was discarded. A cut weighing 0.56 g. was taken; it distilled at 96–98°, $n^{20}D$ 1.5330. The infrared spectrum showed that this cut was largely N-methyl-2-hydroxymethylpyrrole containing some of the unreacted aldehyde. On the basis of the refractive index, the material was 79% alcohol.

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Preparation of Nicotinic and Isonicotinic Anhydride

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Nicotinic and isonicotinic anhydride were first prepared by reaction of their acid chlorides with their sodium salts.[1] The disadvantages of the original method, which requires vacuum distillation of the acid chlorides, have been emphasized by Badgett,[2] who published a simplified procedure for the preparation of nicotinic anhydride, in which the intermediary nicotinyl chloride was obtained and used *in situ*. His procedure, however, involves the use of nitrobenzene, the last traces of which are not readily removed from the product, and it is furthermore inapplicable to isonicotinic anhydride, which is unstable[1] at the high temperature that must be employed.

More recently, a new procedure for the preparation of nicotinyl chloride has been described,[3] in which oxalyl chloride is substituted for the previously employed[2,4] thionyl chloride. Since hydrogen chloride is not formed under these conditions, nicotinyl chloride is obtained directly, and decomposition by distillation from pyridine[4] or by pyrolysis[2] of the nicotinyl chloride hydrochloride produced in the presence of thionyl chloride becomes unnecessary. Wingfield's procedure is an application of a general reaction discovered by Adams and Ulich,[5] who showed that sodium salts of organic acids react with oxalyl chloride to yield either acid chlorides or acid anhydrides, depending on the molar proportions of the reagents. By modifying Wingfield's procedure in the light of these findings, a very convenient and rapid method for preparing directly both nicotinic and isonicotinic anhydride has been developed in this Laboratory.

Experimental

Nicotinic Anhydride.—To a suspension of 32.24 g. (0.2 mole) of potassium nicotinate, which had been ground to pass a 100-mesh sieve and dried at 135°,[3] in 80 ml. of anhydrous benzene was added, with mechanical stirring and cooling in an ice-bath, 12.69 g. (0.1 mole) of oxalyl chloride in 45 ml. of anhydrous benzene during 20 minutes. The cooling bath was removed after another 15 minutes, and the suspension stirred at room temperature for one hour, then at the refluxing temperature for another hour. It was filtered hot, and the solid washed with boiling benzene. The combined filtrate and washings were concentrated to about 100 ml. and cooled, providing 17.23 g. of colorless prismatic needles, m.p. 123–126° (lit. 122–124°,[1] 122.5–123.5°[2]). The product did not depress the melting point of a sample prepared by Badgett's[2] procedure. Another 2.09 g., m.p. 123°, was obtained from the mother liquor by concentrating and adding hexane, bringing the total yield to 85%.

Isonicotinic Anhydride.—The same procedure was used starting with potassium isonicotinate, except that after removing the ice-bath the suspension was stirred at room temperature for two hours, filtered, and the residue washed first with cold benzene, then extracted with hot benzene. The combined light yellow filtrates were concentrated under reduced pressure to about 100 ml. and diluted with an equal volume of hexane to yield 16.56 g. (73%) of colorless elongated prisms, m.p. 112–114°. Recrystallization from benzene–pentane brought the m.p. to 112.7–113.9°. The analytical sample (same m.p.) was obtained by vacuum sublimation (bath 115°).

Anal. Calcd. for $C_{12}H_8O_3N_2$: C, 63.16; H, 3.53; N, 12.28; sapn. equiv., 114. Found: C, 63.36; H, 3.43; N, 12.47; sapn. equiv., 111.

In a preliminary experiment, the compound was obtained in the form of plates, m.p. 103–105° (lit.[1] rhombic prisms, m.p. 103–104°). Subsequent runs yielded the higher-melting polymorphic modification only.

Preparations in which the suspension was refluxed as in the case of nicotinic anhydride gave essentially identical yields and melting points; the product was, however, contaminated with a trace of blue dye, which could be removed by treatment with Norit. The yield was not improved when 0.1 mole of potassium isonicotinate was allowed to react with 0.1 mole of oxalyl chloride to produce isonicotinyl chloride *in situ*, followed by addition of another 0.1 mole of potassium isonicotinate.

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Allylic Rearrangement of Hexachloropropene-1-C^{14}

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Allylic rearrangements of crotyl and methallyl chlorides during reaction have been known for many years. Kundiger and Haney[1] recently reported that 1,1,1-trichloro-2-methyl-2-propene undergoes allylic rearrangement on being heated with thionyl chloride or powdered glass. We wish to report that hexachloropropene also undergoes allylic rearrangement under mild conditions. This conclusion is based on observations with hexachloropropene-1-C^{14} which was synthesized as

$$C^*H_3COOH + C_6H_6 \xrightarrow{PCl_5,\ AlCl_3} C_6H_5COC^*H_3 \xrightarrow{Cl_2} C_6H_5COC^*Cl_3$$

$$\xrightarrow[H_2O]{NaOH} C^*HCl_3 \xrightarrow[AlCl_3]{Cl_2C{=}CCl_2} C^*HCl_2CCl_2CCl_3 \xrightarrow[MeOH]{NaOH} C^*Cl_2{=}CClCCl_3$$

The hexachloropropene was degraded by ozonization, which gave carbon dioxide recovered as barium carbonate and trichloroacetic acid, recovered in most runs as the S-benzylthiuronium salt.

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[1] D. G. Kundiger and H. N. Haney, THIS JOURNAL, **76**, 615 (1954).