_3$ and C_6H_5CHO | NaOH, H_2O , 25° NaOH, C_6H_5OH , 25° HCl, $(C_6H_5)_2O$, 25°, 48 hr. | $RCH=C(OC_6H_5)COCH_3$ (—) $RCH=C(OC_6H_5)COCH=CHR$ (—) $RCH=C(OC_6H_5)COCH_3$ (—) | 268 268 268 |
| 2-HOC $_6H_5$ CHO 4-CH $_2OC_6H_4$ CHO $CH_2COC_7H_{15-n}$ and Cl_2CCHO | NaOH .. CH_3CO_2H | $RCH=C(OC_6H_5)COCH_3$ (40) $RCH=C(OC_6H_5)COCH_3$ (—) $RCHOHCH_2COC_7H_{15-n}$ (20) | 268 268 635 |
|  | HCl | $RCH=C(COCH_3)C_6H_{13-n}$ (—) | 1645 |
| C_6H_5CHO | KOH | $RCH=CHCOC_7H_{15-n}$ (70) | 1743 |
| 2-HO-5-BrC $_6H_3$ CH=CHCOCH $_3$ and 4-(CH $_3$) $_2$ NC $_6H_4$ CHO 4-O $_2$ NC $_6H_4$ CH=CHCOCH $_3$ and  | NaOH .. H_2SO_4 , CH_3CO_2H | 2-HO-5-BrC $_6H_3$ CH=CHCOCH=CHR (80) 4-O $_2$ NC $_6H_4$ CH=CHCOCH=CHR (40) | 1547 647 |
|  | .. | 4-O $_2$ NC $_6H_4$ CH=CHCOCH=CHR (30) | 646 |
| 2-HO-5-O $_2$ NC $_6H_3$ CH=CHCOCH $_3$ and 4-(CH $_3$) $_2$ NC $_6H_4$ CHO | NaOH | 2-HO-5-O $_2$ NC $_6H_3$ CH=CHCOCH=CHR (—) | 1547 |
| $C_6H_5CH=CHCOCH_3$ and CCl_2CHO | CH_3CO_2K , $(CH_3CO)_2O$ | $RCHOHCH_2COCH=CHC_6H_5$ (65) | 287 |
|  | CH_3CO_2H | $RCH=CHCOCH=CHC_6H_5$ (20) | 647 |
|  | H_2SO_4 | $RCH=CHCOCH=CHC_6H_5$ (41) | 646, 1517 |
|  | NaOH | $RCH=CHCOCH=CHC_6H_5$ (—) | 1521, 1793 |
|  | .. | $RCH=CHCOCH=CHC_6H_5$ (52) | 1522 |
|  | .. | $RCH=CHCOCH=CHC_6H_5$ (87) | 1794, 1525, 1539 |
| 3-O $_2$ NC $_6H_4$ CHO C_6H_5CHO | | $RCH=CHCOCH=CHC_6H_5$ (68) $RCH=CHCOCH=CHC_6H_5$ (100) | 1795 1558, 1525, 1539, 1796, 1797 |
| 3,4-(CH $_2O$) $_2C_6H_3$ CHO 4-CH $_2OC_6H_4$ CHO | | $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (—) | 1796 1584 |
|  | Na_2CO_3 | $RCH=CHCOCH=CHC_6H_5$ (57) | 1766 |
| 2-O $_2$ NC $_6H_4$ CH=CHCHO 3-O $_2$ NC $_6H_4$ CH=CHCHO $C_6H_5CH=CHCHO$ 4-(CH $_3$) $_2$ NC $_6H_4$ CHO 3,4-(CH $_2O$) $_2C_6H_3$ CH=CHCHO 3-CH $_2OC_6H_4$ CH=CHCHO $C_6H_5(CH=CH)_2CHO$ Anthracene-9-carboxaldehyde | NaOH Na_2CO_3 | $RCH=CHCOCH=CHC_6H_5$ (19) $RCH=CHCOCH=CHC_6H_5$ (24) $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (40) $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (—) $RCH=CHCOCH=CHC_6H_5$ (—) | 1798, 1594 1798 1589 1799, 1800 1603 1603 1801 1801 |
| 2-HOC $_6H_4$ CH=CHCOCH $_3$ and  | NaOH | $RCH=CHCOCH=CHC_6H_4OH-2$ (—) $RCH=CHCOCH=CHC_6H_4OH-2$ (—) $RCH=CHCOCH=CHC_6H_4OH-2$ (—) $RCH=CHCOCH=CHC_6H_4OH-2$ (85) $RCH=CHCOCH=CHC_6H_4OH-2$ (90) $RCH=CHCOCH=CHC_6H_4OH-2$ (9) $RCH=CHCOCH=CHC_6H_4OH-2$ (—), ($RCH=CH$) $_2CO$ (20) | 347 1796 347 347, 1796 347 347 347, 515 |

Note: References 668-2359 are on pp. 403-438.

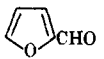
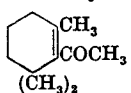
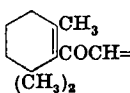
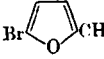
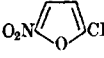
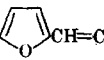
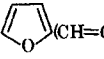
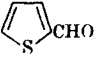
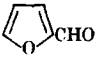
TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|------------------|
| 2-HOC ₆ H ₄ CH=CHCOCH ₃ (contd.) and | | | |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOCH=CHC ₆ H ₄ OH-2 (-) | 347 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OH-2 (75) | 515 |
| C ₆ H ₅ COCH ₂ COCH ₃ and C ₆ H ₅ CHO | KNH ₂ , NH ₃ , then 4-CH ₃ C ₆ H ₄ SO ₃ H (CH ₂) ₅ NH ₂ | RCHOHCH ₂ COCH ₂ COC ₆ H ₅ (-), RCH=CHCOCH ₂ COC ₆ H ₅ (28) RCH=CHCOCH ₂ COC ₆ H ₅ (23)† | 1802, 211 589 |
| C ₆ H ₅ CH ₂ CH ₂ COCH ₃ and  | NaOH | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (46) | 1803 |
| C ₆ H ₅ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (80) | 1803, 1787 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (73) | 1803 |
| 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (52) | 1803 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (80) | 1803 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (73) | 1803 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH ₂ CH ₂ C ₆ H ₅ (34) | 1803 |
| C ₆ H ₅ CH ₂ OCH ₂ COCH ₃ and C ₆ H ₅ CHO | NaOH, H ₂ O, dioxane, 100° | RCH=CHCOCH ₂ OCH ₂ C ₆ H ₅ (30) | 1792 |
| | HCl, 25°, 24 hr. |  (-) | 1792 |
| | HCl, 25°, 48 hr. |  (83) | 1792 |
| CH ₃ COC ₈ H _{17-n} and | | | |
|  | HCl | RCH=C(COCH ₃)C ₇ H _{15-n} (-) | 1645 |
| C ₆ H ₅ CHO | KOH | RCH=CHCOC ₈ H _{17-n} (-) | 1743 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOC ₈ H _{17-n} (-) | 1579 |
| (CH ₃) ₃ C(OH)(CH ₂) ₃ CH(CH ₃)COCH ₃ and C ₂₀ H ₂₄ O ₂ , crocetin dialdehyde | " | R[CH=CHCOCH(CH ₃)(CH ₂) ₃ C(OH)(CH ₃) ₂] (8) | 607 |
| C ₆ H ₅ CH=C(CH ₃)COCH ₃ and C ₆ H ₅ CHO | HCl | RCH=CHCOC(CH ₃)=CHC ₆ H ₅ (-) | 1660 |
| C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOC(CH ₃)=CHC ₆ H ₅ (-) | 1801 |
| 4-CH ₃ OC ₆ H ₄ CH=CHCOCH ₃ and  | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (-) | 1793 |
|  | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (89) | 1794 |
| 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (25) | 1798 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (-) | 1585 |
| 2-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (73) | 1798 |
| 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (13) | 1798 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (42) | 1798 |
| 4-CH ₃ OC ₆ H ₄ CH=CHCHO | " | RCH=CHCOCH=CHC ₆ H ₄ OCH ₃ -4 (-) | 1603 |
| 2-HO-4-CH ₃ OC ₆ H ₃ CH=CHCOCH ₃ and 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₃ OH-2-OCH ₃ -4 (-) | 1547 |
| 2-HO-5-CH ₃ OC ₆ H ₃ CH=CHCOCH ₃ and 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₃ OH-2-OCH ₃ -5 (-) | 1547 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CH=CHCOCH ₃ and 2-HOC ₆ H ₄ CHO | " | RCH=CHCOCH=CHC ₆ H ₃ OCH ₃ -3-OH-4 (60) | 1582 |

Note: References 668-2359 are on pp. 403-438.

† The structure of this compound was not established.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)


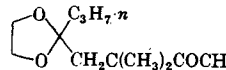
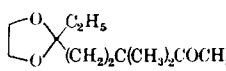

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|------------------------|--|------------------------------|
| $C_6H_5(CH_2)_3COCH_3$ and | | | |
|  | NaOH | $RCH=CHCO(CH_2)_3C_6H_5$ (48) | 1803 |
| C_6H_5CHO | " | $RCH=CHCO(CH_2)_3C_6H_5$ (64) | 1803 |
| $3,4-(CH_2O)_2C_6H_3CHO$ | " | $RCH=CHCO(CH_2)_3C_6H_5$ (68) | 1803 |
| $2-CH_3OC_6H_4CHO$ | " | $RCH=CHCO(CH_2)_3C_6H_5$ (28) | 1803 |
| $4-CH_3OC_6H_4CHO$ | " | $RCH=CHCO(CH_2)_3C_6H_5$ (85) | 1803 |
| $3,4-(CH_3O)_2C_6H_3CHO$ | " | $RCH=CHCO(CH_2)_3C_6H_5$ (61) | 1803 |
| $4-(CH_3)_2NC_6H_4CHO$ | " | $RCH=CHCO(CH_2)_3C_6H_5$ (31) | 1803 |
| $2-HO-3-CH_3OC_6H_4CHO$ and $4-(CH_3)_2NC_6H_4CHO$ | " | $RCH=CHCOCH=CHC_6H_5OH-2-OCH_3-3$ (—) | 1547 |
|  and $3-CH_3OC_6H_4CHO$ | KOH |  (60) | 1804 |
| $n-C_4H_9CH(C_2H_5)CH=CHCOCH_3$ and $(C_2H_5)_2CHCHO$ | NaOH | $RCH=CHCOCH=CHCH(C_2H_5)C_4H_9-n$ (—) | 1470 |
| $CH_3COC_9H_{19-n}$ and | | | |
|  | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1644 |
|  | HCl | $RCH=CH(COCH_3)C_9H_{17-n}$ (—) | 1645 |
| $2-ClC_6H_4CHO$ | NaOH | $RCH=CHCOC_9H_{19-n}$ (—) | 1805 |
| $3-ClC_6H_4CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1805 |
| $4-ClC_6H_4CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (60) | 1805 |
| C_6H_5CHO | KOH | $RCH=CHCOC_9H_{19-n}$ (—) | 1806, 1524, 1791, 1805, 1806 |
| $2-HOC_6H_4CHO$ | HCl NaOH | $RCH=C(COCH_3)C_9H_{17-n}$ (—) $RCH=CHCOC_9H_{19-n}$ (48) | 1791 1805 |
|  | " | $RCH=CHCOC_9H_{19-n}$ (45) | 1766 |
| $3,4-(CH_2O)_2C_6H_3CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1791 |
| $4-CH_3OC_6H_4CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1791 |
| $C_6H_5CH=CHCHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1791 |
|  | " | $RCH=CHCOC_9H_{19-n}$ (90) | 1766 |
| $3,4-(CH_3O)_2C_6H_3CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (72) | 1805 |
| $4-i-C_3H_7C_6H_4CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1805, 1791 |
| $2,4,5-(CH_3O)_3C_6H_2CHO$ | " | $RCH=CHCOC_9H_{19-n}$ (—) | 1608 |
| $n-C_4H_9CH(C_2H_5)(CH_2)_2COCH_3$ and $(C_2H_5)_2CHCHO$ | " | $RCH=CHCO(CH_2)_2CH(C_2H_5)C_4H_9-n$ (—) | 1470 |
| $C_6H_5(CH=CH)_2COCH_3$ and CCl_3CHO | CH_3CO_2K, CH_3CO_2H | $RCHOHCH_2CO(CH=CH)_2C_6H_5$ (36) | 1808 |
|  | NaOH | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1793 |
|  | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1809 |
| C_6H_5CHO | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1676 |
| $2-HOC_6H_4CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1589 |
| $3,4-(CH_2O)_2C_6H_3CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1589 |
| $4-CH_3OC_6H_4CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1589 |
| $3-CH_3O-4-HOC_6H_3CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1589 |
| $C_6H_5CH=CHCHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1595 |
| $3,4-(CH_3O)_2C_6H_3CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1589 |
| $C_6H_5(CH=CH)_2CHO$ | " | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1801 |
| Anthracene-9-carboxaldehyde | Na_2CO_3 | $RCH=CHCO(CH=CH)_2C_6H_5$ (—) | 1801 |
| $C_6H_5(COCH_2)_2COCH_3$ and C_6H_5CHO | $NaNH_2$ | $C_6H_5(COCH_2)_3CHOHC_6H_5$ (45) | 213 |

Note: References 668-2359 are on pp. 403-438.

TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

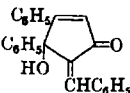
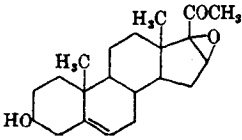
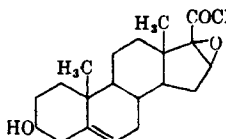
| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|-------|
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCOCH ₃ and  CHO | NaOH | RCH=CHCOCH=CHC ₆ H ₃ (OCH ₃) ₂ -2,4 (80) | 1008 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CH=CClCOCH ₃ and C ₆ H ₅ CHO | .. | RCH=CHCOC(Cl)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (-) | 1705 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOC(Cl)=CHC ₆ H ₃ N(CH ₃) ₂ -4 (-) | 1705 |
| C ₆ H ₅ CH=CHCHO | .. | RCH=CHCOC(Cl)=CHC ₆ H ₄ N(CH ₃) ₂ -4 (-) | 1705 |
| 4-(CH ₃) ₂ NC ₆ H ₃ CH=CHCOCH ₃ and 2-HO-5-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOCH=CHC ₆ H ₃ N(CH ₃) ₂ -4 (-) | 1547 |
| C ₆ H ₅ CHO | .. | RCH=CHCOCH=CHC ₆ H ₄ N(CH ₃) ₂ -4 (75) | 1798 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOCH=CHC ₆ H ₄ N(CH ₃) ₂ -4 (-) | 1798 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOCH=CHC ₆ H ₄ N(CH ₃) ₂ -4 (65) | 1798 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | Na ₂ CO ₃ | RCH=CHCOCH=CHC ₆ H ₄ N(CH ₃) ₂ -4 (66) | 1810 |
|  and CH ₂ C(CH ₃) ₂ COCH ₃ | | | |
| 2,9-Dimethyl-2,8-decadiene- 4,6-diyne-1,10-dial | Al(OC ₄ H ₉ - <i>t</i>) ₃ | $R \left[\begin{array}{c} n\text{-C}_3\text{H}_7 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2\text{CH}_2 \end{array} \right]_2$ (19) | 607 |
| 2,9-Dimethyl-2,4,6,8- decatetraene-1,10-dial | .. | $R \left[\begin{array}{c} n\text{-C}_3\text{H}_7 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2\text{CH}_2 \end{array} \right]_2$ (11) | 607 |
| C ₂₀ H ₂₄ O ₂ , crocetin dialdehyde | KOH | $R \left[\begin{array}{c} n\text{-C}_3\text{H}_7 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2\text{CH}_2 \end{array} \right]_2$ (48) | 607 |
|  and (CH ₂) ₂ C(CH ₃) ₂ COCH ₃ | | | |
| 2,9-Dimethyl-2,8-decadiene- 4,6-diyne-1,10-dial | Al(OC ₄ H ₉ - <i>t</i>) ₃ | $R \left[\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2(\text{CH}_2)_2 \end{array} \right]_2$ (21) | 608 |
| 2,9-Dimethyl-2,4,6,8- decatetraene-1,10-dial | .. | $R \left[\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2(\text{CH}_2)_2 \end{array} \right]_2$ (30) | 608 |
| C ₂₀ H ₂₄ O ₂ , crocetin dialdehyde | KOH | $R \left[\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2(\text{CH}_2)_2 \end{array} \right]_2$ (55) | 608 |
| β- <i>apo</i> -2-Carotenaldehyde | .. | $R \left[\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CHCOC}(\text{CH}_3)_2(\text{CH}_2)_2 \end{array} \right]_2$ (32) | 608 |
| CH ₃ COC ₁₀ H ₂₁ - <i>n</i> and 3-CH ₂ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOC ₁₀ H ₂₁ - <i>n</i> (-) | 1579 |
| 4-CH ₃ OC ₆ H ₄ (CH=CH) ₂ COCH ₃ and 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCO(CH=CH) ₂ C ₆ H ₄ OCH ₃ -4 (-) | 1603 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CH=CHCOCH ₃ and  CHO | .. | RCH=CHCOCH=CHC ₆ H ₂ (OCH ₃) ₃ -2,4,6 (83) | 1008 |
| C ₆ H ₅ CH=C(OC ₆ H ₅)COCH ₃ and C ₆ H ₅ CHO | .. | RCH=CHCOC(OC ₆ H ₅)=CHC ₆ H ₅ (-) | 268 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOC(OC ₆ H ₅)=CHC ₆ H ₅ (-) | 268 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

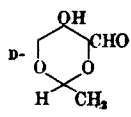
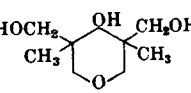
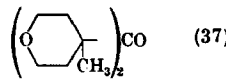
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TABLE XI. CONDENSATION OF ALDEHYDES WITH ALIPHATIC METHYL KETONES
OTHER THAN ACETONE AND 2-BUTANONE (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|----------------------------|---|-------|
| $C_6H_5COC(OH)(C_6H_5)CH_3COCH_3$ and C_6H_5CHO | KOH |  (—) | 324 |
| $C_6H_5(CH=CH)_4COCOCH_3$ and $C_6H_5(CH=CH)_3CHO$ | $(CH_2)_5NH$, CH_3CO_2H | $RCH=CHCOCO(CH=CH)_4C_6H_5$ (100) | 592 |
| $4-CH_3OC_6H_4CH=C(OC_6H_5)COCH_3$ and C_6H_5CHO | NaOH | $RCH=CHCOC(OC_6H_5)=CHC_6H_4OCH_3-4$ (—) | 268 |
| $4-CH_3OC_6H_4CHO$ | " | $RCH=CHCOC(OC_6H_5)=CHC_6H_4OCH_3-4$ (—) | 268 |
|  and | | | |
| C_6H_5CHO | $NaOCH_3$ |  (90) | 1811 |

Note: References 668–2359 are on pp. 403–438.

TABLE XII. CONDENSATION OF ALDEHYDES WITH ACYCLIC NON-METHYL KETONES
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|---|
| HOCH ₂ COCH ₂ OH and CH ₂ O | HCl | Furfural (—) | 975 |
| HOCH ₂ CHO | Glycine | Threopentulose (2), other pentoses (—) | 229, 975 |
| HOCH ₂ CHOHCHO | Ba(OH) ₂ | Fructose, sorbose (—) | 1812 |
| D-HOCH ₂ (CHOH) ₂ CHO | Ca(OH) ₂ | D-gluco-Heptulose (22), D-altru-heptulose (12), D-allo-heptulose (3) | 228 |
|  | Ba(OH) ₂ | D-gluco-Heptulose (20), 5,7-O-ethylidene-D- altru-heptulose (17), 5,7-O-ethylidene-D- manno-heptulose (7) | 227 |
| (C ₂ H ₅) ₂ CO and CH ₂ O | NaOH | CH ₂ CH(CH ₂ OH)COC ₂ H ₅ (75), CH ₂ C(CH ₂ OH) ₂ COC ₂ H ₅ (—), CH ₂ C(CH ₂ OH) ₂ COCH(CH ₂ OH)CH ₃ (—) | 652, 1389, 1400, 1406, 1618, 1622, 1813 |
| | Ca(OH) ₂ |  (—) | 1415 |
| | H ₂ SO ₄ , CH ₃ CO ₂ H |  (37) | 1740 |
| CCl ₃ CHO | CH ₃ CO ₂ K, (CH ₃ CO) ₂ O | RCHOHCH(CH ₃)COC ₂ H ₅ (70) | 287 |
| CH ₃ CHO | KOH | RCHOHCH(CH ₃)COC ₂ H ₅ (71) | 580, 269, 581, 1124 |
| C ₂ H ₅ CHO | " | RCHOHCH(CH ₃)COC ₂ H ₅ (50) | 580, 581 |


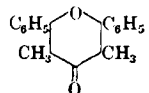

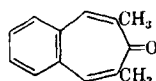

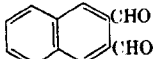
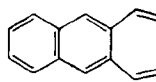
Note: References 668-2359 are on pp. 403-438.

* This product was isolated as the diallyl ether.

THE ALDOL CONDENSATION


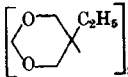
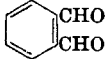
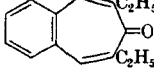
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TABLE XII. CONDENSATION OF ALDEHYDES WITH ACYCLIC NON-METHYL KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|----------------------------------|--|-----------------------------------|
| (C ₂ H ₅) ₂ CO (contd.) and n-C ₃ H ₇ CHO | KOH | RCHOHCH(CH ₃)COC ₂ H ₅ (83) | 580, 581 |
| i-C ₃ H ₇ CHO | NaOH | RCHOHCH(CH ₃)COC ₂ H ₅ (25) | 1124, 274, 1643 |
|  | " | RCH=C(CH ₃)COC ₂ H ₅ (—) | 1526 |
| n-C ₄ H ₉ O ₂ CCHO n-C ₅ H ₁₁ CHO | None, heat KOH | RCHOHCH(CH ₃)COC ₂ H ₅ (81) RCHOHCH(CH ₃)COC ₂ H ₅ (83) | 1468 580, 581 |
| C ₆ H ₅ CHO | " | RCH=C(CH ₃)COC ₂ H ₅ (40),  (20) | 1548, 523, 1663, 1814, 2332 |
| n-C ₆ H ₁₃ CHO | " | RCHOHCH(CH ₃)COC ₂ H ₅ (80) | 580, 581 |
|  | " |  (65) | 1672, 223 |
|  | NaOC ₂ H ₅ | RCH=C(CH ₃)COC ₂ H ₅ (45) | 1487 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CH- CHO, citral | NaOH | RCH=C(CH ₃)COC ₂ H ₅ (33) | 1687, 1492 |
|  | " |  (70) | 1690 |
| C ₂ H ₅ COCHOHCH ₃ and CH ₂ O CH ₃ CHO | KOH " | C ₂ H ₅ COC(OH)(CH ₂ OH)CH ₃ (61) C ₂ H ₅ COC(OH)(CH ₃)CHOHCH ₃ (47) | 230, 1767 230, 1767 |
| (CH ₃ OCH ₂) ₂ CO and O ₂ NCH(CHO) ₂ | NaOH | 2,6-(CH ₃ O) ₂ -4-O ₂ NC ₆ H ₂ OH (62) | 1815 |

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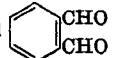
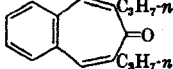

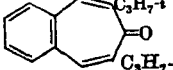
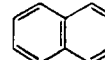
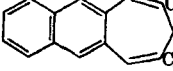

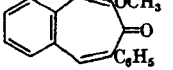
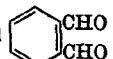
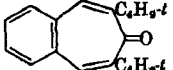
ORGANIC REACTIONS

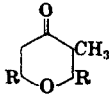
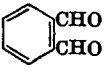
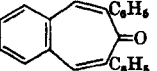
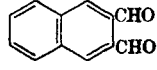
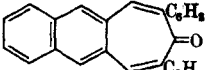
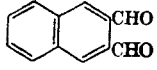
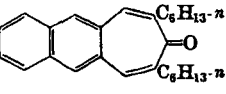
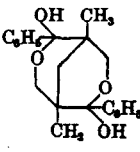
| | | | |
|---|-------------------------|--|-------------------|
| $C_2H_5COC_3H_7$, <i>n</i> and $n-C_3H_7CHO$ | KOH | $n-C_3H_7CHOHCH(CH_2)COC_3H_7$, <i>n</i> (1), $n-C_3H_7CH=C(CH_2)COC_3H_7$, <i>n</i> (9), $n-C_3H_7CH=C(C_2H_5)CHO$ (53) | 222 |
| $C_2H_5COC_4H_9$, <i>n</i> and  | $NaOC_2H_5$ | $RCH=C(CH_3)COC_4H_9$, <i>n</i> † (40) | 1487 |
| $(n-C_3H_7)_2CO$ and CH_2O | H_2SO_4 , CH_3CO_2H |  (32) | 1740 |
| $n-C_3H_7CHO$ | KOH | $RCHOHCH(C_2H_5)COC_3H_7$, <i>n</i> (3.6), $n-C_3H_7CHOHCH(C_2H_5)CHO$ (26), $n-C_3H_7CH=C(C_2H_5)CHO$ (47) | 222 |
| $n-C_4H_9O_2CCHO$ C_6H_5CHO | None, 125° NaOH | $RCHOHCH(C_2H_5)COC_3H_7$, <i>n</i> (84) $RCH=C(C_2H_5)COC_3H_7$, <i>n</i> (19.4), $C_{21}H_{24}O_2$ (15) | 1468 524, 2332 |
|  | $NaOC_2H_5$ |  (73) | 223 |
| $n-C_3H_7CH=C(C_2H_5)CHO$ | KOH | $n-C_3H_7CHOHCH(C_2H_5)COC_3H_7$, <i>n</i> (1.6), $n-C_3H_7CH=C(C_2H_5)COC_3H_7$, <i>n</i> (2.5) | 222 |
| $n-C_4H_9CH(C_2H_5)CHO$ | NaOH | $RCHOHCH(C_2H_5)COC_3H_7$, <i>n</i> (—) | 1652 |
| $(i-C_3H_7)_2CO$ and CH_2O | " | $CH_2OHCH(CH_3)_2COC_3H_7$, <i>i</i> (—) | 1618 |
| $n-C_3H_7CHO$ | $C_6H_5N(CH_3)MgBr$ | $RCHOHCH(CH_3)_2COC_3H_7$, <i>i</i> (82) | 177, 141 |
| $(C_2H_5)_2CHCHO$ | " | $RCHOHCH(CH_3)_2COC_3H_7$, <i>i</i> (67) | 177 |
| C_2H_5CHO | " | $RCHOHCH(CH_3)_2COC_3H_7$, <i>i</i> (80) | 177 |
| $C_2H_5CH_2CHO$ | " | $RCHOHCH(CH_3)_2COC_3H_7$, <i>i</i> (62) | 177 |
| $t-C_4H_9COCH=CHCH_3$ and C_6H_5CHO | $NaOC_2H_5$ | $R(CH=CH)_2COC_4H_9$, <i>t</i> (28) | 513 |
| $C_2H_5COC(CH_3)_2C_2H_5$ and $3,4-(CH_2O)_2C_6H_4CHO$ | Na_2CO_3 | $RCH=C(CH_3)COC(CH_3)_2C_2H_5$ (—) | 1816 |

Note: References 668–2359 are on pp. 403–438.

† The structure of this compound was not established.

TABLE XII. CONDENSATION OF ALDEHYDES WITH ACYCLIC NON-METHYL KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)




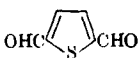
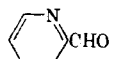
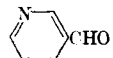
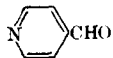
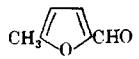
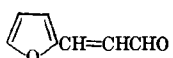
| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---------------------|---|----------|
| $(n-C_4H_9)_2CO$ and  | $NaOC_2H_5$ |  (97) | 223 |
| $(i-C_3H_7)_2CO$ and CH_2O | " | " | " |
| $n-C_3H_7CHO$ | $C_6H_5N(CH_3)MgBr$ | $RCHOHCH(C_2H_5)COC_4H_9$, <i>i</i> (73) | 177, 141 |
| $i-C_3H_7CHO$ | $i-C_3H_7MgCl$ | $RCHOHCH(C_2H_5)COC_4H_9$, <i>i</i> (50) | 141 |
| $i-C_3H_7CHO$ | " | $RCHOHCH(C_2H_5)COC_4H_9$, <i>i</i> (50) | 141 |
| $n-C_4H_9CHO$ | $C_6H_5N(CH_3)MgBr$ | $RCHOHCH(C_2H_5)COC_4H_9$, <i>i</i> (88) | 177 |
|  | $NaOC_2H_5$ |  (27) | 223 |
| $C_2H_5CH_2COC_2H_5$ and  | KOH |  (70) | 1817 |
| $C_2H_5CH_2COCH_2OCH_3$ and  | " |  (83) | 1818 |
| $n-C_3H_7COC(CH_3)_2C_2H_5$ and $3,4-(CH_2O)_2C_6H_4CHO$ | Na_2CO_3 | $RCH=C(C_2H_5)COC(CH_3)_2C_2H_5$ (—) | 1816 |
| $(n-C_5H_{11})_2CO$ and $n-C_3H_7CHO$ | $C_6H_5N(CH_3)MgBr$ | $RCHOHCH(C_2H_5)COC_5H_{11}$, <i>n</i> (15) | 177 |
| $(t-C_4H_9CH_2)_2CO$ and  | $NaOC_2H_5$ |  (4.5) | 223 |
| $4-CH_2OC_2H_5CH=CHCOC_2H_5$ and $3,4-(CH_2O)_2C_6H_4CHO$ | HCl | $C_{22}H_{26}O_4$ (—) | 1673 |

| | | | | |
|--|--|--|--|--|
| 4-CH ₃ OC ₆ H ₄ CHO | NaOH |  | (—) | 1673 |
| (C ₆ H ₅ CH ₂) ₂ CO and C(Cl ₂)=CClCHO C(Cl ₂)=CHCHO O ₂ NCH(CHO) ₂ C ₆ H ₅ CHO | H ₂ SO ₄ NaOH HCl KOH | | [RCH=C(C ₆ H ₅)] ₂ CO (31) [RCH=C(C ₆ H ₅)] ₂ CO (39) 2,6-(C ₆ H ₅) ₂ -4-O ₂ NC ₆ H ₄ OH (100) C ₆ H ₅ CHClCH(C ₆ H ₅)COCH ₂ C ₆ H ₅ (—) RCH=C(C ₆ H ₅)COCH ₂ C ₆ H ₅ (—), [RCH=C(C ₆ H ₅)] ₂ CO (—) | 289 639 1640 1788, 1819 1819 |
|  | " |  | (95) | 1672 |
|  | NaOH |  | (92) | 1690 |
| (n-C ₇ H ₁₅) ₂ CO and  | NaOC ₂ H ₅ |  | (76) | 223 |
| (C ₆ H ₅ COCH ₂) ₂ CH ₂ and CH ₂ O (C ₆ H ₅ COCH ₂) ₂ CHCH ₂ and CH ₂ O | NaOH " | | Polymer (—) C ₆ H ₅ COCH ₂ CH(CH ₂)CH(CH ₂ OH)COC ₆ H ₅ (91) | 1820 1820 |
| [C ₆ H ₅ COCH(CH ₃)] ₂ CH ₂ and CH ₂ O | " |  | (54) | 1820 |
| (C ₆ H ₅ COCH ₂) ₂ CHC ₆ H ₅ and CH ₂ O | " | | C ₆ H ₅ COCH ₂ CH(C ₆ H ₅)CH(CH ₂ OH)COC ₆ H ₅ (89) | 1820 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIII. CONDENSATION OF ALDEHYDES WITH CYCLOPENTANONES
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Cyclopentanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclopentanone Product(s) (Yield, %) | Refs. |
|---|-----------------------------------|----------------------------------|--|------------------------------|
| 2-Oxo-3-Cl | C ₆ H ₅ CHO | HCl | 2-Oxo-3-Cl-5-RCH= (84)* | 1821 |
| 2,2,3-Cl ₃ | " | " | 2,2,3-Cl ₃ -5-RCH= (16)* | 1821 |
| None | CH ₂ O | K ₂ CO ₃ | 2-CH ₂ OH (18), 2,2-(CH ₂ OH) ₂ (32), 2,2,5,5-(CH ₂ OH) ₄ (39) | 276, 278, 1822, 2340 |
| " | " | KOCH ₃ |  (30) | 550 |
| CH ₃ CHO | | K ₂ CO ₃ | 2-RCHOH (31), 2,2-(RCHOH) ₂ (16), 2,2,5,5-(RCHOH) ₄ (32) | 279 |
| " | | KOH | 2-RCH= (8), 2,5-(RCH=) (18), CH ₂ CH=CHCHO† (25) | 290 |
| C(Cl ₂)=CClCHO | | H ₂ SO ₄ | 2,5-(RCH=) ₂ (86) | 289 |
| C(Cl ₂)=CHCHO | | " | 2,5-(RCH=) ₂ (88) | 638 |
| C ₂ H ₅ CHO | | — | 2-RCHOH (—) | 1206 |
| CH ₃ CH=CHCHO | | KOH | 2-RCH= (30) | 301 |
| n-C ₃ H ₇ CHO | | NaOH | 2-RCH= (46), 2,5-(RCH=) ₂ (—) | 286, 1206 |
|  | | NaOC ₂ H ₅ | 2,5-(RCH=) ₂ (48) | 1823, 303, 1824, 1825 |
|  | | NaOH | 2-RCH= (60) | 293, 1826 |
| " | | KOH | 2,5-(RCH=) ₂ (100) | 1826, 1535, 1827, 1828 |
|  | | K ₂ CO ₃ | 2,5-(RCH=) ₂ (—) | 365 |
|  | | NaOH | 2,5-(RCH=) ₂ (Excellent) | 1825 |
|  | | " | 2,5-(RCH=) ₂ (Excellent) | 1825 |
|  | | " | 2,5-(RCH=) ₂ (Excellent) | 1825 |
|  | | " | 2,5-(RCH=) ₂ (Excellent) | 1825 |
| n-C ₄ H ₉ O ₂ CCHO | | None, 100° | 2-RCHOH (82) | 1468 |
| 2-ClC ₆ H ₄ CHO | | NaOH | 2-RCH= (24), 2,5-(RCH=) ₂ (—) | 293, 292 |
| 3-ClC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (—) | 1829 |
| 4-ClC ₆ H ₄ CHO | | " | 2-RCH= (—), 2,5-(RCH=) ₂ (—) | 293, 292 |
| 2-O ₂ NC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (—) | 292 |
| 3-O ₂ NC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (66) | 1830, 292 |
| 4-O ₂ NC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (74) | 1830, 292 |
| C ₆ H ₅ CHO | | — | 2,5-(RCHOH) ₂ (10) | 291 |
| " | | NaOH | 2-RCH= (74) | 299, 290, 295, 1831 |
| " | | " | 2,5-(RCH=) ₂ (95) | 294, 290, 292, 1828, 1831 |
|  | | " | 2,5-(RCH=) ₂ (90) | 1471 |
| 2-HOC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (—) | 1830, 1572, 1832 |
| 4-HOC ₆ H ₄ CHO | | " | 2,5-(RCH=) ₂ (63) | 1830, 1572 |
| n-C ₆ H ₁₃ CHO | | — | 2-RCHOH (—) | 1206 |

Note: References 668-2359 are on pp. 403-438.

* This product may contain some of the isomers containing an α,β -endocyclic double bond.³⁰⁴


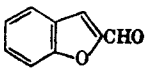
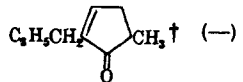
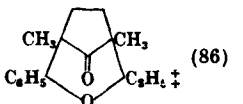
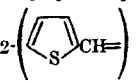
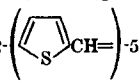
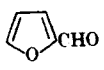
† This is a complete structural formula.

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THE ALDOL CONDENSATION

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TABLE XIII. CONDENSATION OF ALDEHYDES WITH CYCLOPENTANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclopentanone Product(s) (Yield, %) | Refs. |
|---|---|------------------------------------|---|-----------------|
| None (<i>contd.</i>) | 3,4-(CH ₂ O) ₂ C ₂ H ₄ CHO | KOH | 2,5-(RCH=) ₂ (—) | 1830, 292 |
| | .. | NaOC ₂ H ₅ † | 2-RCH= (44) | 295 |
| | 3-CH ₂ OC ₂ H ₄ CHO | NaOH | 2,5-(RCH=) ₂ (—) | 1829 |
| | 4-CH ₂ OC ₂ H ₄ CHO | .. | 2-RCH= (72) | 293 |
| | .. | .. | 2,5-(RCH=) ₂ (—) | 1828, 292, 1563 |
| | 3-CH ₂ O-4-HOC ₂ H ₄ CHO | .. | 2,5-(RCH=) ₂ (—) | 1830 |
| |  | NaOC ₂ H ₅ | 2-RCH= (60) | 1487 |
| |  | NaOH | 2,5-(RCH=) ₂ (—) | 1829 |
| | C ₂ H ₅ CH=CHCHO | .. | 2-RCH= (71), 2,5-(RCH=) ₂ (—) | 290 |
| | .. | .. | 2,5-(RCH=) ₂ (—) | 1828, 292 |
| | 4-CH ₂ CONHC ₂ H ₄ CHO | .. | 2,5-(RCH=) ₂ (—) | 1834 |
| | 2-C ₂ H ₅ OC ₂ H ₄ CHO | .. | 2,5-(RCH=) ₂ (—) | 1598 |
| | 3,4-(CH ₂ O) ₂ C ₂ H ₄ CHO | .. | 2,5-(RCH=) ₂ (—) | 1598 |
| | 4-(CH ₂) ₂ NC ₂ H ₄ CHO | .. | 2,5-(RCH=) ₂ (—) | 292 |
| | 4-(CH ₂) ₂ CHC ₂ H ₄ CHO | KOH | 2,5-(RCH=) ₂ (—) | 1830, 292 |
| 2-CH ₃ | C ₂ H ₅ CHO | NaOCH ₃ | 2-CH ₃ -5-RCH= (—) | 304, 1835, 1836 |
| | .. | HCl |  (—) | 304, 1835-1837 |
| 3-CH ₃ | .. | NaOH | 2,5-(RCH=) ₂ -3-CH ₃ (42) | 1838, 318 |
| 2-CH ₂ CH= | .. | KOH | 2-(CH ₂ CH=)-5-RCH= (—) | 290 |
| 2-C ₂ H ₅ | .. | .. | 2-C ₂ H ₅ -5-RCH= (100) | 290 |
| | C ₂ H ₅ CH=CHCHO | NaOH | 2-C ₂ H ₅ -5-RCH= (—) | 290 |
| 2,4-(CH ₃) ₂ | 3-O ₂ NC ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | 4-O ₂ NC ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | C ₂ H ₅ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | 3,4-(CH ₂ O) ₂ C ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | 4-CH ₂ OC ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | C ₂ H ₅ CH=CHCHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | 4-(CH ₂) ₂ NC ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| | 4- <i>i</i> -C ₂ H ₅ C ₂ H ₄ CHO | .. | 2,4-(CH ₃) ₂ -5-RCH= (—) | 292 |
| 2,5-(CH ₃) ₂ | C ₂ H ₅ CHO | HCl |  (86) | 530 |
| | 4-CH ₂ C ₂ H ₄ CHO | .. | C ₂₂ H ₂₆ O ₂ (25) | 530 |
| | 4- <i>i</i> -C ₂ H ₅ C ₂ H ₄ CHO | .. | C ₂₇ H ₃₄ O ₂ (37) | 530 |
| 3- <i>n</i> -C ₂ H ₅ | 4-O ₂ NC ₂ H ₄ CHO | NaOH | 2,5-(RCH=) ₂ -3- <i>n</i> -C ₂ H ₅ (—) | 1839 |
| 3-C ₂ H ₅ -3-CH ₃ | .. | .. | 2,5-(RCH=) ₂ -3-CH ₃ -3-C ₂ H ₅ (—) | 1839 |
| 3-C ₂ H ₅ -4-CH ₃ | .. | .. | 2,5-(RCH=) ₂ -3-C ₂ H ₅ -4-CH ₃ (—) | 1839 |
| 2-() | C ₂ H ₅ CHO | KOH | 2-()-5-RCH= (82) | 303 |
| 3-C ₂ H ₅ | .. | NaOH | 2,5-(RCH=) ₂ -3-C ₂ H ₅ (—) | 1259 |
| 2-(CH ₂) ₂ CH |  | KOH | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| | C ₂ H ₅ CHO | .. | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| | 4-CH ₂ OC ₂ H ₄ CHO | .. | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| | C ₂ H ₅ CH=CHCHO | .. | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| | 3,4-(CH ₂ O) ₂ C ₂ H ₄ CHO | .. | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| | 4- <i>i</i> -C ₂ H ₅ C ₂ H ₄ CHO | .. | 2-(CH ₂) ₂ CH-5-RCH= (—) | 1840 |
| 2-C ₂ H ₅ CH= | C ₂ H ₅ CHO | .. | 2-(C ₂ H ₅ CH=)-5-RCH= (100) | 290, 1828 |
| 2-C ₂ H ₅ CH ₂ | .. | NaOH | 2-C ₂ H ₅ CH ₂ -5-RCH= (95) | 290, 1835 |

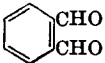
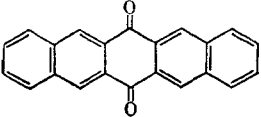
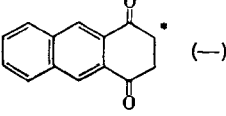
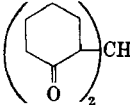
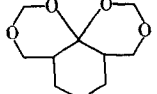
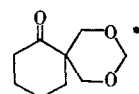
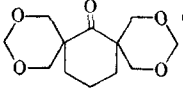
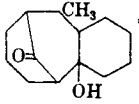
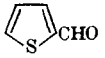
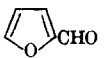
Note: References 663-2359 are on pp. 403-438.

