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A NEW RING OPENING REACTION OF 2-FURALDEHYDE DIPHENYL DITHIOACETAL VIA REDUCTIVE SILYLATION. PREPARATION OF 2,3,4-TRIS(TRIMETHYLSILYL)-3-ALKENYL AND 3,4,4-TRIS(TRIMETHYLSILYL)-2-BUTENYL KETONES

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5-Substituted 2-furaldehyde diphenyl dithioacetals are found to undergo facile ring-opening reaction and to give the corresponding polysilylated ketones when they were treated with metallic sodium in the presence of chlorotrimethylsilane.

In the previous paper, we reported on the reductive silylation reaction of furoic ester, which affords the corresponding 2,4-bis(trimethylsilyl)-3-butynyl ketone.[1] Recently, it has also been found in our laboratory that carbon-sulfur linkage is easily converted into carbon-silicon one through reductive silylation procedure.[2] In connection with studies on ring opening reactions of furan derivatives, we have examined the reductive silylation reaction of diphenyl dithioacetals of 2-furaldehyde and 2-furyl ketone , which is found to provide a convenient method for the preparation of the another types of poly-silylated ketones.

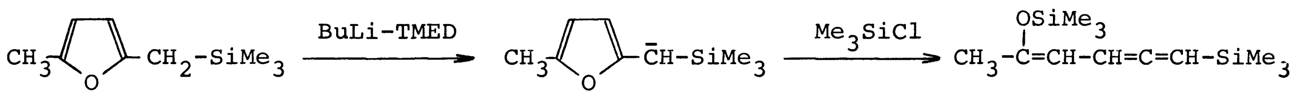
Thus, the dithioacetal 1 ($R^1 \neq H$, $R^2 = H$) was treated with sodium-chlorotrimethylsilane in refluxing tetrahydrofuran for 3 hr. Aqueous work up of the resulting reaction mixture afforded the corresponding ketone 4[3] having 3,4,4-tris(trimethylsilyl)-2-butenyl group in good yield. If desired, the corresponding trimethylsilyl enol ether 2 could be isolated sufficiently by simple distillation of the reaction mixture without hydrolytic work up.

On the other hand, the reaction with diphenyl dithioacetal 1 ($R^1 \neq H$, $R^2 = CH_3$) gave another type of silylated product 5,[4] possessing 2,3,4-tris(trimethylsilyl)-3-alkenyl group, in moderate yield.

Similar results were also obtained when silylated sulfides 6 were treated under similar reaction condition. In these cases, the yield was usually slightly better than those obtained from the dithioacetal.

Further, diphenyl dithioacetal of furoylsilane 7 was found to give 4,6-bis-(trimethylsilyl)-5-hexyn-2-one 8[5] in 53% yield.

In order to clarify the ring-opening process, furfuryltrimethylsilane (I) was treated with butyllithium-tetramethylethylenediamine at -78°C, followed by quenching with chlorotrimethylsilane, which afforded the ring opening product (II) in 63% yield along with the recovered (I) (20%).

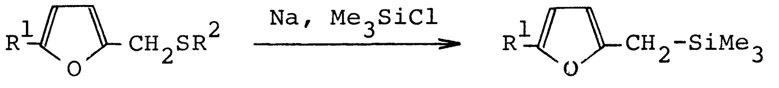


(I) (II)

This result has strongly suggested that introduction of trialkylsilyl group greatly facilitates the ring-opening reaction of furfuryl carbanion. Thus, the reaction is considered to proceed as follows. One of the two phenylthio groups is initially converted into trimethylsilyl one through reductive silylation[2] reaction to yield 6. Then, the second reductive cleagave of another carbon-sulfur bond of 6 takes place to afford the carbanionic species 9, through which ring opening reaction occurs as shown in Scheme 1. On contrary to the formation of (II) through the procedure described above, the resulting vinyl anion 10 may be trapped with the chlorosilane present in this reaction system to give the corresponding bis-silylated dienone 11, prior to the isomerization to allenic enolate.[6,7] On the dienone 11 thus formed, reductive silylation may take place preferentially in 1,6 manner when terminal site of the conjugated system is mono-substituted, while, in the case of di-substituted system, 1,4-reductive silylation may be a predominant process. Thus, the silyl enol ether 2 and 3 are formed selectively from the corresponding diphenyl dithioacetals 1 (R^2 = H and $R^2 \neq$ H), respectively.[7]

In the case of 7, the initial reductive cleagave of carbon-sulfur bond induces ring-opening, followed by removal of benzenethiolate and reductive silylation of the resulting ynone 12 as shown in Schem 2.

