[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

AROYLATIONS OF ETHYL ISOBUTYRATE BY ALKALI TRIPHENYLMETHIDES. ISOLATION OF β-KETO ESTERS BY CHROMATOGRAPHY. USE OF A REAGENT HAVING AN AMINO GROUP[1,2]

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The benzoylation of ethyl isobutyrate to form ethyl benzoyldimethylacetate (I) cannot be effected satisfactorily with the basic reagents usually employed for Claisen type condensations. At least when benzoyl chloride is the acylating agent, the essentially complete metalation of the α-hydrogen of the ester must first be effected, and this requires that the base be not only relatively strong, but also, apparently, rather large or complex in structure. Sodium ethoxide (1) and sodium hydride (2) appear too weakly basic to effect the complete metalation of ethyl isobutyrate, although the latter reagent might do so in a sufficiently high-boiling solvent. Sodium amide is probably a sufficiently strong base, but it reacts preferentially with the carbonyl carbon of ethyl isobutyrate to form isobutyramide (3). The much larger sodium triphenylmethide, even though probably a slightly weaker base than sodium amide, reacts preferentially with the α-hydrogen of ethyl isobutyrate (equation 1), and the resulting sodio ester may be condensed with benzoyl chloride to form β-keto ester I in good yield (equation 2) (4). Potassium triphenylmethide may similarly be employed for this condensation (5). The triphenylmethide ion is particularly suitable for this purpose, since the disappearance of its dark red color serves as an indicator in the metalation of the α-hydrogen of the ester (equation 1). Unless the acid chloride is added soon after this step has been effected, the sodio ester may condense with unchanged ester, a little of which is still present in equilibrium, to form ethyl isobutyrylisobutyrate (6). The relatively complex sodium diisopropylamide (prepared from sodiumphenyl and diisopropylamine) appears to metalate ethyl isobutyrate, but the completion of this step is difficult to determine with this colorless base. In an experiment with this base in which benzoyl chloride was added 15 minutes after adding ethyl isobutyrate, only a 14% yield of β-keto ester I was obtained (7).

1. $HC(CH_3)_2COOC_2H_5 + NaC(C_6H_5)_3 \rightarrow NaC(CH_3)_2COOC_2H_5 + HC(C_6H_5)_3$
2. $C_6H_5COCl + NaC(CH_3)_2COOC_2H_5 \rightarrow \underset{\text{I}}{C_6H_5COC(CH_3)_2COOC_2H_5} + NaCl$

Sodium triphenylmethide also effects the metalation of ethyl methylethylacetate and of ethyl diethylacetate to form the corresponding sodio ester which may be condensed with benzoyl chloride to give β-keto esters II and III, respectively (8).

Although the alkali triphenylmethides are especially suitable for the aroyla-

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[1] Paper LIV on condensations.

[2] Supported in part by the Office of Ordnance Research, U. S. Army.

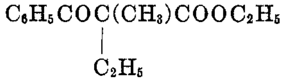
TABLE I

AROYLATION OF ESTERS TO FORM β-KETO ESTERS

Acid Chloride	Ethyl Ester	Reagent	Ethyl β-Keto Ester	B.P.		Yield, %
				°C.	Mm.	
Benzoyl	Isobutyrate	$KC(C_6H_5)_3$	Benzoyldimethylacetate (I)	145–147	14[b]	50
Benzoyl	Isobutyrate	K(VII)[a]	Benzoyldimethylacetate (I)	146–148	15[b]	40
p-Chlorobenzoyl	Isobutyrate	$NaC(C_6H_5)_3$	*p*-Chlorobenzoyldimethylacetate (IVA)	176–178	23[c]	79
Anisoyl	Isobutyrate	$NaC(C_6H_5)_3$	Anisoyldimethylacetate (IVB)	178–179	9[c]	52
Mesitoyl	Isobutyrate	$NaC(C_6H_5)_3$	Mesitoyldimethylacetate (V)	173–175	15[d]	62
Mesitoyl	Isobutyrate	$KC(C_6H_5)_3$	Mesitoyldimethylacetate (V)	168–170	15[d]	43
Mesitoyl	Isobutyrate	K(VII)[a]	Mesitoyldimethylacetate (V)	165–168	15[d]	20
Benzoyl	Diethylacetate	$NaC(C_6H_5)_3$	Benzoyldiethylacetate (III)	173–175	15[e]	41
Benzoyl	Diethylacetate	$KC(C_6H_5)_3$	Benzoyldiethylacetate (III)	178–180	20[e]	22
Benzoyl	Diethylacetate	K(VII)[a]	Benzoyldiethylacetate (III)	180–182	21[e]	22

