[CONTRIBUTION FROM THE SCIENTIFIC RESEARCH INSTITUTE]

On the Formic Acid Rearrangement of 3,4-Dimethyl-1-hexyn-3-ol

BY TATSUO TAKESHIMA

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The formic acid rearrangement of ethynyl carbinols has been extended to 3,4-dimethyl-1-hexyn-3-ol (I). The major rearrangement product (*ca.* 30%) consisted of a mixture of the known α,β- and β,γ-ethylenic ketones, 3,4-dimethyl-3-hexen-2-one (II) and 3,4-dimethyl-4-hexen-2-one (III), respectively. In addition, a small amount (*ca.* 3%) of a new aldehyde, 3,4-dimethyl-2-hexenal (IV), was isolated.

Introduction

The so-called Rupe formic acid rearrangement of ethynyl carbinols has been the subject of many contradictory reports.[1] Accordingly, a series of relatively simple ethynyl carbinols were investigated to determine the nature of this rearrangement in relation to minor differences of substitution. In two previous papers,[2,3] 3-methyl-1-butyn-3-ol and 3-methyl-1-pentyn-3-ol were shown to give β-methylcrotonaldehyde and 3-methyl-3-penten-2-one, respectively, and it was pointed out that each of these two carbinols takes its own course in this rearrangement.

It was the purpose of the present work to examine another fundamental ethynyl carbinol in which the tertiary carbon atom is adjacent to the carbon atom attached to the hydroxyl group. 3,4-Dimethyl-1-hexyn-3-ol (I) was chosen because it was relatively easily available.

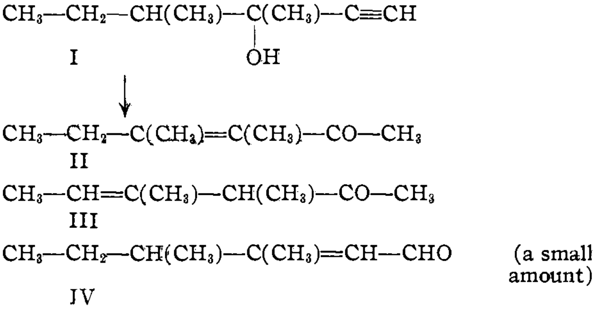
I was refluxed with 80% formic acid for *ca.* 1.5 hours and treated as described in the previous papers.[2,3] The reaction mixture was distilled and five fractions were collected, all of which reacted with carbonyl reagents (consult Table I).

Semicarbazones obtained from fractions 1–4 appeared to be those reported for a pair of homomesitones,[4,5] 3,4-dimethyl-3-hexen-2-one (II) and 3,4-dimethyl-4-hexen-2-one (III).

However, these semicarbazones were difficult to purify and their melting points were too indistinct for characterization purposes. On the other hand, the 2,4-dinitrophenylhydrazones of the above fractions were much more easily purified and exhibited distinct melting points and characteristic appearances (consult Table I). To establish the identity of II and III, these ketones were prepared by an alternate route using known methods[4] and were converted to their 2,4-dinitrophenylhydrazones which compared favorably with those obtained from the rearrangement products.

Fractions 1–4, therefore, consisted of mixtures of II and III. There were obtained four 2,4-dinitrophenylhydrazones from these fractions, corresponding to the two pairs related to II and III, respectively. However, that melting at 75.5–76°, square yellow plates (corresponding to II) was considered to be formed secondarily from that melting at 100–102°, long red plates (corresponding to II), by the acid conditions used in the preparation of the derivatives. The semicarbazone corresponding to the former was not obtained. It may correspond to that of m.p. 166–167° obtained by Abbott and others.[6]

Fraction 5, which had the highest boiling point, proved to be carbonyl compound of formula $C_8H_{14}O$, which gave the 2,4-dinitrophenylhydrazone and semicarbazone shown in Table I. Ozonolysis and oxidation with permanganate gave glyoxal and 3-methyl-2-pentanone as the phenylosazone and the 2,4-dinitrophenylhydrazone, respectively. On the basis of these results, together with the aforesaid unsaturated aldehydic nature, this compound was assigned structure IV.



