amount was insufficient for rigid purification. Reported melting points of glyoxal 2,4-dinitrophenylosazone are: 311–312°,[18] 326–328.[19]

Anal. Calcd. for $C_{14}H_{10}O_8N_8$: N, 26.79. Found: N, 26.25.

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(18) T. L. Jacobs and W. J. Whitcher, THIS JOURNAL, **64**, 2635 (1942).

(19) H. H. Strain, *ibid.*, **57**, 758 (1935).

TOKYO, JAPAN

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF COLUMBIA UNIVERSITY AND THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of Diethyl Dibenzhydrylmalonate[1]

BY ARTHUR C. COPE AND WILLIAM R. LYMAN

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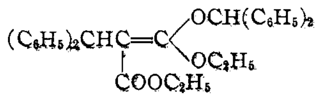
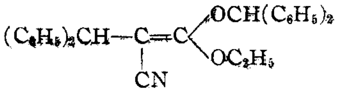
Dibenzhydrylmalonic acid (XVI) has been prepared by reaction of its dibenzhydryl ester XV with hydrogen chloride. The diethyl ester IV of XVI was prepared from the silver salt and ethyl iodide. This ester proved to be identical with a compound first reported by Kohler, which originally was thought to have the O-benzhydryl (ketene acetal) structure I because of the method of synthesis and behavior upon hydrolysis. α-Keto-β,β-dibenzhydryl-β-carbethoxypropionic acid (XI) has been found to undergo an unusual reaction, when heated above the melting point, in which benzhydryl groups rearrange from carbon to oxygen. Carbon monoxide was evolved, and the principal products formed were dibenzhydryl benzhydrylmalonate (XIII) and monoethyl monobenzhydryl benzhydrylmalonate (XIV).

The alkylation products obtained by reaction of benzhydryl bromide with the bromomagnesium derivatives of diethyl benzhydrylmalonate and ethyl benzhydrylcyanoacetate originally were thought to have the O-alkyl (ketene acetal) structures I and II.[2,3] These structures were based on the method of synthesis, which now is known to be inconclusive because reactions of other bromomagnesium enolates have been found to result in either O- or C-substitution,[4,5] and upon degradation of the compounds by acid hydrolysis. Both were stable under the usual conditions of alkaline hydrolysis, but were cleaved by concentrated hydrochloric acid at 175°, yielding benzhydrylacetic acid and benzhydryl ethyl ether.

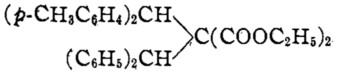

I


II

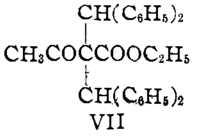
The fact that the alkylation product obtained from the sodium enolate of diethyl benzhydrylmalonate (III) and benzhydryl bromide was identical with the compound originally formulated as I suggested that it actually was diethyl dibenzhydrylmalonate (IV).[6] Indirect evidence for the establishment of formula IV rather than I as correct was obtained by preparing the unsymmetrical disubstituted malonic ester VI, both by alkylation of III with di-*p*-tolylmethyl chloride, and by alkylation of V with benzhydryl bromide. The same product VI was obtained from both alkylations, indicating that the benzhydryl and di-*p*-tolylmethyl groups were attached to the central carbon atom; isomeric but different O-alkyl derivatives (analogous in structure to I) would have been formed by the two routes.[6]

$$\underset{\text{III}}{(C_6H_5)_2CHCH(COOC_2H_5)_2} \longrightarrow \underset{\text{IV}}{[(C_6H_5)_2CH]_2C(COOC_2H_5)_2}$$

$$\underset{\text{V}}{(p\text{-}CH_3C_6H_4)_2CHCH(COOC_2H_5)_2}$$


VI

In the present work, an unambiguous synthesis of IV has been completed, and unusual reactions of intermediates in projected syntheses of IV have been studied. In the first route to IV that was investigated, ethyl dibenzhydrylacetoacetate (VII) was prepared by the alkylation of ethyl benzhydrylacetoacetate. The structure of VII was established by treatment with 20% potassium hydroxide in refluxing 80% ethanol, which resulted in cleavage but failed to saponify the ester group, yielding ethyl dibenzhydrylacetate (VIII). Cleavage of VII with potassium hydroxide in boiling diethylene glycol formed dibenzhydrylacetic acid (IX). The acid IX also was formed from IV under these conditions, and this fact establishes structure IV beyond doubt.



$$CH_3CO\overset{\displaystyle CH(C_6H_5)_2}{\underset{\displaystyle CH(C_6H_5)_2}{C}}COOC_2H_5$$

VII

$$[(C_6H_5)_2CH]_2CHCOOR$$

VIII, R = C_2H_5
IX, R = H

Attempts to oxidize the methyl ketone group of VII to carboxyl with sodium hypochlorite or sodium hypobromite were unsuccessful, the keto ester VII being recovered.

