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ISOMERIZATION OF 1-TRIMETHYLSILYLALLENYL ETHER TO 1-TRIMETHYLSILYLPROPARGYL ETHER. PREPARATION OF 1-METHOXY-1-ALKEN-3-YNES and 2-METHOXY-2,5-DIHYDROFURANS

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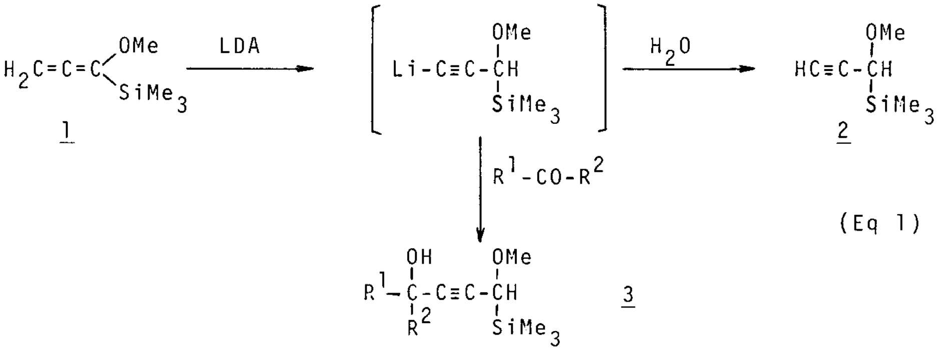
Summary: On treatment of LDA, methyl 1-trimethylsilylallenyl ether isomerizes to lithium acetylide of 1-trimethylsilylpropargyl ether, which can be used efficiently for the preparation of 1-methoxy-1-alken-3-ynes and 2-methoxy-2,5-dihydrofurans.

Allenyl ethers have recently been employed as useful building blocks in organic synthesis. On treatment with alkyllithium, they undergo selective lithiation on α- or γ-carbons, depending on their substitution patterns, which provides an important synthetic methodology for unsaturated carbonyl compound derivatives.[1,2]

During our investigation on the reactivities of methyl 1-trimethylsilylallenyl ether 1, it has been found that the ether 1 isomerizes readily to the propargyl ether 2[3] upon treatment with LDA.[4] Quenching the reaction mixture followed by distillation gave methyl 1-trimethylsilylpropargyl ether 2 in 67% yield. Similarly, treatment of 1 with LDA followed by addition of an aldehyde or ketone led to the formation of the corresponding propargyl alcohol 3 in high yields (Table 1).[5]

The isomerization may possibly proceed through a sequence of deprotonation and protonation processes with LDA and di-isopropylamine, respectively, since it does not take place under the influence of butyllithium.[2]



(Eq 1)

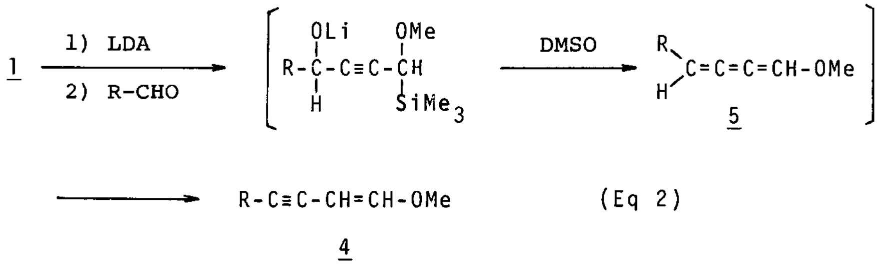
The resulting alcohols 3 have been expected to undergo elimination reaction under appropriate conditions because of their structural feature as acetylenic homologs of β-hydroxyalkyltrimethylsilanes. On standing the lithium alkoxide of 3 obtained from an aldehyde in dry DMSO, the corresponding 1-methoxy-1-alken-3-yne 4 in stead of the expected triene 5 was obtained in good yield together with a small amount of 2-methoxy-2,5-dihyfrofuran 6.

Based on the previous report that described on a facile isomerization of cumulated trienes to enynes,[6] it is reasonable to assume that the initially formed trienes 5 may isomerize to 4 under reaction conditions employed here.

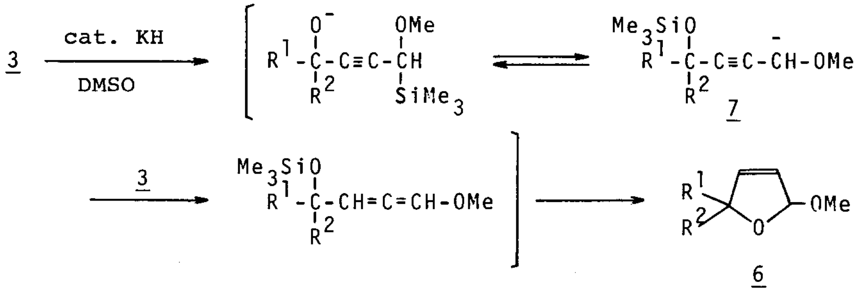
Although it has been documented well that β-hydroxyalkyltrimethylsilanes undergo elimination under both basic and acidic conditions,[7] behaviors of their homologs have scarecely been elucidated up to now. This is a first example of such type of elimination reaction of acetylenic homologs. An intramolecular attack of oxido anion to silyl group is considered to be important in this Peterson type reaction under basic conditions. But the above results clearly show that a similar elimination takes place even if such kind of an intramolecular attack is greatly disfavored due to a distance between oxido anion and silyl group.