† This is a complete structural formula.

‡ This is the structure proposed for the product.

TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---------------------------------|---|-------------------------------------|--|--------------------------------|
| 2-Oxo | $C_6H_5CH=CHCHO$ $C_6H_5CH_2CH_2CHO$ | — — | 2-Oxo-3,6-(RCH=) ₂ (—) 2-Oxo-3,6-(RCH=) ₂ (—) | 327 327 |
| 4-Oxo |  | KOH |  (90),  (—) | 334 |
| None | CH_2O | KOH |  (68) | 1841, 277, 550, 552, 1842 |
| | " | $Ca(OH)_2$ | 2,2,6,6-(CH_2OH) ₄ (40) | 278 |
| | " | $KOCH_3$ | 2- CH_2OH (60) | 550, 277, 278, 1822, 1841 |
| | " | K_2CO_3 | 2,2-(CH_2OH) ₂ (—) | 277 |
| | " (4 mole equiv.) | H_2SO_4 , CH_3CO_2H |  (8),  (—) | 460 |
| | " (10 mole equiv.) | " |  (30) | 460 |
| | CCl_3CHO | CH_3CO_2K , $(CH_3CO)_2O$ | 2-RCHOH (70) | 287 |
| | CH_3CHO | $Ca(OH)_2$ |  (24) | 552-555 |
| | " | NaOH | 2-RCHOH (30) | 285, 82, 277, 1843 |
| | " | Ion-exchange resin Amberlite IR 120 | 2-RCH= (Small) | 283, 82, 277, 285, 1842 |
| | $C(Cl_2)=CClCHO$ | H_2SO_4 | 2,6-(RCH=) ₂ (26) | 289 |
| | $C(Cl_2)=CHCHO$ | HCl | 2,6-(RCH=) ₂ (76) | 639, 638 |
| | C_2H_5CHO | $NaOC_2H_5$ | 2-RCHOH (—) | 1843 |
| | " | NaOH, 15-20° | 2-RCH= (15) | 285, 282, 552, 1843 |
| | $CH_3CH=CHCHO$ | KOH | 2-RCH= (—) | 301 |
| | $n-C_3H_7CHO$ | Ion-exchange resin Amberlite IR 120 | 2-RCH= (—) | 283, 282 |
| | " | NaOH | 2-RCHOH (56) | 1844, 552, 1843 |
| | $C(Cl_2)=CHCH=CHCHO$ | HCl | 2,6-(RCH=) ₂ (70) | 1451 |
| |  | $NaOC_2H_5$ | 2,6-(RCH=) ₂ (51) | 1823, 303, 1824, 1825, 1845 |
| |  | NaOH | 2-RCH= (85) | 1846-1848, 293, 618 |

Note: References 668-2359 are on pp. 403-438.








* This is a complete structural formula.

ORGANIC REACTIONS

THE ALDOL CONDENSATION

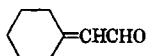
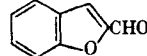
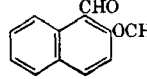
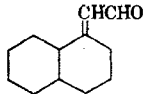
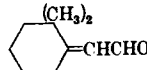
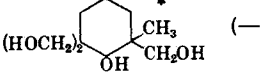
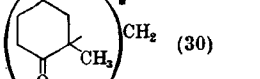


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TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---------------------------------|---|---|--|---|
| None (<i>contd.</i>) |  CHO (<i>contd.</i>) | NaOH | 2,6-(RCH=) ₂ (100) | 1824, 618, 1535, 1827, 1828, 1847, 1848 |
| |  CHO | K ₂ CO ₃ | 2,6-(RCH=) ₂ (—) | 365 |
| |  CHO | NaOH | 2,6-(RCH=) ₂ (Excellent) | 1825 |
| |  CHO | .. | 2,6-(RCH=) ₂ (Excellent) | 1825 |
| |  CHO | .. | 2,6-(RCH=) ₂ (Excellent) | 1825 |
| |  CHO | .. | 2,6-(RCH=) ₂ (Excellent) | 1825 |
| | <i>n</i> -C ₄ H ₉ O ₂ CCHO | None, 100° | 2-RCHOH (84) | 1468 |
| | (C ₂ H ₅) ₂ CHCHO | Ba(OH) ₂ | 2-RCH= (—) | 288 |
| | 4-BrC ₆ H ₄ CHO | NaOH | 2,6-RCH= (89) | 1849, 282 |
| | .. | .. | 2-RCHOH (epimers) (66) | 1850 |
| | 2-ClC ₆ H ₄ CHO | .. | 2-RCH= (70), 2,6-(RCH=) ₂ (—) | 302, 292, 293 |
| | 4-ClC ₆ H ₄ CHO | NaOH, H ₂ O, C ₂ H ₅ OH, rfx., 1.5 hr. | 2,6-(RCH=) (91) | 1849, 292 |
| | .. | NaOH, H ₂ O, rfx., 6 hr. | 2-RCH= (—) | 293 |
| | .. | NaOH, H ₂ O, 25°, 10 hr. | 2-RCHOH (88) | 1850 |
| | 4-IC ₆ H ₄ CHO | NaOH, H ₂ O, C ₂ H ₅ OH, rfx., 1.5 hr. | 2,6-(RCH=) ₂ (84) | 1849 |
| | .. | NaOH, H ₂ O, 25°, 11 hr. | 2-RCHOH (epimers) (84) | 1850 |
| | 2-O ₂ NC ₆ H ₄ CHO | HCO ₂ H | 2,6-(RCH=) ₂ (—) | 292 |
| | 3-O ₂ NC ₆ H ₄ CHO | NaOH | 2,6-(RCH=) ₂ (34) | 1798, 292 |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOH, C ₂ H ₅ OH, warm | 2,6-(RCH=) ₂ (39) | 1798, 292 |
| | .. | NaOH, H ₂ O, 0° | 2-RCHOH (<i>threo</i>) (54), 2-RCHOH (<i>erythro</i>) (30) | 64, 291 |
| | C(Cl ₂)=CH(CH=CH) ₂ -CHO | HCl | 2,6-(RCH=) ₂ (66) | 1451 |
| | C ₂ H ₅ CHO | NaOH, H ₂ O, 25°, 4 hr. | 2-RCHOH (100) | 291, 292, 294 |
| | .. | NaOH, H ₂ O, 25°, 10 days | 2-RCH= (76) | 294, 293, 295, 298, 299, 1097, 1846, 1851, 1852 |
| | .. | NaOH, C ₂ H ₅ OH | 2,6-(RCH=) ₂ (98) | 294, 292, 1097, 1828, 1851, 1852 |
| |  CH=CHCHO | NaOH | 2,6-(RCH=) ₂ (93) | 1471 |
| | 2-HOC ₂ H ₄ CHO | .. | 2,6-(RCH=) ₂ (—) | 1832 |
| | 4-HOC ₂ H ₄ CHO | .. | 2,6-(RCH=) ₂ (—) | 1572 |
| | <i>n</i> -C ₈ H ₁₇ CHO | Ion-exchange resin Amberlite IR 120 | 2-RCH= (—) | 283, 282 |
| | 3,4-(CH ₃ O) ₂ C ₂ H ₂ CHO | NaOC ₂ H ₁₁ - <i>t</i> | 2-RCH= (61) | 295, 299 |
| | .. | NaOH | 2,6-(RCH=) ₂ (—) | 292 |
| | 2-CH ₃ C ₂ H ₄ CHO | KOH | 2-RCH= (71), 2,6-(RCH=) ₂ (—) | 301 |
| | 4-CH ₃ C ₂ H ₄ CHO | .. | 2-RCH= (44) | 298 |
| | .. | NaOH | 2,6-(RCH=) ₂ (70) | 282 |

Note: References 668–2359 are on pp. 403–438.

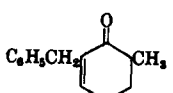
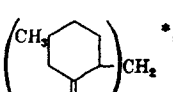


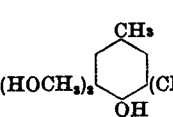
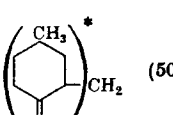


TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---|--|---|---|---|
| None (<i>cont'd.</i>) | 2-CH ₃ OC ₆ H ₄ CHO | NaOH | 2-RCHOH (98) | 291 |
| | 3-CH ₃ OC ₆ H ₄ CHO | KOH | 2-RCH= (70) | 302 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH, H ₂ O, 25° | 2-RCHOH (83) | 291 |
| | " | KOH, H ₂ O, rfx. | 2-RCH= (50) | 298, 1852 |
| | " | NaOH, C ₂ H ₅ OH | 2,6-(RCH=) ₂ (—) | 1572, 292, 1563 |
| |  | NaOH | 2-RCH= (—) | 1853 |
| |  | " | 2,6-(RCH=) ₂ (—) | 1854 |
| | C ₆ H ₅ CH=CHCHO | " | 2,6-(RCH=) ₂ (—) | 292, 1563 |
| | 3-CH ₃ CONHC ₆ H ₄ -CHO | " | 2,6-(RCH=) ₂ (82) | 1798 |
| | 4-CH ₃ CONHC ₆ H ₄ -CHO | " | 2,6-(RCH=) ₂ (75) | 1798, 1834 |
| | 2,4-(CH ₃) ₂ C ₆ H ₃ CHO | " | 2,6-(RCH=) ₂ (70) | 282 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | 2-RCH= (52) | 299 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | NaOC ₂ H ₅ | 2-RCH= (62) | 1798 |
| | " | NaOH | 2,6-(RCH=) ₂ (64) | 1849, 292, 1798 |
| | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | " | 2,6-(RCH=) ₂ (—) | 292, 1855 |
| | <i>i</i> -C ₃ H ₇ (CH ₂) ₂ CH-(CH ₃)CH ₂ CHO | " | 2-RCH= (70) | 1496 |
| | " | KOH, NaOH | 2-RCH= (29), 2,6-(RCH=) ₂ (16) | 1496 |
| | C ₆ H ₅ (CH=CH) ₂ CHO | NaOH | 2,6-(RCH=) ₂ (71) | 1000 |
| |  | " | 2,6-(RCH=) ₂ (—) | 1854 |
| | 2-HO |  | " | 2-RCH= (—), 2,6-(RCH=) ₂ (—) |
| CH ₂ O | | KOH | 2-CH ₂ OH (52) | 230, 1767 |
| 4-HO | | NaOH | 2-(RCH=)-4-HO (68) | 1857, 1858 |
|  | | " | 2-(RCH=)-4-HO (—) | 1857 |
| 2-CH ₃ | | Ca(OH) ₂ |  (—) | 278 |
| " | | KOCH ₃ , CH ₃ OH, < 40° | 2-CH ₃ -2-CH ₂ OH (18) | 550, 1822 |
| " | | KOCH ₃ , CH ₃ OH, rfx., few min. |  (30) | 550, 1842 |
| C(Cl ₂)=CHCHO | | HCl | 2-CH ₃ -2-[C(Cl ₂)=CHCHOH]-6-[C(Cl ₂)=CHCH=] (53) | 638 |
|  | | NaOH | 2-CH ₃ -6-RCH= (60) | 1845 |
|  | | NaOCH ₃ | 2-CH ₃ -6-RCH= (84) | 1272, 618, 1847, 1859, 1860 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---------------------------------|---|---|---|---|
| 2-CH ₃ (contd.) | 4-ClC ₂ H ₄ CHO C ₂ H ₅ CHO | NaOC ₂ H ₅ NaOH | 2-CH ₃ -6-RCH= (32) <i>trans</i> -2-CH ₃ -6-RCH= (69) | 304 1861, 80, 304, 530, 1835-1837, 1851 |
| | .. | HCl |  (83) | 304, 530, 1835, 1836 |
| 3-CH ₃ | CH ₂ O | KOCH ₃ , CH ₃ OH, <40° | 2-CH ₂ OH-5-CH ₃ (-) | 550 |
| | .. | KOCH ₃ , CH ₃ OH, rfx., 2-3 min. |  (83) | 550 |
| |  CHO | NaOH | 2,6-(RCH=) ₂ (-) | 1829 |
| |  CHO | KOH, 6 hr. | 2- or 6-RCH= (70) | 1847, 618 |
| | .. | NaOCH ₃ | 2,6-(RCH=) ₂ (55) | 618 |
| | 2-ClC ₂ H ₄ CHO | NaOH | 6-RCH= (-) | 1862 |
| | 4-ClC ₂ H ₄ CHO | .. | 6-RCH= (-) | 1862 |
| | 2-HO-5-ClC ₂ H ₄ CHO | .. | 6-RCH= (-) | 1863 |
| | 2-O ₂ NC ₂ H ₄ CHO | HCO ₂ H | 2,6-(RCH=) ₂ (-) | 292 |
| | C ₂ H ₅ CHO | KOH | 6-RCH= (45) | 1851, 318, 1862, 1864, 1865 |
| | .. | NaOC ₂ H ₅ | 6- and 2,6-(RCH=) ₂ (-) | 318 |
| | .. | .. | 6-RCH= (-), C ₁₄ H ₂₆ O (-) | 1865 |
| | 2-HOC ₂ H ₄ CHO | NaOH | 6-RCH= (35) | 1832 |
| | 4-HOC ₂ H ₄ CHO | HCl | 2,6-(RCH=) ₂ † (80) | 1572 |
| | 3,4-(CH ₂ O) ₂ C ₂ H ₅ CHO | NaOH | 6-RCH= (-) | 1862 |
| | 4-CH ₂ C ₂ H ₄ CHO | .. | 6-RCH= (-) | 1862 |
| | 4-CH ₂ OC ₂ H ₄ CHO | NaOCH ₃ | 6-RCH= (-) | 1864, 1572, 1862 |
| | .. | HCl | 2,6-(RCH=) ₂ † (-) | 1572 |
| | 2-HO-5- CH ₂ C ₂ H ₄ CHO | NaOH | 6-RCH= (-) | 1863 |
| | 2,3-(CH ₂ O) ₂ C ₂ H ₅ CHO | .. | 6-RCH= (-) | 1862 |
| | 4-(CH ₂) ₂ NC ₂ H ₄ CHO | .. | 6-RCH= (-) | 1862 |
| | 4- <i>i</i> -C ₂ H ₅ C ₂ H ₄ CHO | NaOCH ₃ | 6-RCH= (-), 2,6-(RCH=) ₂ (-) | 1864, 1862 |
| 4-CH ₃ | CH ₂ O | Ca(OH) ₂ |  (83) | 278 |
| | .. | KOCH ₃ | 2-CH ₂ OH-4-CH ₃ (34) | 550, 1822 |
| | .. | .. |  (50) | 550 |
| | C(Cl ₂)=CHCHO | HCl | 2,6-(RCH=) ₂ -4-CH ₃ (70) | 638 |
| |  CHO | NaOH | 2,6-(RCH=) ₂ -4-CH ₃ (100) | 1829, 1845 |
| |  CHO | KOH | 2-(RCH=) ₂ -4-CH ₃ (75) | 1847, 618, 1272, 1860 |
| | .. | NaOCH ₃ | 2,6-(RCH=) ₂ -4-CH ₃ (55) | 618, 1847, 1860 |

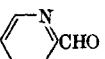
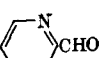
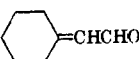
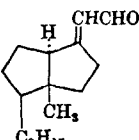
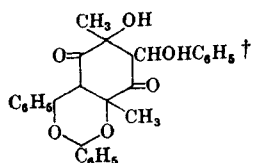
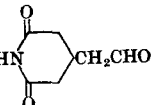
Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

† This structure was suggested but not established.

‡ This product might contain an α,β -unsaturated endocyclic double bond.**

TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. | |
|--|--|--|---|---|------------|
| 4-CH ₃ (contd.) |  | NaOH | 2,6-(RCH=) ₂ -4-CH ₃ (Excellent) | 1825 | |
| |  | NaOH | 2,6-(RCH=) ₂ -4-CH ₃ (Excellent) | 1825 | |
| | 2-O ₂ NC ₆ H ₄ CHO C ₆ H ₅ CHO | HCO ₂ H KOH | 2,6-(RCH=) ₂ -4-CH ₃ (-) 2-(RCH=)-4-CH ₃ (60), 2,6-(RCH=) ₂ -4-CH ₃ (35) | 292 1851, 1866 | |
| | 2-HOC ₆ H ₄ CHO n-C ₆ H ₁₃ CHO | NaOH " | 2,6-(RCH=) ₂ -4-CH ₃ (50) 2-(RCH=)-4-CH ₃ (36) | 1832 284 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | KOH | 2-(RCH=)-4-CH ₃ (65), 2,6-(RCH=) ₂ -4-CH ₃ (-) | 300 | |
| | 4-CH ₃ CONHC ₆ H ₄ -CHO | NaOH | 2,6-(RCH=) ₂ -4-CH ₃ (-) | 1834 | |
| | 4-i-C ₃ H ₇ C ₆ H ₄ CHO C ₂ H ₅ O ₂ C(CH ₂) ₇ CHO | KOH NaOH | 2-(RCH=)-4-CH ₃ (-) 2-(RCH=)-4-CH ₃ (-) | 1867 1868 | |
| | 4-CH ₃ O |  | " | 2-(RCH=)-4-CH ₃ O (25) | 1869, 1856 |
| | | 2-Cholestanylidene-ethanal | " | trans-2-(RCH=)-4-(CH ₃ O) (10), cis-2-(RCH=)-4-(CH ₃ O) (10), 2,6-(RCH=) ₂ -4-CH ₃ O (67) | 1870, 1088 |
| 4-CH ₃ CO ₂ |  | NaOC ₂ H ₅ | 2-(RCH=)-4-CH ₃ CO ₂ (17) | 1871 | |
| 2,5-(OH) ₂ -2,5-(CH ₃) ₂ -4-oxo | C ₆ H ₅ CHO | KOH |  (-) | 1709 | |
| 2,2-(CH ₃) ₂ | " | NaOC ₂ H ₅ HCl | 2,2-(CH ₃) ₂ -6-RCH= (30) 2,2-(CH ₃) ₂ -6-RCH= (46) | 531, 1833 531 | |
| 2,4-(CH ₃) ₂ | 2-ClC ₆ H ₄ CHO | NaOH | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-ClC ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 3-O ₂ NC ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-O ₂ NC ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | C ₆ H ₅ CHO | " | 2,4-(CH ₃) ₂ -6-RCHOH (-) | 292 | |
| | " | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | " | " | 2,4-(CH ₃) ₂ -6-RCHOH (12) | 1872 | |
| 2,5-(CH ₃) ₂ |  | C ₆ H ₅ N(CH ₃)-MgBr | 2,4-(CH ₃) ₂ -6-RCHOH (12) | 1872 | |
| | 3,4-(CH ₂ O ₂)C ₆ H ₅ CHO | NaOH | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | C ₆ H ₅ CH=CHCHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-i-C ₃ H ₇ C ₆ H ₄ CHO | " | 2,4-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 2-ClC ₆ H ₄ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-ClC ₆ H ₄ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 3-O ₂ NC ₆ H ₄ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| | 4-O ₂ NC ₆ H ₄ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | |
| C ₆ H ₅ CHO | " | 2,5-(CH ₃) ₂ -6-RCHOH (-), 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | | |
| 3,4-(CH ₂ O ₂)C ₆ H ₅ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | | |
| 4-CH ₃ OC ₆ H ₄ CHO | " | 2,5-(CH ₃) ₂ -6-RCH= (-) | 292 | | |

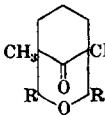
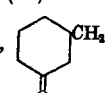
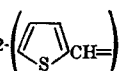
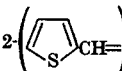
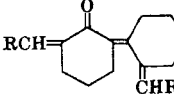
Note: References 668-2359 are on pp. 403-438.

† This structure was suggested but not established.

TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

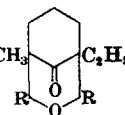
| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---|---|------------------------------------|--|-----------|
| 2,5-(CH ₃) ₂ (cont'd.) | C ₆ H ₅ CH=CHCHO | NaOH | 2,5-(CH ₃) ₂ -6-RCH= (—) | 292 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | 2,5-(CH ₃) ₂ -6-RCH= (—) | 292 |
| | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | .. | 2,5-(CH ₃) ₂ -6-RCH= (—) | 292 |
| 2,6-(CH ₃) ₂ | C ₆ H ₅ CHO | HCl |  (88) | 530 |
| 4-C ₂ H ₅ - <i>i</i> | .. | NaOC ₂ H ₅ | 2,6-(RCH=) ₂ -4-C ₂ H ₅ - <i>i</i> (—) | 320 |
| 2-CH ₃ -2-C ₂ H ₅ § | .. | HCl | 2-CH ₃ -2-C ₂ H ₅ -6-RCH= † (32) | 531 |
| 4-CH ₃ -4-C ₂ H ₅ | .. | (CH ₂) ₅ NH | 2,6-(RCH=) ₂ -4-CH ₃ -4-C ₂ H ₅ (80) | 1873 |
| 3,3,4-(CH ₃) ₃ | 3,4-(CH ₂ O ₂)C ₆ H ₅ CHO | .. | 2,6-(RCH=) ₂ -4-CH ₃ -4-C ₂ H ₅ (80) | 1873 |
| 2-CH ₃ -5-CH ₂ CH=CH ₂ | 4-O ₂ NC ₆ H ₄ CHO | NaOH | 2,6-(RCH=) ₂ -3,3,4-(CH ₃) ₃ (—) | 1839 |
| 2-[(CH ₃) ₂ C=]-5-CH ₃ | C ₆ H ₅ CHO | NaOC ₂ H ₅ | 2-CH ₃ -5-CH ₂ CH=CH ₂ -6-RCH= (20) | 317, 319 |
| | .. | .. | 2-[(CH ₃) ₂ C=]-5-CH ₃ -6-RCH= (—) | 318, 319 |
| | 2-HOC ₆ H ₄ CHO | NaOH | (2-HOC ₆ H ₄ CH=CH) ₂ CO (—),  (—) | 1832 |
| 2-(CH ₂ =CHCH ₂)-4-CH ₃ | C ₆ H ₅ CHO | NaOCH ₃ | 2-(CH ₂ =CHCH ₂)-4-CH ₃ -6-RCH= (40), | 473 |
| | | |  (2.5) | |
| 4- <i>t</i> -C ₄ H ₉ | <i>n</i> -C ₆ H ₁₃ CHO | NaOH | 2-(RCH=)-4-C ₄ H ₉ - <i>t</i> (35) | 284 |
| | 4-CH ₂ CONHC ₆ H ₄ -CHO | .. | 2,6-(RCH=) ₂ -4-C ₄ H ₉ - <i>t</i> (—) | 1834 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | 2,6-(RCH=) ₂ -4-C ₄ H ₉ - <i>t</i> (—) | 1834 |
| 2-CH ₃ -2- <i>n</i> -C ₃ H ₇ | C ₆ H ₅ CHO | NaOCH ₃ | 2-CH ₃ -2- <i>n</i> -C ₃ H ₇ -6-RCH= (—) | 1835 |
| .. | .. | HCl | 2-CH ₃ -2- <i>n</i> -C ₃ H ₇ -6-RCH= (—) | 473, 1835 |
| 2- <i>n</i> -C ₃ H ₇ -4-CH ₃ | .. | NaOCH ₃ | 2- <i>n</i> -C ₃ H ₇ -4-CH ₃ -6-RCH= (30), | 473 |
| .. | .. | .. | C ₁₇ H ₂₄ O ₂ (8) | |
| .. | .. | HCl | 2- <i>n</i> -C ₃ H ₇ -4-CH ₃ -6-RCH= † (38) | 473 |
| 2- <i>i</i> -C ₃ H ₇ -5-CH ₃ | .. | .. | 2- <i>i</i> -C ₃ H ₇ -5-CH ₃ -6-RCH= † (88) | 317-319 |
| 2-() | .. | KOH | 2-()-6-RCH= (80) | 303 |
| 2,3,4,5-(CH ₃) ₄ |  CHO | .. | 2,3,4,5-(CH ₃) ₄ -6-RCH= (86) | 1874 |
| 4,4-(CH ₂) ₅ | C ₆ H ₅ CHO | (CH ₂) ₅ NH | 2,6-(RCH=) ₂ -4,4-(CH ₂) ₅ (80) | 1873 |
| .. | 3,4-(CH ₂ O ₂)C ₆ H ₅ CHO | .. | 2,6-(RCH=) ₂ -4,4-(CH ₂) ₅ (80) | 1873 |
| 2-C ₆ H ₅ | C ₆ H ₅ CHO | NaOH | 2-C ₆ H ₅ -6-RCH= (—) | 1875 |
| 2-[(CH ₂) ₅ C=] |  CHO | .. | 2-[(CH ₂) ₅ C=]-6-RCH= (—) | 282 |
| | C ₆ H ₅ CHO | .. |  (40) | 1178 |

Note: References 668-2359 are on pp. 403-438.

† This structure was suggested but not established.

‡ This product might contain an α,β -unsaturated endocyclic double bond.⁵⁶⁴

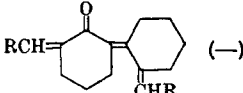
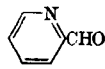


§ The sample of this compound used contained 15% of 2-ethyl-6-methylcyclohexanone which formed



THE ALDOL CONDENSATION

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TABLE XIV. CONDENSATION OF ALDEHYDES WITH CYCLOHEXANONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Cyclohexanone | Aldehyde, RCHO | Catalyst | Substituent(s) in Cyclohexanone Product(s) (Yield, %) | Refs. |
|---|---|----------------------------------|--|-----------|
| 2-[(CH ₂) ₆ C=] (<i>contd.</i>) | 4-CH ₂ OC ₆ H ₅ CHO | NaOH |  (—) | 1178 |
| 4-(CH ₂) ₆ CH |  | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (Excellent) | 1825 |
| | 4-ClC ₆ H ₄ CHO | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (—) | 1876 |
| | 4-FC ₆ H ₄ CHO | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (—) | 1876 |
| | C ₆ H ₅ CHO | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (80) | 1876 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (80) | 1876 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | 2,6-(RCH=) ₂ -4-[(CH ₂) ₆ CH] (—) | 1876 |
| 2-C ₆ H ₅ CH= | C ₆ H ₅ CHO | .. | 2-(C ₆ H ₅ CH=)-6-RCHOH (—) | 1834 |
| | .. | KOH | 2-(C ₆ H ₅ CH=)-6-RCH= (40) | 1852, 294 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | 2-(C ₆ H ₅ CH=)-6-RCH= (35) | 1852 |
| | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | .. | 2-(C ₆ H ₅ CH=)-6-RCH= (50) | 1867 |
| 2-C ₆ H ₅ CH ₂ | C ₆ H ₅ CHO | .. | 2-C ₆ H ₅ CH ₂ -6-RCH= (—) | 1851 |
| 2-C ₆ H ₅ CHOH | .. | NaOH | 2-C ₆ H ₅ CHOH-6-RCH= (48) | 294 |
| 2-(C ₆ H ₅ CH=)-4-CH ₃ | .. | KOH | 2-(C ₆ H ₅ CH=)-4-CH ₃ -6-RCH= (40) | 1851 |
| 3-CH ₃ -3-(4-CH ₃ C ₆ H ₄) |  | NaOH | 3-CH ₃ -3-(4-CH ₃ C ₆ H ₄)-6-RCH= (—) | 1877 |
| 2-(4-CH ₃ C ₆ H ₄ CH ₂) | C ₆ H ₅ CHO | KOH | 2-(4-CH ₃ C ₆ H ₄ CH ₂)-6-RCH= (—) | 1851 |
| 2-[2,3-(CH ₃ O) ₂ C ₆ H ₃] | .. | .. | 2-[2,3-(CH ₃ O) ₂ C ₆ H ₃]-6-RCH= (—) | 1878 |
| 2-(NCCH ₂ CH ₂)-2-C ₆ H ₅ | .. | NaOH | 2-(NCCH ₂ CH ₂)-2-C ₆ H ₅ -6-RCH= (95) | 1875 |
| 2-(4-CH ₃ OC ₆ H ₄ CH=)-4-CH ₃ | .. | KOH | 2-(4-CH ₃ OC ₆ H ₄ CH=)-4-CH ₃ -6-RCH= (100) | 300 |
| 2-(4-CH ₃ OC ₆ H ₄ CH=)-5-CH ₃ | 4-CH ₃ OC ₆ H ₄ CHO | .. | 2-(4-CH ₃ OC ₆ H ₄ CH=)-4-CH ₃ -6-RCH= (—) | 300 |
| | 4-HOC ₆ H ₄ CHO | HCl | 2-(4-CH ₃ OC ₆ H ₄ CH=)-5-CH ₃ -6-RCH= ‡ (82) | 1572 |
| 2-[4-(CH ₃) ₂ NC ₆ H ₄ CH=] | C ₆ H ₅ CHO | NaOC ₂ H ₅ | 2-[4-(CH ₃) ₂ NC ₆ H ₄ CH=]-6-RCH= (90) | 1798 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | 2-[4-(CH ₃) ₂ NC ₆ H ₄ CH=]-6-RCH= (—) | 1798 |
| 2-[2-CH ₃ O-3-C ₂ H ₅ OC ₆ H ₃] | C ₆ H ₅ CHO | KOH | 2-[2-CH ₃ O-3-C ₂ H ₅ OC ₆ H ₃]-6-RCH= (—) | 1878 |
| 2,2-(C ₆ H ₅) ₂ |  | NaOCH ₃ | 2,2-(C ₆ H ₅) ₂ -6-RCH= (66) | 1272 |
| | 2-ClC ₆ H ₄ CHO | KOH | 2,2-(C ₆ H ₅) ₂ -6-RCH= (84) | 1365 |
| | C ₆ H ₅ CHO | .. | 2,2-(C ₆ H ₅) ₂ -6-RCH= (62) | 1365, 304 |


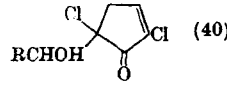

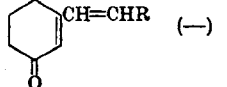
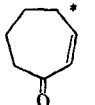

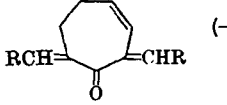
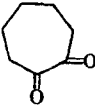
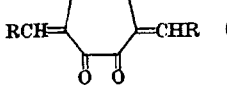
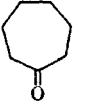
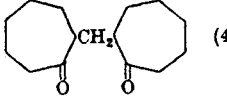

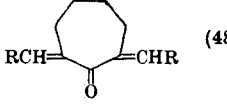

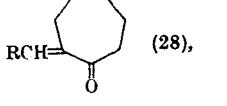

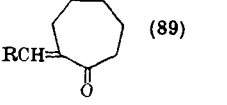
Note: References 668–2359 are on pp. 403–438.

‡ This product might contain an α,β -unsaturated endocyclic double bond.³⁰⁴

TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--------------|--|----------------------------|
|  | C_6H_5CHO | HCl |  (40) | 1821 |
|  | .. | $NaOC_2H_5$ |  (—) | 321 |
|  |  | HCl |  (—) | 1879 |
| | C_6H_5CHO | .. | A, R = $2-(C_4H_5S)$ | 1879 |
| | $3,4-(CH_2O_2)C_6H_5CHO$ | .. | A, R = C_6H_5 (21) | 1879 |
| | $2-CH_2OC_6H_4CHO$ | .. | A, R = $3,4-(CH_2O_2)C_6H_5$ (8) | 1879 |
| | $2-C_{10}H_7CHO$ | .. | A, R = $2-CH_2OC_6H_4$ (22) | 1879 |
| | | .. | A, R = $2-C_{10}H_7$ (31) | 1879 |
|  | C_6H_5CHO | $(CH_3)_2NH$ |  (34) | 1880, 325, 326 |
|  | CH_3O | $KOCH_3$ |  (40) | 550 |
| |  | $NaOC_2H_5$ |  (48) | 1823, 1845 |
| | | | B, R = $2-(C_4H_5S)$ | |
| |  | KOH |  (28), | 1848 |
| | .. | $NaOCH_3$ | B, R = $2-(C_4H_5O)$ (6) | |
| | | | B, R = $2-(C_4H_5O)$ (80) | 1272, 303, 1881 |
| |  | K_2CO_3 | B, R = $2-(C_4H_5S)CHO-5$ (—) | 365 |
| | $2-ClC_2H_4CHO$ | $NaOC_2H_5$ | B, R = $2-ClC_2H_4$ (53) | 1881 |
| | $3-O_2NC_6H_4CHO$ | NaOH | B, R = $3-O_2NC_6H_4$ (—) | 292 |
| | $4-O_2NC_6H_4CHO$ | .. | B, R = $4-O_2NC_6H_4$ (—) | 292 |
| | C_6H_5CHO | KOH |  (89) | 302 |
| | .. | $NaOCH_3$ | B, R = C_6H_5 (78) | 1882, 292, 318, 1881, 2332 |
| | $2-HOC_6H_4CHO$ | NaOH | B, R = $2-HOC_6H_4$ (11) | 1832 |

Note: References 668-2359 are on pp. 403-438.

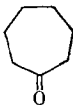
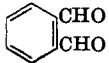
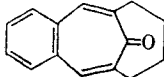
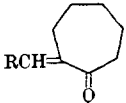
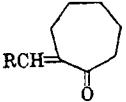
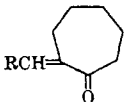
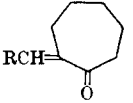
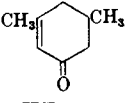
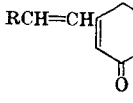
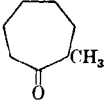

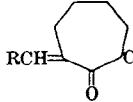
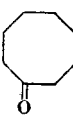
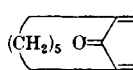
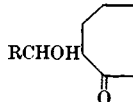
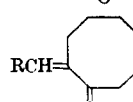
* The cycloheptanone was formed *in situ* from its ethylene ketal.

THE ALDOL CONDENSATION

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TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|--|------------------------------------|
|  (contd.) |  | NaOH |  (31) | 309 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO 4-CH ₃ C ₆ H ₄ CHO | NaOC ₂ H ₅ NaOCH ₃ | B, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (47) B, R = 4-CH ₃ C ₆ H ₄ (60) | 1881, 292 1883, 1881 |
| | 2-CH ₃ OC ₆ H ₄ CHO | KOH; NaOCH ₃ |  (—), B, R = 2-CH ₃ OC ₆ H ₄ (—) | 305 |
| | 3-CH ₃ OC ₆ H ₄ CHO | .. |  (—), B, R = 3-CH ₃ OC ₆ H ₄ (—) | 305 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOCH ₃ |  (50), B, R = 4-CH ₃ OC ₆ H ₄ (35-94) | 1884, 292, 305, 1881 |
| | C ₆ H ₅ CH=CHCHO 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOC ₂ H ₅ .. | B, R = C ₆ H ₅ CH=CH (26) B, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (53) | 1881, 292 1881 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOCH ₃ |  (64), B, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (—) | 1884, 305 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO 4- <i>i</i> -C ₂ H ₇ C ₆ H ₄ CHO 1-C ₁₀ H ₇ CHO | .. NaOC ₂ H ₅ | B, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (90) B, R = 4-(CH ₃) ₂ NC ₆ H ₄ (25) B, R = 4- <i>i</i> -C ₂ H ₇ C ₆ H ₄ (43) B, R = 1-C ₁₀ H ₇ (40) | 1884, 1881 1881 1881 1881 |
|  | C ₆ H ₅ CHO | .. | RCH=CH  (—) | 321, 46, 1837 |
|  |  | NaOCH ₃ |  (75) | 1272 |
|  | O ₂ NCH(CH ₃)CHO | NaOH |  (15) | 310 |
| | C ₆ H ₅ CHO | KOH | RCHOH  (25) | 307 |
| | .. | .. | RCH=  (35) | 307 |

ORGANIC REACTIONS

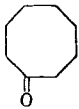
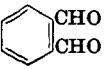
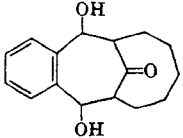
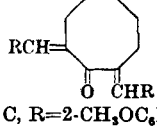
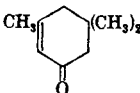
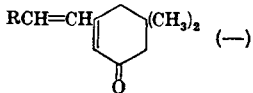
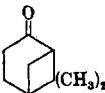
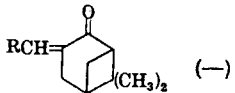
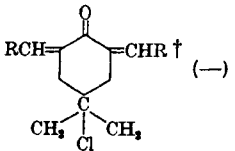
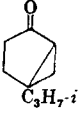
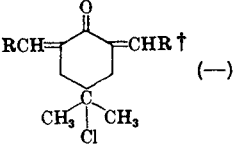
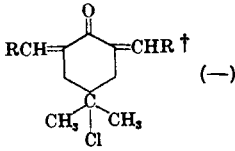
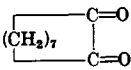
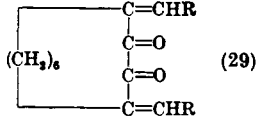
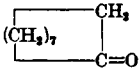
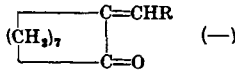
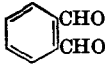
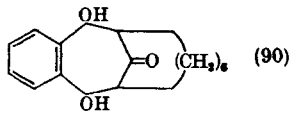
THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)

(R in the product is the group R in the aldehyde RCHO.)

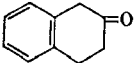
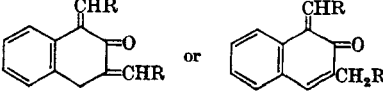
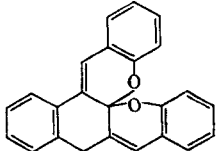
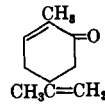
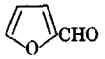
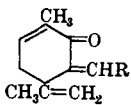
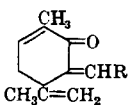
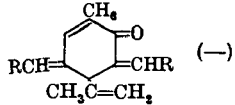
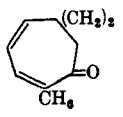
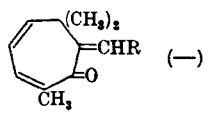
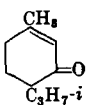
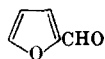
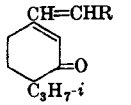
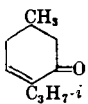
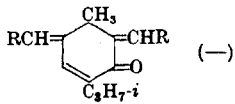
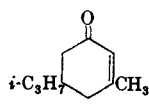
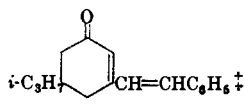
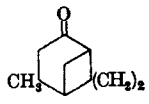
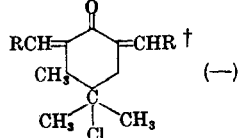
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|------------------------------------|---|-------------------|
|  (contd.) |  | NaOH |  (56) | 309 |
| | 2-CH ₃ OC ₆ H ₄ CHO | NaOC ₂ H ₅ |  (—) C, R=2-CH ₃ OC ₆ H ₄ | 306, 305 |
| | 3-CH ₃ OC ₆ H ₄ CHO | .. | C, R=3-CH ₃ OC ₆ H ₄ (—) | 306, 305 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | C, R=4-CH ₃ OC ₆ H ₄ (—) | 306, 305 |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | C, R=2,4-(CH ₃ O) ₂ C ₆ H ₃ (—) | 306, 305 |
| | 2,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | C, R=2,5-(CH ₃ O) ₂ C ₆ H ₃ (—) | 306, 305 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | C, R=3,4-(CH ₃ O) ₂ C ₆ H ₃ (—) | 306, 305 |
| | 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CHO | .. | C, R=3,4,5-(CH ₃ O) ₃ C ₆ H ₂ (—) | 306, 305 |
|  | C ₆ H ₅ CHO | .. |  (—) | 321, 322, 1837 |
|  | .. | .. |  (—) | 1885, 315 |
| .. | .. | HCl |  (—) | 315 |
|  | .. | .. |  (—) | 315 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. |  (—) | 315 |
|  | C ₆ H ₅ CHO | (CH ₂) ₅ NH |  (29) | 325, 326 |
|  | .. | KOH |  (—) | 307 |
| |  | NaOH |  (90) | 309 |

Note: References 668-2359 are on pp. 403-438.

† This product might contain an α,β -unsaturated endocyclic double bond.³⁰⁴

TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|--|---------------------------------|
|  | C_6H_5CHO | HCl |  (75) | 1886 |
| | 2-HOC ₆ H ₄ CHO | .. |  (35) | 1886 |
|  |  | NaOH |  (15) | 1887 |
| | C_6H_5CHO | .. |  (23) | 1887, 317 |
| | .. | NaOC ₂ H ₅ |  (-) | 316-319 |
|  | .. | NaOC ₂ H ₅ |  (-) | 318 |
|  |  | NaOC ₂ H ₅ |  (-) | 323 |
| | C_6H_5CHO | .. | D, R = 2-(C ₆ H ₅ O) (-) D, R = C ₆ H ₅ (90) | 323, 317, 319, 1888- 1891 |
| | 2-HOC ₆ H ₄ CHO | NaOH or HCl | D, R = 2-HOC ₆ H ₄ (25) | 1891 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOC ₂ H ₅ | D, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (85) | 1891 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOC ₂ H ₅ or HCl | D, R = 4-CH ₃ OC ₆ H ₄ (72) | 1891 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | NaOC ₂ H ₅ | D, R = 4-(CH ₃) ₂ NC ₆ H ₄ (-) | 323 |
| | 2-HO ₂ C-3,4-(CH ₃ O) ₂ -C ₆ H ₂ CHO | .. | D, R = 2-HO ₂ C-3,4-(CH ₃ O) ₂ C ₆ H ₂ (35) | 1891 |
|  | C_6H_5CHO | .. |  (-) | 319, 320 |
|  | .. | .. |  (50) | 1837 |
|  | .. | HCl |  (-) | 315 |

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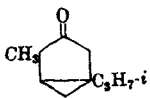
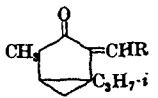
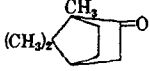
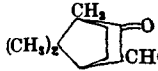

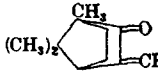
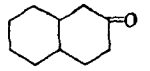

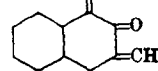
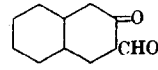
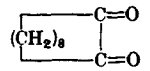
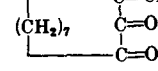
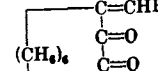
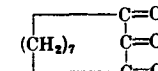
Note: References 668-2359 are on pp. 403-438.

