the latter case. This is equally true in the case of phenyl alkyl and phenyl vinyl sulfones.[5] Thus there is no evidence from infrared data for the popular notation of resonance interaction involving conjugation between carbon–carbon double bonds and the alleged sulfur–oxygen double bond of sulfones. In the case of the alkyl and vinyl sulfoxide, the intense characteristic SO bond frequency at 9.70 μ actually shifts to shorter wave length in the vinyl compound (9.35 μ).[20]

However, although there is no indication of conjugation with carbon–carbon unsaturation having any of the influence on the SO bond to be expected if the SO bond were double, there is abundant evidence in the infrared spectra for resonance shifts of the absorption for the carbon–carbon double bond itself. The normal behavior for an unconjugated vinyl group is clearly indicated by the bands at 5.48, 6.12 and 10.92 μ in methyl allyl sulfide. The 6.12 band is the normal unperturbed C=C stretching frequency, the 10.92 band is the C=C normal wagging frequency and the 5.48 band is its first harmonic.

In methyl vinyl sulfide, these three bands have shifted to 5.85, 6.30 and 11.70 μ, all in accord with the type of resonance interaction previously proposed[3–5] to account for the ultraviolet spectra and copolymerization characteristics of this compound, $\left[-\underset{..}{\ddot{S}}-C{=}C \leftrightarrow -\underset{..}{\dot{S}}{=}C-\dot{C}\right]$. Contributions from the second form would decrease the double bond character between the carbon atoms, accounting for the decreased resistance to stretching and wagging.

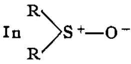
The oxidation of the sulfide group to sulfoxide or sulfone has two pronounced influences on these double bond absorptions of the vinyl group. The first is to reduce markedly the intensity of the C=C absorption relative to the methyl and methylene bands (7.0–7.3 μ). As a result, the only band that is positively identifiable is the stretching frequency, which decreases to 6.20 μ in the sulfoxide and to 6.15 μ in the sulfone.

These same general effects were observed for the case of phenyl vinyl sulfide, sulfoxide and sulfone.[5] Again these observations are in accord with those from ultraviolet spectra and copolymerization,[3–5] all indicating progressively less resonance interaction as the unshared electrons on the sulfur are utilized in bonds to oxygen atoms.

The one other area where one might look for some evidence for resonance involving the sulfur functions is in the C–S frequency. Using sodium chloride optics, we are not able to obtain good resolution of this band, usually occurring around 14.5 μ. Almost all of the compounds showed absorption in this region but unfortunately the shifts are all in the direction opposite to that expected. Compared to the alkyl compounds (14.35–14.50 μ) the allyl sulfur compounds shift to shorter wave length (14.12–14.14 μ, the vinyl to longer (14.60–14.80 μ).

Incidentally, it should be pointed out that the strong conjugation in methyl vinyl sulfide, as indicated by copolymerization data and by ultraviolet and infrared spectra, does not produce any appreciable exaltation of the molecular refraction (Table I).

NOTRE DAME, INDIANA

[20] A shift in this direction, which is also observed for thionyl halides as compared to sulfoxides, may be accounted for by the electronegativity of the groups attached to the sulfur. In  $R_2S^+{-}O^-$, the more electronegative is R, the more positive will be the sulfur. Increased positive charge on the sulfur will increase the ionic contribution to the SO bond strength and will thus shift the vibration to higher frequency (shorter wave length).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

A Study of Some Fluorine-containing β-Diketones[1]

BY J. D. PARK, H. A. BROWN AND J. R. LACHER

RECEIVED DECEMBER 10, 1952

The preparation of seven new β-diketones containing fluorinated groups is reported. The infrared spectra and enolic content of these β-diketones were determined and are noted.[2] Acetylacetone and 1,1,1-trifluoro-2,4-pentanedione were chlorinated and the products identified.