It was possible to condense VII with benzaldehyde in the presence of alcoholic sodium hydroxide, forming ethyl α,α-dibenzhydrylcinnamoylacetate (X) (42%). Oxidation of X with potassium permanganate in acetone yielded the α-keto acid XI

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(1) Abstracted from a thesis submitted in partial fulfillment of requirements for the Ph.D. degree at the Massachusetts Institute of Technology by William R. Lyman.

(2) E. P. Kohler, *Am. Chem. J.*, **34**, 132 (1905).

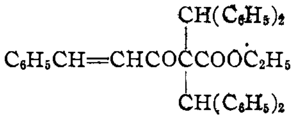
(3) E. P. Kohler and M. Reimer, *ibid.*, **33**, 347 (1905).

(4) E. P. Kohler and W. D. Peterson, THIS JOURNAL, **55**, 1073 (1933).

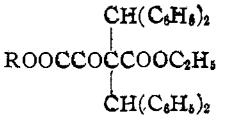
(5) E. P. Kohler and M. Tishler, *ibid.*, **54**, 1596 (1932).

(6) A. C. Cope, *ibid.*, **56**, 721 (1934).

(38%). Attempts to oxidize XI to the monoethyl ester of dibenzhydrylmalonic acid with alkaline


$C_6H_5CH{=}CHCOC(CH(C_6H_5)_2)_2COOC_2H_5$

X


$ROOCCOC(CH(C_6H_5)_2)_2COOC_2H_5$

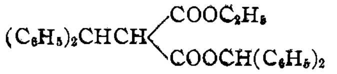
XI, R = H
XII, R = C_2H_5

hydrogen peroxide were unsuccessful. XI was recovered unchanged at room temperature, and at 80° was cleaved as a β-keto ester, forming ethyl dibenzhydrylacetate (VIII). The keto acid XI also was recovered unchanged after attempted oxidation with alkaline potassium permanganate, and after treatment with hydrazoic acid. The ethyl ester XII of the acid XI decomposed with gas evolution when heated in the presence of powdered soft glass at 190–210°. However, although loss of carbon monoxide and formation of IV might be expected in this reaction, the only product that was isolated was a small amount of *sym*-tetraphenylethane.

Thermal decomposition of α-keto acids normally occurs with loss of carbon dioxide to form an aldehyde, or carbon monoxide to form an acid. When XI was decomposed at 190–200°, 78.5–91.3 mole per cent. of carbon monoxide, 4.2–8.2 mole per cent. of carbon dioxide and 25.5–28.2 mole per cent. of water were evolved as gaseous products. Two neutral solid products formed in the decomposition were separated by crystallization from ethanol, and proved to be dibenzhydryl benzhydrylmalonate (XIII) and monoethyl monobenzhydryl benzhydrylmalonate (XIV).

$(C_6H_5)_2CHCH[COOCH(C_6H_5)_2]_2$

XIII

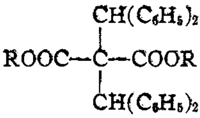

$(C_6H_5)_2CHCH(COOC_2H_5)(COOCH(C_6H_5)_2)$

XIV

The structure of XIII was proved by saponification and decarboxylation with potassium hydroxide in diethylene glycol, forming two equivalents of benzhydrol and one of benzhydrylacetic acid. An authentic sample of XIII was prepared from the silver salt of benzhydrylmalonic acid and benzhydryl bromide, and was identical with XIII obtained by decomposition of XI. The structure of XIV was proved by saponification with dilute alcoholic sodium hydroxide, forming one equivalent of benzhydrol and one of benzhydrylmalonic acid, and confirmed by synthesis of an identical authentic sample from the silver salt of the monoethyl ester of benzhydrylmalonic acid and benzhydryl bromide.

