s-butylbenzene, respectively, in the presence of benzene and catalysts yields a mixture of *t*- and *s*-butylbenzene.

In the presence of silicophosphoric acid and zinc chloride–alumina catalyst *s*-butylbenzene isomerizes partly to *t*-butylbenzene and *t*-butylbenzene to *s*-butylbenzene.

Evanston, Illinois Received October 31, 1949

[Contribution from the Chemistry Departments of McGill University, Middlebury College, and The Johns Hopkins University]

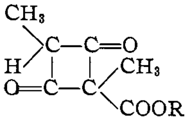
The Sulfuric Acid Condensation Products of Symmetrical Dialkylacetonedicarboxylic Esters

By Evans B. Reid[1]

The observation by Schroeter[2] that the solid dimer of methyl ketene (III)[3,4] results from saponification and decarboxylation of either the methyl or ethyl ester of 1,3-dimethylcyclobutane-2,4-dione carboxylic acid (I), is the main evidence in favor of a cyclobutane structure for the latter compounds. Beyond this, remarkably thorough investigations of the properties of these compounds,[2,5] failed to uncover any facts which could not be accommodated by the cyclobutane structure (I).

These weakly acidic substances were, at first, considered the only products resulting from the action of cold sulfuric acid upon symmetrical dimethylacetonedicarboxylic esters.[6] Later, basic compounds were isolated,[2] to which were assigned 2,6-dialkoxy-γ-pyrone structures (II, where R equals methyl or ethyl).

In the present work both the acidic and the basic substances arising from the sulfuric acid condensation of ethyl α,α′-dimethylacetonedicarboxylate have been examined critically. This has resulted in the conclusions that, whereas the base is correctly represented by the diethoxy-γ-pyrone structure (II), the properties of the acidic body are incompatible with the cyclobutanic formulation (I), and clearly favor the 2-hydroxy-6-ethoxy-γ-pyrone expression (IV), though they do not exclude the 4-hydroxy isomeride (VI).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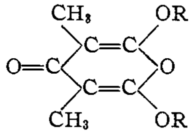
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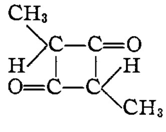
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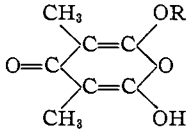
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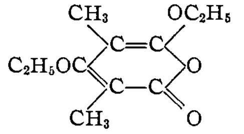
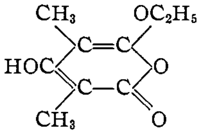

V


VI

The Basic Compound.—This substance proved exceptionally stable. It was inert to phenylhydrazine, and after having been refluxed with distilled water for eight hours was recovered unchanged. Ozone at −30° scarcely attacked it, and on exhaustive treatment at room temperature a true ozonide failed to form. The presence of two ethoxy groups was demonstrated. While typical unsaturation tests were obtained with bromine and neutral permanganate, evidence of oxidation under acidic conditions could only be secured on heating. On the other hand it was susceptible to hydrolysis under weakly basic conditions furnishing pentanone-3. These facts, together with its solubility in acids and insolubility in bases, are rationalized only by the expression 3,5-dimethyl-2,6-diethoxy-γ-pyrone (II).[7]

The Acidic Compound.—In contrast with the basic substance, the so-called ethyl 1,3-dimethylcyclobutane-2,4-dionecarboxylate was exceedingly unstable. The most carefully purified material showed definite signs of decomposition within two weeks. Yet it proved completely inert to hydrogen and Adams catalyst under ordinary conditions. This inertia is difficult to reconcile with the relatively strained cyclobutanedione structure, since ethyl cyclopentanone-1-carboxylate was readily reduced to the corresponding alcohol under the same circumstances.[8]

A peculiar result emerged from hydrolysis studies. Thus, while the substance was readily

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[1] Some of this work is taken from the doctoral dissertation of the author, McGill University, Montreal, 1940. Certain evidence was there presented which tended to show that the cyclobutane structure assigned to the acidic condensation product by Schroeter [*Ber.*, **49**, 2697 (1916)] was not completely satisfactory. An α-alkoxy-γ-pyrone structure (IV, of the present paper), was considered, but was rejected on the basis of experimental evidence then at hand. Part of this earlier work was repeated and extended at Middlebury College, Vermont, in subsequent years. Between 1946–1949, at The Johns Hopkins University, conclusive evidence was obtained in favor of the pyrone structure.

[2] Schroeter, *Ber.*, **49**, 2697 (1916).

