O-SILYL-SUBSTITUTED ENOLS

CARL R. KRÜGER AND EUGENE G. ROCHOW
Mallinckrodt Laboratory of Harvard University, Cambridge, Mass. (U.S.A.)

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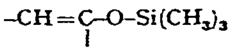
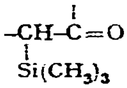
INTRODUCTION

Trialkylsilyl derivatives of enolisable carbonyl compounds were first prepared by Gilman[1], who deduced an *O*-silyl-enol structure from the chemical behavior of this class of compounds. This view was confirmed by West[2], who showed by infrared spectroscopy that the structure of the trimethylsilyl derivatives of ethyl acetoacetate and of acetylacetone corresponds to (a) rather than to (b),



$$-CH{=}\underset{|}{C}{-}O{-}Si(CH_3)_3$$

(a)



$$-\underset{\underset{Si(CH_3)_3}{|}}{CH}{-}\overset{|}{C}{=}O$$

(b)

although other authors[3] had preferred the *C*-substituted structure.

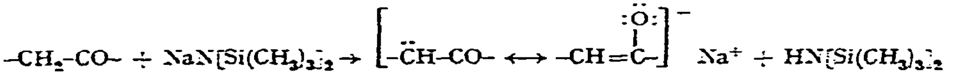
No comparable derivatives of those carbonyl compounds which are somewhat more difficult to enolize have been reported up to now, except the trimethylsilyl derivatives of ethyl acetate and ethyl isobutyrate prepared by Hance and Hauser[4] using sodium triphenylmethide as the base. They claimed that reaction of the sodium enolates with trimethylchlorosilane gave the carbon-substituted products rather than oxygen-substituted compounds, contrary to the results of West. As we show later, both isomers are formed in this reaction.

Our earlier work on the chemical behavior of sodium bis(trimethylsilyl)amide showed that this compound not unexpectedly has very strong basic properties[5], combined with high nucleophilic reactivity[6]. We believed that this base would be of considerable value in organic reactions, especially since it is readily soluble in nonpolar solvents. The work reported herein continues our study of its basic properties.

Non-enolisable carbonyl compounds react[7] with sodium bis(trimethylsilyl)amide (I) according to eqn. (1):

$$>C{=}O + NaN[Si(CH_3)_3]_2 \rightarrow\ >C{=}N{-}Si(CH_3)_3 + NaOSi(CH_3)_3 \qquad (1)$$

Carbonyl compounds with reactive hydrogen in the alpha position, on the other hand, react to form a sodium enolate and bis(trimethylsilyl)amine:



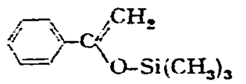
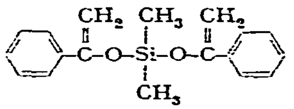
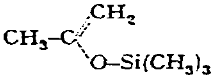
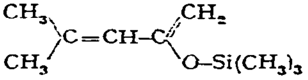
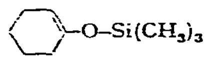
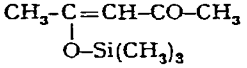
$$-CH_2{-}CO{-} + NaN[Si(CH_3)_3]_2 \rightarrow \left[-\ddot{C}H{-}CO{-} \longleftrightarrow -CH{=}\overset{:\ddot{O}:}{\overset{|}{C}}{-}\right]^{-} Na^{+} + HN[Si(CH_3)_3]_2 \qquad (2)$$

(I) therefore recommends itself as a base in condensation reactions, even sterically hindered ones. We have found, for example, that it is possible to prepare ethyl isobutyrylisobutyrate from ethyl isobutyrate in ether solution at room temperature, in comparatively good yields.

An advantage of (I) over other strong enolising agents lies in the ease of removal of its products after hydrolysis of the reaction mixture; the hexamethyldisiloxane which is formed boils at 101° and is easily distilled. Furthermore, there is no need to store the reagent under an inert gas atmosphere, and the base may be kept for a long time prior to its use without decomposition or deterioration.

Since the reaction of eqn. (2) provides us with many sodium enolates difficult to prepare in any other way, we investigated the reactions of some of these enolates with alkylhalosilanes. In all cases, substitution at the oxygen atom seemingly took precedence over substitution at the carbon atom, producing *O*-silyl-substituted enols. The new substances prepared in this way are listed in Table 1, together with their physical properties. Their structures were proven by IR and NMR spectroscopy.

