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Formation and reactivity of trimethylsilylmethyl cyclopentenones *

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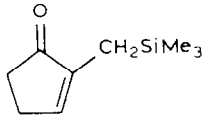
Abstract

Trimethyl-2-propynylsilane readily forms the expected hexacarbonyldicobalt complex with $[Co_2(CO)_8]$ and this reacts with ethene or cyclopentene to yield cyclopentenone derivatives containing allylsilane systems; these fail to yield methylenecyclopentanes on protonation.

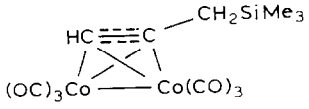
Discussion

We considered that 2-(trimethylsilylmethyl)cyclopent-2-en-1-ones, e.g. **1**, should be readily available by the Khand reaction [1,2] and might provide access to 2-methylenecyclopentanones, including sarkomycin and related antibiotics [3], by allylic electrophilic substitution.

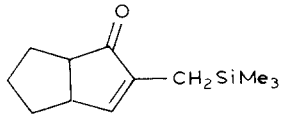
Trimethyl-2-propynylsilane [4] reacted smoothly with octacarbonyldicobalt(0) to give the required precursor, the complex **2**, in high yield. Ethene converted this into the desired cyclopentenone **1**, albeit in modest yield, and cyclopentene gave the analogous product, the bicyclic ketone **3**.



(1)



(2)



(3)

Both ketones were employed in attempts to effect allylic substitution of the silyl group. The monocyclic ketone **1** was substantially unchanged after heating under reflux for 18 h in pure ethanoic acid. Destruction of **1** on heating with toluene-4-

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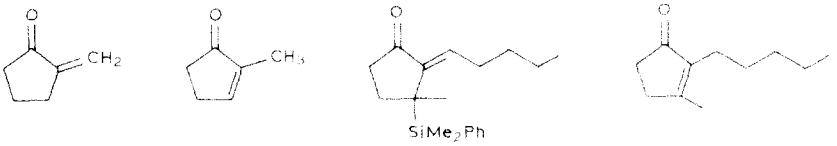
sulfonic acid in benzene was slow. Any 2-methylenecyclopentanone (**4**) formed may well have polymerized under these conditions, but after heating under reflux for six days, 25% of the silane **1** remained unchanged and only a trace (~ 3%) of 2-methylcyclopent-2-en-1-one (**5**) had been formed. Ketone **3** was even more resistant, 83% being recovered unchanged after similar treatment.



(**4**) (**5**) (**6**) (**7**)

Boron(III) fluoride-ethanoic acid was known [5] to transform the keto-silane **6** to dihydrojasmone (**7**), but left compound **1** unchanged after 16 h under the same conditions: only reaction with sulfuric acid in methanol led to reasonably smooth protodesilylation. The product (43%) was exclusively compound **5**; no methylenecyclopentenone could be detected. Under the same conditions, the bicyclic silane **3** yielded a mixture of the isomeric enones **8** (51%) and **9** (18%), with some unreacted ketosilane **3** (5%).

(**8**) (**9**)

Double bond shift into the side chain (to produce the desired methylenecyclopentanones) is clearly less favourable energetically than shift in the reverse direction (as in **6** → **7**). At the same time, the formation of ketone **9** confirms that double bond migration is relatively facile under the reaction conditions. From these considerations, the question arises whether the observed production of 2-methylcyclopent-2-en-1-one (**5**) is the result of direct replacement of silicon by hydrogen or of a two-step process via the methylene ketone **4** as an intermediate. In an attempt to elucidate this question, the ketosilane **1** was treated with D_2SO_4 in CH_3OD; the reaction was significantly slower than with H_2SO_4. The product **5** was found by ^1H NMR spectroscopy to have suffered extensive deuteriation of the methylene position (C(4) and C(5)). The ratio of CH_3/C(3) protons was approximately 10/1, showing that at least some deuteriation had occurred at C(3), but the conclusion that initial D^+ attack at C(3) was involved would be unsafe in view of the extensive scrambling. The results are therefore inconclusive.

Experimental

All reactions involving complex **2** were conducted under dinitrogen. Evaporation was carried out under reduced pressure using a rotary evaporator. Al_2O_3 for chromatography was Spence's grade UG 1 100 mesh which had been neutralized by treatment with ethyl ethanoate, washed with ethanol, then water, and oven dried at 150 °C for 2 h. "Flash"-silica column chromatography was performed using MN-

Kieselgel 60 (0.04–0.063 mm, 230–240 mesh; Macherey–Nagel and Co.) following the procedure of Still, Kahn and Mitra [6].