† The product might contain an α,β -unsaturated endocyclic double bond.³⁰⁴
‡ This structure has been suggested but not established.

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TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--------------------------------|--|--------------------|
|  | C_6H_5CHO | HCl |  (47) | 1837 |
|  | CCl_3CHO | CH_3CO_2K , $(CH_3CO)_2O$ |  (4) | 287 |
|  | CHO | $NaNH_2$ |  (20) E, R = 2-(C_6H_5O) | 618, 1526, 1892 |
| | C_6H_5CHO | Na | E, R = C_6H_5 (-) | 313 |
| | 3,4-(CH_2O_2) C_6H_3CHO | " | E, R = 3,4-(CH_2O_2) C_6H_3 (-) | 1893 |
| | 2- $CH_2C_6H_4CHO$ | $NaNH_2$ | E, R = 2- $CH_2C_6H_4$ (-) | 314 |
| | 3- $CH_2C_6H_4CHO$ | " | E, R = 3- $CH_2C_6H_4$ (-) | 314 |
| | 4- $CH_2C_6H_4CHO$ | " | E, R = 4- $CH_2C_6H_4$ (-) | 314 |
| | 3- $CH_2OC_2H_5CHO$ | Na | E, R = 3- $CH_2OC_2H_5$ (-) | 1893 |
| | 4- $CH_2OC_2H_5CHO$ | " | E, R = 4- $CH_2OC_2H_5$ (-) | 313 |
| | $C_6H_5CH=CHCHO$ | " | E, R = $C_6H_5CH=CH$ (-) | 313 |
| | 2- $CH_2CO_2C_6H_4CHO$ | $NaNH_2$ | E, R = 2- $CH_2CO_2C_6H_4$ (Good) | 314 |
| | 3- $CH_2CO_2C_6H_4CHO$ | " | E, R = 3- $CH_2CO_2C_6H_4$ (Poor) | 314 |
| | 4- $CH_2CO_2C_6H_4CHO$ | " | E, R = 4- $CH_2CO_2C_6H_4$ (Good) | 314 |
| | 4- $C_6H_5OC_2H_4CHO$ | Na | E, R = 4- $C_6H_5OC_2H_4$ (-) | 313 |
| | 4-(CH_3) $_2NC_6H_4CHO$ | $NaNH_2$ | E, R = 4-(CH_3) $_2NC_6H_4$ (-) | 314 |
| | 4- <i>i</i> - $C_2H_5C_6H_4CHO$ | Na | E, R = 4- <i>i</i> - $C_2H_5C_6H_4$ (-) | 313 |
| | 4-(C_2H_5) $_2NC_6H_4CHO$ | $NaNH_2$ | E, R = 4-(C_2H_5) $_2NC_6H_4$ (-) | 314 |
|  |  | NaOH |  (-) F, R = 2-(C_4H_4S) | 1829 |
| | 4- FC_6H_4CHO | " | F, R = 4- FC_6H_4 (-) | 1829 |
| | C_6H_5CHO | — |  † (25) | 291 |
| | " | — | F, R = C_6H_5 (-) | 1894 |
| | 1- $C_{10}H_7CHO$ | NaOH | F, R = 1- $C_{10}H_7$ (-) | 1829 |
|  | C_6H_5CHO | $(CH_3)_3NH$ |  (40), | 325 |
| | " | " |  (15) G, R = C_6H_5 | |
| | " | " | G, R = C_6H_5 (80) | 325, 326 |
| | 3- $CH_2C_6H_4CHO$ | $(CH_3)_3NH$, CH_3CO_2H | G, R = 3- $CH_2C_6H_4$ (47) | 325 |
| | 4- $CH_2C_6H_4CHO$ | " | G, R = 4- $CH_2C_6H_4$ (77) | 325 |
| | 4- $CH_2OC_2H_5CHO$ | " |  (-), G, R = 4- $CH_2OC_2H_5$ (-) | 325 |
| | 4-(CH_3) $_2NC_6H_4CHO$ | " | G, R = 4-(CH_3) $_2NC_6H_4$ (37) | 325 |
| | 4- <i>i</i> - $C_2H_5C_6H_4CHO$ | " | G, R = 4- <i>i</i> - $C_2H_5C_6H_4$ (47) | 325 |

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Note: References 668-2359 are on pp. 403-438.
† This structure has been suggested but not established.

TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------|--|--|--------------------------------------|-------|
| | C ₆ H ₅ CHO | KOH | (21), (16) | 308 |
| | | NaOH | (CH ₂) ₇ (64) | 309 |
| | C ₆ H ₅ CHO | " | RCH= (—) | 1259 |
| | 2-HOC ₄ H ₈ CHO | " | RCH= (—) | 1259 |
| | " | (CH ₂) ₅ NH, CH ₃ CO ₂ H | C ₆ H ₅ (41) | 1895 |
| | 4-(CH ₃) ₂ NC ₄ H ₈ CHO | NaOH | RCH= (—) | 1259 |
| | C ₆ H ₅ CHO | (CH ₂) ₅ NH | (60) | 325 |
| | | NaOH | (CH ₂) ₆ (16) | 309 |
| | 4-O ₂ NC ₄ H ₈ CHO | KOH | (—) | 1896 |
| | C ₆ H ₅ CHO | (CH ₂) ₅ NH | (—) | 325 |
| | " | " | (51) | 326 |
| | | NaOH | (CH ₂) ₆ (79) | 309 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₈ CHO | " | RCH= (—) | 1897 |
| | C ₆ H ₅ CHO | (CH ₂) ₅ NH | (32) | 325 |

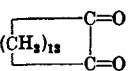
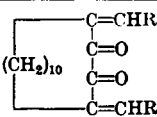
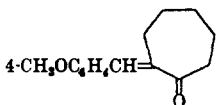
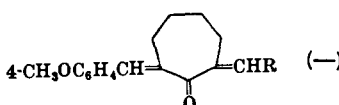
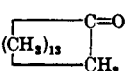
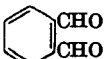
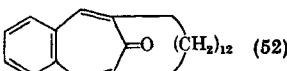
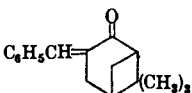
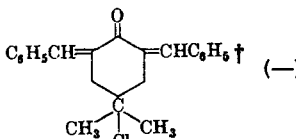
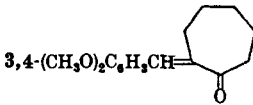
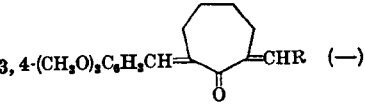
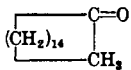
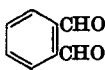
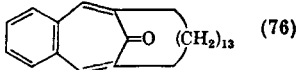
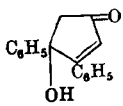
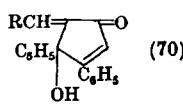
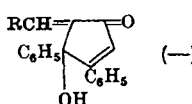
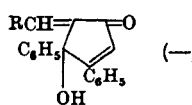
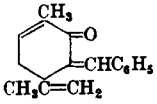
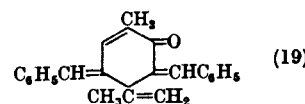
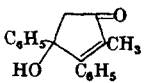
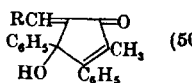
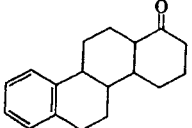
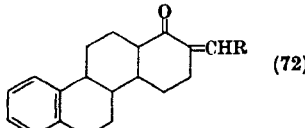
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Note: References 668-2359 are on pp. 403-438.

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TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--------------|---|-------|
|  | C_6H_5CHO | $(CH_2)_5NH$ |  (44) | 325 |
|  | $3,4-(CH_2O)_2C_6H_4CHO$ | $NaOCH_3$ |  (—) | 1884 |
|  |  | $NaOH$ |  (52) | 309 |
|  | C_6H_5CHO | HCl |  (—) | 315 |
|  | $4-CH_2OC_6H_4CHO$ | $NaOCH_3$ |  (—) | 1884 |
|  |  | $NaOH$ |  (76) | 309 |
|  | C_6H_5CHO | KOH |  (70) | 324 |
| | $C_6H_5CH=CHCHO$ | .. |  (—) | 324 |
| | $4-i-C_3H_7C_6H_4CHO$ | .. |  (—) | 324 |
|  | C_6H_5CHO | $NaOC_2H_5$ |  (19) | 316 |
|  | .. | KOH |  (50) | 324 |
|  | | $NaOH$ |  (72) | 1898 |

Note: References 668-2359 are on pp. 403-438.

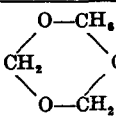
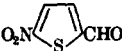







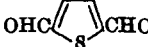

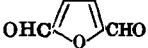




† This product might contain an α,β -unsaturated endocyclic double bond.³⁶⁴

TABLE XV. CONDENSATION OF ALDEHYDES WITH ALICYCLIC KETONES
OTHER THAN CYCLOPENTANONES AND CYCLOHEXANONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------|--|--------------------|---|------------|
| | HO ₂ CCHO | NaOH | (72) | 1899 |
| | | NaOCH ₃ | (50) | 1272 |
| | .. | NaOH | (93) | 1901 |
| | .. | .. | (100) H, R = 2-(C ₄ H ₉ O) | 2118 |
| | | KOH | H, R = 2-(C ₅ H ₄ N) (—) | |
| | | .. | H, R = 4-(C ₅ H ₄ N) (—) | 1900 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | .. | H, R = 2,4-Cl ₂ C ₆ H ₃ (—) | 1900 |
| | 4-ClC ₆ H ₄ CHO | .. | H, R = ClC ₆ H ₄ (—) | 1900 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | H, R = 2-CH ₃ OC ₆ H ₄ (—) | 1900 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | H, R = 4-CH ₃ OC ₆ H ₄ (—) | 1900 |
| | C ₆ H ₅ CH=CHCHO | .. | H, R = C ₆ H ₅ CH=CH (—) | 1900 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | H, R = 4-(CH ₃) ₂ NC ₆ H ₄ (—) | 1900 |
| | C ₆ H ₅ CHO | .. | (75) | 324 |
| | | NaOH | (80) | 1902, 1903 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVI. CONDENSATION OF ALDEHYDES WITH ACETOPHENONE
(R in the product is the group R in the aldehyde RCHO.)

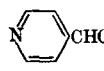
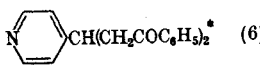
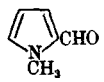
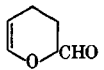
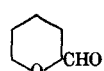
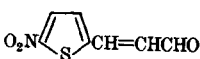
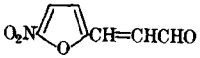
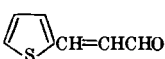
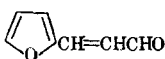
| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|------------------|
| CH ₃ O | NaOCH ₃ |  (20) | 1904, 336 |
| | K ₂ CO ₃ , CH ₃ OH | (CH ₃ OCH ₂) ₂ CHCOC ₆ H ₅ (19), CH ₂ =C(COC ₆ H ₅)CH ₂ OCH ₃ (7) | 1904, 335, 336 |
| | K ₂ CO ₃ , C ₃ H ₇ OH | (C ₂ H ₅ OCH ₂) ₂ CHCOC ₆ H ₅ (5), C ₂ H ₅ OCH ₂ CH ₂ COC ₆ H ₅ (5), HOCH ₂ CH ₂ COC ₆ H ₅ (3) | 1904 |
| | (NH ₄) ₂ CO ₃ | HOCH ₂ CH ₂ COC ₆ H ₅ (-), C ₁₀ H ₂₂ O ₅ (-) | 1905, 1906 |
| | 4-CH ₃ C ₆ H ₄ SO ₃ H | CH ₂ =CHCOC ₆ H ₅ (1) | 1907 |
| | H ₂ SO ₄ | HOCH ₂ CH ₂ COC ₆ H ₅ (25) | 335 |
| | CH ₃ CO ₂ H | RCHOHCH ₂ COC ₆ H ₅ (44) | 636, 1419 |
| | H ₂ SO ₄ | RCH=CHCOC ₆ H ₅ (43) | 289 |
| | H ₂ SO ₄ ; also BaO | RCH=CHCOC ₆ H ₅ (91) | 639, 637, 1908 |
| | CH ₃ CO ₂ H | RCHOHCH ₂ COC ₆ H ₅ (11) | 1909 |
| | NaOH | RCH=CHCOC ₆ H ₅ (90) | 1643, 1910, 1911 |
|  | H ₂ SO ₄ | RCH=CHCOC ₆ H ₅ (48) | 647 |
|  | NaOH | RCHOHCH ₂ COC ₆ H ₅ (30), RCH=CHCOC ₆ H ₅ (36) | 1912 |
|  | H ₂ SO ₄ | RCH=CHCOC ₆ H ₅ (55) | 646, 1517 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (96) | 1913-1915, 1521 |
|  | NaOCH ₃ | RCH=CHCOC ₆ H ₅ (50) | 1522 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (93) | 1916-1920, 1794 |
|  | KOH | RCH=CHCOC ₆ H ₅ (-) | 1540, 1541 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (35) | 1454 |
| i-C ₄ H ₉ CHO | " | RCH=CHCOC ₆ H ₅ (21) | 1459, 1436, 1910 |
|  | K ₂ CO ₃ | C ₆ H ₅ COCH=CH  CH=CHCOC ₆ H ₅ * (-) | 365 |
|  | Na ₂ CO ₃ | C ₆ H ₅ COCH=CH  CH=CHCOC ₆ H ₅ * (74) | 1921 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (42),  CH(CH ₂ COC ₆ H ₅) ₂ * (11) | 545 |
| | " | RCHOHCH ₂ COC ₆ H ₅ (27) | 545 |
|  | " | RCH=CHCOC ₆ H ₅ (40) | 545, 1543 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

TABLE XVI. CONDENSATION OF ALDEHYDES WITH ACETOPHENONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

274

| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|--|
|  | NaOH | RCH=CHCOC ₆ H ₅ (20),  (6) | 545, 1543 |
|  | KOH | RCH=CHCOC ₆ H ₅ (—) | 1541 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (—), RCHOHCH ₂ COC ₆ H ₅ (—) | 1467 |
|  | .. | RCH=CHCOC ₆ H ₅ (40) | 1467 |
| n-C ₄ H ₉ O ₂ CCHO | None, 100° | RCHOHCH ₂ COC ₆ H ₅ (54) | 1468 |
| 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOC ₆ H ₅ (55) | 549 |
| 3,5-Br ₂ -4-HOC ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (54) | 549 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1923 |
| 2-BrC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1924 |
| 3-BrC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (93) | 1924, 1925 |
| 4-BrC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (99) | 1924, 543, 1926 |
| 2-HO-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1927 |
| 2-ClC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (83) | 1924, 1928-1932 |
| 3-ClC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (94) | 1924, 1930, 1933 |
| 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (89) | 1924, 1551, 1930, 1934 |
| 2-FC ₆ H ₄ CHO | BF ₃ , CH ₃ CO ₂ H | RCH=CHCOC ₆ H ₅ (—) | 1935 |
| 4-FC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1935 |
| 2-IC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (76) | 1924 |
| 3-IC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (92) | 1924 |
| 4-IC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (92) | 1924, 1545 |
| 2-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (48) | 1924, 360, 1930, 1936-1939 |
| 3-O ₂ NC ₆ H ₄ CHO | Na ₃ PO ₄ NaOH | RCHOHCH ₂ COC ₆ H ₅ (—) RCH=CHCOC ₆ H ₅ (96) | 361 1924, 360, 1654, 1930, 1938- 1943 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (94) | 1924, 353, 360, 1930, 1938- 1943 |
|  | H ₂ SO ₄ | RCH=CHCOC ₆ H ₅ (48) | 647 |
|  | .. | RCH=CHCOC ₆ H ₅ (56) | 646 |
| C(Cl ₂)=CH(CH=CH) ₂ CHO | HCl | RCH=CHCOC ₆ H ₅ (71) | 1451 |
| C ₆ H ₅ CHO | NaOC ₂ H ₅ | RCH=CHCOC ₆ H ₅ (90) | 5, 353, 640, 1525, 1558, 1940, 1944-1949 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1793 |
| 2-HOC ₆ H ₄ CHO | HCl | RCH=CHCOC ₆ H ₅ (53) | 640, 1940, 1950-1953 |
| 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (53) | 640, 1951, 1953 |
| 4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOC ₆ H ₅ (98) | 1948, 353, 1951, 1953 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (87) | 1794, 1039 |
| 3,4-(HO) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOC ₆ H ₅ (89) | 1948, 348 |
| 2-H ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (16) | 1924 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

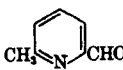
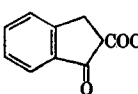
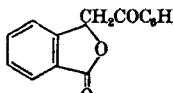
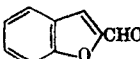
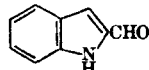
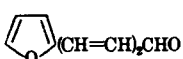
ORGANIC REACTIONS

THE ALDOL CONDENSATION

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TABLE XVI. CONDENSATION OF ALDEHYDES WITH ACETOPHENONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|------------------------------------|---|---|
| 3-H ₄ NC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (44) | 1924 |
| 4-H ₄ NC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (11) | 1924 |
|  | KOH | RCH=CHCOC ₆ H ₅ (—) | 1543 |
| 2,5,6-Br ₃ -3-CH ₂ O-4-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (47) | 1954 |
| 2-O ₂ N-3-CH ₂ O-4-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (42) | 1955 |
| 2,5-Br ₂ -3-CH ₂ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (15) | 1954 |
| 2,6-Br ₂ -3-CH ₂ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (10) | 1954 |
| 3-CH ₂ O-4-HO-5,6-Br ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (20) | 1954 |
| 3,5-Cl ₂ -2-CH ₂ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (Low) | 1955 |
| C ₆ H ₄ (CHO) ₂ -1,2 | KOH |  (6) | 1956, 1574 |
| C ₆ H ₄ (CHO) ₂ -1,3 | NaOH | C ₆ H ₄ (CH=CHCOC ₆ H ₅) ₂ -1,3* (87) | 1957, 1956, 2338 |
| C ₆ H ₄ (CHO) ₂ -1,4 | " | C ₆ H ₄ (CH=CHCOC ₆ H ₅) ₂ -1,4* (96) | 1956, 544, 1958, 2338 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (—) | 1929, 1549, 1940, 1949, 1952, 1959 |
| 2-HO ₂ CC ₆ H ₄ CHO | " |  (—) | 1577 |
| 2-Br-3-CH ₂ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (18) | 1954 |
| 3-CH ₂ O-4-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (33) | 1954 |
| 3-CH ₂ O-4-HO-6-BrC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (52) | 1954 |
| 3-CH ₂ O-4-HO-5-ClC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (10) | 1954 |
| 3-CH ₂ O-4-HO-6-ClC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (10) | 1954 |
| 3-O ₂ N-4-CH ₂ C ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (90) | 1583 |
| 2-O ₂ N-3-CH ₂ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (52) | 1955 |
| 3-CH ₂ O-4-HO-5-O ₂ NC ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (Low) | 1955 |
| 2-CH ₂ C ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (92) | 829, 1939 |
| 3-CH ₂ C ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOC ₆ H ₅ (60) | 1939, 543, 1960 |
| 4-CH ₂ C ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (45) | 353, 1583 |
| 2-CH ₂ OC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (80-90) | 1961, 1930, 1962 |
| 3-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (—) | 1603, 1953, 1940 |
| 4-CH ₂ OC ₆ H ₄ CHO | NaOC ₂ H ₅ | RCH=CHCOC ₆ H ₅ (95) | 1930, 353, 1549, 1563, 1654, 1949, 1952, 1953, 1959, 1963, 1964 |
| 2-HO-5-CH ₂ C ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1965 |
| 2-HO-3-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (36) | 1966 |
| 3-CH ₂ O-4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOC ₆ H ₅ (—) | 1953, 1590 |
|  | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1703 |
|  | (CH ₂) ₂ NH | RCH=CHCOC ₆ H ₅ (59) | 600 |
| 2-O ₂ NC ₆ H ₄ CH=CHCHO | NaOH | RCH=CHCOC ₆ H ₅ (57) | 1798 |
| C ₆ H ₄ CH=CHCHO | " | RCH=CHCOC ₆ H ₅ (84) | 1924, 1563, 1596, 1967, 1968 |
|  | Na ₂ CO ₃ | RCH=CHCOC ₆ H ₅ (90) | 1766 |
| 2-C ₆ H ₄ O-5-BrC ₆ H ₃ CHO | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1927 |
| 3-CH ₂ CONHC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (76) | 1924 |
| 4-CH ₂ CONHC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (23) | 1924 |
| 2-C ₆ H ₄ OC ₆ H ₄ CHO | " | RCH=CHCOC ₆ H ₅ (—) | 1969, 1549 |
| 2,3-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (—) | 1923, 1953 |
| 2,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (49) | 1970 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOC ₆ H ₅ (70) | 411, 1929, 1953, 1971 |

Note: References 668-2359 are on pp. 403-438.

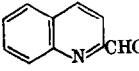
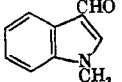
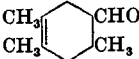
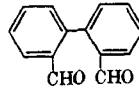
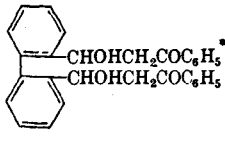
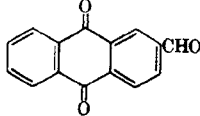
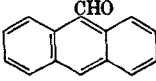
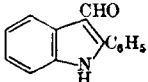
* This is a complete structural formula.

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TABLE XVI. CONDENSATION OF ALDEHYDES WITH ACETOPHENONE (Continued)
(R in the product is the group R in the aldehyde RCHO.)

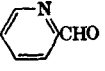
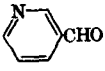
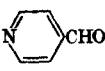
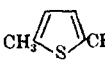
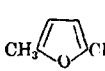
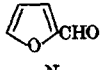
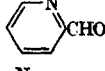
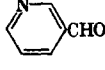
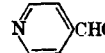
| Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|------------------------------------|--|---------------------------|
| 2-HO-3-C ₂ H ₅ OC ₆ H ₄ CHO | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1590 |
| 3-O ₂ N-4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1601 |
| 4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (60) | 1972, 1601, 1602, 1798 |
| 2-HO-4-(CH ₃) ₂ NC ₆ H ₃ CHO | KOH | RCH=CHCOC ₆ H ₅ (50) | 1973 |
|  | .. | RCH=CHCOC ₆ H ₅ (—) | 1543 |
|  | (CH ₂) ₅ NH | RCH=CHCOC ₆ H ₅ (70) | 600 |
| 1,3,5-(CH ₃) ₃ C ₆ H ₃ CHO | — | RCH=CHCOC ₆ H ₅ (—) | 1607 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOC ₆ H ₅ (—) | 1974 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₃ CHO | NaOH | RCH=CHCOC ₆ H ₅ (98) | 1970 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CHCHO | NaOC ₂ H ₅ | RCH=CHCOC ₆ H ₅ (35) | 1492 |
|  | NaOCH ₃ | RCH=CHCOC ₆ H ₅ (—) | 1678 |
| 1-C ₁₀ H ₇ CHO | NaOH | RCH=CHCOC ₆ H ₅ (—) | 1744 |
| Ferrocenecarboxaldehyde | .. | RCH=CHCOC ₆ H ₅ (92) | 663, 1975 |
| 4-(CH ₃) ₂ NC ₆ H ₃ CH=CHCHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1602 |
| 2- <i>n</i> -C ₄ H ₉ O-3-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1590 |
| 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1923 |
| 2- <i>n</i> -C ₄ H ₉ O-3-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1590 |
| 2- <i>n</i> -C ₄ H ₉ O-3-C ₂ H ₅ OC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1590 |
| 3- <i>n</i> -C ₄ H ₉ O-3-C ₂ H ₅ OC ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (—) | 1590 |
|  | .. |  (55) | 1976 |
| 4-C ₆ H ₅ CH ₂ C ₆ H ₄ CHO | .. | RCH=CHCOC ₆ H ₅ (52) | 1613 |
| 2-C ₆ H ₅ CH ₂ O-3,5-Br ₂ C ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (8) | 549 |
| 2-C ₆ H ₅ CH ₂ O-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOC ₆ H ₅ (81) | 549 |
|  | KOH | RCH=CHCOC ₆ H ₅ (—) | 1977 |
|  | HCl | RCH=CHCOC ₆ H ₅ (68) | 1978 |
|  | (CH ₂) ₅ NH | RCH=CHCOC ₆ H ₅ (67) | 1979 |
| Pyrene-3-carboxaldehyde | NaOC ₂ H ₅ | RCH=CHCOC ₆ H ₅ (100) | 1615 |
| 9-Formyl-1,3,4-benzacridine | NaOH | RCH=CHCOC ₆ H ₅ (75-95) | 372 |
| 10-Formyl-1,2-benzanthracene | .. | RCH=CHCOC ₆ H ₅ (93) | 372 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|---|---|---|-------------------------------|--------------------|------|
| 2-HO-3-Br-5-F | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (—) | 1980 | |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 2-O ₂ NC ₆ H ₃ CHO | Na ₃ PO ₄ | RCHOHCH ₂ COAr (—) | 361 | |
| | 2-O ₂ NC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 1936 | |
| | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 1981 | |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| 4-NO ₂ -3-Br 3-NO ₂ -4-Br 2,4-(HO) ₂ -3-Br-5-NO ₂ | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 3-Br-4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 | |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1982 | |
| 3,5-Br ₂ -4-HO | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 1983 | |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1985 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1985 | |
| | C ₆ H ₅ CHO | H ₂ SO ₄ | RCH=CHCOAr (—) | 1984 | |
| | 3-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| | 4-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 1984 | |
| 2-HO-3-Cl-4-F | 2-Br-5-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 1985 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1985 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 1986 | |
| | 2-HO-3-Cl-5-F | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1986 |
| | | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1986 |
| | | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1986 |
| | | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (40-50) | 1987 |
| 2-HOC ₆ H ₄ CHO | | .. | RCH=CHCOAr (40-50) | 1987 | |
| 4-HOC ₆ H ₄ CHO | | .. | RCH=CHCOAr (40-50) | 1987 | |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | .. | RCH=CHCOAr (40-50) | 1987 | |
| 4-CH ₃ OC ₆ H ₃ CHO | | .. | RCH=CHCOAr (40-50) | 1987 | |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | | .. | RCH=CHCOAr (40-50) | 1987 | |
| 2,5-Cl ₂ | | C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 1988 |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1988 | |
| | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1988 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1988 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1988 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1988 | |
| | 3,4-Cl ₂ |  | .. | RCH=CHCOAr (—) | 1988 |
| | |  | .. | RCH=CHCOAr (—) | 1988 |
| | |  | .. | RCH=CHCOAr (—) | 1988 |
| | |  | .. | RCH=CHCOAr (—) | 1988 |
|  | | .. | RCH=CHCOAr (—) | 1988 | |
| 2-HO-3,5-Cl ₂ |  | KOH | RCH=CHCOAr (75) | 1989 | |
| |  | .. | RCH=CHCOAr (—) | 1990 | |
| |  | .. | RCH=CHCOAr (97) | 371 | |
| |  | .. | RCH=CHCOAr (97) | 370 | |

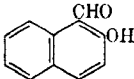
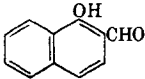
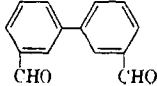
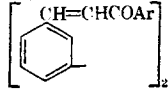

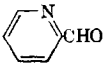
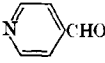
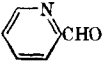
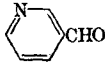
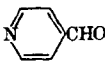
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Note: References 668-2359 are on pp. 403-438.











TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH_3COAr (Continued)
(R in the product is the group R in the aldehyde RCHO .)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|---|---|---------------------------------|------------|
| 2-HO-3,5- Cl_2 (contd.) | $2\text{-Cl}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (65) | 1989, 1991 | |
| | $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (82) | 1989 | |
| | $\text{C}_6\text{H}_5\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (82) | 1989, 1991 | |
| | $2\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (73) | 1989, 1991 | |
| | $3\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (73) | 1989, 1991 | |
| | $4\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (74) | 1989, 1991 | |
| | $3,4\text{-(CH}_2\text{O}_2\text{)}_2\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1991 | |
| | $4\text{-CH}_3\text{C}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (69) | 1989 | |
| | $2\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1991 | |
| | $4\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (66) | 1989, 1991 | |
| | $3\text{-CH}_3\text{O-4-HOC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (60) | 1989 | |
| | $3,4\text{-(CH}_2\text{O)}_2\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1991 | |
| | 2-Br |  | " | $\text{RCH}=\text{CHCOAr}$ (76) | 1989 |
| | |  | " | $\text{RCH}=\text{CHCOAr}$ (87) | 1989 |
| | 3-Br | $\text{C}_6\text{H}_5\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (62) | 1924, 1992 |
| $3\text{-BrC}_6\text{H}_4\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (83) | 1957 | |
| $\text{C}_6\text{H}_5\text{CHO}$ | | NaOH | $\text{RCH}=\text{CHCOAr}$ (94) | 1924, 349 | |
| $\text{C}_6\text{H}_4(\text{CHO})_{2-1,3}$ | | " | $\text{C}_6\text{H}_4(\text{CH}=\text{CHCOAr})_{2-1,3}$ (87) | 1957 | |
| 4-Br |  | HCl |  (98) | 1957 | |
| | $\text{C}(\text{Cl}_2)=\text{CHCHO}$ | BaO | $\text{RCH}=\text{CHCOAr}$ (69) | 1908 | |
| 4-Br |  | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1916 | |
| | $2\text{-HO-3,5-Br}_2\text{C}_6\text{H}_2\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (67) | 549 | |
| | $2\text{-HO-5-BrC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (50) | 549 | |
| | $2\text{-Cl}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (99) | 1924 | |
| | $2\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | Na_3PO_4 | $\text{RCHOHCH}_2\text{COAr}$ (—) | 361 | |
| | " | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1936 | |
| | $3\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (93) | 1924 | |
| | $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (65) | 1993 | |
| | $\text{C}_6\text{H}_5\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (94) | 1924, 349, 540, 1994-1996 | |
| | $3\text{-NCC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (40-70) | 1997 | |
| | $4\text{-NCC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (40-70) | 1997 | |
| | $3\text{-CH}_3\text{O-4-HO-5-BrC}_6\text{H}_2\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (15) | 1955 | |
| | $3\text{-CH}_3\text{O-4-HO-6-BrC}_6\text{H}_2\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (32) | 1955 | |
| $4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1995 | | |
| 3-Br-4-HO |  | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1988 | |
| |  | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1988 | |
| 2-HO-4-Br |  | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1990 | |
| |  | " | $\text{RCH}=\text{CHCOAr}$ (—) | 371 | |
| |  | " | $\text{RCH}=\text{CHCOAr}$ (75) | 370 | |
| | $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$ $\text{C}_6\text{H}_5\text{CHO}$ | NaOH KOH | $\text{RCH}=\text{CHCOAr}$ (85) $\text{RCH}=\text{CHCOAr}$ (—) | 1993 1998 | |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|--|-----------------------|-----------------|------|
| 2-HO-5-Br |  | NaOH | RCH=CHCOAr (100) | 340, 1993 | |
| |  | " | RCH=CHCOAr (—) | 1983, 1990 | |
| |  | KOH | RCH=CHCOAr (—) | 371 | |
| |  | " | RCH=CHCOAr (97) | 370 | |
| | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (60) | 1993 | |
| | 3,5-Br ₂ -4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (80) | 1993 | |
| | 3-BrC ₆ H ₄ CHO | " | RCH=CHCOAr (70) | 1993 | |
| | 3-Br-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (65) | 1993 | |
| | 2-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (70) | 1993 | |
| | 2-HO-5-O ₂ NC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1983 | |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (95) | 340, 1965 | |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (55) | 1993, 340 | |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (50) | 1993 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (80) | 1993, 340 | |
| | 3-Cl-4-CH ₃ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 341 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (90) | 340 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (60) | 340 | |
| | 2,4-(HO) ₂ -5-Br | C ₆ H ₅ CHO | " | RCH=CHCOAr (40) | 2000 |
| | | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (40) | 2000 |
| | | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (45) | 2000 |
| 4-CH ₃ OC ₆ H ₄ CHO | | " | RCH=CHCOAr (45) | 2000 | |
| 3,5-Br ₂ -4-NH ₂ 2-Cl | | 2-O ₂ NC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 1936 |
| | | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (51) | 549 |
| | | 3,5-Br ₂ -4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (7) | 549 |
| | | 2,4-Cl ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1923 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (76) | 1924 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1923 | |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | HCl | RCH=CHCOAr (38) | 1955 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 1923 | |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (96) | 1924, 349 | |
| | 3-Cl 4-Cl | C(Cl) ₂ =CHCHO | HCl | RCH=CHCOAr (75) | 637 |
| C(Cl) ₂ =CHCH=CHCHO | | " | RCH=CHCOAr (72) | 1451 | |
| |  | NaOH | RCH=CHCOAr (78) | 366 | |
| |  | " | RCH=CHCOAr (92) | 2001, 1989 | |
| |  | " | RCH=CHCOAr (40) | 545 | |
| |  | " | RCH=CHCOAr (—) | 1988 | |
| |  | " | RCH=CHCOAr (—) | 1988 | |
| |  | " | RCH=CHCOAr (—) | 1988 | |
| | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (64) | 549 | |
| | 2-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (21) | 549 | |

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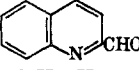

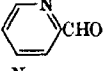
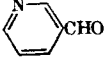
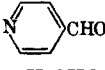



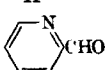
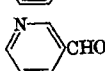
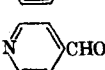
THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

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TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH_3COAr (Continued)
(R in the product is the group R in the aldehyde RCHO .)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|---|---|---|-----------------------------------|---------------------------------|------------|
| 4-Cl (contd.) | 2- $\text{ClC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1923 | |
| | 3- $\text{ClC}_6\text{H}_4\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (53) | 640 | |
| | 4- $\text{ClC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2002 | |
| | 2- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ | Na_2PO_4 | $\text{RCHOHCH}_2\text{COAr}$ (—) | 361 | |
| | " | HCl | $\text{RCH}=\text{CHCOAr}$ (—) | 1936 | |
| | 3- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (90) | 1924 | |
| | 4- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (92) | 1924 | |
| | $\text{C}(\text{Cl}_2)=\text{CH}(\text{CH}=\text{CH})_2\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (70) | 1451 | |
| | $\text{C}_6\text{H}_5\text{CHO}$ | NaOCH_3 | $\text{RCH}=\text{CHCOAr}$ (90) | 540, 349, 1924, 1994, 1996 | |
| | 3- $\text{HOC}_6\text{H}_4\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (42) | 640 | |
| | 4- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (35) | 640 | |
| | 3,4-(CH_2O_2) $\text{C}_6\text{H}_3\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2003 | |
| | 3- $\text{CH}_3\text{O}-4-\text{HO}-5-\text{BrC}_6\text{H}_2\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (31) | 1955 | |
| | 3- $\text{CH}_3\text{O}-4-\text{HO}-6-\text{BrC}_6\text{H}_2\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (76) | 1955 | |
| | 3- $\text{CH}_3\text{O}-4-\text{HOC}_6\text{H}_3\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1923 | |
| | 3,4-(CH_3O) $_2\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1995 | |
| | 4-(CH_3) $_2\text{NC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1800 | |
| |  | NaOCH_3 | $\text{RCH}=\text{CHCOAr}$ (30) | 2004 | |
| | 2- $\text{C}_6\text{H}_5\text{CH}_2\text{O}-5-\text{BrC}_6\text{H}_3\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (24) | 549 | |
| | 2-HO-3-Cl |  | KOH | $\text{RCH}=\text{CHCOAr}$ (80) | 1989 |
| | 3-Cl-4-HO | 2- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | | $\text{C}_6\text{H}_5\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | | 2- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | | 3,4-(CH_2O_2) $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | | 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | | 3- $\text{CH}_3\text{O}-4-\text{HOC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 |
| | 2-HO-4-Cl |  | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1990 |
|  | | " | $\text{RCH}=\text{CHCOAr}$ (—) | 371 | |
|  | | " | $\text{RCH}=\text{CHCOAr}$ (76) | 370 | |
| $\text{C}_6\text{H}_5\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2005, 1992 | |
| 2-HO-5-Cl | |  | NaOH | $\text{RCH}=\text{CHCOAr}$ (60) | 2006 |
| | |  | KOH | $\text{RCH}=\text{CHCOAr}$ (73) | 1989, 2006 |
| | |  | $(\text{CH}_2)_5\text{NH}$ | $\text{RCH}=\text{CHCOAr}$ (32) | 2006 |
| | |  | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1983, 1990 |
| | |  | KOH | $\text{RCH}=\text{CHCOAr}$ (98) | 371, 2006 |
| | |  | " | $\text{RCH}=\text{CHCOAr}$ (95) | 370 |
| | 2-HO-5- $\text{ClC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1983 | |
| 2-HO-5- $\text{O}_2\text{NC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1983 | | |
| $\text{C}_6\text{H}_5\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (30) | 2006, 2005, 2007 | | |
| 2- $\text{HOC}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2005 | | |

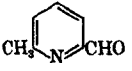
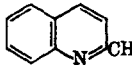

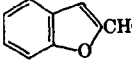

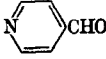
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Note: References 668-2359 are on pp. 403-438.


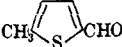
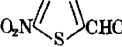
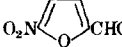





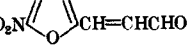

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TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|--|-------------------------------|----------------------------------|------|
| 2-HO-5-Cl (<i>contd.</i>) |  | NaOH | RCH=CHCOAr (—) | 1983 | |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1923 | |
| | 2-Br-4-CH ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2008 | |
| | 2-Cl-4-CH ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 341 | |
| | 2-CH ₃ -4-BrC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2008 | |
| | 2-HO-5-CH ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 1983 | |
| 2,3,4-(HO) ₃ -4-Cl <i>ω</i> -F 3-F |  | .. | RCH=CHCOAr (—) | 1983 | |
| | C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2009 | |
| | .. | NaOH | RCH=CFCOAr (42) | 2010 | |
| | .. | HCl | RCH=CHCOAr (28) | 349 | |
| 4-F |  | — | RCH=CHCOAr (—) | 2011 | |
| | 2-FC ₆ H ₄ CHO | BF ₃ CH ₃ CO ₂ H | RCH=CHCOAr (—) | 1935 | |
| | 4-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1935, 2354 | |
| | 2-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1935 | |
| | 4-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1935 | |
| | C ₆ H ₃ CHO | HCl | RCH=CHCOAr (55) | 349, 2003 | |
| | 3-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (45) | 640 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | BF ₃ CH ₃ CO ₂ H | RCH=CHCOAr (—) | 1935 | |
| | 3-F-4-HO |  | NaOH | RCH=CHCOAr (75-95) | 1854 |
| | |  | .. | RCH=CHCOAr (70) | 1988 |
| 2-HO-5-F |  | .. | RCH=CHCOAr (—) | 1988 | |
| | C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 1980, 2012 | |
| | 2-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980, 2012 | |
| | 3-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2012 | |
| | 4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980, 2012 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1980 | |
| | C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (53) | 1924 | |
| | .. | .. | RCH=CHCOAr (89) | 1924, 349 | |
| | 4-FC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1995 | |
| | 4-IC ₆ H ₃ CHO | .. | RCH=CHCOAr (Good) | 1545 | |
| | C ₆ H ₃ CHO | .. | RCH=CHCOAr (94) | 1924, 349, 1995 | |
| | 4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1995 | |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1995 | | |
| 4-C ₆ H ₃ C ₆ H ₃ CHO | .. | RCH=CHCOAr (91) | 1924 | | |
| 2-HO-5-I | 2-ClC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2013 | |
| .. | C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2013 | |
| .. | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2013 | |
| .. | 2-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2013 | |
| 2-NO ₂ | 2-ClC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2014 | |
| | 4-ClC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2014 | |
| | 2-O ₂ NC ₆ H ₃ CHO | Na ₃ PO ₄ | RCHOHCH ₂ COAr (—) | 361 | |
| | .. | NaOC ₂ H ₅ ; also HCl | RCH=CHCOAr (50) | 1948, 360, 1936 | |
| | 3-O ₂ NC ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (61) | 1948, 360, 1934 | |
| | 4-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (49) | 1948, 360 | |
| | C ₆ H ₃ CHO | HCl | RCH=CHCOAr (98) | 349, 360, 1937, 1939, 2014, 2015 | |

Note: References 668-2359 are on pp. 403-438.

