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 $C_4H_9O_4SNa$: 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 Asinger[3] 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.), $n^{30}D$ 1.4518, d^{30}_4 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-(*t*-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.), $n^{20}D$ 1.4585, m.p. 29–30° (from equal amounts of cyclohexane and benzene). Helberger[1] reports a melting point of 31°.

Anal. Calcd. for $C_3H_6SO_3$: 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.

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

Some Ester Analogs of DDT

BY WALTER T. SMITH, JR., AND JOHN W. RYAN

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Various esters of trichloroacetic acid have been reported in the literature.[1–3] However, 4,4′-dichlorobenzohydryl 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-chlorobenzohydryl trichloroacetate and benzohydryl trichloroacetate. 4-Chlorobenzohydryl 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 trap[4] 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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(1) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(2) T. R. Liston and W. M. Dehn, THIS JOURNAL, **60**, 1264 (1938).

(3) H. Hibbert and M. E. Grieg, *Can. J. Research*, **4**, 254 (1934).

(4) E. W. Dean and D. D. Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

distillation was given further study in the case of benzohydryl trichloroacetate. When this ester was heated in a distilling flask under reduced pressure, a 70% yield of benzohydryl chloride was obtained. The identity of the benzohydryl chloride was established by analysis and by conversion to dibenzohydryl ether.[5] The decomposition also resulted in the evolution of hydrogen chloride and carbon dioxide. Quantitative determination of the hydrogen chloride in the evolved gases showed that nearly one-third of the chlorine in the ester could be accounted for in this way. No free chlorine could be detected in the gaseous products.

When the thermal decomposition of benzohydryl trichloroacetate was carried out at atmospheric pressure, the yield of benzohydryl chloride was reduced to 39% and a 17% yield of tetraphenylethylene was also obtained. The tetraphenylethylene is probably a secondary product of the decomposition, since its formation during the distillation of benzohydryl chloride at atmospheric pressure has been previously reported.[6]

Experimental

4-Chlorobenzohydrol and 4,4'-Dichlorobenzohydrol.—These alcohols were prepared in about 85% yield by reduction of the corresponding ketone with aluminum isopropoxide according to the procedure given by Wilds.[7] The authors are grateful to the Heyden Chemical Corporation for the sample of 4,4'-dichlorobenzophenone used in this work.

Benzohydryl Trichloroacetate.—Benzohydrol (18.4 g., 0.1 mole) and 18 g. (0.11 mole) of trichloroacetic acid were refluxed with 200 ml. of benzene in a flask attached to a water trap.[4] When the theoretical amount of water was collected, the solution was cooled and the unreacted trichloroacetic acid was removed by extraction with 10% sodium bicarbonate solution. The benzene was evaporated under reduced pressure and the remaining oil was taken up in 12 ml. of isoamyl acetate. The solution was kept at −5° for two days. The large crystals which formed were removed by filtration. The filtrate was concentrated to approximately two-thirds of its volume and placed in the refrigerator for two weeks. The resulting crystals were removed, combined with the first crop and recrystallized again from isoamyl acetate. The filtrate was concentrated in order to get good recovery of the product. It was necessary to pulverize the crystals in a mortar and dry them for 24 hours in a desiccator containing flaked paraffin in order to free them of isoamyl acetate. The product was then recrystallized from 95% ethanol to give 21 g. (63%) of benzohydryl trichloroacetate melting at 49.5–51°.

Anal. Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.65; H, 3.36; Cl, 32.27. Found: C, 54.42; H, 3.24; Cl, 32.12.

4-Chlorobenzohydryl Trichloroacetate.—By the procedure outlined above 9 g. (0.055 mole) of trichloroacetic acid and 10.6 g. (0.05 mole) of 4-chlorobenzohydrol gave 8 g. (44%) of 4-chlorobenzohydryl trichloroacetate melting at 45–46°.

Anal. Calcd. for $C_{15}H_{10}Cl_4O_2$: Cl, 38.95. Found: Cl, 38.78.

