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ACYLSILANES FROM THE PYROLYSIS OF SILYL ESTERS OF α-KETOACIDS

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Summary

The pyrolyses of silyl esters of pyruvic acid and phenylglyoxylic acid gave rise to acylsilanes in high yield. An intramolecular rearrangement involving an intermediate siloxycarbene is proposed to account for the reaction.

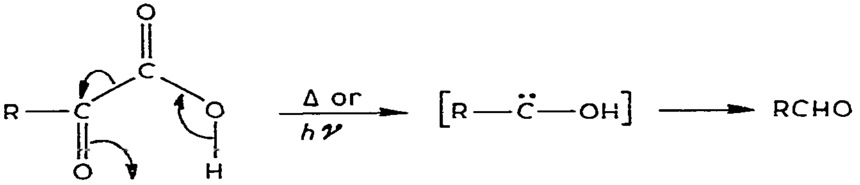
Introduction

It has been clearly established that acylsilanes on photolysis form siloxycarbenes: these have been trapped by a variety of reagents [1-3]. However, in

$$R_3SiCOR' \overset{h\nu}{\rightleftharpoons} R_3SiO\ddot{C}R' \rightarrow \text{products} \qquad (1)$$

the absence of a suitable trapping agent, the siloxycarbene must be able to revert to the parent acylsilane if no other reactions occur. In order to try to confirm this possibility, an alternative synthesis of an appropriate siloxycarbene was sought.

The suggestion that pyruvic acid and other α-ketoacids may decompose by an intramolecular pathway to oxacarbenes, leading to aldehydes [4,5], (eqn. 2), led us to investigate briefly the pyrolysis of silyl esters of α-ketoacids:



(2)

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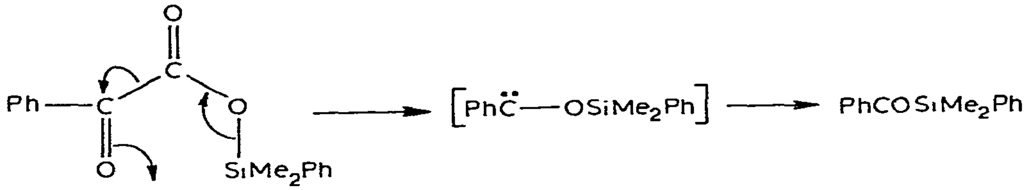
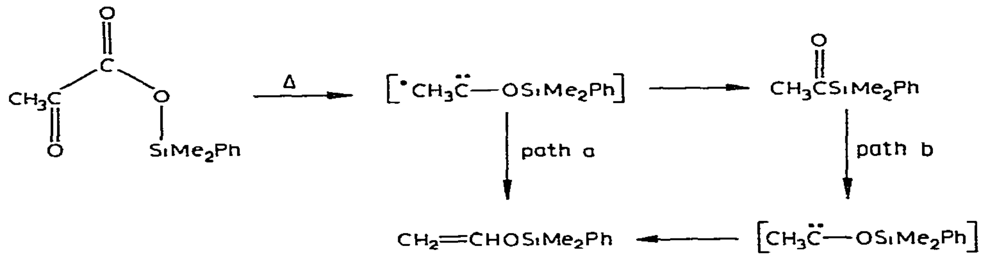
Results

It was found that the pyrolysis of phenyldimethylsilyl phenylglyoxalate cleanly gave only benzoylphenyldimethylsilane (72%), carbon dioxide, and starting material (28%), consistent with an intramolecular decomposition involving a siloxycarbene which subsequently rearranged to acylsilane* (eqn. 3).



(3)

Similarly, phenyldimethylsilyl pyruvate on pyrolysis gave acetylphenyldimethylsilane (40%), vinyloxyphenyldimethylsilane (51%) and recovered starting material. Over shorter periods of time, where much starting material was recovered, it was found that the acylsilane was initially the major product, but that over longer reaction times the amount of acylsilane diminished with a concurrent rise in the yield of vinyloxysilane. Thus, while some of the vinyloxysilane may have arisen by insertion of the siloxycarbene into the adjacent C—H bond (path a) it is evident from this experiment, and by the finding that acetylphenyldimethylsilane itself thermolyses under the same experimental conditions to give the vinyloxysilane, that a major source of the vinyloxy compound is the thermal rearrangement of the intermediately formed acylsilane (path b), which is also believed to involve a siloxycarbene intermediate [6].