The mechanism by which XIII and XIV are formed on decomposition of the α-keto acid XI has not been investigated. Rearrangement of a benzhydryl group from carbon to oxygen occurs in the formation of both compounds, and an intermolecular reaction must be involved in the reaction leading to XIII, for this compound contains three benzhydryl groups while XI contains only two. It is possible that XIII is formed by an ester interchange reaction from two moles of XIV. Monoethyl hydrogen dibenzhydrylmalonate (XVIII) apparently is not an intermediate in the formation of XIV, for XVIII loses carbon dioxide in the normal manner on heating, yielding ethyl dibenzhydrylacetate (VIII).

The remarkable resistance of diethyl dibenzhydrylmalonate (IV) to alkaline hydrolysis undoubtedly is due to steric hindrance by the large benzhydryl groups. It has been shown that *t*-butyl esters are cleaved rapidly by cold solutions of hydrogen chloride in methanol[7] at the bond between oxygen and the *t*-butyl group, which probably occurs because of the stability of the *t*-butylcarbonium ion. Such cleavage is much less subject to steric hindrance than alkaline hydrolysis, and might be expected to occur with benzhydryl esters for reasons similar to those responsible for easy cleavage of *t*-butyl esters. Dibenzhydryl dibenzhydrylmalonate (XV) has been prepared by the alkylation of XIII with benzhydryl bromide, and was cleaved readily by hydrogen chloride at 0°, forming dibenzhydrylmalonic acid (XVI) (81%). The structure of this acid was confirmed by decarboxylation at the melting point, which yielded dibenzhydrylacetic acid (IX). Reaction of the silver salt of dibenzhydrylmalonic acid with ethyl iodide yielded diethyl dibenzhydrylmalonate (IV), which was identical with the product obtained by Kohler's method,[2] completing a synthetic proof of the structure of his product as IV. In another synthesis of an authentic sample of IV, monoethyl monobenzhydryl dibenzhydrylmalonate (XVII) was prepared by alkylation of XIV, and cleaved to monoethyl hydrogen dibenzhydrylmalonate (XVIII) with hydrogen chloride at 0°. Reaction of the silver salt of XVIII with ethyl iodide also yielded the diethyl ester IV.


$ROOC{-}C(CH(C_6H_5)_2)_2{-}COOR'$

XV, R = R' = $CH(C_6H_5)_2$
XVI, R = R' = H
XVII, R = C_2H_5, R' = $CH(C_6H_5)_2$
XVIII, R = H, R' = C_2H_5

Experimental[8]

Ethyl Dibenzhydrylacetoacetate (VII).—The sodium enolate of ethyl benzhydrylacetoacetate[9] was prepared from 5% molar excess of the ester and 6.9 g. (0.3 mole) of powdered sodium in 150 ml. of benzene by stirring at 60–70° until a clear solution was obtained. A solution of benzhydryl bromide[10] (1% molar excess) in an equal volume of benzene was added, and the mixture was protected from moisture with a drying tube and stirred at 55–60° for 72 hours. After cooling, 200 ml. of water was added, the layers were separated, and the benzene layer was washed with water. The aqueous layers were extracted with benzene, and the combined benzene solutions were concentrated under reduced pressure. The residual oil was dissolved in 600 ml. of warm 95% ethanol, and the solution was allowed to cool slowly to room temperature. The white granular crystals of VII that separated were recrystallized twice from ethanol, and then melted at 151–153°; yield 34–42% in several preparations.

Anal. Calcd. for $C_{32}H_{30}O_3$: C, 83.08; H, 6.54. Found: C, 83.08; H, 6.62.

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(7) S. G. Cohen and A. Schneider, *ibid.*, **63**, 3382 (1941).

(8) Melting points are corrected and boiling points are uncorrected.

(9) G. G. Henderson and M. A. Parker, *J. Chem. Soc.*, **71**, 676 (1897); H. Kagi, *Ann.*, **420**, 64 (1920).

(10) C. Courtot, *Ann. chim.*, [9] **5**, 80 (1916).

Attempts to oxidize VII to XVIII by treatment with sodium hypochlorite or sodium hypobromite in the presence of a small amount of pyridine[11] were unsuccessful, the ester VII being recovered unchanged.

