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REACTION OF ENOLATES OF ACYLTRIMETHYLSILANES WITH ALDEHYDES. CANNIZZARO TYPE OXIDATION-REDUCTION REACTION WITH A TRIMETHYLSILYLCARBONYL GROUP

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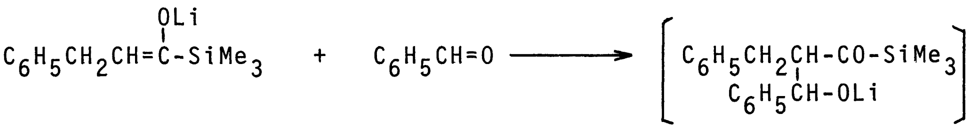
Summary: The reaction of an acyltrimethylsilane enolate with 2 eq of an aldehyde gives a 1:2 adduct, while that with the enolate of an α-chloroacyltrimethylsilane affords an α,β-unsaturated aldehyde as a 1:1 adduct accompanied by the carboxylic acid derived from the starting aldehyde. An oxidation-reduction reaction mechanism on the trimethylsilylcarbonyl group has been proposed.

Various characteristic features of organosilicon compounds have recently been explored and used for carbon chain elongation or introduction of functional groups into organic molecules.[1] In connection with these studies, we have been interested in the reactions of acyltrimethylsilanes or such derivatives as silyl enol ethers[2] or α-haloacyltrimethylsilanes.[3] They usually exhibit behaviors similar to those of the structurally related ketone derivatives, but sometimes show quite unique reactivities.[4]

We recently reported that silyl enol ethers of acyltrimethylsilanes react with various acetals under the influence of boron trifluoride etherate to give the corresponding β-alkoxyacyltrimethylsilanes[5] similarly with silylated ketone enolates.[6] However, the lithium enolates of acyltrimethylsilanes or their α-chloro derivatives have been found to show quite interesting results in the reaction with aldehydes as shown below.

On treating the lithium enolate of an acyltrimethylsilane with benzaldehyde in THF, the initial adduct 2 might be formed,[7] but it was quite unstable and was converted into the corresponding 1:2 adduct 3 during a prolonged reaction period. Especially, when the reaction was carried out with 2 eq of the aldehyde at room temperature overnight, the adduct 3 was isolated in 85% yield. The same adduct was also obtained by the reaction of α-bromoacyltrimethylsilane with benzaldehyde in the presence of zinc.



$$C_6H_5CH_2CH{=}\overset{OLi}{C}\text{-}SiMe_3 \quad + \quad C_6H_5CH{=}O \longrightarrow \left[\begin{array}{c} C_6H_5CH_2\underset{|}{C}H\text{-}CO\text{-}SiMe_3 \\ C_6H_5CH\text{-}OLi \end{array}\right]$$

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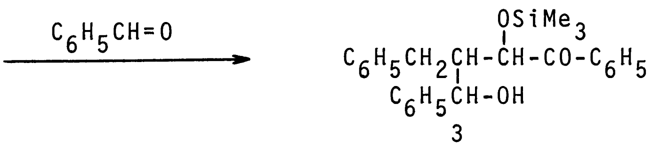

$$\xrightarrow{C_6H_5CH=O} C_6H_5CH_2\underset{C_6H_5CH\text{-}OH}{CH}\text{-}\overset{OSiMe_3}{CH}\text{-}CO\text{-}C_6H_5$$

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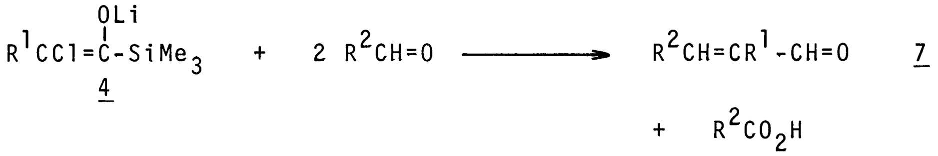
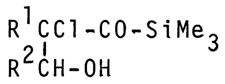
On the contrary, when the lithium enolate of α-chloroacyltrimethylsilane 4 was employed in place of acyltrimethylsilane, neither the corresponding adduct 5 nor the oxirane derivative 6 was isolated, but the α,β-unsaturated aldehyde 7 was formed in a moderate yield. As in the case of acyltrimethylsilane, this reaction also appears to proceed with 2 eq of the aldehyde and the corresponding unsaturated aldehyde was obtained in good yield along with the carboxylic acid by treating 4 with 2 eq of the aldehyde at -78°C for 3 hr followed by work-up of the reaction mixture with aq HCl. The results are shown in the Table.



$$\underset{4}{R^1CCl=\overset{OLi}{C}\text{-}SiMe_3} + 2\ R^2CH=O \longrightarrow R^2CH=CR^1\text{-}CH=O \quad 7$$

$$+ \quad R^2CO_2H$$



$$R^1\underset{R^2CH\text{-}OH}{CCl}\text{-}CO\text{-}SiMe_3$$

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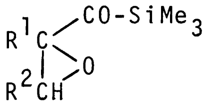