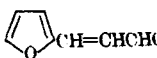
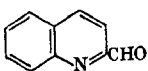
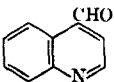



TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|---|--|---|------------|
| 2-NO ₂ (contd.) | 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2016 | |
| | 4-CH ₃ C ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2014 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1937 | |
| | 2,4,6-(CH ₃) ₃ C ₆ H ₂ CHO | KOH | RCH=CHCOAr (—) | 2014 | |
| 3-NO ₂ |  CHO | NaOH | RCH=CHCOAr (—) | 2017 | |
| |  CHO | " | RCH=CHCOAr (—) | 1988 | |
| | 2-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (74) | 1924 | |
| | 2-O ₂ NC ₆ H ₄ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (35) | 1948, 360, 1934, 2018 | |
| | 3-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (80) | 1553, 360, 1940, 1948, 2019 | |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOAr (48) | 1941, 360, 1934, 1948 | |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (75) | 353, 360, 1937, 1939- 1941, 2020, 2021 | |
| | " | HCl | RCH=CHCOAr (100) | 349 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2016 | |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2019 | |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₂ CHO | CH ₃ CO ₂ NH ₄ | RCH=CHCOAr (92) | 1955 | |
| | 3-CH ₃ O-4-HO-6-BrC ₆ H ₂ CHO | CH ₃ CO ₂ NH ₄ , CH ₃ CO ₂ H | RCH=CHCOAr (49) | 1955 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (100) | 356, 1937 | |
| | C ₆ H ₅ CH=CHCHO | " | RCH=CHCOAr (—) | 2022 | |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (89) | 1924, 2019 | |
| | 4-CH ₃ OC ₆ H ₄ CH=CHCHO | " | RCH=CHCOAr (—) | 2022 | |
| | Ferrocenecarboxaldehyde | " | RCH=CHCOAr (30) | 1975 | |
| | 4-NO ₂ |  CHO | H ₂ SO ₄ | RCH=CHCOAr (41) | 647 |
| | |  CHO | NaOH | RCH=CHCOAr (35) | 646 |
| | |  CHO | " | RCH=CHCOAr (90) | 2017, 1793 |
|  CHO | | " | RCH=CHCOAr (77) | 366 | |
|  CHO | | " | RCH=CHCOAr (89) | 2023, 646 | |
|  CHO | | " | RCH=CHCOAr (89) | 2023 | |
|  CHO | | " | RCH=CHCOAr (87) | 2023 | |
| 2-FC ₆ H ₄ CHO | | BF ₃ , CH ₃ CO ₂ H | RCH=CHCOAr (—) | 1935 | |
| 2-O ₂ NC ₆ H ₄ CHO | | Na ₃ PO ₄ , NaOC ₂ H ₅ ; also HCl | RCHOHCH ₂ COAr (—) RCH=CHCOAr (18) | 361 1948, 360, 1936 | |
| 3-O ₂ NC ₆ H ₄ CHO | | NaOC ₂ H ₅ | RCH=CHCOAr (18) | 1948, 360 | |
| 4-O ₂ NC ₆ H ₄ CHO | | " | RCH=CHCOAr (42) | 1948, 360 | |
| " | | HCl | RCH=CHCOAr (15) | 357 | |
|  CHO | | H ₂ SO ₄ | RCH=CHCOAr (55) | 646 | |
|  CH=CHCHO | NaOH | RCH=CHCOAr (78) | 647 | | |

Note: References 668-2359 are on pp. 403-438.



TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------------------------------|---|---------------------------------|-------------------------------|-----------------------------|
| 4-NO ₂ (contd.) | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1937, 360, 1926, 1939, 2021 |
| | .. | HCl | RCH=CHCOAr (100) | 349, 357 |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (60) | 640 |
| | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (40) | 640, 2016 |
| |  (H=CHCHO) | H ₂ SO ₄ | RCH=CHCOAr (80) | 646 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (70) | 2023 |
| | 4-CH ₂ OC ₆ H ₄ CHO | HCl | RCH=CHCOAr (70) | 357, 1937 |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | Na ₂ CO ₃ | RCH=CHCOAr (81) | 1810 |
| |  | NaOH | RCHOHCH ₂ COAr (—) | 2024 |
| | .. | .. | RCH=CHCOAr (85) | 2023, 2024 |
| |  | .. | RCH=CHCOAr (81) | 2023 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CH=CHCHO | Na ₂ CO ₃ | RCH=CHCOAr (72) | 1810 |
| | 9-Formyl-3,4-benzacridine | NaOH | RCH=CHCOAr (75-95) | 372 |
| | 10-Formyl-1,2-benzanthraene | .. | RCH=CHCOAr (75-95) | 372 |
| 2-HO-4-NO ₂ |  | .. | RCH=CHCOAr (91) | 2025 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | HCl | RCH=CHCOAr (13) | 357 |
| | 2-BrC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | 3-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4-ClC ₆ H ₄ CHO | HCl | RCH=CHCOAr (11) | 357 |
| | 2-FC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | 3-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (83) | 357 |
| | 2-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (56) | 2026, 641 |
| | 3-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (66) | 2026, 641, 2021 |
| | 4-O ₂ NC ₆ H ₃ CHO | HCl | RCH=CHCOAr (3) | 357, 641 |
| | 2-HO-3-O ₂ NC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (92) | 2026, 357, 533, 641 |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2028 |
| | 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (27) | 357, 2016, 2029 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (40) | 2026 |
| | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (74) | 357 |
| | 4-OHCC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-CH ₂ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (58) | 357 |
| | 4-CH ₂ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | 3-CH ₂ O-4-HOC ₆ H ₃ CHO | HCl | RCH=CHCOAr (40) | 357 |
| | C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOAr (91) | 2025 |
| | 2-C ₆ H ₄ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | HCl | RCH=CHCOAr (32) | 357 |
| | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | 1-C ₁₀ H ₇ CHO | .. | RCH=CHCOAr (58) | 357 |
| | 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| 2-HO-5-NO ₂ |  | .. | RCH=CHCOAr (60) | 2006 |
| |  | .. | RCH=CHCOAr (100) | 2025, 340, 2006 |

Note: References 668-2359 are on pp. 403-438.

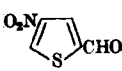
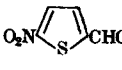
TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|--|----------------------------------|--|-----------------|
| 2-HO-5-NO ₂ (contd.) |  | (CH ₂) ₅ NH | RCH=CHCOAr (33) | 2006 | |
| |  | NaOH | RCH=CHCOAr (31) | 2006 | |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (85) | 357 | |
| | 2-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 | |
| | 3-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 | |
| | 4-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (66) | 357 | |
| | 2-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (61-75) | 340, 357 | |
| | 3-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (58) | 357 | |
| | 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (55) | 357 | |
| | 2-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 | |
| | 3-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 | |
| | 4-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (67) | 357 | |
| | 2-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (75) | 340, 641 | |
| | 3-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 641 | |
| | 4-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (75) | 357, 641 | |
| | 2-HO-3-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (13) | 357 | |
| | 2-HO-5-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1983 | |
| | C ₆ H ₅ CHO | .. | RCH=CHCOAr (97) | 2026, 340, 357, 533, 641, 2006, 2021, 2027, 2030, 2031 | |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (80) | 340, 2028 | |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2028 | |
| | 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2029, 357 | |
| | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (37) | 357 | |
| | 2-NO ₂ -3-HO | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (39) | 357, 2030 |
| | | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (50) | 357 |
| | | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (80) | 340, 2027, 2030 |
| | | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (1) | 357 |
| | | .. | HCl | RCH=CHCOAr (23) | 357 |
| | | C ₆ H ₅ CH=CHCHO | NaOH | RCH=CHCOAr (51) | 2025 |
| | | 2-C ₂ H ₅ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | | 4-i-C ₂ H ₅ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (33) | 357 |
| | | 1-C ₁₀ H ₇ CHO | .. | RCH=CHCOAr (—) | 357 |
| | | 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (24) | 357 |
| | | 4-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | | 3-HO-4-O ₂ NC ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (63) | 1948 |
| | | 2-O ₂ N-5-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (72) | 1948 |
| | | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2016 |
| | | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | 3-HO-4-NO ₂ | 4-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | | 3-HO-4-O ₂ NC ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (66) | 1948 |
| | | 2-O ₂ N-5-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (60) | 1948 |
| | | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2016 |
| | | 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2029 |
| | 3-NO ₂ -4-HO | 2,4-Cl ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | | 2-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | | 3-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| 4-BrC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 2-HO-5-BrC ₆ H ₃ CHO | | .. | RCH=CHCOAr (40) | 1993 | |
| 2-ClC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 3-ClC ₆ H ₄ CHO | | .. | RCH=CHCOAr (47) | 357 | |
| 2-FC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 3-FC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 4-FC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 2-O ₂ NC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 641 | |
| 3-O ₂ NC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 641 | |
| 4-O ₂ NC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 641 | |
| 2-HO-3-O ₂ NC ₆ H ₃ CHO | | .. | RCH=CHCOAr (—) | 357 | |
| 3-HO-4-O ₂ NC ₆ H ₃ CHO | | NaOC ₂ H ₅ | RCH=CHCOAr (53) | 1948 | |
| 3-HO-6-O ₂ NC ₆ H ₃ CHO | | .. | RCH=CHCOAr (84) | 1948 | |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|--------------------------------|----------------------|
| 3-NO ₂ -4-HO (contd.) | 3-O ₂ N-4-HOC ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (27) | 1948 |
| | C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (96) | 2026, 533, 641, 2021 |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2028 |
| | 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2028 |
| | 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2029 |
| | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (39) | 357 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | HCl | RCH=CHCOAr (69) | 357 |
| | C ₆ H ₃ CH=CHCHO | NaOH | RCH=CHCOAr (—) | 2025 |
| | 2-C ₆ H ₄ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4- <i>i</i> -C ₂ H ₅ C ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 1-C ₁₀ H ₇ CHO | .. | RCH=CHCOAr (36) | 357 |
| | 3,4-(C ₆ H ₅ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (15) | 357 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4-BrC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (69) | 357 |
| | 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (56) | 2028 |
| | 3-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 4-FC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (64) | 2028, 2016 | |
| 2-HO-3-O ₂ NC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 | |
| 3-HO-4-O ₂ NC ₆ H ₃ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (70) | 1948 | |
| 2-O ₂ N-5-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (84) | 1948 | |
| C ₆ H ₃ CHO | .. | RCH=CHCOAr (80) | 2028, 533, 2016 | |
| 3-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (40) | 2028 | |
| 4-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2016, 2029 | |
| 2-NO ₂ -5-HO | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (46) | 357 |
| | 4-OHCC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (69) | 357 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2016 |
| | C ₆ H ₃ CH=CHCHO | .. | RCH=CHCOAr (—) | 2025 |
| | 2-C ₆ H ₄ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 1-C ₁₀ H ₇ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3,4-(C ₆ H ₅ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 357 |
| | 3-O ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (5) | 2033 |
| | C ₆ H ₃ CHO | .. | RCH=CHCOAr (20) | 2033 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (25) | 2033 |
| | 4-CH ₃ C ₆ H ₄ CHO | .. | RCH=CHCOAr (20) | 2033 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (25) | 2033 |
| 3-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (25) | 2033 | |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (20) | 2033 | |
| 1-C ₁₀ H ₇ CHO | .. | RCH=CHCOAr (5) | 2033 | |
| 2,4-(HO) ₂ -3-NO ₂ | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | C ₆ H ₃ CHO | .. | RCH=CHCOAr (15) | 2033, 1981 |
| | 2-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | 3-Br-4-CH ₃ OC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (15) | 2033, 1981 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (20) | 2033, 1981 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 1981 |
| | 2-HO |  | HCl | RCH=CHCOAr (21) |
| .. | | NaOCH ₃ | RCHOHCH ₂ COAr (5) | 2034 |
|  | | .. | RCHOHCH ₂ COAr (15) | 2034, 2035 |
| .. | | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CHCOAr (14) | 2034 |

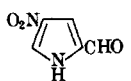
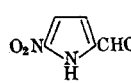



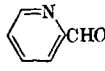
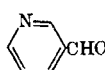
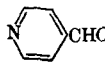
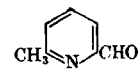
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Note: References 668-2359 are on pp. 403-438.

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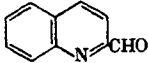
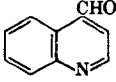
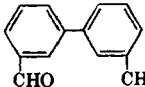
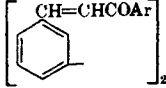
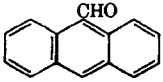
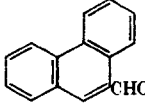
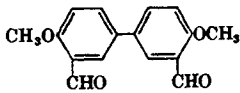
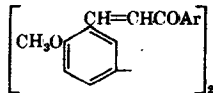
TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------------------------------|---|---|--|----------------------------|
| 2-HO (contd.) |  | NaOH | RCH=CHCOAr (44) | 2034, 2035 |
| |  | " | RCH=CHCOAr (76) | 2034, 2035 |
| |  | " | RCH=CHCOAr (70) | 2034-2037, 369 |
| | " | NaOCH ₃ | RCHOHCH ₂ COAr (23) | 2034 |
| |  | NaOH | RCH=CHCOAr (72) | 2034, 369, 1993, 2038 |
| |  | (CH ₂) ₆ NH | RCH=CHCOAr (25) | 2034, 2035 |
| |  | KOH | RCH=CHCOAr (53) | 2036, 2034, 2037 |
| | " | NaOCH ₃ | RCHOHCH ₂ COAr (37) | 2034, 369 |
| |  | NaOH | RCH=CHCOAr (60) | 2034, 369, 371, 2036, 2037 |
| |  | " | RCH=CHCOAr (17) | 2034, 2037 |
| | | NaOH, NaOCH ₃ , or (CH ₂) ₆ NH, CH ₃ CO ₂ H | RCHOHCH ₂ COAr (27), RCH=CHCOAr (-) | 2034, 369 |
| | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (75) | 1993 |
| | 4-HO-3,5-Br ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (45) | 1993 |
| | 2,3-Cl ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2040 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2040 |
| | 2-HO-3,5-Cl ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (60) | 1993 |
| | 2-BrC ₆ H ₄ CHO | KOH | RCH=CHCOAr (-) | 2012 |
| | 3-BrC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (70) | 1993 |
| | 4-BrC ₆ H ₄ CHO | KOH | RCH=CHCOAr (-) | 2012 |
| | 2-HO-5-BrC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (90) | 1993 |
| | 4-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (74) | 2006 |
| | 2-HO-5-ClC ₆ H ₃ CHO | " | RCH=CHCOAr (85) | 1993 |
| | 2-FC ₆ H ₄ CHO | KOH | RCH=CHCOAr (-) | 2012 |
| | 3-FC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2012 |
| | 4-FC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2012 |
| | 2-IC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2012 |
| | 3-IC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2012 |
| | 4-IC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2012 |
| | 3-O ₂ NC ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2041, 2057 |
| | 4-O ₂ NC ₆ H ₃ CHO | " | RCH=CHCOAr (-), RCHOHCH ₂ COAr (-) | 2057 |
| | 2-HO-5-O ₂ NC ₆ H ₃ CHO | KOH | RCH=CHCOAr (70) | 1993 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (80) | 2042-2044, 1953 |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (60) | 1993, 348, 1953 |
| | 3-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (50) | 1993, 1999, 2039 |
| | 4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (-) | 348, 1999 |
| | 2,4-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 348 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (46) | 2045 |
| |  | " | RCH=CHCOAr (37) | 2036 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|---|------------------------------|
| 2-HO (contd.) | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (40-70) | 1997, 2006 |
| | 2,4-Cl ₂ -4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2040 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (16) | 527, 536, 2044 |
| | 2-Br-4-CH ₃ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (70) | 2046 |
| | 2-Br-5-CH ₂ OC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1985 |
| | 2-Cl-4-CH ₃ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 341 |
| | 3-I-4-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOAr (85) | 2047 |
| | 2-CH ₃ O-5-IC ₆ H ₃ CHO | " | RCH=CHCOAr (85) | 2047 |
| | 2-CH ₃ C ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2048, 1953 |
| | 3-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2048, 1953 |
| | 4-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2048, 1953 |
| | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 1953, 1985 |
| | 3-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1953, 2049 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (54) | 2006, 1953, 2039, 2044, 2050 |
| | 2-HO-3-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 1953, 2039 |
| | 3-HO-4-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (92) | 2051 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1953, 2052 |
| | 4-C ₆ H ₄ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2050 |
| | 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 1953, 2039 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1953, 527 |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | (CH ₂) ₅ NH | RCH=CHCOAr (20) | 2006 |
| |  | KOH | RCH=CHCOAr (29) | 2036, 2034 |
| | .. | NaOCH ₃ | RCHOHCH ₂ COAr (20) | 2034 |
| |  | NaOH | RCH=CHCOAr (40) | 2034 |
| | .. | NaOCH ₃ | RCHOHCH ₂ COAr (10) | 2034 |
| | 2,6-(CH ₃) ₂ -4-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (33) | 1609 |
| | 1-C ₁₀ H ₇ CHO | KOH | RCH=CHCOAr (16) | 2036 |
| | 2-C ₁₀ H ₇ CHO | " | RCH=CHCOAr (55) | 2036 |
| | Ferrocenecarboxaldehyde | NaOH | RCH=CHCOAr (55) | 1975 |
| | 3,4-Dihydroxybenzaldehyde | " | RCH=CHCOAr (54) | 2053 |
| | 4-β-d-glucoside | | | |
| |  | KOH |  (66) | 2047 |
| | 4-C ₆ H ₄ CH ₂ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (60) | 2054 |
| | 3-Hydroxy-4-methoxybenzaldehyde β-d-glucoside | Na ₂ PO ₄ , Na ₂ B ₄ O ₇ , NaOH | RCH=CHCOAr (9) | 2055 |
| | 3-Methoxy-4-hydroxybenzaldehyde β-d-glucoside | " | RCH=CHCOAr (22) | 2055 |
| 4-C ₆ H ₄ CONHC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2057 | |
|  | KOH | RCH=CHCOAr (58) | 2036, 1978 | |
|  | " | RCH=CHCOAr (93) | 2036 | |
|  | .. |  (59) | 2047 | |

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Note: References 668-2359 are on pp. 403-438.

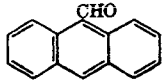
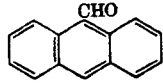
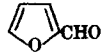
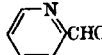
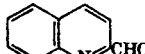
TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------------------------------|---|-----------------------------------|-----------------------|-----------------------------|
| 2-HO (contd.) | | KOH | | (59) 2047 |
| 3-HO | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (41) | 353, 640, 1946 |
| | 3-HOC ₆ H ₄ CHO | HCl | RCH=CHCOAr (30) | 640 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (36) | 640 |
| | 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1971 |
| | | HCl | RCH=CHCOAr (63) | 1978 |
| 4-HO | C(Cl ₂)=CHCHO | " | RCH=CHCOAr (80) | 637 |
| | | NaOH | RCH=CHCOAr (—) | 2056 |
| | 2-HO-3,5-Br ₂ C ₆ H ₂ CHO | " | RCH=CHCOAr (31) | 549 |
| | 2-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (40) | 1993 |
| | 3-ClC ₆ H ₄ CHO | HCl | RCH=CHCOAr (38) | 640 |
| | 4-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (32) | 640 |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2016 |
| | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (—) | 1946 |
| | " | HCl | RCH=CHCOAr (68) | 349, 640 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (14) | 640 |
| | 4-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (52) | 640, 348, 1572, 1948 |
| | " | HCl | RCH=CHCOAr (90) | 357 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (23) | 1948 |
| | 3-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (40-70) | 1997 |
| | 4-NCC ₆ H ₄ CHO | " | RCH=CHCOAr (40-70) | 1997 |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₂ CHO | CH ₃ CO ₂ H | RCH=CHCOAr (46) | 1955 |
| | 3-CH ₃ O-4-HO-6-BrC ₆ H ₂ CHO | " | RCH=CHCOAr (30) | 1955 |
| | 4-CH ₃ OC ₆ H ₄ CHO | HCl | RCH=CHCOAr (68) | 357, 1572, 2016 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2058 |
| | 2-CH ₃ ,4,5-(CH ₃ O) ₂ C ₆ H ₂ CHO | " | RCH=CHCOAr (—) | 2059 |
| | | HCl | RCH=CHCOAr (71) | 1978 |
| 2,4-(HO) ₂ | 2-ClC ₆ H ₄ CHO | KOH | RCH=CHCOAr (64) | 2041 |
| | 3-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (33) | 2041 |
| | 4-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (19) | 2041 |
| | 2-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (0) | 2041 |
| | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (14) | 2041 |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (0) | 2041 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (34-50) | 340, 352, 1940, 1953, 2060 |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 348, 1953, 2061 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (40) | 2062, 348, 1953, 1999, 2063 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (27) | 2064, 348, 2063 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (18) | 2060, 527, 1999, 2065 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2065 |
| | 2-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (20) | 2066, 1953 |
| | 3-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (40) | 2066, 1953 |
| | 4-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (50) | 2066, 1953 |







Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH_3COAr (Continued)
(R in the product is the group R in the aldehyde RCHO .)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|---|---|---|--|---------------------------------|------------|
| 2,4-(HO) ₂ (contd.) | 2- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1953, 1985 | |
| | 3- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1953, 1999 | |
| | 4- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (53) | 2064, 1953, 2067 | |
| | 2-HO-3- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (64) | 2068, 1953 | |
| | 3- $\text{CH}_2\text{O}-4\text{-HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (31) | 2062, 2066 | |
| | 4- $\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 348 | |
| | 2,3-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (42) | 2066, 1953 | |
| | 3,4-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 1953 | |
| |  | " | $\text{RCH}=\text{CHCOAr}$ (40) | 1978 | |
| | 3,4,5-($\text{C}_6\text{H}_4\text{CH}_2\text{O}$) ₃ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (28) | 2069 | |
| 2,5-(HO) ₂ | 2- $\text{ClC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (16) | 2070 | |
| | 2-HO-5- $\text{BrC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2070 | |
| | 3- $\text{O}_2\text{NC}_6\text{H}_3\text{CHO}$ | POCl_3 | $\text{RCH}=\text{CHCOAr}$ (22) | 2070 | |
| | $\text{C}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (35) | 2071, 2072 | |
| | 2- $\text{HOC}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 348, 2071 | |
| | 4- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 348, 2071 | |
| | 3,4-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (25) | 2070 | |
| | 4- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2071 | |
| | 3- $\text{CH}_2\text{O}-4\text{-HOC}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2071 | |
| |  | HCl | $\text{RCH}=\text{CHCOAr}$ (—) | 1978 | |
| | 3,4-(HO) ₂ | $\text{C}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (65) | 1948 |
| | | 4- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (45) | 1948 |
| | | 3,4-(HO) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (55) | 1948, 2073 |
| 3,4-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (—) | 2073 | |
| 2-HO-3,4-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (—) | 348 | |
| 2,3,4-(HO) ₃ | 2-HO-5- $\text{BrC}_6\text{H}_3\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (40) | 1993 | |
| | $\text{C}_6\text{H}_4\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (61) | 352, 348 | |
| | 2- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (45) | 352, 348 | |
| | 3- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (25) | 352 | |
| | 4- $\text{HOC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (—) | 348 | |
| | 3,4-(HO) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (39) | 2045 | |
| | 4- $\text{HOC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2074 | |
| | 3,4-(HO) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (16) | 2075 | |
| | " | NaOH | $\text{RCH}=\text{CHCOAr}$ (39) | 527 | |
| | 2,3,6-(HO) ₃ 2,4,5-(HO) ₃ 2,4,6-(HO) ₃ | $\text{C}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (10) | 1924 |
| " | | " | $\text{RCH}=\text{CHCOAr}$ (50) | 1924 | |
| CH_3O | | None, heat | 4- $\text{CH}_2=\text{NC}_6\text{H}_4\text{COCH}_2\text{CH}_2\text{OH}$ (23) | 598, 359 | |
| i- $\text{C}_3\text{H}_7\text{CHO}$ | | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 1643 | |
|  | | KOH | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (69) | 2076, 359 | |
|  | | NaOH | $\text{RCH}=\text{CHCOAr}$ (42) | 545 | |
| 2-HO-3,5- $\text{Br}_2\text{C}_6\text{H}_2\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (18) | 549 | |
| 4-HO-3,5- $\text{Br}_2\text{C}_6\text{H}_2\text{CHO}$ | | " | $\text{RCH}=\text{CHCOAr}$ (41) | 549 | |
| 2- $\text{O}_2\text{NC}_6\text{H}_3\text{CHO}$ | | HCl | $\text{RCH}=\text{CHCOAr}$ (—) | 1936 | |
| 3- $\text{O}_2\text{NC}_6\text{H}_3\text{CHO}$ | | KOH | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359 | |
| 4- $\text{O}_2\text{NC}_6\text{H}_3\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (—) | 2077 | | |
| " | KOH | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359 | | |
| $\text{C}_6\text{H}_5\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (31) | 1924, 359, 1934, 2078 | | |
| 2,3,6-(HO) ₃ 2,4,5-(HO) ₃ 2,4,6-(HO) ₃ | 3- $\text{H}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOCH_3 | $\text{RCH}=\text{CHCOAr}$ (68) | 2004 | |
| | 3- $\text{NCC}_6\text{H}_4\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (40-70) | 1997 | |
| | 4- $\text{NCC}_6\text{H}_4\text{CHO}$ | " | $\text{RCH}=\text{CHCOAr}$ (40-70) | 1997 | |
| | 3,4-(CH_2O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 359 | |
| | 4- $\text{CH}_2\text{C}_6\text{H}_4\text{CHO}$ | " | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359 | |
| | 4- $\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | " | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359, 2078 | |
| | $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ | " | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359, 2078 | |
| |  | NaOH | $\text{RCH}=\text{CHCOAr}$ (74) | 2023, 2024 | |
| | 4-i- $\text{C}_3\text{H}_7\text{C}_6\text{H}_4\text{CHO}$ | KOH | 4- $\text{RCH}=\text{NC}_6\text{H}_4\text{COCH}=\text{CHR}$ (—) | 359 | |

Note: References 668-2359 are on pp. 403-438.







TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|-------------------------------|------------|
| 4-CN | 4-ClC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (40-70) | 1997 |
| | 2-O ₂ NC ₆ H ₄ CHO | Na ₂ PO ₄ | RCHOHCH ₂ COAr (-) | 361 |
| | " | KOH | RCH=CHCOAr (-) | 1936 |
| | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (40-70) | 1997 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (40-70) | 1997 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (40-70) | 1997, 2357 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (40-70) | 1997, 2357 |
| 2-HO-4-CN |  | " | RCH=CHCOAr (53) | 2006 |
| |  | " | RCH=CHCOAr (56) | 2006 |
| |  | (CH ₂) ₅ NH | RCH=CHCOAr (21) | 2006 |
| |  | NaOH | RCH=CHCOAr (30) | 2006 |
| 2-CH ₃ -3,5-(NO ₂) ₂ | C ₆ H ₃ CHO | " | RCH=CHCOAr (38) | 2006 |
| | " | HCl, CH ₃ CO ₂ H | RCH=CHCOAr (67) | 2079 |
| 4-CO ₂ H | 2-ClC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (60) | 2080, 2350 |
| | 2-O ₂ NC ₆ H ₄ CHO | Na ₂ PO ₄ | RCHOHCH ₂ COAr (-) | 361 |
| | " | KOH | RCH=CHCOAr (-) | 1936, 2350 |
| | C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (60) | 2080, 2350 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (50) | 2080, 2350 |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | " | RCH=CHCOAr (30) | 2080, 2350 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (90) | 2081 |
| 3,4-(CH ₂ O ₂) 3-CO ₂ H-4-HO | C ₆ H ₃ CHO | KOH | RCH=CHCOAr (55) | 2082 |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (35) | 2082 |
| 2-HO-5-CO ₂ H | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (25) | 2082 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (40) | 2082 |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (45) | 2082 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (55) | 2082 |
| | C ₆ H ₃ CHO | " | RCH=CHCOAr (70) | 2082 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (50) | 2082 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2082 |
| | 3,4(CH ₂ O ₂)C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (86) | 2083 |
| | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (40) | 2082 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (55) | 2082 |
| 4-CH ₃ O-5-Br |  | " | RCH=CHCOAr (83) | 370 |
| 2-HO-4-CH ₃ O-5-Br | 2-Cl-4-CH ₃ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (-) | 341 |
| | 3-Cl-4-CH ₃ C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 341 |
| 2-Cl-5-CH ₃ | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (-) | 1985 |
| | 2-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 1936 |
| 3-Cl-4-CH ₃ O | C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (-) | 2003 |
| |  | " | RCH=CHCOAr (-) | 2017 |
| 3-CH ₃ -4-F | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 1995 |
| | 2-O ₂ NC ₆ H ₄ CHO | Na ₂ PO ₄ | RCHOHCH ₂ COAr (-) | 361 |
| 3-NO ₂ -4-CH ₃ | " | HCl | RCH=CHCOAr (-) | 1936 |
| | " | KOH | RCH=CHCOAr (-) | 2084 |
| 3-NO ₂ -4-CH ₃ O | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2085, 2043 |
| | C ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2085 |
| 2-HO-3-NO ₂ -5-CH ₃ | 2-CH ₃ O-3-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (-) | 2085 |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (-) | 2085 |
| 2-HO-3-CH ₃ O-5-NO ₂ | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | - | RCH=CHCOAr (-) | 2043 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | - | RCH=CHCOAr (-) | 2043 |
| 2-HO-3-NO ₂ -4-CH ₃ O | C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (-) | 2074 |
| | " | KOH | RCH=CHCOAr (60) | 2033 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (60) | 2033, 2043 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|---|--------------------------------|
| 2-HO-4-CH ₃ O-5-NO ₂ | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2086 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2087 |
| | 3-Br-4-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2086 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2087 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2074 |
| | " | " | RCH=CHCOAr (55) | 1939 |
| | " | HCl | RCH=CHCOAr (65) | 349, 1939 |
| 4-CH ₃ | C(Cl) ₂ =CHCHO | BaO | RCH=CHCOAr (45) | 1908 |
| |  | NaOC ₂ H ₅ | RCH=CHCOAr (86) | 1914 |
| |  | NaOCH ₃ | RCH=CHCOAr (52) | 1522, 366 |
| |  | NaOC ₂ H ₅ | RCH=CHCOAr (—) | 1860, 537 |
| | 2-HO-3,5-Br ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (67) | 549 |
| | 3,5-Br ₂ -4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (50) | 549 |
| | 2-HO-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (48) | 549, 1965 |
| | 2-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (57) | 353 |
| | 2-O ₂ NC ₆ H ₄ CHO | Na ₃ PO ₄ | RCHOHCH ₂ COAr (—) | 361 |
| | " | NaOH | RCH=CHCOAr (—) | 1938, 1936 |
| | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1938 |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1938 |
| | C ₆ H ₅ CHO | HCl, (CH ₃ CO) ₂ O | RCH=CHCOAr (42) | 353, 349, 538, 1938, 2088-2090 |
| | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2091 |
| | 3,4-(CH ₃ O) ₂ -6-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2092 |
| | 3,4-(CH ₃ O) ₂ -6-ClC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2092 |
| | 4-OHCC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 544 |
| | " | " | C ₆ H ₄ (CH=CHCOAr) ₂ -1,4 (—) | 544 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 1938, 2092 |
| | 3-Br-4-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2092 |
| | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (78) | 549 |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | HCl, CH ₃ CO ₂ H | RCH=CHCOAr (19) | 1955 |
| | 3-CH ₃ O-4-HO-6-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (55) | 1955 |
| | 3-Cl-4-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2092 |
| | 2-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (30) | 353 |
| | 3-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (36) | 353 |
| | 4-CH ₃ C ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOAr (82) | 2089, 353, 1959 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (55) | 353, 1959, 1964, 2092 |
| |  | Na ₂ CO ₃ | RCH=CHCOAr (41) | 1766 |
| | 3-HO-4-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 339 |
| |  | (CH ₃) ₂ NH, 175° | RCH=CHCOAr (61) | 600 |
| |  | NaOH | RCH=CHCOAr (75-95) | 1854 |

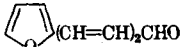
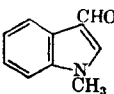
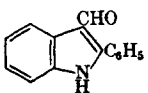
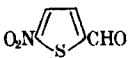
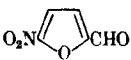




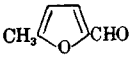
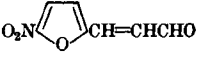
ORGANIC REACTIONS

THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

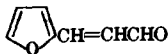
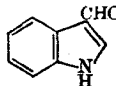
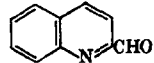
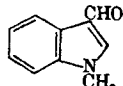
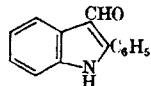
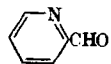
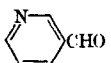
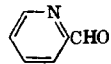
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TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--------------------------------|--|--|-------------------------------|---------------------|
| 4-CH ₃ (contd.) | 2-C ₂ H ₅ O-3,5-Br ₂ C ₆ H ₂ CHO | NaOH | RCH=CHCOAr (45) | 549 |
| |  (CH=CH) ₂ CHO | Na ₂ CO ₃ | RCH=CHCOAr (92) | 1766 |
| | 2-C ₂ H ₅ O-5-BrC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (100) | 549 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1800 |
| |  | (CH ₂) ₅ NH, 200° | RCH=CHCOAr (70) | 600 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CH=CHCHO | NaOH | RCH=CHCOAr (—) | 1938 |
| | 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1923 |
| | 2-C ₆ H ₅ CH ₂ O-3,5-Br ₂ C ₆ H ₂ CHO | " | RCH=CHCOAr (—) | 549 |
| | 2-C ₆ H ₅ CH ₂ O-5-BrC ₆ H ₄ CHO | " | RCH=CHCOAr (71) | 549 |
| |  | (CH ₂) ₅ NH | RCH=CHCOAr (67) | 1979 |
| 2-CH ₃ Se | C ₆ H ₅ CHO | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOAr (67) | 2093 |
| 2-CH ₃ O | " | KOH | RCH=CHCOAr (—) | 1953 |
| 4-CH ₃ O | 4-NCC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (40-70) | 1997 |
| | C(Cl ₂)=CHCHO | BaO | RCH=CHCOAr (56) | 1908 |
| |  | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CHCOAr (40) | 647 |
| |  | " | RCH=CHCOAr (90) | 646 |
| |  | NaOH | RCH=CHCOAr (98) | 1913, 1793, 1914 |
| |  | " | RCH=CHCOAr (75) | 366 |
| |  | " | RCH=CHCOAr (84) | 1794, 1918, 2094 |
| |  | " | RCH=CHCOAr (—) | 1988 |
| |  | " | RCH=CHCOAr (—) | 1988 |
| | 2-HO-3,5-Br ₂ C ₆ H ₂ CHO | " | RCH=CHCOAr (58) | 549 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1923 |
| | 2-BrC ₆ H ₄ CHO | " | RCH=CHCOAr (34) | 1929 |
| | 2-HO-5-BrC ₆ H ₄ CHO | " | RCH=CHCOAr (60) | 549 |
| | 2-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (64) | 353, 1929 |
| | 2-FC ₆ H ₄ CHO | BF ₃ , CH ₃ CO ₂ H | RCH=CHCOAr (—) | 1935 |
| | 4-FC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1935 |
| | 2-O ₂ NC ₆ H ₄ CHO | Na ₂ PO ₄ | RCHOHCH ₂ COAr (—) | 361 |
| | " | NaOH | RCH=CHCOAr (58) | 1798 |
| | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (96) | 356 |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (90) | 2095, 1798 |
| |  | H ₂ SO ₄ , CH ₃ CO ₂ H | RCH=CHCOAr (25) | 646 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (81) | 353, 1994 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

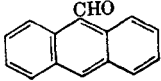

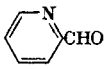
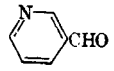
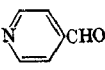


| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|---|--|---|---|---|--|
| 4-CH ₃ O (contd.) | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2097 | |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (74) | 353, 640 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1572 | |
| |  | " | " | RCH=CHCOAr (88) | 1794 |
| | 3-NCC ₆ H ₄ CHO | " | " | RCH=CHCOAr (40-70) | 1997 |
| | 4-NCC ₆ H ₄ CHO | " | " | RCH=CHCOAr (40-70) | 1997 |
| | 4-OHCC ₆ H ₄ CHO | KOH | " | RCH=CHCOAr (—) | 544 |
| | " | " | " | C ₆ H ₅ (CH=CHCOAr) ₂ -1,4 (—) | 544 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | " | RCH=CHCOAr (—) | 1791, 2094 |
| | 3-CH ₃ O-4-HO-5-BrC ₆ H ₃ CHO | HCl, CH ₃ CO ₂ H | " | RCH=CHCOAr (67) | 1955 |
| | 3-CH ₃ O-4-HO-6-BrC ₆ H ₃ CHO | " | " | RCH=CHCOAr (22) | 1955 |
| | 3-CH ₃ OC ₆ H ₄ CHO | NaOCH ₃ | " | RCH=CHCOAr (79) | 2099 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOC ₂ H ₅ | " | RCH=CHCOAr (92) | 2100-2103, 353, 640, 1959, 1971, 2094 |
| | 2-HO-3-CH ₃ OC ₆ H ₃ CHO | NaOH | " | RCH=CHCOAr (61) | 1966 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | " | RCH=CHCOAr (—) | 1923 |
| |  | (CH ₂) ₆ NH, 175° | " | RCH=CHCOAr (60) | 600 |
| | C ₆ H ₅ CH=CHCHO | NaOH | " | RCH=CHCOAr (—) | 1791, 1798 |
| | 3-CH ₃ CONHC ₆ H ₄ CHO | " | " | RCH=CHCOAr (76) | 1798 |
| | 2-CH ₃ -4-CH ₃ OC ₆ H ₃ CHO | NaOCH ₃ | " | RCH=CHCOAr (80) | 2104 |
| | 2,3-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | " | RCH=CHCOAr (—) | 1971 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | " | RCH=CHCOAr (—) | 1929 |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | " | " | RCH=CHCOAr (40) | 1798, 567 |
| |  | NaOCH ₃ | " | RCH=CHCOAr (88) | 2004, 2023, 2024 |
| | 2-HO-4-CH ₃ |  | (CH ₂) ₆ NH, 200° | RCH=CHCOAr (55) | 600 |
| | | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 1923 |
| 2-CH ₃ -4,5-(CH ₂ O) ₂ C ₆ H ₃ CHO | | KOH | RCH=CHCOAr (—) | 2059 | |
| 3,4,5-(CH ₂ O) ₃ C ₆ H ₂ CHO | | NaOCH ₃ | RCH=CHCOAr (—) | 1971 | |
| 4-(CH ₃) ₂ NC ₆ H ₃ CHO | | Na ₂ CO ₃ | RCH=CHCOAr (68) | 1810 | |
| 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | | NaOH | RCH=CHCOAr (—) | 1923 | |
| 2-CH ₃ -4-CH ₃ O-5- <i>i</i> -C ₃ H ₇ C ₆ H ₃ CHO | | " | RCH=CHCOAr (—) | 2105 | |
| 2-C ₆ H ₅ CH ₂ O-3,5-Br ₂ C ₆ H ₃ CHO | | " | RCH=CHCOAr (88) | 549 | |
| 2-C ₆ H ₅ CH ₂ O-5-BrC ₆ H ₃ CHO | | " | RCH=CHCOAr (76) | 549 | |
|  | | (CH ₂) ₆ NH | " | RCH=CHCOAr (78) | 1979 |
| 2-HO-5-CH ₃ | |  | KOH | RCH=CHCOAr (—) | 1990 |
| | |  | " | RCH=CHCOAr (85) | 371 |
| | | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (65) | 2106 |
| | | 4-CH ₃ C ₆ H ₄ CHO | " | RCH=CHCOAr (64) | 2106 |
| | | 4-CH ₃ OC ₆ H ₄ CHO | — | RCH=CHCOAr (—) | 2043 |
| | | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 339 |
| 2-HO-5-CH ₃ | |  | KOH | RCH=CHCOAr (—) | 371 |
| | | 3-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 339 |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 339 | |
| | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (50) | 529 | |
| | 3-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 339 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (60) | 340, 339 | |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (34) | 529 | |
| | 2-Br-4-CH ₃ C ₆ H ₃ CHO | " | RCH=CHCOAr (84) | 2008 | |
| | 2-CH ₃ -4-BrC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2008 | |

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|---|---|---|--|-----------------|------------|
| 2-HO-5-CH ₃ (contd.) | 2-Cl-4-CH ₃ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 341 | |
| | 3-Cl-4-CH ₃ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 341 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (70) | 2107, 529, 2043 | |
| | 2-HO-3-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOAr (18) | 529 | |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (75) | 340, 529 | |
| | C ₆ H ₅ CH=CHCHO | HCl, CH ₃ CO ₂ H | RCH=CHCOAr (—) | 339 | |
| | 2,4-(CH ₃) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 339 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (60) | 529 | |
| | 2,4,6-(CH ₃) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 339 | |
| | 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | " | RCH=CHCOAr (—) | 339 | |
| |  | KOH | RCH=CHCOAr (62) | 2036 | |
| | 2-HO-3-CH ₃ O | 2-HO-3-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (22) | 2108 |
| | | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2108 |
| | | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (27) | 2108, 2109 |
| | 2-HO-4-CH ₃ O |  | " | RCH=CHCOAr (17) | 2037 |
|  | | " | RCH=CHCOAr (16) | 2037 | |
|  | | " | RCH=CHCOAr (21) | 2037 | |
| |  | " | RCH=CHCOAr (8) | 2037 | |
| | 2-BrC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2046 | |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2110, 2099 | |
| | 4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 348 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2110, 2094 | |
| | 2-Br-4-CH ₃ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2046 | |
| | 2-Cl-4-CH ₃ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 341 | |
| | 3-Cl-4-CH ₃ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 341 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2111, 1985 | |
| | 3-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2112 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2113 | |
| | 3-HO-4-CH ₃ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 339 | |
| | 4-Hydroxybenzaldehyde β-d-glucoside | NaOH, Na ₂ B ₄ O ₇ | RCH=CHCOAr (3) | 2055 | |
| | 2-HO-5-CH ₃ O | 2-HO-5-BrC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2070 |
| | | 2-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2070 |
| 3-O ₂ NC ₆ H ₄ CHO | | " | RCH=CHCOAr (—) | 2070 | |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | " | RCH=CHCOAr (34) | 2070 | |
| 2-HO-6-CH ₃ O | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (86) | 2114 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2115 | |
| 2-CH ₃ O-4-HO |  | " | RCH=CHCOAr (—) | 2038 | |
| 3-CH ₃ O-4-HO | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (100) | 2116 | |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2052 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (48) | 2116 | |
| 2,5-(HO) ₂ -4-CH ₃ O | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (43) | 346 | |
| | 2-CH ₃ O-4,6-(HO) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (80) | 2117 | |
| 4-COCH ₃ |  | Na ₂ CO ₃ | 1,4-(RCH=CHCO) ₂ C ₆ H ₄ (—) | 1801 | |
| | 2-ClC ₆ H ₄ CHO | NaOH | 1,4-(RCH=CHCO) ₂ C ₆ H ₄ (32) | 2080 | |
| | C ₆ H ₅ CHO | " | 1,4-(RCH=CHCO) ₂ C ₆ H ₄ (46) | 2080 | |





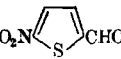
Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

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TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|---|------------------|
| 4-COCH ₃ (contd.) | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | 1,4-(RCH=CHCO) ₂ C ₆ H ₄ (69) | 2080 |
| | C ₆ H ₅ CH=CHCHO | Na ₂ CO ₃ | 1,4-(RCH=CHCO) ₂ C ₆ H ₄ (—) | 1801 |
| 3,4-(CH ₃ O) ₂ -ω-Br | C ₆ H ₅ CHO | HCl, CH ₃ CO ₂ H | RCH=CBrCOAr (—) | 1705 |
| 2,4-(CH ₃ O) ₂ -5-Br | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2119 |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2119 |
| 3-CH ₃ CONH | 2-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1936 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (63) | 1924 |
| 4-CH ₃ CONH | 2-ClC ₆ H ₄ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (69) | 2120 |
| | 2-O ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 1936 |
| | 3-O ₂ NC ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOAr (80) | 2004 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (84) | 1924, 2078 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2078 |
| | C ₆ H ₅ CH=CHCHO | " | RCH=CHCOAr (—) | 2078 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (39) | 2121 |
| 2-HO-5-CH ₃ CONH |  | " | RCH=CHCOAr (57) | 2006 |
| |  | " | RCH=CHCOAr (64) | 2006 |
| |  | " | RCH=CHCOAr (22) | 2006 |
| |  | " | RCH=CHCOAr (30) | 2006 |
| | 4-ClC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2122 |
| | 2-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2122 |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (Good) | 2122 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (100) | 2123, 2006, 2124 |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (14) | 2124, 2122 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (37) | 2124 |
| | OHCC ₆ H ₄ CHO-1,4 | NaOH | RCH=CHCOAr or C ₆ H ₄ (CH=CHCOAr) ₂ -1,4* (—) | 2122 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (36) | 2124 |
| | 3-HO ₂ C-4-HOC ₆ H ₃ CHO | HCl | RCH=CHCOAr (65) | 2124 |
| | 4-CH ₃ C ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2122 |
| | 4-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (33) | 2124 |
| 3-NO ₂ -4-CH ₃ CONH | 2-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1936 |
| 2,4-(CH ₃) ₂ | " | " | RCH=CHCOAr (—) | 1936 |
| | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2048 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2048 |
| 2,5-(CH ₃) ₂ | 2-O ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 1936 |
| | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2048 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2048 |
| 3,4-(CH ₃) ₂ | 2-O ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 1936 |
| | " | Na ₂ PO ₄ | RCHOHCH ₂ COAr (—) | 361 |
| 4-C ₂ H ₅ | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (60) | 2089, 349, 2090 |
| 2-CH ₃ Se-5-CH ₃ | " | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOAr (51) | 2093 |
| 2-CH ₃ -4-CH ₃ O | 2-CH ₃ -4-CH ₃ OC ₆ H ₃ CHO | NaOCH ₃ | RCH=CHCOAr (84) | 2104 |
| 4-C ₂ H ₅ O | 4-CH ₃ OC ₆ H ₄ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (—) | 2100 |
| 2-HO-4,6-(CH ₃) ₂ | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 339 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 339 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 339 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 339 |
| | C ₆ H ₅ CH=CHCHO | " | RCH=CHCOAr (—) | 339 |
| | 2,4,6-(CH ₃) ₃ C ₆ H ₂ CHO | " | RCH=CHCOAr (—) | 339 |
| 2,4-(CH ₃ O) ₂ |  | CH ₃ CO ₂ H, (CH ₃ CO) ₂ O | RCH=CHCOAr (15) | 647 |

Note: References 668-2359 are on pp. 403-438.




