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REDUCTION OF AROMATIC NITRO GROUPS WITH HEXAMETHYLDISILANE[1]: REACTIONS WITH HEXAMETHYLDISILANE AND FLUORIDE ION-II.[2]

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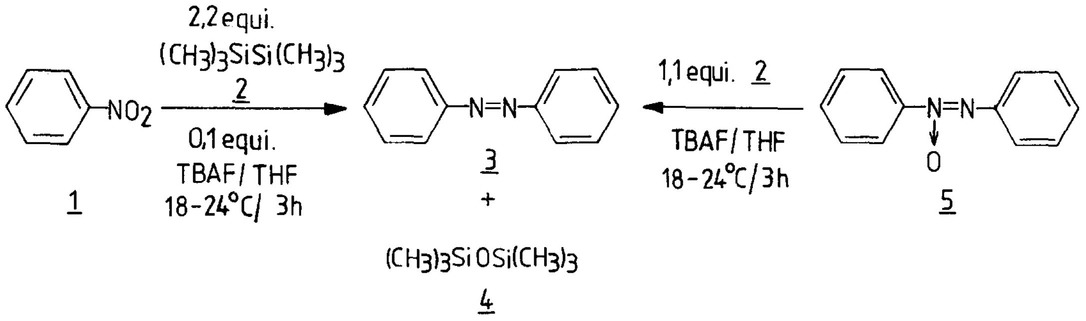
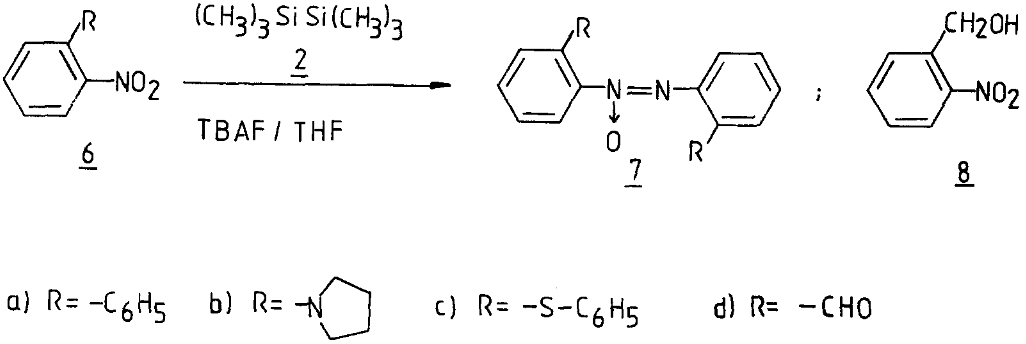
Summary: Reduction of aromatic nitro compounds with hexamethyldisilane and fluoride ion in THF at 24°C gives the corresponding azo- and azoxy compounds in high yields. Hexamethyldisilane converts commercial tetrabutylammoniumfluoride-dihydrate into a highly reactive catalyst.

The facile reduction of aromatic heterocyclic N-oxides by hexamethyldisilane at room temperature in the presence of catalytical amounts of tetrabutylammoniumfluoride (TBAF) in abs. THF[2] prompted us to reexamine the reactions of aromatic nitro compounds with hexamethyldisilane in the presence of TBAF in THF at room temperature. Zon et al.[3] had reduced nitrobenzene (1) with hexamethyldisilane (2) at 240°C to give ca. 22 % of aniline and traces of azobenzene (3), whereas 2-nitrobiphenyl afforded 42 % of carbazole and 4 % of 2-aminodiphenyl.

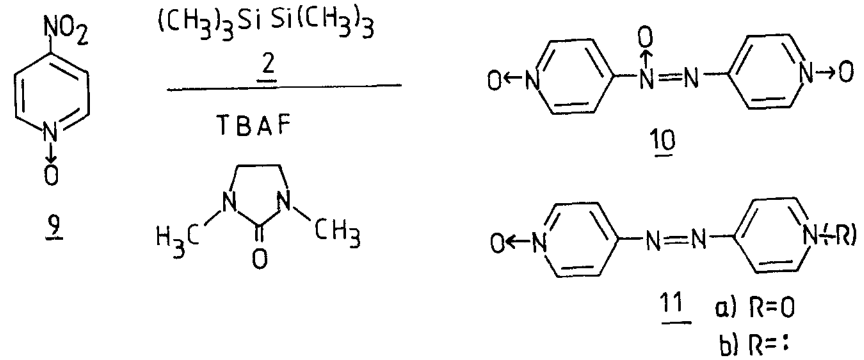
Nitrobenzene (1) reacted readily with hexamethyldisilane (2)[4] in THF in the presence of catalytical amounts of TBAF[5] at 18 - 24°C to afford azobenzene (3) in 84 % yield and hexamethyldisiloxane (4). Analogously, azoxybenzene (5) afforded azobenzene (3) in 95 % yield.



