Pergamon

Tetrahedron Letters, Vol. 35, No. 43, pp. 8031-8032, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01727-1

Peculiarities in the Cleavage by Methyllithium of Unsymmetrical Disilanes

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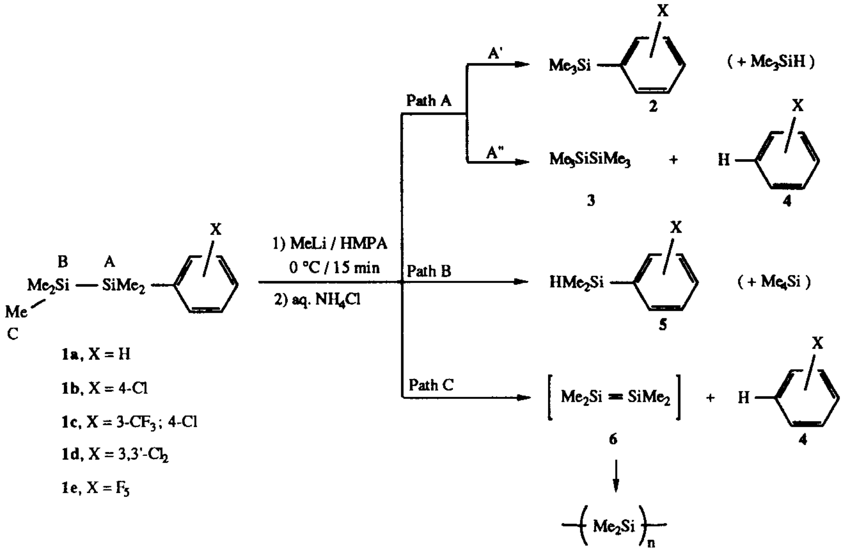
Abstract: *the title reactions did not produce the more stable silyl anions from the disilanes studied, they either occurred by attack at the more electrophilic silicon atom, or led to unexpected products.*

Although the reaction of disilanes with alkali metals is a well known method for the production of silyl metal species [1], the less economic but considerably faster cleavage of the same disilanes by strongly nucleophilic reagents, such as alkoxides [2,3], methyllithium [4] or fluoride ion [5], has often been preferred as an alternative method. Almost invariably, symmetrical disilanes have been considered for this latter type of reaction, and the scarce data reported for unsymmetrical disilanes [3,5] indicate that the Si,Si bond is cleaved in such a way as to generate the more stable silyl metal species (thermodynamic control of the reaction).

Herein we report our first results in this field showing that, depending on the structure of the unsymmetrical disilane, the silicon-silicon bond cleavage can be a substantially more complicated process than it may appear at first glance. Subjecting the disilanes [6] **1a-e** to the cleavage reaction described by W.C. Still [4] (1eq.MeLi/HMPA/0° C/15min.) [7] and quenching the reaction mixtures with aqueous ammonium chloride, the products **2-5** have been observed.[8]

Scheme



In order to make the identification of the cleavage products **2** and **5** easier [9] we chose to scavenge the silyl lithiums formed by a proton as electrophile. We made the following observations.

i) Cleavages of disilanes **1a-c** occur predominantly according to branch A' of Path A (Scheme) leading to trimethylsilyl benzenes **2a-c**, with only minor amounts (or nil) of dimethylhydrosilyl benzenes **5a-c** being formed. In actuality, the product ratios **2a/5a**=95/5, **2b/5b**=93/7 and **2c/5c**=100/0 were obtained for disilanes **1a**, **1b** and **1c**, respectively. These results imply that in each case trimethylsilyllithium, i.e. the least stable "silyl anion" was formed overwhelmingly or exclusively. This in turn suggests that the cleavage reactions have occurred under kinetic rather than thermodynamic control. The question then arizes, what kinetic control means in terms of the site of attack by the nucleophile (methyllithium)? In view of the above results we conclude that the preferred site of attack is not the least hindered silicon atom B (which should have led to predominant formation of silanes **5** after protonation of the more stable silyl anions), instead attack of the more sterically encumbered, but also the more electrophilic silicon atom A is much more efficient.

ii) The reaction of pentamethyl-(3,3'-dichlorophenyl)disilane **1d** with methyllithium under the same conditions (HMPA/0° C/15min., followed by hydrolysis) led to the almost quantitative formation of *meta*-dichlorobenzene **4d** and hexamethyldisilane **3** (Scheme, branch A" of Path A); only a trace amount of trimethylsilyl-3,3'-dichlorobenzene **2d** could be detected (GC analysis) in the crude product mixture. These observations can be rationalized by initial nucleophilic attack occurring again nearly exclusively on silicon atom A leading to a pentacoordinate siliconate anion intermediate [10], which has the choice between expulsion of trimethylsilyl anion (with concomitant formation of **2d**) or expulsion of 3,3'-dichlorophenyl anion (producing **4d** on protonation). The latter scenario appears to predominate largely, presumably due to the much better leaving group capability of 3,3'-dichlorophenyl anion as compared to trimethylsilyl anion.