4,4'-Dichlorobenzohydryl Trichloroacetate.—By the same method used for benzohydryl trichloroacetate, 8.4 g. (0.033 mole) of 4,4'-dichlorobenzohydrol and 6 g. (0.04 mole) of trichloroacetic acid gave 7.5 g. (57%) of 4,4'-dichlorobenzohydryl trichloroacetate melting at 59–59.5°.

Anal. Calcd. for $C_{15}H_9Cl_5O_2$: Cl, 44.48. Found: Cl, 44.43.

Pyrolysis of Benzohydryl Trichloroacetate.—Benzohydryl trichloroacetate was prepared as described above from 20 g. (0.1 mole) of benzohydrol and 18 g. (0.11 mole) of trichloroacetic acid. After removal of benzene, the residue was distilled under reduced pressure. Decomposition started immediately and a yellow liquid distilled slowly at 138–140° (3 mm.). The distillate was redistilled to give 14 g. (70%) of benzohydryl chloride.

Anal. Calcd. for $C_{13}H_{11}Cl$: C, 76.9; H, 5.44. Found: C, 76.55; H, 5.44.

The benzohydryl chloride was further identified by conversion to dibenzohydryl ether melting at 109°.[5]

In another pyrolysis, 25 g. (0.076 mole) of benzohydryl trichloroacetate was placed in a modified claisen flask fitted with a condenser for distillation. The flask was heated for 5 hours in a metal-bath at 280°. Some of the gas evolved was passed into barium hydroxide solution to give an immediate precipitate of barium carbonate. When the gas evolved was passed into water, the water produced a white precipitate of silver chloride when a few drops of silver nitrate solution was added. Chlorine could not be detected in the gaseous mixture by testing with potassium iodide and starch. The pressure in the distillation assembly was then reduced to 1.5 mm. and the flask was heated again. Benzohydryl chloride (4 g., 39%) was collected at 132–134° (1.5 mm.).

The tarry residue in the flask was removed by extraction with benzene after which the benzene was removed by evaporation and the residue was dried in an oven at 110°. The residue was then placed in a soxhlet extractor and extracted with methanol. The methanol was evaporated and the residue was recrystallized three times from benzene to give 2.1 g. (17%) of tetraphenylethylene, identified by melting point and mixed melting point with an authentic sample.

In another pyrolysis of benzohydryl trichloroacetate, analysis of the evolved gases showed that 31.6% of the total chlorine in the benzohydryl trichloroacetate was evolved as hydrogen chloride during the decomposition.

CHEMISTRY DEPARTMENT
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

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[5] E. Wedekind and K. Schenk, *Ber.*, **44**, 201 (1911).

[6] O. Anselmino, *Ber. deut. pharm. Ges.*, **16**, 390 (1906).

[7] A. L. Wilds in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 203.

Prediction of Hydrocarbon Burning Velocities by the Modified Semenov Equation

BY P. L. WALKER, JR., AND C. C. WRIGHT

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The authors,[1] using the thermal theory of Semenov, and Simon,[2] using the diffusion theory of Tanford and Pease, have satisfactorily correlated the experimental burning velocities of a majority of the hydrocarbon–air mixtures investigated by assuming the specific reaction rate constants in the two equations independent of hydrocarbon. The predicted burning velocities of acetylene and ethylene, however, deviated markedly from experimental results for both theories. It was, therefore, concluded that the rate constants for the combustion of these hydrocarbons vary noticeably from all other hydrocarbons investigated.

In the previous correlation by the Semenov equation, due to lack of sufficient data, the energy of activation of all hydrocarbons for the combustion reaction was assumed to be 40 kcal./mole, which approximates the available low temperature data on the oxidation of hydrocarbons. Recent work by Fenn,[3] where he was able to associate lean limit flame temperatures of hydrocarbons with their activation energies, shows that high temperature activation energies for hydrocarbon combustion are considerably lower than the value of 40 kcal./

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[1] P. L. Walker, Jr., and C. C. Wright, THIS JOURNAL, **74**, 3769 (1952).

[2] Dorothy Martin Simon, *Ind. Eng. Chem.*, **43**, 2718 (1951).

[3] John B. Fenn, *ibid.*, **43**, 2865 (1951).