

Anal. Calcd. for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.77; H, 5.17; N, 10.14.

Under milder conditions, cyclization also occurred when phenacyl bromide was used in place of desyl chloride. Using the procedure of Julian, *et al.*, for the preparation of α -anilinopropiophenone¹³ there was obtained a quantitative yield of 2-phenylimidazo[1,2-a]pyridine, m.p. 135–136°, after two recrystallizations from hexane. With sodium carbonate or sodium acetate replacing the sodium bicarbonate in this procedure, the yield dropped to 88 and 33%, respectively.

Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19. Found: C, 80.14; H, 5.34.

The picrate melted at 236–238° after two recrystallizations from acetone.¹⁷

Anal. Calcd. for $C_{13}H_{10}N_2 \cdot C_6H_3N_3O_7$: C, 53.90; H, 3.10. Found: C, 54.39; H, 3.06.

Reaction of 2-Aminopyridine with Benzoylcarbinol.—In an effort to gain additional insight into the mechanism of the Voigt reaction,^{3,12} benzoylcarbinol was treated with 2-aminopyridine. Using the procedure employed in the preparation of N-(2-pyridyl)-desylamine (II), there was obtained from 13.6 g. (0.1 mole) of benzoylcarbinol, 10.3 g. (0.11 mole) of 2-aminopyridine, 100 ml. of toluene and 2 ml. of concd. hydrochloric acid, 5.5 g. of a pale yellow solid, b.p. 142–144° (10 mm.). The compound melted at 150° after two recrystallizations from isopropyl alcohol and showed no depression in melting point when mixed with an authentic sample of 2-aminopyridine benzoate melting at 152–153°.

Anal. Calcd. for $C_{13}H_{10}N_2 \cdot C_7H_5O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.17; H, 5.42; N, 12.82.

The picrate of the free base melted at 216–218°. No depression in melting point was observed on admixture with an authentic sample of 2-aminopyridine picrate.¹⁸

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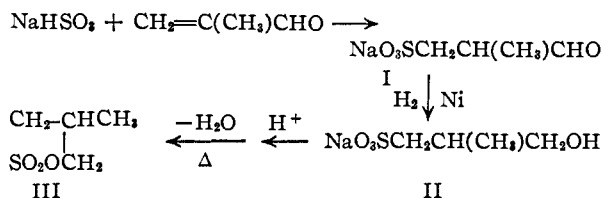
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Reactions of Acrolein and Related Compounds. VIII. Preparation of Sultones

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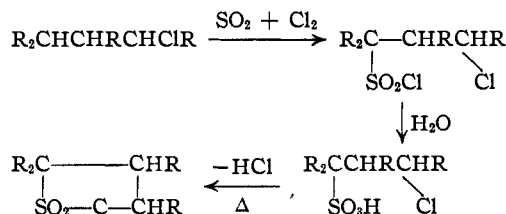
A novel and convenient synthesis of the known and highly reactive 3-hydroxy-2-methyl-1-propanesulfonic acid sultone hereinafter called β -methyl- γ -propanesultone (III) has been realized and may be outlined as



The over-all yield of sultone based on methacrolein was 73%.

Several aliphatic γ -sultones have been previously

prepared by Helberger^{1,2} and by Asinger³ and their associates. The method used by these workers involved sulfochlorination of alkyl halides as shown in the scheme



The aliphatic γ -sultones have been shown^{1,4} to undergo readily a wide variety of reactions.

Earlier attempts by Marckwald and Frahne to synthesize 3-hydroxy-1-propanesulfonic acid sultone, γ -propanesultone, were unsuccessful.⁵ They added bisulfite to acrolein and to allyl alcohol and reduced the acrolein adduct with potassium amalgam presumably to the 3-hydroxy-1-propanesulfonate, but were unable to complete the conversion to the sultone.

In the present process a slight excess (2%) of methacrolein was added to the aqueous solution of sodium bisulfite with the view of removing as completely as possible any bisulfite which might poison the catalyst in the subsequent hydrogenation. The resultant solution was hydrogenated directly over Raney nickel. Saturation of the concentrated reaction mixture with hydrogen chloride resulted in the precipitation of sodium chloride which was removed by filtration. Removal of solvent from the filtrate left a light yellow, viscous oil which on distillation under reduced pressure gave the known³ β -methyl- γ -propanesultone (III).

