A Convenient New Synthesis of t-Alkyl Amines. Amination of the Methine Group with Trichloramine-Aluminium Chloride

By P. KOVACIC, R. J. HOPPER, S. S. CHAUDHARY, J. A. LEVISKY, and V. A. LIEPKALNS

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

IN connection with our investigations of Lewis acid-catalyzed reactions of *N*-halogenoamines, we now report a novel synthesis for t-alkyl amines which has significant theoretical and practical implications. Treatment of methylcyclohexane and *p*-cymene with trichloramine in the presence of aluminium chloride produced 1-amino-1-methylcyclohexane and 8-amino-*p*-cymene, respectively. This is apparently the first example of a one-step synthesis of an alkylamine from the corresponding alkane structure.

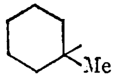
Aminations were carried out with substrate–trichloramine–aluminium chloride in 1–0·1–0·2 molar ratio at 0—10°. The halogenoamine was used as a solution in methylene chloride (with methylcyclohexane) or in ethylene dichloride (with *p*-cymene). The overall procedures were similar to those previously reported.[1,2] On the basis of an equimolar relationship between trichloramine and amine product, methylcyclohexane gave an 83% yield of 1-amino-1-methylcyclohexane. Characterization was accomplished by comparison with authentic material prepared from 1-methylcyclohexene by the Ritter method.[3,4] In the case of *p*-cymene, when t-butyl bromide (equimolar to the catalyst) was incorporated into the reaction mixture, an 80% yield of 8-amino-*p*-cymene, b.p. 76—77°/5·2 mm., n_D^{25} 1·5135, was obtained. This new substance was identified by elemental analysis, n.m.r. and infrared spectra, and comparison with authentic amine provided by an alternate route (adaptation of literature procedures).[5]

In a discussion of the theoretical aspects, attention should be directed to our prior studies of aromatic amination with trichloramine–aluminium chloride.[1,2] Unusual orientation effects were generally observed. For example, alkylbenzenes afforded the *meta*-amino-derivatives as the major basic product. Investigations of the relative reactivities of benzene and alkylbenzenes indicated that σ-complex formation constituted the rate-determining step in amination.[6] On the basis of diverse evidence, a σ-substitution (addition–elimination) mechanism was proposed, *i.e.*, initial generation of a chlorarenonium ion through attack on the aromatic substrate by electrophilic chlorine, subsequent attachment of the nitrogen-containing nucleophile, and then rearomatization *via* elimination of hydrogen chloride.[1,2,6] Concerning this interesting nucleophile which possesses intriguing specificity, there is uncertainty as to which of the various possibilities is actually involved.[2] For the sake of simplicity, amide ion will be employed in the present discussion.

For amination entailing the C–H linkage, the illustrated reaction sequence is postulated.

$$RH \xrightarrow{-H^-} R^+ \xrightarrow{+NH_2^-} RNH_2$$

R=



or p-Me·C_6H_4·CMe_2—

From control experiments carried out with omission of aluminium chloride, no basic organic product was generated. In the absence of t-butyl bromide, apparently hydride abstraction is effected by chloronium ion arising from the complex, $Cl^{\delta+}Cl_2N^{\delta-} \dashrightarrow AlCl_3$. An analogous pathway for carbonium ion formation has been proposed as a mechanistic feature of adamantane bromination.[7] Alternative possibilities will be discussed in the full publication. There can be little doubt that when the alkyl halide is added, presence of the t-butyl cation favours formation of the t-benzyl counterpart. Direct evidence for the hydride mechanism was provided by isolation of isobutane from a similar experiment with t-butyl chloride.

When p-cymene was aminated in the absence of t-butyl halide, the crude base (about 40% yield) consisted of a gross mixture including 8-amino-p-cymene, 2- and 3-amino-p-cymene, 5-amino-m-cymene, and toluidine. The side-chain amine, present in 10% yield, comprised the principal component. These results point to competition for the chloronium ion by the side-chain and aromatic nucleus. With methylcyclohexane, the electrophile would be involved more or less exclusively in the abstraction process.

In terms of synthetic utility, this novel method displays marked promise. Only a very limited number of procedures, *e.g.*, the Ritter reaction, are available for preparation of t-carbinamines.[3] In most cases the previous techniques[8] are characterized by a multiplicity of steps[5] and low yields. In sharp contrast, the alkane–trichloramine–aluminium chloride combination provides high yields of t-alkyl amines by a simple, one-step method. Distillation furnished the products in high purity.

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