from pyridine-water and once from benzene-low boiling petroleum ether yielding white V, m.p. 226–227°. The ultraviolet spectrum in 95% ethanol had an ϵ of 18,000 at 270 mμ.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.8; H, 5.9. Found: C, 89.8; H, 6.2.

Alkylation of the lithium salt of anthrone with methyl iodide. 10,10-Dimethylanthrone (VII). The lithium salt of anthrone was prepared in the manner described for the benzyl chloride reaction using 7.3 g. (0.040 mol.) of anthrone and 0.56 g. (0.080 g. atom) of lithium metal, giving 2 equivalents of lithium methoxide. The toluene and methanol were removed from the salt by gently heating the flask with a steady stream of nitrogen gas passing over the mixture for 3.5 hr. The dry mixture of the lithium salt of anthrone and lithium methoxide was heated in a sealed tube previously flushed with nitrogen, together with 25 ml. (a 10-fold excess) of methyl iodide and 0.2 ml. of *t*-butyl alcohol at 150° for 24 hr., and cooled.

After most of the methyl iodide was distilled, the residue was digested with diethyl ether and acidic products extracted with Claisen's alkali.[14] Removal of the ether from the neutral fraction yielded 6.2 g. (70%) of the dimethylanthrone VII, m.p. 95–105°. Chromatography on alumina gave 5.7 g., 96.5–98° (64%). The ultraviolet spectrum of the analytical sample had an ϵ of 20,000 at 270 mμ.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.4. Found: C, 86.4; H, 6.6.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Alkylations of Acetylacetone and Certain Other β-Diketones at the Terminal Methyl Group through Dicarbanions[1]

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The generality of the alkylation of the dicarbanion of acetylacetone was investigated. Good yields of terminal alkylation products were obtained when the dicarbanion was treated with primary alkyl halides, but only a fair yield was obtained with isopropyl bromide. Tertiary butyl chloride failed to alkylate the dicarbanion. Benzhydryl chloride and β-phenylethyl chloride gave tetraphenylethylene and styrene respectively when treated with the dicarbanion. Both mono- and symmetrical dialkylation products were obtained with *n*-octyl bromide. Benzylation of dipotassio-*o*-hydroxyacetophenone gave exclusively 2,2-dibenzyl-2′-hydroxyacetophenone. Alkylations of the dicarbanions of other β-diketones were also realized. Mechanisms and synthetic applications are indicated.

It was shown recently in this laboratory[3] that acetylacetone can be benzylated at the terminal methyl group rather than at the methylene carbon where alkylation has generally been observed. This was accomplished by converting the β-diketone to its dicarbanion[4] by means of two molecular equivalents of potassium amide in liquid ammonia, and then adding one molecular equivalent of benzyl chloride. The reaction may be represented by Equation 1, in which R is benzyl:

$$CH_3COCH_2COCH_3 \xrightarrow[\text{liq. } NH_3]{2\ KNH_2} \underset{\text{I}}{CH_3CO\bar{C}HCO\bar{C}H_2} \xrightarrow[2.\ NH_4Cl]{1.\ RX} \underset{\text{II}}{CH_3COCH_2COCH_2R} \quad (1)$$

In the present investigation a study was made of the generality of this mode of alkylation. First it was shown that, at least for the alkylation with benzyl chloride, the intermediate dicarbanion I may be prepared by means of sodium amide as well as potassium amide.[5] However, dicarbanion I is evidently not produced satisfactorily with two equivalents of lithium amide in liquid ammonia, since the subsequent addition of benzyl chloride failed to yield the alkylation product, the acetylacetone (61%) being recovered.

In Table I are summarized the yields and other data obtained in the alkylations of dicarbanion I with five primary halides and one secondary halide. It can be seen from this table that the primary halides produced good yields (60–77%), but that isopropyl bromide gave only a fair yield (27%). The alkylation failed with *t*-butyl chloride under similar conditions, and the acetylacetone (64%) was recovered.

Since the *n*-butyl, *n*-heptyl, and *n*-octyl halides employed are usually typical of the homologous series of primary alkyl halides, the reaction represented by Equation 1 may be considered quite general when R is primary.

The lower yield with the secondary halide and the failure with the tertiary halide are not surprising since similar observations have been reported in the alkylations of the more common monocarbanions, for example, that of malonic ester.[6]

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[1] Supported in part by the National Science Foundation.

[2] James B. Duke Fellow, 1958–1959.

[3] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[4] For the present purpose the dipotassio salt of the β-diketone is considered to consist of the 1,3-dicarbanion I, although other resonance forms may contribute more to the structure of the molecule.

[5] Whereas dipotassioacetylacetone is formed as a precipitate in liquid ammonia, disodioacetylacetone remains essentially in solution (black).

[6] See A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 124 (1957).