[a] Potassium derivative of *p*-phenylmethylbenzyldimethyl amine (VII). [b] Ref. 4. [c] Ref. 14. [d] M.p. 41–42°; reported m.p. 42–42.5°, ref. 14. [e] Ref. 26.

tion of aliphatic esters having only one α-hydrogen, they produce as a by-product, triphenylmethane, which is difficult to remove from relatively high-boiling or solid β-keto esters by the ordinary techniques of distillation and recrystallization.



$$C_6H_5COC(CH_3)(C_2H_5)COOC_2H_5$$

II

$$C_6H_5COC(C_2H_5)_2COOC_2H_5$$

III

In the present investigation β-keto esters prepared with the alkali triphenylmethides have been isolated free from the hydrocarbon by-product by means of column chromatography. This technique was applied simply by passing a petroleum ether or petroleum ether-benzene solution of the reaction products through an alumina column and washing the column with the same solvent. Under these conditions, the β-keto ester was adsorbed on the column (along with other oxygen compounds) while the triphenylmethane passed through. The complete removal of this hydrocarbon was indicated when the evaporation of small samples of the washings left no crystalline residue. The β-keto ester was eluted with ethanol and was recovered by distillation or recrystallization.

The β-keto esters prepared with one or both of the alkali triphenylmethides and isolated in this manner include, besides I and III, compounds IVA, IVB, and V which were produced by the aroylations of ethyl isobutyrate with *p*-chlorobenzoyl chloride, anisoyl chloride, and mesitoyl chloride, respectively. The yields are given in Table I, and the analytical results and cleavage products, in Table II. Also in Table I are given the yields of β-keto esters prepared with the potassium derivative of a tertiaryamino-triphenylmethide, designated K(VII),

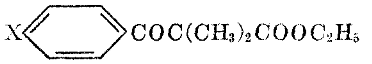
TABLE II

ANALYSIS AND CLEAVAGE OF β-KETO ESTERS OBTAINED BY THE SODIUM TRIPHENYLMETHIDE METHOD

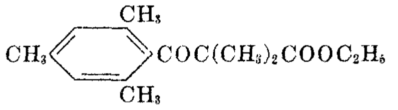
β-Keto Ester	C		H		Cleavage Product	B. P.		Yield, %
	Calc'd	Found	Calc'd	Found		°C.	Mm.	
IVA[a, b]	61.21	61.11	5.94	6.02	*p*-Chloroisobutyrophenone	129–131	15[c]	56
IVB[d]	67.16	68.92	7.24	7.16	*p*-Methoxyisobutyrophenone	157–165	14[e]	41
V[b]	73.28	73.63	8.39	8.53	Mesitylene	161–162	atm.[f]	87
V[g, h]	73.28	73.42	8.39	8.33	—	—	—	—
III[b]	72.57	72.55	8.13	8.19	Diethylacetophenone	128–130	15[i]	63

[a] Calc'd for Cl, 13.92. Found: Cl, 13.87. [b] Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn. [c] M.p. of *semicarbazone* 175–176°, ref. 14. [d] This β-keto ester gave a high value for carbon. [e] M.p. of *semicarbazone* 188–189°, ref. 14. [f] M.p. of dinitro derivative 87°, ref. 14. [g] Obtained by potassium triphenylmethide method. [h] Microanalysis by Clark Microanalytical Laboratory, Urbana, Ill. [i] M.p. of *oxime* 89°, ref. 26.

the by-product of which was separated from the β-keto esters by extraction with acid.