TABLE 1

 b.p.$_{14}$ 93–94° n_D^{20} 1.5008	 b.p.$_1$ 125–126° n_D^{20} 1.5542
 n_D^{20} 1.3932	 b.p.$_{12}$ 52–53° n_D^{20} 1.4460; UV 243 mμ
 b.p.$_{11}$ 58–58.5° n_D^{20} 1.4452	 $CH_3\text{-}\underset{O\text{-}Si(CH_3)_3}{C}{=}CH\text{-}CO\text{-}CH_3$ b.p.$_9$ 68° n_D^{20} 1.4522

EXPERIMENTAL

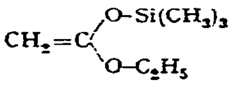
In general, the reactions were carried out as follows: To an ether solution of the carbonyl compound the ether solution of (I) was added at −50 to −70°, or even at room temperature, in a dry nitrogen atmosphere; separation of the enolate started immediately. After the suspension had been kept at low temperatures for 30 min to 2 h, the desired chlorosilane was added, and the suspension was stirred for 30 min to 2 h at room temperature or reflux temperature. After removal of the separated sodium chloride and the solvent, the residues were distilled. In all cases condensation of the enolate with excess of the carbonyl compound could not be avoided completely.

Purification of the reaction products by conventional means failed to produce pure reaction products from acetone and from ethyl acetate. In the first case the boiling point of the 2-(trimethylsiloxy)propene which is formed lies between the boiling points of hexamethyldisilazane (126°) and hexamethyldisiloxane (101°); the presence of the latter is probably due to hydrolysis caused by water from the condensation side reaction. The three compounds could be isolated by preparative gas chromatography.

A similar situation arose in the case of ethyl acetate. Here an azeotropic mixture of both possible isomers, (c) and (d), with hexamethyldisilazane resulted:

$$(CH_3)_3SiCH_2COOC_2H_5$$

(c)



$$CH_2=C\begin{cases}O-Si(CH_3)_3\\O-C_2H_5\end{cases}$$

(d)

These could only be separated by gas chromatography.

Starting materials

Sodium bis(trimethylsilyl)amide was prepared following a procedure given by Wannagat and Niederprüm[8] from sodamide and commercial hexamethyldisilazane. All carbonyl compounds were used in commercially available purity.

All reactions were carried out under an atmosphere of dry nitrogen in a 1-liter three-necked flask equipped with reflux condenser, sealed stirrer, dropping funnel, nitrogen inlet tube, and drying tubes. The apparatus was dried with trimethylchlorosilane vapor and flushed with dry prepurified nitrogen. (The nitrogen is not required by the condensing agent, but only to protect the sodium enolate.)

(a) 2-(Trimethylsiloxy)propene

To a solution of 29 g (0.5 mole) of acetone in 100 ml of dry ether a solution of 91.6 g (0.5 mole) of sodium bis(trimethylsilyl)amide (I) in 300 ml of dry ether was added. The temperature of the reaction mixture was kept at —70° by means of an acetone–dry-ice bath. After completion of the addition, the suspension was allowed to warm to 0° within 6 hours, and then a solution of 54 g (0.5 mole) of trimethylchlorosilane in 50 ml of ether was added slowly. After completion of the reaction, the stirred mixture was refluxed for 3 hours, then filtered through a glass frit under exclusion of moist air. After removal of the solvent by distillation through a 15 cm column filled with glass helices, the remaining residue was separated roughly into a mixture of the desired compound with hexamethyldisiloxane (52 g, b.p. 99–104°) and hexamethyldisilazane (47 g, b.p. 120–126°) by repeated fractionation through a 30 cm column filled with glass helices and fitted with a reflux adapter. There remained 23 g of higher-boiling residues, containing compounds formed by the condensation reaction.

The fraction boiling between 99° and 104° was separated by preparative gas chromatography through a Carbowax column (Autoprep A 700 of Wilkens Instrument & Research Inc.) at a column temperature of 87°; retention time 9.5 min. The over-all yield of 2-(trimethylsiloxy)propene was 17%. (Found: C, 54.76, 54.51; H, 10.71, 10.70; Si, 20.48; mol. wt., 132. $C_6H_{14}OSi$ calcd.: C, 55.31; H, 10.83; Si 21.56%; mol wt., 130.3.)