[3] Staudinger, *ibid.*, **44**, 533 (1911).

[4] The chemistry of the lower aldoketenes is under investigation in these laboratories, and will form the subject of a later communication.

[5] Schroeter, *ibid.*, **59**, 973 (1926).

[6] Schroeter and Stassen, *ibid.*, **40**, 1604 (1907).

[7] Compare Willstätter and Pummerer, *ibid.*, **38**, 1461 (1905).

[8] Reid and Parker, unpublished results from these laboratories.

saponified and decarboxylated by hot baryta, to form the 1,3-dimethylcyclobutane-2,4-dione described by Schroeter,[2,5] it was adamantine to alcoholic potash at room temperature. When warmed with hydriodic acid for sufficient time to cause reaction, decomposition occurred, and when treated with hot dilute hydrochloric acid, pentanone-3 resulted. Again, such behavior is scarcely concordant with a cyclic ester structure.

Grave doubt that the substance possessed the cyclobutanedione structure was engendered by its ready reaction with ethanol containing catalytic amounts of sulfuric acid to regenerate the parent ethyl α,α'-dimethylacetonedicarboxylate. This reaction seems most readily, but not uniquely,[9] interpreted on the basis of the tautomeric 4-hydroxy-6-ethoxy-α-pyrone structure (VI), since it would be merely the reverse of the original cyclization.[10] Decisive evidence against the cyclobutanic structure and in favor of the 2-hydroxy-6-ethoxy-γ-pyrone formulation was afforded in the interconvertibility of the basic and acidic condensation products. Thus, brief treatment of 3,5-dimethyl-2,6-diethoxy-γ-pyrone with warm hydriodic acid smoothly cleaved one ethoxy group, to form the acidic substance. When the latter was treated with diazoethane,[11] two products resulted. One of these was 3,5-dimethyl-2,6-diethoxy-γ-pyrone. The other was a neutral, non-enolic substance whose extreme instability rendered it impossible to obtain satisfactory analysis. However, from its manner of formation, and in view of the known instability of α-pyrones of this type,[11] it is presumed to be 3,5-dimethyl-4,6-diethoxy-α-pyrone (V). When considered together, these last two reactions uniquely demonstrate the non-cyclobutane structure of the acidic condensation product. It must, therefore, be formulated as 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone (IV), which, of course, is capable of reacting in its tautomeric α-pyrone form (VI).

It may be noted that structure IV is capable of rationalizing all the transformations previously ascribed to I, except the formation of 1,3-dimethylcyclobutane-2,4-dione. At present this reaction remains somewhat obscure, since an isomerization of IV to I under the influence of baryta is highly unlikely.[12]

Acknowledgment.—The author wishes to thank Dr. Philip G. Stevens for his kind encouragement during the early stages of this work.

Experimental

Ethyl α,α-Dimethylacetonedicarboxylate.—Ethyl acetonedicarboxylate was prepared in the usual manner,[13] and fractionally distilled through a 22-inch helix-packed column equipped with a total condensation variable take-off head and an electrically heated jacket. The efficiency of the column was twelve theoretical plates. Ethyl acetonedicarboxylate boiled at 137–138° at 12 mm., or 132–133° at 10 mm. It formed a copper derivative with m. p. 146–148°, after recrystallizations from benzene and from alcohol.[14] The semicarbazone had the reported m. p.[15] 94–95°. Dimethylation was effected by the procedure of Schroeter,[2] and upon fractional distillation, the product had b. p. 137–138° at 12 mm. The reported b. p. 128° at 12 mm.[2] is erroneous.

Sulfuric Acid Condensation.—The acidic product was originally obtained through the use of cold concentrated acid.[5] Later, improved yields were claimed with sulfuric acid monohydrate.[2] It was found by trial that the monohydrate produced only traces of product, and that concentrated acid was more efficient. However, to obtain satisfactory yields, it was necessary to employ 100% acid and to adhere strictly to the recommended temperature control. Dissolution of the acidic product in aqueous sodium carbonate followed by reprecipitation caused reduction in yield, but occasioned no improvement in quality. The product was thoroughly washed with water on the filter and recrystallized from dilute ethanol. Long delicate needles formed, possessing a beautiful satiny sheen which dulled after twenty-four hours. Occasionally once-recrystallized product showed the reported m. p. 133–135°, but after several recrystallizations this was raised to 137–138° on slow heating, with some gas evolution above 145°.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.70; H, 6.52. Found: C, 58.97; H, 6.45.