IVA (X = Cl)
IVB (X = OCH3)

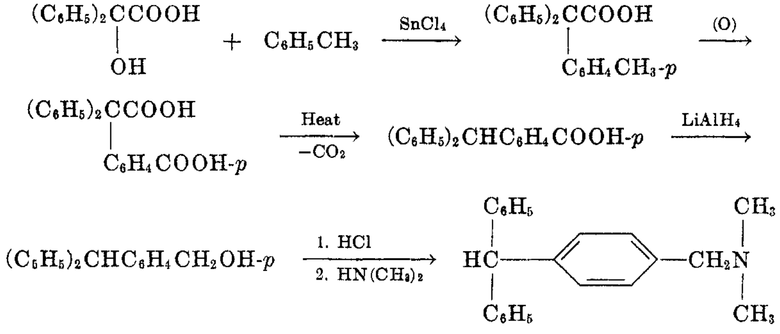


V

It can be seen from Table I that good yields of β-keto esters IVA, IVB, and V and a fairly good yield of β-keto ester III were obtained with sodium triphenylmethide. Moreover, IVA, V, and III were analytically pure (Table II). β-Keto ester IVB analyzed high for carbon, but this appeared not to be due to contamination with triphenylmethane since further chromatographing failed to produce an analytically pure product. The yield for β-keto ester III could probably be improved, since the metalation of the ester was unfortunately allowed to proceed too long and some self-condensation of the ester may have occurred. A much better yield of this β-keto ester has previously been obtained (8) although it may have been contaminated with some triphenylmethane, since only the usual fractional distillation technique was employed. The structures of the β-keto esters were established by ketonic cleavage, except that of β-keto ester V which was cleaved to form mesitylene (Table II).

It can be further seen from Table I that the yields of β-keto esters were lower with potassium triphenylmethide or the potassium derivative of the tertiary-amino-triphenylmethide, K(VII), than with sodium triphenylmethide. In contrast to the latter reagent, which is ether-soluble, the potassium reagents are quite insoluble in this solvent; consequently, the optimum period for the metalation of ethyl isobutyrate before adding the acid chloride is somewhat difficult to determine. Moreover, the potassium triphenylmethide appears to produce self-condensation of the ester more readily than sodium triphenylmethide. Thus, in the benzoylation of ethyl isobutyrate to form β-keto ester I, the yield was 50% when the metalation period was 4½ minutes, but only 28% when it was eight minutes; after this time a 14% yield of the benzoyl derivative of the self-condensation product of the ester (involving the γ-hydrogen) was apparently obtained. A similar acyl derivative of the self-condensation product of ethyl isobutyrate has been isolated employing sodium triphenylmethide only when the acid chloride was added to the reaction mixture after a much longer period (9).

SCHEME A



VI VII

The sodium triphenylmethide reagent was prepared from triphenylchloromethane and sodium amalgam in the usual manner (10). Generally, relatively large amounts of this reagent were made, and aliquots of the standardized solution were employed as desired. On the other hand the potassium triphenylmethide and the potassium derivative of VII were prepared by the metalation of triphenylmethane and VII, respectively. This was accomplished with potassium amide in liquid ammonia, which was replaced by ether, as represented below for triphenylmethane (equation 3). Potassium triphenylmethide has also been prepared in this laboratory from triphenylchloromethane and potassium amalgam but, as when it was made by the metalation of triphenylmethane, it was obtained as a suspension in ether (11).