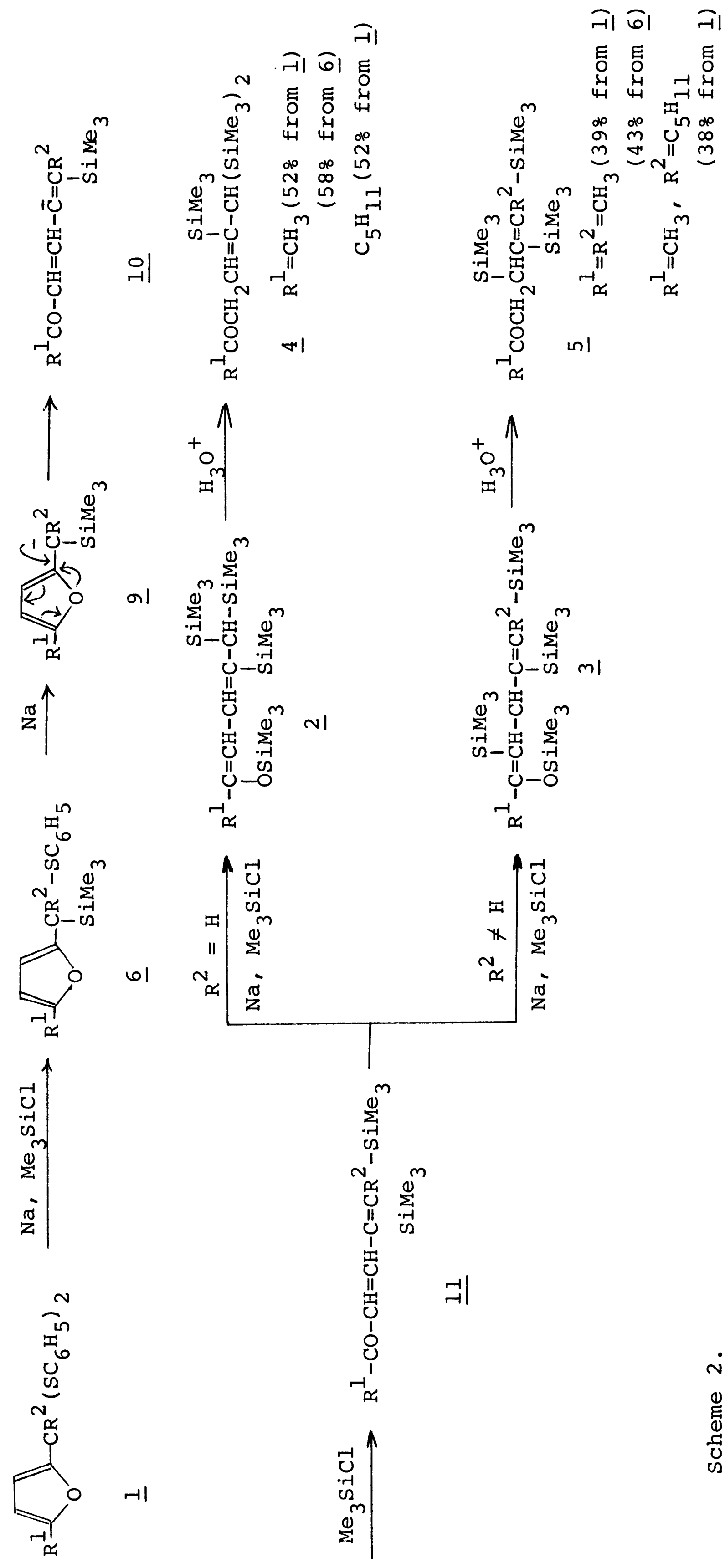
Similar ring opening reaction was also examined with mono-phenylthio substituted material (III), but, under similar reaction condition, this type of compound is shown not to undergo ring opening of furan ring but give simple substitution product (IV) in high yield. The result may be attributable to that the furfuryl anion generated initially is too reactive toward chlorotrimethylsilane to undergo ring opening, probably because it is not stabilized with trimethylsilyl group, and direct silylation may take place preferentially.



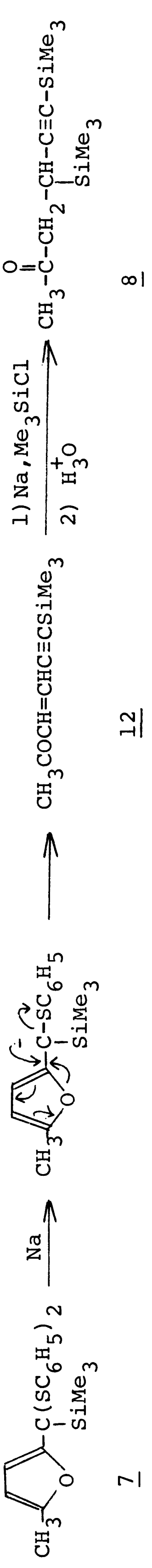
(III) (IV)