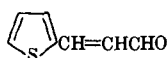
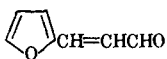
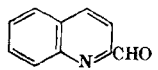
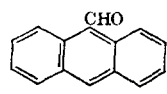
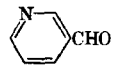
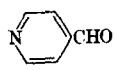
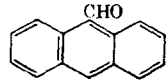

* The structure of the product was not established.

ORGANIC REACTIONS

THE ALDOL CONDENSATION

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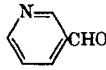
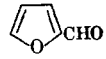
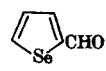
TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|-----------------------|------------------|
| 2,4-(CH ₃ O) ₂ (contd.) |  | NaOH | RCH=CHCOAr (73) | 1008 |
| |  | " | RCH=CHCOAr (61) | 366 |
| |  | " | RCH=CHCOAr (—) | 1794 |
| | 2-ClC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2041 |
| | 4-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2041 |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (Good) | 2095 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 2125, 1940, 2096 |
| |  | " | RCH=CHCOAr (78) | 1008 |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 571 |
| |  | NaOH | RCH=CHCOAr (93) | 1794 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 |
| | 2-CH ₃ O-5-BrC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2119 |
| | 4-CH ₃ C ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2048 |
| | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2119, 1940 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2125, 2101 |
| 2-HO-3-CH ₃ OC ₆ H ₃ CHO | KOH | RCH=CHCOAr (80) | 2068 | |
| 2-HO-5-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (82) | 2068 | |
| 2-HO-6-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (82) | 2068 | |
| 3-HO-4-CH ₃ OC ₆ H ₃ CHO | " | RCH=CHCOAr (74) | 2068 | |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 | |
| 2,5-(CH ₃ O) ₂ | 2,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125, 2061 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | Na ₂ CO ₃ | RCH=CHCOAr (43) | 1810 |
| |  | NaOH | RCH=CHCOAr (—) | 2024 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CH=CHCHO | Na ₂ CO ₃ | RCH=CHCOAr (47) | 1810 |
| |  | HCl | RCH=CHCOAr (36) | 1978 |
| |  | NaOH | RCH=CHCOAr (—) | 2126 |
| |  | (CH ₂) ₅ NH, CH ₃ CO ₂ H | RCH=CHCOAr (49) | 369 |
| | 2-HO-5-BrC ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2070 |
| | 2-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2070 |
| | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2070 |
| | 2-HOC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2127 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (—) | 2070 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1922, 2101 |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2125 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 | |
| 2,6-(CH ₃ O) ₂ |  | HCl | RCH=CHCOAr (70) | 1978 |
| |  | NaOH | RCH=CHCOAr (—) | 2125 |

Note: References 668-2359 are on pp. 403-438.

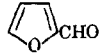
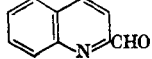
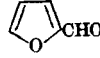
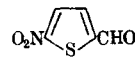
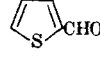
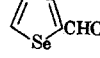
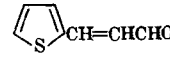
TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. | |
|--|---|--|-----------------------|------------------|------|
| 3,4-(CH ₃ O) ₂ (contd.) | 2-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2128 | |
| | 3-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2128 | |
| | 4-O ₂ NC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2128 | |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 2125, 2058 | |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2097 | |
| | 4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (40) | 2058 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2009 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2125, 2058, 2101 | |
| | C ₆ H ₅ CH=CHCHO | " | RCH=CHCOAr (—) | 2125 | |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 | |
| | 2,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2125, 2129, 2130 | |
| | 3,5-(CH ₃ O) ₂ 2-HO-4-C ₂ H ₅ O | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1971 |
| | | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2131 |
| | | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2173 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | " | RCH=CHCOAr (—) | 2131 | |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | KOH | RCH=CHCOAr (—) | 2132 | |
| 2-HO-5-C ₂ H ₅ O | 3-CH ₃ O-4-C ₂ H ₅ OC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2132 | |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 525, 528 | |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 528 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 526 | |
| | 2-C ₆ H ₅ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 528 | |
| 2-HO-3-CH ₃ O-5-CH ₃ 2-HO-4-CH ₃ O-6-CH ₃ | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (11) | 2134 | |
| | " | KOH | RCH=CHCOAr (—) | 2135 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2135 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (Low) | 2135 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 339 | |
| 2-CH ₃ -4-CH ₃ O-5-HO | 2-CH ₃ -4,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2059 | |
| | | | | | |
| 2-HO-3,4-(CH ₃ O) ₂ | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2009 | |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (45) | 2136 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2136, 2044 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2115, 2137 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2044, 2138 | |
| 2-HO-3,5-(CH ₃ O) ₂ | C ₆ H ₅ CHO | " | RCH=CHCOAr (80) | 2139, 2140 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (85) | 2139, 2140 | |
| | 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (60) | 2139 | |
| 2-HO-3,6-(CH ₃ O) ₂ |  | " | RCH=CHCOAr (—) | 369, 2126 | |
| 2-HO-4,5-(CH ₃ O) ₂ |  | KOH | RCH=CHCOAr (—) | 2141 | |
| 2-HO-4,6-(CH ₃ O) ₂ | 3-O ₂ NC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2074 | |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 2142, 340, 527 | |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (86) | 2114, 340 | |
| | 4-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2143 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2142 | |
| | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2114, 2115 | |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (80) | 340 | |
| | 3-CH ₃ O-4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (60) | 340 | |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (60) | 2115, 2145 | |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (41) | 527, 2145 | |
| | 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | Na ₂ CO ₃ | RCH=CHCOAr (—) | 2146, 2347 | |
| | 2-HO-5,6-(CH ₃ O) ₂ | 2-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2147 |
| 4-CH ₃ OC ₆ H ₄ CHO | | " | RCH=CHCOAr (37) | 346 | |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | " | RCH=CHCOAr (27) | 346 | |
| 4-HO-2,6-(CH ₃ O) ₂ | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 339 | |
| 4-(CH ₃) ₂ N |  | " | RCH=CHCOAr (43) | 366 | |

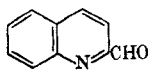
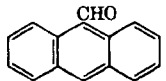
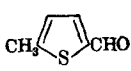
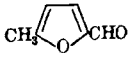
Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|--|------------------|
| 4-(CH ₃) ₂ N (contd.) |  | NaOH | RCH=CHCOAr (—) | 2056 |
| | 4-O ₂ NC ₆ H ₄ CHO | Na ₂ CO ₃ | RCH=CHCOAr (91) | 1810 |
| | C ₆ H ₅ CHO | HCl | RCH=CHCOAr (76) | 349 |
| | 4-CH ₃ OC ₆ H ₄ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1934, 567 |
| | C ₆ H ₅ CH=CHCHO | Na ₂ CO ₃ | RCH=CHCOAr (44) | 1810 |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (77) | 1810 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (92) | 567, 1972 |
| |  | NaOH | RCH=CHCOAr (—) | 2024 |
| | 4-CH ₃ OC ₆ H ₄ CH=CHCHO | Na ₂ CO ₃ | RCH=CHCOAr (30) | 1810 |
| | 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | .. | RCH=CHCOAr (47) | 1810 |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO | .. | RCH=CHCOAr (38) | 1810 |
| 4-(CH ₃) ₂ NC ₆ H ₃ CH=CHCHO | .. | RCH=CHCOAr (17) | 1810 | |
| 9-Formyl-3,4-benzacridine | NaOH | RCH=CHCOAr (75-95) | 372 | |
| 10-Formyl-1,2-benzanthracene | .. | RCH=CHCOAr (75-95) | 372 | |
| 2-CO ₂ C ₂ H ₅ 2-(HO ₂ CCH ₂ O)-4-CH ₃ O | C ₆ H ₅ CHO | .. | RCH=CHCOAr (82) | 2148 |
| | .. | .. | RCH=CHCOAr (—) | 2149 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2149 |
| | 3-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2149 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2149 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2149 |
| | C ₆ H ₅ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (—) | 1607 |
| | 1,3,5-(CH ₃) ₃ C ₆ H ₂ CHO | .. | RCH=CHCOAr (—) | 1607 |
| | CH ₂ O | K ₂ CO ₃ | HOCH ₂ CH ₂ COA (71) | 2150, 519 |
| | 4-BrC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (91) | 2151 |
| | 4-ClC ₆ H ₄ CHO | .. | RCH=CHCOAr (91) | 2151 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | RCH=CHCOAr (100) | 2152 | |
| C ₆ H ₅ CHO | .. | RCH=CHCOAr (—) | 2003 | |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (92) | 2153 | |
| 4-n-C ₃ H ₇ 4-i-C ₃ H ₇ | 2,4,6-(CH ₃) ₃ C ₆ H ₂ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (90) | 2154 |
| | C ₃ H ₇ CHO | NaOCH ₃ | RCH=CHCOAr (63) | 2089, 2090 |
| | .. | .. | RCH=CHCOAr (65) | 2155, 2090 |
| | .. | HCl | RCH=CHCOAr (68) | 349 |
| | .. | NaOH | RCH=CHCOAr (—) | 2156 |
| | 2-HO-3,4,6-(CH ₃) ₃ | KOH | RCH=CHCOAr (—) | 2059 |
| | 2-CH ₃ -4,5-(CH ₃ O) ₂ | .. | RCH=CHCOAr (—) | 2059 |
| | .. | .. | RCH=CHCOAr (—) | 2059 |
| | 2,3,4-(CH ₃ O) ₃ | NaOCH ₃ | RCH=CHCOAr (—) | 1971, 2009, 2084 |
| | .. | KOH | RCH=CHCOAr (80) | 2136, 2101 |
| | 2,4,5-(CH ₃ O) ₃ |  | NaOH | RCH=CHCOAr (—) |
| 2-HOC ₆ H ₄ CHO | | .. | RCH=CHCOAr (—) | 2157 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | | .. | RCH=CHCOAr (—) | 2094 |
| 4-CH ₃ OC ₆ H ₄ CHO | | KOH | RCH=CHCOAr (—) | 2101 |
| 2,4,6-(CH ₃ O) ₃ |  | CH ₃ CO ₂ H, (CH ₃ CO) ₂ O | RCH=CHCOAr (0) | 647 |
| |  | NaOH | RCH=CHCOAr (84) | 1008 |
| |  | .. | RCH=CHCOAr (69) | 366 |
| |  | .. | RCH=CHCOAr (79) | 1008 |
| | 2-HOC ₆ H ₄ CHO | KOH | RCH=CHCOAr (50) | 2158, 2115 |
| | 4-HOC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2143 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2115 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | RCH=CHCOAr (—) | 2101 |
| | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2125, 2143 |
| | 2,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | RCH=CHCOAr (—) | 2125 |






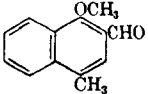
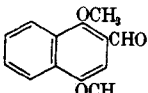
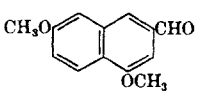
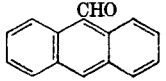

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|--|-----------------------------|
| 2,4,6-(CH ₃ O) ₃ (contd.) | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2125 |
| |  | " | RCH=CHCOAr (—) | 2024 |
| 3,4,5-(CH ₃ O) ₃ | 4-(CH ₃) ₂ NC ₆ H ₃ CH=CHCHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | Na ₂ CO ₃ NaOCH ₃ | RCH=CHCOAr (83) RCH=CHCOAr (—) | 1810 1971, 2009, 2084 |
| 2-HO-4-CH ₃ O-6-C ₂ H ₅ O | 3,4-(C ₂ H ₅ O) ₂ C ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 2159 |
| 2-HO-3-CH ₃ -4,6-(CH ₃ O) ₂ | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | RCH=CHCOAr (50) | 2160 |
| 2-HO-3,4,5-(CH ₃ O) ₃ | C ₆ H ₃ CHO 4-CH ₃ OC ₆ H ₄ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " " " | RCH=CHCOAr (—) RCH=CHCOAr (—) RCH=CHCOAr (—) | 2161 2161 2161 |
| 2-HO-3,4,6-(CH ₃ O) ₃ | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 2,6-(CH ₃ O) ₂ C ₆ H ₃ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH " " | RCH=CHCOAr (—) RCH=CHCOAr (—) RCH=CHCOAr (73) | 2074 2074 2162 |
| 2-HO-4,5,6-(CH ₃ O) ₃ | 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO C ₆ H ₂ CHO 2-C ₆ H ₂ CH ₂ O-4-CH ₃ OC ₆ H ₃ CHO | NaOH KOH " | RCH=CHCOAr (—) RCH=CHCOAr (—) RCH=CHCOAr (78) | 2074 2156 2163 |
| 2,4-(CH ₃ CO) ₂ |  | HCl | RCH=CHCOAr (41) | 1978 |
| 2,5-(CH ₃ CO) ₂ | " | " | RCH=CHCOAr (36) | 1978 |
| 2-HO-3-CH ₃ O-5-(CH ₂ =CHCH ₂) | C ₆ H ₃ CHO | KOH | RCH=CHCOAr (40) | 2164 |
| 2-CH ₃ -5- <i>i</i> -C ₃ H ₇ | " | NaOH | RCH=CHCOAr (—) | 2003 |
| 4- <i>n</i> -C ₄ H ₉ | " | NaOCH ₃ | RCH=CHCOAr (80) | 2155 |
| 4- <i>i</i> -C ₄ H ₉ | " | " | RCH=CHCOAr (83) | 2155 |
| 4- <i>t</i> -C ₄ H ₉ | " | " | RCH=CHCOAr (77) | 2155, 349 |
| 2,4-(C ₂ H ₅ O) ₂ | 2-HO-5-BrC ₆ H ₃ CHO C ₆ H ₃ CHO | NaOH " | RCH=CHCOAr (—) RCH=CHCOAr (—) | 2127 2165 |
| 2,5-(C ₂ H ₅ O) ₂ | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2127 |
| 2-HO-3-CH ₃ O-5- <i>i</i> -C ₃ H ₇ O | C ₆ H ₃ CHO | " | RCH=CHCOAr (70) | 2139 |
| | 4-CH ₃ OC ₆ H ₄ CHO 4- <i>i</i> -C ₃ H ₇ OC ₆ H ₄ CHO | " " | RCH=CHCOAr (70) RCH=CHCOAr (70) | 2139 2139 |
| 2-HO-4,6-(C ₂ H ₅ O) ₂ | C ₆ H ₃ CHO 4-CH ₃ OC ₆ H ₄ CHO | " KOH | RCH=CHCOAr (—) RCH=CHCOAr (—) | 2142, 2166 2166 |
| 2,3,4,6-(CH ₃ O) ₄ | C ₆ H ₃ CHO 3-CH ₃ -4,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | NaOH KOH | RCH=CHCOAr (—) RCH=CHCOAr (—) | 2156 2059 |
| 2-HO-3,4,5,6-(CH ₃ O) ₄ | 2,3,4,6-(CH ₃ O) ₄ C ₆ HCHO 4-C ₆ H ₂ CH ₂ OC ₆ H ₄ CHO | " NaH | RCH=CHCOAr (—) RCH=CHCOAr (—) | 2059 2167 |
| 4-(CH ₂) ₄ CH |  | NaOH | RCH=CHCOAr (—) | 1988 |
| |  | " | RCH=CHCOAr (—) | 1988 |
| 2,4,6-(CH ₃) ₃ -3-CH ₃ CO | 2-ClC ₆ H ₄ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (80) | 2080 |
| | 4-ClC ₆ H ₄ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (85) | 2080 |
| | C ₆ H ₅ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (70) | 2080 |
| | 4-CH ₃ C ₆ H ₄ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (30) | 2080 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (35) | 2080 |
| | 4-(CH ₃) ₂ NC ₆ H ₃ CHO | " | 1,3-(RCH=CHCO) ₂ -C ₆ H(CH ₃) ₃ -2,4,6 (60) | 2080 |
| 4- <i>n</i> -C ₄ H ₉ | C ₆ H ₃ CHO | KOH | RCH=CHCOAr (51) | 2155 |
| 4- <i>i</i> -C ₄ H ₉ CH ₂ | " | NaOCH ₃ | RCH=CHCOAr (86) | 2155 |
| 4- <i>t</i> -C ₄ H ₉ CH ₂ | " | " | RCH=CHCOAr (89) | 2155 |
| 2-CH ₃ -4-CH ₃ O-5- <i>i</i> -C ₃ H ₇ | 2,4-Cl ₂ C ₆ H ₃ CHO 3,4-Cl ₂ C ₆ H ₃ CHO 2-HO-3,5-Cl ₂ C ₆ H ₃ CHO | NaOH " " | RCH=CHCOAr (80) RCH=CHCOAr (80) RCH=CHCOAr (80) | 2168 2168 2168 |

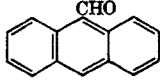

Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|----------------------------------|-----------------------|------------|
| 2-CH ₃ -4-CH ₃ O-5- <i>i</i> -C ₃ H ₇ (<i>conid.</i>) | 2-ClC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (80) | 2168 |
| | 4-ClC ₆ H ₄ CHO | " | RCH=CHCOAr (80) | 2168 |
| | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (—) | 2059 |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 3-CH ₃ O-4-C ₂ H ₅ OC ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 2-CH ₃ -4,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2059 |
| | 1-C ₁₀ H ₇ CHO | NaOH | RCH=CHCOAr (80) | 2168 |
| | C ₆ H ₅ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (50) | 1934 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (Good) | 1934 |
| | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (100) | 2169 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2169 |
| 4-C ₆ H ₅ |  CHO | NaOH | RCH=CHCOAr (51) | 1845, 1829 |
| |  CHO | " | RCH=CHCOAr (100) | 366 |
| |  CHO | NaOC ₂ H ₅ | RCH=CHCOAr (50) | 1823, 1860 |
| | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (90) | 1829, 540 |
| | 3,4-(CH ₃ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (100) | 1829 |
| | 4-CH ₃ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 540 |
| | C ₆ H ₅ CH=CHCHO | " | RCH=CHCOAr (—) | 540 |
| | <i>n</i> -C ₅ H ₁₁  CHO | NaOH | RCH=CHCOAr (—) | 1829 |
| | 2-CH ₃ -4-HO-5- <i>i</i> -C ₃ H ₇ C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 2105 |
| | 2-CH ₃ -4-CH ₃ O-5- <i>i</i> -C ₃ H ₇ C ₆ H ₃ CHO | " | RCH=CHCOAr (75) | 2105 |
| | <i>n</i> -C ₇ H ₁₅  CHO | " | RCH=CHCOAr (—) | 1829 |
| |  | " | RCH=CHCOAr (—) | 1829 |
| |  | " | RCH=CHCOAr (—) | 1829 |
| |  | " | RCH=CHCOAr (—) | 1829 |
|  | HCl | RCH=CHCOAr (68) | 1978 | |
| 3-CH ₃ O-4- <i>n</i> -C ₁₂ H ₂₅ OC ₆ H ₃ CHO | NaOH | RCH=CHCOAr (—) | 1829 | |
| 4-C ₆ H ₅ S |  CHO | " | RCH=CHCOAr (—) | 2017 |
| | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (—) | 1934 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | " | RCH=CHCOAr (—) | 1934 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1934 |
| | C ₆ H ₅ CHO | NaOC ₂ H ₅ | RCH=CHCOAr (—) | 2169 |
| 4-(4-H ₂ NC ₆ H ₄) | NaOCH ₃ | RCH=CHCOAr (—) | 2169 | |
| 4-(CH ₂) ₃ CH | (CH ₂) ₃ C=CHCH ₂ CH ₂ - C(CH ₃)=CHCHO | NaOH | RCH=CHCOAr (—) | 1773 |

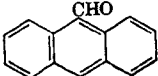
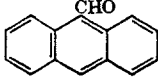
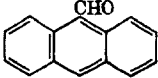
Note: References 668-2359 are on pp. 403-438.

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH₃COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|---|------------|
| 2,4-(HO) ₂ -4-β-d-glucoside | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | NaOH, Na ₂ B ₄ O ₇ | RCH=CHCOAr (10.5) | 2055 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (20) | 2055, 2170 |
| | 4-Hydroxy-3-methoxybenzaldehyde β-d-glucoside | " | RCH=CHCOAr (18) | 2055 |
| | 3-Hydroxy-4-methoxybenzaldehyde β-d-glucoside | NaOH | RCH=CHCOAr (54) | 2053 |
| 4-n-C ₆ H ₁₃ | C ₆ H ₅ CHO | KOH | RCH=CHCOAr (57) | 2155 |
| 2-HO-4-[(C ₂ H ₅) ₂ NCH ₂ -CH ₂ O] | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (25) | 2171 |
| 2-C ₆ H ₅ CO ₂ | 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 355 |
| |  | " | RCH=CHCOAr (68) | 1978 |
| 2-HO-5-C ₆ H ₅ CO | 3-CH ₂ O-4-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 355 |
| | 3-O ₂ NC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2172 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 2-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 3-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 4-HOC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 3-Cl-4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2172 |
| | 2-CH ₂ O-5-BrC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2119 |
| 2-HO-4-C ₆ H ₅ CH ₂ O-5-Br | 2-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2119 |
| 2-HO-4-C ₆ H ₅ CH ₂ O-5-NO ₂ | " | " | RCH=CHCOAr (—) | 2085 |
| 4-(4-CH ₂ OC ₆ H ₄) |  | NaOH | RCH=CHCOAr (—) | 2017 |
| | C ₆ H ₅ CHO | " | RCH=CHCOAr (—) | 1995 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 1995 |
| 4-(4-CH ₂ C ₆ H ₄ O) | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (80) | 2169 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2169 |
| 2-HO-4-C ₆ H ₅ CH ₂ O | C ₆ H ₅ CHO | NaOH | RCH=CHCOAr (—) | 2173 |
| | 2-CH ₂ O-5-BrC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2119 |
| | 2-CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2119 |
| | 3-CH ₂ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (70) | 2054 |
| | 4-CH ₂ OC ₆ H ₄ CHO | KOH | RCH=CHCOAr (—) | 2173 |
| | 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2173 |
| 4-n-C ₇ H ₁₅ | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (85) | 2155 |
| 4-(4-CH ₂ COC ₆ H ₄ S) | " | " | (4-RCH=CHCOC ₆ H ₄) ₂ S (100) | 1934 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ S (100) | 1934 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ S (—) | 1934 |
| | C ₆ H ₅ CH=CHCHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ S (—) | 1934 |
| 4-(4-CH ₂ COC ₆ H ₄ Se) | C ₆ H ₅ CHO | NaOH | (4-RCH=CHCOC ₆ H ₄) ₂ Se (75) | 1934 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ Se (70) | 1934 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ Se (70) | 1934 |
| | C ₆ H ₅ CH=CHCHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ Se (60) | 1934 |
| 4-(4-CH ₂ COC ₆ H ₄ O) | C ₆ H ₅ CHO | NaOCH ₃ | (4-RCH=CHCOC ₆ H ₄) ₂ O (—) | 2169 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ O (—) | 1934 |
| | 4-CH ₂ OC ₆ H ₄ CHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ O (—) | 2169 |
| | C ₆ H ₅ CH=CHCHO | " | (4-RCH=CHCOC ₆ H ₄) ₂ O (—) | 1934 |
| 2-HO-3,5,6-(CH ₃ O) ₃ -4-C ₆ H ₅ CH ₂ O | 4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | NaOH | RCH=CHCOAr (—) | 2066, 2174 |
| 4-n-C ₆ H ₁₇ | 3-CH ₂ O-4-C ₆ H ₅ CH ₂ OC ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 2174 |
| 4-n-C ₆ H ₁₉ | C ₆ H ₅ CHO | NaOCH ₃ | RCH=CHCOAr (42) | 2155 |
| | " | " | RCH=CHCOAr (90) | 2155 |
| 2,4,6-(i-C ₄ H ₉) ₃ | " | NaOH | RCH=CHCOAr (91) | 2175 |
| 2,4-(C ₆ H ₅ CO ₂) ₂ | 3,4-(HO) ₂ C ₆ H ₄ CHO | HCl | RCH=CHCOAr (—) | 2136 |
| | 4-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (—) | 355 |
| | 3-CH ₂ O-4-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (98) | 355 |
| 2,5-(C ₆ H ₅ CO ₂) ₂ | 2-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (82) | 354 |
| | 3-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (67) | 354 |
| | 4-C ₆ H ₅ CO ₂ C ₆ H ₄ CHO | " | RCH=CHCOAr (78) | 354 |

Note: References 668-2359 are on pp. 403-438.

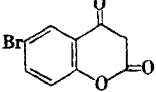
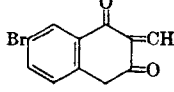
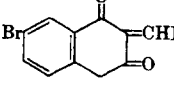
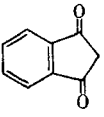
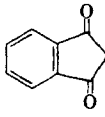
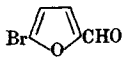
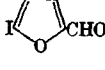

TABLE XVII. CONDENSATION OF ALDEHYDES WITH SUBSTITUTED ACETOPHENONES, CH_3COAr (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Substituent(s) in Acetophenone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|----------------------------------|---------------------------------|-------|
| 2,5-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ (contd.) |  | HCl | $\text{RCH}=\text{CHCOAr}$ (55) | 1978 |
| | 3- CH_3O -4- $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (88) | 354 |
| | 2,4-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (81) | 354 |
| | 3,4-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (78) | 354 |
| | 2,4-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ -6- $\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (42) | 354 |
| | 1,3,5-($\text{C}_6\text{H}_5\text{CO}_2$) ₃ $\text{C}_6\text{H}_2\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 354 |
| 2,6-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ |  | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 1978 |
| 2,4-($\text{C}_6\text{H}_5\text{CH}_2\text{O}$) ₂ | $\text{C}_6\text{H}_5\text{CHO}$ | NaOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2176 |
| | 3,4-(CH_3O) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 2176 |
| 2,5-($\text{C}_6\text{H}_5\text{CH}_2\text{O}$) ₂ | 2,5-(CH_3O) ₂ -3- $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ | NaOCH ₃ | $\text{RCH}=\text{CHCOAr}$ (—) | 2177 |
| 2-HO-3- CH_3 -4,6-($\text{C}_6\text{H}_5\text{CH}_2\text{O}$) ₂ | $\text{C}_6\text{H}_5\text{CHO}$ | KOH | $\text{RCH}=\text{CHCOAr}$ (—) | 2178 |
| 1,3,5-(C_6H_5) ₃ | .. | NaOC ₂ H ₅ | $\text{RCH}=\text{CHCOAr}$ (—) | 1607 |
| 2,3,4-($\text{C}_6\text{H}_5\text{CO}_2$) ₃ | 4- $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{CHO}$ | HCl | $\text{RCH}=\text{CHCOAr}$ (—) | 355 |
| 2,4,6-($\text{C}_6\text{H}_5\text{CO}_2$) ₃ |  | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 1978 |
| | 3- CH_3O -4- $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (90) | 355 |
| | 3,4-($\text{C}_6\text{H}_5\text{CH}_2\text{O}$) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 2179 |
| | 4- $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (85) | 355 |
| | 3- CH_3O -4- $\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (90) | 355 |
| | 3,4-($\text{C}_6\text{H}_5\text{CO}_2$) ₂ $\text{C}_6\text{H}_3\text{CHO}$ | .. | $\text{RCH}=\text{CHCOAr}$ (—) | 2180 |

Note: References 668-2359 are on pp. 430-438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES

(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|---|------------|
|  | (CH ₃) ₂ NC ₆ H ₄ CHO | (CH ₂) ₆ NH, CH ₃ CO ₂ H |  (55) | 2181 |
| | (C ₂ H ₅) ₂ NC ₆ H ₄ CHO | .. |  (42) | 2181 |
|  | C(Cl ₂)=CHCHO | None |  (21) | 639 |
| | | | A, R = C(Cl ₂)=CH | |
| |  | H ₂ SO ₄ , CH ₃ CO ₂ H | A, R = 2-(C ₄ H ₂ BrO) (69) | 2182 |
| |  | .. | A, R = 2-(C ₄ H ₂ IO) (89) | 2182 |
| |  | None, 110° | A, R = 2-(C ₄ H ₃ O) (—) | 2183, 2184 |
| | 2,4-Cl ₂ C ₆ H ₃ CHO | (CH ₂) ₆ NH | A, R = 2,4-Cl ₂ C ₆ H ₃ (77) | 2346 |
| | 4-BrC ₆ H ₄ CHO | (CH ₂) ₆ NH, CH ₃ CO ₂ H | A, R = 4-BrC ₆ H ₄ (74) | 2184 |
| | 2-HOC ₆ H ₄ CHO | None, 110° | A, R = 2-HOC ₆ H ₄ (—) | 2183 |
| | 3-HOC ₆ H ₄ CHO | .. | A, R = 3-HOC ₆ H ₄ (—) | 2183 |
| | 4-HOC ₆ H ₄ CHO | .. | A, R = 4-HOC ₆ H ₄ (—) | 2183 |

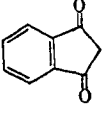
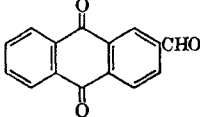
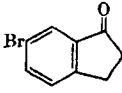
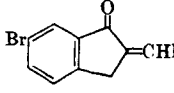
Note: References 668-2359 are on pp. 403-438.

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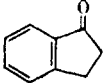
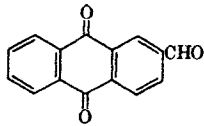
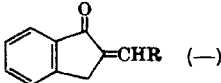
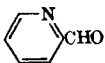
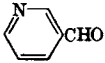
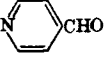
TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)

(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|----------------|--|-----------|
|  (contd.) | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | A, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (83) | 299 |
| | 3-O ₂ N-4-CH ₂ OC ₆ H ₃ CHO | None, 130-140° | A, R = 3-O ₂ N-4-CH ₂ OC ₆ H ₃ (60) | 2185 |
| | C ₆ H ₅ CH=CHCHO | None, 110° | A, R = C ₆ H ₅ CH=CH (—) | 2183 |
| | 2-C ₂ H ₅ OC ₆ H ₄ CHO | .. | A, R = 2-C ₂ H ₅ OC ₆ H ₄ (—) | 2183 |
| | 3-C ₂ H ₅ OC ₆ H ₄ CHO | .. | A, R = 3-C ₂ H ₅ OC ₆ H ₄ (—) | 2183 |
| | 4-C ₂ H ₅ OC ₆ H ₄ CHO | .. | A, R = 4-C ₂ H ₅ OC ₆ H ₄ (—) | 2183 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | A, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (86) | 299, 2184 |
| |  | .. | A, R = 2-(C ₁₄ H ₇ O ₂) (—) | 1977 |
|  | C ₆ H ₅ CHO | .. |  (—) | 2186 |
| | | | B, R = C ₆ H ₅ | |
| | 2-HOC ₆ H ₄ CHO | .. | B, R = 2-HOC ₆ H ₄ (—) | 2186 |
| | 3-HOC ₆ H ₄ CHO | .. | B, R = 3-HOC ₆ H ₄ (—) | 2186 |
| | 4-HOC ₆ H ₄ CHO | .. | B, R = 4-HOC ₆ H ₄ (Poor) | 2186 |
| | .. | HCl | B, R = 4-HOC ₆ H ₄ (—) | 2186 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | NaOH | B, R = 3,4-(HO) ₂ C ₆ H ₃ (Very small) | 2186 |
| | .. | HCl | B, R = 3,4-(HO) ₂ C ₆ H ₃ (—) | 2186 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | B, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (Good) | 2186 |
| | 3-CH ₂ O-4-HOC ₆ H ₃ CHO | .. | B, R = 3-CH ₂ O-4-HOC ₆ H ₃ (Poor) | 2186 |

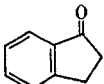
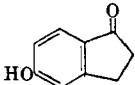
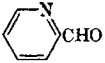
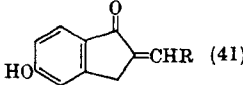
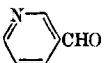
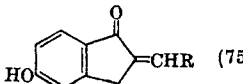
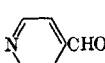
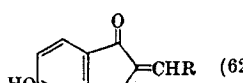


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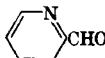
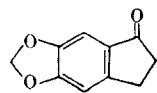
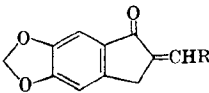
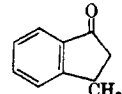
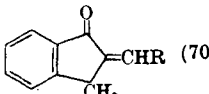
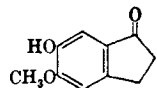
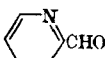
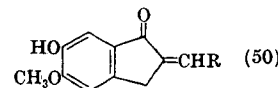
ORGANIC REACTIONS

| | | | | |
|---|---|--|---|--------------------|
|  |  | .. | B, R = 2-(C ₁₄ H ₉ O ₂) (-) | 1977 |
| | C(Cl ₂)=CClCHO | H ₂ SO ₄ |  | 289 |
| | C(Cl ₂)=CHCHO | (CH ₂) ₂ NH, CH ₃ CO ₂ H | C, R = C(Cl ₂)=CCl C, R = C(Cl ₂)=CH (60) | 639 |
| |  | .. | C, R = 2-(C ₅ H ₄ N) (63-81) | 363, 2187, 2333 |
| |  | .. | C, R = 3-(C ₅ H ₄ N) (85) | 363, 2187 |
| |  | .. | C, R = 4-(C ₅ H ₄ N) (55) | 363 |
| | 2-O ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ ; also KOH | C, R = 2-O ₂ NC ₆ H ₄ (75) | 643, 2188, 2189 |
| | C ₆ H ₅ CHO | KOH | C, R = C ₆ H ₅ (95) | 643, 2190, 2345 |
| | 2-HOC ₆ H ₄ CHO | .. | C, R = 2-HOC ₆ H ₄ (100) | 2191, 2192 |
| | 3-HOC ₆ H ₄ CHO | NaOH | C, R = 3-HOC ₆ H ₄ (100) | 2192 |
| | 4-HOC ₆ H ₄ CHO | .. | C, R = 4-HOC ₆ H ₄ (100) | 2192 |
| | 2,4-(HO) ₂ C ₆ H ₃ CHO | HCl | C, R = 2,4-(HO) ₂ C ₆ H ₃ (-) | 2191, 571 |
| | 3,4-(HO) ₂ C ₆ H ₃ CHO | .. | C, R = 3,4-(HO) ₂ C ₆ H ₃ (100) | 2192 |
| | 3,4-(CH ₂ O) ₂ -6-O ₂ NC ₆ H ₂ CHO | (CH ₃ CO) ₂ O | C, R = 3,4-(CH ₂ O) ₂ -6-O ₂ NC ₆ H ₂ (19) | 2188 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOH | C, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (100) | 2192 |
| | 2-HO-4-CH ₂ OC ₆ H ₃ CHO | KOH | C, R = 2-HO-4-CH ₂ OC ₆ H ₃ (-) | 2192 |
| | 3-CH ₃ O-4-HOC ₆ H ₃ CHO | NaOH | C, R = 3-CH ₃ O-4-HOC ₆ H ₃ (-) | 2192 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|--|----------------------------|
|  (contd.) | 3,4-(CH ₂ O) ₂ -6-O ₂ NC ₆ H ₂ CHO 2,4-(CH ₂ O) ₂ C ₆ H ₃ CHO 4-(CH ₃) ₂ NC ₆ H ₄ CHO | (CH ₃ CO) ₂ O KOH NaOH | C, R = 3,4-(CH ₂ O) ₂ -6-O ₂ NC ₆ H ₂ (-) C, R = 2,4-(CH ₂ O) ₂ C ₆ H ₃ (-) C, R = 4-(CH ₃) ₂ NC ₆ H ₄ (100) | 2188 2191 2192, 2345 |
|  |  | (CH ₂) ₂ NH, CH ₃ CO ₂ H |  (41) | 363 |
| |  | .. |  (75) | 363 |
| |  | .. |  (62) | 363 |
| 4-ClC ₆ H ₄ COC ₂ H ₅ | 4-CH ₂ OC ₆ H ₄ CHO | Na ₂ CO ₃ | 4-ClC ₆ H ₄ COC(CH ₃)=CHR (-) | 2194 |
| 2-HO-4-O ₂ NC ₆ H ₃ - COC ₂ H ₅ |  | NaOH | 2-HO-4-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |
| | 4-ClC ₆ H ₄ CHO | .. | 2-HO-4-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |
| | C ₆ H ₅ CHO | .. | 2-HO-4-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |
| 2-HO-5-O ₂ NC ₆ H ₃ - COC ₂ H ₅ |  | .. | 2-HO-5-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |
| | 4-ClC ₆ H ₄ CHO | .. | 2-HO-5-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |
| | C ₆ H ₅ CHO | .. | 2-HO-5-O ₂ NC ₆ H ₃ COC(CH ₃)=CHR (-) | 2193 |

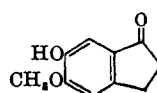
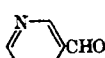
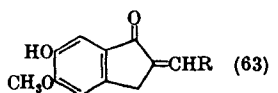
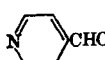
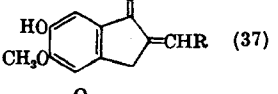
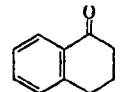
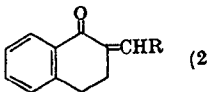
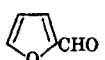
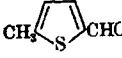
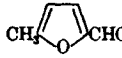
| | | | | |
|---|---|--|---|-------------------------|
| $C_6H_5COC_2H_5$ | CH_2O | Ion-exchange resin Amberlite IRA-400 | $C_6H_5COCH(CH_3)CH_2OH$ (40) | 337, 336, 2195, 2196 |
| | $C(Cl_2)=CClCHO$ $i-C_3H_7CHO$ | HCl $C_6H_5N(CH_3)-MgBr$ | $C_6H_5COC(CH_3)=CHR$ (77) $C_6H_5COCH(CH_3)CHOHR$ (88) | 637 177 |
| |  | NaOH | $C_6H_5COCH(CH_3)C(O)HR$ (40) | 545 |
| | C_6H_5CHO | $C_6H_5N(CH_3)-MgBr$ | $C_6H_5COCH(CH_3)CHOHR$ (—) | 177 |
| | .. | HCl | $C_6H_5COC(CH_3)=CHR$ (96) | 342-345 |
| | $C_6H_4(CHO)_2$, 1,4 | KOH | $C_6H_4[CH=C(CH_3)COC_6H_5]_2$, 1,4 (13) | 544 |
| | $4-CH_3OC_6H_4CHO$ | Na_2CO_3 | $C_6H_5COC(CH_3)=CHR$ (—) | 2194 |
|  | $2-O_2NC_6H_4CHO$ | $(CH_3CO)_2O$ |  (36) | 2188 |
| | $2-HOC_6H_4CHO$ | KOH | D, R = $2-O_2NC_6H_4$ | |
| | $3,4-(CH_3O)_2-6-O_2NC_6H_2CHO$ | $(CH_3CO)_2O$ | D, R = $2-HOC_6H_4$ (Good) | 2191 |
| | $3,4-(CH_3O)_2-6-O_2NC_6H_2CHO$ | " | D, R = $3,4-(CH_3O)_2-6-O_2NC_6H_2$ (34) | 2188 |
| | $(CH_3)_2NC_6H_4CHO$ | KOH | D, R = $3,4-(CH_3O)_2-6-O_2NC_6H_2$ (—) | 2188 |
| | | | D, R = $(CH_3)_2NC_6H_4$ (—) | 2197 |
|  | $C(Cl_2)=CClCHO$ | BF_3 |  (70) | 289, 2345 |
|  |  | $(CH_3)_2NH$ CH_3CO_2H |  (50) | 363 |

Note: References 668-2359 are on pp. 403-438.

