The two solutions were combined immediately and agitated for 5 min. Then 300 ml. of methylene chloride was added. Vigorous agitation was supplied as dilute sulfuric acid was added to reduce the *p*H to about 8.0, where a permanent brown color appeared. The phases were separated and the organic layer was washed with water until the final wash was neutral. When the solvent was evaporated, 131 g. of crude oil (48% yield) was obtained. Crystallization was induced by the addition of pentane to give coarse white granular crystals, m.p. 48–49°.

Anal. Calcd. for $C_{10}H_{13}IO$: I, 45.96; C, 43.50; H, 4.74. Found: I, 46.4; C, 43.23; H, 4.69.

A second crop was obtained from the original aqueous phase by neutralization to a *p*H of 7.2.

Acknowledgment. I am indebted to Dr. A. W. Baker for assistance with the interpretation of infrared spectra and to Mrs. Veda M. Brink and Mrs. Lillian Troxell for assistance with the experimental work.

PITTSBURG, CALIF.

[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Preparation of *alpha* Allyl Ketones from Allyl Alcohol and Ketones

N. B. LORETTE

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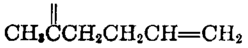
Various ketones and allyl alcohol were allowed to react at elevated temperatures to give *alpha* allyl-substituted ketones. The influence of the reaction time, temperature, reactant ratio, and catalysts on the course of the reaction was studied. The presence of an allyl group on an *alpha* carbon atom of a ketone inhibits further reaction at that atom. A reaction mechanism is proposed.

While carrying out experiments related to recent work[1] in which 5-hexen-2-one was being prepared by heating a solution of 2,2-dimethoxypropane and excess allyl alcohol, it was noted that 5-hexen-2-one (allylacetone) and 3-allyl-5-hexen-2-one continued to be formed after the 2,2-dimethoxypropane had disappeared. This indicated that the allyl alcohol was reacting directly with the ketones present. This was shown to be the case by the formation of 5-hexen-2-one when an acidified mixture of acetone and allyl alcohol was heated.

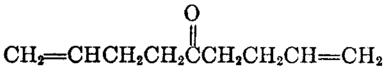
TABLE I

PRODUCT DISTRIBUTION FOR THE REACTION BETWEEN ALLYL ALCOHOL AND ACETONE AT 250–260°

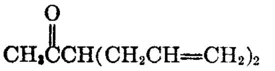
Moles Allyl Alcohol per Mole Acetone	Reaction Time (Hr.)	% Conversion of Acetone to Product		
		I	II	III
1	1	13	Trace	Trace
1	3	24	0.5	1.8
1	6	34	1.7	5.2
3	1	30	0.5	3.2
3	3	37	3.5	8.8
3	6	32	5.8	21.0[a]
5	1	34	1.0	5.7
5	3	39	4.0	21.0[a]
5	6	30	8.5	30.0[a]

I = 

$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2$

II = 

$CH_2{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2$

III = 

$CH_3\overset{\overset{O}{\|}}{C}CH(CH_2CH{=}CH_2)_2$

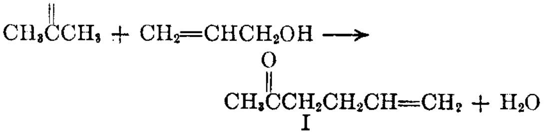
[a] Small amounts of triallylacetones present.

The reaction does not stop at the monoallyl product, however, but proceeds as shown.

The formation of the more substituted ketones was favored by increasing the ratio of allyl alcohol to ketone and by longer reaction time (Table I).

It is known[2] that diallyl ketals will crack and rearrange (Claisen rearrangement) to give *alpha* allyl-substituted ketones but the conditions of the experiments for the direct reaction between allyl alcohol and ketones are quite different from the conditions which favor the formation of ketals. The temperatures used for the direct reaction were 200° to 300°. At these temperatures it is doubtful that any diallyl ketal would be present. Generally, temperatures below 0° are preferred for ketal preparation because at 25° there is very little ketal present at equilibrium.[3]

K. C. Brannock[4] reported that *alpha* allyl aldehydes could be prepared by refluxing an acidified solution of an aldehyde, allyl alcohol, and an inert



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + CH_2{=}CHCH_2OH \longrightarrow \underset{\text{I}}{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2} + H_2O \quad (1)$$

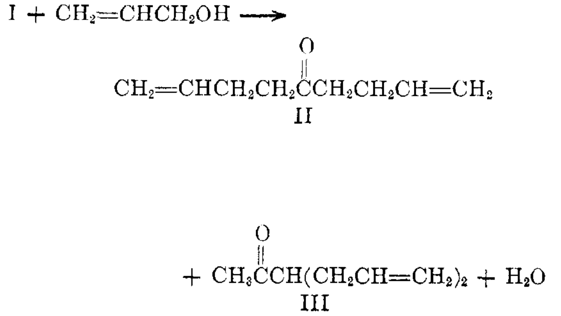
---

[1] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26**, 3112 (1961).

