Preparation of N-(2-Chloroethyl)-4-(phenylazo)aniline

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In the course of other work, a specimen of the title compound (III) was desired. It was therefore synthesized by the following sequence of reactions.



2-Anilinoethanol (I) was first converted to its hvdrochloride, as Ward² has shown that hydrochlorides of such compounds are more readily chlorinated than are the free bases. Compound I-HCl was treated with phosphoryl chloride, to give N-(2chloroethyl)aniline hydrochloride (II) in a yield of 99.5% (lit. yield, 39.2%, using thionyl chloride). (Compound II had previously been prepared, in poor yield, by a variety of methods.³⁻⁷) Compound II was then condensed with benzenediazonium chloride, to afford III.

EXPERIMENTAL

N-(2-Chloroethyl)aniline hydrochloride (II). 2-Anilinoethanol (I. 137 g., 1 mole) was dissolved in 86 ml. (101 g.) of concentrated hydrochloric acid, and the solution was evaporated under diminished pressure (standard-taper joints) to a thick sirup which was dissolved in 100 ml, of absolute ethanol and the solution evaporated to dryness. Treatment with absolute ethanol (100 ml.) was repeated, followed by addition of 100 ml. of benzene and evaporation. Final traces of solvent were removed⁸ at 0.1 mm., to give a quantitative yield of a thick, pale brown gum (I·HCl).

To this hydrochloride (173.7 g.; 1 mole) was added 173 ml. of chloroform, the solution was cooled in ice, a boiling stone and 25 ml. of fresh phosphoryl chloride were added, and the solution was gradually heated under a reflux condenser (standard-taper joints; Drierite tube) until, after 30 min., vigorous gas evolution occurred (bath temp., 51°). The temperature was gradually raised to 58-61° (30 min.) and three 25-ml. portions of phosphoryl chloride were added at

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(2) K. Ward, Jr., J. Am. Chem. Soc., 57, 914 (1935).

(3) G. D. Jones, A. Langsjoen, M. M. C. Neumann, and J. Zomlefer, J. Org. Chem., 9, 125 (1944).

(4) J. Nemirowsky, J. prakt. Chem., [2] 31, 173 (1885).
(5) G. R. Clemo and W. H. Perkin, Jr., J. Chem. Soc., 125, 1804 (1924).

(6) J. von Braun, Ber., 70, 979 (1937).

(7) A. H. Filbey and L. R. Buzbee, Brit. Patent 772,988 (1957); U. S. Patent 2,892,871 (1959).

(8) Using a potassium hydroxide trap and a chloroform-Dry Ice trap.

45-min, intervals (through the condenser), followed by the addition of 80 ml. of phosphoryl chloride and gradual raising of the bath temperature to 84° (2 hr.). The resulting clear solution was kept overnight at room temperature, and the solvents were removed in three steps: (a) at atmospheric pressure (bath temp., 28-160°); (b) at 15 mm.; and (c) at⁸ 0.25 mm. (bath temp., 80-98°), affording 270 g. of brown gum. This was dissolved in 200 ml. of chloroform, the flask was closed by a stopper bearing a pentane thermometer, and the solution was cooled to 0° in ice-salt. Absolute ethanol (45 ml.) was now added (in portions, at 5-min. intervals) so that the temperature did not exceed 2°, and the solution was evaporated under diminished pressure, with addition of six 25-ml. portions of absolute ethanol, to give an almost solid mass of colorless crystals. The suspension was refrigerated, filtered with suction (rubber dam), and the crystals dried in a vacuum desiccator; wt., 117.2 g. The mother liquor afforded a further 74.0 g. of colorless crystals (total yield, 191.2 g. or 99.5%). For recrystallization, the salt was dissolved in 3 vol. of boiling absolute ethanol under reflux, the hot solution filtered, and the filtrate cooled; m.p. $159-160^{\circ}$ (lit. m.p., $155-157^{\circ}, 158^{\circ}, ^{4.6}, 156-158^{\circ}, ^{5}, 155-158^{\circ7}$). Anal. Calcd. for C₈H₁₁Cl₂N: C, 50.02; H, 5.77; Cl, 36.92;

N, 7.29. Found: C, 49.96; H, 5.97; Cl, 36.30; N, 7.62.