TABLE I

ALKYLATIONS OF DIPOTASSIOACETYLACETONE

			Ketone				Copper Chelate		
Alkyl Halide	Product	Yield, %	B.P.	Mm.	Lit. B.P.	Lit. Mm.	M.P.	M.P., Lit.	Infrared Peaks 6.0–6.7 μ[a]
Benzyl chloride	6-Phenyl-2,4-hexanedione	60[b,c]	162–165	16	164–166	16[f]	158.5–160	157–159[f]	6.32, 6.56
Allyl bromide	1-Octene-5,7-dione	65	80–86	15	87–89	16[g]	163–163.5		6.10, 6.40, 6.60
n-Butyl bromide	2,4-Nonanedione	68	101–102	19	101–103	19[h]	139–140	138[l]	6.35, 6.59
n-Heptyl bromide	2,4-Dodecanedione	77	140–143	14	150	15[i]	116–116.5	115.5[i]	6.40, 6.60
n-Octyl bromide	2,4-Tridecanedione	67[d] (49)[e]	155–160	16	150–152	16[j]	117–118	114[m]	6.35, 6.55
i-Propyl bromide	6-Methyl-2,4-heptanedione	27	77–80	21	78–79	20[k]	154–155	154[n]	6.38, 6.60

[a] Infrared spectra were produced with a Perkin-Elmer Infracord by the potassium bromide method. [b] Reported previously, see ref. (3). [c] A 69% yield was obtained from the disodiosalt. [d] Obtained under special conditions. [e] Obtained from the general procedure; also 27% of a dialkylation product was isolated. [f] G. T. Morgan and C. R. Porter, *J. Chem. Soc.*, **125,** 1269 (1924). [g] See ref. (8). [h] F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **72,** 1352 (1950). [i] G. T. Morgan and E. Holmes, *J. Chem. Soc.*, **127,** 2891 (1925). [j] See ref. (18). [k] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67,** 284 (1945). [l] G. T. Morgan and E. Holmes, *J. Chem. Soc.*, **125,** 762 (1924). [m] See ref. (19). [n] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **125,** 743 (1924).

That the alkylation actually occurred at the methyl group was shown by the agreement of the boiling points of the β-diketones and the melting points of their copper chelates with the recorded values (see Table I). Moreover, the infrared spectra of all the copper chelates showed strong adsorption bands at 6.32–6.40 μ and 6.55–6.60 μ (Table I) which is indicative of such β-diketones unsubstituted at the methylene group.[7] The structure of the alkylation product from allyl bromide was further established by independent synthesis from the acylation of allylacetone with ethyl acetate (Equation 2):[8,9]

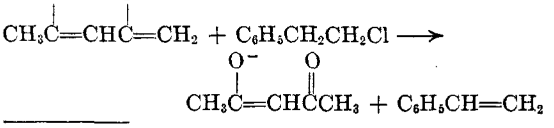
$$CH_2{=}CHCH_2CH_2COCH_3 \xrightarrow[\text{ether}]{NaNH_2} CH_2{=}CHCH_2CH_2COCH_2Na \xrightarrow{CH_3COOC_2H_5} \text{II} \quad (2)$$

$$(R = \text{allyl})$$

It should be pointed out that the 67% yield of mono-alkylation product of type II ($R = n\text{—}C_8H_{17}$) from *n*-octyl bromide was obtained when the halide was added very slowly (in 75 min.) to the reaction mixture. When the halide was added rapidly (in 3 min.) employing 300 ml. of liquid ammonia and 20 ml. of ether as in the general procedure (see Experimental), only 49% of the mono-octylation product was isolated. However, 27% of a dialkylation product was also obtained.[10] The structure of the dialkylation product is considered in the next section. The reason dialkylation was observed only with *n*-octyl bromide is not clear.

Liquid ammonia, with or without small amounts of ether, appears to be a much better medium for the alkylation of dipotassioacetylacetone than does anhydrous ether alone. While the dicarbanion was benzylated in 60% in liquid ammonia, only 9% of the benzylation product was obtained when the reaction was performed in refluxing ether. Similarly, *n*-octyl bromide gave only 23% mono-alkylation and 5% dialkylation in ether.

In contrast to the typical primary alkyl halides, β-phenylethyl chloride, which has a relatively reactive β-hydrogen, failed to alkylate dicarbanion I. Instead, the halide underwent β-elimination to form styrene (89%), most of the acetylacetone being recovered. Since β-phenylethyl chloride is known to undergo β-elimination with ethoxide or amide, but substitution with diphenylmethide carbanion,[11] the dianion of acetylacetone appears to function more like an oxide base than like a carbanion towards this halide. This may be indicated by employing an oxide resonance form of the dianion (Equation 3):



$$CH_3\overset{O^-}{\overset{|}{C}}{=}CH\overset{O^-}{\overset{|}{C}}{=}CH_2 + C_6H_5CH_2CH_2Cl \longrightarrow CH_3\overset{O^-}{\overset{|}{C}}{=}CH\overset{O}{\overset{\|}{C}}CH_3 + C_6H_5CH{=}CH_2 \quad (3)$$

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(7) R. P. Dryden and A. Winston reported [*J. Phys. Chem.*, **62,** 635 (1958)] that the copper chelates of acetylacetone and similar β-diketones unsubstituted at the methylene group show infrared bands at 6.10–6.45 μ and 6.52–6.60 μ whereas the chelates of their 3-substituted derivatives exhibit only the former bands.