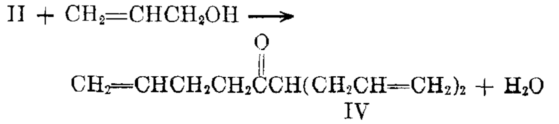
[2] C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1909 (1938).

[3] N. B. Lorette, W. L. Howard, and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 1731 (1959).

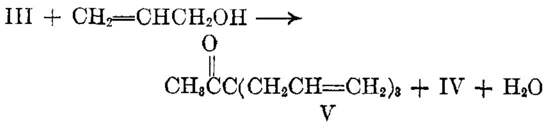
[4] K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).



$$\mathrm{I} + CH_2{=}CHCH_2OH \longrightarrow \underset{\mathrm{II}}{CH_2{=}CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH{=}CH_2} + \underset{\mathrm{III}}{CH_3\overset{O}{\overset{\|}{C}}CH(CH_2CH{=}CH_2)_2} + H_2O \quad (2)$$



$$\mathrm{II} + CH_2{=}CHCH_2OH \longrightarrow \underset{\mathrm{IV}}{CH_2{=}CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH(CH_2CH{=}CH_2)_2} + H_2O \quad (3)$$



$$\mathrm{III} + CH_2{=}CHCH_2OH \longrightarrow \underset{\mathrm{V}}{CH_3\overset{O}{\overset{\|}{C}}C(CH_2CH{=}CH_2)_3} + \mathrm{IV} + H_2O \quad (4)$$

high-boiling solvent. Good evidence was given to show that the diallyl acetal of the aldehyde was an intermediate. It has also been reported[1] that refluxing an acidified solution of allyl alcohol and acetone for ninety-one hours did not produce a detectable amount of 5-hexen-2-one.

Water produced by the reaction of the ketone and allyl alcohol was not simultaneously removed from the reaction system. To show the influence of water on the reaction, as much as two moles of water per mole of ketone was added at the start of the reaction. The total reaction was less, but the amount of decrease was surprisingly small. The presence of water has a very marked inhibitory effect on the formation of ketals from alcohols and ketones.

The reverse reaction of water reacting with an allyl ketone to give the ketone and allyl alcohol does not occur at the reaction conditions used in this work.

Many catalysts were tested during the present investigation and the following generalizations can be made. All materials used that were acids or acid salts (salts whose aqueous solutions had a pH of < 7) were good catalysts. Basic salts inhibited the reaction. Cobaltous phosphate octahydrate was a good catalyst even though it was almost insoluble in the reaction system. Salts that contain at least one ionizable hydrogen atom such as disodium phosphate are good catalysts even though their water solutions may be basic. The results of the catalyst screening experiments are shown in Table II.

TABLE II

Effect of Various Catalysts on the Reaction between Allyl Alcohol and Acetone

Catalyst	% Acetone Converted to Product I	II	III	Ratio III/II
$Zn(C_3H_2O)_2 \cdot 2H_2O$	0.5			
$Mg(C_3H_2O_2)_2 \cdot 4H_2O$	0.7			
NaCl	2.3			
Control (No cat.)	3.7			
CH_3COOH	21	1.1	0.6	0.53
$Co_3(PO_4)_2 \cdot 8H_2O$	21	1.0	0.6	0.60
Na_2HPO_4	22	0.4	0.4	1.0
$CaCl_2$	26	1.5	4.1	2.7
$CoCl_2$	24	1.2	4.1	3.4
NH_4Cl	17	2.0	11.4	5.4
H_2SO_4	20	1.7	11.8	6.9