THE ALDOL CONDENSATION

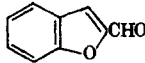
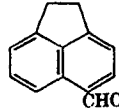
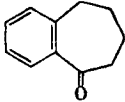
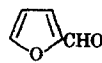
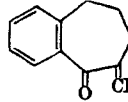
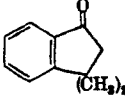
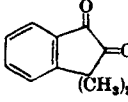
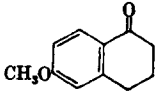
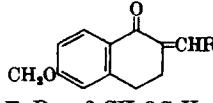
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TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|-----------------------------|---|-----------------------------------|
|  | (cont'd.)  | $(CH_3)_2NH$ CH_3CO_2H |  (63) | 363 |
| |  | " |  (37) | 363 |
|  | CH_2O | NaOH |  (21) E, R = H | 1822, 550, 2198 |
| | $C(Cl_2)=CClCHO$ $C(Cl_2)=CHCHO$ | H_2SO_4 HCl | E, R = $C(Cl_2)=CCl$ (81) E, R = $C(Cl_2)=CH$ (70) | 639, 289 638 |
| |  | NaOH | E, R = $2-(C_4H_5O)$ (—) | 2199 |
| |  | " | E, R = $2-(CH_2C_4H_4S)$ (—) | 1988 |
| |  | " | E, R = $2-(CH_2C_4H_4O)$ (—) | 1988 |
| | $2-O_2NC_6H_4CHO$ | $NaNH_2$ | E, R = $2-O_2NC_6H_4$ (12) | 643 |
| | .. | H_2SO_4 | E, R = $2-O_2NC_6H_4$ (85) | 643, 642 |
| | C_6H_5CHO | KOH | E, R = C_6H_5 (88) | 2200, 301, 1894, 2201, 2348 |
| | $2-CH_3C_6H_4CHO$ | " | E, R = $2-CH_3C_6H_4$ (98) | 301 |

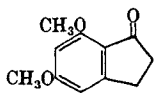
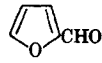
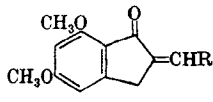
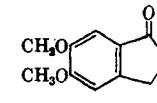
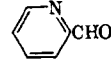
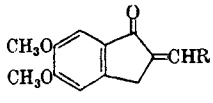
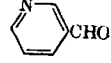
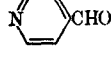
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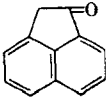

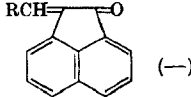
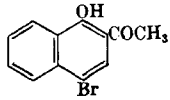
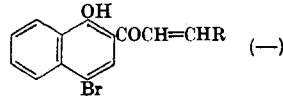
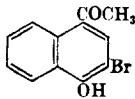
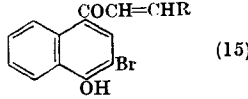
ORGANIC REACTIONS

| | | | | |
|--|---|---|---|----------------------------|
|  | NaOH | E, R = 2-(C ₆ H ₅ O) (95) | 1854 | |
| 2,4,6-(CH ₃) ₃ C ₆ H ₃ CHO | KOH | E, R = 2,4,6-(CH ₃) ₃ C ₆ H ₃ (85) | 301 | |
|  | .. | E, R = 5-C ₁₂ H ₉ (60) | 2202 | |
| 4-ClC ₆ H ₄ COC ₂ H ₅ - <i>n</i> C ₆ H ₅ COC ₂ H ₅ - <i>n</i> | Pyrene-1-carboxaldehyde CH ₂ O C(Cl ₂)=CClCHO CH ₃ (CH ₂) ₄ CHO | .. K ₂ CO ₃ HCl C ₆ H ₅ N(CH ₃) MgBr Na ₂ CO ₃ | E, R = 1-C ₁₄ H ₉ (90) 4-ClC ₆ H ₄ COC(CH ₂ OH)(CH ₃) ₂ (55) C ₆ H ₅ COC(C ₂ H ₅)=CHR (78) C ₆ H ₅ COCH(C ₆ H ₅)CHOHR (40) | 2202 2203 637 177 |
| 4-CH ₃ OC ₆ H ₄ COC ₂ H ₅ | 4-CH ₃ OC ₆ H ₄ CHO | Na ₂ CO ₃ | 4-CH ₃ OC ₆ H ₄ COC(CH ₃)=CHR (-) | 2194 |
|  |  | KOH |  (98) | 1848 |
|  | C ₆ H ₅ CHO | NaOH |  (-) | 2204, 2205 |
|  | 2-CH ₃ OC ₆ H ₄ CHO | NaOC ₆ H ₅ |  (-) | 2206 |
| | 3-CH ₃ OC ₆ H ₄ CHO | .. | F, R = 2-CH ₃ OC ₆ H ₄ | |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | F, R = 3-CH ₃ OC ₆ H ₄ (-) F, R = 4-CH ₃ OC ₆ H ₄ (-) | 2206 2206 |

Note: References 668-2359 are on pp. 403-438.

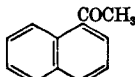


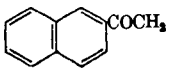
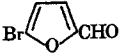


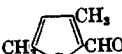
TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

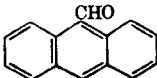
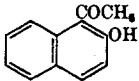
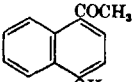
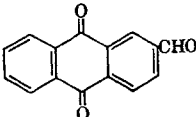
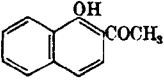
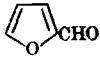
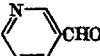
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--|--|-----------|
|  |  | NaOH |  (-) | 2207 |
|  |  | (CH ₂) ₅ NH, CH ₃ CO ₂ H |  (67) | 363 |
| |  | .. | G, R = 2-(C ₅ H ₄ N) | 363 |
| |  | .. | G, R = 3-(C ₅ H ₄ N) (82) | 363 |
| | | | G, R = 4-(C ₅ H ₄ N) (55) | 363 |
| | 2-O ₂ NC ₆ H ₄ CHO | (CH ₃ CO) ₂ O | G, R = 2-O ₂ NC ₆ H ₄ (37) | 2188 |
| | C ₆ H ₅ CHO | KOH | G, R = C ₆ H ₅ (Good) | 2191 |
| | 2-HOC ₆ H ₄ CHO | .. | G, R = 2-HOC ₆ H ₄ (100) | 2191, 571 |
| | 2,4-(HO) ₂ C ₆ H ₃ CHO | HCl | G, R = 2,4-(HO) ₂ C ₆ H ₃ (-) | 2191, 571 |
| | 3,4-(CH ₃ O) ₂ -6-O ₂ NC ₆ H ₂ CHO | (CH ₃ CO) ₂ O | G, R = 3,4-(CH ₃ O) ₂ -6-O ₂ NC ₆ H ₂ (-) | 2188 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | G, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (-) | 2191 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | G, R = 2-CH ₃ OC ₆ H ₄ (Good) | 2191 |
| | 3,4-(CH ₃ O) ₂ -6-O ₂ NC ₆ H ₂ CHO | (CH ₃ CO) ₂ O | G, R = 3,4-(CH ₃ O) ₂ -6-O ₂ NC ₆ H ₂ (36) | 2188 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | KOH | G, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (Good) | 2191 |
| C ₆ H ₅ COC ₂ H ₅ - <i>n</i> | CH ₃ CHO | C ₆ H ₅ N(CH ₃) MgBr | C ₆ H ₅ COCH(C ₂ H ₅ - <i>n</i>)CHOHR (50) | 177 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ - COC ₂ H ₅ | 4-CH ₃ OC ₆ H ₄ CHO | Na ₂ CO ₃ | 2,4-(CH ₃ O) ₂ C ₆ H ₃ COC(CH ₃)=CHR (-) | 2194 |
| 4-CH ₃ OC ₆ H ₄ COC ₂ H ₅ - <i>n</i> | 4-CH ₃ OC ₆ H ₄ CHO | HCl | 4-CH ₃ OC ₆ H ₄ COC(C ₂ H ₅)=CHR (-) | 2102 |
| 4-CH ₃ OC ₆ H ₄ COC ₂ H ₅ - <i>i</i> | CH ₂ O | K ₂ CO ₃ | 4-CH ₃ OC ₆ H ₄ COC(CH ₂ OH)(CH ₃) ₂ (17) | 2203 |

| | | | | |
|---|---|------|--|------------|
|  |  | NaOH |  | 1801, 2208 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | H, R = 2-(C ₄ H ₃ O) | |
| | 4-CH ₂ OC ₆ H ₄ CHO | .. | H, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (-) | 2208 |
| | 3-CH ₂ O-4-HOC ₆ H ₃ CHO | .. | H, R = 4-CH ₂ OC ₆ H ₄ (-) | 2208 |
| | C ₆ H ₅ CH=CHCHO | .. | H, R = 3-CH ₂ O-4-HOC ₆ H ₃ (-) | 2208 |
| | 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | H, R = C ₆ H ₅ CH=CH (-) | 2208 |
| | | | H, R = 4-(CH ₃) ₂ NC ₆ H ₄ (-) | 2208 |
|  | 2-HO-5-BrC ₆ H ₃ CHO | .. |  | 1993 |
| | C ₆ H ₅ CHO | .. | I, R = 2-HO-5-BrC ₆ H ₃ | |
| | 2-HOC ₆ H ₄ CHO | .. | I, R = C ₆ H ₅ (-) | 2209 |
| | 4-CH ₂ OC ₆ H ₄ CHO | .. | I, R = 2-HOC ₆ H ₄ (-) | 1993 |
| | | | I, R = 4-CH ₂ OC ₆ H ₄ (-) | 2210 |
|  | 2-HO-5-BrC ₆ H ₃ CHO | .. |  | 1993 |
| | C ₆ H ₅ CHO | .. | J, R = C ₆ H ₅ | |
| | 2-HOC ₆ H ₄ CHO | .. | J, R = 2-HOC ₆ H ₄ (18) | 2211 |
| | 3-HOC ₆ H ₄ CHO | .. | J, R = 3-HOC ₆ H ₄ (18) | 2211 |
| | 4-HOC ₆ H ₄ CHO | .. | J, R = 4-HOC ₆ H ₄ (18) | 2211 |
| | 4-CH ₂ OC ₆ H ₄ CHO | .. | J, R = 4-CH ₂ OC ₆ H ₄ (18) | 2211 |

Note: References 668-2359 are on pp. 403-438.

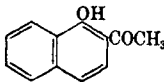
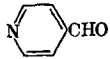
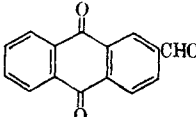
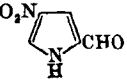
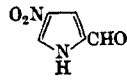
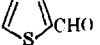
TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES OTHER THAN ACETOPHENONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)






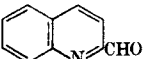
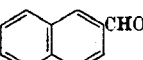


| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|----------------------------------|---|------------|
|  |  | NaOC ₂ H ₅ | 1-C ₁₀ H ₇ COCH=CHR (45) | 1823, 1845 |
| |  | .. | 1-C ₁₀ H ₇ COCH=CHR (68) | 1823, 1860 |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOH | 1-C ₁₀ H ₇ COCH=CHR (-) | 1791 |
| | C ₆ H ₅ CHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 2212 |
| | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 1744, 2212 |
| | 4-CH ₂ C ₆ H ₄ CHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 2212 |
| | 4-CH ₂ OC ₆ H ₄ CHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 2212 |
| | C ₆ H ₅ CH=CHCHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 1791 |
| | 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | .. | 1-C ₁₀ H ₇ COCH=CHR (-) | 2212 |
| | 9-Formyl-3,4-benzacridine | .. | 1-C ₁₀ H ₇ COCH=CHR (75-95) | 372 |
| | 10-Formyl-1,2-benzanthracene | .. | 1-C ₁₀ H ₇ COCH=CHR (75-95) | 372 |
|  | C(Cl) ₃ =CHCHO | BaO | 2-C ₁₀ H ₇ COCH=CHR (25) | 1908 |
| |  | NaOH | 2-C ₁₀ H ₇ COCH=CHR (-) | 1644 |
| |  | NaOC ₂ H ₅ | 2-C ₁₀ H ₇ COCH=CHR (57) | 1823, 1845 |
| |  | .. | 2-C ₁₀ H ₇ COCH=CHR (85) | 1823, 1860 |
| | 4-FC ₆ H ₄ CHO | NaOH | 2-C ₁₀ H ₇ COCH=CHR (-) | 1995 |
| | C ₆ H ₅ CHO | .. | 2-C ₁₀ H ₇ COCH=CHR (-) | 2212 |
| |  | .. | 2-C ₁₀ H ₇ COCH=CHR (-) | 2017 |

| | | | | |
|---|---|----------------------------------|--|------|
| | 3- <i>i</i> -C ₂ H ₇ -4-CH ₃ O-6-CH ₃ C ₆ H ₄ CHO | .. | 2-C ₁₀ H ₇ COCH=CHR (75) | 2105 |
| |  | HCl | 2-C ₁₀ H ₇ COCH=CHR (80) | 1978 |
| | Pyrene-3-carboxaldehyde | NaOC ₂ H ₅ | 2-C ₁₀ H ₇ COCH=CHR (100) | 1615 |
| | 9-Formyl-3,4-benzacridine | NaOH | 2-C ₁₀ H ₇ COCH=CHR (75-95) | 372 |
| | 10-Formyl-1,2-benzanthracene | .. | 2-C ₁₀ H ₇ COCH=CHR (75-95) | 372 |
|  | 2-HO-5-BrC ₆ H ₄ CHO | .. | 2-HOC ₁₀ H ₆ COCH=CHR-1 (80) | 1993 |
|  | 2-ClC ₆ H ₄ CHO | KOH | 4-HOC ₁₀ H ₆ COCH=CHR-1 (78) | 2213 |
| | 3-ClC ₆ H ₄ CHO | .. | 4-HOC ₁₀ H ₆ COCH=CHR-1 (72) | 2213 |
| | 4-ClC ₆ H ₄ CHO | .. | 4-HOC ₁₀ H ₆ COCH=CHR-1 (76) | 2213 |
| | 2-HOC ₆ H ₄ CHO | .. | 4-HOC ₁₀ H ₆ COCH=CHR-1 (62) | 2213 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | 4-HOC ₁₀ H ₆ COCH=CHR-1 (81) | 2213 |
| |  | NaOH | 4-HOC ₁₀ H ₆ COCH=CHR-1 (-) | 1977 |
|  |  | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 2214 |
| |  | KOH | 1-HOC ₁₀ H ₆ COCH=CHR-3 (71) | 371 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

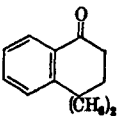
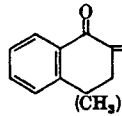
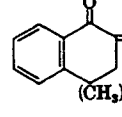
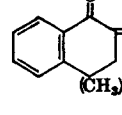
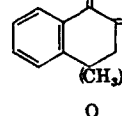
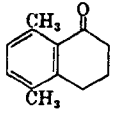
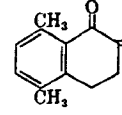
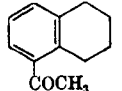
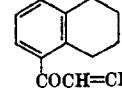
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|----------|---|------------------|
|  | (<i>contd.</i>)  | KOH | 1-HOC ₁₀ H ₆ COCH=CHR-2 (73) | 370 |
| | 2-HO-5-BrC ₆ H ₄ CHO | NaOH | 1-HOC ₁₀ H ₆ COCH=CHR-2 (60) | 1993 |
| | C ₆ H ₅ CHO | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 2215, 1929, 2044 |
| | 2-HOC ₆ H ₄ CHO | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (60) | 1993 |
| | 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 2215, 1929, 2044 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 1929, 2044, 2216 |
| | 4-C ₂ H ₅ OC ₆ H ₄ CHO | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 2214 |
| |  | .. | 1-HOC ₁₀ H ₆ COCH=CHR-2 (-) | 1977 |
| Acetylferrocene |  | .. | C ₅ H ₅ FeC ₅ H ₄ COCH=CHR (15) | 1975 |
| |  | .. | C ₅ H ₅ FeC ₅ H ₄ COCH=CHR (16) | 1975 |
| |  | .. | C ₅ H ₅ FeC ₅ H ₄ COCH=CHR (75) | 1975 |

| | | | | |
|--|---------------------------------------|-------------------------------|--|------|
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (65) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (19) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (50) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (44) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (32) | 1975 | |
| 4-ClC ₆ H ₄ CHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (50) | 1975 | |
| 4-O ₂ NC ₆ H ₄ CHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (50) | 1975 | |
| C ₆ H ₅ CHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (83) | 1975, 2217, 2218 | |
| 4-NCC ₆ H ₄ CHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (40) | 1975 | |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (30) | 1975 | |
| C ₆ H ₅ CH=CHCHO | .. | $C_5H_5FeC_5H_4COCH=CHR$ (40) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (22) | 1975 | |
|  | .. | $C_5H_5FeC_5H_4COCH=CHR$ (35) | 1975 | |
| Ferrocenecarboxaldehyde | .. | $C_5H_5FeC_5H_4COCH=CHR$ (44) | 1975 | |
| C ₆ H ₅ CO  | 4-ClC ₆ H ₄ CHO | NaOCH ₃ | C ₆ H ₅ CO  =CHR (47) | 2219 |

Note: References 668-2359 are on pp. 403-438.

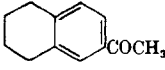
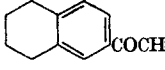
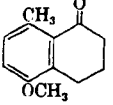
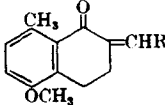
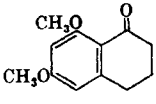

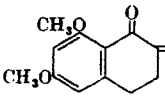
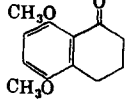
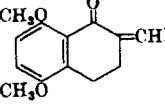
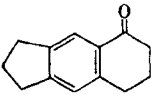
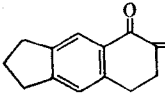
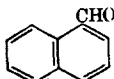
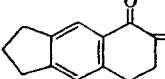
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TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|---|-----------|
|  | 4-Cl-2-O ₂ NC ₆ H ₄ CHO | CH ₃ CO ₂ H, H ₂ O, Fe, 100° |  (90) | 645 |
| | 2-O ₂ N-5-ClC ₆ H ₄ CHO | .. |  (94) | 645 |
| | 2-O ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ , CH ₃ CO ₂ H |  (94) | 642 |
| | C ₆ H ₅ CHO | KOH |  (76) | 643, 2205 |
|  | 2-O ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ , CH ₃ CO ₂ H |  (48) | 644 |
|  | C ₆ H ₅ CHO | NaOH |  (77) | 2220 |

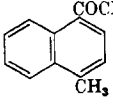
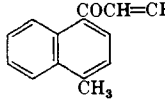
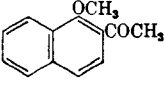
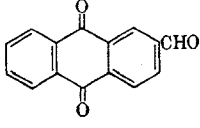
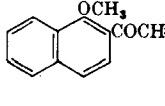
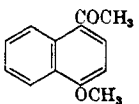
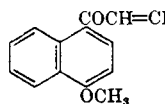
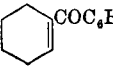
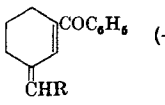
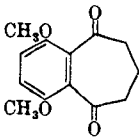
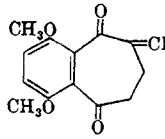
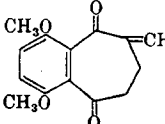
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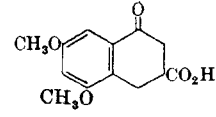
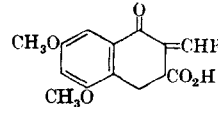
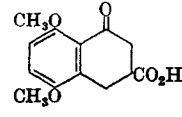
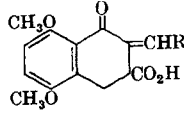
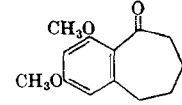

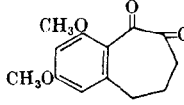
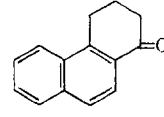
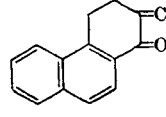
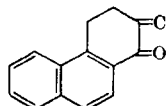
ORGANIC REACTIONS

| | | | | |
|---|--|----------------------------------|---|------|
|  | 3- <i>i</i> -C ₆ H ₄ -4-CH ₃ O-6-CH ₃ -C ₆ H ₄ CHO | .. |  COCH=CHR (75) | 2105 |
|  | 2-OHCC ₆ H ₄ CHO | KOH |  CHR (-) | 2221 |
|  |  CHO | NaOH |  CHR (54) | 2207 |
|  | 2-HO ₂ CC ₆ H ₄ CHO | KOH |  CHR (65) | 2221 |
| 2-HO-5-(C ₂ H ₅ CONH)-C ₆ H ₄ COC ₂ H ₅ | 4-O ₂ NC ₆ H ₄ CHO | .. | 2-HO-5-(C ₂ H ₅ CONH)C ₆ H ₄ -COC(CH ₃)=CHR (-) | 2222 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₂ -COC ₂ H ₅ | CH ₂ O | K ₂ CO ₃ | 2,4,6-(CH ₃) ₃ COC ₆ H ₂ -COC(CH ₃)=CHR (70) | 2150 |
| | 2,4,6-(CH ₃) ₃ C ₆ H ₂ CHO | NaOC ₂ H ₅ | 2,4,6-(CH ₃) ₃ COC ₆ H ₂ -COC(CH ₃)=CHR (51) | 2154 |
|  | C ₆ H ₅ CHO | KOH |  CHR (60) | 2223 |
| |  | .. |  CHR (60) | 2223 |

Note: References 668-2359 are on pp. 403-438.

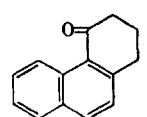
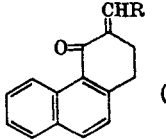
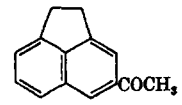
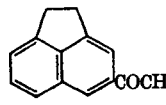
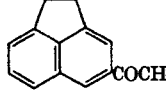
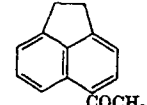
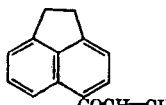
TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES OTHER THAN ACETOPHENONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

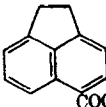
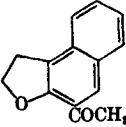
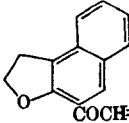
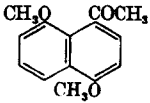

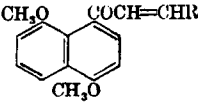
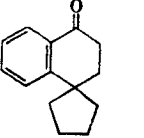
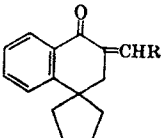
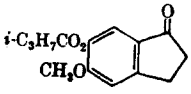
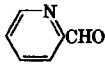
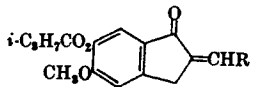
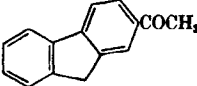
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|----------------------------------|--|-------|
|  | 2-O ₂ NC ₆ H ₄ CHO | HCl |  COCH=CHR (-) | 1936 |
|  |  | NaOH |  COCH=CHR (-) | 1977 |
|  | .. | .. |  COCH=CHR (-) | 1977 |
|  | C ₆ H ₅ CHO | NaOC ₂ H ₅ |  COC ₂ H ₅ (-) | 316 |
|  | CH ₂ CHO | HCl |  CHR (63) | 2224 |
| | C ₆ H ₅ CHO | .. |  CHR (58) | 2224 |

| | | | | |
|---|---|--------------------------------|--|------|
|  | 2-Cl-5-CH ₃ OC ₆ H ₃ CHO | KOH |  (44) | 2225 |
|  | 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " |  (50) | 2225 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₂ -COCH=CHCH ₃ | 4-ClC ₆ H ₄ CHO | NaOH | 2,4,6-(CH ₃) ₃ C ₆ H ₂ CO(CH=CH) ₂ R (45) | 2226 |
|  |  | " |  (—) | 2207 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₂ -COC ₂ H ₅ | CH ₂ O | K ₂ CO ₃ | 2,4,6-(CH ₃) ₃ C ₆ H ₂ COC(CH ₃) ₂ -CH ₂ OH (40) | 2150 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₂ -COCH ₂ CH ₂ OCH ₃ | " | " | 2,4,6-(CH ₃) ₃ C ₆ H ₂ -COC(CH ₂ OCH ₃)=CH ₂ (65) | 519 |
|  | Pyrene-1-carboxaldehyde | KOH |  (60) | 2202 |
| | Phenanthrene-9-carboxaldehyde | " |  (—) | 362 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES OTHER THAN ACETOPHENONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

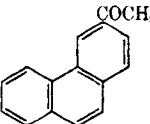
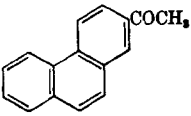
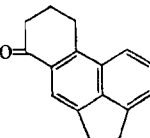
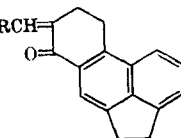
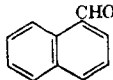
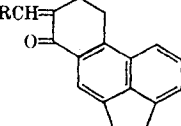
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|------------------------------------|--|---------------------|
|  | Pyrene-1-carboxaldehyde | KOH |  (—) | 2202 |
| C ₆ H ₅ COCH ₂ C ₆ H ₅ | C(Cl) ₂ =CClCHO | H ₂ SO ₄ | C ₆ H ₅ COC(C ₆ H ₅)CHOHR (31) | 289 |
| | 2-ClC ₆ H ₄ CHO | HCl | C ₆ H ₅ COC(C ₆ H ₅)=CHR (—) | 2227 |
| | 4-O ₂ NC ₆ H ₄ CHO | NaOH | C ₆ H ₅ COC(C ₆ H ₅)CHOHR (epimers) | 64, 2188 |
| | C ₆ H ₅ CHO | (CH ₃) ₂ NH | C ₆ H ₅ COC(C ₆ H ₅)=CHR (77) | 597, 548, 2228-2232 |
| | 4-CH ₃ C ₆ H ₄ CHO | HCl | C ₆ H ₅ COC(C ₆ H ₅)=CHR (—) | 2227 |
| | 4-CH ₃ OC ₆ H ₄ CHO | " | C ₆ H ₅ COC(C ₆ H ₅)=CHR (—) | 2227 |
| | 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | " | C ₆ H ₅ COC(C ₆ H ₅)=CHR (—) | 2227 |
| | 4- <i>i</i> -C ₂ H ₅ C ₆ H ₄ CHO | " | C ₆ H ₅ COC(C ₆ H ₅)=CHR (—) | 2227 |
|  | 9-Formyl-3,4-benzacridine | NaOH |  (75-95) | 372 |
| | 10-Formyl-1,2-benzanthracene | " |  (75-95) | 372 |
|  | 2-ClC ₆ H ₄ CHO | — |  (—) | 2233 |

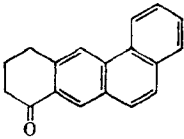
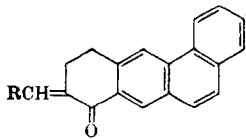
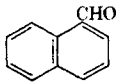
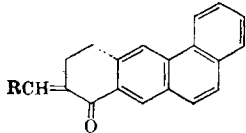
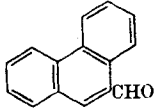
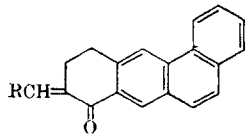
| | | | | |
|---|---|-------------------------------|--|------|
| | 9-Formyl-3,4-benzacridine | NaOH |  (75-95) | 372 |
|  | C_6H_5CHO | KOH |  (—) | 2234 |
| bis-Acetylferrocene | " | NaOH | $C_{10}H_8Fe(COCH=CHR)_2$ (75) | 2235 |
|  |  | " |  (—) | 1829 |
|  | 2- $O_2NC_6H_4CHO$ | H_2SO_4 , CH_3CO_2H |  (84) | 644 |
|  |  | $(CH_3)_2NH$, CH_3CO_2H |  (59) | 363 |
|  | CH_2O | KOH | Polymer (—) | 2236 |

Note: References 668-2359 are on pp. 403-438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES OTHER THAN ACETOPHENONES (Continued)

(R in the product is the group R in the aldehyde RCHO.)

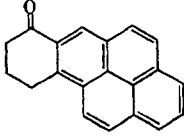
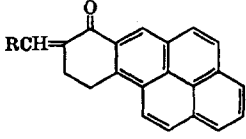
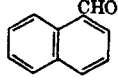
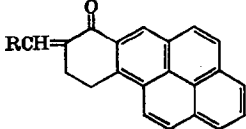
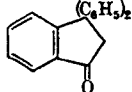
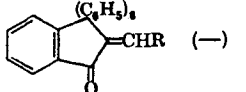
| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|--------------|---|-------|
|  | C_6H_5CHO | HCl | 3- $C_{14}H_9COCH=CHR$ (60) | 2238 |
|  | 4- $O_2NC_6H_4CHO$ | " | 2- $C_{14}H_9COCH=CHR$ (60) | 2238 |
| 4- $(CH_3)_2NC_6H_4CH_2-$ COC $_6H_5$ | C_6H_5CHO | " | 2- $C_{14}H_9COCH=CHR$ (60) | 2238 |
| 4- $(CH_3)_2NC_6H_4COCH_2-$ C $_6H_5$ | CH_2O | $(CH_2)_2NH$ | 4- $(CH_3)_2NC_6H_4CH(CH_2OH)COC_6H_5$ (80) | 598 |
| | " | " | 4- $(CH_3)_2NC_6H_4COCH(CH_2OH)C_6H_5$ (60) | 598 |
|  | C_6H_5CHO | KOH |  (70) | 2202 |
| |  | " |  (65) | 2202 |

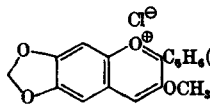
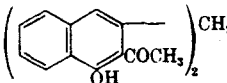
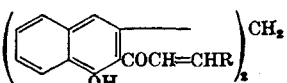
| | | | | |
|--|--|--|---|--|
| $C_6H_5COCH_2COCH_2C_6H_5$ 2,4,6-(CH_3) ₃ C_6H_2 - $CH_2COC_6H_5$ 2,4,6-(CH_3) ₃ C_6H_2 - $COCH_2C_6H_5$ | 2-HOC ₆ H ₄ CHO CH ₂ O 4-ClC ₆ H ₄ CHO C ₆ H ₅ CHO | (CH_2) ₅ NH K ₂ CO ₃ NaOH .. | $C_6H_5COCH_2COC(C_6H_5)=CHR$ (63) 2237 2,4,6-(CH_3) ₃ $C_6H_2C(=CH_2)COC_6H_5$ (80) 2239 2,4,6-(CH_3) ₃ $C_6H_2COC(C_6H_5)=CHR$ (83) 2240 2,4,6-(CH_3) ₃ $C_6H_2COC(C_6H_5)=CHR$ (82) 2241 | |
|  | C ₆ H ₅ CHO | KOH |  (70) 362 | |
|  | CHO | .. |  (—) 362 | |
|  | CHO | .. |  (—) 362 | |
| 2,4,6-(CH_3) ₃ $C_6H_2COCH_2$ - CH ₂ C ₆ H ₅ 2,3,5,6-(CH_3) ₄ C ₆ HCOCH ₂ - C ₆ H ₅ (C ₆ H ₅ COCH ₂ CH ₂) ₂ | 4-ClC ₆ H ₄ CHO .. C ₆ H ₅ CHO .. | NaOH NaOCH ₃ | 2,4,6-(CH_3) ₃ C_6H_2 - COC(CH ₂ C ₆ H ₅)=CHR (—) 2242 2,3,5,6-(CH_3) ₄ C ₆ HCOC(C ₆ H ₅)=CHR (81) 2240 2,3,5,6-(CH_3) ₄ C ₆ HCOC(C ₆ H ₅)=CHR (70) 2240 [C ₆ H ₅ COC(=CHR)CH ₂] ₂ (—) 2243 | |

Note: References 668–2359 are on pp. 403–438.

TABLE XVIII. CONDENSATION OF ALDEHYDES WITH CARBOCYCLIC AROMATIC KETONES
OTHER THAN ACETOPHENONES (Continued)



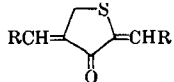
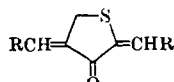

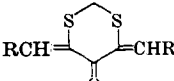


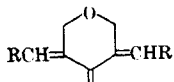
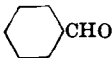

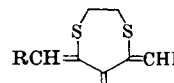

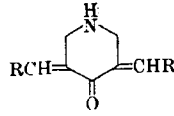


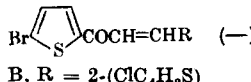
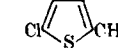

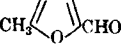
(R in the product is the group R in the aldehyde RCHO.)

| Ketone | Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---------------------------------------|--------------------------------|---|-------|
|  | C ₆ H ₅ CHO | KOH |  (80) 2202 | |
|  | CHO | .. |  (—) 2202 | |
| 2,4,6-(CH_3) ₃ $C_6H_2CH_2$ - COC ₆ H ₄ (CH_3) ₂ -2,4,6 | CH ₂ O | K ₂ CO ₃ | 2,4,6-(CH_3) ₃ $C_6H_2C(CH_3)=$ C(OH)C ₆ H ₄ (CH_3) ₂ -2,4,6 (50) 2244 | |
|  | 2-ClC ₆ H ₄ CHO | NaOH |  (—) 2247 | |
| | | | K, R = 2-ClC ₆ H ₄ (<i>cis</i> and <i>trans</i>) | |

| | | | | |
|---|---|--------------------------------|--|-----------|
| | 4-ClC ₆ H ₄ CHO | .. | K, R = 4-ClC ₆ H ₄ (-) | 2247 |
| | C ₆ H ₅ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = C ₆ H ₅ (-) | 2247 |
| | 2-CH ₃ C ₆ H ₄ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = 2-CH ₃ C ₆ H ₄ (-) | 2247 |
| | 3-CH ₃ C ₆ H ₄ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = 3-CH ₃ C ₆ H ₄ (-) | 2247 |
| | 2-CH ₃ OC ₆ H ₄ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = 2-CH ₃ OC ₆ H ₄ (-) | 2247 |
| | 4-CH ₃ OC ₆ H ₄ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = 4-CH ₃ OC ₆ H ₄ (-) | 2247 |
| | 2-C ₂ H ₅ OC ₆ H ₄ CHO | .. | (<i>cis</i> and <i>trans</i>) K, R = 2-C ₂ H ₅ OC ₆ H ₄ (-) | 2247 |
| 2,4-(C ₆ H ₅ CH ₂ O) ₂ C ₆ H ₃ - COCH ₂ OCH ₃ | 2-HO-4,5-(CH ₂ O) ₂ C ₆ H ₂ CHO | HCl |  C ₆ H ₃ (OCH ₂ C ₆ H ₅) ₂ -2,4 | (-) 2245 |
| 2,4,6-(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₂ - CH ₂ COC ₆ H ₅ | CH ₂ O | K ₂ CO ₃ | 2,4,6-(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₂ C(COC ₆ H ₅)=CHR | (96) 2239 |
| | C ₆ H ₅ CHO | NaOH | 2,4,6-(<i>i</i> -C ₃ H ₇) ₂ C ₆ H ₂ C(COC ₆ H ₅)=CHR | (70) 2240 |
|  (CH ₂) ₂ | 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. |  (CH ₂) ₂ | (75) 2246 |

Note: References 668-2359 are on pp. 403-438.