iii) On the basis of the presently available data we tentatively propose Path C (Scheme) as the most likely route for the cleavage of pentamethylpentafluorophenyldisilane **1e** to occur. Indeed, the reaction takes place instantaneously on dropwise addition of methyllithium, and is accompanied by the formation of gas bubbles, as well as of a slightly beige-brown coloured precipitate. The accessible properties of the isolated solid compound (IR spectrum, m.p.>250 °C, insolubility in all common organic solvents) suggest that it may be polydimethylsilylene. Formation of this polymer can be accommodated by nucleophilic attack on one of the terminal methyl groups of **1e** (Site C, Scheme) leading to ethane (gas bubbles), tetramethyldisilene **6** and pentafluorophenyl anion (also a good leaving group). The latter species gives pentafluorobenzene **4e** on protonation (detected by GC analysis of the mother liquor of the reaction mixture), while disilene **6** can undergo polymerisation directly or through the intermediacy of octamethylcyclotetrasilane (by anionic ring opening polymerisation, ROP). It should be added that trace amounts of **2e** and **5e** could also be detected in the crude product mixture [11].

Thus, although some aspects of this latter cleavage reaction should be further ascertained, an important conclusion can be drawn from the above results: *none of the disilanes 1a-e generates the more stable silyl anionic species when cleaved by methyllithium; these reactions do not take place under thermodynamic control.*

However, the presence of electron donating substituents on the phenyl ring of **1a** instead of electron withdrawing ones, as in **1b-e**, as well as the use of nucleophilic reagents other than methyllithium, and of other reaction conditions may well impart quite different outcomes to the cleavage of unsymmetrical disilanes.

References and Notes

1. See for example: Davis D.D. and Gray C.E., *Organometal. Chem. Rev. A*, **1970**, *6*, 283, and references cited therein.
2. a) Sakurai H., Okada A., Kira M. and Yonezawa K., *Tetrahedron Lett.*, **1971**, 1511; b) Sakurai H. and Okada A., *J. Organomet. Chem.*, **1972**, *35*, C13; c) Sakurai H. and Kondo F., *ibid.*, **1975**, *92*, C46
3. Buncel E., Venkatachalam T.K. and Edlund U., *ibid.*, **1992**, *437*, 85
4. Still W.C., *J. Org. Chem.*, **1976**, *41*, 3063
5. Hiyama T., Obayashi M., Mori I. and Nozaki H., *ibid.*, **1983**, *48*, 912
6. Disilanes **1a-e** have been synthesized according to the equation:

$$\mathrm{Ar-Br}\ \xrightarrow[\text{2) Me}_3\text{SiSiMe}_2\text{Cl / -78 °C to RT}]{\text{1) 2 eq. t-BuLi / Et}_2\text{O / -78 °C / 1 h}}\ \text{1a-e (43-68 \%)}$$

   and purified by column chromatography (SiO_2, eluent pentane/cyclohexane, 9/1 v/v).
7. Under these conditions the cleavage reactions were complete for disilanes **1c-e**, whereas a small amount (3-4%) of unreacted **1a** or **1b** was detected in the corresponding product mixtures.
8. Compounds **2-5** have been identified and quantified by GC analysis (comparison to authentic compounds [9] and calibration using dodecane as internal standard) of the crude product mixtures.
9. Authentic **2a-e** and **5a-e** were synthesized in ways analogous to that used for **1a-e** (ref.6).
10. For a discussion of the mechanisms of nucleophilic substitution on silicon, see for example: Bassindale A.R. and Taylor P.G. in *The Chemistry of Organic Silicon Compounds"*, Eds. Patai S. and Rappoport Z., John Wiley & Sons, Chichester (UK), **1989**, Vol. 1, p. 839.
11. The essentially complete absence of attack on silicon atom A (Scheme), as compared to **1d**, is probably due to steric hindrance by the *ortho*-fluorine atoms. For Taft's steric constants of *ortho*-substituents, see for example: Leffler J.E. and Grunwald E., *"Rates and Equilibria of Organic Reactions"*, John Wiley & Sons, New-York, **1963**.

(*Received in UK* 30 *June* 1994; *revised* 24 *August* 1994; *accepted* 2 *September* 1994)