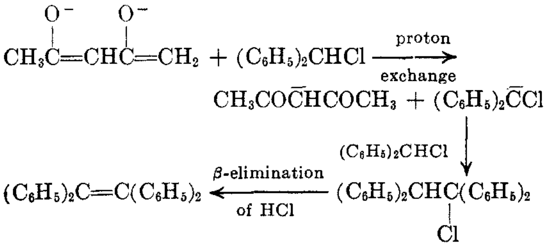
(8) G. Leser, *Bull. soc. chim. France*, [3], **27,** 64 (1902).

(9) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8,** 122–123 (1954).

(10) When the reaction was carried out in a mixture of 150 ml. each of liquid ammonia and anhydrous ether the yields of mono- and dialkylation products were 31 and 42% respectively.

(11) C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79,** 3142 (1957).

Benzhydryl chloride, which has a more reactive α-hydrogen than benzyl chloride, failed to alkylate dicarbanion I. The halide, instead, underwent self-alkylation accompanied by β-elimination to give tetraphenylethylene (98%). Since benzhydryl chloride is known to undergo such a self-condensation with the amide ion[12] but the substitution type reaction with the diphenylmethide carbanion,[11] the dianion of acetylacetone again seems to function more like a strong base than as a nucleophilic carbanion. This may be represented by Equation 4:



$$\begin{aligned}&CH_3\overset{O^-}{\overset{|}{C}}=CH\overset{O^-}{\overset{|}{C}}=CH_2 + (C_6H_5)_2CHCl \xrightarrow[\text{exchange}]{\text{proton}} CH_3CO\overline{C}HCOCH_3 + (C_6H_5)_2\overline{C}Cl\\ &\qquad\Big\downarrow{\scriptstyle (C_6H_5)_2CHCl}\\ &(C_6H_5)_2C=C(C_6H_5)_2 \xleftarrow[\text{of HCl}]{\beta\text{-elimination}} (C_6H_5)_2CH\underset{Cl}{\underset{|}{C}}(C_6H_5)_2 \qquad (4)\end{aligned}$$

Although all of the above results were obtained with acetylacetone, similar results might be expected with other β-diketones having a terminal methyl group. In fact the benzylations of the terminal methyl groups of benzoylacetone,[3] acetylcyclohexanone,[13] and acetylcyclopentanone[13] have been reported. The alkylation of the dicarbanions of β-diketones of type II is discussed below.

Alkylations of β-diketones of type II. In contrast to acetylacetone and benzoylacetone,[3] β-diketones of type II can form two different dicarbanions (III and IV) depending on whether a methyl or 5-methylene hydrogen undergoes the secondary ionization. It has recently been shown in this

$$\underset{\text{III}}{RCH_2CO\overset{-}{C}HCO\overset{-}{C}H_2} \qquad \underset{\text{IV}}{R\overset{-}{C}HCO\overset{-}{C}HCOCH_3}$$

laboratory[13] that 6-phenyl-2,4-hexanedione (II. R = $CH_2C_6H_5$) can be benzylated through a dicarbanion of type III to 1,7-diphenyl-3,5-heptanedione (Va) in 65% yield. No products corresponding to alkylation of a dicarbanion of type IV were observed.

In the present study other β-diketones of type II were alkylated. As with 6-phenyl-2,4-hexanedione only products corresponding to alkylations of a dicarbanion of type III were obtained.

The first ketone studied was 2,4-tridecanedione (II. R = n-C_8H_{17}) which was derived from the alkylation of the dicarbanion of acetylacetone with n-octyl bromide. This β-diketone was converted to its dicarbanion by means of two molecular equivalents of potassium amide in liquid ammonia and then alkylated with one molecular equivalent of n-octyl bromide (Equation 5): That the product (71%) actually had structure Vb was shown by alkaline cleavage to give capric acid and methyl nonyl ketone (isolated as the semicarbazone) in yields of 84 and 89% respectively (Equation 6):

$$\underset{\text{II}}{RCH_2COCH_2COCH_3} \xrightarrow[\text{liq. } NH_3]{2\ KNH_2} \text{III} \xrightarrow[2.\ NH_4Cl]{1.\ R'X} RCH_2COCH_2COCH_2R' \qquad (5)$$

Va. R = R′ = $CH_2C_6H_5$
b. R = R′ = n-C_8H_{17}
c. R = $CH_2C_6H_5$, R′ = n-C_4H_9

$$\text{Vb} \xrightarrow[2.\ \text{HCl}]{1.\ \text{KOH}} CH_3(CH_2)_8COOH + CH_3CO(CH_2)_8CH_3 \qquad (6)$$