(4)

It has been reported that alkyl pyruvates, such as benzyl pyruvate, do not thermally decompose by concerted decarboxylation, but instead decompose by a two bond cleavage mechanism to acetyl and benzyl radicals, the former of which completely decarbonylate to methyl radicals prior to coupling or hydrogen abstraction [7]. This was confirmed under our experimental conditions, since benzyl pyruvate, when pyrolysed, gave bibenzyl (35%) and ethylbenzene (34%) by radical coupling, together with recovered starting material and traces of other unidentified material. These results effectively preclude the possibility (thermodynamically improbable) that the silyl pyruvates were decomposing to acetyl and silyl radicals which combined to form the observed acylsilane, since under the experimental conditions the acetyl radicals would not have survived decarbonylation.

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* The alternative 4-centre pathway appears less probable on steric grounds.

These findings give strong support to the propositions that siloxycarbenes are intermediates in the thermal decomposition of silyl α-ketocarboxylate esters, and that such siloxycarbenes, in the absence of other reactions, isomerise to acylsilanes.

Experimental

Tetrahydrofuran and ether were distilled from sodium immediately before use. Identities and proportions of mixtures were determined by NMR techniques (Varian T60) or by gas chromatography (Varian Aerograph Series 200, with a 20′ × ¼″ aluminium column containing 20% SE 30 on Chromasorb W, using a column temperature of 282°C and helium as carrier gas). NMR and IR spectra were run in carbon tetrachloride solution. Microanalyses were performed by A.B. Gygli of Toronto.

Phenyldimethylsilyl pyruvate

Silver pyruvate was prepared in 96% yield by stirring 10 ml (0.14 mol) of pyruvic acid and 31.8 g (0.14 mol) of silver trifluoroacetate in 100 ml tetrahydrofuran in the dark for 1.5 h. The precipitate was filtered and washed with ether.

Silver pyruvate (10 g) and 8.5 ml of phenyldimethylchlorosilane in 100 ml dry pentane were stirred in the dark for 4 h. After filtration and removal of the solvent, distillation at 73-75°C/0.28 mmHg gave 86% of phenyldimethylsilyl pyruvate; n_D^{22} 1.4947; NMR: δ 7.2-7.7, m, 5H (Ph); 2.26, s, 3H (CH_3CO); 0.59, s, 6H (Me_2Si) ppm; IR 5.7, 5.8 (C=O), 6.98, 9.0 (Si—Ph), 7.97 (SiMe) μ (Found: C, 59.40; H, 6.20. $C_{11}H_{14}O_3Si$ calcd.: C, 59.43; H, 6.35%).

Phenyldimethylsilyl phenylglyoxalate

This compound, prepared analogously to the above in 83% yield, had b.p. 140-142°C/0.16 mmHg, n_D^{22} 1.5461; NMR: δ 7.2-8.0, m, 10H (Ph); 0.70, s, 6H ($SiMe_2$) ppm; IR: 5.80, 5.90 (C=O), 6.90 (C—Ph), 7.0, 9.0 (Si—Ph), 8.0 (SiMe) μ (Found: C, 68.15; H, 5.71. $C_{16}H_{16}O_3Si$ calcd.: C, 67.58; H, 5.67%).

Acetylphenyldimethylsilane

Following the dithane route to acylsilanes [8], the anion of 2-methyl-1,3-dithiane was coupled with phenyldimethylchlorosilane to give, after recrystallisation from pentane methanol, a 68% yield of 2-phenyldimethylsilyl-2-methyl-1,3-dithiane, m.p. 79-80°C; NMR: δ 7.2-7.5, m, 5H (Ph); 1.73, s, 3H (Me), 1.6-3.4, m, 6H (ring); 0.46, s, 6H ($SiMe_2$) ppm.

Hydrolysis of this with mercuric chloride and cadmium carbonate (10 and 5 mol equivalents respectively) in water/acetone/benzene, followed by work-up and distillation gave 58% of acetylphenyldimethylsilane, b.p. 60-63°C/1.9 mmHg, further purified by preparative GLC: n_D^{22} 1.5138; NMR: δ 7.3-7.7, m, 5H (Ph); 2.12, s, 3H (CH_3CO); 0.43, s, 6H (Me_2Si) ppm; IR: 6.08 (C=O), 7.0, 9.0 (Si—Ph), 8.0 (SiMe) μ (Found: C, 67.18; H, 7.58. $C_{10}H_{14}OSi$ calcd.: C, 67.36; H, 7.91%).

Vinyloxyphenyldimethylsilane

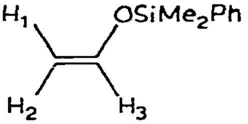
Molar equivalents of bis(formylmethyl)mercury and phenyldimethylchloro-

TABLE 1 .