On keeping for ten days it acquired a sharp odor as it began to decompose to a yellow oil. The fresh crystals gave a deep red color with alcoholic ferric chloride.

Tests on 3,5-Dimethyl-2-hydroxy-6-ethoxy-γ-pyrone.—Hydrogen at 40 p. s. i. g., and Adams catalyst failed to effect any reduction during a five-hour treatment. The product was recovered unchanged. Excess alcoholic potassium hydroxide was likewise without effect. After standing for seven days the solvent was removed. Acidification with dilute hydrochloric acid regenerated the substance in almost quantitative yield. When a sample was brought to reflux in 50% hydrochloric acid, hydrolytic fission began to occur almost immediately. The product was pentanone-3, which was proved by direct comparison with authentic material. Dissolution in constant boiling hydriodic acid occasioned initial cooling. After warming to 40° for two minutes the solution was cooled, diluted, and the excess acid destroyed by the cautious addition of diethyl ether. Evaporation left a brown oil which effervesced vigorously on heating, but from which no 1,3-dimethylcyclobutane-2,4-dione could be isolated.

1,3-Dimethylcyclobutane-2,4-dione.—The improved yield of this compound claimed by Schroeter[2] could not be duplicated, but that reported originally[6] was improved as follows. Ten grams (0.056 mole) of the acidic condensation product was added, with stirring, to a hot filtered solution of 20 g. of barium hydroxide octahydrate in 30 ml. of water. The resulting pasty mass was refluxed gently, until a test portion no longer formed a white precipitate on addition of dilute hydrochloric acid. This required from three to four hours. The excess barium ion was precipitated with carbon dioxide and filtered. The filter-cake was washed with small amounts of water, and sucked as dry as possible. The filtrate was concentrated to a small bulk on the steam-bath under a jet of air, at such a rate that the temperature of the mixture remained below 80°.

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[9] Compare Roberts, Armstrong, Trimble and Burg, THIS JOURNAL, **71**, 843 (1949).

[10] Litynski and Malachowski, *Chem. Zentr.*, **99**, II, 448 (1928).

[11] Litynski and Malachowski, *loc. cit.*, found the anhydride of acetonedicarboxylic acid to form 4,6-dimethoxy-α-pyrone, even when only one equivalent of diazomethane was used.

[12] After this work was completed, the author learned, through the kindness of Dr. R. B. Woodward, Harvard University, that similar conclusions regarding the structure of the acidic condensation product had been reached in his laboratory, and that, further, the cyclobutanic structure for the decarboxylated product had been substantiated.

[13] Adams and Chiles, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. I, 1941, p. 237.

[14] von Pechmann, *Ber.*, **24**, 4095 (1891), reported 145°.

[15] Haller and March, *Bull. soc. chim.*, [3] **31**, 440 (1904).

Addition of ice-cold concentrated hydrochloric acid to the cold solution caused immediate separation of the flocculent product. This was collected on the filter and dried. The yield was 1.02 g., or about 17%. Recrystallization from benzene furnished 0.85 g. of short white needles, m. p. 139°. For comparison, the same product was prepared from the analogous methyl compounds. 1,3-Dimethylcyclobutane-2,4-dione was obtained from methyl-α,α'-dimethylacetonedicarboxylate in about 10% yield. In contradistinction to its progenitor, this substance is quite stable. After keeping for nine years, a specimen still retained its luster, and had m. p. 133–135°. The substance gave an instantaneous enol test in aqueous ferric chloride.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.15. Found: C, 63.98; H, 6.87.

Alcoholysis of 3,5-Dimethyl-2-hydroxy-6-ethoxy-γ-pyrone.—Nine grams (0.049 mole) was dissolved in 100 ml. of commercial absolute ethanol[16] containing 1 ml. of concentrated sulfuric acid. After warming under reflux for six hours it was poured into ice-water saturated with sodium chloride. The characteristic fruit odor of acetonedicarboxylic ester was immediately apparent. The ester separated and was combined with the ether extract of the aqueous layer, shaken with sodium carbonate solution and washed with water. After drying over sodium sulfate, the ether was removed and the residual oil distilled. A small low-boiling fraction was obtained which was presumed to be ethyl α-propionylpropionate. The main fraction, 5 g., consisted of an enolic oil, b. p. 107° at 2.5–3.0 mm., and 137–138° at 12 mm. This was shown to be ethyl α,α-dimethylacetonedicarboxylate by direct comparison with authentic material. It was recondensed with 100% sulfuric acid, forming 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone, m. p. and mixed m. p. 136–138°.