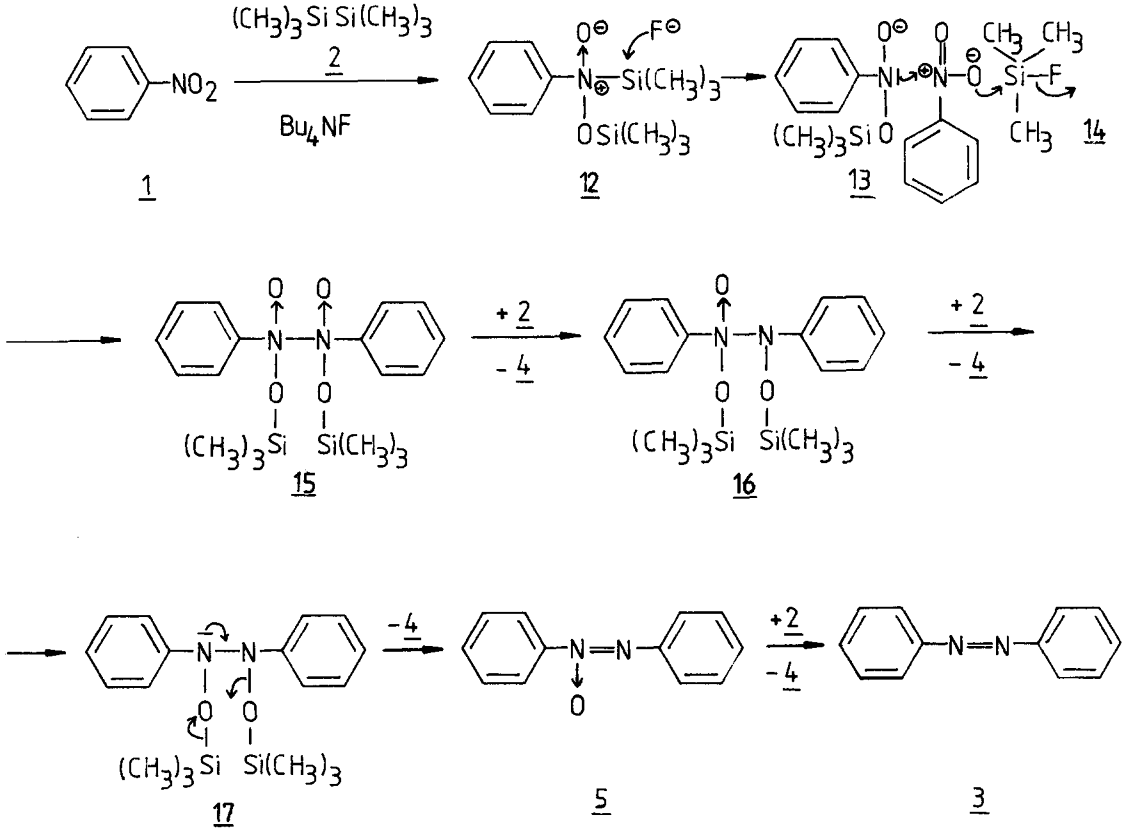
Performing reductions of (1) in 1 : 1 mixtures of THF-anisole or THF-N,N-dimethylaniline did not give any p-methoxy- or p-dimethylamino-diphenylamine, but only azobenzene (3) and azoxybenzene (5) indicating the absence of a singlet nitrene-intermediate. Furthermore, reduction of 2-substituted nitrobenzenes like 2-nitrobiphenyl (6a), 2-pyrrolidinonitrobenzene (6b) or 2-nitrodiphenylsulfide (6c) with (2) and TBAF in THF did not give any insertion products like carbazole from (6a) or phenothiazine from (6c) but exclusively the corresponding substituted azoxybenzenes (7a) (mp. 159°C)6), (7b) (mp. 129-131°C) and (7c) (mp. 93°C) in 70 - 85 % yield, as well as small amounts of the corresponding azo compounds. The bulky ortho substitutents inhibit apparently the further reduction of (7a) - (7c) to the corresponding substituted azobenzenes. Reduction of o-nitrobenzaldehyde (6d) in THF at 24°C proceeded only in the presence of equivalent amounts of TBAF5) to afford the light sensitive o-nitrobenzyl alcohol (8) (mp. 73°C) in ca. 80 % yield, but practically no azo- or azoxy compound.