Moreover, the infrared spectra of its copper chelate (blue-gray) showed strong infrared adsorption bands at 6.40 and 6.60 μ which is indicative of such a β-diketone.[7]

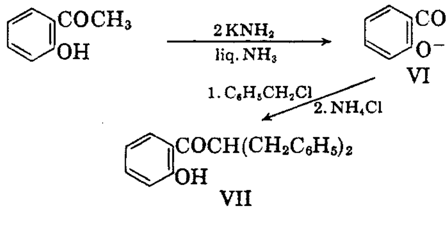
The β-diketone and chelate were identical with the dialkylation product obtained when the dicarbanion of acetylacetone was rapidly alkylated with n-octyl bromide (see above).

Secondly, 6-phenyl-2,4-hexanedione (II. R = $CH_2C_6H_5$), obtained as described above, was converted to its dicarbanion and alkylated with n-butyl bromide to give β-diketone Vc (67%). That the ketone actually had structure Vc was shown through an independent synthesis, by the condensation of methyl hydrocinnamate with methyl amyl ketone (Equation 7).[9] Also its copper chelate (blue) showed strong infrared adsorption at 6.40 and 6.60 μ which is characteristic of such a β-diketone.[7] The β-diketone Vc was also synthesized (52%) by the alkylation of the dicarbanion of 2,4-nonanedione (II, R = n-C_4H_9) with benzyl chloride.

$$CH_3(CH_2)_4COCH_3 \xrightarrow[\text{ether}]{NaNH_2} CH_3(CH_2)_4COCH_2Na \xrightarrow{C_6H_5CH_2CH_2COOCH_3} \text{Vc} \qquad (7)$$

The stepwise dialkylation of acetylacetone through intermediate dicarbanions of type I and III thus affords a convenient means for the synthesis of high molecular weight β-diketones.

Alkylation of o-hydroxyacetophenone. Although o-hydroxyacetophenone is not a typical β-diketone, it seemed of interest to determine whether it could be alkylated at the methyl group through the intermediate dianion VI. When o-hydroxyacetophenone was added to two molecular equivalents of potassium amide in liquid ammonia and the resulting suspension treated with one molecular equivalent of benzyl chloride (Equation 8) no mono-benzylation product was isolated:



(8)

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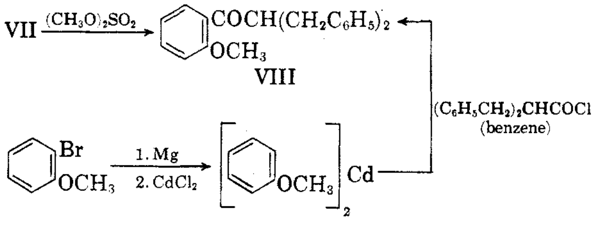
[12] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78,** 1653 (1956).

[13] T. M. Harris and C. R. Hauser, *J. Am. Chem. Soc.*, **81,** 1160 (1959).

Instead, the dibenzylation product VII was obtained (69–74% based on benzyl chloride) and unreacted *o*-hydroxyacetophenone was recovered (53%). Presumably the dianion of the mono-alkylation product was an intermediate. Rather surprisingly, when the reaction was performed using two molecular equivalents of benzyl chloride, a poorer yield (23%) of the dialkylation product was isolated. Again no mono-benzylation products were observed.

The dialkylation product gave a purple color with 1% methanolic ferric chloride, formed an oxime, and was thus assigned the structure VII. The structure of the dialkylation product was established as VII by converting it to its methyl ether VIII (79%) with dimethyl sulfate. This ether was independently synthesized (Scheme A) from di-(*o*-methoxyphenyl)-cadmium and dibenzylacetyl chloride.[14] That the ethers were the same was shown by comparison of the boiling points, refractive indices, and infrared spectra.

SCHEME A



EXPERIMENTAL[15]

General procedure for the alkylation of dipotassioacetylacetone. To a stirred solution of 0.2 mol. of potassium amide in 300 ml. of liquid ammonia[3] was added through a powder funnel 10 g. (0.1 mol.) of acetylacetone as the freshly precipitated ammonium salt.[16] After stirring 0.5 hr. the resulting white suspension was considered to contain 0.1 mol. of dipotassioacetylacetone.

To the stirred suspension of dipotassioacetylacetone was added in 3 min. 0.1 mol. of alkyl halide in 10–20 ml. of anhydrous ether. The resulting mixture was stirred 1 hr. and neutralized by the rapid addition of 12 g. of solid ammonium chloride. The ammonia was replaced by ether and the ethereal suspension extracted with water to remove the inorganic salts. The aqueous solution was acidified with 3*N* hydrochloric acid and extracted three times with ether. The combined ethereal solutions were dried over Drierite, filtered, and the solvent removed under reduced pressure. The residual liquid was vacuum distilled to give the 1-alkyl-2,4-pentanedione.