Ethyl Dibenzhydrylacetate (VIII).—Ethyl dibenzhydrylacetoacetate (VII) (3 g.) was added to 50 ml. of 20% potassium hydroxide in 80% ethanol and heated under reflux for 28 hours. The ethanol was removed by distillation, and ice and water were added to the residue. The solid that formed was separated by filtration, dissolved in ether, and concentrated after filtration to remove inorganic material. The residue was crystallized from 50 ml. of 95% ethanol and yielded 1.53 g. (56%) of VIII, m.p. 109.5–111°. An analytical sample that was recrystallized twice from 95% ethanol melted at 112–113°.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.67; H, 6.71. Found: C, 85.65; H, 6.77.

The ester VIII also was prepared from dibenzhydrylacetic acid (described below) through the silver salt (obtained in 93% yield) by reaction with ethyl iodide in benzene (88% yield); m.p. 109–110°. The procedure was similar to one described below for preparation of XV.

Dibenzhydrylacetic Acid (IX).—Diethyl dibenzhydrylmalonate (IV) (2.74 g.) was added to a solution of 1 g. of potassium hydroxide in 6 ml. of diethylene glycol and 0.5 ml. of water. The mixture was heated with a flame (70 minutes) so that the diethylene glycol refluxed and part of the water distilled. The ester melted and dissolved as it was saponified. The contents of the flask solidified on cooling and were pulverized in a mortar with 70 ml. of water. The suspension was extracted with 120 ml. of ether in three portions, and the extracts were washed with 30 ml. of water. The combined aqueous solutions were heated to expel ether, cooled and acidified with hydrochloric acid. The acid IX that separated was collected on a filter, dried and recrystallized from 50 ml. of 50% ethanol; yield 1.57 g., m.p. 182.5–183.5°. An additional 0.06 g. obtained from the mother liquor made the total yield 75%.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.63; H, 5.97.

The acid IX also was obtained from ethyl dibenzhydrylacetoacetate (VII) by a similar procedure.

Ethyl α,α-Dibenzhydrylcinnamoylacetate (X).—Freshly distilled benzaldehyde (7.8 g.) and the sodium hydroxide solution prepared by dissolving 1.6 g. of sodium in 60 ml. of 95% ethanol were added to a solution of 17 g. of VII in 400 ml. of boiling 95% ethanol. The mixture was heated under reflux for 3.3 hours and cooled overnight at 5°. The crude reddish-brown solid that separated was boiled with 75 ml. of isopropyl alcohol, and the hot suspension was filtered; X separated from the filtrate as light yellow crystals in a yield of 8.4 g. (42%), m.p. 167–170°. Varying proportions of the reactants, shorter or longer reaction times, and crystallization from ethanol or butanol gave yields of 30–40%. Recrystallization from ethanol gave an analytical sample of X as white needles, m.p. 169–170°.

Anal. Calcd. for $C_{39}H_{34}O_3$: C, 85.05; H, 6.22. Found: C, 85.01; H, 6.50.

α-Keto-β,β-dibenzhydryl-β-carbethoxypropionic Acid (XI).—A solution of 19.5 g. of X in 300 ml. of acetone was added to a solution of 26 g. of potassium permanganate in 200 ml. of water and 700 ml. of acetone. The mixture was shaken and allowed to stand at room temperature for 63 hours, with cooling by cold water during the first 5 hours to keep the temperature from rising. The excess permanganate was reduced with sodium bisulfite solution, and the mixture was filtered to separate manganese dioxide, which was washed thoroughly with aqueous acetone. The acetone was distilled from the filtrate under reduced pressure, and the solid that separated was collected on a filter and washed with ether to remove unoxidized X, leaving 8.5 g. (45%) of the white, crystalline potassium salt of XI. This salt is relatively insoluble in water or acetone but soluble in mixtures of the two, and can be recrystallized from 95% ethanol.

The potassium salt was shaken in a separatory funnel with 170 ml. of 20% hydrochloric acid and 90 ml. of ether, and the aqueous layer was extracted with two 90-ml. portions of ether. The combined ether solutions were washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residual oil was crystallized from 80% ethanol, yielding 6.92 g. (86% from the potassium salt. 38% over-all) of the keto acid XI, m.p. 177–179° (dec.).

Anal. Calcd. for $C_{32}H_{28}O_5$: C, 78.01; H, 5.73. Found: C, 77.81; H, 5.85.