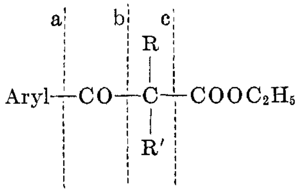
$$3.\quad HC(C_6H_5)_3 + KNH_2 \xrightarrow[\text{2. Ether}]{\text{1. Liquid NH}_3} KC(C_6H_5)_3 + NH_3$$

When the potassium reagents were employed in the condensations, the by-product, triphenylmethane or tertiary amine VII, was largely recovered and reconverted to its potassium derivative for use in subsequent condensations. Tertiary amine VII was synthesized as represented in Scheme A, compounds VI and VII being reported for the first time.

It would obviously be advantageous to prepare also the sodium triphenylmethide by the metalation of triphenylmethane since this starting material could then be recovered after the reagent is employed in condensations and reused. Triphenylmethane is metalated by sodium amide in liquid ammonia but, on replacing the ammonia by ether in order to obtain a suitable medium for the aroylations with acid chlorides, the sodium triphenylmethide reverts to sodium amide and triphenylmethane accompanied by the complete discharge of the characteristic red color of the triphenylmethide ion (5). Similar results have been obtained by us on replacing the ammonia with ethylene glycol dimethyl ether and by another worker in this laboratory (12) on replacing the ammonia with *n*-butyl ether, dioxane, triethylamine, or toluene. This difference in stability between the sodium and potassium triphenylmethides under these conditions appears to be associated with the coordinating capacities of the metallic cation since, like the sodium reagent, lithium triphenylmethide, prepared from lithium amide and triphenylmethane in liquid ammonia, reverts to the starting materials on replacing the ammonia by ether (12). Sodium triphenylmethide has been prepared in benzene by the metalation of triphenylmethane with sodiumphenyl, but it was not employed for the aroylation of an ester; it was carbonated to form triphenylacetic acid in 77% yield (7).

Although the optimum conditions for the aroylations of esters with the ether-insoluble potassium reagents are not easily determined, such a difficulty does not arise in self-condensations of esters for which these reagents should be as satisfactory as the ether-soluble sodium triphenylmethide. In agreement with this ethyl isovalerate has been self-condensed in 64% yield by potassium triphenylmethide (5), which is even better than the yield (45–60%) reported with the sodium reagent (1). We have realized this condensation in 45% yield employing the potassium derivative of amine VII. Even sodium triphenylmethide in liquid ammonia may be employed for effecting the self-condensations of certain esters. Thus, we obtained a 59% yield of the self-condensation product of ethyl *n*-butyrate with this reagent. However, for the self-condensations of esters such as ethyl isobutyrate and ethyl isovalerate, we have preferred diisopropylaminomagnesium bromide which effects these reactions particularly rapidly (13).

Comparison of methods of synthesis of β-keto esters of type VIII. The aroylations of aliphatic esters having only one α-hydrogen described above, particularly those employing sodium triphenylmethide with chromatography, furnish a satisfactory general method for the synthesis of β-keto esters of type VIII in which condensation at position (b) is involved.



$$\text{Aryl}-\text{CO}-\overset{\text{R}}{\underset{\text{R}'}{\text{C}}}-\text{COOC}_2\text{H}_5$$

VIII

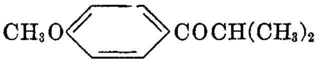
Another general method, also involving condensation at position (b), was described recently (14) in which a Reformatsky type reaction was employed with aroyl chlorides, ethyl α-bromoisobutyrate, and zinc. This method, involving the intermediate formation of the zinc bromide derivative of the ester, may be illustrated for the preparation of β-keto ester I by equations 4 and 5. Analogous reactions have been effected with certain phenyl esters (14) and with benzonitrile (15), but aroyl chlorides appear to be more satisfactory.

