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Leo A. Paquette,* Robert H. Meisinger
Robert E. Wingard, Jr.[19]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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1,2-Alkyl Shift, from Carbon to Positive Nitrogen, in Simple, Open-Chain *N*,*N*-Dichloroalkylamines

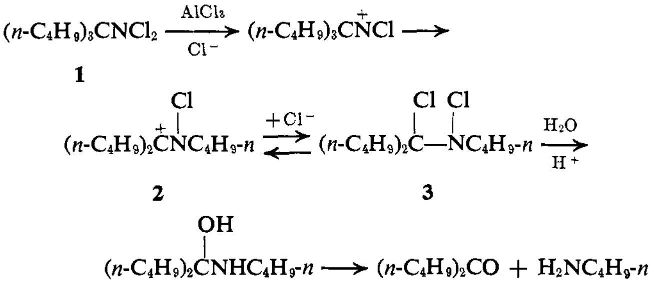
Sir:

1,2-Alkyl shifts from carbon to carbon[1a] and from carbon to oxygen[1b] involving electron-deficient species are well established for uncomplicated alkyl structures. However, apparently no analogous situation has been observed for rearrangement from carbon to positive nitrogen arising from an *N*-halamine. Examples in this category which are reported[2,3] contain mono-, bi-, or tricyclic units characterized by some degree of strain, usually quite appreciable. The Stieglitz rearrangement,[2] believed to fit in this general class, entails migration of an aryl group.

We now present the first examples of 1,2-alkyl shift from carbon to electron-deficient nitrogen generated from simple, open-chain *N*-halamines. The reactions proceeded quite cleanly in high yields. Treatment of *N*,*N*-dichlorotri-*n*-butylcarbinamine (**1**) with aluminum chloride gave a rearranged product which was converted to *n*-butylamine (84% yield) and di-*n*-butyl ketone (94% yield) on exposure to aqueous acid. Similarly, *N*,*N*-dichlorodi-*n*-butyl-*sec*-butylcarbinamine formed *sec*-butylamine (51% yield) and *n*-butylamine (46% yield), along with di-*n*-butyl ketone (55% yield) and *n*-butyl *sec*-butyl ketone (43% yield).

By analogy to prior mechanistic interpretations,[2,3] the reaction is thought to take place according to the indicated pathway (Scheme I).

Scheme I



$$(n\text{-}C_4H_9)_3CNCl_2 \xrightarrow[Cl^-]{AlCl_3} (n\text{-}C_4H_9)_3C\overset{+}{N}Cl \longrightarrow$$

1

$$(n\text{-}C_4H_9)_2\overset{+}{C}(Cl)NC_4H_9\text{-}n \underset{}{\overset{+Cl^-}{\rightleftharpoons}} (n\text{-}C_4H_9)_2C(Cl)\text{—}N(Cl)C_4H_9\text{-}n \xrightarrow[H^+]{H_2O}$$

2 **3**

$$(n\text{-}C_4H_9)_2C(OH)NHC_4H_9\text{-}n \longrightarrow (n\text{-}C_4H_9)_2CO + H_2NC_4H_9\text{-}n$$

In the absence of catalyst, rearrangement was negligible. There is little basis for comment concerning the synchronous *vs.* stepwise nature of the migration. Rearranged product might be in the form of either **2** or **3**. The similarity in the ratio of *sec*-butylamine:*n*-butylamine (1.1) to the ratio of di-*n*-butyl ketone:*n*-butyl *sec*-butyl ketone (1.3) from *N*,*N*-dichloro-di-*n*-butyl-*sec*-butylcarbinamine supports the proposed scheme, as does the close correspondence in yields of *n*-butylamine and di-*n*-butyl ketone from **1**. The order of migratory aptitudes, *sec*-butyl:*n*-butyl = 2.2 (statistically corrected), is also in keeping with the mechanistic approach.

Our investigation of the open-chain types is continuing. The indicated procedure was followed. **1** was obtained by chlorination[4] (1 hr) of tri-*n*-butylcarbinamine.[5] A mixture of crude **1** (~0.025 mol) and aluminum chloride (0.05 mol) in 60 ml of methylene chloride was stirred at $-30°$ for 1.5 hr. After addition of concentrated hydrochloric acid, solvent was removed *in vacuo*. Steam distillation gave ketone product in the volatile fraction. Extraction of the residue with methylene chloride provided minor amounts of starting amine hydrochloride and intractable solid. The aqueous acid portion was made basic and distilled into acid for the isolation of *n*-butylamine.

Di-*n*-butyl-*sec*-butylcarbinamine, bp 75.5° (0.28 mm), prepared according to the procedure[5] for the tri-*n*-butyl analog, was characterized by ir and nmr spectra and elemental analyses.

Yields are based on the *N*,*N*-dichloramine with the assumption of minor contamination by *N*-chloramine.

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Timothy A. Kling, Myrna B. Nazareno, Peter Kovacic*
Department of Chemistry, University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

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