2,2-Dichloroethanol.—This compound was prepared by the reduction of dichloroacetyl chloride by lithium aluminum hydride in absolute ether. Details are given in the accompanying paper.[4]

2,2,2-Trichloroethanol.—The method of Chalmers[5] given in "Organic Syntheses" was followed.

Esters.—The procedure for the synthesis of all twelve esters reported in this paper was essentially as follows.

2,2,2-Trichloroethyl *p*-Chlorobenzoate.—In a 200-ml. round-bottom flask, fitted with a reflux condenser and dropping funnel, was placed 18.5 g. (0.12 mole) of 2,2,2-trichloroethanol. All openings were protected by calcium chloride tubes and the flask was heated in an oil-bath maintained at 110-115°. *p*-Chlorobenzoyl chloride (21.7 g., 0.12 mole) was added slowly over a period of twenty minutes. Hydrogen chloride was evolved vigorously and heating was continued for seventy-five minutes after which no further evolution could be noted.

On cooling in the oil-bath the reaction mixture became solid. It was recrystallized several times from 95% alcohol giving 30 g., 84% yield, of white crystals melting at 49-49.5°; very soluble in benzene, acetone and hot 95% ethanol.

Anal. Calcd. for $C_9H_6Cl_4O_2$: Cl, 49.3. Found: Cl, 49.2, 49.4.

Acknowledgment.—Toxicity tests were carried out in the laboratories of the Niagara Chemical Division, Food Machinery Corporation, Middleport, New York.

Summary

The mono-, di- and trichloroethanol esters of *p*-chloro-, *o*-chloro-, 2,4-dichloro- and 3,4-dichlorobenzoic acids have been synthesized.

Preliminary toxicity tests gave no indication of insecticidal activity.

BUFFALO, NEW YORK RECEIVED NOVEMBER 19, 1948

---

[4] Sroog, Chih, Short and Woodburn, THIS JOURNAL, 71, 1710 (1949).

[5] Chalmers, "Organic Syntheses," Coll. Vol. II, p. 598 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Reduction of Chloro-acid Derivatives by Lithium Aluminum Hydride: Synthesis of Dichloroethanol

BY CYRUS E. SROOG, CHEN MING CHIH, FRANKLIN A. SHORT AND HENRY M. WOODBURN

Nystrom and Brown[1] have reported the reduction of ketones, aldehydes, acid chlorides, esters, anhydrides, simple acids and certain types of substituted acids to form alcohols in yields exceeding 80%. Successful results with substances possessing aromatically bound halogen were reported but no reductions of those containing aliphatically bound halogen. Our need for relatively large amounts of 2,2-dichloroethanol led us to investigate this method of converting dichloroacetic acid derivatives to the alcohol and ultimately resulted in a method for the synthesis of the desired compound in 65% yield.

The conventional method for making 2,2-dichloroethanol requires the production of dichloroacetal, hydrolysis of this substance to dichloroacetaldehyde and reduction of the latter to the desired alcohol. In our hands the process gave disappointing results, in addition to requiring many hours of time. Except for the final drying and distillation, the synthesis described below can be completed in about four hours.

The reduction was accomplished by the slow addition of the halogen compound to an ether suspension of lithium aluminum hydride and was equally successful with the free acid, the ethyl ester and the acid chloride. The fact that the chloroalcohol formed the major part of the product, indicated that the principle reaction occurred at the carboxyl end of the molecule.

The study was then extended to the free acid, the ethyl ester and the acid chloride of monochloroacetic acid and trichloroacetic acid. Results were similar to those obtained before, although considerably poorer yields of alcohol resulted from the free acids.

A summary of results is given in Table I.

TABLE I

PRODUCTION OF ALCOHOLS FROM CHLOROACID DERIVATIVES

Reactant	Alcohol produced	Yield, %
$CHCl_2CO_2H$	$CHCl_2CH_2OH$	65
$CHCl_2CO_2Et$	$CHCl_2CH_2OH$	65
$CHCl_2COCl$	$CHCl_2CH_2OH$	63
CH_2ClCO_2H	CH_2ClCH_2OH	13
CH_2ClCO_2Et	CH_2ClCH_2OH	37
$CH_2ClCOCl$	CH_2ClCH_2OH	62
CCl_3CO_2H	CCl_3CH_2OH	31
CCl_3CO_2Et	CCl_3CH_2OH	65
CCl_3COCl	CCl_3CH_2OH	64

After this work had been completed, Henne, Alm and Smook[2] published a description of the lithium aluminum hydride reduction of trifluoroacetyl chloride. Like the reactions above, this offers an attractive method for the preparation of the haloalcohol.

Experimental

The chloroalcohols prepared in this work were made by completely analogous reactions whether the free acid, the ester or the acid chloride was the source material. The stoichiometric relationships given by Nystrom and Brown[1] were used. Details of only one specific case are given below.

The lithium aluminum hydride was purchased from Metal Hydrides Incorporated. Organic reagents were C. P. Eastman Kodak Co. products.

---

[1] Nystrom and Brown, THIS JOURNAL, 69, 1197, 2548 (1947).

[2] Henne, Alm and Smook, *ibid.*, 70, 1968 (1948).

