solidified oil left after steam distilling the mixture gave a 50% yield of α-benzyl-α-phenyl-thiourea (m. p. 138–139°). In a similar manner β-furoyl-α,α-diphenylthiourea, XXXV, yielded unsymmetrical diphenylthiourea (m. p. 217°).

Thiazolidine Formation.—With phenylaminoethanol, furoyl isothiocyanate yielded α-ethanol-β-furoyl-α-phenylthiourea, XXXVI. Treatment with 80% sulfuric acid gave 2-furoylimino-3-phenylthiazolidine, XXXVII. Alkaline hydrolysis of this product formed the same 173–174° melting compound obtained from II.

Summary

Benzoyl isothiocyanate has been utilized in synthesizing a number of new heterocyclic compounds.

Furoyl isothiocyanate has been prepared and a number of its derivatives have been described. Methods of hydrolyzing some of these compounds have been given.

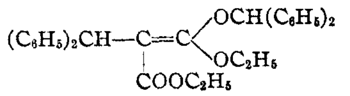
LAWRENCE, KANSAS RECEIVED DECEMBER 8, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of Ethyl Di-diphenylmethylmalonate

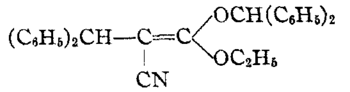
BY ARTHUR C. COPE[1]

While several O-alkyl and acyl derivatives of the enolic form of ketones and ketonic esters are known, very few O-alkyl derivatives of ester enols (ketene acetals) are recorded. Of the latter class of compounds only two have been obtained by direct alkylation of ester enolates. They are ethyl O-diphenylmethyl diphenylmethylmalonate (I)[2] and the corresponding derivative of ethyl cyanoacetate (II).[3] A study of I was undertaken in order to determine if it could be transformed into the corresponding dialkyl malonic ester (III) by a rearrangement involving migration of the diphenylmethyl group from oxygen to carbon.



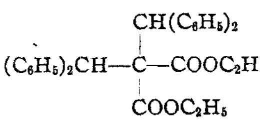
$$(C_6H_5)_2CH-\underset{\substack{|\\COOC_2H_5}}{C}=C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix}$$

I



$$(C_6H_5)_2CH-\underset{\substack{|\\CN}}{C}=C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix}$$

II

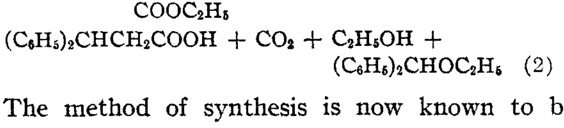


$$(C_6H_5)_2CH-\overset{\substack{CH(C_6H_5)_2\\|}}{\underset{\substack{|\\COOC_2H_5}}{C}}-COOC_2H_5$$

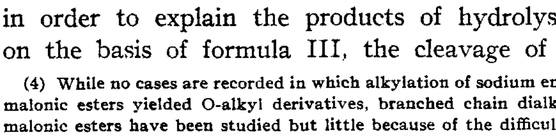
III

Before attempting the rearrangement of I into III it seemed advisable to prepare III by the ordinary malonic ester synthesis and determine its properties. However, the product obtained by alkylating the sodium derivative of ethyl diphenylmethylmalonate with diphenylmethyl bromide proved to be identical with the compound originally prepared by Kohler and regarded as a ketene acetal (I). This observation must lead to one of two conclusions: either the ketene acetal structure (I) is incorrect and the compound is really ethyl di-diphenylmethylmalonate (III), or the malonic ester synthesis in this case has given an O-alkyl derivative.[4]

The structure I was based on the method of synthesis and the products of hydrolysis.



$$C_6H_5CH{=}C(COOC_2H_5)_2 + C_6H_5MgBr \longrightarrow (C_6H_5)_2CH-\underset{\substack{|\\COOC_2H_5}}{C}=C\begin{matrix}\diagup OMgBr\\ \diagdown OC_2H_5\end{matrix} \xrightarrow{(C_6H_5)_2CHBr} (C_6H_5)_2CH-\underset{\substack{|\\COOC_2H_5}}{C}=C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix} \quad (1)$$



$$(C_6H_5)_2CH-\underset{\substack{|\\COOC_2H_5}}{C}=C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix} + 2H_2O \xrightarrow[175^\circ]{40\%\ HCl} (C_6H_5)_2CHCH_2COOH + CO_2 + C_2H_5OH + (C_6H_5)_2CHOC_2H_5 \quad (2)$$

The method of synthesis is now known to be inconclusive as evidence for structure I, since other bromo-magnesium enolates have been observed to yield C-acyl derivatives.[5,6] However, in order to explain the products of hydrolysis on the basis of formula III, the cleavage of a

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[1] National Research Fellow in Chemistry. The author wishes to express his indebtedness to Professor E. P. Kohler for advice and criticism.

