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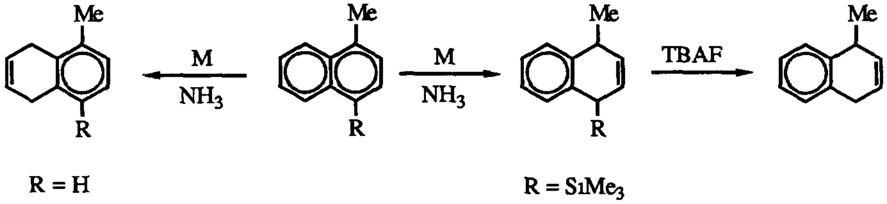
SILICON MODIFIED REDUCTION AND REDUCTIVE ALKYLATION-APPLICATION TO THE PHENANTHRENE SYSTEM

Peter W. Rabideau* and **Zbigniew Marcinow**
Department of Chemistry, Purdue School of Science at Indianapolis
Indiana University-Purdue University at Indianapolis
Indianapolis, IN 46223

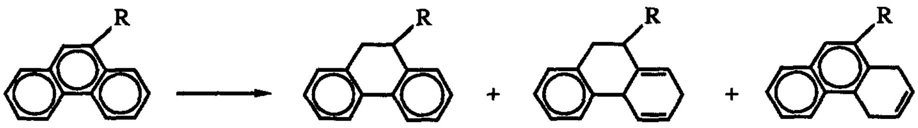
Summary. *A trimethylsilyl (TMS) substituent is used to control the metal-ammonia reduction of phenanthrenes The TMS group is then removed by tetrabutylammonium fluoride (TBAF) and replaced by either H or R '*

The Birch Reduction, together with related metal-ammonia processes, has become an important synthetic method [1] The reaction is limited, however, in that the regiochemistry is dictated by the electron density distribution in the anionic intermediates We recently introduced a method for the regiochemical control of this reaction in the naphthalene system by the use of silicon to direct reduction.[2] For example, 1-methyl-naphthalene reduces exclusively in the unsubstituted ring to produce 5-methyl-1,4-dihydronaphthalene However, 1-methyl-4-trimethylsilylnaphthalene reduces in the substituted ring so that subsequent removal of the trimethylsilyl (TMS) group with tetrabutylammonium fluoride (TBAF) affords the "misorientated" reduction product, 1-methyl-1,4-dihydronaphthalene We have since learned that "silicon modified reduction" can be employed to control overreduction in cases where it is difficult to stop the reaction after only two hydrogens have been incorporated In addition, we have also developed a procedure for "silicon modified reductive alkylation " That is, the reduction can be controlled by silicon which is subsequently replaced by alkyl rather than hydrogen



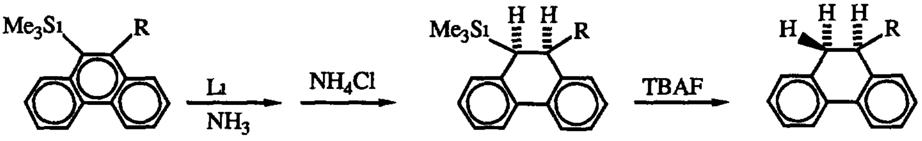
Early efforts to reduce phenanthrene were rather unsuccessful with little product formed and/or overreduction to form tetrahydro products[3] (Scheme 1) The use of catalytic amounts of iron and reaction times of 1-3 hrs provided a substantial improvement with yields of 70-80% [4] However conditions under which all of the starting materials were consumed (i e , excess metal) produced unacceptable levels of overreduction and the use of less metal resulted in substantial amounts of unreacted starting material. The necessary compromise was to accept some level (20-30%) of both unreduced and overreduced material

Scheme 1



1, R = H, Me, Et

We now report the production of 9,10-dihydrophenanthrene and its 9-methyl and 9-ethyl derivatives in essentially quantitative yields by a silicon modified reduction Hence the TMS derivatives 2 (R = H, Me, Et), which are readily available from reaction of the corresponding bromoarenes[5] with n-butyllithium/ClSiMe$_3$, are smoothly reduced with lithium/ammonia solutions[6] to produce the dihydro compounds 3 The reason



