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Preliminary communication

NOVEL CYCLIC DIENOLATES FROM DIFUNCTIONAL SILANES AND β-DIKETONES

J.A. CELLA*
General Electric Company, Corporate Research & Development, Schenectady, New York 12301 (U.S.A.)
and T.D. MITCHELL
General Electric Company, Silicone Products Business Division, Waterford, New York 12188 (U.S.A.)

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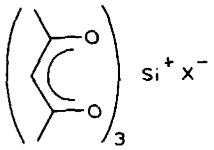
Summary

β-Diketones react with dialkyl- (or aryl-)dichlorosilanes in the presence of triethylamine at room temperature to afford silylated cyclic dienolates. These derivatives, formally synthetic equivalents of β-dicarbonyl dianions, do not require strongly basic conditions for their generation.

Silylation of β-dicarbonyl compounds can produce different products depending upon the functionality of the silane employed. Tetrafunctional silanes react with β-dicarbonyl compounds to produce cationic hexacoordinate complexes, **1** [1]. Trifunctional silanes yield hexa- or penta-coordinate cationic or neutral complexes, **2** or **3** depending on the method of preparation [2]. Mono- and di-functionalsilanes yield "normal" enol ether derivatives [2d,3] **4** and **5**. While the preparation of trialkylsilyl ethers, **4**, is uncomplicated in most cases, difficulties in the preparation of bis-enol ethers from difunctional compounds have been encountered [2d,3a]. For example, reaction of 2,4-pentanedione with dimethyldichlorosilane in the presence of



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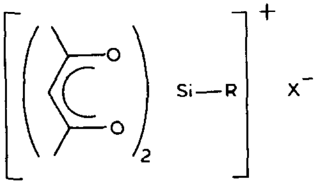

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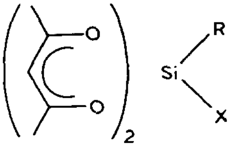

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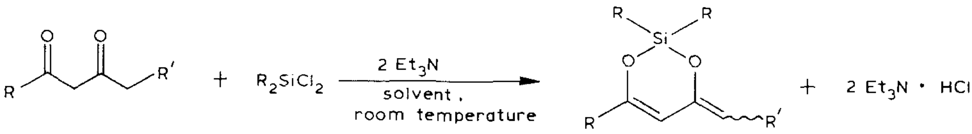
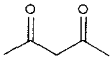
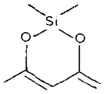
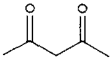
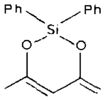
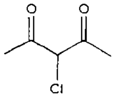
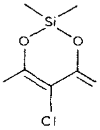
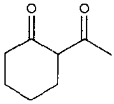
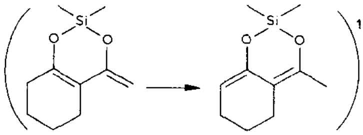
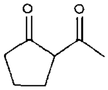
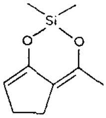
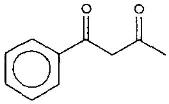
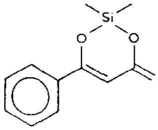
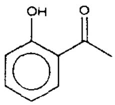
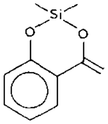
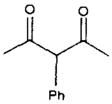
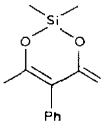
TABLE 1

PREPARATION OF CYCLIC DIENOLATES OF β-DICARBONYL COMPOUNDS



β-Dicarbonyl compound	Silane	Product	Yield (%)[a]
	$(CH_3)_2SiCl_2$		45
	Ph_2SiCl_2		75
	$(CH_3)_2SiCl_2$		56
	$(CH_3)_2SiCl_2$	 (8) (9) [10]	68
	$(CH_3)_2SiCl_2$		56
	$(CH_3)_2SiCl_2$		68
	$(CH_3)_2SiCl_2$		79
	$(CH_3)_2SiCl_2$		50

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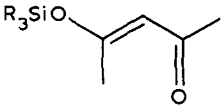
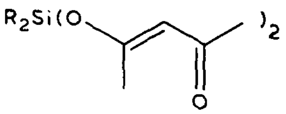
[a] Yields are based on isolated products (unoptimized).