[2] Kohler, *Am. Chem. J.*, **34**, 132 (1905).

[3] Kohler and Reimer, *ibid.*, **33**, 348 (1905).

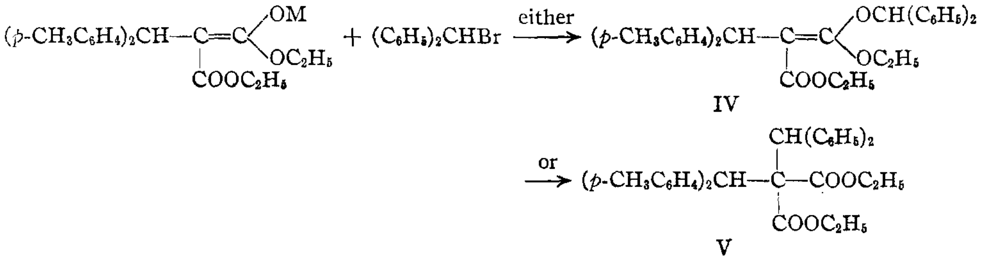
[4] While no cases are recorded in which alkylation of sodium enol malonic esters yielded O-alkyl derivatives, branched chain dialkyl malonic esters have been studied but little because of the difficulty encountered in introducing the second alkyl group. Because of this fact and since the products of hydrolysis of the compound are more easily explained on the basis of formula I, it seemed unwise to interpret the method of synthesis as evidence for formula III.

[5] Kohler and Peterson, THIS JOURNAL, **55**, 1073 (1933).

[6] Kohler and Tishler, *ibid.*, **54**, 1596 (1932).

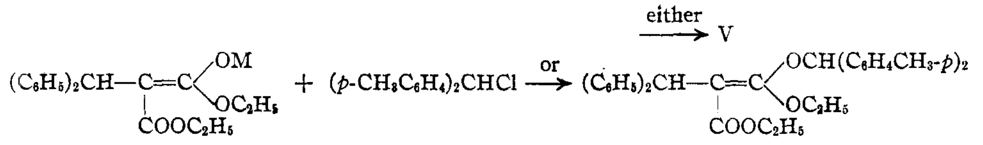
diphenylmethyl group must be assumed to occur prior to the hydrolysis of the ester. This would not be predicted.

Efforts to establish the structure of the compound through its reactions or through an independent synthesis which must yield III have not yet been successful, but it has been possible to solve the problem by synthesizing a closely related unsymmetrical homolog. The method is outlined in the following equations.



$$(p\text{-}CH_3C_6H_4)_2CH{-}\underset{COOC_2H_5}{C}{=}C\begin{smallmatrix}OM\\OC_2H_5\end{smallmatrix} + (C_6H_5)_2CHBr \xrightarrow{\text{either}} \underset{\text{IV}}{(p\text{-}CH_3C_6H_4)_2CH{-}\underset{COOC_2H_5}{C}{=}C\begin{smallmatrix}OCH(C_6H_5)_2\\OC_2H_5\end{smallmatrix}}$$

$$\xrightarrow{\text{or}} \underset{\text{V}}{(p\text{-}CH_3C_6H_4)_2CH{-}\overset{CH(C_6H_5)_2}{\underset{COOC_2H_5}{C}}{-}COOC_2H_5} \qquad (3)$$