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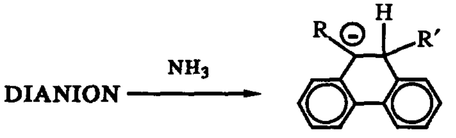
2, R = H, Me, Et

3

Quantitative

for the improved results can be rationalized as follows Dianions are formed from both 1 and 2 which are protonated by ammonia to produce monoanions However, in the unsilylated case, the monoanion (5) is quite basic (simply benzylic) and is also protonated by ammonia to produce a (neutral) 9,10-dihydrophenanthrene (9,10-DHP) which is itself reduced under these conditions Silylation not only makes the



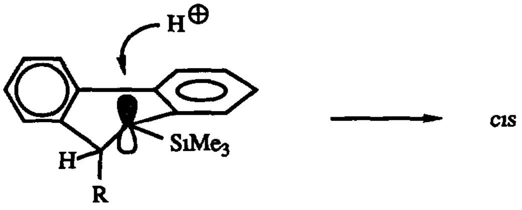
R = H; protonated by NH$_3$

R = SiMe$_3$, resistant to protonation

5

arene more reactive, but now the monoanion is stabilized and persists under the reaction conditions as long as the temperature is kept low (-78°C). This prevents overreduction. Subsequent removal of TMS is easily accomplished with tetrabutylammonium fluoride (TBAF) in THF.

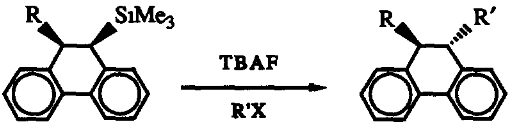
The geometry of the dihydro products (3) was assigned on the basis of the $J_{H_9H_{10}}$ coupling constants. These values (5.3 Hz for R = Me and 5.0 Hz for R = Et) are quite consistent with previous values for a pseudoaxial/pseudoequatorial relationship between H_9 and H_{10} indicating 3 to be the cis isomer[7] This is also consistent with a pseudoaxial position for R in the monoanion (5') with protonation taking place from the opposite (and pseudoaxial) side



5'

We have also learned that the trimethylsilyl group can be replaced with alkyl (Me or Et) This is especially important for phenanthrenes since normal reductive alkylation does not produce 9-alkyl- or 9,10-dialkyl-9,10-DHP's, but rather 4a-alkyl-2,4a,9,10-tetrahydrophenanthrenes. This results from protonation of the 9,10-DHP monoanion (as discussed above), and a subsequent second reduction producing a tetrahydro monoanion which persists in ammonia.

This silicon modified reductive alkylation is accomplished in the following way: (1) using anhydrous TBAF,[8] (2) keeping the reaction temperature low (-30 °C) to slow competition with residual water in the TBAF, and (3) having R'X present with the DHP before the TBAF is added. The results summarized in Table 1 indicate good to excellent yields. Moreover, the trans isomers are produced, and this is the opposite result as compared to reduction of 9,10-dialkylphenanthrenes which afford cis isomers[4,9]



R' = Me, Et

Table 1. Desilylation/Alkylation of Cis-9-R-10-TMS-9,10-DHP

R	R'X	Trans-9-R-10-R'-DHP	9-R-DHP
H	MeI	90	10
H	Et I	82	18
Me	MeI	92	8
Me	Et I	78	22

[a] Run at -30 °C in THF with anhydrous TBAF for 2 hrs. Yields are uncorrected GLPC

We expect that this new procedure will represent an important route for the "reductive alkylation" of aromatic compounds Studies are currently underway to determine the applicability to other polynuclear aromatic systems

ACKNOWLEDGMENT

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5 For example, see the bromination procedure in reference 4

6 Lithium (2.5 mol) was added to the arylsilane in THF/NH_3 (1 2) at -78°C After 20 minutes the solution was quenched with solid ammonium chloride

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9. In the case of 9-methyl-10-ethyl-DHP, trans assignment was made on the basis of the small $J_{9,10}$ coupling constant (1.8 Hz) [7] The trans dimethyl is a known compound [4]

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