

trates were adjusted to pH 2-3 with nitric acid; 25% AgNO₃ was added till the precipitation was complete. The white silver salt was washed with water to remove all excess HNO₃ and AgNO₃. The silver salt was suspended in 35 ml. of water and treated exhaustively with H₂S. Silver sulfide was removed and the filtrate concentrated to dryness *in vacuo*. The dried residue was crystallized from 3 ml. of *n*-butyl alcohol. The resulting product was collected by filtration, washed with petroleum ether and dried *in vacuo* at 55° for 2 hours. One hundred twenty mg. of 1-methyl-*v*-triazole-4,5-dicarboxylic acid, m.p. 174-175° dec., was obtained. An additional 70 mg. of product could be obtained from the mother liquor by the careful addition of petroleum ether, m.p. 170° dec.

Anal. Calcd. for C₅H₅O₄N₃: C, 35.09; H, 2.95; O, 37.39; N, 24.56. Found: C, 35.02; H, 3.02; O, 37.28; N, 24.68.

(b) Oxidation of 1-methylbenzotriazole⁴ was performed as under (a), m.p. 175-176° dec.; mixture of 1-methyl-*v*-triazole-4,5-dicarboxylic acid from (a) and (b), m.p. 174-175° dec.

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N-Methyl-2-pyrrolealdehyde and N-Methyl-2-hydroxymethylpyrrole

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The formylation of pyrrole with dimethylformamide to give 2-pyrrolealdehyde, and the reduction of the aldehyde to 2-hydroxymethylpyrrole, was reported recently.¹

A compound previously reported² as 2-hydroxymethylpyrrole was shown to be the pinacol formed by a bimolecular reduction of 2-pyrrolealdehyde.

This communication records the formylation of N-methylpyrrole with dimethylformamide to give N-methyl-2-pyrrolealdehyde, and the reduction of this aldehyde with sodium borohydride to the previously unreported N-methyl-2-hydroxymethylpyrrole. The elemental analysis, molar refractivity and infrared spectrum were in accord with the postulated structure. All efforts, however, to prepare a derivative of this simplest alcohol of the N-methylpyrrole series were unsuccessful, as was also the case for 2-hydroxymethylpyrrole.¹ Treatment with acetic anhydride in pyridine, benzoyl chloride and 2,4-dinitrobenzoyl chloride in pyridine and in ether with potassium carbonate, dilute aqueous potassium permanganate, picric acid, trinitrobenzene, α -naphthyl isocyanate and triphenylmethylchloride in pyridine gave polymeric material. Shaking an ether solution of the alcohol with aqueous sodium bisulfite to remove traces of the aldehyde also resulted in polymerization of the alcohol.

Unequivocal proof of the identity of the alcohol was obtained by preparing the same compound by two other routes. The preparation of 3-hydroxymethylindole by Leete and Marion³ by alkaline hydrolysis of gramine methiodide led us successfully to apply this technique to the methiodide of N-methyl-2-dimethylaminomethylpyrrole. A crossed-Cannizzaro reaction of N-methyl-2-pyrrolealdehyde yielded the same product. Satisfactory

(1) R. M. Silverstein, E. E. Ryskiewicz and S. W. Chaikin, *THIS JOURNAL*, **76**, 4485 (1954).

(2) M. S. Taggart and G. H. Richter, *ibid.*, **56**, 1385 (1934).

(3) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).

agreement of the boiling points, refractive indices, and infrared spectra established that the products obtained from these three diverse procedures were identical.

Experimental

N-Methyl-2-pyrrolealdehyde.—The procedure which was used for the formylation of pyrrole¹ was applied to N-methylpyrrole. The product was obtained in 25% yield; boiling point 73-75° (11 mm.), lit.⁴ 75-76° (12 mm.); semicarbazone 206-208°, lit.⁵ 207-208°.

A better yield was obtained from a simpler procedure based on the method of Rogers⁶ for the formylation of 2,4-diphenylpyrrole with N-methylformanilide:

To 7.3 g. of dimethylformamide in a flask fitted with a stirrer, condenser and drying tube, was added 17.8 g. of phosphorus oxychloride. After 10 minutes, the flask was placed in a 60° bath, and 4.1 g. of N-methylpyrrole was added dropwise over a period of 30 minutes. The mixture was stirred at 60° for an additional hour, then poured on 100 g. of ice. Hydrolysis was completed by adding 75 g. of sodium acetate and heating the mixture just to boiling. The mixture was cooled and extracted with ether. The ether solution was washed with sodium carbonate, dried and evaporated, and the residue was distilled at 73-75° at 11 mm.; yield 2.7 g. (48%).