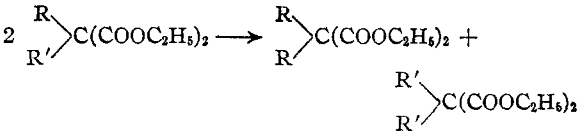
$$(C_6H_5)_2CH{-}\underset{COOC_2H_5}{C}{=}C\begin{smallmatrix}OM\\OC_2H_5\end{smallmatrix} + (p\text{-}CH_3C_6H_4)_2CHCl \xrightarrow{\text{either}} \text{V}$$

$$\xrightarrow{\text{or}} \underset{\text{VI}}{(C_6H_5)_2CH{-}\underset{COOC_2H_5}{C}{=}C\begin{smallmatrix}OCH(C_6H_4CH_3\text{-}p)_2\\OC_2H_5\end{smallmatrix}} \qquad (4)$$

(M = Na or MgBr)

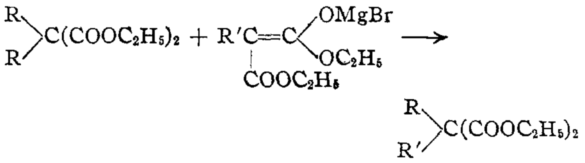
Obviously, if the same product is obtained from both reactions it must be the C-alkyl derivative (V). O-Alkylation would give the isomeric but not identical compounds IV and VI. Actually, operating through the sodium enolates the same product was obtained from both reactions (3 and 4); consequently it must have structure V. Having proved the alkylation to yield a dialkyl malonic ester in this case, the method of synthesis (through the sodium enolate) establishes formula III rather than I for the di-diphenylmethyl derivative. By analogy ethyl di-diphenylmethyl cyanoacetate, formerly considered to be an O-alkyl derivative (II), is probably the dialkylcyanoacetic ester $[(C_6H_5)_2CH]_2C(CN)COOC_2H_5$.

It was originally intended to carry out the syntheses (3 and 4) through the bromomagnesium enolates. While (4) gave the desired product in 81% yield, (3) gave a mixture from which three compounds were isolated. They proved to be (1) V, the expected product; (2) III, ethyl di-diphenylmethylmalonate; (3) ethyl di-di-*p*-tolylmethyl malonate, $[p\text{-}CH_3C_6H_4)_2CH]_2C(COOC_2H_5)_2$, VII. The formation of III and VII involves the disproportionation of an unsymmetrical dialkyl malonic ester into the two symmetrical homologs



$$2\ {}^{R}_{R'}\!>\!C(COOC_2H_5)_2 \longrightarrow {}^{R}_{R}\!>\!C(COOC_2H_5)_2 + {}^{R'}_{R'}\!>\!C(COOC_2H_5)_2$$

This novel disproportionation can be accounted for only by a cleavage of the diarylmethyl groups at some stage of the reaction. The cleavage may either precede or follow the synthesis; that is, it may occur either in the enolate or in the dialkyl malonic ester. However, there is no basis for assuming that the enolate could be cleaved in this manner, while direct evidence was obtained that the dialkyl malonic esters can be cleaved by reagents present in the alkylation experiments. Thus ethyl di-di-*p*-tolylmethyl malonate (VII) reacted with the bromomagnesium enolate of ethyl diphenylmethylmalonate to give ethyl diphenylmethyl di-*p*-tolylmethylmalonate (V).

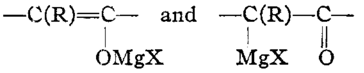


$$ {}^{R}_{R}\!>\!C(COOC_2H_5)_2 + R'\underset{COOC_2H_5}{C}{=}C\begin{smallmatrix}OMgBr\\OC_2H_5\end{smallmatrix} \longrightarrow {}^{R}_{R'}\!>\!C(COOC_2H_5)_2$$

Obviously in this reaction an R group of the dialkylmalonic ester has been separated by cleavage. The MgBr grouping of the enolate is essential for the cleavage, for the corresponding sodium enolate was found to be incapable of producing the disproportionation indicated in the above equation. This was expected since in the syntheses (3 and 4) with the sodium enolates no disproportionation products were obtained. The mechanism of the cleavage will be investigated further in connection with a study of the properties of III and related compounds which is in progress.