When 5-hexen-2-one was allowed to react with allyl alcohol, Equation 2, the reaction always occurred at both the methylene and methyl *alpha* carbon atoms. Examination of the amounts of II and III formed in the catalyst screening experiments (Table II), indicated that the more acidic the reaction system, the greater the formation of III relative to II. In more general terms, it appeared that the more acidic the reaction medium, the greater the reactivity at the more highly substituted *alpha* carbon atom relative to the amount of reaction at the less substituted *alpha* carbon atom. To check the validity of this generalization, 3-allyl-5-hexen-2-one (III) was allowed to react with allyl alcohol with various amounts of phosphoric acid present (Equation 4). In an experiment using 0.09 g. of phosphoric acid for the catalyst, the reaction favored the formation of IV over V by a ratio of four to one. When the amount of catalyst was increased tenfold, the ratio of the products formed was reversed so that the formation of V was favored over IV by a ratio of seventeen to one (see Table III).

TABLE III

Effect of Acid Concentration on the Product Distribution for the Reaction between Allyl Alcohol and 3-Allyl-5-hexen-2-one

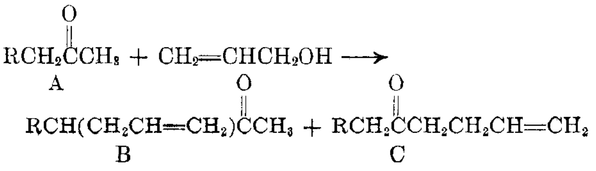
H_3PO_4, G.	% Conversion of III to Product IV	V	% Unchanged III
0.09	4.9	1.2	93
0.36	8.0	16.0	73
0.90	2.0	35.0	56
1.8	4.1	16.0	21 + Tar
(8 Hr., 0.4 g. $Co_3(PO_4)_2 \cdot 8H_2O$)	9.0	0.3	91

The use of cobaltous phosphate octahydrate for catalysis of reaction (4) resulted in the most striking example of the reaction favoring the methyl group. Conversion of III was low but there was thirty times more IV than V formed.

The presence of an allyl group attached to an *alpha* carbon atom of a ketone caused that atom to be less reactive than if a *n*-propyl group were attached. This was demonstrated by using 5-hexen-2-one and 2-hexanone in the reaction with allyl alcohol. Comparative experiments (Table IV) using three different catalysts indicated the *alpha* methylene group of 2-hexanone to be as much as 130% more reactive than the *alpha* methylene carbon atom of 5-hexen-2-one. The influence of two allyl groups attached to the same *alpha* carbon atom was shown to favor reaction at the methyl group by a four to one ratio when III was allowed to react with allyl alcohol. Under the same conditions, reaction at the methyne *alpha* carbon atom of 3-propyl-2-hexanone was favored seven to one.

TABLE IV

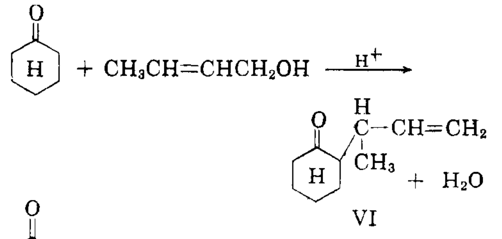
INFLUENCE OF AN ALLYL GROUP ATTACHED TO AN *alpha* CARBON ATOM



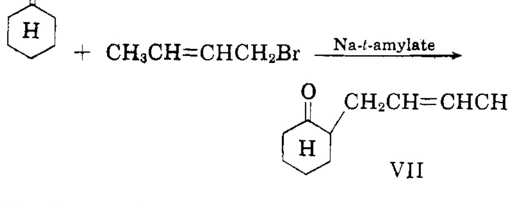
$$\underset{A}{RCH_2\overset{O}{\overset{\|}{C}}CH_3} + CH_2{=}CHCH_2OH \longrightarrow \underset{B}{RCH(CH_2CH{=}CH_2)\overset{O}{\overset{\|}{C}}CH_3} + \underset{C}{RCH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH{=}CH_2}$$

R	Catalyst	Quantity, G.	% of A Converted to B	% of A Converted to C	Ratio B/C
Allyl	Lactic acid (85%)	1.8	4.7	4.9	0.9
Propyl	Lactic acid (85%)	1.8	11.0	5.6	1.9
Allyl	$CaCl_2$	0.4	27	11	2.5
Propyl	$CaCl_2$	0.4	48	7.8	6.1
Allyl	H_3PO_4 (85%)	0.18	32	10	3.2
Propyl	H_3PO_4 (85%)	0.18	47	9.4	5.0

To show whether or not the reaction proceeded by a Claisen rearrangement, the infrared spectrograms of the products of reactions (5) and (6) were compared.



