mercuration reaction. At present, therefore, it seems unwise to the authors to attempt an assignment of geometric configuration to the dichloropropenes on the basis of an interpretation of their $CuCl_2^-$ catalyzed hydrolysis rates in terms of the steric course of mercuration reactions.

The chloroalcohol obtained by hydrolysis of α-1,3-dichloropropene is readily dehydrochlorinated by aqueous sodium hydroxide while that obtained from the *beta* isomer is not.[1] On the basis that chlorofumaric acid is dehydrochlorinated more readily than chloromaleic acid, Hatch and Roberts concluded that the *alpha* dichloride and chloroalcohol were the *trans* isomers (presumably B and B′).

However a survey of the literature indicates that in general dehydrohalogenation of vinyl halides takes place most readily when the hydrogen and halide are *trans* to each other.[6] For example, chlorofumaric acid,[6] *trans*-2-bromo-2-butene[7] and *cis*-dichloroethylene[8] all dehydrohalogenate more readily than the isomers of opposite geometric configuration. From these facts it would seem better to reach a conclusion opposite to that of Hatch and Roberts and to assign the structures A and A′ to the *alpha* isomers and B and B′ to the *beta* isomers.

In the opinion of the authors a definite assignment of geometric configuration for the 1,3-dichloropropenes cannot be made on the basis of available experimental evidence. It is possible that further studies of the mechanisms of dehydrohalogenation of substituted vinyl halides and of the cuprous chloride–chloride ion complex catalyzed hydrolysis reactions would clarify this situation.

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Nicotinic Anhydride

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Preparation of nicotinic anhydride by the reaction of nicotinyl chloride with sodium nicotinate and subsequent distillation of the anhydride from the reaction mixture has been reported previously.[1] However, the synthesis of pure nicotinyl chloride from nicotinic acid[2,3] or from nicotinic acid nitrate[4] is difficult, time-consuming, and poorly productive because of the troublesome separation of the acid chloride from pyridine hydrochloride by distillation.

A simplified method for the preparation of nicotinic anhydride from nicotinic acid has been developed in this Laboratory. Excellent yields of essentially pure product are obtained by a process in which distillation procedures are eliminated and the anhydride is crystallized from the liquid portion of the reaction mixture. The improvement over previously reported methods is achieved by high temperature removal of hydrogen chloride from nicotinyl chloride hydrochloride in inert solvents.

Preparation

Into a 500-cc. three-necked, round-bottom flask equipped with a condenser fitted with a calcium chloride drying tube, air-tight stirrer and dropping funnel, were placed 40.6 g. (0.33 mole) of nicotinic acid and 100 cc. of anhydrous nitrobenzene. Over a period of ten minutes, 39.3 g. (0.33 mole) of redistilled thionyl chloride was added dropwise. The temperature of the reaction mixture was raised gradually to 210° and maintained for one hour, or until all gas evolution had ceased. The reaction mixture was allowed to cool, then 53.1 g. (0.33 mole) of potassium nicotinate was introduced in one portion, and the mixture was heated to 210° for three hours, after which it was allowed to cool to approximately 100° and poured into a 1500-cc. beaker. One liter of anhydrous benzene and 10 g. of Norit were added. The mixture was then boiled for about ten minutes and filtered through a heated Buchner funnel, and the filtrate was cooled to room temperature. The 49.5 g. of nicotinic anhydride which crystallized had a melting point of 119.8–121.5°.[5] Concentrating the mother liquors to approximately 150 cc. gave a second crop of crystals, which weighed 14.6 g. and had a melting point of 119.1–121.3°. A third crop of 2.5 g. was obtained by further concentration and crystallization, bringing the total weight of nicotinic anhydride to 66.6 g. This represented a yield of 88.9%. The combined crops of crystals recrystallized once from hot benzene gave a pure anhydride melting at 122.5–123.5°. However, the crude anhydride was of sufficient purity to be used in most syntheses.

Anal. Calcd. for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28. Found: C, 63.15; H, 3.63; N, 12.23.

Direct reaction of 1 mole of potassium nicotinate with 0.5 mole of thionyl chloride gave lower yields than this procedure. Use of other solvents in the preparation of nicotinic anhydride was investigated. Nitrobenzene gave the best yields and product. The following table shows the solvent used and yield of anhydride obtained.

Solvent	Yield, %
Nitrobenzene	88.9
o-Dichlorobenzene	78.3
Deobase[6]	47.9
p-Cymene	26.6

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(2) Späth and Spitzer, *Ber.*, **59B**, 1477–1486 (1926).

(3) Meyer and Graf, *ibid.*, **61**, 2202–2215 (1928).

(4) Douglass and Forman, This Journal, **56**, 1609 (1934).

(5) Melting points reported are uncorrected.

(6) Deobase is deodorized kerosene. It was redistilled and only the cut boiling at 205–215° was used.

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The Preparation of 1-Phenyl-1,3-butadiene

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In connection with a study of Diels–Alder reactions of aryl-substituted dienes, an investiga-

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