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A NOVEL METHOD OF CONVERSION OF PRIMARY AMINES INTO ALDEHYDES.

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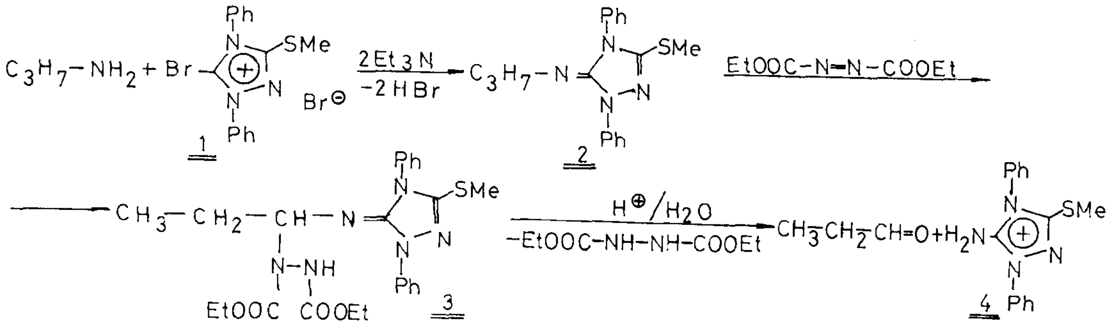
While several methods are available for the conversion of primary amines containing secondary alkyl groups into ketones, no satisfactory method exists for the conversion of primary amines containing *primary* alkyl groups into aldehydes.[1,2] I wish to describe here a novel method which may prove a suitable approach for solving the latter problem. The method is outlined in the following Scheme, using the conversion of 1-propylamine into propanal as an example.



The reagent 1 was obtained by refluxing 3-methyl-1,4-diphenylisothiosemicarbazide[3] for 2 h with 13 moles of 98-100% formic acid, adding aqueous KBr soln (8 moles), and treating the resulting 3-methylthio-1,4-diphenyl-*s*-triazolium bromide (77%; m.p. 208-9°C) in dry $CHCl_3$ solution with Br_2 (1 mole) to obtain the corresponding perbromide (85%; m.p. 146-7°C, dec); when treated with a slight excess of dry Et_3N in dry $CHCl_3$ at 0°C, the perbromide was smoothly transformed (through a nucleophilic carbene[3]) into 1 (76%; m.p. 226-7°C, dec).

1 and 1-propylamine react in the presence of 2 moles of dry Et_3N in

dry CHCl$_3$ exothermally to yield **2** (91%; m.p. 90-1°C). The latter, when refluxed with crude diethyl azodicarboxylate[4] in CHCl$_3$, furnishes **3** (89%; m.p. 151°C) which is hydrolyzed by aqueous acid to propanal (94%), diethyl 1,2-hydrazinedicarboxylate (74%) and **4** (isolated in 48% yield as the free base, m.p. 92-3°C). Isolation and purification of the intermediates **2** and **3** is unnecessary. The method has been extended for the conversion of n-decyl-, benzyl- and phenethylamine into decanal (71%), benzaldehyde (94%) and phenylacetaldehyde (46%), respectively. The isopropylamino analogue (92% yield; m.p. 130°C) of **2**, however, does not react with diethyl azodicarboxylate under similar conditions.

Compound **1** is closely related to the 2-fluoro-1-methylpyridinium ion and its analogues which have recently been succesfully applied for achieving carboxyl condensation reactions.[5] The possibility of using compound **1** as the reagent in such reactions was therefore explored. In agreement with expectation, triazole **1** and 2 equivalents, each, of benzoic acid and dry Et$_3$N at 25°C furnished benzoic anhydride (43%), 3-methylthio-1,4-diphenyl-Δ^2-*s*-triazolin-5-one (61%; m.p. 103°) and Et$_3$N.HBr (94%), while **1**, treated first at 0°C with 1 equivalent of benzoic acid and 2 equivalents of Et$_3$N and then with 1 equivalent of PhNH$_2$, gave benzanilide (62%) and the above triazolinone (79%).

All new compounds gave correct microanalyses and were characterized by their IR and PMR spectra. Known products were identified by comparison with authentic products.

References

1. V. Calo and P.E. Todesco, *J.C.S. Perkin I*, 1652 (1972)
2. E.J. Corey and Kazau Achiwa, *J.Amer.Chem.Soc*. **91**, 1429 (1968)
3. G. Doleschall, *Tetrahedron* **32**, 2549 (1976)
4. J.C. Kauer, *Org. Syntheses*, Coll. Vol. 4, p. 411 (1963)
5. *e.g.* T. Mukaiyama et al, *Heterocycles* **4**, 1707 (1976); **6**, 1509 (1977); *Chem. Lett*. 1163 (1975); 49, 741 (1976)