paper extends this study, reporting the reaction of ethyl chloroacetate with ethyl acetoacetate to give ethyl α-acetosuccinate, of ethylene chlorohydrin with malonic ester to give γ-butyrolactone, and of propylene α-chlorohydrin with malonic ester to give γ-valerolactone, each of these syntheses being catalyzed by aluminum chloride.

The synthesis of ethyl α-acetosuccinate from ethyl chloroacetate and ethyl acetoacetate in the presence of either an acidic or a basic catalyst suggests that ethyl chloroacetate gives the same carbonium ion in both instances. Moreover, the formation of γ-lactones from chlorohydrins and malonic ester in the presence of aluminum chloride indicates that the following type of carbonium ion is present

$$HO{-}CH_2{-}CH_2{-}Cl + AlCl_3 \longrightarrow \overset{\ominus}{AlCl_4} + HO{-}CH_2{-}\overset{\oplus}{CH_2}$$

Experimental

Diethyl α-Acetosuccinate.—Twenty grams of coarsely powdered anhydrous aluminum chloride (much larger amounts gave tars only) was placed in a standard joint flask fitted with a guard tube and a dropping funnel. A solution of 6.5 g. of ethyl acetoacetate and 6.0 g. of ethyl chloroacetate in 25 ml. of chloroform was added dropwise at room temperature. After the evolution of hydrogen chloride ceased, the mixture was decomposed with ice hydrochloric acid, the chloroform layer was separated and the aqueous layer was extracted with chloroform. The chloroform solution was washed with water, then with very dilute alkali, finally with water, and was then dried over anhydrous sodium sulfate. Removal of the solvent left an oil which was fractionated, giving a fore-run of unreacted starting materials at atmospheric pressure and then 2 to 3 g. of an oil, b.p. 115–120° at 10 mm. pressure. Carbon–hydrogen analysts of this oil indicated that it was ethyl α-acetosuccinate. The phenylhydrazone melted at 155–157°[3] and semicarbazone melted at 164–165°.

Anal. Calcd. for $C_{11}H_{19}N_3O_5$: C, 48.4; H, 6.9. Found: C, 48.6; H, 7.2.

The phenylhydrazone and semicarbazone were also prepared from diethyl α-acetosuccinate synthesized by the base-catalyzed reaction described by Fittig[3] and by Adkins.[4]

α-Acetosuccinic Acid.—Nine and one-half grams of diethyl α-acetosuccinate was placed in a flask cooled externally by ice and 30 ml. of hydrochloric acid (sp. gr. 1.17) was added. After standing for 48 hours at a temperature below 10°, and the subsequent removal of the solvent at 55–60° (25–30 mm.), there was obtained 1.5 g. of white solid, m.p. 181–183°, which melted at 183–184° after two recrystallizations from water.

Anal. Calcd. for $C_6H_8O_5$: C, 45.0; H, 5.0; neut. equiv., 80. Found: C, 45.2; H, 5.3; neut. equiv., 81, 84.

γ-Valerolactone.—To a suspension of 50 g. of coarsely powdered aluminum chloride in 50 ml. of chloroform was added, dropwise, a solution of 16 g. of diethyl malonate and 10 g. of propylene α-chlorohydrin. When the evolution of hydrogen chloride ceased (about 18 hr.), the mixture was decomposed with iced 10% hydrochloric acid and was then refluxed for 40 hours. The product, which smelled like benzaldehyde, was worked up in the usual manner, giving 3.8 g. of an oil, b.p. 100–101° at 8 mm.,[5] which had a neutralization equivalent of 105 (calculated value, 100). Oxidation of 3.3 g. of this oil with 3.0 ml. of concentrated nitric acid (sp. gr. 1.41) gave 1.1 g. of succinic acid, identified by mixed melting point.[6]

γ-Butyrolactone.—The substitution of ethylene chlorohydrin for propylene α-chlorohydrin in the above procedure gave γ-butyrolactone in 60–80% yield. The lactone product, b.p. 85–100° at 12 mm., gave neutralization equivalent values of 81 and 87, and was oxidized to succinic acid by the action of nitric acid.