Trimethyl-2-propynylsilane was prepared [4] from 2-propynylmagnesium bromide and chlorotrimethylsilane, and contained 12–23% of allenyltrimethylsilane.

Hexacarbonyl(trimethyl-2-propynylsilane)dicobalt (2)

To a stirred solution of octacarbonyldicobalt(0) (18.8 g, 55 mmol) in light petroleum (b.p. 40–60 °C) at room temperature, trimethyl-2-propynylsilane (8 g, 55 mmol) was added over 15 min and stirring was continued for 5 h. The mixture was filtered through Kieselguhr, the solvent removed from the filtrate and the residue chromatographed on neutral alumina. Light petroleum (b.p. 30–40 °C) eluted the complex **2** (18.7 g, 85%), a deep purple oil. ^{1}H NMR: δ ($CDCl_3$) 0.12 (s, 9H, CH_3), 2.48 (d, 2H, J 1.28 Hz, CH_2), 5.98 ppm (t, 1H, HC≡). Analysis. Found: C, 36.6; H, 3.2; $C_{12}H_{12}Co_2O_6Si$ calc: C, 36.2; H, 3.0%.

2-(Trimethylsilylmethyl)cyclopent-2-en-1-one (1)

A steel autoclave containing the complex **2** (8.7 g, 22 mmol) and benzene (100 ml) was filled with ethene to a pressure of 60 atm and then heated to 90 °C for 36 h. After cooling, the reaction mixture was filtered through Kieselguhr, and the residue washed with trichloromethane. The filtrate was evaporated to dryness, and this residue chromatographed on alumina to separate unreacted complex (1.4 mmol) from the crude product. The latter was further purified by 'flash' silica chromatography followed by distillation (Kugelrohr; 130–140 °C/20 torr) and obtained as a colourless oil (994 mg, 29%). IR; ν(CO) ($CHCl_3$) 1685 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 0.04 (s, 9H, CH_3), 1.62 (d, 2H, J 1.28 Hz, CH_2Si), 2.34 (m, 2H, H(5)), 2.51 (m, 2H, H(4)) and 7.09 ppm (m, 1H, H(3)); ^{13}C NMR: δ($CDCl_3$) −1.82 (q, CH_3), 14.34 (t, CH_2Si), 26.09 (t, C(5)), 33.86 (t, C(4)), 143.85 (s, C(2)), 153.88 (d, C(3)) and 209.32 ppm (s, C(1)). Analysis. Found: C, 63.8; H, 9.6; $C_9H_{16}OSi$ calc: C, 64.2; H, 9.6%.

cis-4,5,6,6a-Tetrahydro-2-(trimethylsilylmethyl)-1-3aH-pentalenone (3)

A mixture of the complex **2** (15.9 g, 40 mmol), cyclopentene (13.6 g, 200 mmol) and benzene (250 ml) was heated under reflux for 24 h, then cooled, filtered through Kieselguhr, and the filtrate evaporated to dryness. Successive chromatography of the residue on neutral alumina and 'flash' silica columns and distillation (Kugelrohr; 74–78 °C/0.2 torr) gave the product **3** as a colourless, low-melting solid (2.33 g, 28%). IR: ν(CO) (film) 1695, ($CHCl_3$) 1685 cm^{-1}; ^{1}H NMR: δ ($CDCl_3$) 0.05 (s, 9H, CH_3), 1.70 (br. m, 8H, H(4–6) and CH_2Si), 2.72 (m, 1H, H(6a)), 3.21 (m, 1H, H(3a)), 6.98 ppm (m, 1H, H(3)). Analysis. Found: C, 68.7; H, 9.5. M^+, m/z 208.1285. $C_{12}H_{20}OSi$ calc: C, 69.2; H, 9.7%; M^+, 208.1283.

Attempted protonations of 2-(trimethylsilylmethyl)cyclopent-2-en-1-one (1)

(i) Using ethanoic acid. The silane **1** (126 mg, 0.75 mmol) was heated under reflux in freshly purified ethanoic acid (5 ml) for 18 h. Only starting material (104 mg, 85%) was recovered.