Introduction

Perfluorinated acetic, propionic, butyric and valeric acids were esterified by treating the acids with an equivalent quantity of ethyl alcohol in the presence of concentrated sulfuric acid[3] (approximately 1.5 moles per mole of alcohol). Subsequently, these esters were condensed in good yields with various ketones in the presence of sodium methoxide. Ethyl trifluoroacetate was found to react successfully with cyclopentanone, cyclohexanone, 1-indanone and 1-tetralone. The esters of perfluorinated acetic, propionic, butyric and valeric acids were condensed with acetone with equal success. In each case, the yield of the β-diketones was better than 75%.

Copper chelates of all the β-diketones synthesized in this study were prepared. The physical properties of the β-diketones and copper chelates are shown in Table I.

The enolic content of eight β-diketones contain-

[1] Abstracted from a thesis submitted by H. A. Brown in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Colorado, June, 1952.

[2] The spectra referred to in the body of this paper have been deposited as Document number 4016 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[3] Private communication, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

TABLE I

SUMMARY OF PROPERTIES OF SOME FLUORINATED β-DIKETONES

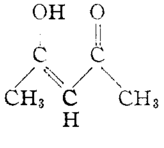
Compound	Yield, %	B.p. or m.p.,[a] °C.	Mm.	$n^{20}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Copper chelate M.p., °C.	Copper chelate Carbon, % Calcd.	Copper chelate Carbon, % Found	Copper chelate Hydrogen, % Calcd.	Copper chelate Hydrogen, % Found	Enol, %[b]
$CF_3COCH_2COCH_3$[c]	..	107[c]	760	$1.3893^{21°}$	...	...	..	..	189	...	...	..	..	92.5
$CF_3CF_2COCH_2COCH_3$	84.5	111-112	631	1.3729	35.30	35.56	2.46	2.16	111.6-112	30.68	30.92	1.72	1.96	120.3
$CF_3(CF_2)_2COCH_2COCH_3$	78.5	55.5-56.8	38-39	1.3646	33.08	33.15	1.98	2.10	55-55.2	29.51	29.53	1.42	1.56	118.5
$CF_3(CF_2)_3COCH_2COCH_3$	80.0	68-68.5	33-34	1.3589	31.59	31.59	1.65	1.89	77.5-78	28.69	28.50	1.20	1.15	120.0
$C_5H_7O-CO-CF_3$[d]	82.3	66	21-22	1.4312	46.67	46.79	3.91	3.73	175-176	39.86	40.13	2.87	2.64	92.7
$C_6H_9O-CO-CF_3$[e]	85.7	76-77	20-21	1.4522	49.48	49.48	4.67	4.58	182-182.5	42.72	34.11	3.59	3.56	90.8
$C_9H_7O-CO-CF_3$[f]	84.2	72.5-73	....	....	57.89	57.90	3.09	2.97	272	51.02	50.91	2.34	2.25	90.2
$C_{10}H_9O-CO-CF_3$[g]	81.2	51-52	....	....	59.51	59.60	3.75	3.73	291-292	52.80	53.12	2 96	3.17	98.6

[a] All melting points were determined on a Fisher-Johns block. All boiling points and melting points are uncorrected. Analyses by Clark Microanalytical Laboratories, Urbana, Illinois. [b] This value represents the average of three determinations agreeing within 1%. [c] Physical constants previously reported by J. C. Reid and M. Calvin, THIS JOURNAL, **72**, 2948 (1950). [d] 2-Trifluoroacetylcyclopentanone. [e] 2-Trifluoroacetylcyclohexanone. [f] 2-Trifluoroacetylindanone-1. [g] 2-Trifluoroacetyltetralone-1.