The copper chelates, formed by adding a hot, filtered aqueous solution of copper acetate to a methanolic solution of β-diketone, were crystallized from methanol or a mixture of benzene and ligroin (b.p. 60–90°).

The results are summarized in Table I.

Benzylation of disodioacetylacetone. To a stirred suspension of 0.1 mol. of sodium amide in 300 ml. of liquid ammonia[17] was added 5 g. (0.05 mol.) of acetylacetone as the freshly precipitated ammonium salt.[16] After stirring 0.5 hr. the resulting black solution was assumed to contain 0.05 mol. of disodioacetylacetone.

To this black solution was added in 3 min. 6.3 g. (0.05 mol.) of benzyl chloride in 10 ml. of anhydrous ether. After stirring 1 hr. the solution was neutralized with 6.0 g. of solid ammonium chloride and worked up as described above. The residual liquid after the removal of the ether was converted directly to the copper chelate of 6-phenyl-2,4-hexanedione (II. R = $CH_2C_6H_5$), 7.6 g. (69%), m.p. 159–160 (lit.[3] 158.5–160°).

Octylation of dipotassioacetylacetone. To a stirred suspension of 0.1 mol. of dipotassioacetylacetone in 300 ml. of liquid ammonia was added in 75 min. 19.3 g. (0.1 mol.) of *n*-octyl bromide in 20 ml. of anhydrous ether. The resulting suspension was stirred 1 hr. and neutralized with solid ammonium chloride (12 g.). The ammonia was replaced by ether and the ethereal suspension processed in the usual manner. Distillation afforded 14.1 g. (67%) of 2,4-tridecanedione (II. R = n-C_8H_{17}), b.p. 155–160° at 16 mm. lit.,[18] 150–152° at 16 mm.). The β-diketone gave an orange enol test with 1% methanolic ferric chloride and formed a blue copper chelate which was crystallized from methanol, m.p. 117–118° (lit.,[19] 114° and[18] 110°).

When the alkylation was carried out as described in the general procedure (halide added in 3 min.) the yield of 2,4-tridecanedione was 49% and a dialkylation product was obtained. This was processed in the following manner: The pot residue after the distillation of the mono-alkylation product was cooled and crystallized from methanol to give 10,12-henicosanedione Vb (27%), m.p. 39–39.5°. This β-diketone gave an orange color with 1% methanolic ferric chloride.

Anal. Calcd. for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42; mol. wt., 325. Found: C, 77.73; H, 12.21; mol. wt., 335.

A sample of the β-diketone was converted to a blue-gray copper chelate which was crystallized from benzene-ligroin (b.p. 60–90°), m.p. 109.5–110°.

Anal. Calcd. for $C_{42}H_{78}O_4Cu$: C, 70.99; H, 11.06; Cu, 8.96. Found: C, 71.47 and 71.38; H, 11.05 and 11.14; Cu, 8.84 and 8.76.

Independent synthesis of 1-octene-5,7-dione (II. R = $-CH_2CH{=}CH_2$). To a stirred suspension of 0.2 mol. of sodium amide in 300 ml. of anhydrous ether was added 9.8 g. (0.10 mol.) of allylacetone in 20 ml. of ether, followed after 5 min. by 17.6 g. (0.20 mol.) of ethyl acetate in 40 ml. of ether according to the general sodium amide method A.[17] After refluxing 3 hr. the suspension was cooled and poured onto 200 g. of crushed ice containing 25 ml. of concentrated hydrochloric acid. The ether layer was separated and combined with three ether washings of the aqueous solution. After drying over Drierite, the ethereal solution was filtered and the ether removed under reduced pressure. The residue was dissolved in hot methanol and a hot, filtered, aqueous solution of copper acetate was added. The crude copper chelate (11.8 g., 69%, m.p. 163–164.5°) was decomposed with hydrochloric acid and the aqueous suspension extracted with petroleum ether (b.p. 30–60°). The

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[14] Although di-(*m*-methoxyphenyl)-cadmium reacts with rearrangement, it has been shown that the ortho derivative reacts normally. See W. G. Dauben and J. W. Collette, *J. Am. Chem. Soc.*, **81**, 967 (1959).

[15] Melting points and boiling points are uncorrected. Melting points were taken on a Fisher-Johns melting point apparatus. Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[16] The direct addition of acetylacetone to the liquid ammonia solution of alkali amide was so vigorous that the reaction was difficult to control. The ammonium salt was prepared by freezing the acetylacetone in a Dry Ice-acetone bath and then adding liquid ammonia. The excess liquid ammonia was evaporated at room temperature and the residual salt added to the amide solution.

[17] See ref. (9), p. 122.

[18] C. Weygand and H. Baumgartel, *Ber.*, **62B**, 574 (1929).