N-(2-Chloroethyl)-4-(phenylazo)aniline hydrochloride (III). Aniline (9.3 g.; 0.1 mole) in 125 ml. of 2 N hydrochloric acid at 0° was diazotized with 6.9 g. of sodium nitrite in 100 ml. of water at 0°. The solution of benzenediazonium chloride (at 0°) was slowly added (10 min.), with stirring, to a solution of 19.2 g. of II in 250 ml. of absolute methanol at 0°. The mixture was then stirred during a further 4 hr.; after 1 hr. at 0°, the temperature was allowed to rise slowly to room temperature. Dark-red crystals gradually separated; these were removed by filtration and dried to constant weight at 0.1 mm. at 25°; wt., 10.0 g. The mother liquor, kept overnight at 0°, afforded a further 2.7 g. of crystals. A portion (8.6 g.) of the crystals was shaken with 258 ml. (30 vol.) of absolute ethanol, the suspension was filtered, and to the filtrate was added 3.0 ml. of concentrated hydrochloric acid, giving 7.2 g. of dark red crystals, m.p. 178–179°. Anal. Calcd. for $C_{14}H_{15}Cl_2N_3$: C, 56.77; H, 5.11; Cl, 23.94;

N, 14.19. Found: C, 56.39; H, 5.34; Cl, 23.88; N, 14.13.

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The Reaction of Phosphorus Pentachloride with N-Methyltrifluoroacetamide. N-Methyltrifluoroacetimidoyl Chloride and 1,3-Dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine

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The reaction of mono-N-substituted amides with phosphorus pentachloride is a much used and general preparative method for imidoyl chlorides.¹ In the various sources investigated the only products mentioned were the imidoyl chloride,

^{(1) (}a) H. Eilingsfeld, M. Seefelder, and H. Weidinger, Angew. Chem., 72, 836 (1960). (b) J v. Braun and W. Rudolph, Ber., 67B, 1762 (1934). (c) A. H. Blatt, Org. Syntheses, III, 818 (1955).

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phosphorus oxychloride, and hydrogen chloride. The yields of imidoyl chlorides are frequently not mentioned, as the crude product may be used directly in the next step of a reaction sequence.¹⁰ Consequently it is generally not possible to judge if, and to what extent, side reactions have occurred. The reaction of *N*-methyltrifluoroacetamide with phosphorus pentachloride is one case in which a "side reaction" becomes the main reaction. Fortyfour per cent of the expected *N*-methyltrifluoroacetimidoyl chloride (I) and 52% of 1,3-dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine (II) were formed. ion attacks nitrogen rather than oxygen. The O

$$CF_{s}CNHCH_{s} + PCL^{+} \longrightarrow IV + H^{+}$$

strongly electronegative trifluoromethyl group may have a leveling effect upon the electron densities of the nitrogen and the oxygen of the amide making them about equally attractive, electrostatically speaking, to the phosphonium ion. At the present no data are available which could be used to confirm or reject either route.

N-Methyltrifluoroacetimidoyl chloride (I) is a stable low boiling liquid. Its stability would be



The reaction is almost equally divided along routes a and b. Imidoyl chloride formation (route a) probably proceeds by initial attack of the tetrachlorophosphonium ion on the oxygen of Nmethyltrifluoroacetamide to give the intermediate,

$$\begin{array}{c} O \\ CF_{3}CNHCH_{3} + PCl_{4}^{+} \longrightarrow \begin{bmatrix} O - PCl_{4} \\ CF_{3}C = NCH_{3} \end{bmatrix} + H^{+} \\ III \\ III \\ & \begin{array}{c} Cl \\ I \\ III \\ & \end{array} \\ CF_{3}C = NCH_{3} + POCl_{3} \\ I \end{array}$$

III which, in turn, would give I by a nucleophilic attack of chloride ion on the imidoyl carbon or by an intramolecular displacement by chloride (SNi) from the internal phosphorus tetrachloride group.