The fact that water and not hydrogen chloride was eliminated during this distillation establishes the fact that no significant amount of the hydroxy acid was converted to the chloroacid during treatment with hydrochloric acid.

β -Methyl- γ -propanesultone also has been prepared through the peroxide-catalyzed addition of sodium bisulfite to methallyl alcohol. The yield of sultone based on methallyl alcohol charged was 52%. Probably the reason the yield is lower here than from methacrolein is that in this latter case the initial addition proceeded to only about 88% conversion.

Preparations of γ -propanesultone were carried out from acrolein and from allyl alcohol by procedures identical with the above. The melting point of the product was in agreement with that given by Helberger.¹ The yield from acrolein was 16% while that from allyl alcohol was only 5%.

In addition to the conversion of the aldehyde group of the bisulfite adduct of methacrolein to a

(1) J. H. Helberger, *Reichsanzi Wirtshafsaufbau Chem. Br. Prof. Nr.*, 15, (U. S. Office of Publication Board, P.B. 52013) 269 (1942); *C. A.*, 41, 4101 (1947).

(2) J. H. Helberger, G. Manecke and H. M. Fischer, *Ann.*, 562, 23 (1949); *C. A.*, 43, 6569 (1949).

(3) F. Asinger, F. Ebeneder and H. Eckholdt, U. S. Office of Publication Board, P.B. 70183, Frame 893.

(4) J. H. Helberger, G. Manecke and R. Heyden, *Ann.*, 565, 22 (1949).

(5) W. Marckwald and H. H. Frahne, *Ber.*, 31, 1854 (1898).

hydroxyl group it has also been converted to an amine, 3-amino-2-methyl-1-propanesulfonic acid, by hydrogenation over Raney nickel in the presence of concentrated ammonium hydroxide.

Experimental

Sodium 3-Hydroxy-2-methyl-1-propanesulfonate from Methacrolein.—Methacrolein, 154 g. (2.2 moles), was added dropwise with stirring and cooling to a solution of 190 g. (1 mole) of sodium metabisulfite in 520 ml. of water at 6–8°. When about 95% of the methacrolein had been added, the temperature rose sharply to 15–20° although the rate of addition had not been changed. During the addition of the remaining methacrolein the temperature dropped to 5°.

An attempt to isolate the sodium salt of β -sulfoisobutyraldehyde gave a glass which could not be crystallized. Hydrogenation of the above reaction mixture over Raney nickel at 50° and 1500 p.s.i. was complete in one hour. The catalyst was still active after the run, but the third run on the same catalyst was only 35% hydrogenated in 3.5 hours.

The catalyst was removed by filtration and the product was concentrated to dryness. The product weighed 371 g. (19 g. over theory) and probably still contained water. A small sample of the sodium 3-hydroxy-2-methyl-1-propanesulfonate which was recrystallized from methanol melted at 216–217°.

Anal. Calcd. for $C_4H_8O_4SNa$: C, 27.27; H, 5.15; Na, 13.1. Found: C, 27.30, 27.48; H, 5.15, 5.23; Na, 12.9, 13.0.

β -Methyl- γ -propanesultone.—A 186-g. sample of the above crude sodium 3-hydroxy-2-methyl-1-propanesulfonate was dissolved in 1400 ml. of hot methanol and treated with an excess of gaseous hydrogen chloride. After the mixture had been cooled, the sodium chloride which separated was collected on a filter. The methanol was evaporated from the filtrate and the product was distilled from a claisen flask. The slightly yellow distillate, b.p. 115–130° (1.5 mm.), weighed 100 g. This corresponds to a 73.5% yield. The boiling point reported by Asinger³ for this sultone was 135° (5 mm.). β -Methyl- γ -propanesultone obtained by redistillation through a Vigreux column had the following properties: b.p. 89–91° (<0.5 mm.), n_D^{20} 1.4518, d_4^{20} 1.2931, 1.2932, soluble in acetone, chloroform and benzene but insoluble in cold water and petroleum ether. After recrystallization from ether, the sultone melted at 28.8–29.3°.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.28; H, 5.92; sapn. equiv., 136. Found: C, 35.56, 35.52; H, 5.95, 5.94; sapn. equiv., 136.