[19] G. T. Morgan and E. Holmes, *J. Chem. Soc.*, **125**, 760 (1924).

organic solution was dried over Drierite, filtered, and the solvent removed under reduced pressure. Distillation of the residue afforded 6.25 g. (45%) of 1-octene-5,7-dione, b.p. 83–84° at 16 mm. (lit.[8] 87–89° at 16 mm.). The infrared spectrum of this β-diketone was identical with the spectrum of the β-diketone prepared by the alkylation of dipotassioacetylacetone with allyl bromide.

A sample of the β-diketone was reconverted to the copper chelate (blue) which was crystallized from methanol, m.p. 162–162.5° and not depressed on admixture with the copper chelate from the alkylation reaction. Repeated recrystallization from methanol raised the melting point to 163–163.5°.

Anal. Calcd. for $C_{16}H_{22}O_4Cu$: C, 56.21; H, 6.49; Cu, 18.38. Found: C, 56.21; H, 6.42; Cu, 18.42.

Reaction of dipotassioacetylacetone with β-phenylethyl chloride. The reaction was carried out as described in the general procedure using 0.1 mol. of dipotassioacetylacetone and 14.1 g. (0.1 mol.) of β-phenylethylchloride. A few crystals of hydroquinone were added to the dried ether solution before the removal of the solvent. The residue was dissolved in methanol and a hot, filtered solution of 12 g. of copper acetate in 200 ml. of 50% aqueous methanol was added. The mixture was cooled and the copper chelate filtered. The filter cake was washed successively with water and petroleum ether (b.p. 30–60°) until the washings were essentially clear, yielding 9.2 g. (70%) of the copper chelate of acetylacetone.

The filtrate was separated and the organic solution was combined with two petroleum ether washings of the aqueous solution. The dried organic solution was cooled in ice and a 10% solution of bromine in carbon tetrachloride was slowly added until the bromine color persisted for 5 min. The excess bromine was decomposed by the addition of a 10% sodium bisulfite solution. The organic layer was separated, washed with a 10% sodium bisulfite solution followed by water, dried over Drierite, filtered, and the solvent removed under reduced pressure. The residual solid was crystallized from aqueous ethanol to give 23.3 g. (89%) of styrene dibromide, m.p. 68–70° (lit.[20] 72–73°). After recrystallization from ethanol the m.p. and mixed m.p. with authentic styrene dibromide were 72.5–73°.

Reaction of dipotassioacetylacetone with benzhydryl chloride. To a stirred suspension of 0.1 mol. of dipotassioacetylacetone in 300 ml. of liquid ammonia was added in 5 min. 20.3 g. (0.1 mol.) of benzhydryl chloride in 10 ml. of anhydrous ether. An orange color appeared immediately. After stirring 1 hr. the suspension was neutralized by the addition of 12 g. of solid ammonium chloride and the ammonia was replaced by ether. Water was added to the ethereal suspension and the mixture was filtered to give 8.55 g. of tetraphenylethylene, m.p. 221.5–223.5° and 223.5–224.5° when mixed with an authentic sample (lit.[21] 223–224°).

The filtrate was separated and the ethereal solution combined with several ether washings of the aqueous solution. After drying over Drierite, the solvent was filtered and distilled under reduced pressure. The residual mixture was filtered and the filter cake washed with petroleum ether (b.p. 30–60°) until the washings were clear, yielding 7.65 g. of tetraphenylethylene, m.p. and mixed m.p. 223.5–224.5°. Total tetraphenylethylene 16.2 g. (98%).

The filtrate was concentrated, dissolved in hot methanol and converted to the copper chelate of acetylacetone (7.0 g., 54%).

Independent synthesis of 10,12-henicosanedione (Vb). To a stirred solution of 0.1 mol. of potassium amide in 300 ml. of liquid ammonia was added 10.6 g. (0.05 mol.) of 2,4-tridecanedione in an equal volume of anhydrous ether. The resulting gray suspension was stirred 0.5 hr. and 9.65 g. (0.05 mol.) of *n*-octyl bromide in an equal volume of anhydrous ether was rapidly added. After stirring 1 hr. the suspension was neutralized by the addition of excess ammonium chloride and the ammonia was replaced by ether. The ethereal suspension was extracted with water, combined with two ether washings of the aqueous solution, dried over Drierite, filtered, and the ether removed under reduced pressure. The residual solid was crystallized from methanol to give 11.55 g. (71%) of 10,12-henicosanedione, m.p. 38–39° and not depressed on admixture with the dialkylation product from dipotassioacetylacetone and *n*-octyl bromide.

Alkaline cleavage of 10,12-henicosanedione (Vb). A solution of 3.24 g. (10 mmol.) of β-diketone Vb and 2 g. of potassium hydroxide in 60 ml. of 80% ethanol was refluxed 10 hr. The ethanol was evaporated and ether and water were added to the residue. The ether layer was separated, dried over magnesium sulfate, filtered, and the ether was removed under reduced pressure. The residue was treated with semicarbazide hydrochloride and sodium acetate to give 1.9 g. (89%) of the semicarbazone of methyl nonyl ketone, m.p. 121.5–122.5° (lit.[22] 122–123°).

