CHEMISTRY LETTERS, pp. 1223-1226, 1985.

# ANION RADICAL-INDUCED DESILYLATION OF ORGANOSILANE. REACTIONS OF BENZYLSILANES WITH ALDEHYDES AND RELATED COMPOUNDS IN THE PRESENCE OF BUTYLLITHIUM OR LITHIUM METAL

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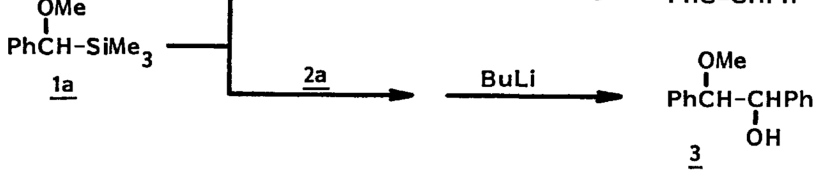
By the action of butyllithium or lithium metal in such polar aprotic solvent as DMF or HMPA in the presence of aldehydes or related compounds, some benzylsilanes suffer from anion radical-induced desilylation forming benzyl carbanions which add to the aldehydes and related compounds.

The selective desilylation and deprotonation of organosilanes leading to two different types of carbanionic species are now possible by the proper use of nucleophiles (or silylophiles) and bases.1) This chemoselectivity depends upon the nucleophilicity and basicity of the bases as well as the acidity of the most acidic hydrogen of organosilanes. Although alkyl lithium reagents are generally excellent bases for the generation of silyl-stabilized carbanions, they bring about desilylation when no acidic hydrogen is present in organosilanes.2)

The present communication describes a rare example of anion radical-induced desilylation reaction of organosilane, which has been observed in the reactions of benzylsilanes with aldehydes and related compounds in HMPA or DMF in the presence of butyllithium or lithium metal.

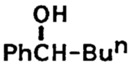
As expected, the α-hydrogen of (α-methoxybenzyl)trimethylsilane 1a was readily deprotonated by butyllithium in both tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) in 5 min at 0 °C and the resulting red-colored carbanion of silyl-stabilized type was trapped with benzaldehyde 2a as 1-methoxy-1,2-diphenylethene in 83 and 41% yields, respectively.3)



Scheme 1.

During the investigation to find the optimum conditions, we came across a surprising fact that the same reaction led to a dramatically different result when the order of addition of the reagents was changed. When butyllithium was added to a mixture of 1a and 2a in HMPA at 0 °C, the reaction mixture immediately turned deep blue. This color survived for about an hour and gradually changed into dark brown. After 17 h at room temperature under nitrogen, this reaction produced 92% of 2-methoxy-1,2-diphenylethanol 3 as the 1:1 mixture of erythro and threo isomers as shown in Scheme 1.4)

Table 1. Reactions of a benzylsilane 1a with benzaldehyde 2a a)

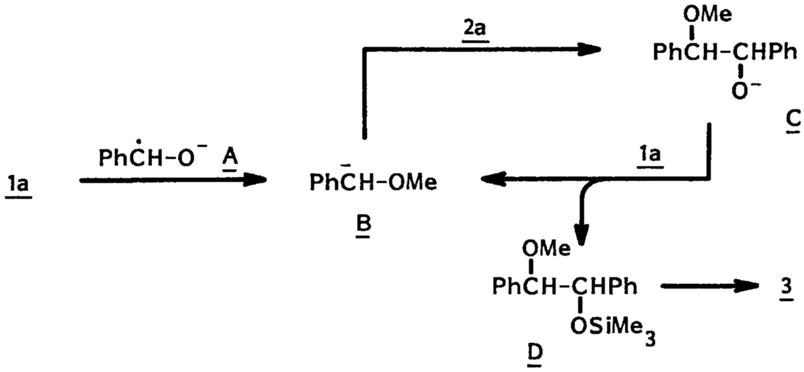
| Reaction conditions | | | | | |
|---|---|---|---|---|---|
| Solvent | Base | Base/1a | Temp | Time/h | Product (yield/%)b) |
| HMPA | BuLi | 1 | rt | 17 | 3 (92) |
| HMPA | BuLi | 0.1 | rt | 17 | 3 (67) |
| HMPA | BuLi | 1 | 0 °C | 5 min | 3 (30) |
| DMF | BuLi | 1 | rt | 18 | 3 (87) |
| THF | BuLi | 1 | rt | 17 | 1 (79)<br> $PhCH(OH)\text{-}Bu^n$ (90) |
| HMPA | Li | 1 | rt | 2.5 | 3 (79) |
| HMPA | Li | cat. | rt | 2.5 | 3 (70) |
| HMPA | NaOMe | 1 | rt | 14 | 3 (57) |

