The Photochemical Reactions of Ethyl Pyruvate in 2-Propanol and in Cyclohexane

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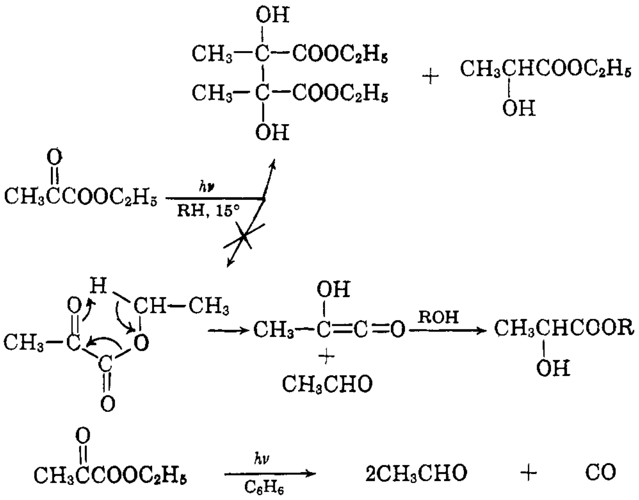
Ketones with γ-hydrogen undergo Type II photochemical processes.[3] The photochemistry of ethyl pyruvate was investigated to ascertain whether it would also undergo an analogous process. The α-hydrogen of the ester function is sterically similar to the γ-hydrogen of aliphatic ketones. Photolysis of ethyl pyruvate would then yield acetaldehyde and a hydroxyketene. If the irradiation is carried out in an alcohol other than ethanol, the hydroxyketene formed would react with the alcohol to form the lactate ester.

Hammond and co-workers[4] studied the direct and sensitized photolysis of ethyl pyruvate in benzene solution. They found the principal products to be carbon monoxide and acetaldehyde. Hammond's work demonstrated the nature of the reacting species to be a triplet.



The irradiation of ethyl pyruvate in 2-propanol and in cyclohexane with a low-pressure mercury vapor lamp at 15° resulted in reductive dimerization with the formation of diethyl dimethyltartrate. A small amount of ethyl lactate also was formed, but no product which may be attributed to a process analogous to Type II was isolated. The main product may be a mixture of *meso* and racemic forms, but no separation of these components was achieved by distillation or gas chromatography. The mechanism of the reduction dimerization is believed to be analogous to that for the formation of benzpinacol from benzophenone.[5,6]

Experimental

Irradiation of Ethyl Pyruvate.—A solution of freshly distilled ethyl pyruvate (30 g., 0.25 mole) in 275 ml. of Spectro Grade 2-propanol was placed in a low pressure mercury resonance lamp.[7] The irradiation apparatus was fitted with a Freidrich condenser and immersed in a water bath which maintained the temperature of the solution between 15–20°. The outlet of the condenser was connected, in series, to a Dry Ice trap and then through a three-way stopcock to a gas buret filled with saturated potassium chloride solution. The gas buret was isolated from the system by means of the stopcock and the apparatus was flushed with high purity nitrogen for 30 min. The nitrogen flow was then discontinued and the gas buret was reopened to the system. The solution was irradiated with vigorous magnetic stirring for a period of 72 hr. Throughout the irradiation there was no gas evolution nor was there any material condensed in the Dry Ice trap. The solution then was transferred to a flask and fractionally distilled at atmospheric pressure with the aid of a Heligrid column rated at 50 theoretical plates. Acetone (9.05 g.) was collected, after which time the temperature of the distillate rose steadily until pure 2-propanol began to distil. The remaining 2-propanol was removed with the same column at reduced pressure, b.p. 54° (230 mm.).

The fractionation was next continued with the aid of a 3-ft. tantalum wire spiral column under reduced pressure to yield the following fractions: fraction I, b.p. 57–58° (15 mm.), 1.90 g.; fraction II, b.p. 54–61° (0.1 mm.), 0.73 g.; fraction III, b.p. 61–63° (0.1 mm.), 24.01 g.; residue, 1.60 g.