4. $BrC(CH_3)_2COOC_2H_5 + Zn \rightarrow BrZnC(CH_3)_2COOC_2H_5$

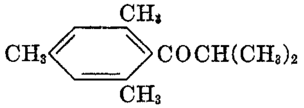
5. $C_6H_5COCl + BrZnC(CH_3)_2COOC_2H_5 \rightarrow \underset{\text{I}}{C_6H_5COC(CH_3)_2COOC_2H_5} + ZnBrCl$

Each of these two general methods has certain advantages. The alkali triphenylmethide method has the advantage that an ordinary ester such as ethyl isobutyrate is used whereas the Reformatsky reaction requires the usually less available α-bromo ester. On the other hand relatively high-boiling or solid β-keto esters from the latter method may be isolated merely by distillation or recrystallization.

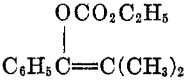
Condensation at position (b) to form VIII employing either the triphenylmethide or the Reformatsky method has been more satisfactory than condensations at position (a) or (c). Indeed we were unable to effect satisfactorily a condensation at position (c) through the carbethoxylation of *p*-methoxyisobutyrophenone (IX) with ethyl chlorocarbonate or of isobutyromesitylene (X) with ethyl carbonate employing sodium amide. Haller and Bauer (16) have shown that the O-carbethoxylation of isobutyrophenone occurs with ethyl chlorocarbonate using sodium amide to form the enol ester XI.



IX



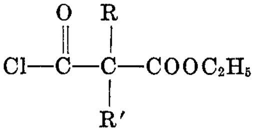
X



$$C_6H_5\overset{\overset{\Large |}{OCO_2C_2H_5}}{C}{=}C(CH_3)_2$$

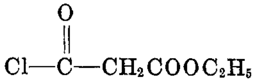
XI

Condensation at position (a) to form VIII, involving the Friedel-Crafts type of acylation of an aromatic compound with a di-substituted ethyl malonyl chloride (XII) has apparently not been attempted, although such a reaction with benzene and ethyl malonyl chloride itself (XIII) has been reported in good yield (17).



$$Cl{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}{-}COOC_2H_5$$

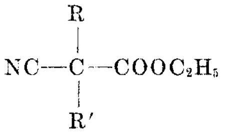
XII



$$Cl{-}\overset{\overset{O}{\|}}{C}{-}CH_2COOC_2H_5$$

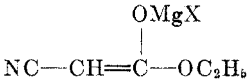
XIII

It might appear that condensation at (a) to form VIII could be realized with a di-substituted ethyl cyanoacetate (XIV) and an aroylmagnesium halide similar to that observed with ethyl cyanoacetate and ethylmagnesium iodide, which is one of the well-known methods for preparing ethyl propionylacetate. However, the latter reaction involves the condensation of an intermediate magnesium enolate of the cyanoacetate XV with the Grignard reagent, and such an enolate would not be possible with XIV, the ester group of which would probably react with the Grignard reagent to a greater extent than the nitrile group (18).



$$NC\text{—}\overset{R}{\underset{R'}{C}}\text{—}COOC_2H_5$$

XIV



$$NC\text{—}CH{=}\overset{OMgX}{C}\text{—}OC_2H_5$$

XV

Also the direct condensations at position (b) to form VIII are considered superior to indirect methods involving the dialkylation of the β-keto esters of type XVI, since, not only would the unsubstituted β-keto ester usually first have to be prepared, but the dialkylation product would presumably be rather difficult to isolate entirely free from the monoalkylated and unalkylated products. Ethyl benzoylacetate, which is commercially available, has been dimethylated and diethylated, but a special procedure for purification was recommended (19).

$\text{Aryl-CO-CH}_2\text{-COOC}_2\text{H}_5$

XVI

EXPERIMENTAL[3]

Aroylations of esters (*Table I*). Ethyl isobutyrate, b.p. 110–111°, and ethyl diethylacetate,[4] b.p. 151° were aroylated by one or more of the methods described below, the first two of which are modifications of earlier procedures for the benzoylations of ethyl isobutyrate (4, 5). Benzoyl chloride, b.p. 73° at 10 mm.; *p*-chlorobenzoyl chloride, b.p. 114° at 14 mm.; anisoyl chloride, b.p. 111° at 3 mm.; were purified commercial products. Mesitoyl chloride, b.p. 126° at 20 mm., was prepared from mesitoic acid and thionyl chloride as described previously (20).