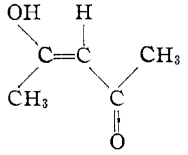
ing fluorinated groups was determined by the usual K. Meyer "indirect method." The procedure employed was checked by determining the enolic content of two β-diketones previously investigated. It is obvious from the results shown in Table I that the trifluoromethyl and other fluorinated groups exert a very noticeable effect on the keto-enol equilibrium. In all eight of the β-diketones investigated, the enolic content was found to be over 90%. In three of the β-diketones containing highly fluorinated groups, the enolic content was determined to be approximately 120%. This apparent anomaly has been reported for other compounds. Meyer[4] reported that he found 179-202% enol when he determined the enolic content of acetylacetone in pyridine as a solvent. Reid and Calvin[5] found that 0.06 *M* solution of isovaleroyltrifluoroacetone in benzene at 25° consistently gave a value of 115% enol.

If the stability of the enol form depends in part upon hydrogen bonding between the enolic hydroxyl group and a carbonyl group or some other group, then the large enolic content found in the fluorinated β-diketones investigated in this work could be explained.

In the case of the enol form of acetylacetone two stereoisomers are possible as indicated by Henecka[6]



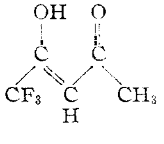
"*syn*" form



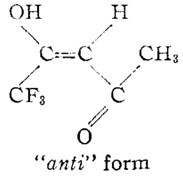
"*anti*" form

Examination of the Fisher-Hirshfelder models indicates that hydrogen bonding cannot occur in the "*anti*" form.

However, if we now consider the possible stereoisomers of the enolic form of trifluoroacetylacetone we have increased the possibility for hydrogen bonding. In the "*syn*" isomer, hydrogen bonding can occur not only with the carbonyl oxygen but also with a fluorine atom of the $-CF_3$ group. In the "*anti*" isomer hydrogen bonding between the enolic OH hydrogen and the carbonyl group is still not possible; however, O-H · · · F bonding can occur and would tend to stabilize this isomer.



"*syn*" form



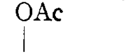
"*anti*" form

This hypothesis offers an explanation for the very high enolic content found in the fluorinated β-diketones investigated in this work. The existence of the O-H · · · X type intramolecular bond, where X is a chlorine atom, has been postulated[7] to explain the infrared absorption spectrum of *o*-chlorophenol.

In the four open-chain, fluorinated β-diketones examined, a very strong band was observed at 6.23 μ. This band was assigned to the C=O (enol) vibration. The C=O band in the cyclic derivatives was located at somewhat shorter wave lengths (6.11-6.17 μ). In all of the fluorinated β-diketones very strong absorption bands were observed in the 7.5-9.0 μ region and these were assigned as due to C-F vibrations.

In most β-diketones, in which the methylene group between the two carbonyl groups is unsubstituted, the C=O absorption band is found at considerably longer wave lengths (6.1-6.3 μ) than the "normal" carbonyl band (5.4-6.1 μ).

If, however, the methylene hydrogens were replaced by two chlorine atoms or other groups, enolization involving the methylene hydrogens would be impossible. As a result the C=O band at 6.1-6.3 μ should shift to shorter wave lengths and the first carbonyl overtone should become more intense. This, indeed, was found to be the case with dibenzoylmethane and dibenzoyldibromomethane. A similar effect was observed with acetylacetone[8] and 3,3-dichloro-2,4-pentanedione and 1,1,1-trifluoro-2,4-pentanedione and 3,3-dichloro-1,1,1-trifluoro-2,4-pentanedione.

A similar effect has been observed by Rasmussen, *et al.*,[8] in the infrared spectra of acetylacetone and acetylacetone acetate  $(CH_3\overset{\overset{OAc}{|}}{C}{=}CH{-}COCH_3)$. The C=O band in acetylactone is found at 6.16 μ, whereas when acetylacetone is acetylated, the band shifts to 5.9 μ.

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(4) K. Meyer, *Ber.*, **45**, 2843, 2848, 2858 (1912).

(5) J. C. Reid and M. Calvin, THIS JOURNAL, **72**, 2952 (1950).

