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# THE PREPARATION AND REACTIONS OF LITHIO TERT-BUTYLBIS(TRIMETHYLSILYL)ACETATE. A SYNTHESIS OF α-SILYLATED VINYL ESTERS.

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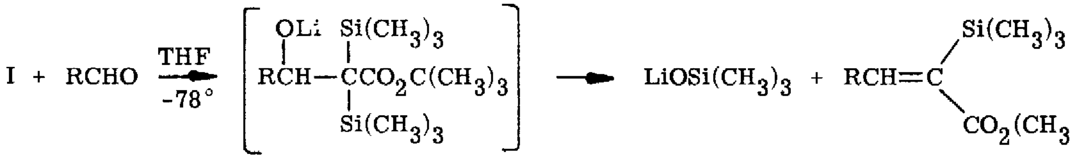
Lithio tert-butyl bis(trimethylsilyl)acetate, I, obtained by reaction of the corresponding ester, II, with lithium diisopropylamide (eq 1), reacts with aldehydes to give good yields of α-silylated vinyl esters (eq 2). As suggested previously for the mono-silyl analogue of I,[2] reaction is presumed to occur by elimination of trimethylsilyloxide from the intermediate adduct, III.

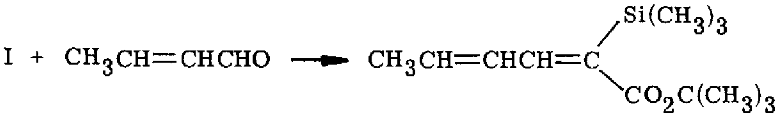
$$\underset{\text{II}}{HC[Si(CH_3)_3]_2CO_2C(CH_3)_3} + LiN[CH(CH_3)_2]_2 \xrightarrow[\text{THF}]{-78^\circ} \underset{\text{I}}{LiC[Si(CH_3)_3]_2CO_2C(CH_3)_3} + HN[CH(CH_3)_2]_2 \qquad (1)$$



$$I + RCHO \xrightarrow[-78^\circ]{\text{THF}} \left[ \underset{\text{III}}{RCH(OLi)-C(Si(CH_3)_3)_2CO_2C(CH_3)_3} \right] \longrightarrow LiOSi(CH_3)_3 + RCH{=}C(Si(CH_3)_3)(CO_2(CH_3)_3) \qquad (2)$$

III

Results obtained with a variety of aldehydes are shown in Table I. As can be seen from data in the table, the reagent adds in a 1,2-fashion with conjugated aldehydes such as crotonaldehyde (eq 3).



$$I + CH_3CH{=}CHCHO \longrightarrow CH_3CH{=}CHCH{=}C(Si(CH_3)_3)(CO_2C(CH_3)_3) \qquad (3)$$

Table I. Reaction of Aldehydes with Lithio tert-Butylbis(trimethylsilyl)acetate

| Aldehyde | Product | Yield, %[a] |
|---|---|---|
| Formaldehyde | $CH_2{=}C[Si(CH_3)_3]CO_2C(CH_3)_3$[b] | 70 (35) |
| Acetaldehyde | $CH_3CH{=}C[Si(CH_3)_3]CO_2C(CH_3)_3$[c] | 80 (58) |
| Isobutyraldehyde | $(CH_3)_2CHCH{=}C[Si(CH_3)_3]CO_2C(CH_3)_3$[d] | 90 (74) |
| Crotonaldehyde | $CH_3CH{=}CHCH{=}C[Si(CH_3)_3]CO_2C(CH_3)_3$[e] | 85 — |
| Benzaldehyde | $C_6H_5CH{=}C[Si(CH_3)_3]CO_2C(CH_3)_3$[f] | 79 (65) |

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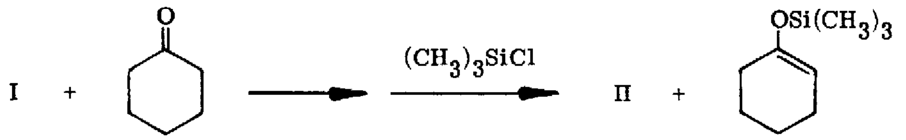
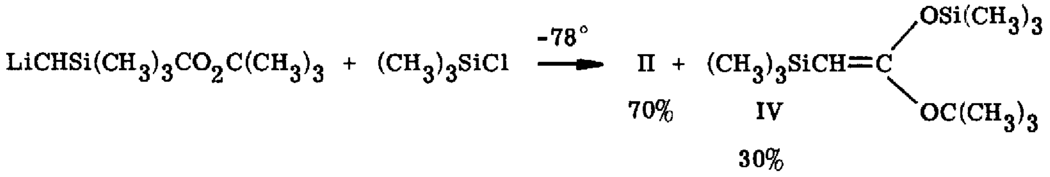
[a] GLPC yields (Se-30 column), isolated yields in parentheses. [b] PMR spectrum ($CCl_4$): doublet δ 6.50 (1H), doublet δ 5.77 (1H), singlet δ 1.47 (9H), singlet δ 0.17 (9H). IR (neat): 1700, 1720 $cm^{-1}$ (C=O), 1590 $cm^{-1}$ (C=C). [c] PMR spectrum ($CCl_4$), cis-isomer: quartet δ 6.0 (1H), doublet δ 1.90 (3H), singlet δ 1.47 (9H), singlet δ 0.10 (9H). trans-isomer: quartet δ 6.90 (1H), doublet δ 1.87 (3H), singlet δ 1.47 (9H), singlet δ 0.20 (9H). [d] PMR spectrum ($CCl_4$) mixture of isomers: 2 doublets δ 6.53, δ 5.60 (1H), multiplet δ 2.87 (1H), singlet δ 1.43 (9H), doublet δ 1.0 (6H), singlets δ 0.17, δ 0.10 (9H). [e] PMR spectrum ($CCl_4$), mixture of isomers: multiplet δ 7.4-5.6 (3H), doublet δ 1.80 (3H), singlet δ 1.47 (9H), singlets δ 0.13, δ 0.23 (9H). [f] PMR spectrum ($CCl_4$), mixture of isomers: singlet δ 7.13 (5H), singlet δ 6.5 (1H), singlet δ 1.37 (9H), singlet δ 0.20 (9H). IR (neat): 1710 $cm^{-1}$ (C=O), 1660 $cm^{-1}$ (C=C).