(*b*) *α-(Trimethylsiloxy)styrene*

To a solution of 24 g (0.2 mole) of acetophenone in 100 ml of benzene a solution of 36.6 g of (I) (0.2 mole) in 500 ml of dry benzene was added at 0–5°. During the addition the solution became yellow, and then the separation of the enolate started. The suspension was stirred for 5 h more, and then 21.6 g (0.2 mole) of trimethylchlorosilane in 50 ml of benzene was added. During the addition the color changed to orange and the suspension warmed up slightly. The mixture was refluxed for an additional 3 h and filtered after cooling, as described under (*a*). After removal of the solvent the residue was fractionated several times through a 30 cm column as under (*a*) with a reflux ratio of 1:10 to remove unreacted acetophenone. The final yield of pure α-(trimethylsiloxy)styrene was 14.4 g (37.5 %), b.p.$_{13.5}$ 93–94°. (Found: C, 68.54; H, 8.35; Si, 14.56. $C_{11}H_{16}OSi$ calcd.: C, 68.70; H, 8.39; Si, 14.60 %.)

(*c*) *Bis(α-styryloxy)dimethylsilane*

This compound was prepared in similar fashion. Starting with 48 g acetophenone (0.4 mole), 73.2 g of (I) (0.4 mole) and 25.8 g of dimethyldichlorosilane (0.2 mole), the yield of (*c*) was 33 g (67 %). (Found: C, 73.30; H, 6.98; Si, 9.44; mol. wt., 281. $C_{18}H_{20}O_2Si$ calcd.: C, 72.90; H, 6.80; Si, 9.47 %; mol. wt., 296.5.)

(*d*) *1-(Trimethylsiloxy)cyclohexene*

Starting with 19.6 g (0.2 mole) of cyclohexanone in 50 ml of dry benzene, and with 36.6 g (0.2 mole) of (I) in 400 ml of benzene and 21.6 g (0.2 mole) of trimethylchlorosilane, the yield of (*d*) was 20.1 g (59 %). (Found: C, 63.68; H, 10.75; Si, 16.33; mol. wt., 175. $C_9H_{18}OSi$ calcd.: C, 63.46; H, 10.65; Si, 16.49 %; mol. wt., 170.3.)

(*e*) *2-(Trimethylsiloxy)-4-methyl-1,3-pentadiene*

Fifty-five g of (I) (0.3 mole) was dissolved in 300 ml of absolute ether, cooled to —55°, and then a solution of 29.5 g (0.3 mole) of mesityl oxide in 300 ml of dry ether was added slowly, allowing the mixture to warm up to room temperature. During this time separation of the enolate occurred. The suspension was stirred for 3 h at room temperature; then a solution of 32.4 g (0.3 mole) of trimethylchlorosilane in 50 ml dry ether was added and the mixture refluxed for 3 h. The product (*e*) was separated and purified as described under (*b*). The yield was 14 g (30 %) of slightly yellow oil. (Found: C, 61.03; H, 10.64; Si, 16.25; mol. wt., 165. $C_9H_{18}OSi$ calcd.: C, 63.46; H, 10.65; Si, 16.49 %; mol. wt., 170.3.) It was proved by spectroscopic means that this compound also was present in the higher boiling residue of reaction (*a*), as a result of condensation of acetone.

(*f*) *O-(Trimethylsilyl)-O-ethylketeneacetal and ethyl (trimethylsilyl)acetate*

Thirty-five g (0.4 mole) of ethyl acetate, dissolved in 500 ml of dry ether, was cooled to —65° and then a solution of 73.2 g of (I) (0.4 mole) in 250 ml of ether was added within 30 minutes, causing precipitation of the enolate. After stirring for an additional 30 minutes at low temperature, 43.2 g (0.4 mole) of trimethylchlorosilane in 50 ml of absolute ether was added. The reaction mixture slowly warmed up to room temperature. It was stirred for an additional 3 hours, then filtered, and the solvent removed by careful distillation through a 60 cm column filled with glass helices. The remaining residue was separated by distillation at normal pressure through the same column into hexamethyldisilazane (b.p. 124–127°), an intermediate fraction (b.p. 130–156°), and ethyl (trimethylsilyl)acetate (b.p. 157–158° after repeated fractionation) (n_D^{20} 1.4158). (Found: C, 52.23; H, 10.20; Si, 16.80; mol. wt., 156. $C_7H_{16}O_2Si$ calcd.: C, 52.44; H, 10.06; Si, 17.53; mol. wt., 160.3.) The intermediate fraction was once more concentrated (to b.p. 136–144°) and thereafter separated by gas chromatography through a Carbowax column at 125° into hexamethyldisilazane (ret. time 6.2 min), *O*-(trimethylsilyl)-*O*-ethylketeneacetal (ret. time 15 min) and ethyl (trimethylsilyl)acetate (ret. time 24.5 min). The final yields were 62.1 g of hexamethyldisilazane (96.5 %), 14.2 g of ethyl (trimethylsilyl)acetate (22.3%), and 8.8 g of the new acetal (13.7 %). (Found: C, 51.97; H, 9.91; Si, 17.00; mol. wt., 155. $C_7H_{16}O_2Si$ calcd.: C, 52.44; H, 10.06; Si, 17.53 %; mol. wt., 160.3.)