An attempt to oxidize XI at room temperature with the alkaline hydrogen peroxide obtained from sodium peroxide and ice-water resulted in recovery of XI unchanged. An attempted oxidation with alkaline hydrogen peroxide at 80° for 3 hours resulted in ketonic cleavage instead and formed ethyl dibenzhydrylacetate (VIII) (59%), identical by m.p. and mixed m.p. with the authentic sample described above. After heating with hydrogen peroxide in acetic acid XI was recovered unchanged, as was the case on treatment with chromic acid in aqueous acetic acid at room temperature or on heating briefly. The acid XI also was recovered after boiling with dilute aqueous alkaline potassium permanganate for one hour.

Treatment of XI with hydrazoic acid in chloroform under various conditions resulted in recovery of the acid unchanged.

Ethyl α-Keto-β,β-dibenzhydryl-β-carbethoxypropionate (XII).—A solution of 1.0 g. of the α-keto acid XI in 30 ml. of absolute ethanol was cooled with ice, saturated with dry hydrogen chloride, stoppered and allowed to stand at room temperature for 3.5 days. The solution was concentrated under reduced pressure, and the residue was dissolved in ether and washed with sodium bicarbonate solution and water. The ether solution was concentrated and the residue was dissolved in 20 ml. of 95% ethanol, treated with Norit, and crystallized by cooling. The yield of the ester XII obtained in two crops was 0.74 g. (73%), m.p. 120–121°.

Anal. Calcd. for $C_{34}H_{32}O_5$: C, 78.45; H, 6.20. Found: C, 78.44; H, 6.00.

A sample (0.50 g.) of the α-keto ester XII was mixed with 0.05 g. of powdered soft glass and heated; gas evolution began at 190° and the temperature was maintained at 210° for two hours, until evolution of gas had practically ceased. Crystallization of the residue from 25 ml. of 95% ethanol yielded 0.10 g. of *sym*-tetraphenylethane as the only solid product that could be isolated; m.p. 194–203°, and after one recrystallization from ethanol, m.p. and mixed m.p. with an authentic sample, 208–211°.

Thermal Decomposition of α-Keto-β,β-dibenzhydryl-β-carbethoxypropionic Acid (XI).—Weighed samples of the α-keto acid XI were decomposed by heating in a small flask at 190–200° for 20 minutes, until gas evolution ceased, in a stream of nitrogen (introduced from a gas buret), which passed over the sample and through tubes containing Drierite (for determination of the amount of water formed) into a second gas buret. The gaseous products of decomposition, diluted with a known volume of nitrogen, were collected in the second buret over saturated salt solution, and analyzed in an Orsat apparatus. Data from decomposition of 1.279- and 1.375-g. samples were as follows, with the yields of gaseous products expressed as fractional molar equivalents: carbon monoxide, 0.785, 0.913; carbon dioxide, 0.042, 0.082; water, 0.282, 0.255.

The red residue from decomposition of 3.44 g. of the α-keto acid XI under the conditions described above was dissolved in ether and washed with water. Distillation of the ether left a residue that was crystallized from 75 ml. of 95% ethanol, yielding 0.70 g. of a white crystalline product, m.p. 145–148°. One recrystallization from ethanol yielded 0.57 g. of pure dibenzhydryl benzhydrylmalonate (XIII), m.p. 152–153.5°.

Anal. Calcd. for $C_{42}H_{34}O_4$: C, 83.68; H, 5.69. Found: C, 83.60; H, 5.88.

Concentration of the mother liquor yielded 1.3 g. of another product as impure yellowish crystals, m.p. 85–90°. Two recrystallizations from ethanol yielded 0.60 g. of pure, white crystalline monoethyl monobenzhydryl benzhydrylmalonate (XIV).

Anal. Calcd. for $C_{31}H_{28}O_4$: C, 80.16; H, 6.07; OC_2H_5, 9.70. Found: C, 80.19; H, 6.20; OC_2H_5, 9.69.

Structure of Dibenzhydryl Benzhydrylmalonate (XIII).—A solution of 0.30 g. of the ester XIII (obtained by heating XI) and 0.50 g. of potassium hydroxide in 6 ml. of diethylene glycol and 0.5 ml. of water was heated for 10 minutes so

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[11] R. C. Fuson, J. W. Bertetti and W. E. Ross, THIS JOURNAL, 54, 4380 (1932).

that the water distilled out of the solution. The cooled residue was poured into 50 ml. of water, allowed to stand until the solid formed had coagulated, and filtered, separating 0.15 g. (86%) of benzhydrol, m.p. and mixed m.p. with an authentic sample, 65–67°. The filtrate was acidified with hydrochloric acid, and the precipitated acid was recrystallized from 95% ethanol, yielding 0.08 g. (74%) of benzhydrylacetic acid, m.p. and mixed m.p. with an authentic sample, 154.5–156°.