(6) H. Henecka, *Chem. Ber.*, **81**, 189 (1948).

(7) L. Zumwalt and R. Badger, THIS JOURNAL . **62** .305 (1940).

(8) R. S. Rassmussen, *et al.*, *ibid.*, **71**, 1068 (1949

That the direct chlorination of acetylacetone as well as its halogenation with sulfuryl chloride gave 3,3-dichloro-2,4-pentanedione was shown by comparison of the boiling points, refractive indices and infrared spectra of samples prepared by both methods. Furthermore, this material does not give a copper salt while its isomer, 1,1-dichloro-2,4-pentanedione does.

That the dichlorinated derivative of 1,1,1-trifluoro-2,4-pentanedione was 1,1,1-trifluoro-3,3-dichloro-2,4-pentanedione was shown by the facts that it did not give a copper salt and was cleaved by dilute sodium hydroxide solution to give a mixture of trifluoroacetic acid and 1,1-dichloroacetone.

Experimental[9]

Preparation of β-Diketones.—The procedure employed to prepare the β-diketones described in this work is essentially the same as that outlined by Reid and Calvin[10] and Barkley and Levine[11] with slight modifications. Compounds 2, 3 and 4 (Table I) were prepared by treating the ethyl esters of perfluoropropionic, perfluorobutyric and perfluorovaleric acids (1 mole) with acetone (1 mole) in the presence of sodium methoxide (1.1 moles). Compounds 5, 6, 7 and 8 (Table I) were prepared by treating cyclopentanone, cyclohexanone, indanone and tetralone (1 mole), respectively, with ethyl trifluoroacetate (1 mole) in the presence of sodium methoxide (1.1 moles).

The copper chelates of these compounds were prepared by treating the β-diketone with saturated copper acetate solution. The copper chelates of compounds 7 and 8 were found to be exceptionally stable to 10% sulfuric acid and were not decomposed. However, these compounds readily react with hydrogen sulfide.

The data for these compounds are given in Table I.

Preparation of Halogenated β-Diketones. 1. Chlorination of 1,1,1-Trifluoro-2,4-pentanedione.—The 1,1,1-trifluoro-2,4-pentanedione was prepared[9] by condensing ethyl trifluoroacetate with acetone in the presence of sodium methoxide.

One hundred and thirty-three grams (0.86 mole) of the β-diketone was placed in a long glass cylinder fitted with a fritted-glass gas dispersion tube projecting through the wall of the cylinder and extending to the bottom. The top of the cylinder was connected to an efficient reflux condenser, which was in turn connected to a series of traps consisting of an ice-water-trap, a Dry Ice-trap and finally a cylinder filled with water to dissolve hydrogen chloride evolved during the reaction. Chlorine diluted with nitrogen was passed through the β-diketone until the chlorine absorption became sluggish; then the mixture was illuminated with a strong ultraviolet source and an infrared heat lamp and chlorine and nitrogen were passed through the mixture until no more chlorine was absorbed. At first the reaction was very vigorous and exothermic but slowed down toward the end of the chlorine addition.

Nitrogen was passed through the mixture for an additional hour. The mixture was then fractionated, giving 83.7 g. of a compound which analyzed for $C_5H_3Cl_2F_2O_2$ (Calcd. Cl, 31.80; found Cl, 32.09) and 58.6 g. of more highly chlorinated material.

The dichloro product is very lachrymatory and is a nasal irritant. The more highly chlorinated products are also lachrymatory but are much weaker. The dichloro product (as well as the others) does not form a copper chelate with cupric acetate. This evidence in conjunction with the infrared data indicated that the dichloro product was 3,3-dichloro-1,1,1-trifluoro-2,4-pentanedione ($CF_3COCCl_2COCH_3$). The more highly chlorinated products were not isolated and identified.