(*A*) *Sodium triphenylmethide method.* A 1 liter three-necked flask fitted with a mercury-sealed stirrer, an efficient reflux condenser, and a calibrated addition funnel was thoroughly flushed with dry nitrogen. Into the addition funnel was siphoned under nitrogen approximately 400 ml. (0.2 mole) of a standardized ether solution of sodium triphenylmethide which had been prepared from 1 mole of triphenylchloromethane and 3% sodium amalgam (10). The reagent was drained into the flask, and an equimolar amount (0.2 mole) of ethyl isobutyrate was added to the stirred solution. After the deep red color of the reagent had faded to light orange (usually within 5 minutes, only one minute when some of the finely divided mercury had been siphoned over with the reagent), an equimolar quantity (0.2 mole) of the aroyl chloride in 100 ml. of dry ether was added rapidly and the stirring was continued for two hours. Water was added to dissolve the precipitated sodium chloride, and the mixture acidified with 10% acetic acid. The ether layer was washed with 10% sodium bicarbo-

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[3] Melting points and boiling points are uncorrected. Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

[4] We are indebted to Carbide and Carbon Chemicals Corp. for a generous sample of **2-ethylbutyric acid** from which this ester was made.

nate solution, followed by water, and dried over Drierite. After filtering, the solvent was removed and the residue shaken with 50 ml. of petroleum ether. The mixture was filtered and the crystals of triphenylmethane were washed with several small portions of cold petroleum ether. The combined filtrate and washings were passed through a well-packed (21) activated alumina column (Merck Reagent Grade) in a vertical glass tube (6 x 30 cm.) (tapered at one end) through which had just been passed petroleum ether. The column was then washed with petroleum ether until free from triphenylmethane, as determined by the absence of crystals on evaporating small samples of the washings. The rate of flow was approximately 30 drops per minute, although finer mesh alumina required a slight head of pressure to obtain a satisfactory flow rate. When the column had been freed from triphenylmethane (usually 300–500 ml. of solvent were required), the adsorbed material was eluted with ethyl alcohol (commercial absolute). The ethanol was distilled from the solution and the crude product was distilled *in vacuo*. Usually more β-keto ester was obtained by passing the petroleum ether washings through a fresh column of alumina followed by elution with ethanol.

In a similar manner ethyl diethylacetate was added to an equivalent of the sodium triphenylmethide reagent and, after 18 hours (when the color of the reagent had been completely discharged), an equivalent of benzoyl chloride was added. The reaction mixture was worked up and chromatographed as described above.

(*B*) *Potassium triphenylmethide method.* The deep red suspension of 0.1 mole of potassium triphenylmethide in 300 ml. of dry ether was prepared (5) in a 1-liter round-bottom three-neck flask fitted with a dropping-funnel, a stirrer sealed by a rubber gasket, and a reflux condenser having a drying tube. Practically all the ammonia was removed from the suspension by stirring and refluxing for about 4 hours at which time dry nitrogen was passed into the flask for 5 minutes. After loosening the reagent from the sides of the flask by vigorous shaking, 0.1 mole of ethyl isobutyrate, in 100 ml. of dry ether was added. The mixture was shaken vigorously 4 to 5 minutes when the characteristic red color of the reagent had changed to orange. Then, 0.1 mole of the freshly distilled acid chloride in 50 ml. of dry ether was added rapidly and the mixture was stirred for 20 minutes. After adding a small amount of wet ether (to destroy any potassium or potassium amide), the mixture was decomposed with ice and hydrochloric acid. The ether solution was washed with cold 10% sodium hydroxide and dried over sodium sulfate followed by Drierite. The solvent was distilled and the residue was taken up in 150 ml. of dry ligroin (b.p. 30–60°) and 45 ml. of dry benzene. The solution was then passed through a chromatographic column (4.5 x 35 cm.), composed of well-packed activated alumina (Aluminum Co. of America). After most of the ligroin-benzene solution had been collected, the column was washed with several small portions of a fresh mixture of equal volumes of ligroin and benzene, until the last of the successive sample of the collected solution on evaporation gave no residue of triphenylmethane or other material. In this way 23.8 g. (98%) of white crystals of triphenylmethane, (m.p. 91–92°) were recovered. Finally, the column was eluted with 200 ml. of ethanol. The ethanol was distilled and the residue was fractionated *in vacuo*.