The formation of trifluoroacetyl chloride and the diazadiphosphetidine, II (route b), may occur by an intramolecular rearrangement of III to give IV followed by either an SN2 attack of chloride ion or an SNi reaction to give trifluoroacetyl chloride and N-methyltrichlorophosphinimine. The latter then dimerizes to give II.



Intermediate 1V also could be formed by an alternative path in which tetrachlorophosphonium

expected in the absence of hydrogen on the carbon adjacent to the imidoyl carbon.^{1b} The infrared spectrum shows a strong band at 5.90 μ due to the >C=N⁻ stretching frequency. Dry hydrogen chloride and I form a solid addition compound which is stable up to about -20° . The composition of the complex was not determined, but it is probably a one-to-one adduct by analogy with the trichloroacetimidoyl chloride-hydrogen chloride adduct and certain N-substituted imidoyl chloridehydrogen chloride adducts.²

1,3-Dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine (II) is a white crystalline solid melting at 174-179°. The melt begins to evolve gas at 250°. The same compound was prepared by Chapman et al.,³ by the reaction of phosphorus pentachloride with methylammonium chloride. These authors report a melting point of 160° with decomposition. However, the infrared spectrum of their compound is the same as that of compound II. The molecular weight of II was determined by mass spectrometry.⁴ Parent peaks were observed at 330, 332, 334, 336, and 338 in intensities approximating the calculated relative intensities of 18, 36, 30, 13, and 3, respectively, based on the Cl³⁵ and Cl³⁷ isotope distribution expected for a compound containing six chlorine atoms. The calculated relative amounts of masses 340 and 342 are very small and were not detectable. There were no peaks observed beyond 338 indicating the absence of trimer or tetramer. Fractional sublimation failed to reveal any material less

⁽²⁾ v. F. Klages and W. Grill, Ann., 594, 21 (1955).

⁽³⁾ A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, *J. Chem. Soc.*, 1825 (1961).

⁽⁴⁾ The mass spectrum was determined by Maynard H. Hunt of this laboratory on a Bendix Model 12 mass spectrometer.

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volatile than the dimer, again ruling out higher polymers.

The proton magnetic resonance spectrum of II was obtained in phosphorus oxychloride at 105° to differentiate between the two possible isomeric structures, II and V.⁵ The spectrum was a simple



1:2:1 triplet which would result from the coupling of each proton with two symmetrically disposed phosphorus atoms as in II. The proton magnetic resonance spectrum of V would consist of a doubled doublet-i.e., four lines of equal intensity. This confirms structure II. Chapman et al.³ also proposed structure II on the basis of infrared and Raman spectra and other data.

The unusual stability of this compound, as indicated by its thermal stability and ascribed by Chapman³ to the delocalization of the ring electrons, is being investigated further.

Michaelis⁶ proposed an alternating phosphorusnitrogen four-membered ring for his phosphinimine dimer $(C_6H_5N-POCl)_2$, and it is likely that the N-phenyltrichlorophosphinimine reported by Gilpin⁷ was also a dimer containing the same fourmembered phosphorus-nitrogen ring.

It seems reasonable that compound II, its homologs, and analogs have previously been formed in other reactions of phosphorus pentachloride and N-alkyl- or N-arylamides of various organic acids but have gone undetected, either because they occurred only in small amounts, or because the imidoyl chlorides were used without purification.

EXPERIMENTAL

Reaction of N-methyltrifluoroacetamide with phosphorus pentachloride. One hundred and forty grams (1.1 moles) of N-methyltrifluoroacetamide and 230 g. (1.1 moles) of phosphorus pentachloride were combined in a 500-ml. round bottomed flask fitted with a Vigreux column and a distillation head leading to a Dry Ice-acetone trap. The reaction vessel was heated to melt the amide and gas evolution commenced immediately. Heating was continued to maintain a brisk evolution of gas. Gas evolution ceased when all the phosphorus pentachloride had dissolved. Heating was continued until the distillate temperature reached 60°.

