

CONVERSION OF HETEROCYCLIC N-OXIDES INTO α -ALKYLATED HETEROCYCLES.

TRIMETHYLSILANOL AS LEAVING GROUP — IV^{1,2}.

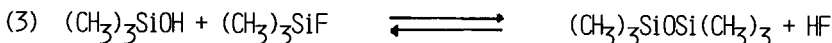
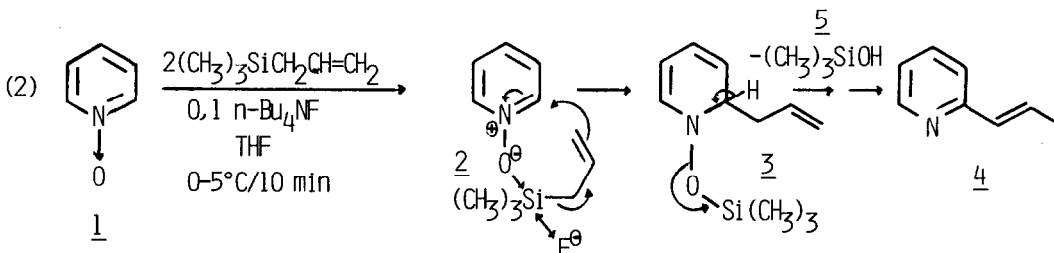
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Summary: Aromatic heterocyclic N-oxides are readily converted into α -alkylated heterocycles by allyl- or benzyltrimethylsilane and fluoride ion.

In our recently described¹ cyanation of heterocyclic aromatic N-oxides with trimethylsilyl cyanide the strong affinity of the "hard" trimethylsilyl group for the "hard" N-oxide oxygen and the "soft" cyano group for the "soft" α -carbon atom leads to a selective 1,2-addition followed by elimination of trimethylsilanol to give 2-cyanopyridines, 2-cyanoquinoline and 1-cyanoisoquinoline in high yields¹.

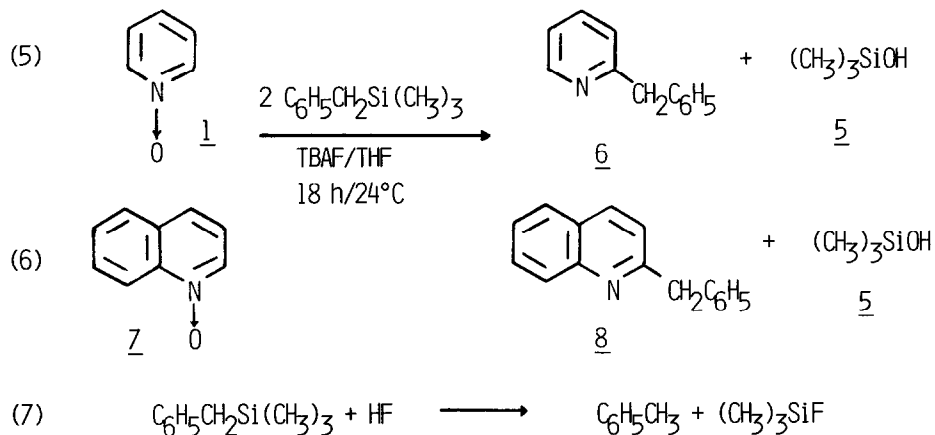
Since allyltrimethylsilane forms on treatment with tetra-n-butylammonium fluoride (TBAF) the "hard" trimethylsilyl fluoride and the tetra-n-butylammonium salt of the "soft" allylic anion^{3,4} (equation 1), we reacted anhydrous pyridine-N-oxide 1 with 2 equiv. of allyltrimethylsilane in tetrahydrofuran (THF) in the presence of 0,1 equiv. of TBNF. At +5°C the reaction proceeded in less than 10 min to afford after workup and distillation 2-propenylpyridine 4 in 56% yield as the only reaction product. 4 was identified by its typical ¹H NMR spectrum as well as by its picrate, mp. 162°C (lit.⁵ 164°C).



We assume that the reaction proceeds via the initial 1,2-adduct 3 followed by elimination of trimethylsilanol 5 to 2-allylpyridine which is isomerized during the reaction to 2-propenylpyridine 4 (equation 2). The trimethylsilanol 5 probably reacts then with trimethylsilyl fluoride to form hexamethyldisiloxane and HF (equation 3) which converts a second equivalent of allyltrimethylsilane into the volatile trimethylsilyl fluoride and propylene (equation 4).

3-Methyl as well as 4-methylpyridine-N-oxide gave analogously the 1,2-addition products 2-propenyl-3-methylpyridine (picrate mp. 173-175°C) as well as 2-propenyl-4-methylpyridine (picrate mp. 200°C dec.) in 69% and 73% yield⁶.

We furthermore reacted pyridine-N-oxide 1 and quinoline-N-oxide 7 with 2 equiv. of benzyltrimethylsilane⁷ in the presence of catalytic amounts of TBAF in THF for 1 - 2 h at +5°C and obtained 2-benzylpyridine 6 [picrate mp. 137-139°C (lit.⁸ mp. 140°C)] in 70% yield (equation 5) as well as 2-benzylquinoline 8 [picrate mp. 154°C (lit.⁹ mp. 158-159°C)] in 65% yield (equation 6).



We assume that HF generated according to equation (3) will react with the second equivalent of benzyltrimethylsilane (equation 7) to give toluene and trimethylsilyl fluoride in analogy to equation (4).

Further examples of fluoride catalyzed additions of silylated synthons to heterocyclic N-oxides and related systems will be reported in the full paper.

References

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- 6) All products were identified by their typical ¹H-NMR-spectra.
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(Received in Germany 10 December 1982)