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[3] Fittig [*Ann.*, **283**, 67 (1894)] and Emery [*ibid.*, **295**, 94 (1897)] reported a melting point of 155–156°.

[4] H. Adkins, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 262.

[5] Leuchs and co-workers (*Ber.*, **42**, 1228 (1909)) reported a boiling point of 83–84° at 13 mm. for γ-valerolactone.

[6] Fittig and Messerschmidt (*Ann.*, **208**, 97, 107 (1881)) described, but without details, the nitric acid oxidation of γ-valerolactone.

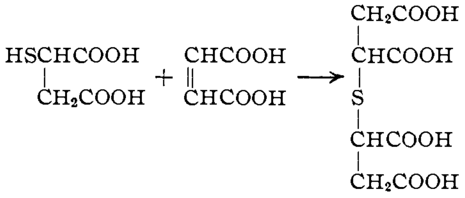
Synthesis of Thiodisuccinic Acid[1,2]

By A. W. Schwab

Received October 2, 1953

Esters of thiodisuccinic acid have been reported,[3,4] but the free acid has not been prepared. Tetrabutyl thiodisuccinate is sold under the trade name "Flexol" Plasticizer TWS. Interest in the use of thiodisuccinic acid as a possible chelating agent has stimulated its preparation. The acid is pentadentate and the sulfur atom may be expected to function as a coördinating atom in the formation of chelate rings especially with the heavy metal ions.

Synthesis of the free acid was accomplished by the addition of mercaptosuccinic acid to the ethylenic bond of maleic acid. Mercaptosuccinic acid adds in the manner



$$\begin{array}{l} HSCHCOOH \\ \quad | \\ CH_2COOH \end{array} + \begin{array}{l} CHCOOH \\ \quad \| \\ CHCOOH \end{array} \longrightarrow \begin{array}{l} CH_2COOH \\ | \\ CHCOOH \\ | \\ S \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{array}$$

Carboxymethylmercaptosuccinic acid has been prepared by the addition of mercaptoacetic acid to maleic acid.[5–7]

Experimental

Mercaptosuccinic acid (15.0 g., 0.1 mole) and maleic acid (11.6 g., 0.1 mole) in 100 ml. of water were heated on the steam-bath for 2 hours. Upon standing overnight, crystals separated. The crystalline product was filtered, washed with cold water, and purified by recrystallization from water. After drying, 11.0 g. of a product was obtained which melted at 196–197°. The neutral equivalent was 67.2 (theory 66.5).

Anal. Calcd. for $C_8H_{10}O_8S$: C, 36.1; H, 3.8; S, 12.0. Found: C, 36.1; H, 3.8; S, 12.1.

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[1] From one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Article not copyrighted.

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The *p*-bromophenacyl tetraester melted at 170–171°.

Anal. Calcd. for $C_{40}H_{30}O_{12}SBr_4$: C, 45.5; H, 2.85; S, 3.04; Br, 30.4. Found: C, 45.6; H, 2.92; S, 3.24; Br, 30.6.

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Function of Organic Material in the Photochemical Formation of Hydrogen Peroxide at Zinc Oxide Surfaces[1]

BY CHARLES B. VAIL, JAMES P. HOLMQUIST AND LOCKE WHITE, JR.

RECEIVED AUGUST 28, 1953

The photochemical formation of hydrogen peroxide in aqueous zinc oxide suspensions has been the subject of several investigations,[2–6] including the recent works of Markham and Laidler[7] and Rubin, Calvert, Rankin and MacNevin.[8] In each of these cases the effectiveness of certain organic materials to increase the yield of peroxide was noted and some efforts were made to determine the function of those materials. Most authors have considered the additives as reactants, rather than peroxide stabilizers, and have supported that contention with experimental evidence of oxidation of the additive. Markham and Laidler, for example, reported the formation of catechol in suspensions containing phenol, and Rubin, *et al.*, recovered carbon dioxide from potassium oxalate suspensions. In no case, however, has there been a quantitative proof that the additive participates directly in the peroxide reaction. The objective of this research was to establish the fate of the additive and the stoichiometry of the reactions involved.