N-Methyltrifluoroacetimidoyl chloride (I). The condensate in the trap was distilled to give 49 g. of low boiling material and 70 g. (44% yield) of N-methyltrifluoroacetimidoyl chloride, b.p. $47-48^{\circ}/705$ mm. The infrared absorption spectrum showed a very strong sharp band at 5.90 μ attributed to the >C=N⁻, and the typical trifluoromethyl group bands in the 8 to 9 μ region.

(5) The NMR spectrum of II was recorded and interpreted by Donald W. Moore of this laboratory.

- (6) A. Michaelis, Ann., 407, 290 (1915).
 (7) J. E. Gilpin, Am. Chem. J., 29, 352 (1897).

Anal. Caled. for C3H3ClF3N: C, 24.76; H, 2.07; Cl, 24.37 F, 39.17. Found: C, 24.68; H, 2.28; Cl, 24.62; F, 39.20.

Trifluoroacetyl chloride. The 49 g. of low boiling material, which was recondensed in a Dry Ice-acetone trap, contained an appreciable amount of solid at -78° . An infrared spectrum at 15 mm. pressure of the gas, formed by warming the condensate, was identical with the spectrum of trifluoroacetyl chloride at the same pressure. At 440 mm. pressure the infrared spectrum of the gas from the condensate, gave, in addition to the trifluoroacetyl chloride spectrum, bands at 3.38 μ and 3.54 μ , due to the presence of hydrogen chloride,⁸ and a small peak at 5.90 μ , due to the presence of a small amount of N-methyltrifluoroacetimidoyl chloride.

Trifluoroacetyl chloride and hydrogen chloride do not form a solid complex at -78° , but *N*-methyltrifluoroacetim-idoyl chloride, a liquid at -78° , combines with hydrogen chloride to give a solid which accounts for the solid in the trap at -78° . The solid was warmed slowly from -78° to -20° with no sign of melting or dissociation. Above -20° shrinkage began to occur and at -10° the solid liquified and gas evolution occurred.

1,3-Dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine (II). The residue in the initial reaction vessel was heated on the steam bath under reduced pressure to remove the phosphorus oxychloride, leaving 87 g. (52% yield) of 1,3 - dimethyl - 2,2,2,4,4,4 - hexachloro - 1,3,2,4 - diazadiphosphetidine, m.p. 170-176°. Sublimation at 140°/0.1 mm., gave II, m.p. 174-179°. When the melt was further heated in the capillary melting point tube gas evolution occurred at 250°.

Anal. Caled. for CH₃Cl₃NP: C, 7.22; H, 1.82; Cl, 63.93; N, 8.42; P, 18.61. Found: C, 7.63; H, 2.41; Cl, 63.16; N, 8.42; P, 18.46.

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(8) R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, Anal. Chem., 28, 1239 (1956).

Synthesis of Phenyl-1,2-ethenediol Cyclic Carbonate¹

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Previous reports describe the synthesis and polymerization of 1,2-ethenediol cyclic carbonate (I, vinylene carbonate).² Compared to other 1,2disubstituted ethylenes, the ring structure of I appeared to enhance the reactivity in vinyl poly-

⁽¹⁾ Presented in part before the Division of Organic Chemistry at the 140th National Meeting, American Chemical Society, Chicago, Ill., September 1961.

^{(2) (}a) M. S. Newman and R. W. Addor, J. Am. Chem. Soc., 75, 1263 (1953); 77, 3789 (1955). (b) K. Hayashi and G. Smets, J. Polymer Sci., 27, 275 (1958). (c) J. M. Judge and C. C. Price, J. Polymer Sci., 40, 439 (1959). (d) C. G. Overberger, H. Biletch, and R. G. Nickerson, J. Polymer Sci., 27, 381 (1958). (e) W. K. Johnson and T. L. Patton J. Org. Chem., 25, 1042 (1960).