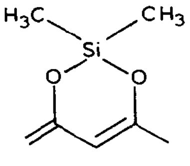
(4)



(5)

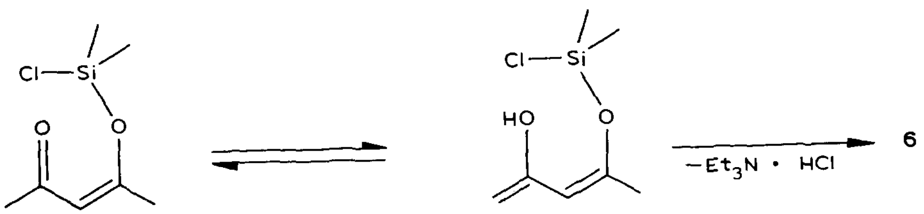
triethylamine produced 5 (R = CH_3) in only 20% yield [2d]. The intriguing possibility that hexacoordinate complexes might be produced in this reaction led us to study the products in more detail.

When 2,4-pentanedione (2 equiv.), dimethyldichlorosilane (1 equiv.), and triethylamine (2 equiv.) were allowed to react at 0° C to room temperature for 30 to 60 minutes in toluene, no evidence for chelated silanes was found. Careful workup of the reaction mixture, however, led to the isolation of significant quantities of the bis-silylated dienolate 6 [4]. The structure of 6 is evident from its proton NMR, mass spectrum and elemental analysis [5]. Indeed when 6 is prepared intentionally using one equivalent of 2,4-pentanedione per mole of dimethyldichlorosilane, respectable yields can be obtained.



(6)

The ready formation of 6 under mild conditions is somewhat surprising since bis-silylation of β-dicarbonyl compounds with monofunctional silanes generally requires the use of strong bases [6] (i.e., lithium diisopropylamide) or highly reactive silylating agents [7] (i.e., $(CH_3)_3SiOTf$)* to effect the second silylation. The facility with which bis-silylation occurs in this case may be due to intramolecular trapping of enol in the monosilylated intermediate, 7 [8].



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The bis-silylation of β-diketones with dimethyldichlorosilane appears to be quite general as depicted by the results in Table 1. The silylated dienolates prepared by this method could be of significant synthetic value as masked dianions of β-diketones [6,9], particularly since their formation does not require the use of strong bases and should be tolerant of other functionality.

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*OTf = triflate = trifluoromethanesulfonate.

A limitation to their utility in this regard is their exceptional reactivity. Silylated dienolate, **6**, hydrolyzes instantly on exposure to moist acetone. Attempted reaction of **6** with electrophilic reagents such as bromine in carbon tetrachloride or various carbonyl compounds in the presence of Lewis acids results in formation of considerable resinous material. This high reactivity may be due to the strain associated with incorporation of silicon atom into a 6-membered ring with three sp^2 carbon centers.

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4 Bis enol ether 5 was also produced in low yield. Yields of 6 fall off rapidly if air or moisture are not rigorously excluded during workup and distillation.

5 Compound 6: Found: C, 53.66; H, 7.72. $C_7H_{12}O_2Si$ calcd.: C, 53.85; H, 7.69%. NMR δ $(CDCl_3)$ 5.0 (s, 1, vinyl H), 3.95 (s, 1, =CH), 3.78 (s, 1, =CH), 1.73 (s, 3, CH_3) and 0.10 ppm (s, 6, $SiCH_3$). All compounds listed in Table 1 gave satisfactory elemental and spectral analyses.

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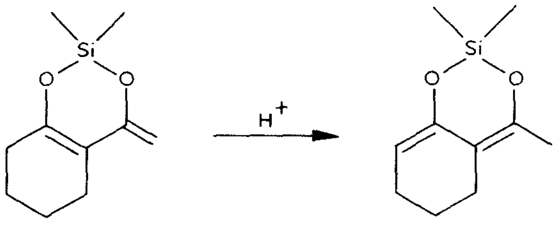
10 Reaction of 2-acetylcyclohexanone with dimethyldichlorosilane initially produces 8. On standing in $CDCl_3$ (presumably containing traces of acid), 8 is converted to 9.



(8) (9)