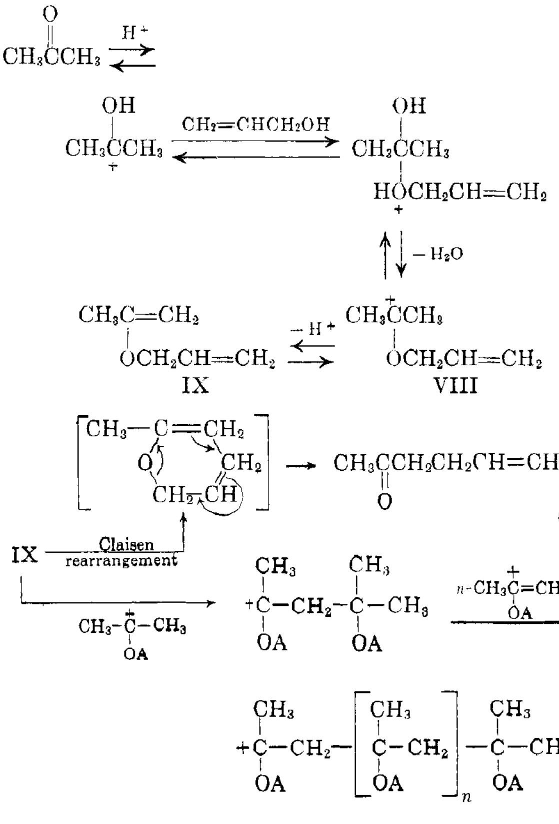
(5)



(6)

The infrared spectrograms showed that the double bond of VI was terminal and that of VII was internal. Since the product of reaction (5) contained a terminal double bond, it was concluded that the structure assigned for compound VI was correct and that it was the result of a Claisen rearrangement of an intermediate reaction species.

The following reaction mechanism is proposed as the possible route to the various products observed.



(7)

(8)

A = $CH_2{=}CHCH_2{-}$

In an acid medium, acetone forms a carbonium ion. This can react with allyl alcohol followed by the elimination of water to form a new carbonium ion. The ejection of a proton by intermediate VIII can give allylisopropenyl ether IX. If the concentration of the ether is low, then the known Claisen rearrangement (reaction 8) will be the predominant reaction, and the rearrangement is the rate-determining step. As the acid concentration is increased, there is a corresponding increase in the amount of ether. This increase in ether concentration favors the second-order carbonium ion polymerization. This mechanism is in accord with our experimental results. At higher acid concentrations there was much polymer formation.

When a hydrogen atom of a methyl group of the carbonium ion (VIII) was substituted with a propyl group, the elimination of a proton took place preferentially from the carbon atom containing the least number of hydrogen atoms. This is in accord with the Saytzeff rule.

Under conditions of very low acid catalyst concentration or no catalyst, the reaction is slow and the products indicate a nonselective pyrolysis reaction. It is thought that under these conditions the ejection of the proton from VIII is nonselective.[5]

EXPERIMENTAL

For most experiments a 300-ml. capacity rocking autoclave was charged with 150 ml. of the reaction mixture and heated for the desired time at the chosen temperature. The crude reaction mixture was then analyzed by vapor chromatography. The reaction mixture was water washed, dried with potassium carbonate, and distilled for recovery of the products. Actual recovered yields were usually above 90% of the values indicated by vapor chromatography to be present in the original crude reaction mixture.

Direct distillation of the products of the reaction of allyl alcohol and acetone can be used to recover unchanged acetone; however, recovery of the allyl alcohol is complicated by a ternary azeotrope (b.p. 88–89°) composed of water (22% vol.), allyl alcohol (70%), and 5-hexen-2-one (8%). No azeotrope is formed when a mixture of allyl alcohol and 5-hexen-2-one is distilled.

Mesityl oxide appeared only when a molar excess of acetone to allyl alcohol was used. The formation of allyl ether was rarely more than 2% of the starting allyl alcohol and then only when strong acid catalysts such as sulfuric acid or *p*-toluenesulfonic acid were used. If the reaction temperature was maintained below about 260°, over 95% of the starting ketone could be accounted for as allyl ketones and unchanged starting ketone. As higher reaction temperatures were used, the product contained increasing amounts of dark polymeric tar.