$$\mathrm{CH_3{-}CH_2{-}CH(CH_3){-}\underset{\displaystyle OH}{\underset{|}{C}}(CH_3){-}C{\equiv}CH}$$

I

$$\downarrow$$

$$\mathrm{CH_3{-}CH_2{-}C(CH_3){=}C(CH_3){-}CO{-}CH_3}$$

II

$$\mathrm{CH_3{-}CH{=}C(CH_3){-}CH(CH_3){-}CO{-}CH_3}$$

III

$$\mathrm{CH_3{-}CH_2{-}CH(CH_3){-}C(CH_3){=}CH{-}CHO}$$ (a small amount)

IV

Thus, the bulk of the rearrangement product consisted of a mixture of the two unsaturated methyl ketones. In addition, a small amount of the unsaturated aldehyde was formed. This special case thus corresponds to the usual one. Likewise, α,β- and β,γ-ethylenic ketones are simultaneously produced in this rearrangement under acid conditions.

Acknowledgment.—I am indebted to Mr. K. Furuhashi and Mr. K. Muto for the elementary analyses contained within. I also wish to thank Mr. H. Yasuda, Miss N. Suzuki and Miss S. Yokoyama for their kind assistance.

Experimental

3-Methyl-2-pentanone.—The ketone used in the preparation of I was prepared by hydrogenating 3-methyl-3-penten-2-one over palladium. Seventy-three grams of a fraction boiling at 116–119° was obtained (on one distillation) from 100 g. of the ethylenic ketone, yield *ca.* 72%.

3,4-Dimethyl-1-hexyn-3-ol (I).—The preparation followed, on the whole, the same method as in the previous papers.[2,3] Ninety-six grams of the carbinol boiling at 152–155° was obtained from 93 g. of 3-methyl-2-pentanone; yield 82%.

The Formic Acid Rearrangement of 3,4-Dimethyl-1-hexyn-3-ol (I).—Seventy-one grams of I was boiled gently under reflux with 700 g. of *ca.* 80% formic acid for *ca.* 1.5 hr.,

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[1] A. W. Johnson, "The Chemistry of Acetylenic Compounds," Vol. I, E. Arnold and Co., London, 1946, pp. 127–130; F. G. Fischer, L. Ertel and K. Löwenberg, *Ber.*, **64B**, 30 (1931); C. D. Hurd and W. D. McPhee, THIS JOURNAL, **71**, 398 (1949).

[2] T. Takeshima, *J. Sci. Research Inst.* (*Tokyo*), **45**, 103 (1951).

[3] T. Takeshima, *ibid.*, **45**, 211 (1951).

[4] A. E. Abbott, G. A. R. Kon and R. D. Satchell, *J. Chem. Soc.*, **2**, 2514 (1928).

[5] These α,β and β,γ-ethylenic ketones are known to show tautomeric behavior.

[6] Each two semicarbazone of II and III are considered to correspond to the geometric isomers of the ketones. See reference (4).

TABLE I

REARRANGEMENT PRODUCTS FROM I

Fraction	B.p. °C.	Mm.	Yield, g. from 71 g. of I	Constituent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. weight Calcd.	Mol. weight Found
1	157–160	*ca.* 760	*ca.* 4	III predominating	...	...	...	...	...	
2	160–163.5	*ca.* 760	*ca.* 8	III, II	76.14	75.85	11.18	11.30	...	...
3	163.5–165	*ca.* 760	*ca.* 4.3	III, II	...	...	...	...	...	...
4	59–73	15	*ca.* 6	II predominating	...	...	...	...	...	...
5	78–79	15	*ca.* 2	IV	76.14	76.09	11.18	10.93	126.2	121

DERIVATIVES OF THE CARBONYL COMPOUNDS

		2,4-Dinitrophenylhydrazone M.p., °C.	2,4-Dinitrophenylhydrazone Appearance	Semicarbazone M.p., °C.	Semicarbazone Reported m.p., °C.
From II	(a)	100–102	Red long plates	185–186	186
	(b)	75.5–76	Yellow square plates	.....	(166–167[a])
From III	(a)	94.5–95	Yellow flattened sharp needles	*ca.* 200	203–204
	(b)	104.5–105	Deep yellow long plates	164–165	163
From IV		173–174	Orange-red plates	160–161	......