On standing in stoppered, clear-glass bottles, crude samples of the sultone turned dark but decomposition was slight since redistillation gave high recovery of product.

Sodium 3-Hydroxy-2-methyl-1-propanesulfonate and β -Methyl- γ -propanesultone from Methallyl Alcohol.—A mixture of 36 g. (0.5 mole) of methallyl alcohol, 47.5 g. (0.25 mole) of sodium metabisulfite, 1.5 ml. of 2,2-bis(*i*-butylperoxy)-butane, 60 ml. of water and 100 ml. of methanol was heated with shaking in a stainless steel vessel at 130° for one hour. Iodine titration of the product indicated 12.3% unreacted bisulfite. The product was concentrated to a heavy sirup under reduced pressure. Following the addition of 50 ml. of concentrated hydrochloric acid to the sirup, the resulting slurry was saturated with gaseous hydrogen chloride. The precipitated sodium chloride was removed by filtration and the product was concentrated under reduced pressure to a thick sirup which was distilled from a claisen flask. The distillate, b.p. 110–115° (1 mm.), wt. 28 g., represents a 52% yield. Recrystallization of 2.5 g. from ether gave 2 g. of product which alone and in mixture with β -methyl- γ -propanesultone from methacrolein melted at 28.5–29°.

γ -Propanesultone was prepared from acrolein (16% yield) and from allyl alcohol (5% yield) by procedures essentially identical to the above. The sultone from acrolein had the following properties: b.p. 95–100° (1 mm.), n_D^{20} 1.4585, m.p. 29–30° (from equal amounts of cyclohexane and benzene). Helberger¹ reports a melting point of 31°.

Anal. Calcd. for $C_3H_6SO_2$: ester value, 0.819 eq./100 g. Found: ester value, 0.796 eq./100 g.

3-Amino-2-methyl-1-propanesulfonic Acid.—A 0.6-mole batch of sodium β -sulfoisobutyraldehyde was prepared by the method described above. Ammonia, 62 g. (3.65 moles), was added to the product and the mixture was hydrogenated over Raney nickel at 100° and 1000 p.s.i. The catalyst was removed by filtration and the filtrate was evaporated to a hygroscopic glass. This material was acidified with an excess of concentrated hydrochloric acid and the sodium chloride was removed by filtration. After evaporation of the solvent the product was recrystallized from aqueous methanol giving 3-amino-2-methyl-1-propanesulfonic acid, m.p. 260–265°, in 44% yield based on methacrolein.

Anal. Calcd. for $C_4H_{11}O_3NS$: C, 31.36; H, 7.24; N, 9.15; S, 20.93. Found: C, 31.31; H, 7.33; N, 8.87; S, 20.93.

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Some Ester Analogs of DDT

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Various esters of trichloroacetic acid have been reported in the literature.^{1–3} However, 4,4'-dichlorobenzohydril trichloroacetate has not been reported previously. This compound is of interest since it has some of the same structural characteristics of DDT, but differs by the insertion of the ester linkage into the molecule. In this paper is reported the preparation of this ester along with the preparation of 4-chlorobenzohydril trichloroacetate and benzohydril trichloroacetate. 4-Chlorobenzohydril trichloroacetate is of particular interest because it contains an asymmetric carbon and offers the future possibility of comparing the insecticidal activity of its optically active forms.

These esters were conveniently prepared by refluxing a solution of the alcohol and trichloroacetic acid in benzene in a flask fitted with a water trap⁴ and reflux condenser. An excess of trichloroacetic acid was used to minimize the amount of unreacted alcohol remaining in the reaction mixture. The excess trichloroacetic acid was removed by extraction with dilute alkali. The esterification proceeded rapidly and was complete in about one hour.

The esters decomposed when distilled at reduced pressure and could only be isolated in a pure state by a tedious process of crystallization. The most satisfactory solvent for inducing crystallization was isoamyl acetate. After the esters were obtained in a crystalline form, they could be recrystallized from ethyl alcohol. This last recrystallization was necessary in order to remove traces of isoamyl acetate, which were otherwise quite difficult to remove.

Preliminary tests indicate that these esters have considerable activity against red spiders, but little or no activity when tested against house flies, aphids, milkweed bugs, bean beetle larvae and army worms. The authors are indebted to the Rohm and Haas Company for the testing of these compounds.

The decomposition of the esters during attempted

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