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SYNTHESIS OF CYCLIC ACYLSILANES

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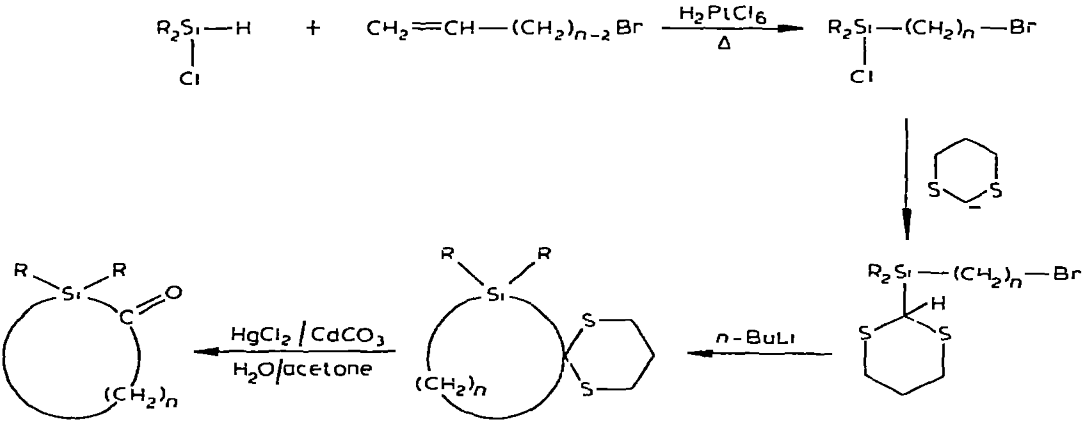
Summary

An improved route to cyclic acylsilanes, involving the synthesis of intermediate disubstituted spirodithianes and their hydrolysis, is described.

To date the only reported route to cyclic acylsilanes has involved the synthesis and hydroboration of a silacyclohexene, followed by oxidation of the resulting 1-silacyclohexan-2-ol, a tedious and time-consuming process [1,2]. The success of the dithiane route to acyclic acylsilanes [3,4] prompted the development of the route outlined in Scheme 1 to the corresponding cyclic compounds, which has been found to be an improvement on the previous method.

Each of the reactions in this sequence is well-known and little comment is required. It was noted that phenyl-substituted dithianes were much more resistant toward hydrolysis than their methyl analogues, as has been noted previously



(R = Me, Ph, n = 3,4,5)

TABLE 1

PROPERTIES OF ω-HALOALKYLCHLOROSILANES

$RR'SiCl(CH_2)_nX$	Yield (%)	B.p. (°C)	Refractive Index
$Ph_2SiCl(CH_2)_3Cl$[a]	67	135°/0 01 mm	n_D^{21} 1.5760
$Ph_2SiCl(CH_2)_4Br$	52	151-153°/0.02 mm	
$PhMeSiCl(CH_2)_4Br$	73	108-110°/0.02 mm	n_D^{22} 1 5425
$Me_2SiCl(CH_2)_4Br$	83	64-68°/0.02 mm	
$Ph_2SiCl(CH_2)_5Cl$	51	150-153°/0 01 mm	
$PhMeSiCl(CH_2)_5Cl$	63	110-111°/0.01 mm	n_D^{22} 1.5198
$Me_2SiCl(CH_2)_5Cl$	58	77-78°/3.4 mm	

[a] From PhLi + $Cl_3Si(CH_2)_3Cl$. Other products were obtained by the addition of R_2SiClH to $CH_2{=}CH{-}(CH_2)_{n-2}X$ using H_2PtCl_6.

[5]. Dimethylsiladithianes hydrolyse in minutes, with the vigorous evolution of CO_2, whereas the diphenyl compounds generally required prolonged refluxing. In the case of diphenylsilacyclopentanone, the dithiane precursor was resistant to hydrolysis under the usual conditions, and no acylsilane could be obtained.

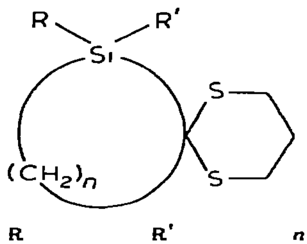
Data on the compounds prepared are given in Tables 1, 2, and 3, and typical conditions are given in the Experimental section. Yields have not necessarily been optimised.