2. Chlorination of Acetylacetone. a. Using Sulfuryl Chloride.—3,3-Dichloro-2,4-pentanedione ($CH_3COCCl_2COCH_3$) was prepared[12] by slowly dropping sulfuryl chloride (2 moles) into acetylacetone (1 mole) contained in a flask surrounded by an ice-bath. The mixture was stirred for an additional hour at room temperature.

The product was distilled and the middle fraction, b.p. 77° (19–20 mm.), $n^{20}D$ 1.4568, of three cuts was used for infrared spectra determination.

b. Using Elementary Chlorine.—In a manner similar to that used in the chlorination of trifluoroacetylacetone, 70 g. (1 mole) of chlorine was slowly passed into 50 g. (0.5 mole) of acetylacetone dissolved in 50 ml. of carbon tetrachloride. In this experiment, however, the chlorination was allowed to proceed without illumination. Next the solvent was removed and the residue distilled under reduced pressure. Refractionation ultimately gave 21.3 g. of a material which boiled at 77.5–78° at 20–21 mm. which was used in the infrared work. This material did not form a copper chelate, and the boiling point and refractive index ($n^{20}D$ 1.4570) correspond to 3,3-dichloro-2,4-pentanedione obtained by treating sulfuryl chloride with acetylacetone.

3. Preparation of Dibenzoyldibromomethane.—Following the directions in reference 13, this compound was prepared and then was recrystallized from hot 95% ethyl alcohol three times to obtain a pure sample (m.p. 94–95°[12]) for infrared spectra determination.

Hydrolysis of 1,1,1-Trifluoro-3,3-dichloro-2,4-pentanedione ($CF_3COCCl_2COCH_3$).—The hydrolysis of this compound in aqueous sodium hydroxide leads to extensive decomposition and hence the following procedure was adopted: Thirty-four and four-tenths grams (0.154 mole) of the dichloro product was placed in a 100-ml. round-bottom flask fitted with a reflux condenser. The flask was then heated to about 40° and 8.63 g. of solid potassium hydroxide pellets was added slowly to the dichloro product. A very vigorous reaction was observed and a solid material settled to the bottom of the flask. After all the potassium hydroxide had been added, the mixture was gently refluxed for about 10 minutes. The reflux condenser was replaced with a Claisen adapter and the liquid in the flask was removed under reduced pressure collecting it in a Dry Ice-cooled receiver.

By this method 22.2 g. of liquid and 19.7 g. of solid residue (remaining in the flask) were obtained.

Fractionation of the liquid gave 15 g. of material boiling at 40–43° (50–51 mm.). This material in alcohol forms a white semicarbazone derivative, m.p. 160–161°, when treated with aqueous semicarbazide hydrochloride. This material was subsequently shown to be 1,1-dichloroacetone.[14]

The solid material from the hydrolysis was dissolved in hot water to remove it from reaction vessel and then it was evaporated to dryness. Treatment of this material with 12 ml. of concentrated sulfuric acid gave 9.6 g. of trifluoroacetic acid which was converted to the ester (b.p. 56° (630 mm.)) and then to the amide (m.p. 74–75°[15]) by bubbling ammonia through the ester.

Determination of Enolic Content.—For the determination of the enolic content of the fluorinated β-diketones, the indirect method of K. Meyer[16] was elected because it was found to give more satisfactory results than the direct titration method utilizing a standard bromine solution. The results of this investigation are summarized in Table I and the procedure employed as follows:

A sample of the selected β-diketone, about 0.2 g., was weighed into a 125-ml. glass-stoppered erlenmeyer flask. The flask was then placed on a constant temperature bath (20°) and after approximately one-half hour 20 ml. of absolute methyl alcohol (also at 20°) was added to the flask. Immediately 15 ml. of freshly prepared 5–6% bromine solution (methyl alcohol) was added to the flask and after 5 seconds, 10 ml. of 10% phenol (methyl alcohol) was added. Finally, 10 ml. of 10% potassium iodide solution was added and then the flask was allowed to stand in the dark for one hour. The liberated iodine was then titrated with 0.1 *N* sodium thiosulfate using starch as an indicator.