Reduction of the rather polar and insoluble 4-nitropyridine-N-oxide (9) in N,N'-dimethylimidazoline-2-one7) furnished the azoxy compound (10) (mp. 229°C)8), which precipitated in 52 % yield from the reaction mixture. Chromatography of the mother liquor furnished a further amount of 26 % of (10) as well as 12 % of a mixture of the azo compounds (11a) and (11b)8). Since nitrosobenzene dimerizes with TBAF in THF to azoxybenzene (5)9), the reduction of nitrosobenzene to azobenzene (3) as well as reactions of olefinic and saturated nitro compounds with (2) and TBAF will be discussed in a future paper.



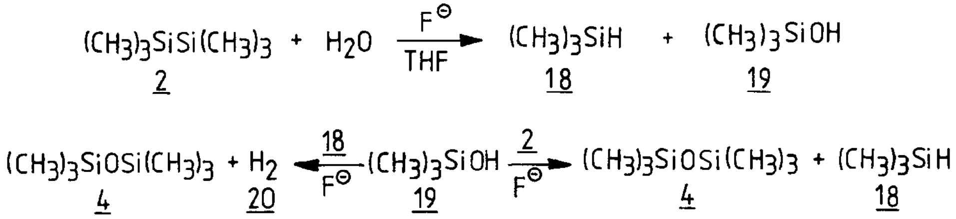
The present data suggest that hexamethyldisilane (2) adds to nitrobenzene (1) in the presence of TBAF to form (12) as the first intermediate (cf. ref. 3) which reacts with fluoride ion to (13) and $(CH_3)_3SiF$ (14). (13) will then add to nitrobenzene (1) and $(CH_3)_3SiF$ (14) to form (15), which is subsequently reduced by hexamethyldisilane (2) and TBAF to (16) and hexamethyldisiloxane (4). Further reduction of (16) by (2) leads via (17) to azoxybenzene (5), which can be detected by t.l.c. as intermediate. Finally, reduction of azoxybenzene (5) with (2) and TBAF affords azobenzene (3).



Since commercial TBAF solution[5)] contains up to 5 % H_2O it consists mainly of the dihydrate of TBAF. Gradual addition within 16 h of hexamethyldisilane (2) at 10°C to a one molar commercial solution of TBAF in THF leads to an increasingly vigorous and exothermic reaction with gas evolution, which only ceases after ca. 2 - 2.5 equivalents of (2) have been added.

Thus, hexamethyldisilane (2) reacts apparently with the water present in TBAF·2 H_2O to give the volatile trimethylsilane (18) (bp. 7°C) and via trimethylsilylfluoride (14) trimethylsilanol (19). Trimethylsilanol (19) can subsequently react either with hexamethyldisilane (2) to afford hexamethyldisiloxane (4) and trimethylsilane (18) or with trimethylsilane (18) to afford (4) and hydrogen (20). Hexamethyldisiloxane (4), trimethylsilylfluoride (14) and trimethylsilane (18)($\frac{m}{e}$ = 74, 73, 59, 43, 28) were determined by GC/MS. The resulting reactive TBAF solution in THF is stable for weeks at -24°C but decomposes gradually and sometimes violently at room temperature forming two layers which consist mainly of hexamethyldisiloxane (4), some trimethylsilylfluoride (14), n-butyl fluoride and tributylamine, the latter of which can be easily isolated by distillation.

The ready formation of trimethylsilane (18), which is formed in larger amounts, when equivalent amounts of the TBAF·2 H_2O reagent are employed, could also account for some reductions e.g. of o-nitrobenzaldehyde (6d) to o-nitrobenzyl alcohol (8). Experiments are underway to prove the suggested mechanisms and to test this highly active form of TBAF in THF[10)], which might be responsible for the smooth reactions observed so far.



$$\underset{\underline{2}}{(CH_3)_3SiSi(CH_3)_3} + H_2O \xrightarrow[THF]{F^{\ominus}} \underset{\underline{18}}{(CH_3)_3SiH} + \underset{\underline{19}}{(CH_3)_3SiOH}$$

$$\underset{\underline{4}}{(CH_3)_3SiOSi(CH_3)_3} + \underset{\underline{20}}{H_2} \xleftarrow[F^{\ominus}]{18} \underset{\underline{19}}{(CH_3)_3SiOH} \xrightarrow[F^{\ominus}]{2} \underset{\underline{4}}{(CH_3)_3SiOSi(CH_3)_3} + \underset{\underline{18}}{(CH_3)_3SiH}$$

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