In the syntheses through the bromomagnesium enolates, disproportionation occurred in reaction (3) but not in (4). The difference is probably due to the physical characteristics of the addition compounds formed as the first step in alkylation, for in (4) an insoluble addition compound separates as soon as the alkyl halide is added, while in (3) the addition product is soluble and consequently available for further reaction (cleavage). The difference in the course of the reactions might also be related to the fact that in (4) a chloride was used in alkylation while in (3) a bromide was employed. It was impossible to decide this directly because no alkylation took place under the same conditions when $(C_6H_5)_2CHCl$ was substituted for $(C_6H_5)_2CHBr$ in (3).

The structures I and II were originally utilized as evidence for 1,4-addition of the Grignard reagent, the argument being that since the alkyl group was linked to oxygen in the product, the magnesium also must have been attached to oxygen. The present work which invalidates these structures proves that alkylation cannot be employed to determine the location of the magnesium in compounds in which the two formulas



$$-\underset{\text{OMgX}}{\underset{|}{\text{C}}}\text{(R)}=\text{C}- \quad\text{and}\quad -\underset{\text{MgX}}{\underset{|}{\text{C}}}\text{(R)}-\underset{\text{O}}{\underset{\|}{\text{C}}}-$$

are possible. It has been shown recently that acylation likewise cannot be used in differentiating between such formulas,[5] for in the cases studied the nature of the R group rather than the structure of the magnesium compound appeared to determine whether O-acyl or C-acyl derivatives were formed.

Experimental Part

Kohler[2] described ethyl di-diphenylmethylmalonate (III) as crystallizing in thin rectangular plates, m. p. 132°. The product obtained in this research from both the sodium and bromomagnesium enolates crystallized in this form and when pure had m. p. 136–136.5°. After several months of work with the compound, however, a sample which had been exposed to the air of the laboratory for a few days had m. p. 176–177°. Several samples simultaneously gave this new melting point, and all of them when immersed in a bath at 140° melted, then resolidified and melted again at 176°. After once melting or recrystallizing all the samples had m. p. 176° with no lower melting point obtainable on rapid heating. The high melting form is much less soluble in alcohol than the low melting, and crystallizes from alcohol or acetic acid in prisms. Many attempts to prepare the low melting form both in this Laboratory and elsewhere[7] after the high melting form had once been obtained were unsuccessful; the form of m. p. 176° was always obtained directly in spite of all the care taken to exclude seed crystals. The two forms must be isomorphous and not isomeric, since the transition to the high melting variety took place slowly even in the dark at room temperature and in the solid state. Isomerization would be very unlikely under these conditions; moreover, no isomers are possible on the basis of the correct formula (III).

1. Ethyl Di-diphenylmethylmalonate (III)

A. Through the Grignard Reaction.—The reaction was carried out as by Kohler.[2] The phenylmagnesium bromide from 5.84 g. of magnesium and 37.7 g. of bromobenzene in 100 cc. of ether was cooled in ice and 48 g. of ethyl benzalmalonate added (with stirring) sufficiently rapidly to cause the solution to reflux gently. The solution was refluxed for thirty minutes, then 50 g. of diphenylmethyl bromide was added and the refluxing continued for three hours. The solution was cooled and ice added, followed by hydrochloric acid. The ether layer was separated and the aqueous solution extracted with ether. Distillation of the ether left a crystalline residue which was recrystallized from acetic acid in minute prisms; yield 85 g. (89%), m. p. 176–177°. Exactly similar preparations made before the high melting form was obtained had given the same yield of thin rectangular plates from alcohol, m. p. 136–136.5°.

Anal. (high melting form). Calcd. for $C_{33}H_{32}O_4$: C, 80.44; H, 6.55; mol. wt., 492.3. Found: C, 80.44; H, 6.38; mol. wt. (camphor), 485.

B. Through the Sodium Enolate.—Ethyl diphenylmethylmalonate[2] (3.90 g. or 20% excess of 0.01 mole) was added to 0.23 g. of powdered sodium under 50 cc. of dry benzene. The mixture was refluxed for one hour to dissolve the sodium, and then 2.47 g. (0.01 mole) of diphenylmethyl bromide added. After three hours of refluxing dilute hydrochloric acid was added to the cooled solution and the product extracted and purified as in (1A); yield 3.8 g. (77%); m. p. 176–177°, mixed melting point with the product from (1A) was 176–177°. Before the transition to the high melting form occurred a similar preparation had given the low melting form, m. p. 136–136.5°; mixed melting point with the product of the same melting point from (1A) was 136–136.5°.