The reaction fails with ketones, probably for steric reasons, and only enolization of the ketone occurs. Thus, addition of cyclohexanone to solutions of I gave only recovered tert-butylbis(trimethylsilyl)acetate and the lithium enolate of cyclohexanone, identified by trapping as the vinyl ether with trimethylchlorosilane (eq 4). Similar behavior was observed with acetone in place of cyclohexanone.



(4)

Compound II was prepared by silylation of lithio tert-butyltrimethylsilylacetate[2] (eq 5). The reaction gave a 70% yield of the desired carbon-silylated product, II, together with 30% of the oxygen-silylated product IV (GLPC analysis). The reaction mixture was quenched

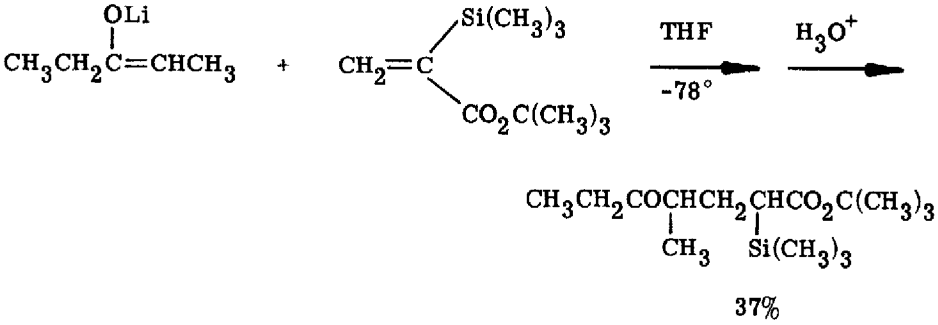


$$\mathrm{LiCHSi(CH_3)_3CO_2C(CH_3)_3} + \mathrm{(CH_3)_3SiCl} \xrightarrow{-78^\circ} \underset{70\%}{\mathrm{II}} + \underset{\mathrm{IV}\ 30\%}{\mathrm{(CH_3)_3SiCH{=}C\begin{matrix}\diagup \mathrm{OSi(CH_3)_3} \\ \diagdown \mathrm{OC(CH_3)_3}\end{matrix}}} \qquad (5)$$

with dilute acid and distilled to give 50-60% yields of pure II, bp 61°/0.4 mm. The dominance of carbon silylation observed in this reaction is surprising since other α-substituted acetate enolates react under similar conditions to give almost exclusive oxygen silylation.[3]

The following procedure for the preparation of I and its reaction with acetaldehyde is representative. A 100-ml round-bottomed flask equipped with magnetic stirring, septum inlet, and mercury bubbler is flushed with nitrogen and charged with 50 ml of a 1.0 M-solution of lithium diisopropylamide[2] in tetrahydrofuran (THF). The flask is cooled to Dry-ice temperatures and II (13.3 ml, 50 mmoles) is added dropwise over a 5-minute period. After an additional one hour of stirring, 2.8 ml of acetaldehyde (50 mmoles) is injected. The solution is then allowed to reach room temperature and quenched by addition of 35 ml of 3N hydrochloric acid. The aqueous layer is extracted with pentane and the combined organic layers are dried with anhydrous potassium carbonate and vacuum distilled to give 6.2 g (58%) of tert-butyl-2-trimethylsilyl-2-butenoate, bp 59°/0.3 mm.

Stork[4] and Boeckman[5] have shown that α-silyl vinyl ketones undergo Michael addition reactions with a number of electrophiles. α-Silyl vinyl esters, now readily available by the present procedure, may prove to be an equally useful class of Michael acceptors. In line with this, we have observed the addition of the lithium enolate of 3-pentanone to tert-butyl-2-trimethylsilyl-2-propenoate under aprotic conditions (eq 6).



$$\mathrm{CH_3CH_2\overset{OLi}{C}{=}CHCH_3} + \mathrm{CH_2{=}C\begin{matrix}\diagup \mathrm{Si(CH_3)_3} \\ \diagdown \mathrm{CO_2C(CH_3)_3}\end{matrix}} \xrightarrow[-78^\circ]{\mathrm{THF}} \xrightarrow{\mathrm{H_3O^+}} \underset{37\%}{\mathrm{CH_3CH_2CO\underset{CH_3}{C}HCH_2\underset{Si(CH_3)_3}{C}HCO_2C(CH_3)_3}} \qquad (6)$$

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