11. *A Tracer Study of the Hydrolysis of Ethyl ββ-Diethoxyacrylate.*

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The uncatalysed and the acid-catalysed hydrolysis of ethyl ββ-diethoxyacrylate in $H_2{}^{18}O$ have been studied. The former involves quantitative transfer of the label into the diethyl malonate produced, but the catalysed reaction does not. The former reaction proceeds by an addition–elimination mechanism, and in the latter fission of the ether linkage occurs between the saturated carbon and the oxygen atom.

OUR initial aim was to see whether the inactive dienophiles, keten acetals, could be modified into active dienophiles.[1] It was thought that this might be brought about by introduction of an ethoxycarbonyl group at the terminal unsaturated carbon atom, since ethyl ββ-diethoxyacrylate was reported to be able to react with water,[2] presumably by addition. However, the ester does not add cyclopentadiene or 2,3-dimethylbutadiene: at temperatures below 160° it is recovered unchanged; at higher temperatures, 170—180°, it undergoes thermal decomposition into ethylene and diethyl malonate [3] in 71% yield. Similar unreactivity is exhibited in Michael additions.

We then studied the mechanism of hydrolysis of the ester. This reaction occurs in

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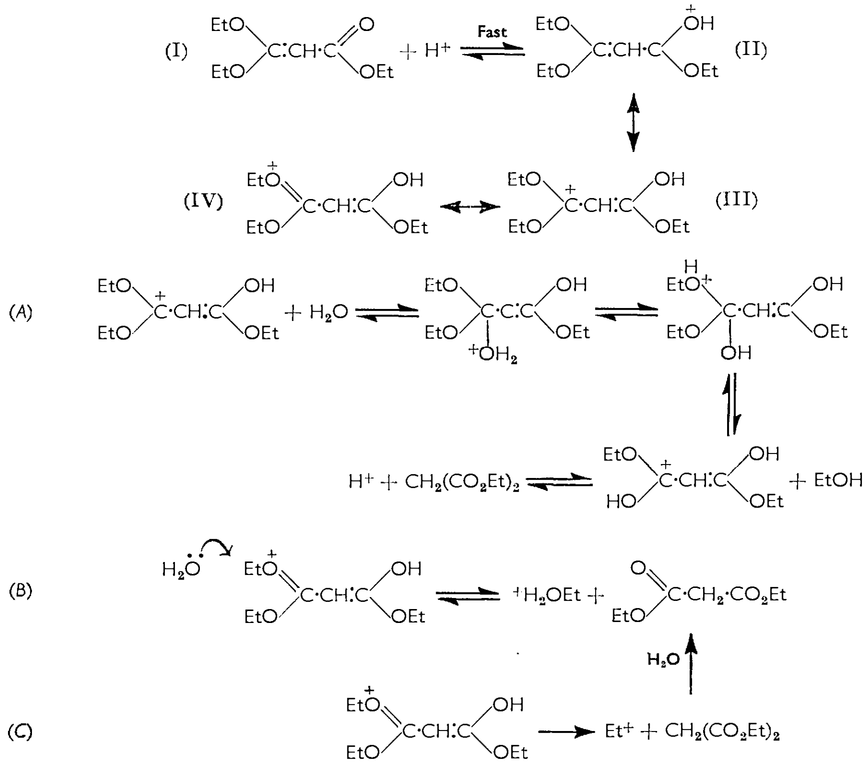
[1] Bartlett and Tate, *J. Amer. Chem. Soc.*, 1956, **78**, 2473.

[2] Reitter and Weindel, *Ber.*, 1907, **40**, 3358.

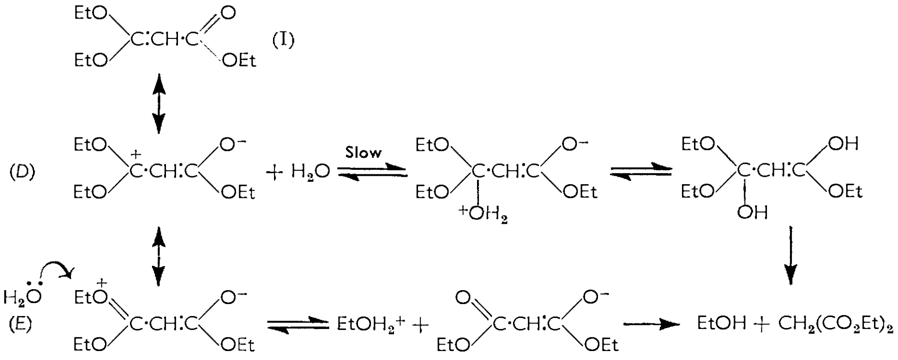
[3] McElvain, Anthes, and Shapiro, *J. Amer. Chem. Soc.*, 1942, **64**, 6525; McElvain and Stevens, *ibid.*, 1946, **68**, 1917.

acidic[4] or neutral[1] conditions, providing diethyl malonate in high yield. The acid-catalysed hydrolysis is very fast, but reaction in water is very slow. Possible mechanisms for the reaction are as follows:

Acid-catalysed reaction:



Uncatalysed reaction:



Mechanisms *A* and *D* differ from *B*, *C*, and *E* in the mode of splitting of the ether linkage. Whereas the types *A* and *D* require attack by a water molecule at the saturated carbon atom, types *B*, *C*, and *E* require attack at the terminal unsaturated carbon atom. These types could be differentiated by conducting the hydrolysis in water enriched in oxygen-18, since mechanisms *A* and *D* require that the final product is devoid of isotope oxygen, whereas mechanisms *B*, *C*, and *E* require incorporation of the label into the ester product.