(ii) Using toluene-4-sulfonic acid. A solution of toluene-4-sulfonic acid hydrate (143 mg, 0.75 mmol) in benzene (20 ml) was dried by azeotropic distillation of half of the solvent. The silane **1** (126 mg) was then added and the mixture heated under reflux for 6 d, resulting in some decomposition. The cooled, filtered, washed

(aqueous sodium hydrogen carbonate) and dried solution was separated into two fractions by 'flash' silica chromatography. One yielded unreacted silane **1** (31 mg, 25%) and the other was shown, by GLC and ^{1}H NMR spectroscopy, to contain a small quantity (< 3%) of 2-methylcyclopent-2-en-1-one (**5**).

(iii) Using $BF_3 \cdot 2CH_3CO_2H$. To the silane **1** (126 mg) in dry dichloromethane (2 ml) under dinitrogen, $BF_3 \cdot 2CH_3CO_2H$ (0.115 ml, 155 mg, 0.825 mmol) was added and the mixture heated under reflux for 16 h, when TLC showed no change.

(iv) Using $H_2SO_4 \cdot CH_3OH$. To an ice-cooled solution of the silane **1** (126 mg) in methanol (5 ml), concentrated sulfuric acid (5 ml, 98%) was added over 50 min, maintaining the temperature below 20 °C. The mixture was then stirred at room temperature until TLC showed no more starting material (60 h), then poured into water (100 ml) and extracted with trichloromethane (4 × 20 ml). The dried ($MgSO_4$) extract was evaporated to dryness and the residue distilled (Kugelrohr, 55–65 °C/15 torr) to yield 2-methylcyclopent-2-en-1-one (**5**) (30 mg, 42%) (Lit. [7]: b.p. 54 °C/15 torr) identified by its IR and ^{1}H NMR spectra [7].

(v) Using $D_2SO_4 \cdot CH_3OD$. The preceding experiment was repeated using the silane **1** (126 mg) with methanol-d_1 (2 ml) and D_2SO_4 (2 ml; 98% in D_2O). No product could be detected by TLC after 20 h stirring at room temperature and the mixture was therefore warmed to 60 °C (bath temperature) under dinitrogen for 4 h, when no more starting material was detected. The ketonic product (36 mg) was isolated as before. Its IR spectrum showed only very weak C–H stretching bands at 2922 and 2840 cm^{-1}; in the ^{1}H NMR ($CDCl_3$) spectrum, the peaks at δ 2.32 (H(5)) and 2.50 ppm (H(4)) were very weak and the peaks at δ 1.73 (CH_3) and 7.30 ppm (H(3)) were in the ratio of *ca.* 10:1.

Protodesilylation of cis-4,5,6,6a-tetrahydro-2-(trimethylsilylmethyl)-1-3aH-pentalenone (3)

Treatment of **3** with toluene-4-sulfonic acid, as under (iii) above, led to the recovery of unreacted starting material (83%).

Sulfuric acid (5 ml, 98%) was added over 40 min to an ice-cooled solution of the silane **3** (210 mg, 1.01 mmol) in methanol (5 ml) maintained below 20 °C. After 2 d stirring at room temperature, TLC revealed no change and the mixture was therefore heated under reflux for 24 h, when most of the starting material had been consumed. Workup as for the product from silane **1** in (iv) above yielded three fractions on 'flash' silica chromatography: the unchanged silane **3** (11 mg, 5%), 2-methyl-4,5,6,6*a*-tetrahydro-1-3*aH*-pentalenone (**8**) (70 mg, 51%) (IR: ν_{max}, 3010, 2950, 2920, 2850, 1700, 1640, 1420, 1370, 1190, 1040 and 930 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 1.44 (br.m, 9H, H(4–6) and CH_3), 2.52 (m, 1H, H(6a)), 3.02 (m, 1H, H(3a)) and 7.05 ppm (m, 1H, H(3)); M^+ *m/z* 136.0873; $C_9H_{12}O$ calc: 136.0888) and 2-methyl-2,3,5,6-tetrahydro-1-4*H*-pentalenone (**9**) (25 mg, 18%) (IR: ν_{max}, 2958, 2920, 2858, 1702, 1641, 1428, 1378, 1192 and 930 cm^{-1}; ^{1}H NMR: δ($CDCl_3$) 1.26 (d, 3H, CH_3) and 2.00–3.00 ppm (m, 9H, H(2–6)); M^+, *m/z* 136.0882; $C_9H_{12}O$ calc: 136.0888).

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