Except where specifically noted, all products were isolated as chromatographically pure materials. The products, 5-hexen-2-one, n_D^{24} 1.4182, d_{24} 0.838, b.p. 55° (50 mm.), 1,8-nonadien-5-one, n_D^{25} 1.4462, d_{25} 0.860, b.p. 77° (15 mm.), and 3-allyl-5-hexen-2-one, n_D^{24} 1.4450, d_{24} 0.859, b.p. 68° (15 mm.), were identical with those obtained by the cracking and rearrangement of diallyl ketals in previous work.[1]

Effect of reaction time and ratio of reactants on the reaction of allyl alcohol and acetone. For the data in Table I, 150 ml. of the reaction solution having the indicated mole ratio of allyl alcohol to acetone was maintained at 250–260° for the specified time. The reaction was catalyzed with 0.09 g. of 85% phosphoric acid. The product data in the table are based on chromatographic analysis of the crude reaction products.

Effect of water on the reaction of 3-pentanone and allyl alcohol. The autoclave was charged with 150 ml. of a solution of allyl alcohol, 3-pentanone (3:1 mole ratio), and 0.18 g. of 85% phosphoric acid. After a 2-hr. reaction period at 240–250°, there was a 44% yield of 4-methyl-6-hepten-3-one (X), n_D^{23} 1.4253, d_{23} 0.835, b.p. 153 (762 mm.) (lit.,[6] b.p. 153–156), and 56% unchanged 3-pentanone in the crude product. The experiment was repeated with the addition of 1 mole of water per mole of pentanone in the starting solution, and there was present in the crude product a 29% yield of X and 70% unchanged pentanone. When repeated with 2 moles of water per mole of starting ketone, there was obtained a 25% yield of X and 75% unchanged 3-pentanone.

Catalyst screening experiments. The data in Table II were obtained by heating 150 ml. of a solution of allyl alcohol and acetone (3:1 mole ratio) to 240–250° for 1 hr. with 0.4 g. of catalyst.

Effect of acid concentration on product distribution. The data of Table III were obtained by allowing a 150-ml. charge of a solution of allyl alcohol and 3-allyl-5-hexen-2-one to react at 240–250° for 2 hr. with various amounts of catalysts present.

4-Allyl-1,8-nonadien-5-one (IV). A solution consisting of 0.75 mole of 1,8-nonadien-5-one, 1.5 moles of allyl alcohol and 0.18 g. of phosphoric acid was heated to 240–250° for 2 hr. The crude products contained 0.53 mole of the starting 1,8-nonadien-5-one and 0.21 mole of IV. After water washing and drying the crude products with potassium carbonate, the remaining material was distilled to give the unchanged 1,8-nonadien-5-one and chromatographically pure IV, n_D^{25} 1.4590, d_{25} 0.867, and b.p. 96° (9 mm.).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.18. Found: C, 80.80; H, 10.17.

3,3-Diallyl-5-hexen-2-one (*V*). The method of Conia[7] was used. To a cooled solution of 0.78 mole of sodium *tert*-amylate dissolved in 500 ml. of toluene was added 0.8 mole of 3-allyl-5-hexen-2-one followed by the slow addition of 0.8 mole of allyl bromide. The reaction solution was then refluxed for 1.5 hr., cooled, water washed, and dried with potassium carbonate. Distillation of the dried solution resulted in the recovery of 0.1 mole of 3-allyl-5-hexen-2-one and 0.6 mole of V (7% of isomeric 4-allyl-1,8-nonadien-5-one was present), n_D^{25} 1.4702, d_{25} 0.888, b.p. 86° (6 mm.), (lit.,[7] n_D^{18} 1.4733, d_{18} 0.894).

Attempted hydrolysis of 3-allyl-5-hexen-2-one. A solution composed of 0.75 mole of 3-allyl-5-hexen-2-one, 1.5 moles of water, and 0.18 g. of phosphoric acid was heated at 270–280° for 2 hr. in the autoclave. By vapor chromatography there was shown to be 94% of the starting 3-allyl-5-hexen-2-one present. There was no 5-hexen-2-one, 3,3-diallyl-5-hexen-2-one, or 4-allyl-1,8-nonadien-5-one detected.

Influence of one allyl group attached to an alpha carbon atom on direction of reaction. The data of Table IV were obtained by allowing 150 ml. of a solution of allyl alcohol, ketone (3:1 mole ratio), and the indicated catalyst to react for 2 hr. at 240–250°.