[a] It was not ascertained whether or not this semicarbazone corresponds to the 2,4-dinitrophenylhydrazone of m.p. 75.5–76°.

cooled, and then poured onto ice and concentrated solution of *ca.* 950 g. of potassium carbonate, extracted with ether, dried by calcium chloride, the ether driven off, and again dried.[2,3]

The product was separated into several fractions: a distillate up to 157° was rejected; (1) b.p. 157–160°, *ca.* 4 g.; (2) b.p. 160–163.5°, *ca.* 8 g. (the greater part distilled at 162–163°); (3) b.p. 163.5–165°, *ca*, 4.3 g.; (4) b.p. 59–73° (15 mm.), *ca.* 6 g. (the greater part distilled at 61–68° (15 mm.); (5) b.p. 78–79° (15 mm.), *ca.* 2 g.; yield *ca.* 34% altogether.

All these fractions were almost colorless or faintly yellow, barely soluble in water and easily soluble in common organic solvents. They readily decolorized bromine water.

Fractions 1–4 had a camphoraceous odor, and were indifferent or slightly reactive toward Schiff reagent (fraction 4 was somewhat reactive), indifferent toward Fehling solution. From fraction 1 a small amount of white precipitate was produced by ammoniacal silver nitrate, possibly the silver salt of the unchanged carbinol. Fraction 4 contained a small amount of the aldehyde of the fraction 5 (see below), which was obtained in the form of its 2,4-dinitrophenylhydrazone. Fraction 2, which was the main one, was analyzed.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.85; H, 11.30.

It was apparent that imperfect separation of the ketones was accomplished by distillation. However, III predominated in fraction 2 and II was enriched in fraction 4.

Fraction 5 had a stimulative smell like an aldehyde, leaving somewhat the camphoraceous odor of the lower-boiling fractions, and was reactive toward Schiff reagent (deep purple-pink color somewhat slowly produced). It reduced ammoniacal silver nitrate solution[7]; on heating, it merely turned Fehling solution into turbid green. This behavior is somewhat similar to that of β-methylcrotonaldehyde.[8]

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18; mol. wt., 126.2. Found: C, 76.09; H, 10.93; mol. wt. (Rast), 121.

2,4-Dinitrophenylhydrazones from Fractions 1–4.—A solution of 2,4-dinitrophenylhydrazine in alcoholic sulfuric acid was used. Some water was added to the reaction mixture when the precipitation of the derivatives was not satisfactory.

(a) The product from fraction 1 was fairly soluble in methanol and was crystallized twice from this solvent, deep yellow long plates, m.p. 104.5–105° (one 2,4-dinitrophenylhydrazone of III).

Anal. Calcd. for $C_{14}H_{18}O_4N_4$; N, 18.29. Found: N, 18.26.

In addition, some tarry matter was obtained.

From the same fraction which was left for a few weeks at room temperature (*ca.* 25–30°), another derivative was obtained, which was easily soluble in methanol, and also in pyridine, and was more suitably recrystallized from the latter to yield yellow flattened sharp needles, m.p. 94–95° (the other 2,4-dinitrophenylhydrazone of III).

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.07.

(b) From fraction 2, a fair amount of tarry matter was obtained in spite of fractional crystallization with methanol or pyridine, in addition to the 2,4-dinitrophenylhydrazone of m.p. 104.5–105°; the tarry matter was kept for some days in a desiccator containing sulfuric acid and analyzed.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.40.

Thus, the tarry matter may be a mixture of different 2,4-dinitrophenylhydrazones of $C_8H_{14}O$-ketones.