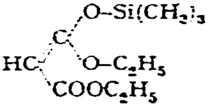
(*g*) *Condensation of ethyl isobutyrate*

To 34.8 g of ethyl isobutyrate (0.3 mole) in 400 ml of dry ether a solution of 54.9 g of (I) in 200 ml of dry ether was added during a period of 6 hours at room temperature. Thereafter the suspension was stirred for 80 hours at room temperature, and hydrolysed in a mixture of 100 ml of water and 50 ml of acetic acid. The ether phase was washed with 10 % Na_2CO_3 solution and water, then dried with Drierite. The yield of ethyl isobutyrylisobutyrate (b.p.$_{14}$ 86–88°, n_D^{20} 1.4231) was 15 g. (27 %). (Found: C, 64.32; H, 9.82. $C_{10}H_{18}O_3$ calcd.: C, 64.46; H, 9.74 %.)

SPECTRA AND STRUCTURE

The substituted enol structures of all the newly-prepared substances were proved by use of ^1H NMR spectra. The terminal $=CH_2$ group shows a typical AB pattern, as was to be expected. In Table 2 there are listed the chemical shifts of the unsaturated group and the $Si(CH_3)_3$-group, together with the values of the coupling constant J. It might be noted that in the case of 2-(trimethylsiloxy)propene the chemical shifts δ_A and δ_B are equal, and the pattern therefore degenerates into an A_2-pattern, showing only one single line. Similar observations were made by Whipple[9] *et al.*, investigating 2-substituted propenes. In the case of isopropenyl ethers only one single absorption also is observed, in the pertinent region. Long-range splitting effects between the different CH_3, $=CH-$ and $=CH_2$ groups in 2-(trimethylsiloxy)-4-methyl-1,3-pentadiene [δ $Si(CH_3)_3$ 0.203 p.p.m.] gives rise to 3 broad unresolved absorptions in the expected region, but no assignments can be given.

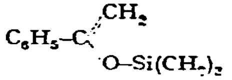
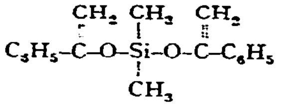
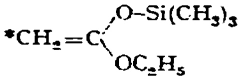
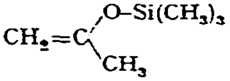
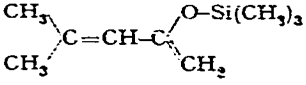
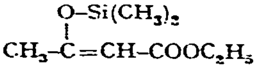
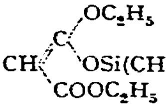
In this context we examined the NMR spectra of the already-prepared silyloxycrotonate[2] and found the absorptions also given in Table 2. These support the structure given by West[2]. *O*-Substitution also occurs in the case of silyl-substituted malonic ester; we found the absorptions which also are given in Table 2. The structure therefore is assumed to be



Investigation of the IR spectra of all compounds prepared gave similar results. In all spectra the typical C=O frequency between 1660 cm^{-1} and 1720 cm^{-1} is

TABLE 2

CHEMICAL SHIFTS (in p.p.m.) AND *J* VALUES

	δ Si(CH$_3$)$_3$ (*p.p.m.*)	=*CH$_2$*		
		J$_{AB}$	*δ A* (*p.p.m.*)	*δ B* (*p.p.m.*)
	0.251	1.3	4.33	4.73
 $C_6H_5\text{-}\overset{\overset{\displaystyle CH_2}{\Vert}}{C}\text{-}O\text{-}\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{Si}}\text{-}O\text{-}\overset{\overset{\displaystyle CH_2}{\Vert}}{C}\text{-}C_6H_5$	0.38	1.9	4.59	4.90
	0.191	2.2	2.90	3.06
	0.18	—	3.95	3.95
	0.203		methyl 1.82	
 $CH_3\text{-}\overset{\overset{\displaystyle O\text{-}Si(CH_3)_3}{\vert}}{C}=CH\text{-}COOC_2H_5$	0.22		methyl 1.87	CH 5.1
	0.27		CH 4.16	