Infrared Spectra.—The infrared spectra were determined using a Perkin-Elmer automatic recording infrared spectrophotometer, model 12-C.

Acknowledgment.—The authors wish to thank the Minnesota Mining and Manufacturing Com-

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[9] All boiling and melting points are uncorrected.

[10] J. C. Reid and M. Calvin, This Journal, **72**, 2948 (1950).

[11] L. B. Barkley and R. Levine, *ibid.*, **73**, 4625 (1951).

[12] A. Combes, *Compt. rend.*, **111**, 273 (1890).

[13] "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., p. 244.

[14] G. Knopfer, *Monatsh.*, **32**, 765 (1911).

[15] H. Gilman and R. G. Jones, This Journal, **65**, 1458 (1943).

[16] K. Meyer, *Ann.*, **380**, 212 (1911).

pany for the perfluorinated acids used in this work. Thanks are also due to the Office of Naval Research which partially supported this research.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

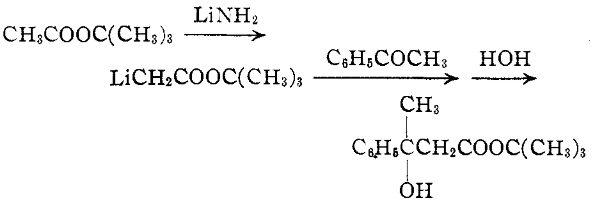
Role of Metallic Cation in Aldol Condensation of Metallo Esters with Acetophenone to Form β-Hydroxy Esters. Reversal to Claisen Acylation or Self-condensation of the Ketone[1]

BY CHARLES R. HAUSER AND W. H. PUTERBAUGH[2]

RECEIVED MAY 18, 1953

The metallic cation plays an important role in the aldol type condensation of metallo acetic esters with acetophenone to form β-hydroxy esters, since the reaction may be realized satisfactorily with lithio, zinchalo and magnesiumhalo esters but not with sodio esters. The aldol condensation was realized with a sodio ester under special conditions but, under usual conditions, metal–hydrogen exchange between the sodio ester and the α-hydrogen of the ketone occurred to form a β-diketone. Moreover, sodio β-hydroxy esters were found to be relatively unstable; they underwent the reverse aldol condensation even in refluxing ether. The reverse aldol condensation was realized also with lithio- and zinchalo-β-hydroxy esters, but much more drastic conditions were required. The success of the aldol condensation of lithio, zinchalo and magnesiumhalo esters with acetophenone is ascribed to the coördinating capacities of the metallic cations.

The aldol type of condensation of certain esters having α-hydrogen with the carbonyl group of ketones or aldehydes to form β-hydroxy esters, such as that of *t*-butyl acetate with acetophenone to form β-hydroxy ester I, have been realized through the intermediate formation of the lithio ester,[3,4] zincchloro ester[3] and magnesiumbromo ester,[5] but not with the sodio ester.[3] The reaction is illustrated below with lithium amide. These condensations, particularly that with the zincchloro ester, are related to the well-known Reformatsky reaction in which an intermediate zinchalo ester is formed by the action of zinc on an α-halo ester.