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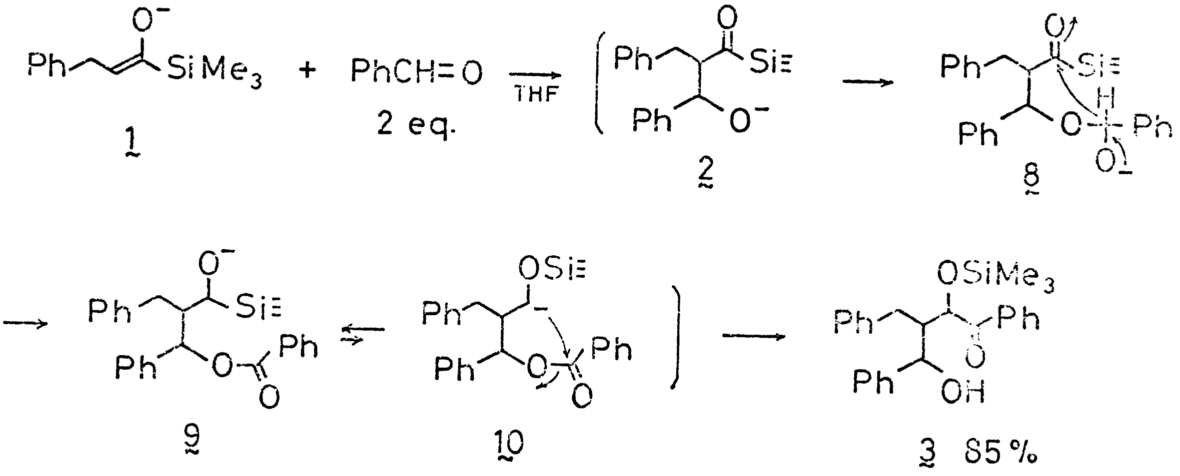
These unusual results may be explained by assuming a Cannizzaro type oxidation-reduction process shown in Scheme 1 and 2. Thus, in the reaction of an acyltrimethylsilane enolate, the adduct 2 initially formed may further react with benzaldehyde to yield the intermediate 8. Intramolecular oxidation-reduction reaction[8] between the trimethylsilylcarbonyl group and the lithium alkoxide moiety appears to take place at this stage to give 9, which is in equilibrium with 10 resulting from transfer of the silyl group to the oxido anion.[9] Intramolecular acylation reaction of the resulting carbanionic species 10 may yield the corresponding 1:2 adduct 3 (see Scheme 1).

In the case of the lithium enolates of α-chloroacyltrimethylsilanes, similar reaction paths involving oxidation-reduction may be conceivable. Thus, the intermediate 12 may be formed through the addition of the initially formed adduct 11 to another molecule of the aldehyde, and the reduction of the trimethylsilylcarbonyl group may take place with the internally formed lithium alkoxide moiety.[3] As shown in the previous paper,[3] the resulting intermediate 13 undergoes a facile rearrangement of the silyl group to the neighboring carbon atom bearing chlorine atom to yield the β-acyloxy α-trimethylsilyl aldehyde 14, from which the corresponding α,β-unsaturated aldehyde may be formed via the β-elimination of the trimethylsilyl carboxylate during an acidic work-up (see Scheme 2).

Scheme 1



Scheme 2

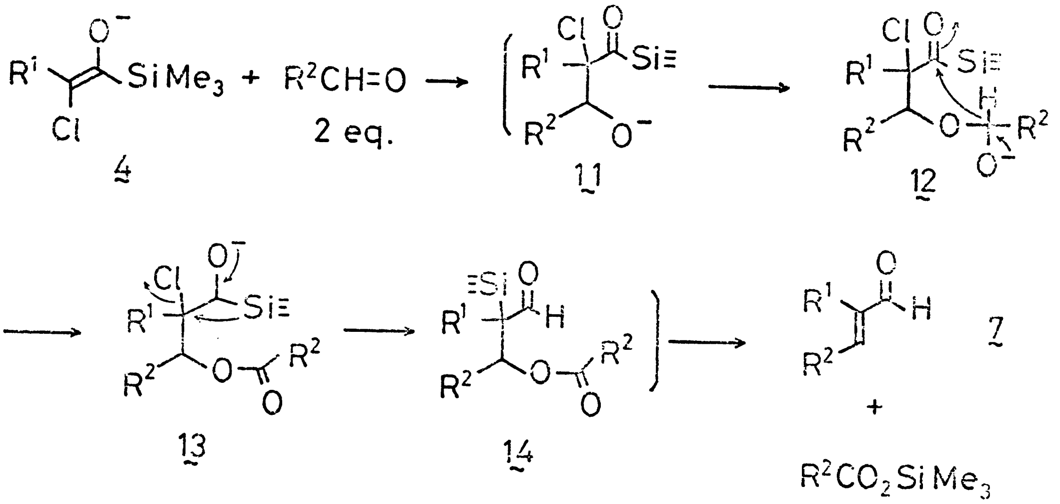


Table. Reactions of Lithium Enolates of α-Chloroacyltrimethylsilanes 4 with Aldehydes

R^1	R^2	Yield of 7 (%)
C_4H_9	C_6H_5	97 (100)[a]
C_4H_9	$C_6H_5CH_2CH_2$	83 (78)
C_4H_9	C_5H_{11}	59 (67)
$C_6H_5CH_2$	C_6H_5	97 (72)
$C_6H_5CH_2$	$C_6H_5CH_2CH_2$	80 (73)
$C_6H_5CH_2$	C_5H_{11}	67 (65)

[a] Yields of the carboxylic acids.

References and Notes

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6) T. Mukaiyama, Angew. Chem. Int. Ed. Engl., 16, 817 (1977).
7) On quenching the reaction mixture after short reaction period, the corresponding 1:1 adduct 2 might be obtained. See, W. A. Kleschick, C. T. Buse, and C. H. Heathcock, J. Am. Chem. Soc., 99, 247 (1977).
8) Trimethylsilylcarbonyl groups are shown to be reduced by Grignard reagents possessing β-hydrogen. See, A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, J. Am. Chem. Soc., 82, 5102 (1960).
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