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SYNTHESIS OF N,N,N'-TRICHLOROAMIDINES BY A NOVEL OXIDATIVE CHLORINATION REACTION

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The syntheses of mono substituted halo amidines have been reported and, in general, involve the displacement of one hydrogen atom of an amidine group with chlorine, bromine, or iodine (1,2). N-Chloroformamidine and N-chloroacetamidine have been prepared in high yield by the action of hypochlorous acid on the corresponding amidine hydrochloride. N-Iodobenzamidine has been prepared by the action of basic iodine-potassium iodide solution on benzamidine hydrochloride (3). Other syntheses of N-halo amidines have been described using N-alkyl and N-aryl substituted amidines (4). We wish to report the synthesis of the first examples of N,N,N'-trichloroamidines, by a novel method of chlorination involving the oxidation of chloride ion with fluorine, and the use of the N,N,N'-trichloroamidines as chlorinating agents for olefins.

Excellent yields of N,N,N'-trichloroamidines were prepared by bubbling a mixture of 5% to 20% fluorine in nitrogen through an aqueous solution of an alkyl amidine hydrochloride and excess potassium chloride. The reactions were carried out at 0°C (5) in a glass tube without stirring. The N,N,N'-trichloroamidines separated out as heavy orange liquids and were isolated by extracting with fluorotrichloromethane, drying the extracts, and removing the solvent in vacuo. At this point the trichloroamidines are better than 95% pure and can be further purified by vacuum distillation.

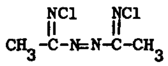
N,N,N'-trichloroamidines are light yellow liquids which possess a sharp, chlorine-like odor.

When butyramidine hydrochloride was chlorinated in this manner, a 90% yield of N,N,N'-trichlorobutyramidine (I) was obtained: b.p. 34°-35°C/0.15 mm; n_D^{25} 1.5266; λ_{max} 3.32μ, 6.23μ, 6.82μ, 8.01μ, 8.51μ, 14.22μ; n.m.r. of neat sample, 7.20τ ($-C\underline{H}_2-C{=}N-$), 8.26 ($CH_3-C\underline{H}_2$), 8.99 ($C\underline{H}_3-$). Elemental analysis requires C, 25.33; H, 3.72; N, 14.78; Cl, 56.07. Found: C, 26.00; H, 3.96; N, 14.61; Cl, 55.43. Similarly, chlorination of acetamidine hydrochloride gave a 65% yield of N,N,N'-trichloroacetamidine (II): b.p. 50°-51°C/4.5 mm; λ_{max} 6.22μ, 7.02μ, 7.32μ, 8.34μ, 11.08μ, 12.67μ, 14.3μ. Elemental analysis requires C, 14.88; H, 1.87; N, 17.36; Cl, 65.87. Found: C, 15.3; H, 1.8; N, 17.33; Cl, 65.7. The chlorination of heptafluorobutyramidine hydrochloride, however, yielded only the mono-chlorinated product, N'-chloro-heptafluorobutyramidine (III), m.p. 27°C; λ_{max} 2.96μ, 6.05μ, 7.47μ, 8.0-8.5μ, 8.90μ, 10.33μ, 10.80μ, 13.28μ; n.m.r. 4.31τ ($-NH_2$). Elemental analysis requires C, 19.48; H, 0.82; N, 11.37; Cl, 14.38. Found: C, 19.8; H, 0.84; N, 11.01; Cl, 13.78.

It was found that compounds I, II, and III could also be prepared by using hypochlorous acid or chlorine gas as the chlorinating agent. However, the yields were poor, 5% to 10%, and a large amount of decomposition products accompanied the reactions. It is evident that, in these systems and in the fluorine-KCl system, the chloronium ion is the chlorinating agent. In the fluorine-KCl system, chloride ion is oxidized by fluorine to chloronium ion which in turn displaces an amidine hydrogen, giving the overall effect of the equation,

$$2\ RC(=NH)NH_2 + 6\ Cl^- + 3F_2 \longrightarrow 2\ RC(=NCl)NCl_2 + 6\ HF$$

Both I and II are stable but are reactive compounds. When dissolved in methylene chloride and treated with a catalytic amount of activated charcoal, one-half equivalent of chlorine gas was liberated. With olefins they reacted to give good yields of the corresponding 1,2-dichlorohydrocarbon. Compound II reacted with 1-octene and cyclohexene yielding 1,2-dichloroöctane and *trans*-1,2-dichlorocyclohexane, respectively, and bis(N-chloroacetimido)azene (IV).



$$CH_3-\overset{\overset{NCl}{\|}}{C}-N=N-\overset{\overset{NCl}{\|}}{C}-CH_3$$

IV

Compound IV is an orange crystalline solid, possessing a sharp chlorine-like odor: m.p. 81°; I.R., λ_{max}^{nujol} 6.27μ, 8.25μ, 9.70μ, 10.15μ, 11.48μ, 13.5μ; n.m.r. in $CDCl_3$ 7.51τ ($-CH_3$); λ_{max}^{hexane} 273mμ; log ε = 4.26. Elemental analysis requires C, 26.01; H, 3.31; N, 30.6; Cl, 38.8. Found: C, 26.01; H, 3.65; N, 30.42; Cl, 40.18. Molecular weight requires 181; found: 183.

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5. When the reaction involving fluorine and butyramidine hydrochloride was carried out at ambient temperature, only butyramidine hydrofluoride was produced.