The Decomposition of Acylated Malonic Esters for the Preparation of β-Keto Esters

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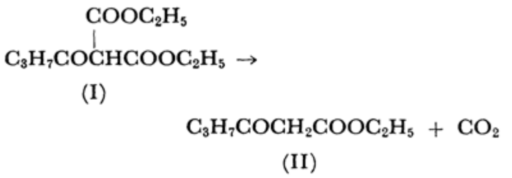
The β-keto esters are very important substances as intermediates for organic synthesis, and many studies to prepare them have been described. The decomposition of the acylated malonic esters is one convenient method. Such decomposition agents of the acylated malonic esters as toluene-sulfonic acid[1], β-naphthalene-sulfonic acid,[2] sulfuric acid[3] and magnesium oxide[4] have been reported by some workers. Of these Brändström's method,[4] in which magnesium oxide in glacial acetic acid was used, seems to be the most promising one for the preparation of β-keto esters; the other methods give low yields and are tedious. This paper will report an advantageous method of decomposing acylated malonic esters to β-keto esters.

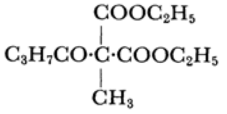
When diethyl butyrylmalonate (I) was heated in an aqueous solution, carbon dioxide evolved and ethyl β-ketocaproate (II) was obtained in a good yield. Moreover, this reaction was found to proceed more rapidly in aqueous acetic acid; thereby the formation of ethyl acetate was observed.



$$\underset{\text{(I)}}{C_3H_7CO\overset{COOC_2H_5}{\overset{|}{C}H}COOC_2H_5} \rightarrow \underset{\text{(II)}}{C_3H_7COCH_2COOC_2H_5} + CO_2$$

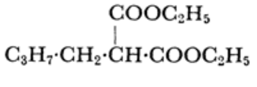
However, the decomposition of I did not take place either in glacial acetic acid or without a solvent, so it can be said that the decomposition reaction needs water. Thus, it seems that I dissociates partly to the corresponding monocarboxylic acid as intermediate.

Moreover, diethyl butyrylmethylmalonate (III) or diethyl butylmalonate (IV) could not be converted to the corresponding β-keto ester under similar conditions. This fact might appear to suggest that I might be decomposed in an enol-form, because III or IV could not take an enol-form, in which an enol-double bond was conjugated with a carbonyl group of the ester. Therefore, the decomposition reaction of I might reasonably be explained as follows: the hydroxy group of an



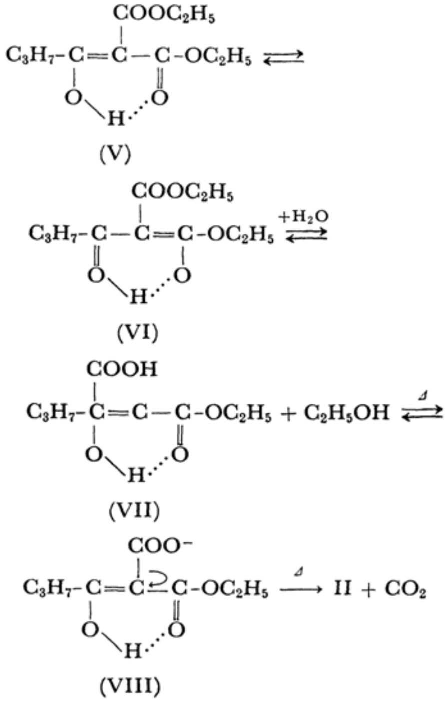
$$C_3H_7CO\cdot\underset{\underset{CH_3}{|}}{\overset{\overset{COOC_2H_5}{|}}{C}}\cdot COOC_2H_5$$

(III)



$$C_3H_7\cdot CH_2\cdot\overset{\overset{COOC_2H_5}{|}}{C}H\cdot COOC_2H_5$$

(IV)



(V)

(VI)

(VII)

(VIII)

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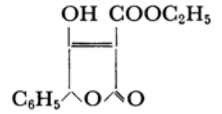
[1] R. S. Breslow, E. Baumgarten and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944).

[2] B. Riegel and W. M. Lilienfeld, *ibid.*, **67**, 1273 (1965).

[3] R. E. Bowman, *J. Chem. Soc.*, **1950**, 322.

[4] A. Brandstrom, *Acta Chem. Scand.*, **5**, 820 (1951).

Table 1

Substance	Solvent	Time, hr	β-Ketoester	Recovered
$C_3H_7COCH(COOC_2H_5)_2$	Water	2	64%	28%
	Water	6	79	7
	1 N CH_3COOH	1	63	35
	1 N CH_3COOH	3	77	17
	6 N CH_3COOH	1	60	35
	CH_3COOH	1	10	80
	3 N CH_3COOH	10 min	87	—

enol-form forms an intramolecular hydrogen bond with an ester group (V or VI), and thereby the other ester group exists in equilibrium with the carboxylic acid in an aqueous solution (VII, VIII). The resultant six-membered chelate ring then loses the exo-carboxyl group as carbon dioxide, thus yielding II.

In. aqueous acetic acid, the formation of ethyl acetate can be explained in terms of the acidolysis.

In a similar manner, when α-carbethoxy-γ-phenyltetronic acid (IX), as an example of cyclic compounds, was boiled in aqueous acetic acid, decarboxylation occured easily and γ-phenyltetronic acid (X) was obtained in a good yield. These results are summarized in Table 1.

Experimental

Diethyl Butylmalonate was prepared according to the method of Adams and Kamm.[5] Bp 135°C/26 mmHg.

Diethyl Butyrylmalonate was prepared by a method similar to that of Lund.[6] Bp 98°C/2 mmHg.

Diethyl Butyrylmethylmalonate. Diethyl methylmalonate was prepared according to the method of McElvan;[7] it was then converted with butyric acid chloride to diethyl butyrylmethylmalonate according to the method of Lund.[8] Bp 80°C/0.5 mmHg.

α-Carbethoxy-γ-phenyltetronic Acid was prepared according to the method of Böcker.[8] Mp 140°C.

Ethyl β-Ketocaproate. Diethyl butyrylmalonate (24.4 g, 0.1 mol) was boiled with 200 ml of 1 N acetic acid for 3 hr, and then the mixture was extracted with two 100-ml portions of ether. The ether layer was washed once with 100 ml of a saturated sodium bicarbonate solution and then with 100 ml of water. The ether solution was dried over anhydrous sodium sulfate, the ether was evaporated, and the residue was distilled. Yield, 12.0 g (77%); bp 50°C/5 mmHg (Found: C, 60.50; H, 8.88%. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%).

γ-Phenyltetronic Acid. Ten grams of α-carbethoxy-β-phenyltetronic acid were boiled with 30 ml of 3 N acetic acid for 10 min. The mixture was then acidified with hydrochloric acid, and the precipitate was recrystallized from water. Yield, 6 g (80%); mp 128°C (Found: C, 67.90; H, 4.53%. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58%).

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5) R. Adams and R. M. Kamm, "Organic Synthesis," Coll. Vol. I, p. 250 (1948).

6) H. Lund, *Ber.*, **67**, 935 (1934).

7) R. F. B. Cox and S. M. McElvan, "Organic Synthesis," Coll. Vol. II, p. 279 (1948).

8) R. Anschutz and R. Bocker, *Ann.*, **368**, 53 (1909).