Deoxygenative Reduction of Nitroxyl and Carbonyl Groups

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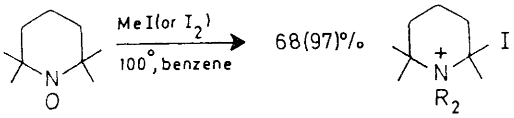
Summary 2,2,6,6-Tetramethylpiperidinoxyl reacts with methyl iodide or iodine to yield 2,2,6,6-tetramethylpiperidinium iodide; carbonyl groups are reduced to methylene by silanes in the presence of iodides.

We report the unprecedented†‡ reduction by MeI or I_2 of an alicyclic nitroxyl radical to the corresponding amine.§ The [MeI, C_6D_6] system gave (**1**; $R = 1\cdot0H$) while the [CD_3I, C_6H_6] and [CD_3I, C_6D_6] systems gave (**1**; $R = 0\cdot84D$).

We have observed reduction in good yield of the carbonyl to a methylene group in the systems (n-$C_7H_{15}COCH_3$, Ph_2SiH_2, n-$C_6H_{13}I$, 190°), (PhCHO, Ph_3SiH or Ph_2SiH_2, PhI or n-$C_6H_{13}I$, 168—190°) and (PhCOMe, Ph_2SiH_2, n-$C_6H_{13}I$ or PhI, 134—168°) in benzene, wherein the iodide is necessary for significant conversion into the hydrocarbon but is insignificantly consumed itself.



(1)

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† Aryl nitroxyls and hydroxylamines autodisproportionate thermally (2,2,6,6-tetramethylpiperidinoxyl is thermally stable in benzene at 100°) into the corresponding amine, the favoured mechanisms being inapplicable to non-aromatic compounds: A. Calder, A. R. Forrester, and S. P. Hepburn, *J.C.S. Perkin I*, 1973, **456**, and references therein.

‡ The reaction $(PhCH_2)_2NOH + PhCH_2Cl \xrightarrow{120—130°} (PhCH_2)_2\overset{+}{N}H_2Cl^-$ (28—33%) has been reported: B. Behrend and K. Leuchs, *Annalen*, 1890, **257**, 203.

§ Identified by i.r. and 270 MHz n.m.r. spectra and elemental (C,H,N,I) analysis and by comparison with the product obtained in 88% yield from the reaction between 2,2,6,6-tetramethylpiperidine and anhydrous HI in ether.