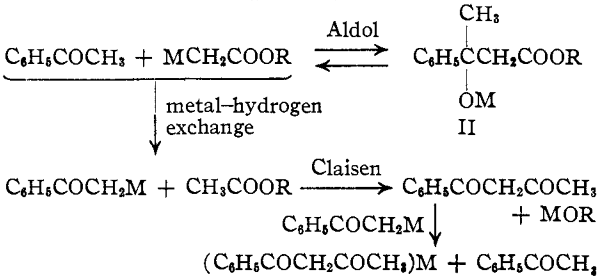


$$CH_3COOC(CH_3)_3 \xrightarrow{LiNH_2} LiCH_2COOC(CH_3)_3 \xrightarrow{C_6H_5COCH_3} \xrightarrow{HOH} C_6H_5\overset{CH_3}{\underset{OH}{C}}CH_2COOC(CH_3)_3$$

I

It has now been found that, whereas β-hydroxy ester I is obtained in 76% yield on refluxing acetophenone with lithio-*t*-butyl acetate for two hours in ether, a different product, benzoylacetone, is produced by a similar treatment of this ketone with sodio-*t*-butyl acetate or with sodio-ethyl acetate (prepared by means of sodium triphenylmethide). The β-diketone evidently arises from metal–hydrogen exchange between the sodio ester and α-hydrogen of the ketone, followed by Claisen acylation of the resulting sodio ketone with the regenerated ester as represented in scheme A in which M stands for the metal. The yield of benzoylacetone was only 6%[6] with sodio-*t*-butyl acetate (much of the original ester and ketone being recovered) but was 94%[6] with sodio-ethyl acetate from which was generated the relatively good acylating agent, ethyl acetate. However, since a 30% yield of β-hydroxy ester I was isolated from sodio-*t*-butyl acetate and acetophenone on stopping the reaction after only 15 minutes, some of the aldol condensation must first have occurred and then reversed completely during the usual two-hour treatment in accordance with scheme A (when M is sodium).[7]

SCHEME A



$$C_6H_5COCH_3 + MCH_2COOR \overset{\text{Aldol}}{\rightleftarrows} C_6H_5\overset{CH_3}{\underset{OM}{C}}CH_2COOR \quad \text{II}$$

$$\Big\downarrow \text{metal–hydrogen exchange}$$

$$C_6H_5COCH_2M + CH_3COOR \xrightarrow{\text{Claisen}} C_6H_5COCH_2COCH_3 + MOR$$

$$\Big\downarrow C_6H_5COCH_2M$$

$$(C_6H_5COCH_2COCH_3)M + C_6H_5COCH_3$$

These results indicated that the metallo-β-hydroxy ester (II), the form in which the β-hydroxy ester is present in the reaction mixture before acidification, is much less stable when the metallic cation (M) is sodium than when it is lithium. This was confirmed with sodio- and lithio-β-hydroxy esters prepared from the β-hydroxy esters and sodium amide and lithium amide, respectively (Table I). Thus, on refluxing two hours in ether, sodio salt II (R = ethyl) was converted completely to benzoylacetone and acetophenone in accordance with scheme A, whereas the corresponding lithio salt was only slightly decomposed, 75% of the orig-

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[1] Paper LI on Condensations; supported in part by a grant from the Duke University Research Council.

[2] Carbide and Carbon Chemicals Company Fellow, 1950–1952.

[3] C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **73**, 2972 (1951).

[4] C. R. Hauser and W. H. Puterbaugh, *ibid.*, **75**, 1068 (1953).

[5] K. Sisido, H. Nozaki and O. Kurihara, *ibid.*, **74**, 6254 (1952).

[6] The yield of β-diketone is calculated on the basis that only half of the sodio ketone from the metal–hydrogen exchange is available for the Claisen acylation, the other half being used to convert the β-diketone to its metallo salt or chelate as represented in scheme A. See J. T. Adams and C. R. Hauser, THIS JOURNAL, **66**, 1220 (1944).

[7] It seems likely that, in certain of the reported Claisen acylations of ketones with esters by sodium reagents to form β-diketones, some of the aldol condensation to form the β-hydroxy ester also first occurred and then reversed. Of course, only the aldol condensation may occur between ethyl acetate and a ketone or an aldehyde having no α-hydrogen; for example, this ester undergoes with benzaldehyde, in the presence of sodium ethoxide, an aldol condensation accompanied by dehydration to form ethyl cinnamate.