The aqueous layer from the cleavage mixture was saturated with carbon dioxide and extracted with ether to remove any unreacted β-diketone. The aqueous solution was then acidified with cold, dilute hydrochloric acid and extracted twice with ether. The ether solution was dried over magnesium sulfate, filtered, and the solvent removed yielding 1.45 g. (84%) capric acid, m.p. 24–27° (lit.[23] 31.5°). A portion of the acid was converted to its *p*-bromophenacyl ester, m.p. 66–67° (lit.[23] 67°).

1-Phenyl-3,5-decanedione (Vc). (A) *From the dicarbanion of 6-phenyl-2,4-hexanedione* (II. R = $—CH_2C_6H_5$). To a stirred solution of 0.1 mol. of potassium amide in 300 ml. of liquid ammonia was added 9.51 g. (0.05 mol.) of 6-phenyl-2,4-hexanedione in 7 ml. of anhydrous ether. The resulting dark red solution was stirred 0.5 hr. and 6.85 g. (0.05 mol.) of *n*-butyl bromide in 5 ml. of anhydrous ether was added over 1.5 min. The color faded and the resulting yellow suspension was stirred 0.5 hr. After neutralization by the addition of 6 g. of solid ammonium chloride the ammonia was replaced by ether and the mixture worked up in the usual manner. Distillation afforded 8.25 g. (67%) of 1-phenyl-3,5-decanedione (Vc), b.p. 148–152° at 2 mm. Repeated distillation gave b.p. 146° at 1 mm. The β-diketone gave an orange enol test with 1% methanolic ferric chloride.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.87; H, 8.89

A portion of the β-diketone was converted to its copper chelate which was crystallized from methanol, m.p. 124–124.5°.

Anal. Calcd. for $C_{32}H_{42}O_4Cu$: C, 69.35; H, 7.64; Cu, 11.35. Found: C, 69.48; H, 7.68; Cu, 11.47.

(B) *From the dicarbanion of 2,4-nonanedione* (II. R = n-C_4H_9). To a stirred solution of 0.2 mol. of potassium amide in 300 ml. of liquid ammonia was added 15.6 g. (0.1 mol.) of 2,4-nonanedione in 5 ml. of anhydrous ether. The resulting green suspension was stirred 0.5 hr. and 12.6 g. (0.1 mol.) of benzyl chloride in 5 ml. of anhydrous ether was added in 3 min. The resulting suspension was stirred 1 hr. and neutralized by the addition of 12 g. of solid ammonium chloride. The ammonia was replaced by ether and the mixture worked up in the usual manner. Distillation afforded 12.8 g. (52%) of β-diketone Vc, b.p. 147–152° at 1 mm. The infrared spectrum of this β-diketone was identical with the spectrum of the β-diketone prepared by method A.

A portion of the β-diketone was converted to its copper chelate, m.p. 125–126° and not depressed on admixture with the chelate from A.

Independent synthesis of β-diketone Vc. To a stirred suspension of 0.2 mol. of sodium amide in 300 ml. of anhydrous

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[20] C. R. Hauser, J. C. Shivers, and P. S. Skell, *J. Am. Chem. Soc.*, **67**, 409 (1945).

[21] J. Schmidlin, *Ber.*, **39**, 4203 (1907).

[22] Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. III, p. 464.

[23] Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, **Vol. I**, p. 421.

ether was added 22.8 g. (0.2 mol.) of methyl amyl ketone in 25 ml. of ether, followed after 5 min. by 16.4 g. (0.1 mol.) of methyl hydrocinnamate in 25 ml. of ether according to the general sodium amide method B.[17] After refluxing 1.5 hr. the suspension was cooled and poured into 200 g. of crushed ice containing 18 ml. of concentrated hydrochloric acid. The ether layer was separated and combined with an ether washing of the aqueous solution. The combined ether solutions were washed successively with 100 ml. of a saturated sodium bicarbonate solution and 100 ml. of water. After drying over Drierite, the ether was filtered and solvent removed under reduced pressure. The residual liquid was distilled to give 14.65 g. (60% based on ester) of β-diketone Vc, b.p. 150–155° at 1.5 mm. The infrared spectrum of this β-diketone was identical with the spectra of the β-diketones prepared by methods A and B.

A portion of the β-diketone was converted to its copper chelate, m.p. 125–126°, not depressed on admixture with the chelates from methods A and B.