Tertiary alcohols 3 obtained from ketones almost remained unchanged under the present reaction conditions. Under typical acidic conditions, e.g. BF_3OEt_2 in CH_2Cl_2 at 0°C,[7] alcohols 3 decompose to give a complex mixture.

Another useful transformation to dihydrofuran 6 is also effected under the influence of ca. 0.1 equiv of potassium hydride in DMSO as shown in Eq 3. A facile protonation of the carbanionic species 7 with the parent alcohol 3 followed by cyclization may account for the formation of 6.



(Eq 2)



(Eq 3)

Table 1. Preparation of Propargyl Alcohols 3.[a]

R^1	R^2	Yield(%) of 3
C_6H_5	H	81
$C_6H_5CH_2CH_2$	H	92
C_8H_{17}	H	83
$-(CH_2)_5-$		89
$-(CH_2)_6-$		86
$-(CH_2)_7-$		81
$-(CH_2)_3-C(CH_3)=CH-$		95

a) The reaction was performed as follows. After the ether 1 (0.30 mmol) was treated with an ethereal solution of LDA (0.31 mmol) at 0°C for 1 hr, an appropriate aldehyde or ketone was added and it was stirred for 10 min at that temperature.

Table 2. Preparation of 1-Methoxy-1-alken-3-ynes 4.

R	Yield(%) of 4	(E/Z ratio)	Yield(%) of 6
$C_6H_5CH_2CH_2$	65[a]	(77/23)	23
$C_6H_5CH_2CH_2$	71[b]	(73/27)	12
C_9H_{19}	72[a]	(73/27)	trace
C_9H_{19}	75[b]	(71/29)	11
$C_2H_5CH(CH_3)$	57[a]	(77/23)	17
$C_2H_5CH(CH_3)$	61[b]	(69/31)	8[c]
$C_6H_5C(CH_3)_2$	55[b]	(81/19)	13[c]

[a] An aldehyde was treated with the lithium acetylide prepared from the ether 1 and LDA as described above. After removal of the solvent and di-isopropylamine in vacuo, dry DMSO was added and it was stirred for 1.5 hr at room temperature. After quenching, hexane extracts were purified by column chromatography to give 4 and 6. Ratio of E to Z was determined by NMR. [b] Lithium acetylide prepared from the propargyl ether 2 and butyllithium was used. [c] Isolated as the corresponding 2-alkylfuran.

Table 3. Preparation of Dihydrofurans 6.[a)]

R^1	R^2	Yield(%) of 6
$C_6H_5CH_2CH_2$	H	57
C_8H_{17}	H	56
$-(CH_2)_5-$		71
$-(CH_2)_6-$		77
$-(CH_2)_3-C(CH_3)=CH-$		87

a) The reaction was performed as follows. To a THF (0.2 ml) solution of the propargyl alcohol 3 (0.38 mmol) a DMSO (1 ml) solution of KH (4 mg) was added and it was stirred for 1 hr at room temperature.

These products, 4 and 6, are expected to be useful nucleophilic and electrophilic reagents, respectively, in synthetic organic chemistry. We are now studying their synthetic utilities.

References and Notes

1) S. Hoff, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, 87, 916 (1968); J. C. Clinet and G. Linstrumelle, *Tetrahedron Lett.*, 1137 (1978).
2) J. C. Clinet and G. Linstrumelle, *Tetrahedron Lett.*, 21, 3987 (1980).
3) For the isomerization of allenyllithiums to lithium acetylides, see J. Klein and S. Brenner, *J. Org. Chem.*, 36, 1319 (1971). Another important feature of this procedure is that the ether 2 is not available from methyl propargyl ether: Y. Leroux and R. Mantione, *Tetrahedron Lett.*, 591 (1977); R. Mantione and Y. Leroux, *ibid.*, 593 (1971); Y. Leroux and C. Romen, *ibid.*, 2585 (1973).
4) Use of LDA prepared from alkyllithium containing lithium bromide gave much more satisfactory results.
5) Attempts for alkylation of the lithium acetylide gave less satisfactory results.
6) R. Kuhn and H. Fischer, *Chem. Ber.*, 94, 3060 (1961); P. P. Montijn, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, 86, 129 (1967).
7) E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981, p. 141--164.

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