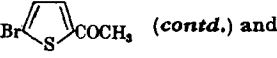
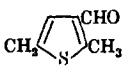
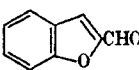

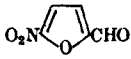
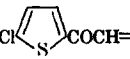


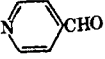
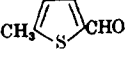
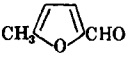
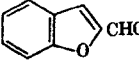
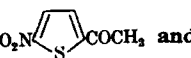
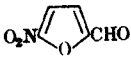
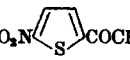

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|-------------------------------|---|--------------------|
|  and  | NaOH |  (99) | 2248 |
| C_6H_5CHO | " |  (46) | 2248 |
|  and C_6H_5CHO | $(CH_2)_5NH$ |  (78) | 2249 |
|  and  | NaOH |  (92) | 2250 |
| $4-O_2NC_6H_4CHO$ | $(CH_2)_5NH$, CH_3CO_2H | A, R = $2-(C_6H_5O)$ | 599 |
| C_6H_5CHO | NaOH | A, R = C_6H_5 (70) | 2250, 599, 2251 |
|  | " | A, R = C_6H_{11} (—) | 2250 |
| $3,4-(CH_2O)_2C_6H_3CHO$ | $(CH_2)_5NH$, CH_3CO_2H | A, R = $3,4-(CH_2O)_2C_6H_3$ (55) | 599 |
| $3-CH_2C_6H_4CHO$ | " | A, R = $3-CH_2C_6H_4$ (33) | 599 |
| $4-CH_2C_6H_4CHO$ | " | A, R = $4-CH_2C_6H_4$ (50) | 599, 2250 |
| $4-CH_2OC_6H_4CHO$ | " | A, R = $4-CH_2OC_6H_4$ (42) | 599, 2251 |
| $C_6H_5CH=CHCHO$ | NaOH | A, R = $C_6H_5CH=CH$ (65) | 2250, 2251 |
| $4-C_2H_5OC_6H_4CHO$ | $(CH_2)_5NH$, CH_3CO_2H | A, R = $4-C_2H_5OC_6H_4$ (56) | 599 |
| $2,3-(CH_3O)_2C_6H_3CHO$ | " | A, R = $2,3-(CH_3O)_2C_6H_3$ (50) | 599 |
| $3,4-(CH_3O)_2C_6H_3CHO$ | " | A, R = $3,4-(CH_3O)_2C_6H_3$ (58) | 599 |
| $4-(CH_3)_2NC_6H_4CHO$ | " | A, R = $4-(CH_3)_2NC_6H_4$ (42) | 599 |
| $4-i-C_3H_7C_6H_4CHO$ | " | A, R = $4-i-C_3H_7C_6H_4$ (69) | 599 |
| $1-C_{10}H_7CHO$ | " | A, R = $1-C_{10}H_7$ (58) | 599 |
|  and C_6H_5CHO | $(CH_2)_5NH$ |  (92) | 2249 |
|  and C_6H_5CHO | HCl, CH_3CO_2H |  (58) | 2252, 2253 |
|  and  | NaOH |  (—) | 2017 |
|  | " | B, R = $2-(ClC_4H_2S)$ | 2017 |
|  | " | B, R = $2-(C_4H_3O)$ (—) | 2017 |
|  | " | B, R = $2-(CH_3C_4H_2O)$ (—) | 1988 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)

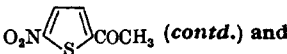
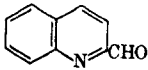
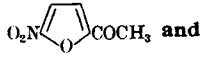
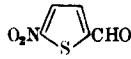
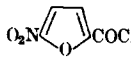

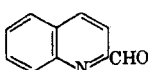
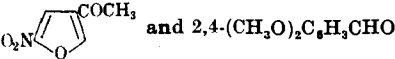
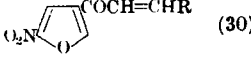
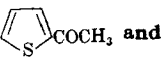
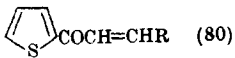
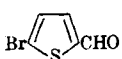
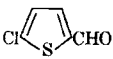
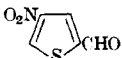
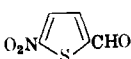
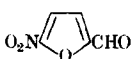
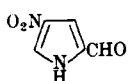
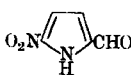
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|---|------------|
| Br  (contd.) and | | | |
| 3,4-Cl ₂ C ₆ H ₃ CHO | NaOH | B, R = 3,4-Cl ₂ C ₆ H ₃ (-) | 2017 |
| 4-ClC ₆ H ₄ CHO | .. | B, R = 4-ClC ₆ H ₄ (-) | 2017 |
| 4-FC ₆ H ₄ CHO | .. | B, R = 4-FC ₆ H ₄ (-) | 2017 |
| C ₆ H ₅ CHO | .. | B, R = C ₆ H ₅ (-) | 2017 |
|  | .. | B, R = 3-[(CH ₃) ₂ C ₄ HS] (-) | 2017 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | B, R = 4-CH ₃ OC ₆ H ₄ (-) | 2017 |
|  | .. | B, R = 2-(C ₆ H ₅ O) (75-95) | 1854 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | B, R = 4-(CH ₃) ₂ NC ₆ H ₄ (-) | 2017 |
| 1-C ₁₀ H ₇ CHO | .. | B, R = 1-C ₁₀ H ₇ (-) | 2017 |
| Cl  and | | | |
|  | H ₂ SO ₄ |  COCH=CHR (-) | 2144 |
| | | C, R = 2-(O ₂ NC ₆ H ₄ O) | |
|  | NaOH | C, R = 2-(C ₄ H ₂ S) (-) | 2017 |
|  | .. | C, R = 2-(C ₄ H ₂ O) (-) | 2017 |
|  | .. | C, R = 4-(C ₅ H ₄ N) (-) | 1988 |
|  | .. | C, R = 2-(CH ₃ C ₄ H ₄ S) (-) | 1988 |
|  | .. | C, R = 2-(CH ₃ C ₄ H ₄ O) (-) | 1988 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | .. | C, R = 3,4-Cl ₂ C ₆ H ₃ (-) | 2017 |
| 4-ClC ₆ H ₄ CHO | .. | C, R = 4-ClC ₆ H ₄ (-) | 2017 |
| 4-FC ₆ H ₄ CHO | .. | C, R = 4-FC ₆ H ₄ (-) | 2017 |
| C ₆ H ₅ CHO | .. | C, R = C ₆ H ₅ (-) | 2017, 2254 |
|  | .. | C, R = 2-(C ₆ H ₅ O) (75-95) | 1854 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | C, R = 4-(CH ₃) ₂ NC ₆ H ₄ (-) | 2017 |
| 1-C ₁₀ H ₇ CHO | .. | C, R = 1-C ₁₀ H ₇ (-) | 2017 |
| O₂N  and | | | |
|  | H ₂ SO ₄ , CH ₃ CO ₂ H |  COCH=CHR (32) | 1779 |
| | | D, R = 2-(O ₂ NC ₆ H ₄ O) | |
|  | NaOH | D, R = 2-(C ₄ H ₂ O) (20) | 1779 |
| 4-O ₂ NC ₆ H ₄ CHO | H ₂ SO ₄ , CH ₃ CO ₂ H | D, R = 2-O ₂ NC ₆ H ₄ (90) | 647 |
| C ₆ H ₅ CHO | .. | D, R = C ₆ H ₅ (60) | 647 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | D, R = 4-CH ₃ OC ₆ H ₄ (81) | 647 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---------------------------|---|---------------------|
|  (contd.) and | | | |
| $C_6H_5CH=CHCHO$ | $H_2SO_4,$ CH_3CO_2H | D, R = $C_6H_5CH=CH$ (60) | 647 |
| $2,4-(CH_3O)_2C_6H_3CHO$ | " | D, R = $2,4-(CH_3O)_2C_6H_3$ (54) | 647 |
|  | NaOH | D, R = $2-(C_8H_7N)$ (—) | 2024 |
| $2,4,6-(CH_3O)_3C_6H_2CHO$ | $H_2SO_4,$ CH_3CO_2H | D, R = $2,4,6-(CH_3O)_3C_6H_2$ (50) | 647 |
|  and | | | |
|  | " |  COCH=CHR (51) E, R = $2-(O_2NC_4H_2S)$ | 1779 |
|  | " | E, R = $2-(C_4H_3S)$ (70) | 1779 |
| $4-O_2NC_6H_4CHO$ | " | E, R = $4-O_2NC_6H_4$ (35) | 646 |
| C_6H_5CHO | " | E, R = C_6H_5 (50) | 646 |
| $4-CH_3OC_6H_4CHO$ | " | E, R = $4-CH_3OC_6H_4$ (33) | 646 |
| $4-O_2NC_6H_4CH=CHCHO$ | " | E, R = $4-O_2NC_6H_4CH=CH$ (45) | 646 |
| $C_6H_5CH=CHCHO$ | " | E, R = $C_6H_5CH=CH$ (54) | 646 |
|  | NaOH | E, R = $2-(C_8H_7N)$ (—) | 2024 |
| $4-CH_3OC_6H_4CH=CHCHO$ | $H_2SO_4,$ CH_3CO_2H | E, R = $4-CH_3OC_6H_4CH=CH$ (25) | 646 |
| $2,4,6-(CH_3O)_3C_6H_2CHO$ | " | E, R = $2,4,6-(CH_3O)_3C_6H_2$ (50) | 646 |
|  and $2,4-(CH_3O)_2C_6H_3CHO$ | " |  COCH=CHR (30) | 646 |
|  and | | | |
| $C(Cl_2)=CClCHO$ | H_2SO_4 |  COCH=CHR (80) F, R = $C(Cl_2)=CCl$ | 289 |
|  | NaOH | F, R = $2-(BrC_4H_2S)$ (—) | 2017 |
|  | " | F, R = $2-(ClC_4H_2S)$ (—) | 2017 |
|  | " | F, R = $2-(O_2NC_4H_2S)$ (55) | 2034, 2035 |
|  | $NaOCH_3$ | F, R = $2-(O_2NC_4H_2S)$ (10) | 2034 |
| " | $H_2SO_4,$ CH_3CO_2H | F, R = $2-(O_2NC_4H_2S)$ (20) | 2034, 2035, 2144 |
|  | " | F, R = $2-(O_2NC_4H_2O)$ (12) | 1779 |
|  | NaOH | F, R = $2-(O_2NC_4H_2NH)$ (66) | 2034, 2035 |
|  | " | F, R = $2-(O_2NC_4H_2NH)$ (57) | 2034, 2035 |

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

















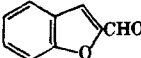
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Note: References 668-2359 are on pp. 403-438.

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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---------------------------------|---|---|
|  COCH ₃ (contd.) and | | | |
|  CHO | NaOH | F, R = 2-(C ₄ H ₅ S) (90) | 1845, 1030, 1520, 1823, 2035, 2255 |
|  CHO | NaOCH ₃ | F, R = 2-(C ₄ H ₅ Se) (56) | 1915, 2351 |
|  CHO | KOH | F, R = 2-(C ₄ H ₅ O) (90) | 1779, 1520, 1823, 2254, 2255 |
|  CHO | NaOH | F, R = 2-(C ₄ H ₅ NH) (83) | 2034, 2035 |
| OHC  CHO | K ₂ CO ₃ |  COCH=CH  CH=CHCO  * (—) | 365 |
| OHC  CHO | Na ₂ CO ₃ |  COCH=CH  CH=CHCO  * (76) | 1921 |
| CH ₃  CHO | NaOH | F, R = 2-(CH ₃ C ₄ H ₄ S) (—) | 2017 |
| CH ₃  CHO | " | F, R = 2-(CH ₃ C ₄ H ₄ O) (—) | 1988 |
| 2,4-Cl ₂ C ₆ H ₃ CHO | " | F, R = 2,4-Cl ₂ C ₆ H ₃ (82-95) | 2254 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | " | F, R = 3,4-Cl ₂ C ₆ H ₃ (82-95) | 2254, 2017 |
| 2-ClC ₆ H ₄ CHO | " | F, R = 2-ClC ₆ H ₄ (82-95) | 2254 |
| 4-ClC ₆ H ₄ CHO | " | F, R = 4-ClC ₆ H ₄ (82-95) | 2254 |
| 3-O ₂ NC ₆ H ₄ CHO | " | F, R = 3-O ₂ NC ₆ H ₄ (93) | 2023 |
| 4-O ₂ NC ₆ H ₄ CHO | " | F, R = 4-O ₂ NC ₆ H ₄ (—) | 2017, 1793 |
| C ₆ H ₅ CHO | " | F, R = C ₆ H ₅ (82-95) | 2254, 1030, 1520, 1914, 1915, 2255, 2256 |
|  CH=CHCHO | " | F, R = 2-(C ₄ H ₅ S)CH=CH (—) | 1793 |
|  CH=CHCHO | " | F, R = 2-(C ₄ H ₅ O)CH=CH (91) | 1779 |
| 3-HOC ₆ H ₄ CHO | NaOCH ₃ | F, R = 3-HOC ₆ H ₄ (—) | 2257 |
| 4-HOC ₆ H ₄ CHO | NaOH | F, R = 4-HOC ₆ H ₄ (32) | 2258 |
| 3-CF ₃ C ₆ H ₄ CHO | " | F, R = 3-CF ₃ C ₆ H ₄ (82-95) | 2254 |
| 1,3-C ₆ H ₄ (CHO) ₂ | " | 1,3-( COCH=CH) ₂ C ₆ H ₄ * (80) | 1956 |
| 1,4-C ₆ H ₄ (CHO) ₂ | " | 1,4-( COCH=CH) ₂ C ₆ H ₄ * (76) | 1956, 1958 |
| 2-CH ₃ OC ₆ H ₄ CHO | " | F, R = 2-CH ₃ OC ₆ H ₄ (83) | 1914 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | F, R = 4-CH ₃ OC ₆ H ₄ (86) | 1914, 1793 |
|  CHO | " | F, R = 2-(C ₈ H ₅ O) (75-95) | 1854 |
| 4-O ₂ NC ₆ H ₄ CH=CHCHO | " | F, R = 4-O ₂ NC ₆ H ₄ CH=CH (40) | 647 |
| C ₆ H ₅ CH=CHCHO | " | F, R = C ₆ H ₅ CH=CH (—) | 1793 |

Note: References 668-2359 are on pp. 403-438.



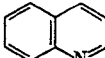


















* This is a complete structural formula.

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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)





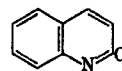

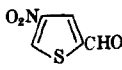

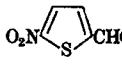

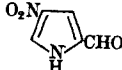
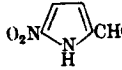
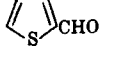
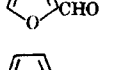
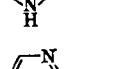
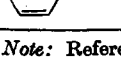

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---------------------------------|--|---------------------------|
|  COCH₃ (contd.) and | | | |
|  (CH=CH ₂)CHO | NaOH | F, R = 2-(C ₄ H ₃ O)CH=CHCH=CH (85) | 1779 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | F, R = 2,4-(CH ₃ O) ₂ C ₆ H ₃ Cl (77) | 1008 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | F, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (-) | 2017 |
|  CHO | .. | F, R = 2-(C ₈ H ₇ N) (-) | 2024 |
| 4-CH ₃ OC ₆ H ₄ CH=CHCHO | .. | F, R = 4-CH ₃ OC ₆ H ₄ CH=CH (-) | 1793 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | .. | F, R = 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ (95) | 1008 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CHCHO | .. | F, R = (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CH (69) | 1773 |
| 1-C ₁₀ H ₇ CHO | .. | F, R = 1-C ₁₀ H ₇ (-) | 2017 |
| Ferrocenecarboxaldehyde | .. | F, R = C ₅ H ₅ FeC ₅ H ₄ (69) | 1975 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CHCHO | .. | F, R = 2,4-(CH ₃ O) ₂ C ₆ H ₃ CH=CH (83) | 1008 |
| 2-CH ₃ -4-HO-5-i-C ₃ H ₇ -C ₆ H ₂ CHO | .. | F, R = 2-CH ₃ -4-HO-5-i-C ₃ H ₇ -C ₆ H ₂ (75) | 2105 |
| 2-CH ₃ -4-CH ₃ O-5-i-C ₃ H ₇ -C ₆ H ₂ CHO | .. | F, R = 2-CH ₃ -4-CH ₃ O-5-i-C ₃ H ₇ -C ₆ H ₂ (75) | 2105 |
|  COCH₃ and | | | |
|  CHO | NaOCH ₃ |  COCH=CHR (51) | 1915, 2351 |
| | | G, R = 2-(C ₄ H ₃ S) | |
|  CHO | NaOH | G, R = 2-(C ₄ H ₃ Se) (-) | 2351 |
| OHC  CHO | Na ₂ CO ₃ |  COCH=CH  CH=CHCO  CHO* (78) | 1921 |
| C ₆ H ₅ CHO | NaOH | G, R = C ₆ H ₅ (83) | 366 |
| 4-ClC ₆ H ₄ CHO | .. | G, R = 4-ClC ₆ H ₄ (72) | 366 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | G, R = 4-O ₂ NC ₆ H ₄ (100) | 366 |
| 4-CH ₃ C ₆ H ₄ CHO | .. | G, R = 4-CH ₃ C ₆ H ₄ (66) | 366 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | G, R = 4-CH ₃ OC ₆ H ₄ (73) | 366 |
| 4-(CH ₃) ₂ NC ₆ H ₃ CHO | .. | G, R = 4-(CH ₃) ₂ NC ₆ H ₃ (30) | 366 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | G, R = 2,4-(CH ₃ O) ₂ C ₆ H ₃ (100) | 366 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | .. | G, R = 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ (61) | 366 |
| 4-C ₆ H ₅ C ₆ H ₄ CHO | .. | G, R = 4-C ₆ H ₅ C ₆ H ₄ (89) | 366 |
|  COCH₃ and | | | |
| O ₂ N  CHO | .. |  COCH=CHR (24) | 1779 |
| | | H, R = 2-(O ₂ NC ₄ H ₂ S) | |
|  CHO | .. | H, R = 2-(C ₄ H ₃ S) (70) | 1779, 2255 |
|  CHO | .. | H, R = 2-(C ₄ H ₃ O) (92) | 1794, 2255 |
| OHC  CHO | Na ₂ CO ₃ |  COCH=CH  CH=CHCO  CHO* (71) | 1921 |
| 3-O ₂ NC ₆ H ₄ CHO | NaOH | H, R = 3-O ₂ NC ₆ H ₄ (92) | 2023 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | H, R = 4-O ₂ NC ₆ H ₄ (83) | 646 |
| C ₆ H ₅ CHO | .. | H, R = C ₆ H ₅ (86) | 1794, 1535, 1919, 2255 |
|  CH=CHCHO | .. | H, R = 2-(C ₄ H ₃ S)CH=CH (93) | 1779 |
| 3-HOC ₆ H ₄ CHO | NaOCH ₃ | H, R = 3-HOC ₆ H ₄ (-) | 2257 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--------------------|---|--------------------------|
|  COCH ₃ (contd.) and | | | |
|  CH=CHCHO | NaOH | H, R = 2-(C ₄ H ₃ O)CH=CH (80) | 1794, 1535 |
| 1,3-C ₆ H ₄ (CHO) ₂ | " | 1,3-() ₂ C ₆ H ₄ * (57) | 1956 |
| 1,4-C ₆ H ₄ (CHO) ₂ | " | 1,4-() ₂ C ₆ H ₄ * (51) | 1956, 1958 |
| 2-CH ₃ OC ₂ H ₄ CHO | " | H, R = 2-CH ₃ OC ₂ H ₄ (-) | 1918 |
| 4-CH ₃ OC ₂ H ₄ CHO | " | H, R = 4-CH ₃ OC ₂ H ₄ (92) | 1794, 1918 |
| 3-O ₂ NC ₆ H ₄ CH=CHCHO | " | H, R = 3-O ₂ NC ₆ H ₄ CH=CH (51) | 646 |
| C ₆ H ₅ CH=CHCHO | " | H, R = C ₆ H ₅ CH=CH (96) | 1794 |
| 2,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | H, R = 2,4-(CH ₂ O) ₂ C ₆ H ₃ (90) | 1794 |
|  CHO | " | H, R = 2-(C ₈ H ₇ N) (-) | 2024 |
| 4-CH ₃ OC ₂ H ₄ CH=CHCHO | " | H, R = 4-CH ₃ OC ₂ H ₄ CH=CH (80) | 1794 |
| C ₆ H ₅ (CH=CH) ₂ CHO | " | H, R = C ₆ H ₅ (CH=CH) ₂ (35) | 2260 |
| 2,4-(CH ₂ O) ₂ C ₆ H ₃ CH=CHCHO | " | H, R = 2,4-(CH ₂ O) ₂ C ₆ H ₃ CH=CH (78) | 1794 |
|  COCH ₃ and | | | |
|  CHO | " |  COCH=CHR (18) I, R = 2-(O ₂ NC ₄ H ₃ S) | 2034, 2035 |
|  CHO | NaOCH ₃ |  COCH ₂ CHOHR (20) | 2034 |
|  CHO | NaOH | I, R = 2-(O ₂ NC ₄ H ₃ S) (-) | 2035 |
|  CHO | " | I, R = 2-(O ₂ NC ₄ H ₃ NH) (20) | 2034, 2035 |
|  CHO | " | I, R = 2-(O ₂ NC ₄ H ₃ NH) (52) | 2034, 2035 |
|  CHO | " | I, R = 2-(C ₄ H ₃ S) (55) | 2034, 2035 |
|  CHO | " | I, R = 2-(C ₄ H ₃ O) (100) | 2259, 2034 |
|  CHO | " | I, R = 2-(C ₄ H ₃ NH) (40) | 364, 2034, 2035, 2355 |
|  CHO | " | I, R = 2-(C ₈ H ₇ N) (50) | 2034 |

ORGANIC REACTIONS


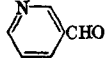
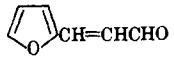
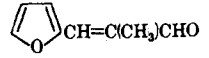
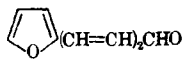
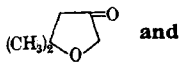
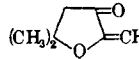
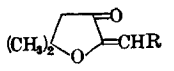

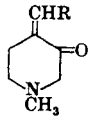
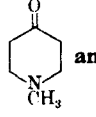
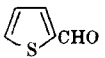
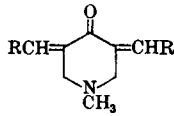
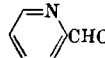
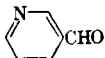
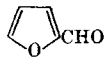
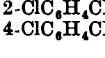
THE ALDOL CONDENSATION

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

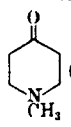
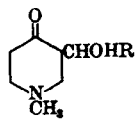
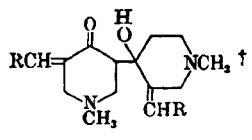
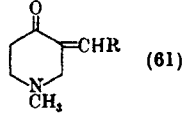
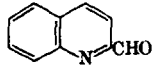
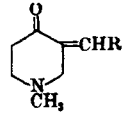
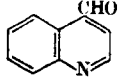
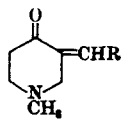
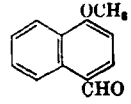

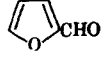
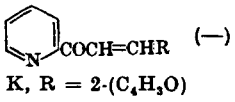
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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|------------|
|  COCH ₃ (contd.) and | | | |
|  CHO | NaOH | I, R = 3-(C ₆ H ₄ N) (40) | 2034 |
| 2-ClC ₆ H ₄ CHO | .. | I, R = 2-ClC ₆ H ₄ (91) | 1781 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | I, R = 3-O ₂ NC ₆ H ₄ (73) | 1781 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | I, R = 4-O ₂ NC ₆ H ₄ (90) | 1781 |
| C ₆ H ₅ CHO | KOH | I, R = C ₆ H ₅ (52) | 364 |
|  CH=CHCHO | Na ₂ CO ₃ | I, R = 2-(C ₄ H ₃ O)CH=CH (81) | 1766 |
| 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | KOH | I, R = 3,4-(CH ₂ O ₂)C ₆ H ₃ (75) | 364 |
| 4-CH ₃ C ₆ H ₄ CHO | NaOH | I, R = 4-CH ₃ C ₆ H ₄ (57) | 1781 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | I, R = 4-CH ₃ OC ₆ H ₄ (72) | 1781 |
|  CH=C(CH ₃)CHO | Na ₂ CO ₃ | I, R = 2-(C ₄ H ₃ O)CH=C(CH ₃) (50) | 1766 |
| C ₆ H ₅ CH=CHCHO | NaOH | I, R = C ₆ H ₅ CH=CH (—) | 2259 |
|  (CH=CH) ₂ CHO | Na ₂ CO ₃ | I, R = 2-(C ₄ H ₃ O)CH=CHCH=CH (72) | 1766 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | NaOH | I, R = 4-(CH ₃) ₂ NC ₆ H ₄ (60) | 1781 |
| Ferrocenecarboxaldehyde | .. | I, R = C ₅ H ₅ FeC ₅ H ₄ (74) | 1975 |
|  and | | | |
| i-C ₃ H ₇ CHO | .. |  (35) | 2261, 2262 |
| C ₆ H ₅ CHO | .. |  (50) | 2263 |
|  and C ₆ H ₅ CHO | KOH |  (25) | 2264 |
|  and | | | |
|  CHO | .. |  (—) | 2265 |
|  CHO | .. | J, R = 2-(C ₄ H ₃ S) | 2265 |
|  CHO | .. | J, R = 2-(C ₆ H ₄ N) (—) | 2265 |
|  CHO | .. | J, R = 3-(C ₆ H ₄ N) (—) | 2265 |
|  CHO | .. | J, R = 2-(C ₄ H ₃ O) (—) | 2265 |
| 2-ClC ₆ H ₄ CHO | .. | J, R = 2-ClC ₆ H ₄ (90) | 2266, 2267 |
| 4-ClC ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 4-ClC ₆ H ₄ (89) | 2267 |
| 4-FC ₆ H ₄ CHO | KOH | J, R = 4-FC ₆ H ₄ (—) | 2265 |
| 3-O ₂ NC ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 3-O ₂ NC ₆ H ₄ (82) | 2267 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)












| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|------------|
|  (contd.) and | | | |
| 4-O ₂ NC ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 4-O ₂ NC ₆ H ₄ (100) | 2267, 2268 |
| C ₆ H ₅ CHO | KOH | J, R = C ₆ H ₅ (44),  (36) | 2266-2268 |
| | .. |  † (70) | 2269 |
| | .. |  (61) | 2266 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | J, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (—) | 2265 |
| 2-CH ₂ C ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 2-CH ₂ C ₆ H ₄ (69) | 2267 |
| 4-CH ₂ C ₆ H ₄ CHO | .. | J, R = 4-CH ₂ C ₆ H ₄ (63) | 2267, 2265 |
| 4-CH ₂ OC ₆ H ₄ CHO | .. | J, R = 4-CH ₂ OC ₆ H ₄ (66) | 2267, 2265 |
| C ₆ H ₅ CH=CHCHO | KOH | J, R = C ₆ H ₅ CH=CH (—) | 2265 |
| 4-CH ₂ CONHC ₆ H ₄ CHO | .. | J, R = 4-CH ₂ CONHC ₆ H ₄ (—) | 2265 |
| 4-(CH ₂) ₄ NC ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 4-(CH ₂) ₄ NC ₆ H ₄ (58) | 2267, 2265 |
|  CHO | KOH | J, R = 2-(C ₆ H ₄ N) (39),  (40) | 2266 |
|  CHO | .. |  (95) ‡ | 2266 |
| | .. | J, R = 4-(C ₆ H ₄ N) (79) § | 2266 |
| 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 4- <i>i</i> -C ₃ H ₇ C ₆ H ₄ (36) | 2267 |
| 1-C ₁₀ H ₇ CHO | KOH | J, R = 1-C ₁₀ H ₇ (88) | 2266, 2265 |
| 4-(CH ₂) ₄ NC ₆ H ₄ CHO | .. | J, R = 4-(CH ₂) ₄ NC ₆ H ₄ (—) | 2265 |
|  CHO | .. | J, R = 1-(CH ₂ OC ₁₀ H ₈) (—) | 2265 |
| 4-C ₆ H ₅ C ₆ H ₄ CHO | None, C ₂ H ₅ OH, rfx. | J, R = 4-C ₆ H ₅ C ₆ H ₄ (—) | 2267 |
| Phenanthrene-9-carboxaldehyde | KOH | J, R = 9-C ₁₄ H ₉ (—) | 2265 |
|  COCH ₃ and | | | |
|  CHO | (C ₂ H ₅) ₂ NH |  (—) K, R = 2-(C ₄ H ₃ O) | 2270 |

Note: References 668-2359 are on pp. 403-438.

- † This structure was suggested but not established.
‡ This was obtained with a 1:1 molar ratio of reactants.
§ This was obtained with a 2:1 molar ratio of aldehyde to ketone.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|----------------|
|  COCH ₃ (contd.) and | | | |
|  CHO | NaOH | K, R = 2-(C ₅ H ₄ N) (40) | 545 |
| 2,4-Cl ₂ C ₆ H ₃ CHO | .. | K, R = 2,4-Cl ₂ C ₆ H ₃ (89) | 534 |
| 2,5-Cl ₂ C ₆ H ₃ CHO | .. | K, R = 2,5-Cl ₂ C ₆ H ₃ (89) | 534 |
| 3,4-Cl ₂ C ₆ H ₃ CHO | .. | K, R = 3,4-Cl ₂ C ₆ H ₃ (89) | 534 |
| 2-ClC ₆ H ₄ CHO | .. | K, R = 2-ClC ₆ H ₄ (99) | 534 |
| 3-ClC ₆ H ₄ CHO | .. | K, R = 3-ClC ₆ H ₄ (99) | 534 |
| 2-Cl-4-HOC ₆ H ₃ CHO | .. | K, R = 2-Cl-4-HOC ₆ H ₃ (95) | 534 |
| 2-O ₂ NC ₆ H ₄ CHO | .. |  COCH ₂ CHOHR (-) | 2271 |
| 3-O ₂ NC ₆ H ₄ CHO | NaOCH ₃ | K, R = 3-O ₂ NC ₆ H ₄ (96) | 2004, 534 |
| 4-O ₂ NC ₆ H ₄ CHO | NaOH | K, R = 4-O ₂ NC ₆ H ₄ (94) | 534, 2270 |
| C ₆ H ₅ CHO | .. | K, R = C ₆ H ₅ (99) | 534, 545, 2271 |
| 2-HOC ₆ H ₄ CHO | .. | K, R = 2-HOC ₆ H ₄ (97) | 534, 2270 |
| 4-HOC ₆ H ₄ CHO | .. | K, R = 4-HOC ₆ H ₄ (90) | 534 |
| 4-HO ₂ CC ₆ H ₄ CHO | .. | K, R = 4-HO ₂ CC ₆ H ₄ (98) | 534 |
| 1,3-C ₆ H ₄ (CHO) ₂ | .. | 1,3-( COCH=CH) ₂ C ₆ H ₄ * (58) | 1956 |
| 1,4-C ₆ H ₄ (CHO) ₂ | .. | 1,4-( COCH=CH) ₂ C ₆ H ₄ * (68) | 1956 |
| 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | .. | K, R = 3,4-(CH ₂ O ₂)C ₆ H ₃ (91) | 534, 2270 |
| 2-CH ₃ OC ₆ H ₄ CHO | .. | K, R = 2-CH ₃ OC ₆ H ₄ (98) | 534 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | K, R = 4-CH ₃ OC ₆ H ₄ (91) | 534, 2270 |
| 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | K, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (98) | 534 |
| 2,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | K, R = 2,4-(CH ₃ O) ₂ C ₆ H ₃ (98) | 534 |
| 2,5-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | K, R = 2,5-(CH ₃ O) ₂ C ₆ H ₃ (98) | 534 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | K, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (92) | 534, 2270 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | K, R = 4-(CH ₃) ₂ NC ₆ H ₄ (60) | 534 |
| Ferrocenecarboxaldehyde | .. | K, R = C ₅ H ₅ FeC ₅ H ₄ (45) | 1975 |
|  COCH ₃ and | | | |
|  CHO | .. |  COCH=CHR (95) L, R = 2-(C ₄ H ₃ O) | 2272, 2270 |
| 4-O ₂ NC ₆ H ₄ CHO | (C ₂ H ₅) ₂ NH | L, R = 4-O ₂ NC ₆ H ₄ (-) | 2270 |
| C ₆ H ₅ CHO | NaOH | L, R = C ₆ H ₅ (22) | 534, 2270 |
| 2-HOC ₆ H ₄ CHO | (C ₂ H ₅) ₂ NH | L, R = 2-HOC ₆ H ₄ (-) | 2270 |
| 3-HOC ₆ H ₄ CHO | NaOH | L, R = 3-HOC ₆ H ₄ (97) | 534 |
| 4-HOC ₆ H ₄ CHO | .. | L, R = 4-HOC ₆ H ₄ (50) | 534 |
| 2-HO ₂ CC ₆ H ₄ CHO | .. | L, R = 2-HO ₂ CC ₆ H ₄ (98) | 534 |
| 4-CH ₃ OC ₆ H ₄ CHO | (C ₂ H ₅) ₂ NH | L, R = 4-CH ₃ OC ₆ H ₄ (-) | 2270 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | .. | L, R = 3-CH ₃ O-4-HOC ₆ H ₃ (-) | 2270 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | L, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (-) | 2270 |
|  COCH ₃ and | | | |
|  CHO | NaOH |  COCH=CHR (77) M, R = 2-(C ₄ H ₃ O) | 2272, 2270 |

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THE ALDOL CONDENSATION



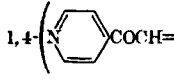
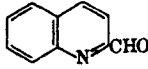

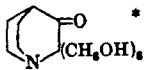
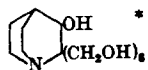
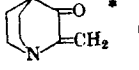
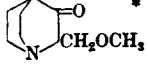
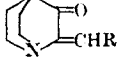
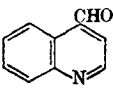
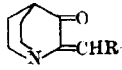
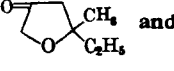
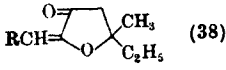

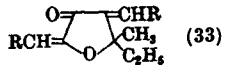
Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|---|----------------|
|   (contd.) and | | | |
| 3-ClC ₆ H ₄ CHO | NaOH | M, R = 3-ClC ₆ H ₄ (88) | 534 |
| 4-ClC ₆ H ₄ CHO | " | M, R = 4-ClC ₆ H ₄ (99) | 534 |
| 2-Cl-4-HOC ₆ H ₃ CHO | " | M, R = 2-Cl-4-HOC ₆ H ₃ (98) | 534 |
| 2-O ₂ NC ₆ H ₄ CHO | " | M, R = 2-O ₂ NC ₆ H ₄ (60) | 534 |
| 4-O ₂ NC ₆ H ₄ CHO | " | M, R = 4-O ₂ NC ₆ H ₄ (60) | 534 |
| C ₆ H ₅ CHO | " | M, R = C ₆ H ₅ (99) | 534, 545, 2270 |
| 2-HOC ₆ H ₄ CHO | " | M, R = 2-HOC ₆ H ₄ (90) | 534, 2270 |
| 3-HOC ₆ H ₄ CHO | " | M, R = 3-HOC ₆ H ₄ (97) | 534 |
| 4-HOC ₆ H ₄ CHO | " | M, R = 4-HOC ₆ H ₄ (86) | 534 |
| 1,4-C ₆ H ₄ (CHO) ₂ | " | 1,4-()C ₆ H ₄ * (33) | 1956 |
| 2-HOCC ₆ H ₄ CHO | " | M, R = 2-HOCC ₆ H ₄ (98) | 534 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | " | M, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (60) | 534, 2270 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | M, R = 4-CH ₃ OC ₆ H ₄ (99) | 534, 2270 |
| 3-CH ₃ O-4-HOC ₆ H ₃ CHO | (C ₆ H ₅) ₂ NH | M, R = 3-CH ₃ O-4-HOC ₆ H ₃ (-) | 2270 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | NaOH | M, R = 4-(CH ₃) ₂ NC ₆ H ₄ (60) | 534, 2270 |
|  | " | M, R = 2-(C ₆ H ₅ N) (-) | 2024 |
|  and | | | |
| CH ₃ O | K ₂ CO ₃ , H ₂ O |  * (21-54),  * (15) | 450 |
| | K ₂ CO ₃ , H ₂ O, CH ₃ OH |  * (54),  * (16) | 450 |
| C ₆ H ₅ CHO | (CH ₂) ₅ NH |  (75) | 2273, 2274 |
|  | (CH ₂) ₅ NH, CH ₂ CO ₂ H |  (50) | 2273 |
|  and | | | |
| CH ₃ CHO | NaOH |  (38) N, R = CH ₃ | 2261, 2262 |
| C ₆ H ₅ CHO | " | N, R = C ₆ H ₅ (17) | 2261, 2262 |
| n-C ₇ H ₁₅ CHO | " | N, R = n-C ₇ H ₁₅ (22) | 2261, 2262 |
| i-C ₇ H ₁₅ CHO | " | N, R = i-C ₇ H ₁₅ (35) | 2261, 2262 |
|  | " | N, R = 2-(C ₆ H ₅ O) (29) | 2261, 2262 |
| C ₆ H ₅ CHO | " |  (33) O, R = C ₆ H ₅ | 2261, 2262 |
| n-C ₇ H ₁₅ CHO | " | N, R = n-C ₇ H ₁₅ (32) | 2261, 2262 |
| 4-CH ₃ OC ₆ H ₄ CHO | " | N, R = 4-CH ₃ OC ₆ H ₄ (46) † | 2261, 2262 |
| | " | O, R = 4-CH ₃ OC ₆ H ₄ (68) § | 2261, 2262 |

Note: References 668-2359 are on pp. 403-438.

* This is a complete structural formula.

† This was obtained with a 1:1 molar ratio of reactants.

§ This was obtained with a 2:1 molar ratio of aldehyde to ketone.

ORGANIC REACTIONS

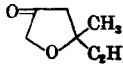
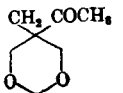
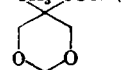
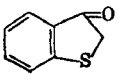
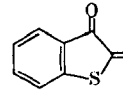
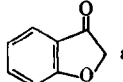
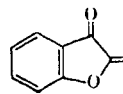
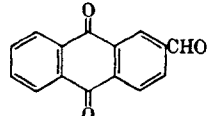
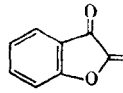
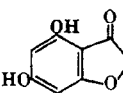
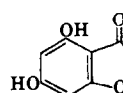
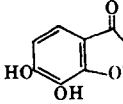
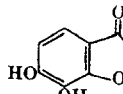
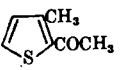
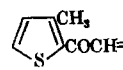
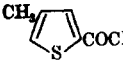
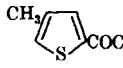
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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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ORGANIC REACTIONS

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--|--|--|
|  (contd.) and 4-(CH ₃) ₂ NC ₆ H ₄ CHO (CH ₃) ₂ C=CH(CH ₂) ₂ CH(CH ₃)CH ₂ CHO 4-C ₆ H ₅ C ₆ H ₄ CHO | NaOH | O, R = 4-(CH ₃) ₂ NC ₆ H ₄ (51) N, R = (CH ₃) ₂ C=CH(CH ₂) ₂ CH(CH ₃)CH ₂ (49) O, R = 4-C ₆ H ₅ C ₆ H ₄ (55) | 2261, 2262 2261, 2262 2261, 2262 |
|  and CH ₂ O | .. | CH ₃ COCH(CH ₂ OH) ₂ *  (—) | 2275 |
|  and C(Cl ₂)=CClCHO | BF ₃ |  =CHR (80) | 289 |
|  and 3-CH ₃ O-4-HOC ₆ H ₃ CHO | HCl |  =CHR (55) | 2052, 2342 |
|  CHO | NaOH |  =CHR (—) | 1977 |
|  and C ₆ H ₅ CHO | KOH |  =CHR (—) P, R = C ₆ H ₅ | 2165 |
| 2-CH ₃ OC ₆ H ₄ CHO 4-CH ₃ OC ₆ H ₄ CHO 3-CH ₃ O-4-HOC ₆ H ₃ CHO | (CH ₃ CO) ₂ O, rfx. | P, R = 2-CH ₃ OC ₆ H ₄ (—) P, R = 4-CH ₃ OC ₆ H ₄ (—) P, R = 3-CH ₃ O-4-HOC ₆ H ₃ (60) | 2276 2277 2278 |
| 3-HO-4-CH ₃ OC ₆ H ₃ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 3,4-(C ₆ H ₅ O) ₂ C ₆ H ₃ CHO | .. KOH NaOH | P, R = 3-HO-4-CH ₃ OC ₆ H ₃ (50) P, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (—) P, R = 3,4-(C ₆ H ₅ O) ₂ C ₆ H ₃ (—) | 2278 2276 2159 |
|  and 3,4-(HO) ₂ C ₆ H ₃ CHO | (CH ₃ CO) ₂ O |  =CHR (—) | 2279 |
|  and C ₆ H ₅ CHO | NaOH |  =CHR (82-95) | 2254 |
|  and C ₆ H ₅ CHO | .. |  =CHR (82-95) | 2254 |

Note: References 668-2359 are on pp. 403-438.

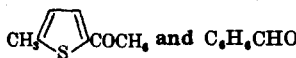
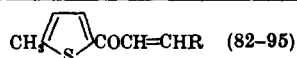
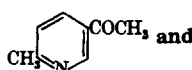
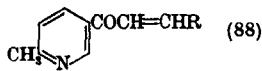
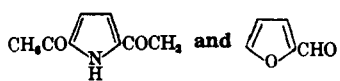
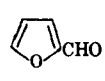
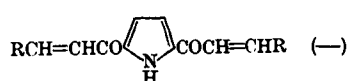
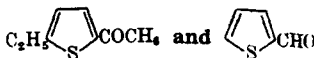
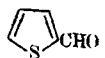
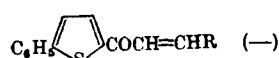
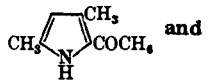
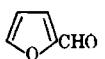
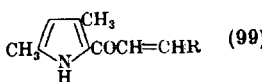
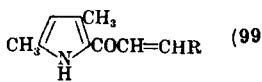
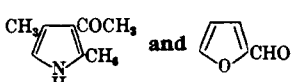
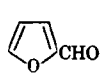
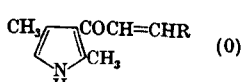
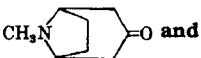
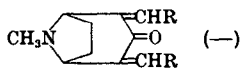
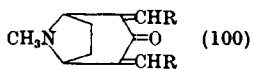
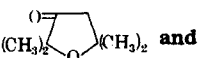
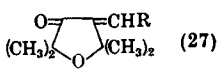
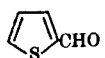
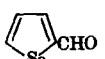
* This is a complete structural formula.

|| The product was initially isolated as a triacetate and was subsequently deacetylated.