Ethyl Di-*p*-tolylmethylmalonate, $(p\text{-}CH_3C_6H_4)_2CHCH(COOC_2H_5)_2$.—Ethyl *p*-tolual malonate was prepared by heating 48 g. of *p*-tolualdehyde with a slight excess of ethyl malonate (70 g.) and 2 g. of piperidine on the steam-bath for eighteen hours. Piperidine and toluic acid were removed by extraction of the reaction mixture in ether with dilute hydrochloric acid and sodium hydroxide and the product distilled in vacuum. The fraction of b. p. 165–170° (2 mm.) weighed 56 g. (53%). Condensation of the forerun in the same manner increased the yield to 77 g. (73%). The product was recrystallized from ligroin; m. p. 50–51°.[8]

Ethyl *p*-tolualmalonate (13.1 g. or 0.05 mole) in dry ether was added to the *p*-tolylmagnesium bromide prepared from 1.52 g. of magnesium and a slight excess (12 g.) of

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(7) The author is indebted to Professor S. M. McElvain for carrying out the preparation of III through the Grignard reaction at the University of Wisconsin. He also obtained the high melting form directly, with no evidence of the form of m. p. 136°.

(8) Chrzaszczewska, *Roczniki Chemji*, **6**, 33 (1925); *Chem. Zentr.*, II, 2905 (1926), gives m. p. 46–47°.

p-bromotoluene in 50 cc. of ether; the Grignard reagent was cooled and the ester added with sufficient rapidity to cause the solution to reflux. The addition product is soluble in ether. After thirty minutes of refluxing the bromomagnesium enolate was decomposed with ice and hydrochloric acid and the product distilled in vacuum. The yield was 15.8 g. (90%); m. p. 192–196 (1 mm.). The distillate solidified and was recrystallized from ligroin in needles, m. p. 71–71.5°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.53; H, 7.39. Found: C, 74.72; H, 7.47.

The ester (2.0 g.) was refluxed for one hour with 20 cc. of 20% potash in 50% alcohol. After distillation of the alcohol the residue was diluted and acidified with concd. hydrochloric acid. Crystalline di-*p*-tolylmethylmalonic acid was precipitated. The yield was quantitative, m. p. 179–180° (dec.). Recrystallization from 80% alcohol gave the pure acid crystallizing in fine needles, m. p. 184° (dec.).

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.44; H, 6.08; neut. eq., 149. Found: C, 72.29; H, 6.16; neut. eq., 148.6.

A sample of the malonic acid heated to slightly above the melting point for five minutes was converted through loss of carbon dioxide into β,β-di-*p*-tolylpropionic acid, which crystallized at once on cooling, m. p. 183–185°. The acid was purified by extraction from ether with dilute sodium hydroxide and crystallization from alcohol in needles, m. p. 187–188°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.27; H, 7.14; neut. eq., 254. Found: C, 80.15; H, 7.18; neut. eq., 256.1.

2. Ethyl Di-di-*p*-tolylmethylmalonate (VII)

A. Through the Grignard Reaction.—Ethyl *p*-tolualmalonate (5.24 g. or 0.02 mole) in ether was added to the *p*-tolylmagnesium bromide prepared from 0.61 g. of magnesium and 7 g. of *p*-bromotoluene in the usual manner. After thirty minutes of refluxing 5.20 g. (0.022 mole) of di-*p*-tolylmethyl chloride[9] in ether was added. A crystalline addition compound separated during the addition of the halide. After three hours of refluxing ice and hydrochloric acid were added and the product crystallized from alcohol in stout plates, m. p. 148–149°; yield 9.60 g. (88%).

Anal. Calcd. for $C_{37}H_{40}O_4$: C, 80.97; H, 7.35. Found: C, 80.83; H, 7.48.

B. Through the Sodium Enolate.—In the manner described in (1B) the enolate was prepared from 3.90 g. of ethyl di-*p*-tolylmethyl malonate and 0.23 g. of sodium. Di-*p*-tolylmethyl chloride (2.31 g. or 0.01 mole) was added and the solution refluxed for three hours. The product crystallized from alcohol in plates identical in appearance with those described above; yield 4.30 g. (80%), m. p. 148–149°.

