

which are being actively studied by physicochemical means. The study of their therapeutic effects may lead to interesting developments. As they contain easily reactive halogen atoms, they might be useful in making other compounds of mercury, or in organic synthesis.

The experimental details of the preparation and properties of the substances, as well as the analytical data, will be published in a later paper on their constitution.

THE CHEMICAL LABORATORIES OF THE COLLEGE  
BARODA, INDIA

KUVERJI GOSAI NAIK,  
MAHADEO DATTATRAYA AVASARE

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**The Catalytic Bromination of Aliphatic Acid Chlorides.**—The use of iron, ferric chloride, aluminum chloride, etc., in brominating and chlorinating aromatic compounds has found widespread application. In the aliphatic series, however, the use of iron as a catalyst in introducing bromine within the molecule has been limited chiefly to saturated and unsaturated hydrocarbons.

Meyer<sup>1</sup> and Kronstein<sup>2</sup> have presented a series of papers dealing with the bromination of hydrocarbons using iron as a catalyst. Willstätter and Bruce<sup>3</sup> used iron powder in preparing 1,2-dibromocyclobutane, and recently Mereshkowsky<sup>4</sup> has studied the ratio of reaction products obtained in the bromination of hydrocarbons and their bromine derivatives by using iron wire, ferric bromide, aluminum, and aluminum trichloride as catalysts. In brominating acetic acid and its homologs the use of sulfur as catalyst is well known.

During the course of researches on derivatives of camphoronic acid,  $(\text{CH}_3)_2\text{C}(\text{COOH})-\text{C}(\text{CH}_3)(\text{COOH})-\text{CH}_2\text{COOH}$  (a description of which will appear later), it was found necessary to brominate anhydrocamphoronyl chloride,  $\text{C}_6\text{H}_{11}(\text{CO})_2\text{OCOCl}$ . The bromination hitherto has been carried out by Bredt<sup>5</sup> either by heating one or both isomers with bromine in a sealed tube at elevated temperatures, or in an open vessel on the water-bath, the reaction product being a mixture of two isomeric bromo-anhydrocamphoronyl chlorides in which it is known that the bromine is attached to the primary carbon atom of the molecule. The latter scheme required about 12 hours for complete reaction to take place.

The above procedure was modified by treating anhydrocamphoronic acid,  $\text{C}_6\text{H}_{11}(\text{CO})_2\text{OCOOH}$ , formed in quantitative yields by heating pure, optically-active camphoronic acid under a vacuum at  $180^\circ$  in an oil-bath with 1.1 molecular equivalents of phosphorus pentachloride in a flask

<sup>1</sup> Meyer, *Ber.*, **24**, 4247 (1891); **25**, 3304 (1892).

<sup>2</sup> Kronstein, *Ber.*, **24**, 4245 (1891); **26**, 2436 (1893); **54**, 1 (1921).

<sup>3</sup> Willstätter and Bruce, *Ber.*, **40**, 3983 (1907).

<sup>4</sup> Mereshkowsky, *Ann.*, **431**, 113 (1923).

<sup>5</sup> Bredt, *Ann.*, **299**, 142 (1899).

bearing a ground-glass tube and condenser together with a separatory funnel sealed to its side. The mixture was warmed and when the reaction had ceased, without distilling the phosphorus oxychloride, a small amount of iron powder (0.2–0.5 g.) was added. Then, while the mixture was heated on the water-bath, 1.1 molecular equivalents of bromine was slowly added through the separatory funnel. A violent bromination of the camphoronyl chlorides followed. After all the bromine had been added the mixture was heated for 45 minutes to insure complete reaction. At the end of this time, when no fumes of bromine could be detected, the flask was removed and allowed to stand at room temperature for 24 hours to permit the crystallization of the  $\alpha$ -bromo-anhydrocamphoronyl chloride. The contents of the flask were filtered and the crude product, obtained in yields of 75%, was repeatedly washed with small amounts of absolute ether to remove both its readily soluble isomer and ferric bromide. The solid was dissolved in hot benzene, boiled with Norite two or three times and finally allowed to cool. Transparent crystals of the pure product melting at 168° were obtained. The original filtrate contained some  $\alpha$ -bromo acid chloride together with ferric bromide and the  $\beta$ -, or isomeric, bromo acid chloride. The latter compound has never been obtained in a pure state.

This method of catalytic halogenation appears to have considerable value in the catalytic preparation of  $\alpha$ -halogen acids. It is the intention of the writer to continue investigation of the reaction, extending it not only to other acid chlorides, but also to other classes of aliphatic compounds to which it has not been applied.

CHEMICAL LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS  
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WALTHER F. GOEBEL

**The Purity of Alpha-Gamma-Dichlorohydrin Prepared by the Action of Hydrogen Chloride on Glycerol.**—In the preparation of  $\alpha, \gamma$ -dichlorohydrin from glycerol by the action of hydrogen chloride there is the possibility of forming considerable amounts of  $\alpha, \beta$ -dichlorohydrin (the dichloride of allyl alcohol). The complete separation of such a mixture by distillation would be very difficult. In order to obtain information in regard to the purity of the dichlorohydrin prepared in this way, we investigated the action of *p*-nitrobenzoyl chloride on the final product of the reaction which was collected over a 3° range and over a 7° range. The preparation and distillation was carried out as described in "Organic Syntheses," Vol. II, p. 29. Five g. of the material was mixed with 20 g. of pyridine and 8 g. of *p*-nitrobenzoyl chloride; the mixture was heated for 3 hours on the steam-bath, then allowed to stand overnight and finally treated with dil. hydrochloric acid and extracted with ether. After the removal of nitrobenzoic acid by means of aqueous sodium carbonate, the ether