THE ALDOL CONDENSATION

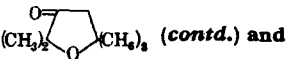

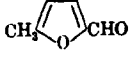
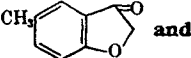
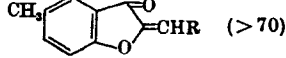
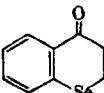
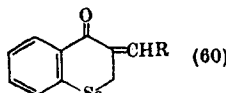
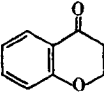
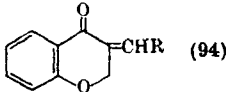
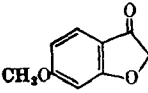
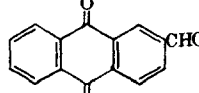
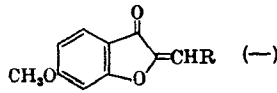
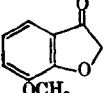
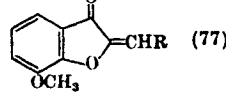
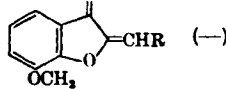
375

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|----------|--|------------|
|  and C_6H_5CHO | NaOH |  =CHR (82-95) | 2254 |
|  and 4-BrC ₆ H ₄ CHO | " |  =CHR (88) Q, R = 4-BrC ₆ H ₄ | 367 |
| 2-ClC ₆ H ₄ CHO | " | Q, R = 2-ClC ₆ H ₄ (88) | 367 |
| 4-ClC ₆ H ₄ CHO | " | Q, R = 4-ClC ₆ H ₄ (69) | 367 |
| 2-O ₂ NC ₆ H ₄ CHO | " | Q, R = 2-O ₂ NC ₆ H ₄ (27) | 367 |
| 3-O ₂ NC ₆ H ₄ CHO | " | Q, R = 3-O ₂ NC ₆ H ₄ (33) | 367 |
| 4-O ₂ NC ₆ H ₄ CHO | " | Q, R = 4-O ₂ NC ₆ H ₄ (78) | 367 |
| C ₆ H ₅ CHO | " | Q, R = C ₆ H ₅ (49) | 545 |
| 4-NCC ₆ H ₄ CHO | " | Q, R = 4-NCC ₆ H ₄ (68) | 367 |
| 4-HO ₂ CC ₆ H ₄ CHO | " | Q, R = 4-HO ₂ CC ₆ H ₄ (44) | 367 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | " | Q, R = 4-(CH ₃) ₂ NC ₆ H ₄ (50) | 367 |
| 4-CH ₃ CONHC ₆ H ₄ CHO | " | Q, R = 4-CH ₃ CONHC ₆ H ₄ (68) | 367 |
|  and  | " | RCH=CHCO  =CHR (—) | 2259 |
|  and  | " |  =CHR (—) | 2017 |
|  and | | | |
|  | |  =CHR (99) | 2259 |
| C ₆ H ₅ CH=CHCHO | " |  =CHR (99) | 2259 |
|  and  | " |  =CHR (0) | 2259 |
|  and C ₆ H ₅ CHO | KOH |  =CHR (—) | 2280 |
| 3,4-(CH ₂ O ₂)C ₆ H ₄ CHO | " |  =CHR (100) | 2280 |
|  and | | | |
| <i>i</i> -C ₃ H ₇ CHO | " |  =CHR (27) S, R = <i>i</i> -C ₃ H ₇ | 2281, 1355 |
|  | " | S, R = 2-(C ₄ H ₃ S) (100) | 2282 |
|  | " | S, R = 2-(C ₄ H ₃ Se) (100) | 2282 |

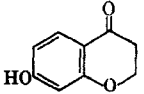
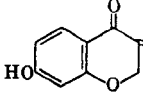
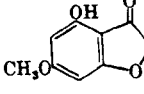
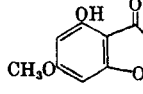
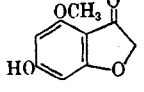
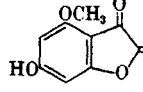
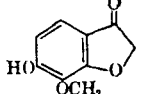
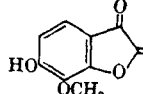
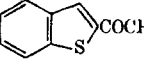
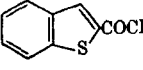
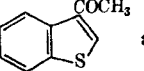
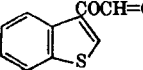
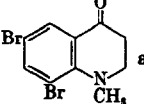

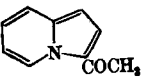
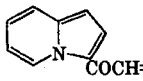
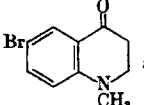
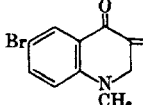
Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|---------------------|
|  (contd.) and | | | |
|  | KOH | S, R = 2-(C ₄ H ₇ O) (85) | 2281, 2282 |
|  | .. | S, R = 2-(CH ₃ C ₄ H ₅ O) (100) | 2282 |
| C ₆ H ₅ CHO | .. | S, R = C ₆ H ₅ (97) | 2283, 2284 |
| 2-O ₂ NC ₆ H ₄ CHO | .. | S, R = 2-O ₂ NC ₆ H ₄ (90) | 2281 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | S, R = 3-O ₂ NC ₆ H ₄ (43) | 2281 |
| 2-HOC ₆ H ₄ CHO | .. | S, R = 2-HOC ₆ H ₄ (77) | 2285 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | S, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (95) | 2281, 2284 |
| 2-CH ₂ OC ₆ H ₄ CHO | .. | S, R = 2-CH ₂ OC ₆ H ₄ (-) | 2285 |
| C ₆ H ₅ CH=CHCHO | .. | S, R = C ₆ H ₅ CH=CH (80) | 2281 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | S, R = 4-(CH ₃) ₂ NC ₆ H ₄ (74) | 2281 |
|  and | | | |
| 3-O ₂ NC ₆ H ₄ CHO | HCl, CH ₃ CO ₂ H |  (> 70) T, R = 3-O ₂ NC ₆ H ₄ | 339 |
| 4-HOC ₆ H ₄ CHO | .. | T, R = 4-HOC ₆ H ₄ (>70) | 339 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | T, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (-) | 2276 |
| 2,4-(CH ₂) ₂ C ₆ H ₃ CHO | HCl, CH ₃ CO ₂ H | T, R = 2,4-(CH ₂) ₂ C ₆ H ₃ (>70) | 339 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | KOH | T, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (-) | 2276 |
| 2,4,6-(CH ₃) ₃ C ₆ H ₂ CHO | HCl, CH ₃ CO ₂ H | T, R = 2,4,6-(CH ₃) ₃ C ₆ H ₂ (>70) | 339 |
|  and C ₆ H ₅ CHO | NaOH |  (60) | 2286 |
|  and | | | |
| C ₆ H ₅ CHO | HCl |  (94) U, R = C ₆ H ₅ | 2032, 2287-2289 |
| 3-HOC ₆ H ₄ CHO | .. | U, R = 3-HOC ₆ H ₄ (-) | 2290 |
| 3,4-(HO) ₂ C ₆ H ₃ CHO | .. | U, R = 3,4-(HO) ₂ C ₆ H ₃ (45) | 2291 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | U, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (45) | 2291 |
| 2-CH ₂ OC ₆ H ₄ CHO | .. | U, R = 2-CH ₂ OC ₆ H ₄ (82) | 2032 |
| 3-CH ₂ OC ₆ H ₄ CHO | .. | U, R = 3-CH ₂ OC ₆ H ₄ (75) | 2290 |
| 4-CH ₂ OC ₆ H ₄ CHO | .. | U, R = 4-CH ₂ OC ₆ H ₄ (88) | 2032, 2291 |
| 3-CH ₂ O-4-HOC ₆ H ₃ CHO | .. | U, R = 3-CH ₂ O-4-HOC ₆ H ₃ (65) | 2291 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | U, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (99) | 2032, 2290, 2291 |
|  and  | NaOH |  (-) | 1977, 2343 |
|  and | | | |
| 3-CH ₂ O-4-HOC ₆ H ₃ CHO | HCl |  (77) | 2109 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. |  (-) | 2109 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

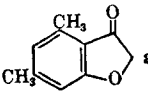
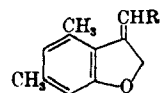
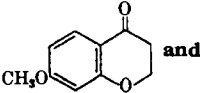
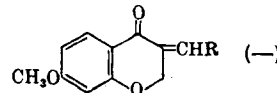
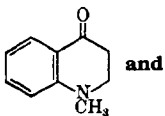
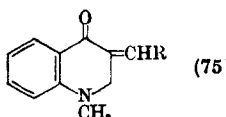
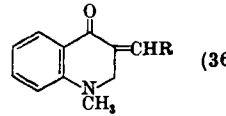
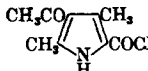
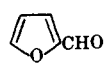
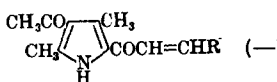
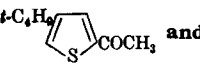
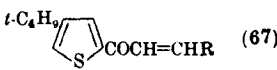
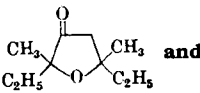
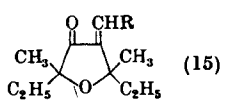
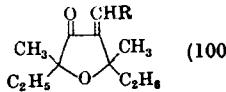
| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---|---|------------------------------|
|  and 3,4-(HO) ₂ C ₆ H ₃ CHO | HCl |  (99) V, R = 3,4-(HO) ₂ C ₆ H ₃ | 2292, 2291 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 4-CH ₃ OC ₆ H ₄ CHO 3-CH ₃ O-4-HOC ₆ H ₃ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. NaOC ₂ H ₅ HCl NaOC ₂ H ₅ | V, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (60) V, R = 4-CH ₃ OC ₆ H ₄ (41) V, R = 3-CH ₃ O-4-HOC ₆ H ₃ (80) V, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (50) | 2291 2292 2291 2291 |
|  and 3,4-(HO) ₂ C ₆ H ₃ CHO | (CH ₃ CO) ₂ O, r.f.x. |  (66) | 2278, 2293 |
|  and 3,4-(HO) ₂ C ₆ H ₃ CHO | .. |  (43) | 2278 |
|  and 3,4-(HO) ₂ C ₆ H ₃ CHO | (CH ₃ CO) ₂ O |  (—) | 2294 |
|  and C ₆ H ₅ CHO | NaOH |  (—) | 1801 |
|  and 3-O ₂ NC ₆ H ₄ CHO | KOH |  (100) W, R = 3-O ₂ NC ₆ H ₄ | 2295 |
| C ₆ H ₅ CHO 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO Ferrocenecarboxaldehyde | NaOH | W, R = C ₆ H ₅ (84) W, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (48) W, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (57) W, R = C ₅ H ₅ FeC ₅ H ₄ (25) | 2295 2295 2295 1975 |
|  and 4-(CH ₃) ₂ NC ₆ H ₄ CHO | (CH ₃) ₂ NH |  (—) | 368 |
|  and C ₆ H ₅ CHO | NaOH |  (—) | 2296 |
|  and 4-(CH ₃) ₂ NC ₆ H ₄ CHO | (CH ₃) ₂ NH |  (78) | 368 |

Note: References 668-2359 are on pp. 403-438.

|| The product was initially isolated as a triacetate and was subsequently deacetylated.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|---|--|------------|
|  and 3-HOC ₆ H ₄ CHO | HCl, CH ₃ CO ₂ H |  (—) X, R = 3-HOC ₆ H ₄ | 339 |
| 4-HOC ₆ H ₄ CHO | .. | X, R = 4-HOC ₆ H ₄ (—) | 339 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | X, R = 4-CH ₃ OC ₆ H ₄ (—) | 339 |
| C ₆ H ₅ CH=CHCHO | .. | X, R = C ₆ H ₅ CH=CH (—) | 339 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | X, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (—) | 339 |
|  and 2-BrC ₆ H ₄ CHO | NaOH |  (—) Y, R = 2-BrC ₆ H ₄ | 1929 |
| 2-ClC ₆ H ₄ CHO | .. | Y, R = 2-ClC ₆ H ₄ (—) | 1929 |
| 3,4-(CH ₃ O) ₂ C ₆ H ₃ CHO | HCl | Y, R = 3,4-(CH ₃ O) ₂ C ₆ H ₃ (99) | 2032, 2291 |
|  and C ₆ H ₅ CHO | NaOH |  (75) | 368 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | (CH ₃) ₂ NH |  (36) | 368 |
|  and  | NaOH |  (—) | 2259 |
|  and (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CHCHO | .. |  (67) | 1773 |
|  and 2-HOC ₆ H ₄ CHO | KOH |  (15) | 2285 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. |  (100) | 2282 |

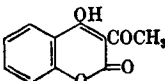
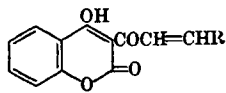
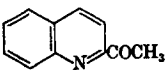

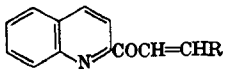
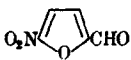
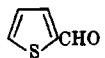
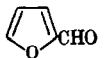
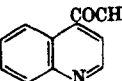
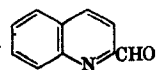
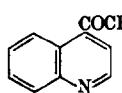
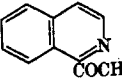
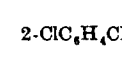
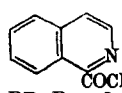
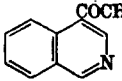
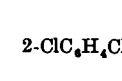
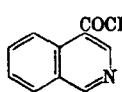
Note: References 668-2359 are on pp. 403-438.

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THE ALDOL CONDENSATION

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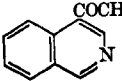
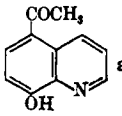
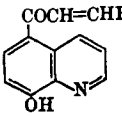
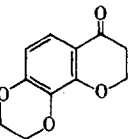
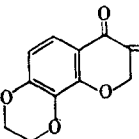
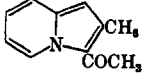
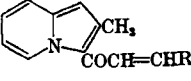
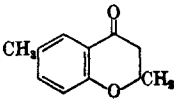
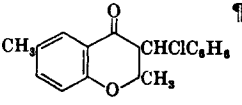
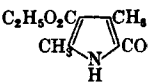

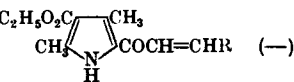
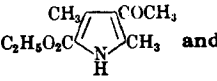
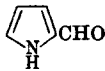
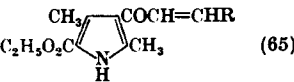
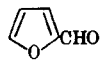
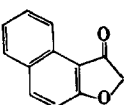
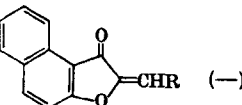
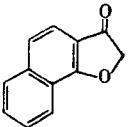
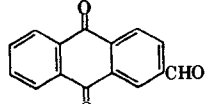
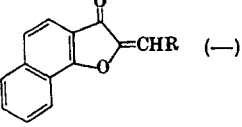
TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|----------------------------------|--|------------|
|  and 2-O ₂ NC ₆ H ₄ CHO | NaOH |  (37) Z, R = 2-O ₂ NC ₆ H ₄ | 2298 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | Z, R = 4-O ₂ NC ₆ H ₄ (40) | 2298 |
| C ₆ H ₅ CHO | .. | Z, R = C ₆ H ₅ (-) | 2298 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | NaOC ₂ H ₅ | Z, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (60) | 2299, 2298 |
| 4-CH ₃ OC ₆ H ₄ CHO | NaOH | Z, R = 4-CH ₃ OC ₆ H ₄ (45) | 2298 |
|  and  | NaOH |  (38) AA, R = 2-(O ₂ NC ₆ H ₄ S) | 2301, 2356 |
|  | .. | AA, R = 2-(O ₂ NC ₆ H ₄ O) (10) | 2301, 2356 |
|  | .. | AA, R = 2-(C ₄ H ₃ S) (94) | 2301, 2356 |
|  | .. | AA, R = 2-(C ₄ H ₃ O) (96) | 2301, 2356 |
| 4-O ₂ NC ₆ H ₄ CHO | .. | AA, R = 4-O ₂ NC ₆ H ₄ (95) | 2301, 2356 |
| C ₆ H ₅ CHO | .. | AA, R = C ₆ H ₅ (96) | 2301, 2356 |
| 4-H ₃ NC ₆ H ₄ CHO | .. | AA, R = 4-H ₃ NC ₆ H ₄ (50) | 2301, 2356 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | AA, R = 4-CH ₃ OC ₆ H ₄ (95) | 2301, 2356 |
| C ₆ H ₅ CH=CHCHO | .. | AA, R = C ₆ H ₅ CH=CH (96) | 2301, 2356 |
| 2,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | AA, R = 2,4-(CH ₂ O) ₂ C ₆ H ₃ (95) | 2301, 2356 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | AA, R = 4-(CH ₃) ₂ NC ₆ H ₄ (60) | 2301, 2356 |
| 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CHO | .. | AA, R = 2,4,6-(CH ₃ O) ₃ C ₆ H ₂ (87) | 2301, 2356 |
|  and  | NaOCH ₃ |  (65) | 2004 |
|  and  | NaOH |  (93) BB, R = 2-ClC ₆ H ₄ | 1770 |
| 2-ClC ₆ H ₄ CHO | .. | BB, R = C ₆ H ₅ (73) | 1770 |
| C ₆ H ₅ CHO | .. | BB, R = 3,4-(CH ₂ O) ₂ C ₆ H ₃ (74) | 1770 |
| 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | BB, R = 4-CH ₃ OC ₆ H ₄ (88) | 1770 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | BB, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (90) | 1770 |
| 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | .. | | |
|  and  | NaOH |  (71) CC, R = 2-ClC ₆ H ₄ | 1770 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|------------------------------|
|  (contd.) and C ₆ H ₅ CHO 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO 4-CH ₃ OC ₆ H ₄ CHO 2,3-(CH ₃ O) ₂ C ₆ H ₃ CHO | (CH ₂) ₃ NH NaOH | CC, R = C ₆ H ₅ (52) CC, R = 3,4-(CH ₂ O ₂)C ₆ H ₃ (95) CC, R = 4-CH ₃ OC ₆ H ₄ (76) CC, R = 2,3-(CH ₃ O) ₂ C ₆ H ₃ (66) | 1770 1770 1770 1770 |
|  and 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO | .. |  (94) | 2297 |
|  and 3,4-(OCH ₂ CH ₂ O)C ₆ H ₃ CHO | HCl, CH ₃ CO ₂ H |  (75) | 2302 |
|  and C ₆ H ₅ CHO | NaOH |  (—) | 2303 |
|  and C ₆ H ₅ CHO | HCl |  (84) | 2304 |
|  and  | NaOH |  (—) | 2259 |
|  and  | KOH |  (65) DD, R = 2-(C ₄ H ₇ NH) | 364 |
|  | .. | DD, R = 2-(C ₄ H ₇ O) (69) | 364, 2259 |
| C ₆ H ₅ CHO 3,4-(CH ₂ O ₂)C ₆ H ₃ CHO 4-(CH ₃) ₂ NC ₆ H ₄ CHO | | DD, R = C ₆ H ₅ (66) DD, R = 3,4-(CH ₂ O ₂)C ₆ H ₃ (51) DD, R = 4-(CH ₃) ₂ NC ₆ H ₄ (65) | 364 364 364 |
|  and 4-CH ₃ OC ₆ H ₄ CHO | .. |  (—) | 2276 |
|  and  | NaOH |  (—) | 1977 |

Note: References 668-2359 are on pp. 403-438.

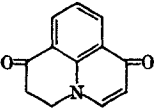
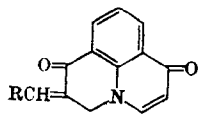
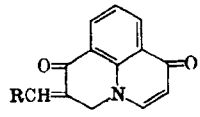
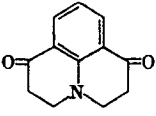
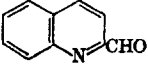
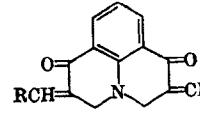
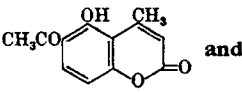
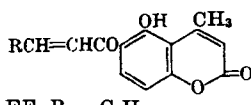
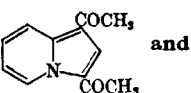
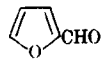
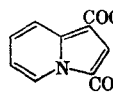
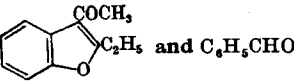
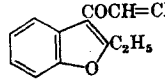
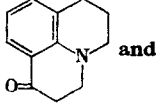
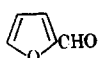
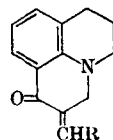
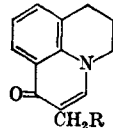
¶ This product was converted quantitatively to the benzal derivative by heating at 180°.

ORGANIC REACTIONS

THE ALDOL CONDENSATION

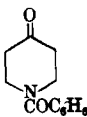
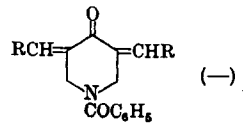
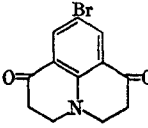
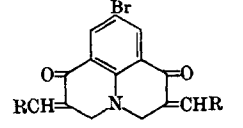
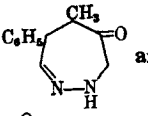
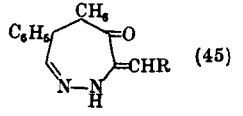
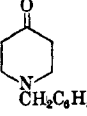
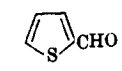
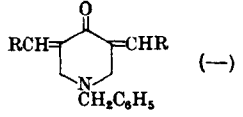
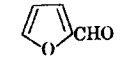
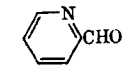
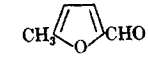
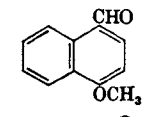
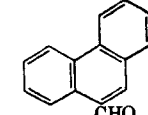
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TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--------------|--|-----------|
|  and C_6H_5CHO | $(CH_2)_5NH$ |  (—) | 368 |
| $4-(CH_2)_2NC_6H_4CHO$ | .. |  (—) | 368 |
|  and  | KOH |  (25) | 368, 2341 |
|  and C_6H_5CHO | NaOH |  (—) EE, R = C_6H_5 | 2300 |
| $2-HOC_6H_4CHO$ | KOH | EE, R = $2-HOC_6H_4$ (—) | 2300 |
| $3,4-(HO)_2C_6H_3CHO$ | .. | EE, R = $3,4-(HO)_2C_6H_3$ (—) | 2300 |
| $4-CH_3OC_6H_4CHO$ | .. | EE, R = $4-CH_3OC_6H_4$ (—) | 2300 |
| $3-CH_3O-4-HOC_6H_3CHO$ | .. | EE, R = $3-CH_3O-4-HOC_6H_3$ (—) | 2300 |
|  and  | NaOH |  (—) FF, R = $2-(C_6H_5O)$ | 2305 |
| $2-O_2NC_6H_4CHO$ | .. | FF, R = $2-O_2NC_6H_4$ (—) | 2306 |
| $3-O_2NC_6H_4CHO$ | .. | FF, R = $3-O_2NC_6H_4$ (—) | 2306 |
| $4-O_2NC_6H_4CHO$ | .. | FF, R = $4-O_2NC_6H_4$ (—) | 2306 |
| C_6H_5CHO | .. | FF, R = C_6H_5 (—) | 2305 |
| $3,4-(CH_2O)_2C_6H_3CHO$ | .. | FF, R = $3,4-(CH_2O)_2C_6H_3$ (—) | 2305 |
| $4-CH_3C_6H_4CHO$ | .. | FF, R = $4-CH_3C_6H_4$ (—) | 2305 |
| $C_6H_5CH=CHCHO$ | .. | FF, R = $C_6H_5CH=CH$ (—) | 2305 |
| $4-(CH_2)_2NC_6H_4CHO$ | .. | FF, R = $4-(CH_2)_2NC_6H_4$ (—) | 2306 |
| $4-i-C_3H_7C_6H_4CHO$ | .. | FF, R = $4-i-C_3H_7C_6H_4$ (—) | 2305 |
|  and C_6H_5CHO | .. |  (—) | 1703 |
|  and  | .. |  (62) | 2307 |
| C_6H_5CHO | .. |  (—) | 2307 |

Note: References 668-2359 are on pp. 403-438.

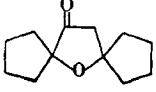
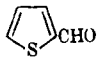
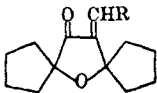
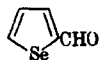
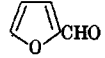
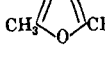
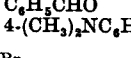
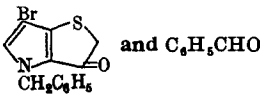
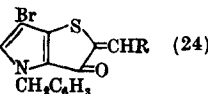
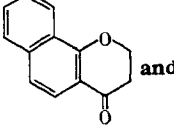
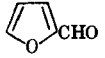
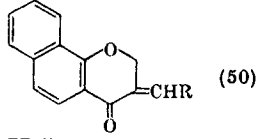
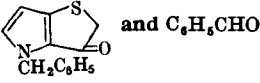
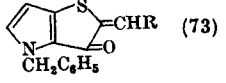


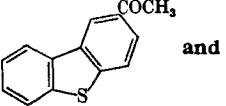
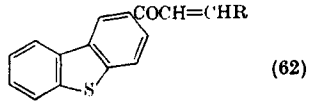
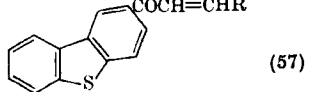
TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|------------------------------------|---|--|
|  and 2-ClC ₆ H ₄ CHO | HCl |  (—) GG, R = 2-ClC ₆ H ₄ | 358 |
| 4-ClC ₆ H ₄ CHO 3-O ₂ NC ₆ H ₄ CHO 4-O ₂ NC ₆ H ₄ CHO C ₆ H ₅ CHO 3,4-(CH ₂ O ₂)C ₆ H ₄ CHO 2-CH ₂ OC ₆ H ₄ CHO 4-CH ₂ OC ₆ H ₄ CHO | .. | GG, R = 4-ClC ₆ H ₄ (73) GG, R = 3-O ₂ NC ₆ H ₄ (61) GG, R = 4-O ₂ NC ₆ H ₄ (52) GG, R = C ₆ H ₅ (97) GG, R = 3,4-(CH ₂ O ₂)C ₆ H ₄ (99) GG, R = 2-CH ₂ OC ₆ H ₄ (—) GG, R = 4-CH ₂ OC ₆ H ₄ (91) | 358 358 358 358 358 358 358 |
|  and C ₆ H ₅ CHO | (CH ₂) ₅ NH |  (—) | 368 |
|  and C ₆ H ₅ CHO | NaOC ₂ H ₅ |  (45) | 2308 |
|  and C ₆ H ₅ CHO | | | |
|  | KOH |  (—) HH, R = 2-(C ₄ H ₃ S) | 2265 |
|  | .. | HH, R = 2-(C ₄ H ₃ O) (—) | 2265 |
|  | .. | HH, R = 2-(C ₅ H ₄ N) (—) | 2265 |
|  | .. | HH, R = 2-(CH ₃ C ₄ H ₃ O) (—) | 2265 |
| 4-FC ₆ H ₄ CHO C ₆ H ₅ CHO 3,4-(CH ₂ O ₂)C ₆ H ₄ CHO 4-CH ₂ OC ₆ H ₄ CHO C ₆ H ₅ CH=CHCHO 4-CH ₂ CONHC ₆ H ₄ CHO 4-(CH ₂) ₂ NC ₆ H ₄ CHO 1-C ₁₀ H ₇ CHO | .. | HH, R = 4-FC ₆ H ₄ (—) HH, R = C ₆ H ₅ (—) HH, R = 3,4-(CH ₂ O ₂)C ₆ H ₄ (—) HH, R = 4-CH ₂ OC ₆ H ₄ (—) HH, R = C ₆ H ₅ CH=CH (—) HH, R = 4-CH ₂ CONHC ₆ H ₄ (—) HH, R = 4-(CH ₂) ₂ NC ₆ H ₄ (—) HH, R = 1-C ₁₀ H ₇ (—) | 2265 2265 2265 2265 2265 2265 2265 2265 |
|  | .. | HH, R = 1-(CH ₂ OC ₁₀ H ₈) (—) | 2265 |
|  | .. | HH, R = 9-(C ₁₄ H ₉) (—) | 2265 |

Note: References 668-2359 are on pp. 403-438.

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

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| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|--------------------|---|--------------|
|  and | | | |
|  | KOH |  (96) | 2282 |
|  | .. | II, R = 2-(C ₄ H ₃ S) | 2282 |
|  | .. | II, R = 2-(C ₄ H ₃ Se) (100) | 2282 |
|  | .. | II, R = 2-(C ₄ H ₃ O) (62) | 2282 |
|  | .. | II, R = 2-(CH ₃ C ₄ H ₂ O) (70) | 2282 |
| C ₆ H ₅ CHO 4-(CH ₃) ₂ NC ₆ H ₄ CHO | NaOH KOH | II, R = C ₆ H ₅ (43) II, R = 4-(CH ₃) ₂ NC ₆ H ₄ (92) | 2309 2282 |
|  and C ₆ H ₅ CHO | NaOH |  (24) | 2310 |
|  and | | | |
|  | .. |  (50) | 1929 |
| C ₆ H ₅ CHO 3,4-(CH ₂ O) ₂ C ₆ H ₃ CHO | .. | JJ, R = 2-(C ₆ H ₅ O) JJ, R = C ₆ H ₅ (50) | 1929 1929 |
|  and C ₆ H ₅ CHO | .. |  (73) | 2310 |
| C ₆ H ₅ CH ₂  COCH ₃ and (CH ₃) ₂ C=CHCH ₂ CH ₂ C(CH ₃)=CHCHO | .. |  (65) | 1773 |
|  and | | | |
| C ₆ H ₅ CHO | NaOCH ₃ |  (62) | 2004 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. |  (57) | 2004 |

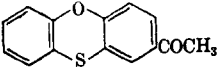
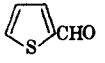
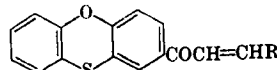
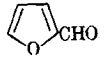
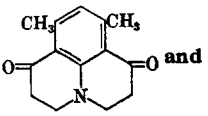
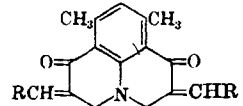
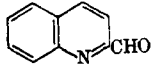
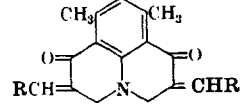

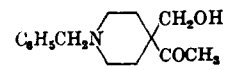
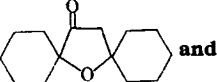
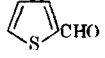
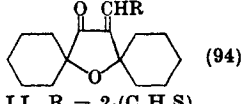
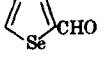
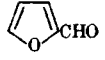
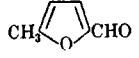
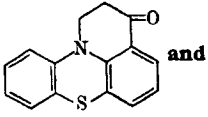
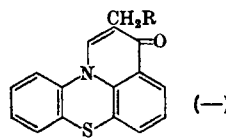
Note: References 668-2359 are on pp. 403-438

ORGANIC REACTIONS

THE ALDOL CONDENSATION

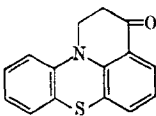
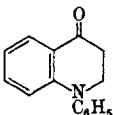
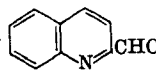
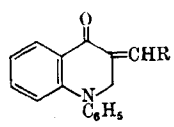
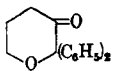

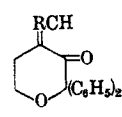
393

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (Continued)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|--|----------------------------------|--|------------|
|  and  | NaOC ₂ H ₅ |  (81) KK, R = 2-(C ₄ H ₃ S) | 2312 |
|  | .. | KK, R = 2-(C ₄ H ₃ O) (82) | 2312 |
| 4-ClC ₆ H ₄ CHO | .. | KK, R = 4-ClC ₆ H ₄ (75) | 2312 |
| C ₆ H ₅ CHO | .. | KK, R = C ₆ H ₅ (83) | 2312 |
| 4-CH ₃ OC ₆ H ₄ CHO | .. | KK, R = 4-CH ₃ OC ₆ H ₄ (90) | 2312 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | .. | KK, R = 4-(CH ₃) ₂ NC ₆ H ₄ (70) | 2312 |
|  and 4-(CH ₃) ₂ NC ₆ H ₄ CHO | KOH |  (93) | 368 |
|  | .. |  (—) | 368 |
| C ₆ H ₅ CH ₂ N  COCH ₃ and CH ₂ O | NaOH |  (31) | 450 |
|  and  | KOH |  (94) LL, R = 2-(C ₄ H ₃ S) | 2282 |
|  | .. | LL, R = 2-(C ₄ H ₃ Se) (70) | 2282 |
|  | .. | LL, R = 2-(C ₄ H ₃ O) (95) | 2282 |
|  | .. | LL, R = 2-(CH ₃ C ₄ H ₃ O) (92) | 2282 |
| C ₆ H ₅ CHO | NaOH | LL, R = C ₆ H ₅ (55) | 2309 |
| 4-(CH ₃) ₂ NC ₆ H ₄ CHO | KOH | LL, R = 4-(CH ₃) ₂ NC ₆ H ₄ (90) | 2282 |
|  and 4-ClC ₆ H ₄ CHO | None |  (—) MM, R = 4-ClC ₆ H ₄ | 2313, 2328 |
| 3-O ₂ NC ₆ H ₄ CHO | .. | MM, R = 3-O ₂ NC ₆ H ₄ (—) | 2313, 2328 |

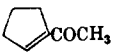
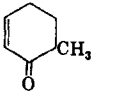
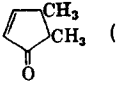
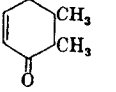
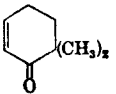
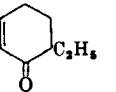
Note: References 668-2359 are on pp. 403-438

TABLE XIX. CONDENSATION OF ALDEHYDES WITH HETEROCYCLIC KETONES (*Continued*)
(R in the product is the group R in the aldehyde RCHO.)

| Ketone and Aldehyde, RCHO | Catalyst | Product(s) (Yield, %) | Refs. |
|---|------------------|---|--|
|  (<i>contd.</i>) and C_6H_5CHO $4-CH_3OC_6H_4CHO$ $4-(CH_3)_2NC_6H_4CHO$ | None | MM, R = C_6H_5 (—) MM, R = $4-CH_3OC_6H_4$ (—) MM, R = $4-(CH_3)_2NC_6H_4$ (—) | 2313, 2328 2313, 2328 2313, 2328 |
|  and  | KOH |  (80) | 368 |
|  and  | NaOH |  (—) | 2314 |

Note: References 668–2359 are on pp. 403–438.

TABLE XX. INTRAMOLECULAR CONDENSATION OF KETOALDEHYDES

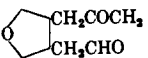
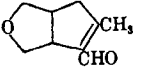
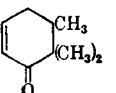
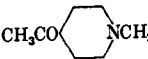
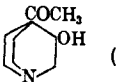
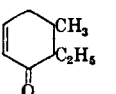
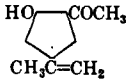
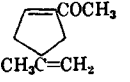
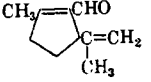
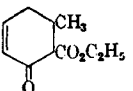
| Ketoaldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|--|-----------------------------------|--|----------|
| $\text{CH}_2\text{CO}(\text{CH}_2)_4\text{CHO}^*$ | NaOH |  (73) | 2315 |
| $\text{CH}_2\text{COCH}(\text{CH}_3)(\text{CH}_2)_2\text{CHO}^\dagger$ | KOCH_3 |  (40) | 447, 448 |
| $\text{CH}_2\text{COCH}(\text{CH}_2)\text{CH}(\text{CH}_2)\text{CHO}$ | $\text{CH}_3\text{CO}_2\text{Na}$ |  (74) | 2316 |
| $\text{CH}_2\text{COCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}^\dagger$ | KOCH_3 |  (35) | 447, 448 |
| $\text{CH}_2\text{COC}(\text{CH}_3)_2(\text{CH}_2)_2\text{CHO}^\dagger$ | .. |  (12) | 447, 448 |
| $\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)(\text{CH}_2)_2\text{CHO}^\dagger$ | .. |  (20) | 447, 448 |

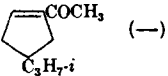
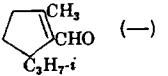
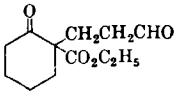
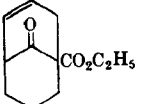
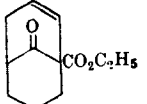
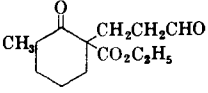
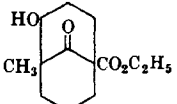
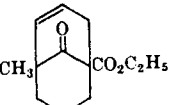
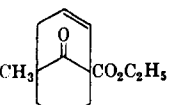
Note: References 668-2359 are on pp. 403-438.

* The ketoaldehyde was formed *in situ* from 2-benzyloxymethylene-1-carbethoxymethylcyclohexan-1-ol.

† The ketoaldehyde was formed *in situ* by Michael addition of the appropriate ketone to acrolein, α -methylacrolein, or crotonaldehyde.

TABLE XX. INTRAMOLECULAR CONDENSATION OF KETOALDEHYDES (Continued)

| Ketoaldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|--|----------|
|  | $(\text{CH}_2)_2\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$; also KOH, KOC_4H_9-t , Al_2O_3 |  (30) | 438 |
| $\text{CH}_2\text{COC}(\text{CH}_3)_2\text{CH}(\text{CH}_2)\text{CH}_2\text{CHO}^\dagger$ | KOCH_3 |  (22) | 447, 448 |
| CH_2CO  $\text{NCH}_2\text{CHO}^\dagger$ | HCl |  (10) | 450 |
| $\text{CH}_2\text{COCH}(\text{C}_2\text{H}_5)\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}^\dagger$ | KOCH_3 |  (30) | 447, 448 |
| $\text{CH}_2\text{CO}(\text{CH}_2)_2\text{CHCH}_2\text{CHO}$ $\text{CH}_3\text{C}=\text{CH}_2$ | KOH |  (25),  (25) | 444 |
| | $(\text{CH}_2)_2\text{NH}$, $\text{CH}_3\text{CO}_2\text{H}$ |  (59) | 445 |
| $\text{CH}_2\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)(\text{CH}_2)_2\text{CHO}$ | NaOC_2H_5 |  (53) | 2317 |

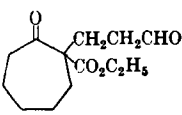
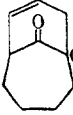
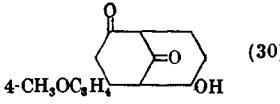
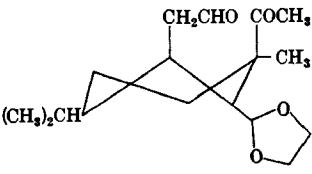
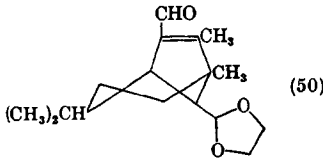
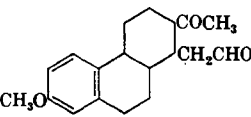
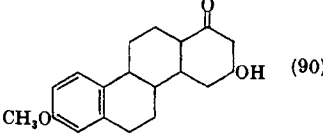
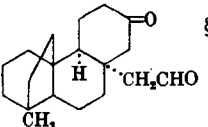
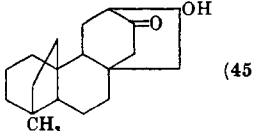
| | | | |
|---|--|---|------------|
| $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}(\text{C}_3\text{H}_7-i)\text{CH}_2\text{CHO}$ | KOH |  (—) | 436, 437 |
| | $(\text{CH}_2)_5\text{NH}, \text{CH}_3\text{CO}_2\text{H}$ |  (—) | 436 |
|  | H_2SO_4 |  (—),  (—) | 451 |
| | | (I:II = 4.7) | |
|  | HCl, $\text{CH}_3\text{CO}_2\text{H}$ |  (80) | 2318, 2358 |
| | H_2SO_4 |  (30),  (11) | 2318, 451 |

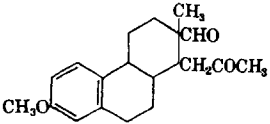
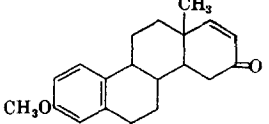
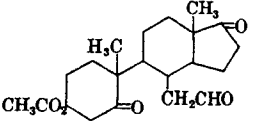
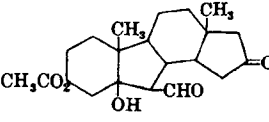
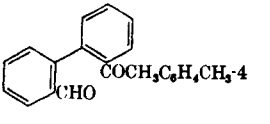
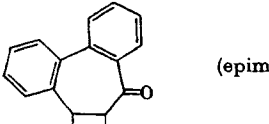
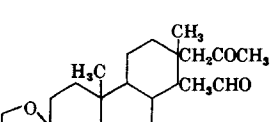
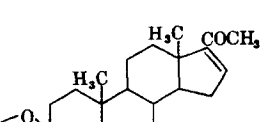
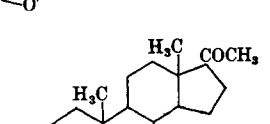
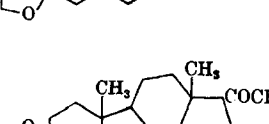
Note: References 668–2359 are on pp. 403–438.

† The ketoaldehyde was formed *in situ* by Michael addition of the appropriate ketone to acrolein, α -methylacrolein, or crotonaldehyde.

‡ The ketoaldehyde was formed *in situ* from the diethyl acetal.

TABLE XX. INTRAMOLECULAR CONDENSATION OF KETOALDEHYDES (Continued)

| Ketoaldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|---------------------------------------|---|-------|
|  | H_2SO_4 , then KOH |  (16) | 2319 |
| $4\text{-CH}_3\text{OC}_6\text{H}_4\text{-C}_6\text{H}_4\text{-C(=O)-CH}_2\text{CH}_2\text{CHO}^\ddagger$ | HCl, $\text{CH}_3\text{CO}_2\text{H}$ |  (30) | 2320 |
|  | NaOH |  (50) | 439 |
|  | KOH |  (90) | 1316 |
|  | H_2SO_4 |  (45) | 449 |

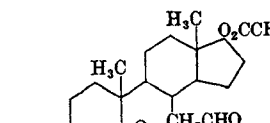
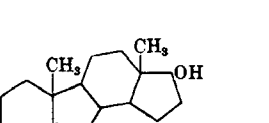

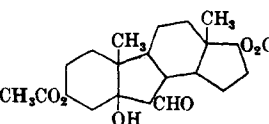
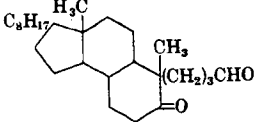
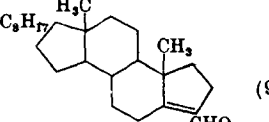
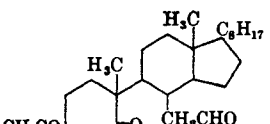
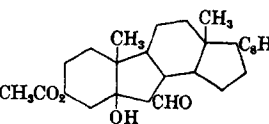
| | | | |
|---|---|---|-----------|
|  | $\text{CH}_3\text{CO}_2\text{Na}, \text{CH}_3\text{CO}_2\text{H}$ |  (—) | 2321, 442 |
|  | Al_2O_3 |  (64) | 441, 442 |
|  | Florisil |  (epimers) (60) | 70 |
|  | KOH |  (73) | 434 |
|  | Al_2O_3 |  (—) | 2322 |

Note: References 668-2359 are on pp. 403-438.

‡ The ketoaldehyde was formed *in situ* from the diethyl acetal.

§ The ketoaldehyde was formed *in situ* from the ketal.

TABLE XX. INTRAMOLECULAR CONDENSATION OF KETOALDEHYDES (Continued)

| Ketoaldehyde | Catalyst | Product(s) (Yield, %) | Refs. |
|---|--|---|----------|
|  | KOH |  (25) | 435 |
|  | Al_2O_3 |  (68) | 441, 442 |
|  | $\text{HCl}, \text{CH}_3\text{CO}_2\text{H}$ |  (90) | 440 |
|  | Al_2O_3 |  (74) | 441, 442 |

Note: References 668-2359 are on pp. 403-438.

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