When the ethyl isobutyrate was allowed to react with the potassium triphenylmethide reagent for about 8 minutes, before adding benzoyl chloride, there was obtained, after chromatographic adsorption and distillation, only a 28% yield of ethyl benzoyldimethylacetate (I), b.p. 146–149° at 15 mm., and a 14% yield of what appeared to be ethyl benzoylisobutyrylisobutyrate, b.p. 195–198° at 15 mm., 189–191° at 12 mm.

In a similar manner ethyl diethylacetate was added to the potassium triphenylmethide reagent and, after 3 hours, an equivalent of benzoyl chloride was added. The reaction mixture was worked up and chromatographed as described above.

(*C*) *Method using the potassium derivative of* VII. To 0.08 mole of potassium amide in 200 ml. of liquid ammonia was added rapidly 0.08 mole of amine VII (prepared as described below) in 100 ml. of dry ether and the liquid ammonia was replaced by ether as described for potassium triphenylmethide. This new reagent, which is somewhat darker red than potassium triphenylmethide, was assumed to be formed quantatively from amine VII and potassium amide. To the reagent (0.08 mole) was added 0.08 mole of ethyl isobutyrate and, after 2 to 3 minutes when the color had changed to orange, 0.1 mole of the acid chloride was added essentially as described in Method B. After decomposing the reaction mixture with ice and hydrochloric acid, the ether solution was further extracted with acid until free from amine VII and then washed with sodium bicarbonate, followed by water, and dried. The solvent was removed and the residue fractionated *in vacuo*. Amine VII was recovered in yields of 50–85% from the acid extracts.

The benzoylation of ethyl diethylacetate was carried out in a similar manner, the acid chloride being added after the ester and reagent had reacted for 7 minutes.

Self-condensations of esters. (*A*) *With sodium triphenylmethide in liquid ammonia.* Triphenylmethane (0.2 mole) was added to stirred sodium amide (0.2 mole) in 200 ml. of liquid ammonia, and the resulting red mixture was stirred 20 minutes. Ethyl isobutyrate (0.2 mole) in 50 ml. of dry ether was then added, and the stirring was continued for 1.5 hours. The yellow mixture was decomposed with 0.2 mole of solid ammonium chloride, followed by ice and hydrochloric acid, to give a 59% yield of ethyl α-*n*-butyryl-*n*-butyrate, b.p. 100–104° at 12 mm. (reported 102–105° at 12 mm.) (22).

(*B*) *With the potassium derivative of amine* VII. Ethyl isovalerate was self-condensed by this reagent (16 hours' stirring at room temperature, the reaction mixture being worked up as described above for the aroylations) to give a 45% yield of ethyl isovalerylisovalerate, b.p. 116.5–119° at 15 mm., (reported 118–119° at 15 mm.) (5).

p-Diphenylmethylbenzyl alcohol (VI). *p*-Diphenylmethylbenzoic acid was prepared in three steps by the method of Bistizycki (23, 24) employing much larger quantities of material. Benzilic acid (131 g., 0.58 mole, m.p. 150–151°) and 1600 ml. of dry toluene were condensed with 113.5 g. (0.437 mole) of stannic chloride to form 127 g., 0.417 mole (72%) of *p*-tolyldiphenylacetic acid, m.p. 205–207° [reported m.p. 205° (23, 24). Alkaline-permanganate oxidation of this intermediate gave 119 g., 0.358 mole (86%) of *p*-carboxyphenyldiphenylacetic acid, m.p. 246° [reported m.p. 246–247° (23, 24)], which on decarboxylation at its melting point gave 85 g. (0.294 mole, 82%) of *p*-diphenylmethylbenzoic acid, m.p. 163–164°, [reported m.p. 162° (23, 24)].