Alkylation of o-hydroxyacetophenone. To a stirred solution of 0.2 mol. of potassium amide in 300 ml. of liquid ammonia was added 13.6 g. (0.1 mol.) of *o*-hydroxyacetophenone in 20 ml. of anhydrous ether. A vigorous reaction occurred and a yellow precipitate formed. The suspension was stirred 10 min. and 12.6 g. (0.1 mol.) of benzyl chloride in 20 ml. of anhydrous ether was added in 3 min. The resulting yellow solution was stirred 1 hr. and neutralized by the addition of 12 g. of solid ammonium chloride. The ammonia was replaced by ether and the ethereal suspension was extracted with water. After being combined with three ether washings of the acidified aqueous solution, the ether solution was dried over Drierite, filtered, and the ether removed under reduced pressure. The residue was crystallized from methanol to give 2,2-dibenzyl-2′-hydroxyacetophenone (VII) (69–74% on benzyl chloride), m.p. 71–72°. Recrystallization from methanol raised the m.p. to 73–73.5°. The solid gave a purple color with 1% methanolic ferric chloride.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37; mol. wt., 316. Found: C, 83.28 and 83.25; H, 6.45 and 6.31; mol. wt., 327.

The filtrate was evaporated and the residue dissolved in ether. The ethereal solution was extracted with 10% sodium hydroxide which was subsequently acidified with 3*N* hydrochloric acid. The acidic solution was extracted with ether and the ether was evaporated. The residual liquid was converted to the phenylhydrazone of *o*-hydroxyacetophenone (52.5%), m.p. 109.5–110°, not depressed on admixture with an authentic sample.

An oxime was prepared by refluxing a solution of VII (1.00 g., 3.17 mmol.), hydroxylamine hydrochloride (1.0 g.) and potassium hydroxide (4.0 g.) in 20 ml. of 95% ethanol for 2 hr. The solution was then poured into 150 ml. of water and the suspension filtered. The filtrate was acidified with hydrochloric acid and allowed to stand overnight when a white precipitate settled out. Filtration yielded 0.8 g., m.p. 88–92° of a material which appeared to be a mixture. After several fractional crystallizations from hexane the material melted at 121–121.5°.

Anal. Calcd. for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.64; H, 6.50; N, 4.15.

Methylation of VII. To a hot solution of 3.16 g. (10 mmol.) of VII in 20 ml. of ethanol was added alternately in five portions, 4 g. of sodium hydroxide in 10 ml. of water and 10 ml. of dimethyl sulfate. Vigorous refluxing occurred after each addition of dimethyl sulfate. After the final portion of dimethyl sulfate had been added a solution of 1 g. of sodium hydroxide in 2 ml. of water was added and the mixture refluxed 2.5 hr. After cooling, the alkaline solution was extracted three times with ether. The ether was dried over Drierite, filtered, and the solvent removed under reduced pressure. Distillation of the residue afforded 2.6 g. (79%) of 2,2-dibenzyl-2′-methyoxyacetophenone VIII, b.p. 193–196° at 0.4 mm., n_D^{26} 1.5896. After two redistillations, b.p. 193–195° at 0.2 mm., n_D^{25} 1.5900.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.54; H, 6.83.

Independent synthesis of VIII. Di-(*o*-methoxyphenyl)-cadmium was prepared by a procedure similar to that described by Cason and Prout for diisoamylcadmium.[24]

To 1.37 g. (0.0564 g.-atom) of magnesium shavings in 20 ml. of anhydrous ether was slowly added a solution of 10.5 g. (0.0563 mol.) of *o*-bromoanisole in 100 ml. of anhydrous ether and the resulting mixture was refluxed for 2.25 hr. The mixture was then cooled in ice and 5.50 g. (0.030 mol.) of anhydrous, powdered cadmium chloride was added. The ice bath was removed and the mixture was refluxed for 0.75 hr., when it gave a negative Gilman's test for Grignard reagent. The ether was rapidly distilled and thiophene-free benzene added. To the resulting suspension was added 11.6 g. (0.045 mol.) of dibenzylacetyl chloride (b.p. 148–152° at 0.5 mm.), prepared from dibenzylacetic acid and thionyl chloride (refluxed 8 hr.), in 50 ml. of benzene. The mixture was refluxed 2.5 hr., cooled, and decomposed by the cautious addition of 80 g. of ice followed by 40 ml. of 3*N* hydrochloric acid. The benzene layer was separated and combined with two ether washings of the aqueous solution. The combined organic solutions were washed successively with 50 ml. of water, 50 ml. of a saturated sodium bicarbonate solution, and 50 ml. of water. After drying over Drierite the ether was filtered and solvent removed under reduced pressure. Distillation afforded 5.10 g. (35%) of ether VIII, b.p. 187–190° at 0.25 mm., n_D^{25} 1.5887. Redistillation gave b.p. 196–198° at 0.4 mm., n_D^{25} 1.5891. The infrared spectrum of this compound was identical with the spectrum of the methylation product of VII.

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(24) See J. Cason and F. S. Prout, *Org. Syntheses,* **Coll. Vol. III,** 601 (1955).