(c) Fraction 3 gave nearly the same derivatives as fraction 2 but in addition a small amount of a much less soluble one was first obtained on allowing the reaction mixture to stand. On recrystallization from pyridine, it formed orange-red plates, m.p. 173–174°, and proved to be the derivative of IV (see below).

(d) From fraction 4, in addition to some of the above derivative of m.p. 173–174°, characteristic yellow laminae were obtained which were crystallized twice from methanol, yellow square plates, m.p. 75–76° (one of the 2,4-dinitrophenylhydrazones of II), easily soluble in methanol.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.33.

This fraction was shaken thoroughly with a solution of sodium sulfite in order to remove the aldehyde, and the above derivative could then be obtained in fairly pure state.

A fair amount of reddish precipitate was produced from this fraction if water was added after the reaction mixture had stood for awhile, this substance turned yellowish on standing in the mixture for a few hours; a similar phenomenon was also observed in the case of fraction 3. This is understandable from the behavior of the 2,4-dinitrophenylhydrazone of m.p. 100–102° which, in this case, could not be obtained in sufficiently pure state.

Some of the 2,4-dinitrophenylhydrazone of m.p. 75–76° was also obtained from the lower-boiling fractions.

Semicarbazones from Fractions 1–4.—The semicarbazones were prepared in aqueous alcoholic solution. Even though fractionally crystallized, the derivatives obtained gave generally indistinct melting points.

(a) The less soluble semicarbazone formed colorless plates or long plates, m.p. *ca.* 200° (one semicarbazone of III). It was mainly obtained from the lower-boiling fractions. This semicarbazone was the only one obtained in a satisfactory state of purity.

Anal. Calcd. for $C_9H_{17}ON_3$: C, 58.98; H, 9.35; N, 22.93. Found: C, 59.19; H, 9.07; N, 22.87.

(b) One of the more soluble semicarbazones was obtained (mainly from the lower-boiling fractions) in the form of colorless plates or flattened needles, m.p. *ca.* 165° (the other semicarbazone of III).

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.93. Found: N, 22.61.

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(7) The ammoniacal silver nitrate was also reduced, on heating, by fractions 1–4; however, the circumstance was evidently different from that in the case of fraction 5, the latter being quick and remarkable.

(c) The other of the more soluble semicarbazones was obtained (mainly from the higher-boiling fractions) in the form of colorless plates, m.p. *ca.* 170° (semicarbazone of II).

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.93. Found: N, 22.65.

(d) Finally, all the precipitates obtained from the intermediate fractions of the ketones were recrystallized and analyzed.

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.93. Found: N, 22.31.

A few portions of semicarbazones each of which had also vague melting points such as *ca.* 125°, *ca.* 136°, *ca.* 145°, were obtained in the case of above-mentioned fractional crystallization. They may be "eutectics"[4,8] or simply mixtures.

Conversion of the Semicarbazones Derived from the Fractions 1–4, into the Corresponding 2,4-Dinitrophenylhydrazones.—Each of the above-mentioned semicarbazones were heated for a short time with an excess of saturated solution of oxalic acid with shaking, and the ketone regenerated was converted into the corresponding 2,4-dinitrophenylhydrazone. Alternately, the 2,4-dinitrophenylhydrazones were prepared by adding the requisite or somewhat excessive amount of 2,4-dinitrophenylhydrazine reagent directly to each semicarbazone. The identical derivative was always obtained from a given semicarbazone by these two methods.

These 2,4-dinitrophenylhydrazones were identical with those obtained directly from the rearrangement products. (a) From the semicarbazone of m.p. *ca.* 200° was obtained the 2,4-dinitrophenylhydrazone of yellow flattened sharp needles, m.p. 94.5–95°.

Anal.[9] Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.05.

(b) From the semicarbazone of m.p. *ca.* 165° was obtained the 2,4-dinitrophenylhydrazone of deep yellow long plates, m.p. 104–105° (the analysis was omitted).