a) The base was added at 0 °C. All the reactions were carried out under nitrogen using 1.5 equivalent of 2a. b) Isolated yields as mixtures of erythro and threo isomers (1:1).

In order to figure out the reaction mechanism, especially the concerned active species, and then to know the scope of this unusual reaction, various reaction conditions were applied to the reaction between 1a and 2a. The results are listed in Table 1.

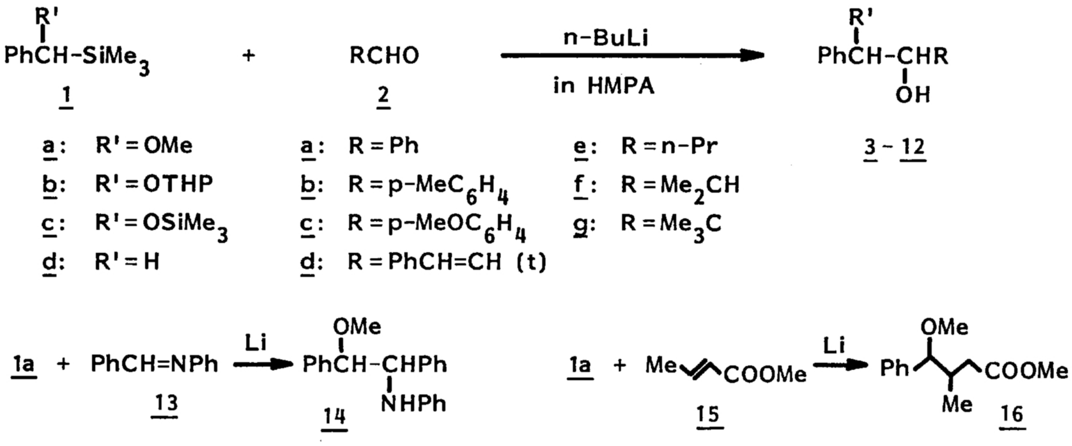
A catalytic amount of butyllithium (10 mol%) was found sufficient though the yield was not excellent. The reactions in Table 1 were continued until all 1a was consumed on TLC. When the reaction was quenched after 5 min at 0 °C, 30% of 3 was obtained. Dimethylformamide (DMF) was also effective as a solvent, while the reaction in THF did not show the characteristic blue color giving no trace of 3. The only product was the adduct of butyllithium to 2a, 1-phenyl-1-pentanol (90%), and most of 1a was recovered unchanged. Lithium metal, either an equivalent or catalytic amount, was found a good initiator for this reaction. This time again, the color of mixture was deep blue.5)

From the above results, a possible reaction mechanism was figured out as shown in Scheme 2. The first step is the single electron transfer from butyllithium to 2a or from lithium metal to HMPA and then further transfer to 2a generating an anion radical A.6) This anion radical A then abstracts the silyl group from 1a forming the carbanion B, which adds to 2a giving the adduct C. The alkoxide C serves as a desilylating reagent for the followed reaction so that the sequence of desilylation of 1a and addition of the resulting anion to 2a is autocatalyzed. The probability of desilylation of 1a with an alkoxide ion was confirmed by the reaction using sodium methoxide as shown in Table 1.



Scheme 2.