A mixed melting point with the product from (2A) was 148–149°.

3. Ethyl Diphenylmethyl Di-*p*-tolylmethylmalonate (V)

A. Through the Grignard Reaction (Equation 4).—Ethyl benzalmalonate (4.96 g. or 0.02 mole) was added to the phenylmagnesium bromide prepared from 0.61 g. of magnesium and 5 g. of bromobenzene. After thirty minutes refluxing 5.2 g. (0.022 mole) of di-*p*-tolylmethyl chloride in ether was added. The addition compound separated at once. After three hours of refluxing ice and hydrochloric acid were added and the product recrystallized from alcohol. The yield was 8.30 g. (81%); m. p. 122–123°. The compound crystallized as large diamond shaped tables from methyl alcohol.

Anal. Calcd. for $C_{35}H_{36}O_4$: C, 80.72; H, 6.97. Found: C, 80.69; H, 7.09.

B. Through the Grignard Reaction (Equation 3).—Ethyl *p*-tolualmalonate (5.24 g. or 0.02 mole) was added to the *p*-tolylmagnesium bromide prepared from 0.61 g. of magnesium and 7 g. of *p*-bromotoluene. After thirty minutes of refluxing 5.45 g. (0.022 mole) of diphenylmethyl bromide in ether was added. In this case no solid addition compound separated; after one to two hours an oil separated but remained suspended in the ether while the solution was stirred. After three hours of refluxing ice and hydrochloric acid were added and the oily product crystallized from alcohol. Crystallization took place very slowly, best from dilute solution at room temperature. Cooling or concentration produced oils. The solid material was separated from time to time and the solution concentrated slowly. The crystalline mixture melted over a wide range and was fractionally crystallized. Ethyl di-diphenylmethylmalonate (III) was separated easily because of its low solubility in hot alcohol and was purified by recrystallization from acetic acid; yield 0.70 g. (7%), m. p. 176–177°; mixed melting point with the product from 1A or B 176–177°. Ethyl di-di-*p*-tolylmethylmalonate (VII) was separated as the fraction next least soluble in alcohol; yield 1.20 g. (12%), m. p. 148–149°, mixed with the product from 2A or B, 148–149°. From the most soluble fractions ethyl diphenylmethyl di-*p*-tolylmethylmalonate (V) was sepraated; yield 0.40 g. (4%) m. p. 121–122°, mixed with the product from (3A) 121–123°. These yields could undoubtedly be raised by a more careful fractionation. A duplicate experiment gave the same products.

In a similar experiment in which a corresponding quantity of diphenylmethyl chloride was substituted for the bromide, an insoluble addition product was formed immediately, but on working up the reaction mixture in the usual manner after three hours of refluxing no crystalline product could be obtained. Distillation gave 6.1 g. (86%) of ethyl di-*p*-tolylmethylmalonate, b. p. 190–195° (1 mm.), m. p. 71–71.5° after crystallization from ligroin. The diphenylmethyl chloride was recovered as a lower boiling fraction. Consequently the apparent reaction had stopped with the formation of the addition compound. On carrying out the reaction at the boiling point of benzene alkylation occurred, but a mixture similar to that described in (2B) was obtained.

C. Through the Sodium Enolate (Equation 4).—The enolate was prepared from 3.90 g. of ethyl diphenylmethylmalonate and 0.23 g. of sodium under 50 cc. of benzene. Di-*p*-tolylmethyl chloride (2.31 g.) was added and the solution refluxed for three hours. The product was crystallized from alcohol; yield 3.21 g. (63%), m. p. 122–123°, mixed with the product from (3A) 122–123°.

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[9] Norris and Blake, THIS JOURNAL, **50**, 1808 (1928).

D. Through the Sodium Enolate (Equation 3).—The enolate was prepared from 4.25 g. of ethyl di-*p*-tolylmethylmalonate and 0.23 g. of sodium under 50 cc. of benzene; 2.72 g. of diphenylmethyl bromide was added and the solution refluxed for three hours. On crystallization from alcohol 2.05 g. (40%) of a product of m. p. 122–123° was obtained which was identical with that formed in 3A, B and C; mixed melting points showed no depression. A side reaction in this case was coupling of the halide, which was indicated by the isolation of 0.22 g. (12%) of tetraphenylethane.