2-Hexanone. This compound was prepared by the hydrogenation of 5-hexen-2-one at 25° using 5% platinum on alumina, n_D^{25} 1.3990, d_{25} 0.804, b.p. 68° (100 mm.).

Allyl derivatives of 2-hexanone. From the products of the reaction of allyl alcohol and 2-hexanone, there were recovered by distillation 3-allyl-2-hexanone (XI), n_D^{25} 1.4300, d_{25} 0.832, b.p. 71° (17 mm.) and 1-nonen-5-one (XII), n_D^{25} 1.4307, d_{25} 0.837, b.p. 81° (17 mm.).

Anal. Calcd. for XI and XII, $C_9H_{16}O$: C, 77.09; H, 11.50. Found for XI: C, 77.42; H, 11.55. Found for XII: C, 77.08; H, 11.41.

Additional evidence that the structures are correct was given by infrared spectra. A methyl carbonyl group was present in XI and absent in XII.

Effect of two allyl groups attached to the same alpha carbon atom on the direction of reaction. When 150 ml. of a solution of 3 moles of allyl alcohol and 1 mole of 3-allyl-5-hexen-2-one catalyzed with 0.09 g. of 85% phosphoric acid was allowed to react for 2 hr. at 230–240°, the conversion of III to IV was 4.9% and to V was 1.2%.

In a similar experiment 3-propyl-2-hexanone XIII was allowed to react with allyl alcohol. Eleven per cent of the starting XIII was converted to 3-allyl-3-propyl-2-hexanone and 1.5% converted to 4-propyl-8-nonen-5-one (XIV). The results of this experiment must be considered as approximations since no XIV was available for a chromatographic standard. However, it is the opinion of the author that any error in the yield figures is less than ±10% of the yield values given.

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(5) The referee noted that the loss of a proton from VIII should be independent of acid catalyst concentration, but that the acid catalyzed equilibration of the two enol ethers should be more rapid the higher the acid concentration. The ratio of products in the acid and neutral conditions could be kinetically controlled. It is agreed that the alternative explanation is quite possible.

(6) A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1850 (1941).

(7) J. M. Conia, *Bull. soc. chim. France*, **1956**, 1392.

3-Propyl-2-hexanone (XIII). A 95% yield of 3-propyl-2-hexanone, n_D^{25} 1.4190, d_{25} 0.817, b.p. 52° (6 mm.), was obtained by the hydrogenation of 360 ml. of 3-allyl-5-hexen-2-one in the presence of 1 g. of 5% platinum on alumina.

3-Allyl-3-propyl-2-hexanone (XV). To a solution of 0.87 mole of sodium *tert*-amylate dissolved in 500 ml. of toluene was added 0.9 mole of 3-propyl-2-hexanone at a reaction temperature of 50° (at a lower temperature the *tert*-amylate tended to precipitate from the toluene). Allyl bromide was added slowly so that the reaction temperature was maintained between 50–80°. The mixture was refluxed for 1 hr., water washed, dried with potassium carbonate, and distilled. There were recovered 0.27 mole of 3-propyl-2-hexanone and 0.52 mole of XV, n_D^{25} 1.4470, d_{25} 0.861, b.p. 82° (4 mm.). The compound was not obtained chromatographically pure but contained about 7% of what was believed to be the isomeric 4-propyl-8-nonen-5-one.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.31; H, 12.15.

2-(1-Methylallyl)cyclohexanone (VI). The autoclave was charged with 220 ml. of a mixture containing 2 moles of crotyl alcohol and 1 mole of cyclohexanone. The charge was catalyzed with 0.09 g. phosphoric acid and heated for 3 hr. at 240–250°. The crude reaction mixture was flash distilled at reduced pressure and the final 56 ml. was shown by vapor phase chromatography to have two components present in about equal amounts. The 56-ml. portion was carefully distilled through a vacuum-jacketed column and collected in seven fractions containing 6 to 12 ml. each. Except for a part of fraction 1, all fractions were collected at 101.5–102° (19 mm.). Fraction 3 contained about equal amounts of the two materials and fraction 7 contained 5–15% of the component which had the shorter retention time on the chromatographic column, with the balance being the component with the longer retention time. The physical properties of fraction 3 were n_D^{25} 1.4688, d_{25} 0.924 and for fraction 7, n_D^{25} 1.4698, d_{25} 0.926.