Sodium Borohydride Reduction of N-Methyl-2-pyrrolealdehyde.—A solution of 2.0 g. of sodium borohydride in 15 ml. of methyl alcohol was added portionwise to a stirred solution of 2.04 g. of N-methyl-2-pyrrolealdehyde in 10 ml. of methyl alcohol. The temperature was held below 55° by intermittent cooling. After one hour, 25 ml. of water was added. The solution was saturated with potassium carbonate, and extracted with ether. After the ether solution was dried and the ether was removed, the residue was distilled at 98-100° at 11 mm. The distillate was a moderately viscous, colorless oil; yield 1.26 g. (61%). *Anal.* Calcd. for N-methyl-2-hydroxymethylpyrrole: C, 64.8; H, 8.11; (R)_D, 32.2. Found: C, 64.5; H, 8.11; (R)_D 31.9; n^{20}_D 1.5268, d^{20}_4 1.070. The infrared spectrum showed the hydrogen-bonded hydroxyl band at 3.00 μ . After two weeks in the refrigerator, the liquid crystallized. Two recrystallizations from a petroleum ether-benzene mixture gave white crystals melting at 28-30°.

Hydrolysis of N-Methyl-2-dimethylaminomethylpyrrole Methiodide.—The quaternary ammonium salt was prepared as described by Herz and Rogers.⁷ Attempted alkaline hydrolysis of this compound under the very mild conditions used by Leete and Marion³ for gramine methiodide was not successful. The desired alcohol was obtained, albeit in poor yield, as follows: To a stirred refluxing mixture of 125 ml. of 10% sodium hydroxide and 125 ml. of benzene was added, over a period of 20 minutes, 7.0 g. of N-methyl-2-dimethylaminomethylpyrrole methiodide in 75 ml. of water. After refluxing for an additional hour, the benzene layer was separated. The residue following evaporation of the benzene weighed 0.60 g. The aqueous alkaline solution was refluxed and stirred with another 125-ml. portion of benzene for three hours. An additional 1.1 g. of residue was thus extracted. Distillation of the combined residues gave 0.30 g. (11%) of a moderately viscous oil which distilled at 95° at 11 mm., n^{20}_D 1.5268. The infrared spectrum was identical with that of the product obtained by sodium borohydride reduction of N-methyl-2-pyrrolealdehyde.

Crossed-Cannizzaro Reaction of N-Methyl-2-pyrrolealdehyde.—A procedure for the preparation of *p*-tolylcarbinol⁸ was adapted for our purpose: To a solution of 3.0 g. of potassium hydroxide in 6 ml. of methyl alcohol was added a mixture of 2.33 g. of N-methylpyrrolealdehyde and 2 ml. of formalin (37% formaldehyde). The mixture was allowed to stand overnight at room temperature, held at 60° for one hour, diluted with 20 ml. of water, saturated with potassium carbonate and extracted with ether. The ether solution was dried, the solvents removed and the residue was distilled at 11 mm. in a Claisen flask. A forerun of 1.0 g.

(4) E. Fischer, *Ber.*, **46**, 2504 (1913).

(5) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. I, Edwards Bros., Ann Arbor, Mich., 1943, p. 175.

(6) M. A. T. Rogers, *J. Chem. Soc.*, 596 (1943).

(7) W. Herz and J. L. Rogers, *THIS JOURNAL*, **73**, 4921 (1951).

(8) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 590.

was discarded. A cut weighing 0.56 g. was taken; it distilled at 96–98°, n_D^{20} 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 unstable¹ 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 pyridine⁴ or by pyrolysis² 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's² 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 C₁₂H₈O₃N₂: C, 63.16; H, 3.53; N, 12.28; sapon. equiv., 114. Found: C, 63.36; H, 3.43; N, 12.47; sapon. 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.

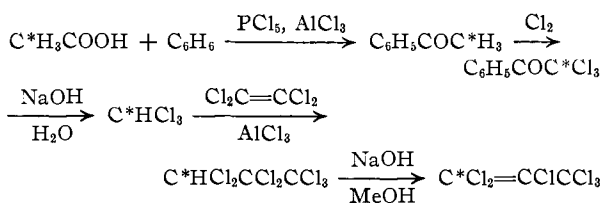
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Allylic Rearrangement of Hexachloropropene-1-C¹⁴

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Allylic rearrangements of crotyl and methallyl chlorides during reaction have been known for many years. Kundiger and Haney¹ 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-C¹⁴ which was synthesized as



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.

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

- (1) R. Graf, *Biochem. Z.*, **229**, 164 (1930).
- (2) C. O. Badgett, *THIS JOURNAL*, **69**, 2231 (1947).
- (3) H. N. Wingfield, Jr., W. R. Harlan and H. R. Hanmer, *ibid.*, **75**, 4364 (1953).
- (4) H. Meyer and R. Graf, *Ber.*, **61**, 2202 (1928).
- (5) R. Adams and L. H. Ulich, *THIS JOURNAL*, **42**, 599 (1920); cf. R. Adams, W. V. Wirth and H. E. French, *ibid.*, **40**, 424 (1918).