In order to determine whether the dialkyl malonic esters could be cleaved by the bromomagnesium enolate of a monoalkyl malonic ester, the following experiment was performed. The bromomagnesium enolate of ethyl diphenylmethylmalonate was prepared by the addition of 8.2 g. (a slight excess) of ethyl benzalmalonate in 50 cc. of dry benzene to the filtered phenylmagnesium bromide prepared from 5.2 g. of bromobenzene and excess magnesium in 50 cc. of ether. Ethyl di-di-*p*-tolylmethylmalonate (VII) (2.69 g. or 0.005 mole) was added and the solution refluxed for twenty hours. The oily product was refluxed for five hours with 20% potash in 50% alcohol to remove the ethyl diphenylmethylmalonate (the dialkyl malonic esters are not saponified under these conditions), and the unsaponifiable material crystallized from alcohol. Ethyl diphenylmethyl di-*p*-tolylmethylmalonate (V), m. p. 122–123°, was isolated in 39% yield (1.0 g.).

The corresponding sodium enolate did not cause this cleavage. This was established by refluxing 0.005 mole of V and VII with 0.03 mole of the sodium enolate of ethyl diphenylmethylmalonate in 75 cc. of benzene for twenty hours. In each case following the same procedure as outlined above over 90% of the unchanged dialkyl malonic esters was recovered.

Summary

Ethyl di-diphenylmethyl malonate has been proved to be a dialkyl malonic ester (III) rather than a ketene acetal (I), as was originally proposed. By analogy the corresponding derivative of ethyl cyanoacetate is probably a dialkyl cyanacetic ester rather than an O-alkyl derivative (II). In the hydrolysis of these remarkably stable esters the first reaction is the cleavage of a diphenylmethyl group. This cleavage originally led to the formulation of the compounds as O-alkyl derivatives, but must be interpreted now as resulting from the breaking of a carbon to carbon linkage weakened by the substituent groups.

In the synthesis of an unsymmetrical dialkyl malonic ester $RR'C(COOC_2H_5)_2$ through the bromomagnesium enolate disproportionation occurred and the two symmetrical homologs $RRC(COOC_2H_5)_2$ and $R'R'C(COOC_2H_5)_2$ were also produced.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED DECEMBER 12, 1933

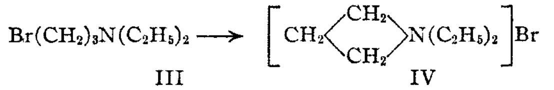
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Quaternary Ammonium Salts from Bromopropyldialkylamines. IV. Formation of Four-Membered Rings

BY C. F. GIBBS AND C. S. MARVEL

Amines of the type $Br(CH_2)_nN(CH_3)_2$ have been found to undergo self-condensation to yield monomeric cyclic, dimeric cyclic or linear polymeric quaternary ammonium salts depending on the value of n.[1] We have now discovered that the size of the alkyl groups on the nitrogen atom affects the course of the reaction in the case of compounds in which n has the value 3. Thus, although bromopropyldimethylamine[2] (I) reacts with itself to give a linear polymeric quaternary ammonium salt (II), the corresponding diethyl derivative (III) under the same conditions reacts intramolecularly to give a cyclic quaternary ammonium salt (IV).

$$\underset{\text{I}}{x\,Br(CH_2)_3N(CH_3)_2} \longrightarrow \underset{\text{II}}{\{Br[(CH_2)_3N(CH_3)_2]_{x-1}(CH_2)_3N(CH_3)_2\}Br_{x-1}}$$



III IV

The cyclic structure of the quaternary ammonium salt is established by its properties. It is crystalline, gives a neutral water solution, contains only ionizable bromine, and has a molecular weight which corresponds to that of the monomeric salt. The isomeric compound, diethylallylamine hydrobromide, which might form if bromopropyldiethylamine should lose hydrogen bromide and this acid should add to the nitrogen, has been prepared. Comparison of this

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[1] Lehman, Thompson and Marvel, THIS JOURNAL, **55**, 1977 (1933).

[2] Gibbs, Littmann and Marvel, *ibid.*, **55**, 753 (1933).