An authentic sample of XIII was prepared from benzhydrylmalonic acid,[2] by first converting 7.30 g. of the acid to the silver salt (according to the general procedure of Lüttringhaus and Schade[12]), which was obtained in a yield of 12.64 g. (97%). A suspension of the silver salt in 100 ml. of benzene was stirred and heated under reflux while 12.20 g. of benzhydryl bromide in 50 ml. of benzene was added dropwise (5 minutes) and for 20 minutes longer. The mixture was cooled, filtered to remove silver bromide, and concentrated under reduced pressure. The residue was crystallized from 1500 ml. of 95% ethanol and yielded 10.33 g. (70%) of analytically pure XIII, m.p. and mixed m.p. with a sample obtained from the thermal decomposition of XI, 152.5–153.5°.

Structure of Monoethyl Monobenzhydryl Benzhydrylmalonate (XIV).—A solution of 0.14 g. of the ester XIV (obtained by heating XI) in 50 ml. of 5% sodium hydroxide in 50% ethanol was heated under reflux for two hours, and concentrated to remove the ethanol. The residue was diluted with water and extracted with ether. Concentration of the ether extracts and crystallization of the residue from 10 ml. of pentane yielded 0.029 g. (53%) of benzhydrol. Acidification of the alkaline aqueous solution, extraction with ether, concentration of the extracts and crystallization of the residue from a mixture of 15 ml. of ether and 20 ml. of commercial pentane yielded 0.054 g. (67%) of benzhydrylmalonic acid, identified by melting point and the formation of benzhydrylacetic acid by decarboxylation that occurred on melting.

An authentic sample of XIV was prepared in 88% yield from the silver salt (prepared by the general procedure of ref. 12) of monoethyl hydrogen benzhydrylmalonate by treatment with benzhydryl bromide in benzene under conditions similar to those described above for preparation of XIII. The authentic sample of XIV after recrystallization from ethanol melted at 112–113° and showed no depression in mixed melting point with XIV from the thermal decomposition of the α-keto acid XI.

Dibenzhydryl Dibenzhydrylmalonate (XV).—The sodium enolate of dibenzhydryl benzhydrylmalonate was prepared by stirring a solution of 9.0 g. of the ester XIII in 250 ml. of dry toluene with 0.33 g. of powdered sodium for five hours at 100°. A solution of 3.54 g. of benzhydryl bromide in 10 ml. of toluene was added, and the mixture was stirred for five hours at 100° and allowed to stand for 4 days at room temperature. The toluene solution was washed twice with water and concentrated under reduced pressure. The residue could not be crystallized successfully, so it was heated under reflux for 1.5 hours with 600 ml. of 5% sodium hydroxide in 80% ethanol to saponify any of the original ester XIII that was present. After distillation of the ethanol under reduced pressure ether and water were added, and 1.76 g. of a white crystalline solid that was insoluble in either phase was separated; m.p. 125–130°. Concentration of the ether solution and crystallization of the residue from ethanol yielded an additional 1.13 g., m.p. 127–132°. The first of these crops of crude XV was recrystallized from 400 ml. of 95% ethanol and yielded 1.41 g. of pure XV, m.p. 140–141° (the total yield of XV melting above 137° was 2.41 g. or 22%).

Anal. Calcd. for $C_{55}H_{44}O_4$: C, 85.90; H, 5.77. Found: C, 85.86; H, 5.91.

Dibenzhydrylmalonic Acid (XVI).—The ester XV (0.57 g.) was dissolved in 40 ml. of ethyl acetate and 10 ml. of absolute ethanol, and the solution was saturated with hydrogen chloride at 0° and allowed to stand at that temperature for four hours. The solution was concentrated to dryness under reduced pressure, and a solution of the residue in 30 ml. of ether was extracted with two 20-ml. portions of 2% potassium hydroxide and 10 ml. of water. The combined aqueous layers were heated on a steam-bath to remove ether, cooled and acidified with hydrochloric acid. The precipitated organic acid was collected on a filter, dried and recrystallized from 60 ml. of benzene. The yield of XVI was 0.262 g. (81%), m.p. 188–191° (dec., softening at 183°).

Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.78; H, 5.54. Found: C, 79.93; H, 5.78.

A sample (0.2 g.) of the acid XVI was decarboxylated by heating above the melting point until gas evolution ceased. Crystallization of the residue from benzene yielded 0.11 g. of dibenzhydrylacetic acid (IX), identified by m.p. and mixed m.p. with an authentic sample of IX described above.

Synthesis of Diethyl Dibenzhydrylmalonate (IV) from the Acid XVI.—The silver salt was prepared from 100 mg. of XVI by the general procedure of ref. 12 in a yield of 127 mg. (85%). A suspension of the salt in 25 ml. of benzene was warmed on a steam-bath with 0.20 ml. of ethyl iodide for 25 minutes. The mixture was filtered and centrifuged to remove silver iodide, concentrated to dryness, and the residue was crystallized from 7 ml. of 95% ethanol. The yield of the ester IV was 76 mg., m.p. and mixed m.p. with a sample prepared by alkylation of III,[6] 178–180°.

Monoethyl Monobenzhydryl Dibenzhydrylmalonate (XVII).—The sodium enolate was prepared from 15.0 g. of the ester XIV and 0.62 g. of powdered sodium in 150 ml. of dry benzene, by stirring under reflux for 4.5 hours. A solution of 6.65 g. of benzhydryl bromide in 50 ml. of benzene was added, and the mixture was stirred and heated under reflux for 4.5 hours. After cooling, the benzene solution was washed with dilute hydrochloric acid and water, and then was concentrated under reduced pressure. The residue was heated under reflux for four hours with 300 ml. of 5% sodium hydroxide in 65% ethanol to saponify any XIV remaining, and concentrated under reduced pressure to remove ethanol. The aqueous residue was extracted with ether, and the extracts were washed with water, dried over sodium sulfate, and concentrated under reduced pressure. Crystallization of the residue from 600 ml. of 95% ethanol yielded 4.29 g. (25%) of XVII, m.p. 128–131°. An analytical sample was recrystallized from ethanol as needles with a constant melting point of 132.5–133.5°.

Anal. Calcd. for $C_{44}H_{38}O_4$: C, 83.78; H, 6.07; OC_2H_5, 7.14. Found: C, 83.59; H, 6.18; OC_2H_5, 7.19.

Monoethyl Hydrogen Dibenzhydrylmalonate (XVIII).—A solution of 1.00 g. of the ester XVII in 50 ml. of dry ether and 25 ml. of absolute ethanol was saturated with hydrogen chloride at 0°, stoppered, and allowed to stand at that temperature for four hours. The solvent was removed under reduced pressure and the residue was dissolved in ether and washed with water. After distillation of the ether, the residue was crystallized from 95% ethanol. The yield of XVIII was 0.616 g. (83%), m.p. 169–171° (dec.). An analytical sample that was recrystallized several times from ethanol melted at 169–171° (dec., with softening at 160°, inserted at 150° and the temperature raised 5° per minute).

Anal. Calcd. for $C_{31}H_{28}O_4$: C, 80.16; H, 6.08. Found: C, 79.91; H, 6.24.

A sample (0.20 g.) of XVIII was decarboxylated by heating above the melting point until no more gas was evolved. The ethyl dibenzhydrylacetate that was formed was recrystallized from 95% ethanol, and was obtained in a yield of 0.136 g. (75%), m.p. and mixed m.p. with an authentic sample of VIII, 109–111°.

Synthesis of Diethyl Dibenzhydrylmalonate (IV) from XVIII.—The monoethyl ester XVIII (0.193 g.) was converted to the silver salt (0.206 g., 87%) by the general procedure of ref. 12. The silver salt and 0.1 ml. of ethyl iodide were added to 10 ml. of benzene and the mixture was warmed on the steam-bath for 15 minutes. The silver iodide was separated by filtration, and the filtrate was concentrated to dryness. The residue was crystallized from 15 ml. of 95% ethanol, and yielded 0.149 g. (72%) of IV, m.p. 172–178°. After one recrystallization from ethanol the IV from this preparation had m.p. and mixed m.p. with a sample prepared by alkylation of III[6] of 177–179°.

CAMBRIDGE, MASS.

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[12] A. Lüttringhaus and D. Schade, *Ber.*, **74**, 1566 (1941).