2,2-Dichloroethanol by Reduction of 2,2-Dichloroacetyl Chloride.—A one-liter three-necked flask fitted with a reflux condenser, mercury sealed stirrer and dropping funnel was charged with 275 ml. of rigorously dried ether. To this was added 13.6 g. (0.36 mole) of pulverized lithium aluminum hydride (20% excess). Stirring produced a milky suspension. After fifteen minutes the addition of 88.6 g. (0.60 mole) of 2,2-dichloroacetyl chloride was begun and continued at a rate determined by the refluxing of the ether. Two hours and a half was required for the addition, vigorous stirring being maintained throughout the addition and for thirty minutes thereafter.

Excess hydride was destroyed by dropwise addition of water while the flask was cooled in a water-bath. Considerable heat was evolved and a white curdy precipitate, presumed to be aluminum hydroxide, was formed. Hydrolysis of the intermediate was effected by the addition of 500 ml. of 10% sulfuric acid.

The pale yellow ether layer, combined with two ether extracts of the aqueous layer, was dried over anhydrous magnesium sulfate, the ether removed by distillation at reduced pressure and the organic residue fractionated under vacuum through an 18′ column packed with glass helices. The fraction collected between 37° and 38.5° (6 mm.) amounted to 44 g. or 63%. At 739 mm. pressure this boiled at 145° (Heilbron lists 146°, pressure unknown).

Analysis for chlorine was carried out by the Rauscher method.[3]

Anal. Calcd. for $C_2H_4Cl_2O$: Cl, 61.7. Found: Cl, 61.2, 61.3.

Summary

The three chloroacetic acids, their esters and acid chlorides are reduced smoothly by lithium aluminum hydride, the principle product in most cases being the chloroalcohol. The method is recommended as a procedure for the synthesis of 2,2-dichloroethanol.

---

(3) Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).

BUFFALO, N. Y. RECEIVED NOVEMBER 19, 1948

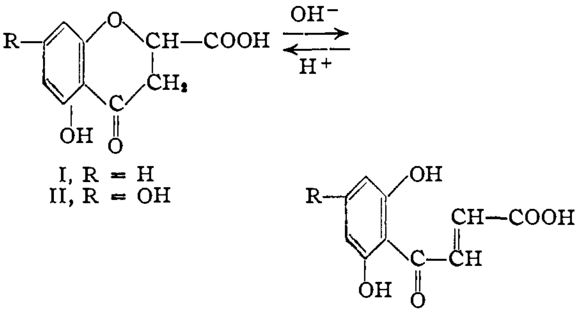
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VICK CHEMICAL COMPANY]

Ultraviolet Absorption Study of Some Substituted β-Aroylacrylic Acids and 2-Carboxy-γ-chromones and Chromanones

BY CHARLES I. JAROWSKI[1] AND GLENN B. HESS[1]

In the preceding paper evidence was presented for the assignment of the 2-carboxy-5,7-dihydroxy-γ-chromanone structure to the acid obtained by the acylation of phlorglucinol with maleic anhydride. Arguments were also set forth to indicate that alkaline hydrolysis of 2-carbethoxy-5-hydroxy-γ-chromanone followed by acidification resulted in the formation of the corresponding acid.[2]

A study of the ultraviolet absorption of some 2-carboxy-γ-chromones, 2-carboxy-γ-chromanones and β-aroylacrylic acids was initiated in order to add more evidence in favor of the structures postulated. Furthermore it was of interest to determine if the following chalcone–γ-chromanone type of equilibrium did occur with the two acids studied



I, R = H
II, R = OH

for it was quite possible that alkaline hydrolysis of the ethyl ester of I had opened the γ-chromanone ring but that acidification resulted in cyclization of the desired β-(2,6-dihydroxybenzoyl)-acrylic acid to give the closed structure.

Some chromophorically related compounds were likewise included in order to gain a better insight into the structural features accounting for the characteristic bands observed.

Experimental

The compounds listed in Table I were previously prepared in this Laboratory by methods already described in the literature.

Absorption Measurements.—Absorption determinations were made on a Beckmann Model DU Quartz spectrophotometer, using 1 cm. cemented quartz cuvettes and a hydrogen discharge lamp as the light source. Samples were made up in the range of 0.1% w./v. and dilutions to 0.01 and 0.001% were made with the same solvent. Samples which were run in 0.05 *N* alcoholic potassium hydroxide were made up to a concentration of 0.1% w./v. and dilutions were made with alcoholic potassium hydroxide.

All samples except β-mesitoylacrylic acid followed Beer's law in the concentrations used. β-Mesitoylacrylic acid gave anomalous results in the range from 250–300 millimicrons in the shift from 0.001 to 0.01% concentration. Results shown in this range are the absorptions for the 0.01% solution.

Discussion of Results

In Fig. 1 are shown the absorption curves obtained by plotting log ε as a function of the wave length expressed in mμ. The groups of curves have been displaced vertically by one log ε unit.

---

[1] Present address: Chas. Pfizer & Co., Inc., 11 Bartlett St., Brooklyn, N. Y.

[2] Jarowski, Moran and Cramer THIS JOURNAL, 71, 944 (1949).