Some other aldehydes successfully reacted with 1a under the similar conditions producing β-methoxy alcohols 3-8 in satisfactory yields (Scheme 3 and Table 2). The β-alkoxy alcohols 9-11 obtained from the silanes 1b and 1c could be readily deprotected giving quantitative yields of the corresponding 1,2-diols.



Scheme 3.

N-Benzylideneaniline 13 and methyl crotonate 15 also reacted with the carbanion derived from 1a under the conditions of using catalytic amount of lithium metal providing the β-amino ether 14 and γ-alkoxy ester 16, respectively, while the reaction with 13 in the presence of butyllithium led to the exclusive formation of butyllithium adduct to 13, N-(1-phenylpentyl)aniline.

Table 2. Reactions of benzylsilanes 1 with aldehydes 2 and related compounds 13, 15 a)

| Benzyl-silane | Acceptor | Base | Base/1 | Acceptor/1 | Time/h | Product | | | Yield/% b) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | R' | R | |
| 1a | 2a | BuLi | 1 | 1.5 | 17 | 3 | OMe | Ph | 92 |
| 1a | 2b | BuLi | 1 | 1.5 | 16 | 4 | OMe | p-MeC$_6$H$_4$ | 83 |
| 1a | 2d | BuLi | 1 | 1.5 | 17 | 5 | OMe | PhCH=CH (t) | 76 |
| 1a | 2e | BuLi | 1 | 1.5 | 16.5 | 6 | OMe | n-Pr | 60 |
| 1a | 2f | BuLi | 1 | 1.5 | 17 | 7 | OMe | Me$_2$CH | 70 |
| 1a | 2g | BuLi | 1 | 1.5 | 17 | 8 | OMe | Me$_3$C | 63 |
| 1b | 2a | BuLi | 1 | 1.5 | 16 | 9 | OTHP | Ph | 55 |
| 1b | 2g | BuLi | 1 | 2.0 | 17 | 10 | OTHP | Me$_3$C | 61 |
| 1c | 2c | BuLi | 1 | 1.5 | 13 | 11 | OSiMe$_3$ | p-MeOC$_6$H$_4$ | 29 |
| 1d | 2a | BuLi | 1 | 1.5 | 17 | 12 | H | Ph | 60 |
| 1a | 13 | Li | cat. | 1.5 | 2.5 | 14 | | | 80 |
| 1a | 15 | Li | cat. | 1.5 | 3 | 16 | | | 43 |

a) Carried out in HMPA at room temperature. b) All isolated yields as erythro and threo mixtures (1:1).

## References

1) As reviews: I. Fleming, "Organic Silicon Chemistry," in "Comprehensive Organic Chemistry," ed by D. H. R. Barton and W. D. Ollis, Pergamon, Oxford (1979), Vol. 3, p. 539; E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981); W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Heidelberg (1983).

2) W. C. Still, J. Org. Chem., 41, 3063 (1976); P. Magnus and G. Roy, J. Chem. Soc., Chem. Commun., 1979, 822; P. Magnus and G. Roy, Organometallics, 1, 553 (1982).

3) The silyl-stabilized carbanion generated from 1a and butyllithium in THF was allowed to react with a variety of carbonyl compounds (sixteen kinds) giving 94-62% of the E/Z mixtures of vinyl ethers (S. Kanemasa, J. Tanaka, H. Nagahama, and O. Tsuge, submitted for publication).

4) All the new compounds reported herein gave satisfactory spectral data as well as elemental analyses. Some products were identified by the comparison with the authentic samples prepared from 1a and aldehydes in the presence of a fluoride ion (O. Tsuge, S. Kanemasa, H. Nagahama, and J. Tanaka, Chem. Lett., 1984, 1803).

5) The blue solution of alkali metal in HMPA has been characterized as the anion radical formation: K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, J. Am. Chem. Soc., 92, 2783 (1970); H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, ibid., 92, 2800 (1970) and the references cited therein.

6) The anion radical of HMPA can not be excluded as a possible initiator, especially in the reaction system using lithium metal in HMPA.

(Received May 27, 1985)