Anal. Calcd. for $C_{10}H_{15}O$: C, 78.89; H, 10.60. Found for fraction 3: C, 79.28: H, 10.77. Found for fraction 7: C, 78.96; H, 10.76.

The infrared spectrograms for both fractions were almost identical and consistent for the structure of VI. It is believed that the two components are diastereoisomers of VI.

2-Crotylcyclohexanone. In the manner already described, 0.9 mole of cyclohexanone was alkylated with 0.9 mole of crotyl bromide in the presence of 0.8 mole of sodium *tert*-amylate at 10–20°. The reaction mixture was water washed and distilled. A 53% yield of 2-crotylcyclohexanone was obtained, n_D^{25} 1.4713, d_{25} 0.925, b.p. 87° (6 mm.).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 79.02; H, 10.67.

The infrared spectrum was consistent with the structure of 2-crotylcyclohexanone.

Allyl-substituted cyclopentanones. From a 3:1 molar stock solution of allyl alcohol and cyclopentanone, a 150-ml. sample was put in the autoclave with 0.18 g. of phosphoric acid. The material was heated for 2 hr. at 240–250°. There was a 95% conversion of the cyclopentanone and a 42% yield of 2-allylcyclopentanone, 20% 2,2-diallylcyclopentanone, and a 37% yield of 2,5-diallylcyclopentanone. The 2-allylcyclopentanone, n_D^{24} 1.4582, d_{24} 0.924, b.p. 62° (10 mm.), was the same as the material previously prepared.[1]

Chromatographically pure samples of the 2,2- and 2,5-diallylcyclopentanones were obtained by distillation of the combined products of several experiments through a 4-ft. vacuum-jacketed distillation column packed with $^1/_8$-in. glass helices. 2,2-Diallylcyclopentanone had n_D^{25} 1.4760, d_{25} 0.929, b.p. 85° (7 mm.).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.10; H, 9.76.

2,5-Diallylcyclopentanone had n_D^{25} 1.4683, d_{25} 0.912, b.p. 91° (7 mm.).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.02; H, 9.74.

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[CONTRIBUTION FROM WALKER LABORATORY, RENSSELAER POLYTECHNIC INSTITUTE]

Indan Analogs of Hexestrol and Diethylstilbestrol[1]

CHARLES A. PANETTA[2] AND STANLEY C. BUNCE

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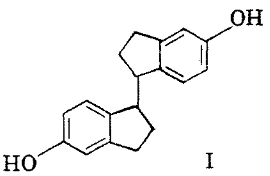
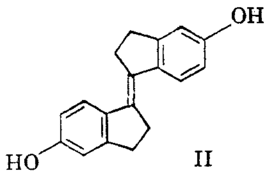
meso-5,5′-Dihydroxy-1,1′-biindan (I), an indan analog of hexestrol, has been prepared from 5-methoxy-1-indanone by conversion to its ketazine, hydrogenation to 5,5′-dimethoxy-1,1′-azoindan, and pyrolysis. Both racemic and *meso*-5,5′-dimethoxy-1,1′-biindan were formed (VI); the latter was demethylated to form *meso*-5,5′-dihydroxy-1,1′-biindan (I).

The syntheses of 5,5′-dimethoxy-1,6′-biindan (VII), 6,6′-dimethoxy-5,5′-biindan (VIII), 5-bromo-6-methoxyindan, 5-iodo-6-methoxyindan, 4-iodo-5-methoxyindan, 5-chloro-6-methoxyindan, 5-nitro-1-indanone, 5-methoxy-1-indenecarboxylic acid (X), 2,2′-diiodo-3,3′-dihydroxy-1,1′-biindan (XII), and 2-(α-chloroacetyl)-5-methoxy-1-indanone (IX) are also reported.

Our interest in the preparation and properties of compounds structurally similar to the estrogenic hormones[3] led us to attempt the preparation of 5,5′-dihydroxy-1,1′-biindan (I) and 5,5′-dihydroxy-$\Delta^{1,1'}$-biindan (II), which are indan analogs of the artificial estrogens, hexestrol, and diethylstilbestrol.



I



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[1] Abstracted from the Ph.D. thesis of Charles A. Panetta, Rensselaer Polytechnic Institute, 1960.

[2] Present address: Chemical Development Department, Bristol Laboratories Inc., Syracuse, N. Y.

[3] For the previous paper in this series see J. G. Bennett, Jr., and S. C. Bunce, *J. Org. Chem.*, **25**, 73 (1960).