* Shift of the CH_2 group in the isomeric $(CH_3)_3SiCH_2COOC_2H_5$ is 1.78 p.p.m.

missing. Instead the characteristic frequencies of the unsaturated groups appear: $\nu(C{=}C)$ 1648–1658 cm^{-1} (medium) and 892 cm^{-1} (strong). Besides that absorption, all compounds show the typical absorptions of the $Si(CH_3)_3$ group, and in the range between 1020 cm^{-1} and 1040 cm^{-1} a characteristic $\nu_{as}[Si\text{-}O(C)]$ vibration. Fig. 1 shows the IR spectrum of 2-(trimethylsiloxy)propene.

The NMR spectra were taken in 5% carbon tetrachloride solution with tetramethylsilane as internal reference with a VARIAN A-60 spectrograph at room temperature. The IR spectra were obtained with thin films, using a Perkin-Elmer grating spectrometer, Model 238.

DISCUSSION

In all the cases which were investigated, halosilanes react with sodium enolates of ketones to form the corresponding *O*-silylated enols. This fact may be due to the relatively high bond energy of the Si–O bonding system (108 kcal/mole), thus stabilizing the enol structure. Attempts to prepare the isomeric *C*-substituted ketones in a pure state by different methods have failed so far. Unfortunately we could not reproduce one procedure[10] already given to prepare (trimethylsilyl)acetone, in this respect being in accord with other observers[3].

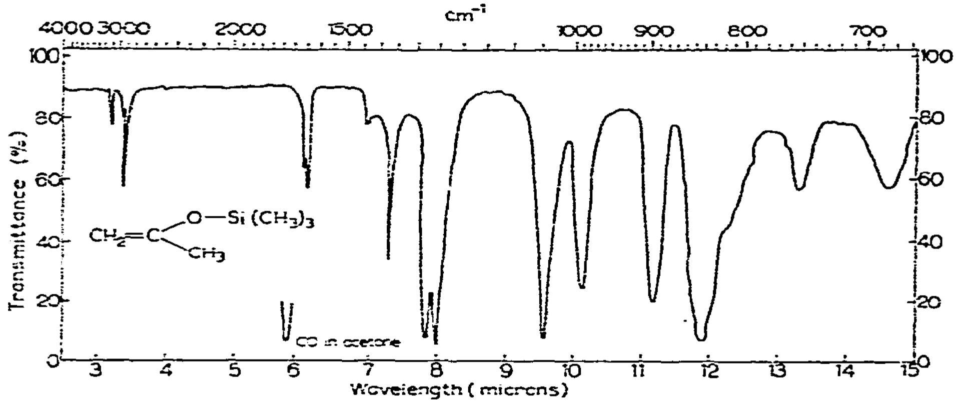


Fig. 1. IR spectrum of 2-(trimethylsiloxy)propene.

In the case of the enolates of esters, both substitution types seem to be possible. As far as we know, the reported preparation of *O*-(trimethylsilyl)-*O*-ethylketeneacetal is the first preparation of a keteneacetal starting with the sodium enolate of an ester, as the earlier work of Scheibler[11] in this field is reported to be not reproducible[12].

All of the *O*-silyl-substituted substances prepared in this work are hydrolytically unstable; hydrolysis yields the corresponding carbonyl compound and a silanol or a disiloxane. Attempts to polymerize these olefinic compounds in a controlled manner have failed so far. Cationic as well as anionic catalysts caused Si–O–C bond fission, whereas catalysts of the free-radical type caused uncontrolled resinification.

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SUMMARY

Although sodium bis(trimethylsilyl)amide reacts with non-enolisable carbonyl compounds to yield silyl-substituted imines and sodium silanolate, carbonyl compounds with active hydrogen are easily enolised and react differently, yielding bis(trimethylsilyl)amine and a sodium derivative of the carbonyl compound. The reaction of the resulting sodium enolates with halosilanes yields *O*-silyl-substituted enols, the structures of which have been proven by NMR and IR spectroscopy.

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