R^1 = H R^2 = C_6H_5 84%
R^2 = CH_3 R^2 = C_2H_5 78%

The following procedure is illustrative. To the refluxing THF (100 ml) solution suspended with sodium dispersion (7.36 g, 0.4 mol) was added THF (50 ml) solution of 5-methyl-2-furaldehyde diphenyl dithioacetal (6.25 g, 0.02 mol) and chlorotrimethylsilane (34.6 g, 0.32 mol) during 15 min under vigorous stirring. After additional heating for 3 hr, it was cooled and the deposited material was removed off by filtration. Removal of the solvent followed by distillation afforded 2-trimethylsiloxy-5,6,6-tris(trimethylsilyl)-2,4-hexadiene 2 (R^1 = CH_3), bp 105-110 °C/0.35 Torr. The product, $CH_3C(OSiMe_3)=CH_a-CH_b=CSiMe_3CH_c(SiMe_3)$, exhibited the following spectral data. Nmr (CCl_4, benzene as internal standard); δ 0.10 (s, 9H), 0.13 (s, 9H), 0.20 (s, 9H), 0.28 (s, 9H), 1.20 (s, 0.6H, H_c), 1.33 (s, 0.4H, H_c), 1.90 (s, 3H), 5.41 (d, J = 12 Hz, 0.6H, H_b), 5.65 (d, J = 11 Hz, Scheme 1.



Scheme 2.



0.4H, H_b), 6.54 (d, J = 11 Hz, 0.4H, H_a), and 6.77 (d, J = 12 Hz, 0.6H, H_a). Ir (neat); 3050, 2950, 1644, 1250, 1190, 1140, 1040, 976, 845, 758, 690, and 625 cm^{-1}.

The silyl enol ether (0.403 g, 1.04 mmol) obtained above was treated with 0.5 ml of hydrochloric acid (1.2 N) in THF (6 ml) for 5 min at room temperature. Then, it was washed with aq $NaHCO_3$ solution and was extracted with hexane. Removal of the solvent and tlc separation of the residue afforded 5,6,6-tris-(trimethylsilyl)-4-hexen-2-one (0.300 g, 92%), 4 ($R^1 = CH_3$), which showed the following spectral data. Nmr (CCl_4, benzene as internal standard); δ 0.09 (s, 9H), 0.13 (s, 9H), 0.17 (s, 9H), 1.18 (s, 1H), 2.15 (s, 3H), 3.20 (d, J = 7 Hz) and 3.31 (d, J = 8 Hz) as 2H, 5.94 (t, J = 7 Hz) and 6.01 (t, J = 8 Hz) as 1H. Ir (neat); 2950, 1740, 1728, 1600, 1359, 1251, 1160, 1040, 840, and 690 cm^{-1}.

References and Notes

1) I. Kuwajima, K. Atsumi, and I. Azegami, J. Chem. Soc., Chem. Commun., 76 (1977).

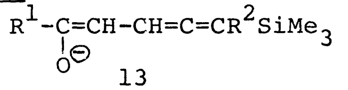
2) I. Kuwajima, T. Abe, and K. Atsumi, Chem. Lett., 383 (1978).

3) 4 (R^1=CH_3): see the text. 4 (R^1=C_5H_{11}): b.p. 115-120 °C/0.08 Torr. Key spectral data were similar with those of 4 (R^1=CH_3).

4) 5 (R^1=R^2=CH_3): two geometrical isomers (A) and (B) were separated by tlc. (A): b.p. 85-90 °C/0.8Torr. Nmr (CCl_4, benzene as internal standard); δ 0.08 (s, 9H), 0.18 (s, 9H), 0.25 (s, 9H), 1.93 (s, 3H), 2.09 (s, 3H), and 2.5∿3.0 (m, 3H). Ir (neat); 2949, 1725, 1250, 838, and 756 cm^{-1}. (B): b.p. 80-85 °C/0.8 Torr. Nmr; δ 0.08 (s, 9H), 0.20 (s, 18H), 1.83 (s, 3H), 2.09 (s, 3H), and 2.5∿3.0 (m, 3H). Ir (neat); 2949, 1725, 1250, 840, and 760 cm^{-1}. 5 (R^1=CH_3, R^2=C_5H_{11}): b.p. 127-132 °C/0.15 Torr. Key spectral data were similar with those of 5 (R^1=R^2=CH_3).

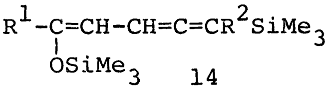
5) 8: b.p. 70-74 °C/0.4 Torr. Nmr; δ 0.22 (s, 9H), 0.24 (s, 9H), 2.25 (s, 3H), and 2.2∿2.7 (m, 3H). Ir (neat); 2945, 2880, 2150, 1724, 1253, 842, and 761 cm^{-1}.

6) Apparently, 10 is different species from the corresponding allenic enolate 13,



$R^1-\underset{O^{\ominus}}{\underset{|}{C}}=CH-CH=C=CR^2SiMe_3$

13



$R^1-\underset{OSiMe_3}{\underset{|}{C}}=CH-CH=C=CR^2SiMe_3$

14

which may be explicable for the formation of 11 under such a reaction condition.

7) Intermediary formation of silylated enol 14, in place of 11, can be excluded, since (II) does not undergo such kind of reductive silylation under the reaction condition employed here.

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