3,5-Dimethyl-2,6-diethoxy-γ-pyrone from 3,5-Dimethyl-2-hydroxy-6-ethoxy-γ-pyrone.—Fifteen grams (0.08 mole) of freshly prepared and recrystallized acidic condensation product was suspended in 500 ml. of absolute ether, and cooled to ice temperature. To this was added as quickly as the one-liter flask could accommodate the effervescence, an ethereal solution of diazoethane prepared from 15 g. (0.13 mole) of ethylnitrosourea[17] according to the general directions for diazomethane.[18] After one hour the solution was concentrated and exhaustively extracted with cold 1–3 hydrochloric acid. Addition of cold dilute sodium hydroxide to these extracts gave 3.3 g. of the basic pyrone; yield 20%, m. p. 87–88°, alone, and admixed with authentic material.

After shaking the residual solution with cold potassium hydroxide solution, the ether was evaporated, leaving 7.3 g. of almost colorless oil. On standing, a faint green color developed, and whereas no enol test (ferric chloride) could at first be obtained, it became progressively more pronounced. Chilling to −78° caused crystallization of the main body. Recrystallization of this solid from ligroin furnished white scales, m. p. 53–55°. Within a few hours the crystals had changed to the green oil. It is presumed that the non-enolic white solid is the isomeric 3,5-dimethyl-4,6-diethoxy-γ-pyrone, although analysis did not furnish concordant results.

3,5-Dimethyl-2,6-diethoxy-γ-pyrone.—This basic condensation product was isolated from the sulfuric acid mother liquor by the known procedure,[2] and after several recrystallizations from ligroin had the reported m. p. 87–88°.

Anal.[19] Calcd. for $C_{11}H_{16}O_4$: C, 62.24; H, 7.60. Found: C, 62.15; H, 7.71.

The compound was very stable, a five-year old specimen had approximately the same m. p. It dissolved completely in dilute hydrochloric acid, and was thrown down on addition of base. A Zeisel determination showed 2.02 ethoxy groups present.[20] Attempts to form a phenylhydrazone were fruitless. Ozone at −30° had scarcely any action, and treatment at room temperature for thirty-one hours was necessary for reaction with a 10-g. sample in 300 ml. of chloroform. Ten and one-half grams of green-yellow oil formed, possessing a strong peroxide odor. One gram of this was boiled with 10 ml. of water for eight hours without producing visible change. In carbon tetrachloride a sample of the pyrone discharged the color of a bromine solution, without the formation of hydrogen bromide, and treatment of the substance with neutral 2% potassium permanganate caused immediate oxidation. A sample in dilute sulfuric acid containing chromium trioxide was stable for twelve hours, and required heating at 100° to effect slow oxidation. On boiling the compound with distilled water for eight hours, no gas was evolved and, on cooling, the pyrone was recovered unchanged. However, at *p*H 9, refluxing for three hours caused extensive decomposition. The product was pentanone-3, which was identified by comparison with authentic material.

3,5-Dimethyl-2-hydroxy-6-ethoxy-γ-pyrone from 3,5-dimethyl-2,6-diethoxy-γ-pyrone.—One and six-hundredths grams (0.005 mole) of the basic pyrone was added to seven ml. of 57% hydriodic acid, and the mixture was warmed to 40° on the steam-bath. As soon as solution was effected, it was chilled. White crystals resulted. These were collected on the filter, washed with water and shaken with 5% aqueous potassium hydroxide. The insoluble portion was unchanged γ-pyrone. The basic filtrate was acidified at ice temperature with cold 1–3 hydrochloric acid. The resulting white precipitate was collected and dried. The yield was 0.10 g., or 11%. On recrystallization from dilute alcohol, long satiny needles formed. The m. p., alone and admixed with freshly recrystallized authentic material, was 136–138°.

Summary

The sulfuric acid condensation of ethyl α,α'-dimethylacetonedicarboxylate has been shown to form 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone and 3,5-dimethoxy-2,6-diethoxy-γ-pyrone. These compounds have been interconverted; and 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone has been shown to react with ethanol to form ethyl α,α'-dimethylacetonedicarboxylate.

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[16] This alcohol, unfortunately, was later shown to contain a small amount of water. Otherwise, undoubtedly, a better yield of ester would have formed.

[17] Arndt, *Angew. Chem.*, **46**, 47 (1933).

[18] Arndt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 166.

[19] Microanalysis by Miss June Sheeler of The Johns Hopkins University.

[20] The author wishes to thank Mr. Milton Sack for this determination.