PRODUCTS FROM THE PYROLYSIS OF ORGANOSILICON COMPOUNDS

Compound	Reaction time (min)	Products and proportions (%)
$PhCOCO_2SiMe_2Ph$	110	$PhCOSiMe_2Ph$ (72)[a] Starting material (28) CO_2 (not determined)
$MeCOCO_2SiMe_2Ph$	~18	$CH_3COSiMe_2Ph$ (40) $CH_2{=}CHOSiMe_2Ph$ (51)[b] Starting material (9) CO_2
$MeCOSiMe_2Ph$	20	$CH_2{=}CHOSiMe_2Ph$ (83) Starting material (17)
$CH_3COCO_2CH_2Ph$[c]	9	$PhCH_2CH_2Ph$ (35)[d] $PhCH_2CH_3$ (34)[e] Starting material (31)

[a] Ref. 9. IR: 6.18 (C=O) μ; NMR: 7.1-7.9, m, 10H (Ph); 0.56, s, 6H ($SiMe_2$) ppm. [b]



NMR: δ 7.2-7.8, m, 5H (Ph); 6.33, d of d, (J_{cis} 6, J_{trans} 14 Hz), 1H (H_3); 4.38, d (J 14 Hz); 1H (H_1); 4.05, d (J 6 Hz) 1H (H_2); 0.42, s, 6H ($SiMe_2$) ppm; IR: 6.12 μ (C=C). [c] NMR: δ 7.32, s, 5H (Ph); 5.17, s, 2H (CH_2); 2.32, s, 3H (Me)ppm. [d] NMR: δ 7.1, s, 10H (Ph); 2.89, s, 4H (CH_2) ppm. [e] NMR: δ 7.19, s, 5H (Ph); 2.62, q, 2H (CH_2); 1.22, t, 3H (CH_3) ppm.

silanes were stirred in tetrahydrofuran at 25°C for 30 min following published procedures [10]. Work-up and distillation at 50-52°C/1.9 mmHg gave 58% of the desired compound, n_D^{22} 1.4957, identical in all respects to the product obtained from the pyrolyses (Found: C, 67.22; H, 7.81. $C_{10}H_{14}OSi$ calcd.: C, 67.36; H, 7.91%).

Pyrolysis experiments

Pyrolyses were effected by direct heating, using a Bunsen burner, of an evacuated flask connected to a water-cooled condenser (reflux configuration), and thence through a liquid nitrogen trap to a mechanical pump. A thermocouple indicated the flask temperature to be approximately 650°C. Data for the pyrolyses are given in Table 1. In the case of phenyldimethylsilvl pyruvate, a

TABLE 2

PYROLYSES OF PHENYLDIMETHYLSILYL PYRUVATE

Pyrolysis time (min)	Decomposition (%)	Proportions of products (%)		
		A[a]	B[b]	C[c]
6	39	61	32	7
12	76	24	49	27
20	98	2	17	81

[a] A = $MeCOCO_2SiMe_2Ph$. [b] B = $MeCOSiMe_2Ph$. [c] C = $CH_2{=}CHOSiMe_2Ph$.

1.0 g sample was pyrolysed under the above conditions, and samples were removed at various intervals: proportions of compounds, determined from NMR integrations, are given in Table 2.

Acknowledgement

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References

1 J.M. Duff and A.G. Brook, Can. J. Chem., 51 (1973) 2869.
2 A.G. Brook, H.W. Kucera and R. Pearce, Can. J. Chem., 49 (1971) 1618.
3 A.G. Brook, R. Pearce and J.B. Pierce, Can. J. Chem., 49 (1971) 1622.
4 G. Vesley and P. Leermakers, J. Phys. Chem., 68 (1964) 2364.
5 J. Calvert and J. Pitts, Photochemistry, J. Wiley and Sons Inc., New York, 1966, 432.
6 A.R. Bassindale, A.G. Brook and J. Harris, J. Organometal. Chem., 90 (1975) C6.
7 R. Louw and E.C. Kooyman, Rec. Trav. Chim. Pays-Bas, 86 (1967) 1041.
8 A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, J. Amer. Chem. Soc., 89 (1967) 431.
9 A.G. Brook, M.A. Quigley, G J.D. Peddle, N.V. Schwartz and C.M. Warner, J. Amer. Chem. Soc., 82 (1960) 5102.
10 A.N. Nesmeyanov, I.F. Lutsenko and V.A. Brattsev, Dokl. Akad. Nauk S.S.S.R., 128 (1959) 551.