Experimental

All reactions involving the use of organometallic reagents were carried out in anhydrous solvents under an atmosphere of dry nitrogen. The following are typical of the conditions used to give the compounds listed in Tables 1, 2, and 3.

TABLE 2

PROPERTIES OF SUBSTITUTED DITHIANES

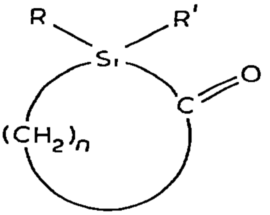


R	R'	n	Yield (%)	M.p.[a] or b p. (°C)
Ph	Ph	3	53	134-135
Ph	Ph	4	48	143-144.5[b]
Me	Ph	4	62	66.5-67.5[c]
Me	Me	4	50	105-109/0.03 mm[d]
Ph	Ph	5	36	92-93
Me	Me	5	58	103-107/0.02 mm

[a] Temperatures not followed by a pressure are melting points. [b] Found. C, 67.54; H, 6.87. $C_{20}H_{24}SiS_2$ calcd.: C, 67.38; H, 6.78%. [c] Found: C, 61.38; H, 7 32. $C_{15}H_{22}SiS_2$ calcd.. C, 61.17; H, 7.53%. [d] Found: C, 51.37; H, 8.73. $C_{10}H_{20}SiS_2$ calcd.. C, 51.65; H, 8.67%.

TABLE 3

CYCLIC ACYLSILANES[a]



R	R′	n	Yield (%)	B.p. (°C)
Ph	Ph	3	0	
Ph	Ph	4	52	65-66[b]
Ph	Me	4	79	94-97/0.05 mm[c]
Me	Me	4	58	44/3.6 mm[d]
Me	Me	5	53	43-44/1.5 mm[e]
Ph	Ph	5	44	Impure oil

[a] Spectroscopic data for these compounds will be found in ref. 6. [b] Mixed melting point with authentic sample was not depressed. [c] n_D^{22} 1.5488. Found: C, 70.54, H, 7.84. $C_{12}H_{16}SiO$ calcd.: C, 70.53; H, 7.89%. [d] n_D^{22} 1.4635. Found: C, 58.87; H, 9.83. $C_7H_{14}SiO$ calcd.: C, 59.09, H, 9.92%. [e] n_D^{22} 1.4707. Found C, 61.56; H, 10.29. $C_6H_{16}SiO$ calcd.: C, 61.49; H, 10.32%.

Preparation of 1-methylphenylchlorosilyl-4-bromobutane

A mixture of 30.0 g (0.224 mol) of 4-bromobutene, 38.0 g (0.246 mol) of methylphenylchlorosilane and ten drops of 0.4 *M* solution of chloroplatinic acid in n-propanol was heated in an efficient reflux apparatus to 100°, at which point the heat source was removed. The temperature rose rapidly to 150° and levelled off at 165°, with foaming and vigorous refluxing (*Caution*). The temperature was maintained at 140-160° for 10 min and then the material was distilled to yield 47 g (73%) of the desired compound, b.p. 108-112° /0.02 mm.

Preparation of 1-methyl-1-phenyl-1-sila-7,11-dithiaspiro[5.5]undecane

To a solution of 25.6 g (0.214 mol) of 1,3-dithiane in 300 ml of anhydrous tetrahydrofuran (THF), cooled to −20° by a dry-ice/carbon tetrachloride bath, was added 138 ml (0.221 mol) of 1.6 *N* n-butyllithium. After 2 h at −20°, a solution of 62 g (0.214 mol) of 1-methylphenylchlorosilyl-4-bromobutane in 100 ml THF was added all at once, and the mixture was allowed to warm to room temperature overnight.

To 300 ml of anhydrous diethyl ether and 200 ml of THF, cooled to −20°, were added, simultaneously over about 1 h, the above dithiane solution and 138 ml (0.221 mol) of n-butyllithium in hexane (by syringe) at such a rate that more than one equivalent of dithiane was always present in the reaction vessel. After the addition, the metallation was allowed to continue at −20° for an additional 1.5 h, and the mixture was then cooled to −80° in a dry-ice/acetone bath.

