Reaction of t-Alkyl Chlorides with Trichloramine–Aluminium Chloride

By P. KOVACIC and M. K. LOWERY

(Department of Chemistry, Case Institute of Technology, Cleveland, Ohio)

WE have discovered a new method for the formation of t-alkyl amines involving treatment of the corresponding t-alkyl chloride with trichloramine in the presence of aluminium chloride. From t-butyl chloride and t-pentyl chloride, the corresponding amines were formed in yields of 88% and 82%, respectively, based on an equimolar relationship between trichloramine and basic product. The compounds were identified by comparison with the authentic materials.

Best results were realized with substrate: trichloramine: aluminium chloride in 4 : 1 : 2 molar ratio at −10°. The overall procedure was similar to those previously reported,[1,2] except that the alkyl halide was added to a mixture of the other reaction components. The amine product was steam distilled into dilute hydrochloric acid. Evaporation under reduced pressure provided the amine hydrochloride which, on treatment with 50% caustic alkali and subsequent distillation, gave the free amine.

The following mechanism is suggested.

$$Cl_3N + AlCl_3 \rightleftarrows Cl^{\delta+}(Cl_2NAlCl_3)^{\delta-}$$

$$RCl \xrightarrow[AlCl_3]{-Cl^-} R^+ \xrightarrow{NCl_2^-} RNCl_2 \xrightarrow[-Cl^+]{+H^+} RNH_2$$

In a control experiment carried out in the absence of aluminium chloride, no reaction occurred. The catalyst apparently complexes with the alkyl halide to form a carbonium ion which is then attacked by the nitrogen-containing nucleophile. A somewhat arbitrary designation, NCl_2^-, is used for the nucleophile since its exact nature is not known.[1b] It is significant that with the appropriate reaction conditions and work-up procedure, we were able to isolate *NN*-dichloro-t-butylamine from t-butyl chloride as precursor. The authentic material[3] used for characterization was prepared from t-butylamine and calcium hypochlorite.

Our prior use of trichloramine–aluminium chloride for amination involved aromatic compounds[1] and alkanes[2] as substrates. The present work provides good evidence for participation of carbonium ion intermediates.

Investigation of the neutral layer yielded various polychlorinated isobutanes, including 1,2,3-trichloro-2-methylpropane, 1,1,2,3-tetrachloro-2-methylpropane, and 1,2,3-trichloro-2-chloromethylpropane (identified by elemental analyses, n.m.r. spectra, and comparison of their physical properties with the literature values[4]). A reasonable reaction pathway is given (illustrated with 1,2,3-trichloro-2-methylpropane).

$$(CH_3)_3\cdot CCl \xrightarrow[-HCl]{AlCl_3} (CH_3)_2\cdot C{=}CH_2 \xrightarrow{+Cl^+}$$

$$(CH_3)_2\cdot\overset{+}{C}CH_2Cl \xrightarrow{-H^+} CH_2{=}C(Me)\cdot CH_2Cl \xrightarrow{+Cl^+}$$

$$ClCH_2\cdot\overset{+}{C}(Me)\cdot CH_2Cl \xrightarrow{+Cl^-} (ClCH_2)_2\cdot C(Me)Cl$$

Trichloramine, chlorine, and $RNCl_2$ could serve as sources of chloronium-type ion.

The reaction of trichloramine with t-alkyl chlorides provides a novel method for the synthesis of t-alkyl amines. The interesting specificity of the nucleophile is emphasized by the easy elimination which occurs on treatment of t-alkyl halides with amines.[5] With few exceptions, *e.g.*, the Ritter reaction, the classical routes to t-carbinamines are characterized by a multiplicity of steps.[5] The Ritter technique has been utilized for preparation of t-butylamine and t-pentylamine in a two-step sequence entailing use of an olefin or alcohol as substrate.[6,7]

(Received, August 16th, 1966; Com. 606.)

---

[1] (a) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Amer. Chem. Soc.*, 1965, **87**, 1262; (b) P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, 1966, **88**, 100; (c) P. Kovacic and J. A. Levisky, *ibid.*, p. 1000.

[2] P. Kovacic, R. J. Hopper, S. S. Chaudhary, J. A. Levisky, and V. A. Liepkalns, *Chem. Comm.*, 1966, 232.

[3] H. Zimmer and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1954, **76**, 3856.

[4] A. O. Rogers and R. E. Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 1027.

[5] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", Wiley, New York, 1953, ch. 24.

[6] J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, 1948, **70**, 4048.

[7] M. Mousseron, R. Jacquier, and H. Christol, *Bull. Soc. chim. France*, 1957, 600.