Previous investigations have used, for the most part, relatively complex molecules such as phenols, acetanilide, etc. The effectiveness of these materials is satisfactory, but so many oxidation products can be derived from any one that an analysis of the irradiated suspension is difficult at best. A more desirable additive would be a compound such as an oxalate or formate which has only one normal oxidation product. Fortunately, such compounds are effective[8] and actually produce greater yields than most others. Furthermore, they were both readily available with carbon-14 labeling which greatly facilitated the tracing of their fate.

Experimental Procedure

The chemicals used were reagent grade; the zinc oxide was J. T. Baker Analyzed. In all experiments redistilled water, freed of carbon dioxide, was employed. Commercial cylinder oxygen and water-pumped nitrogen were used with no further purification.

The light source was a General Electric A-H6 lamp operated from a d.c. power supply. A fairly narrow band of light was isolated around 366 mμ by means of Corning glass filters No. 7380 and 5860.

Reactions were carried out in a Pyrex cell which rather resembled a gas washing bottle. The lower half, however, was made from a large test-tube provided with a flat window near the bottom. The reaction mixture, 0.5 g. of ZnO in 85 ml. of solution, was placed in the cell along with a magnetic stirrer bar, and the assembled vessel was fastened together securely.

The irradiation period was preceded by five minutes of equilibration during which oxygen was bubbled into the stirred suspension at about 100 ml./min. After equilibration the exit tube atop the reaction cell was connected by rubber tubing to a filter stick immersed in dilute sodium hydroxide, and irradiation was commenced. Upon completion of the irradiation period, which ranged from one to three hours, 35 ml. of dilute HCl was introduced from a vessel inserted in the inlet line to the cell. The resulting acid solution was warmed and swept with nitrogen for 30 minutes. Inactive Na_2CO_3 was then added as carrier to the $C^{14}O_2$ absorbed in the alkali, and the combined carbonates were precipitated as $BaCO_3$. The dried $BaCO_3$ was used for radioactivity measurements.

Determinations of the radioactivity were made in accordance with the gas-phase procedure of Skipper, Bryan, White and Hutchison.[9] A few of the "high" activity samples from oxalate runs were measured on planchets with a Nuclear Measurements Corporation proportional counter. In both instances the total count, not the specific activity, was sought. Blank runs were made by the same procedure without irradiation, and the activities of the irradiated runs were corrected accordingly. The activities of the blanks never exceeded 5% of those for the runs. The yield of CO_2 was calculated from the net total count and the specific activity of the initial additive solution. To determine the latter value an aliquot of the solution was oxidized to CO_2 by a wet oxidation procedure[10] and then assayed by the method described above.

The analysis for hydrogen peroxide was made with a portion of the residual acid solution according to the colorimetric (titanium sulfate) procedure of Eisenberg.[11] The oxalate ion, however, was found to intensify the color of the titanium complex in rough proportion to the oxalate concentration. Standardization curves, therefore, were prepared for each concentration.

Isotopic Exchange.—In the initial planning of this work, consideration was given to a possible isotopic exchange of carbon atoms between the labeled additive and inactive CO_2 accidentally incorporated in the system. The low activity of the blanks, however, showed that if exchange did occur, there was very little CO_2 present to participate. Nevertheless, the possibility existed that larger and variable amounts of inactive CO_2 might accidentally contaminate other samples. Therefore, the exchange was investigated.

Solutions of 0.01 *M* NaO_2CH and 0.01 *M* C-14 enriched Na_2CO_3 were mixed and agitated vigorously. Aliquots were withdrawn periodically and precipitated as $BaCO_3$. The $BaCO_3$ was assayed for radioactivity by the procedures described above. The results, shown in Table I, indicate that no significant exchange occurred even in 72 hours.

TABLE I

Time, hr.	Specific activity of Na_2CO_3, μc./mole	Time, hr.	Specific activity of Na_2CO_3, μc./mole
0	1.00	3	1.00
5 (min.)	0.95	5	0.98
0.5	.92	7	.98
1	.98	24	.97
2	.98	72	.96

There is some deviation from the initial activity, yet there is no clearly defined trend. The deviations may have been

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[1] This work was supported by the Charles F. Kettering Foundation.

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