(c) The 2,4-dinitrophenylhydrazone which was first obtained from the semicarbazone of m.p. *ca.* 170° was crystallized thrice from methanol or methanol containing some pyridine, lustrous long red plates, m.p. 99–101° (the other 2,4-dinitrophenylhydrazone of II).

Anal.[10] Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 17.73.

The 2,4-dinitrophenylhydrazone of m.p. 75–76° (yellow square plates) was obtained from this semicarbazone if the reaction mixture was left for more than a few hours (increased acidity seemed to increase the velocity). This substance also was obtained by the action of acid on the lustrous long red plates.

Preparation of 3,4-Dimethyl-3-hexen-2-one (II) and 3,4-Dimethyl-4-hexen-2-one (III) and Their Derivatives. (a).—The preparation of II followed the simplified method of Descude.[4] II was converted into its semicarbazone, colorless plates, m.p. 185–186°, identical with that obtained by Abbott and others.[4]

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.93. Found: N, 22.81.

Its 2,4-dinitrophenylhydrazone, lustrous long red plates, had m.p. 99–101°.

The same 2,4-dinitrophenylhydrazone was obtained also from the above semicarbazone.

Anal.[11] Calcd. for $C_{14}H_{18}O_4N_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.49; H, 5.77; N, 18.34.

The 2,4-dinitrophenylhydrazone of m.p. 75.5–76°, yellow square plates, was obtained from this red one in the manner indicated above.

(b) From the lower-boiling fraction, b.p. 40–45° (10–8 mm.), from the distillation of II, was obtained a semicarbazone, colorless plates or long plates, m.p. *ca.* 200°, which was considered to be identical with that of III[12]; reported m.p. 203–204°.[4]

Anal. Calcd. for $C_9H_{17}ON_3$: C, 58.98; H, 9.35; N, 22.93. Found: C, 59.11; H, 8.96; N, 22.88.

The 2,4-dinitrophenylhydrazone obtained from this fraction was that of m.p. 94.5–95°, yellow flattened sharp needles, which also was obtained from the above semicarbazone.

(c) Another isomeride of III was prepared by isomerization of II with sodium methoxide,[4] and was converted into its derivatives. Its semicarbazone formed colorless long plates, m.p. 164–165°, reported m.p. 163°.[4]

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.93. Found: N, 22.77.

Its 2,4-dinitrophenylhydrazone formed deep yellow long plates, m.p. 104.5–105°, and was obtained also from the above semicarbazone.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.29. Found: N, 18.05.

Some Notes on the 2,4-Dinitrophenylhydrazones of the Ketones.—None of the specimens of the 2,4-dinitrophenylhydrazones of the same ketones showed any depression in melting point.

Mixtures of different ones showed depressions of melting points except that of the ones of m.p. 94–95° and m.p. 104–105°, which always gave intermediate melting point. These two derivatives, however, seemed evidently to be different (the analogous phenomenon was reported for the two semicarbazones of III[4]).

Semicarbazone and 2,4-Dinitrophenylhydrazone from Fraction 5.—The aldehyde fraction 5 reacted with semicarbazide and 2,4-dinitrophenylhydrazine to give single characteristic derivatives.

The semicarbazone was recrystallized from methanol, colorless plates, m.p. 160–161°. It is much less soluble in methanol than those of the ketones.

Anal. Calcd. for $C_9H_{17}ON_3$: C, 58.98; H, 9.35; N, 22.93. Found: C, 58.81; H, 9.26; N, 23.12.

The 2,4-dinitrophenylhydrazone was recrystallized from pyridine, orange-red plates, m.p. 173–174°, sparingly soluble in methanol, rather soluble in boiling methanol.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.70; H, 5.83; N, 18.03.

It also was obtained from the above semicarbazone.