Fraction I was identified as mainly ethyl lactate with a small amount of ethyl pyruvate. The infrared spectrum very closely resembled that of ethyl lactate, but it gave a positive test with 2,4-dinitrophenylhydrazine reagent. The presence of ethyl pyruvate (15%) was confirmed by gas chromatography.

Fraction II was found to be mainly impure fraction III, and fraction III was identified as the diethyl ester of dimethyltartaric acid, $n^{21}\text{D}$ 1.4410.

Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.30; H, 7.75. Found: C, 51.56; H, 8.10.

Identification of Diethyl Dimethyltartrate.—The compound (3 g.) was dissolved in 80 ml. of distilled water and mixed with 9.0 g. of paraperiodic acid. The reaction mixture was maintained at room temperature for 4 hr., neutralized with barium hydroxide, and filtered. The filtrate was continuously extracted with ether for 24 hr. The ethereal solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent afforded 1.83 g. of a material which was identified as pyruvic acid by comparison with the infrared spectrum of an authentic sample. Prior to the continuous extraction, an aliquot (5 ml.) of the filtrate was treated with 2,4-dinitrophenylhydrazine reagent and yielded a 2,4-dinitrophenylhydrazone, m.p. 214°, which was identical in all respects with an authentic sample of pyruvic acid 2,4-dinitrophenylhydrazone.

Irradiation of Ethyl Pyruvate in Cyclohexane.—A solution of ethyl pyruvate (25 g., 0.21 mole) in 275 ml. of Spectro Grade cyclohexane was irradiated as above for a period of 48 hr. There was no gas evolution throughout the irradiation and no material condensed in the trap. The cyclohexane was removed by fractionation through the Heligrid column under reduced pressure, b.p. 46° (225 mm.). The reaction mixture was then fractionated under reduced pressure through the tantalum wire column to yield: fraction I, b.p. 56.5–57.0° (20 mm.), 9.12 g.; fraction II, b.p. 61.8–63.0° (0.1 mm.), 7.14 g.; residue, 4.76 g.

Fraction I was identified as mainly unchanged ethyl pyruvate (36% recovery), and Fraction II was identified as diethyl dimethyltartrate (29% yield). The cyclohexane fraction was fractionated again at atmospheric pressure by means of the Heligrid column after the addition of acetone (75 ml.) to remove cyclohexane by azeotropic distillation. The acetone–cyclohexane azeotrope was collected at 53°. When the temperature of the distillate reached 80°, the fractionation was discontinued. The residue then was tested for unsaturation and found to decolorize bromine in carbon tetrachloride, indicating the presence of cyclohexene.

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[1] Alfred P. Sloan Foundation Fellow.

[2] National Institutes of Health Predoctoral Fellow, 1959-1962.

[3] (a) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); (b) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958); (c) W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962).

[4] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2395 (1961).

[5] (a) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); (b) J. N. Pitts, Jr., *et al.*, *ibid.*, **81**, 1068 (1959).

[6] NOTE ADDED IN PROOF.—After this manuscript was submitted for publication, E. S. Huyser and D. C. Neckers reported [*J. Org. Chem.*, **29**, 276 (1964)] that phenylglyoxalates, a group of α-keto esters, undergo a photochemical process analogous to Type IIp rocess of ketones at elevated temperatures.

[7] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 245 (1949).

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Reactions of 1-Chloro-2,3-epithiopropane

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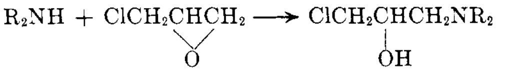
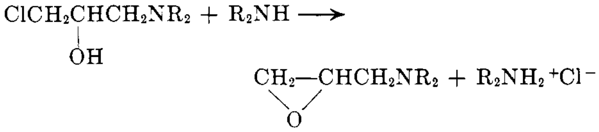
There have been numerous investigations reported on the reaction of epichlorohydrin with amines, of which the references listed[1,2] are representative. In these reactions, with either primary or secondary amines, it has been established that the following sequence can occur, with the final product dependent mainly on the relative molar amount of amine used.


