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A SIMPLE REDUCTION OF AROMATIC HETEROCYCLIC N-OXIDES WITH HEXAMETHYLDISILANE[1]: REACTIONS WITH HEXAMETHYLDISILANE AND FLUORIDE ION I

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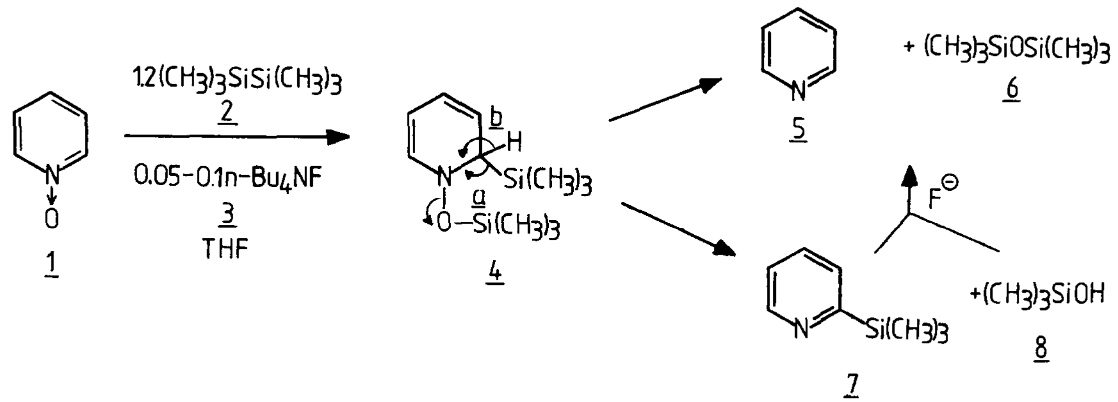
Summary: Aromatic heterocyclic N-Oxides are readily reduced at room temperature by hexamethyldisilane in the presence of fluoride ion in THF.

Pyridine-N-Oxides can be reduced by phenoxypentamethyldisilane at 135°C but not by hexamethyldisilane[2] whereas hexachlorodisilane effects such reductions at 24°C[3]. Hexamethyldisilane, however, reduces quinones at 60°C in the presence of iodine as catalyst[4].

When we reacted pyridine-N-oxide (1) with hexamethyldisilane (2) in the presence of catalytical amounts of tetrabutylammoniumfluoride (TBAF) in abs. THF[5] at room temperature in order to synthesize 2-trimethylsilylpyridine (7)[6], we found that we had smoothly converted pyridine-N-oxide (1) and hexamethyldisilane (2) into pyridine (5), which was isolated as its picrate in 90 % yield, and hexamethyldisiloxane (6). 5 and 6 were also estimated independently by GC-MS. In this reaction, it is crucial to add ca. 1.1 equiv. of hexamethyldisilane (2) in THF slowly to pyridine-N-oxide (1) and ca. 0.05 - 0.1 equiv. of TBAF (3)[5] in abs. THF whereupon the reaction temperature rises to ca. 35°C. Addition of 0.1 equiv. of TBAF (3)[5] in abs. THF to an equimolar solution of pyridine-N-Oxide (1) and hexamethyldisilane (2) in abs. THF resulted twice after an initiation-period in an explosion and complete destruction of the apparatus.



We assume that fluoride-ion cleaves the Si-Si-bond in hexamethyldisilane (2) to the "hard" trimethylsilylfluoride and the "soft" trimethylsilyl anion, which adds to the "soft" α-carbon atom in pyridine-N-oxide (1). This is followed by silylation of the "hard" N-oxide-oxygen by trimethylsilylfluoride regenerating fluoride ion. The intermediate (4) then eliminates hexamethyldisiloxane (6) via reaction path a) to afford pyridine. However we cannot as yet exclude that 2-trimethylsilylpyridine (7) is actually formed as intermediate via reaction path b) by elimination of trimethylsilanol (8), which then reacts with 2-trimethylsilylpyridine (7) in the presence of fluoride ion to afford pyridine (5) and hexamethyldisiloxane (6).

The reductions of other systems like nitrones are presently being investigated. Interestingly, Hiyama, et al. described recently7) that they could only achieve reactions between aldehydes or 1,3-dienes and hexamethyldisilane-TBAF in HMPT but not in THF.

The examples summarized in Table 1 demonstrate the scope of this reduction of heterocyclic aromatic N-oxides. 20 m mol N-oxide were usually dissolved in ca. 50 ml abs. THF and the hexamethyldisilane (2) added in ca. 10 ml abs. THF.

Table 1

N-oxide	hexamethyldisilane / TBAF5) (equiv.)	reaction-temperature and -time	tert. base (yield)
pyridine-N-oxide	1.2 / 0.05	24-35°C / 3 h	pyridine, 90 % as picrate, mp. 160°C
3-methylpyridine-N-oxide	1.1 / 0.05	18-23°C / 7 h	3-picoline, 85 % as picrate, mp. 146°C
4-dimethylamino-pyridine-N-oxide	1.5 / 0.1	24-30°C / 8 h	4-dimethylaminopyridine 84 % (DMAP), mp. 112°C
3-cyano-pyridine-N-oxide	2.0 / 0.1	24-26°C / 24 h	3-cyanopyridine, 51 %, mp. 48°C
quinoline-N-oxide	1.2 / 0.5	24-38°C / 16 h	quinoline, 72 % as picrate mp. 198°C
isoquinoline-N-oxide	1.5 / 0.05	23-26°C / 3 h	isoquinoline, 92 % distilled product

References and Notes:

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