The above solution was then transferred by syringe in 80 ml portions into a flask containing 1l of refluxing ether, precautions being taken to avoid condensation of moisture on the syringe needle. After completion of the transfer the solution was refluxed for 5 h and then worked up by removal of the solvents under reduced pressure. The residue was taken up in ether, which was then washed with 10% aqueous sodium bicarbonate, and then saturated sodium chloride solution. After drying, the residue obtained on removal of the ether was distilled in a Kugelrohr apparatus, all volatile material up to 260°/0.01 mm being collected. This was crystallised from pentane to yield 39.4 g (62%) of substituted dithiane, m.p. 66.5-67.5°.

In other preparations, dimethylsilyl-substituted dithianes were purified by fractional distillation, and diphenyl-substituted dithianes were not distilled at all, but were crystallised directly, first from methanol—benzene, and then from hexane.

Hydrolysis of 1-phenyl-1-methyl-1-sila-7,11-dithiaspiro[5.5] undecane

A solution of 36.4 g (0.124 mol) of the above dithiane in 200 ml of acetone was added to a mixture of 170 g (0.62 mol) mercuric chloride, 43 g (0.25 mol) of cadmium carbonate, 80 ml of water, 800 ml of acetone and 300 ml of benzene. After 4 h reflux, the material was filtered, and the precipitate washed well with 1/1 acetone/benzene. The volatile solvents were removed under reduced pressure, and the residue was taken up in ether. This solution was thoroughly washed with saturated sodium chloride solution to remove mercuric chloride. After drying with anhydrous magnesium sulphate, and removal of the ether, the residue was distilled in a Kugelrohr apparatus at 0.01 mm and the distillate was collected in a dry-ice/acetone trap. The distillate was extracted with ether, and the ether layers were washed with 5% hydrochloric acid, dilute sodium bicarbonate, and then saturated sodium chloride solution. After drying, and removal of the ether, distillation gave 20.0 g (79%) of 1-phenyl-1-methyl-1-silacyclohexan-2-one, b.p. 94-97°/0.05 mm, identical with authentic material [2] in all respects.

Similar procedures were employed in hydrolysing the dithiane precursors of the diphenylsilyl species, except that 16 h reflux was employed, and the acylsilanes were, of necessity, purified by column chromatography, since their boiling points were too high for convenient distillation.

Hydrolysis of 1,1-dimethyl-1-sila-7,11-dithiaspiro[5.5] undecane

The dimethyldithiane (40 g) in 100 ml of DMSO was added to a mixture of 250 g (0.91 mol) of mercuric chloride, 100 g (0.58 mol) of cadmium carbonate, 40 ml water, 200 ml of DMSO and 800 ml of diethylene glycol. Vigorous evolution of CO_2 occurred, which quickly subsided. The mixture was then warmed to 60° for 2 h, and then the volatile components of the mixture were distilled under high vacuum with a trap cooled by dry-ice/acetone. About 200 ml of a mixture of acylsilane, water and DMSO were thus collected. Water was added and the acylsilane was ether extracted, and washed with water. Work-up and distillation, gave 14.5 g (58%) of 1,1-dimethyl-1-silacyclohexan-2-one, b.p. 44°/3.6 mm.

Acknowledgement

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References

1 A.G. Brook and J.B. Pierce, J. Org. Chem., 30 (1965) 2566.
2 A.G. Brook, H.W. Kucera and D.M. MacRae, Can. J. Chem., 48 (1970) 818.
3 A.G. Brook, J.M. Duff, P.F. Jones and N.R. Davis, J. Amer. Chem. Soc., 89 (1967) 431.
4 E.J. Corey, D. Seebach and R. Freedman, J. Amer. Chem. Soc., 89 (1967) 434.
5 P.F. Jones, M.Sc. Thesis, University of Toronto, 1967.
6 A.G. Brook in Advances in Organometallic Chemistry, Vol. 7, Academic Press, New York (1968) P95.