(1)

I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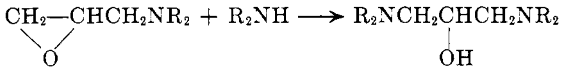
II


(3)

III

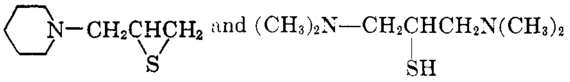
In work at this laboratory, reactions of amines with the sulfur analog of epichlorohydrin, 1-chloro-2,3-epithiopropane, have been investigated. In *no* case, regardless of the molar ratio of reactants, the manner of addition, the solvent, or the conditions of the reaction, have sulfur analog compounds corresponding to I, 1-N-substituted amino-3-chloro-2-propanethiols, been isolated.

With secondary amines, sulfur analog products corresponding to II, 1-N-disubstituted amino-2,3-epithiopropanes, and to III, 1,3-bis(N-disubstituted amino)-2-propanethiols, were formed in relative amounts dependent chiefly on the amount of amine used. Tables I and II list the physical constants, analytical data, and some derivatives for the compounds prepared. Although the course of the reactions has not been definitely established, it is believed that the same sequence occurs as in the case of epichlorohydrin, with step 2 proceeding at a much faster rate than step 1. Direct nucleophilic displacement of chlorine by amine to give products of type II in one step does not seem likely in view of the usual lower relative speed, under the conditions used, of this type of reaction as compared to the opening of the sulfide ring, nor in view of the usual close analogy of reactions of oxirane and thiirane rings with nucleophilic reagents. Using a reactant mole ratio of 1:1, especially if the amine was added to the sulfide, with both in ether or petroleum ether (b.p. 30–60°) solution, gave predominantly the amino sulfides as products in yields varying from fair to moderately good based on the available amine. With dimethylamine, however, polymerization of the amino sulfide occurred very easily during distillation and on standing at room temperature, so that the product could not be directly analyzed. When methanol was used as solvent with dimethylamine or diethylamine, only polymers were obtained. With the three heterocyclic amines tried, methanol could be used as solvent and the amino sulfides could be isolated, but in lower yield than when ether was used as solvent, due to some polymerization. The amino sulfides, once isolated, reacted very readily with additional amine (except in the case of di-*n*-butylamine as noted subsequently) to form the 1,3-bis(N-disubstituted amino)-2-propanethiols.

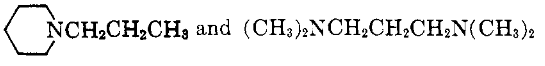
With a reactant ratio of 2 or more moles of amine to 1 of sulfide, both types of products were generally obtained. Apparently steric hindrance plays a role in determining the ratio of these products, since, for example, in the case of di-*n*-butylamine none of the 1,3-bis(dibutylamino)-2-propanethiol was ever formed regardless of the amount of amine used or conditions of the reaction.

In order to demonstrate the direction of ring opening in both steps 1 and 3, desulfurization by commercial Raney nickel catalyst of one of the amino sulfides and one of the diaminopropanethiols was employed.

The following structures were shown to be correct,

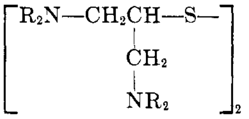


since, on treatment of each individually with Raney nickel in ethanol, these compounds were obtained.



Thus both 1-chloro-2,3-epithiopropane and the 1-N-disubstituted amino-2,3-epithiopropanes open in the so-called "normal" manner by cleavage at the primary carbon–sulfur bond when treated with amines.

In some cases the 1,3-bis(N-disubstituted amino)-2-propanethiols were oxidized with alcoholic iodine to the following corresponding disulfides.



$$\left[R_2N{-}CH_2\underset{\substack{|\\ CH_2\\ |\\ NR_2}}{CH}{-}S{-}\right]_2$$

These were either isolated and purified directly as the dihydroiodide salts or the free tetraaminodisulfide was isolated and then converted to the tetrahydrochloride salt.

In the reaction of primary amines with 1-chloro-2,3-epithiopropane, no simple compounds could be isolated and amino sulfide polymers appeared to be the only products. This was not unexpected, since the amino sulfide monomer contains a secondary amine group which can react readily with the sulfide ring in another molecule, thus leading to polymers of the following type.

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(1) H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **68**, 1291 (1946).

(2) D. L. Heywood and B. Phillips, *ibid.*, **80**, 1257 (1958).