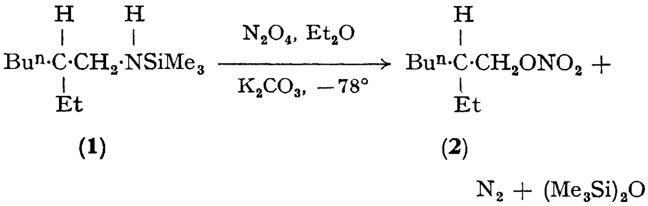
Nitrodeamination of a Trimethylsilylamine: Conversion of Amines into Nitrates

By FRED WUDL* and THOMAS B. K. LEE

(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York,* 14214)

Summary Treatment of *N*-2-ethylhexyl-*N*-trimethylsilylamine with dinitrogen tetroxide affords 2-ethylhexyl nitrate in fair yield.

REACTION between dinitrogen tetroxide and hexylamine in dichloromethane at −80°, as reported by White and Feldman,[1] afforded hexylnitroamine (53% yield) and hexyl nitrate (6% yield). We have found that trimethylsilylation of the amine function changes the course of the reaction drastically. Thus, *N*-2-ethylhexyl-*N*-trimethylsilylamine† may be deaminated cleanly at −78° with N_2O_4 to afford 2-ethylhexyl nitrate in *ca.* 60% yield.



$$\mathrm{Bu^{n}\cdot\overset{H}{\underset{Et}{C}}\cdot CH_2\cdot\overset{H}{N}SiMe_3 \xrightarrow[K_2CO_3,\ -78^{\circ}]{N_2O_4,\ Et_2O} Bu^{n}\cdot\overset{H}{\underset{Et}{C}}\cdot CH_2ONO_2 + N_2 + (Me_3Si)_2O}$$

(1) **(2)**

In a typical experiment, when a solution of 1 equiv. of N_2O_4 (Matheson) in anhydrous ether was added to a well-stirred suspension of anhydrous potassium carbonate in a solution of (**1**) in anhydrous ether at −78°, a fast, quantitative evolution of nitrogen occurred within $\frac{1}{2}$ to 1 min.‡

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† The commercially available amine was trimethylsilylated with Pierce Chemical's "tri-sil" and the product distilled. Gas chromatographic analysis (ref. 4) of the product showed *ca.* 1% of non-silylated amine and a trace of hexamethyldisiloxane.

‡ The nitrogen was collected over water in a calibrated cylinder. An induction period of *ca.* 1 min. was sometimes observed before nitrogen evolution began.

At room temperature, the reaction mixture was treated with water, the layers were separated, and the organic phase was dried and evaporated to give a yellow oil (*ca.* 70%). G.c. analysis§ showed only 3 minor unidentified peaks (*ca.* 20%) and a major peak (*ca.* 80%) corresponding to (**2**). A sample purified *via* preparative g.c. had the following spectroscopic properties:¶ n.m.r. ($CDCl_3$ with Me_4Si) δ 0·9—1·9 (m, 15H), 4·45 (d, 2H); i.r. (neat) ν_{max} 2900, 1625, 1462, 1377, 1279, 987, 965, 873·4, 763 [almost identical with the i.r. spectrum of butyl nitrate (Sadtler i.r. spectrum No. 13495)]. The mass spectrum exhibited a fragmentation pattern typical of branched and long chain nitrates:[2] no M^+; base peak, m/e 57; major peaks at m/e 55, 43, 41, 39.

The data conform with the structure assigned to (**2**). A further proof of structure is the quantitative, (*ca.* 60% yield based on crude reaction mixture) reduction (lithium aluminium hydride)[3] of the nitrate to the known 2-ethylhexanol.

This nitrodeamination reaction is general; *i.e.*, trimethylsilylamino-groups attached to primary, secondary, benzylic, and secondary benzylic carbon atoms undergo the reaction with comparable yield.[4] So far, we know little about the detailed mechanism except that the deamination proceeds with retention of configuration at carbon.[4] The reaction is also very sensitive to changes in solvent and temperature.[1,4]

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§ Carbowax 20-M, 5% on Chromosorb W, 80—100 mesh, 7 ft. column. Injector, 170°; column, 105°; detector, 200°.

¶ This compound gave satisfactory elemental analysis.

[1] E. H. White and W. R. Feldman, *J. Amer. Chem. Soc.*, 1967, **79**, 5832.

[2] R. T. M. Fraser and N. C. Paul, *J. Chem. Soc.* (*B*), 1968, 659.

[3] P. A. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Benjamin, New York, 1966, vol. II, pp. 455—506.

[4] F. Wudl and T. B. K. Lee, unpublished results.