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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DIVISION OF CHEMISTRY
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RECEIVED JANUARY 27, 1947

Nicotinic Anhydride

BY C. O. BADGETT

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.

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

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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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(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

BY E. C. COYNER AND G. A. ROPP[1]

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

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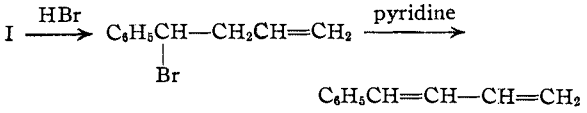
(1) Research Corporation Fellow.

tion of the preparation of 1-phenyl-1,3-butadiene from four phenylbutenols (I–IV) has been made.

I $C_6H_5CH(OH)CH_2CH{=}CH_2$[2]
II $C_6H_5CH{=}CHCH(OH)CH_3$[3]
III $C_6H_5CH(OH)CH{=}CHCH_3$[4]
IV $C_6H_5CH_2CH(OH)CH{=}CH_2$[5]

Alcohols (I–III) were obtained by the Grignard reaction, but attempts to prepare (IV) by this reaction using the procedure of Delaby, who reported a 5% yield, gave only phenylbutadiene dimer, b. p. 250° (33 mm.),[6] and higher polymers. Alcohol (IV) is therefore probably the least stable of the four studied.

1-Phenyl-3-buten-1-ol (I) is the most stable of the alcohols (*vide infra*) and was obtained in 77% yield; it was used in preparing 1-phenyl-1,3-butadiene (46% yield from alcohol) *via* the reactions



$$\text{I} \xrightarrow{\text{HBr}} C_6H_5\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_2CH{=}CH_2 \xrightarrow{\text{pyridine}} C_6H_5CH{=}CH{-}CH{=}CH_2$$

Data on the relative stability of alcohols (I–III) under dehydrating conditions were obtained by measuring the rates of water formation in solutions of each of the alcohols in benzene containing 0.1% concentrated sulfuric acid. The determined stabilities are (I) > (II) = (III). This procedure gave isolable quantities of diene monomer (6%) from (III) only.

Experimental

1-Phenyl-1,3-butadiene.—Dry hydrogen bromide was passed into a solution of 54.3 g. of 1-phenyl-3-buten-1-ol in 230 cc. C. P. benzene under reflux for five hours. Ninety per cent. of the theoretical amount of water was separated from the reaction mixture after two hours. After the benzene solution was washed free of acid with dilute aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate, it was added to 39.5 g. of pyridine and a few mg. of hydroquinone, and the resulting solution was mechanically stirred and heated under reflux for eleven hours. The supernatant liquid was decanted from the yellow, tacky precipitate which was then washed twice with benzene and was found to contain 93.5% of the theoretical amount of bromide ion; it was almost completely soluble in water. The benzene washings were combined with the decanted solution and the whole was washed seven times with water and dried over anhydrous magnesium sulfate. A small amount of hydroquinone was added and the benzene was removed *in vacuo*. The residue was a red oil which gave, upon distillation, 22 g. of 1-phenyl-1,3-butadiene [46%, based on (I)], b. p. 75–79° (6.5 mm.),[7] m. p. 1–3°.[6]

Dehydration of 1-Phenyl-3-buten-1-ol, 4-Phenyl-3-buten-2-ol and 1-Phenyl-2-buten-1-ol.—A solution of each alcohol in an equal volume of benzene containing about 0.1% concentrated sulfuric acid was heated under reflux and the returning condensate was passed over a trap from which the water was periodically withdrawn and its volume measured. Under these conditions 1-phenyl-3-buten-1-ol (I) was dehydrated only 16% in three hours while both 4-phenyl-3-buten-2-ol (II) and 1-phenyl-2-buten-1-ol (III) gave about 35% of the theoretical amount of water during the first hour and no additional water after three hours. The reaction mixtures were washed free of acid with dilute aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate and distilled in the presence of hydroquinone *in vacuo*. In addition to polymeric residues which were obtained from all of the alcohols, phenylbutadiene, b. p. 96–99° (25 mm.), was obtained from the reaction with 1-phenyl-2-buten-1-ol (III) in 6% yield and 63% unchanged alcohol was recovered from the reaction with 1-phenyl-3-buten-1-ol (I).

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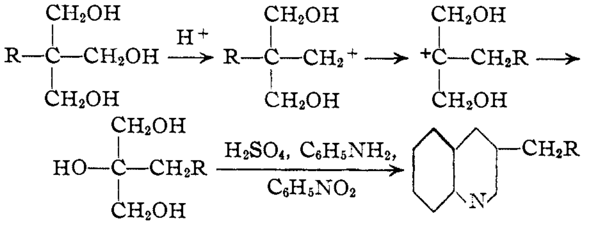
Evidence of Rearrangement of Polymethylol Compounds Related to Neopentane

BY ROBERT W. BROWN[1] AND GREGG DOUGHERTY

The neopentyl system in polymethylol compounds of the type $R_2C(CH_2OH)_2$ and $RC(CH_2OH)_3$ is much more stable than it is in neopentyl alcohol, as is shown by the fact that the halides of these polyalcohols can be prepared without rearrangement by treatment with hydrogen halides.[2] The report of Fischer and Winter,[3] however, that methyl isopropyl ketone and isovaleraldehyde are formed in small amounts by the action of sulfuric acid on 2,2-dimethylpropanediol-1,3 at 200° suggests that some sort of rearrangement of the carbon skeleton takes place under sufficiently drastic conditions.

The trimethylol compounds are largely destroyed by treatment with concentrated acids at high temperatures, but as rearrangement of these compounds with migration of the alkyl group would lead to β-alkylglycerols, it appeared that the conditions of the Skraup synthesis might lead to isolable derivatives.



When 2-(hydroxymethyl)-2-methylpropanediol-1,3 was heated with aniline, nitrobenzene, and sulfuric acid, a vigorous reaction set in at about 160°. After six hours of heating at 160–170° a heavy tar was obtained, which after steam distillation and removal of primary and secondary amines by diazotization gave 10–25% yields of 3-ethylquinoline.

Under the same conditions 2-(hydroxymethyl)-2-ethylpropanediol-1,3 reacted in the same manner as the lower homolog; the product in this case being 3-propylquinoline.

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