Oxidation of the Fraction 5 by Permanganate.—To a suspension of 1 g. of this fraction in 30 ml. of water, was added gradually a solution of 3.4 g. of potassium permanganate in 70 ml. of water at 3–8° with stirring. The mixture was held at this temperature for 30 minutes with stirring. A small amount of sodium bisulfite was then added, the mixture was filtered, and the residue was washed with methanol. The combined washings and filtrate were extracted with ether and the extracts were dried with potassium carbonate and distilled. The greater part of the distillate consisted of the solvent accompanied by a small amount of a carbonyl compound which was obtained in the form of a 2,4-dinitrophenylhydrazone of m.p. 72–73°, yellow flattened needles. The latter is in good agreement with the melting point of this derivative. of 3-methyl-2-pentanone (reported, 71.5–72.5°[13]; 72°[14]; 71.2°[15]). An additional amount could be obtained from the distillation residue.

Anal. Calcd. for $C_{12}H_{18}O_4N_4$: C, 51.42; H, 5.75; N, 19.99. Found: C, 50.97; H, 5.71; N, 20.31.

Ozonolysis of Fraction 5.—A suspension of 1 g. of this fraction in 10 ml. of water was cooled with ice and ozonized oxygen was passed through for *ca.* 3 hr. The reaction mixture was then placed in a separating funnel and allowed to stand.

The aqueous portion (acid reaction), on treatment with phenylhydrazine, yielded glyoxal phenylosazone, m.p. 169–170°, pale yellow crystals from ethanol, in good agreement with reported properties.[16,17]

The aqueous portion also yielded glyoxal 2,4-dinitrophenylosazone, darkening and contracting near 300°. The

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[8] *Cf.* J. Colonge and K. Mostafavi, *Bull. soc. chim.*, [5] **52**, 1478 (1938); J. Colonge, *ibid.*, [4] **49**, 426 (1931).

[9] Specimen obtained by the direct method of conversion.

[10] Specimen obtained by the direct method of conversion.

[11] Specimen obtained from the ketone regenerated.

[12] *Cf.* ref. 4, p. 2518.

[13] W. Dirscherl and H. Nahm, *Ber.*, **73B**, 448 (1940).

[14] F. Kogl and H. Erxleben, *Z. physiol. Chem.*, **227**, 51 (1934).

[15] N. L. Drake and F. P. Veitch, Jr., THIS JOURNAL, **57**, 2623 (1935).

[16] E. Fischer, *Ber.*, **17**, 575 (1884).

[17] Beilstein, "Organische Chemie," Erganzungs-Werk, Band 15, p. 38; *cf.* Hauptwerk, Band 15, p. 154.

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.

TOKYO, JAPAN

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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).

[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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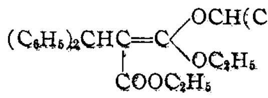
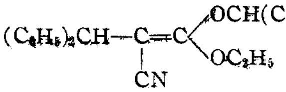
Dibenzhydrylmalonic acid (XVI) has been prepared by reaction of its dibenzhydryl ester XV with hydrogen chloride. The diethyl ester IV of XVI was prepared from the silver salt and ethyl iodide. This ester proved to be identical with a compound first reported by Kohler, which originally was thought to 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



$(C_6H_5)_2CHC(COOC_2H_5){=}C(OCH(C_6H_5)_2)(OC_2H_5)$

I



$(C_6H_5)_2CH{-}C(CN){=}C(OCH(C_6H_5)_2)(OC_2H_5)$

II

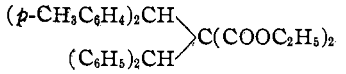
inconclusive because reactions of other bromomagnesium enolates have been found to result in either O- or C-substitution,[4,5] and upon degradation of the compounds by acid hydrolysis. Both were stable under the usual conditions of alkaline hydrolysis, but were cleaved by concentrated hydrochloric acid at 175°, yielding benzhydrylacetic acid and benzhydryl ethyl ether.

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]

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

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

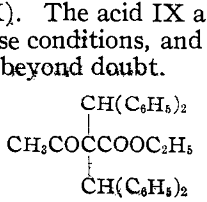
V



$[(p\text{-}CH_3C_6H_4)_2CH][(C_6H_5)_2CH]C(COOC_2H_5)_2$

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.



$CH_3COC[CH(C_6H_5)_2]_2COOC_2H_5$

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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