To 9.19 g. (0.238 mole) of finely powdered lithium aluminum hydride (Metal Hydrides, Incorp.) suspended in 400 ml. of dry ether was added 54.5 g. (0.19 mole) of *p*-diphenylmethylbenzoic acid in 700 ml. of dry ether at a rate to maintain gentle reflux according to the general method of Nystrom and Brown (25). There was obtained 42 g. (81%) of *p*-diphenylmethylbenzyl alcohol (VI), which after recrystallization from a mixture of nine parts of ethanol (95%) and one part of ligroin (b.p. 60–90°), melted at 67–67.5°.

Anal. Calc'd for $C_{20}H_{18}O$: C, 87.59; H, 6.57.
Found: C, 87.63; H, 6.64.

p-Diphenylmethylbenzyldimethyl amine (VII). A suspension of 42 g. (0.154 mole) of *p*-diphenylmethylbenzyl alcohol (VI) in 300 ml. of ligroin (b.p. 60–90°) was saturated with hydrogen chloride at 0°, allowed to stand 2 hours at this temperature, and then 24 hours at room temperature with hydrogen chloride being passed in slowly. After drawing off the water formed in the reaction, the ligroin solution was dried over Drierite. Dry air was passed through the solution until free from hydrogen chloride, and the solvent was distilled. To a solution of the residual alkyl chloride in 200 ml. of absolute ethanol, cooled to 0°, was added 23 g. (0.5 mole) of anhydrous dimethylamine and the mixture was allowed to stand at room temperature for 24 hours with occasional shaking. The ethanol was distilled and the residue was taken up in ether. The ether solution was washed with water, dried over sodium sulfate, and the solvent removed. After distilling low-boiling material, the residue was fractionated to give 36.1 g. (79%) of *p*-diphenylmethylbenzyldimethylamine (VII), b.p. 194–196° at 2 mm.

Anal. Calc'd for $C_{22}H_{23}N$: N, 4.65. Found: N, 4.58, 4.69.

The *methiodide* of VII, prepared with two equivalents of methyl iodide in ethanol, melted at 233–235° (dec.).

Anal. Calc'd for $C_{23}H_{26}IN$: C, 62.32; H, 5.87; N, 3.16.
Found: C, 62.36; H, 5.87; N, 3.06.

Analyses and cleavage of β-keto esters. (Table II). Although the β-keto esters were prepared previously (14, 19), they were analyzed in order to show that they were uncontaminated with triphenylmethane. Their structures were established by cleavage with mixtures of acetic and sulfuric acids (26). The resulting ketones or mesitylene (from β-keto ester V) were identified by their boiling points and appropriate derivatives.

SUMMARY

1. Aroylations of ethyl isobutyrate and of ethyl diethylacetate with aroyl chlorides have been effected by sodium and potassium triphenylmethides to form β-keto esters of the type Aroyl-$CR_2COOC_2H_5$, which were isolated free from the by-product triphenylmethane by means of column chromatography.

2. Certain of these types of aroylations have been effected also by the potassium derivative of a tertiaryamino-triphenylmethane, the by-product of which was extracted from the β-keto ester with acid.

3. These methods have been compared with one another and with those described previously. Under certain circumstances the present methods are superior.

4. The synthesis of the tertiaryamino-triphenylmethane (VII) used in this work has been described.

5. Some observations concerning the use of the alkali triphenylmethides for self-condensations of esters and the stabilities of these reagents have been mentioned.

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