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[4] McElvain and Mallineaux, *J. Amer. Chem. Soc.*, 1952, **74**, 1811.

However, mechanism *B* cannot be distinguished from *C* in this way, and, for this, product studies are needed. The experiments were performed with both the ester (I) and diethyl malonate (for control) in the usual manner; the results are assembled in the Table (water containing 1·31% of $H_2{}^{18}O$ was used). They show quantitative transfer of the label in the uncatalysed reaction, whereas in the acid-catalysed reaction the labelling in the diethyl malonate produced results from the secondary oxygen-exchange. This indicates that the uncatalysed reaction proceeds by the addition–elimination mechanism of type *D*, whereas the reaction in acid solution may occur by a mechanism *B* or *C*. The characteristic difference between mechanisms *B* and *C* is that the former involves a specific water molecule in the rate-determining step whereas the latter does not. The data here presented do not permit a distinction between these two mechanisms.

Compound	Conditions	^{18}O atom % excess	No. of ^{18}O atoms in ester produced
Ester (I)	Neutral	0·277	0·99
Et_2 malonate	,,	0	0
Ester (I)	Acidic	0·226	—
Et_2 malonate	,,	0·226	—

In a similar study of acid-catalysed formation of enol ethers, Wiberg and Saegebarth[5] showed that the reaction is a reversible addition–elimination. This suggests that, in contrast to enol ethers, ionic species analogous to (III) are of little probability or that their ability to undergo nucleophilic attack by the solvent molecules is relatively low. On the other hand, ionic species of the structure (IV) are very liable to lose a carbonium ion and yield a stable product.

The ability of our ester (I) to undergo a reaction of type *D* contrasts with its lack of reactivity in Michael addition. This can be rationalised in terms of mesomeric and steric effects.[6]

A preliminary account of this study has already been given elsewhere.[7]

EXPERIMENTAL

Ethyl ββ-diethoxyacrylate, b. p. 122°/10 mm., n_D^{25} 1·4597, $\lambda_{max.}$ (in EtOH) 236 mμ (log ε 4·16), was prepared from ethyl cyanoacetate in an overall yield of 33% by Glickman and Cope's method.[8]

Pyrolysis of the Ester (I).—The ester (28 g.) was heated at 170—180° for 8 hr. The ethylene produced was passed into a solution of bromine (25 g.) in carbon tetrachloride (250 ml.), giving ethylene dibromide (22 g., 78%). The residue was fractionally distilled, giving diethyl malonate (17 g., 71%), b. p. 55—60°/4 mm., n_D^{20} 1·4142, and a solid (0·13 g.), m. p. 60° (from ethanol) (Found: C, 56·8; H, 6·9%), which was not investigated.

Tracer Study.—Water containing 1·31% of $H_2{}^{18}O$ was supplied by the Isotope Department, The Weizmann Institute of Science, Rehovot.

Location of Bond-fission.—(*a*) *Hydrolysis in water.* Hydrolysis of the ester is accompanied by disappearance of the absorption band at 236 mμ, and the reaction was followed by measuring the optical density at that wavelength.

Ethyl ββ-diethoxyacrylate (10 g.) was shaken with enriched water (16 ml.) at room temperature for 48 hr. Benzene (50 ml.) was added and the organic layer was separated, dried ($MgSO_4$), and evaporated. Distillation of the residue provided diethyl malonate (8 g., 80%), b. p. 55°/4 mm., n_D^{15} 1·4174.

(*b*) *Hydrolysis in acid solution.* When the ester (10 g.) was added to enriched water (16 ml.) containing sulphuric acid (0·2 g.), the reaction was instantaneous, as shown by spectrophotometry. Diethyl malonate was isolated as described above, having the same characteristics and in the same yield.

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[5] Wiberg and Saegebarth, *J. Org. Chem.*, 1960, **25**, 832.

[6] The yields in the Michael additions of diethyl malonate to acrylic esters decrease from 76% in the parent compound to 35% in methyl *ββ*-dimethylacrylate, and to 14% in *β*-ethoxyacrylic ester (Bergmann, Ginsburg, and Pappo, " Organic Reactions," Vol. X, Chapman & Hall, Ltd., 1959, p. 179).

[7] Sarel, Breuer, and Menahem, *Bull. Res. Council Israel*, 1961, **10**, *A*, 48.

[8] Glickman and Cope, *J. Amer. Chem. Soc.*, 1945, **67**, 1017.

Oxygen-exchange of Diethyl Malonate in Water and in Acidic Solution.—The oxygen-exchange experiments were performed for control purposes, by adding diethyl malonate (6 g.) to enriched water (16 ml.) containing sulphuric acid (0·2 g.) and, after short shaking, the ester was recovered by means of benzene and the usual working up. The exchange experiment in water was performed by shaking a mixture of diethyl malonate and enriched water at room temperature for 2 days.

Isotopic Analysis.—Oxygen-18 analyses were performed by the modified method[9] of Rittenberg and Ponticorvo.[10]

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[9] Anbar and Guttman, *Internat. J. Appl. Radiation Isotopes*, 1959, **5**, 233.
[10] Rittenberg and Ponticorvo, *Internat. J. Appl. Radiation Isotopes*, 1956, **1**, 208.