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BROMOALKYL- AND BROMOVINYL-SILANES

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Summary

Several vinylsilanes and one vinylgermane were brominated; the resulting bromoalkyl compounds were dehydrobrominated in refluxing pyridine to bromovinyl compounds. 1-Triphenylsilyl-2-phenylethane could be mono-, di- or tri-brominated with *N*-bromosuccinimide.

During the course of studies on the stereochemistry of bromination of vinylsilanes, and the debromination, dehydrobromination and debromosilylation of the bromo adducts, as recently reported [1], a number of additional systems were investigated. These are described here briefly, since some of the types of compounds, particularly the α-bromovinyl-silanes, have been found to have synthetic utility [2,3].

It was found that bromination of a wide variety of triphenylvinylsilanes, and the only vinylgermane investigated, was readily effected using bromine in carbon tetrachloride in the presence of ultraviolet light. In the absence of UV light, the reactions were much slower, and the yields poorer, except when the double bond was activated by an aryl group, as in the β-silylstyrenes where no UV light was required when CH_2Cl_2 or $CHCl_3$ (but not CCl_4) was solvent [1]. The reactions carried out are listed in Table 1.

Many of the dibromides were cleanly dehydrobrominated by refluxing pyridine to yield bromovinyl derivatives, as shown in Table 2. With the simple 1,2-dibromoethyl derivatives, hydrogen was lost from the carbon alpha to silicon and the bromine came from the beta carbon atom, as has been previously observed with the dibromosilylstyrenes [1] and other compounds [4]: however, when the α-carbon was more highly substituted (Me, Br) the loss of bromine was necessarily from the α-carbon atom. When 1,1,2-tribromo-1-triphenylsilyl-2-phenylethane was heated, it underwent debromosilylation yielding β,β-dibromostyrene, and triphenylbromosilane as previously observed with other dibromosilylstyrenes [1,5]. The brominated germane which decomposed in refluxing pyridine, gave

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TABLE 1

HALOGENATION OF VINYLMETALLOIDS

Vinylmetalloid	Dibromide	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)		NMR data [a] δ (ppm)
				C	H	
$Ph_3SiCH{=}CH_2$ [b]	$Ph_3SiCHBrCH_2Br$	95	106—107 [c]	53,77 (53,82)	4,20 (4,06)	7,2—7,8; 3,4—4,3 (m, ABC, 3H) (CCl_4)
$Ph_3SiCH{=}CH_2$	$Ph_3SiCHClCH_2Cl$	84	120—123 [d]	66,90 (67,22)	5,01 (5,08)	7,2—7,7; 3,6—4,25 (m, ABC, 3H) (CCl_4)
$Ph_3SiCBr{=}CH_2$ [b]	$Ph_3SiCBr_2CH_2Br$	85	166—167 [c]	45,99 (45,73)	3,18 (3,26)	7,2—8,0; 4,42 (s, 2H)
$Ph_3SiCMe{=}CH_2$ [b]	$Ph_3SiCMeBrCH_2Br$	92	149—150 [d]	54,92 (54,86)	4,44 (4,38)	7,2—7,7; 4.24, 4.04 (m, AB, J 11 Hz); 1,98 (s)
(*Z*)-$Ph_3SiCBr{=}CHPh$ [b]	$Ph_3SiCBr_2CHBrPh$	78	154—156 [d]	52,01 (51,94)	3,54 (3,52)	7,1—7,8; 5,79 (s)
(*E*)-$Ph_3SiCBr{=}CHPh$ [b]	$Ph_3SiCBr_2CHBrPh$	77	154—156 [d]			
$Ph_3GeCH{=}CH_2$ [b]	$Ph_3GeCHBrCH_2Br$	78	118—120 [d]	49,16 (48,94)	3,74 (3,69)	7,3—7,8; 3,61—4,48 (m, ABC, 3H)

[a] NMR spectra run in $CDCl_3$, unless otherwise noted. [b] Ultraviolet light employed. [c] Recrystallised from ethanol. [d] Recrystallised from methylene chloride/methanol.

TABLE 2

DEHYDROBROMINATIONS OF SOME BROMOALKYLMETALLOIDS WITH REFLUXING PYRIDINE

Bromide	Reaction time (h)	Product	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)		NMR data [a] δ (ppm)
					C	H	
$Ph_3SiCHBrCH_2Br$	4,5	$Ph_3SiCBr{=}CH_2$	82	128—129 [b]	66,10 (65,73)	4,66 (4,69)	7,2—7,8; 6,68, 6,36 (2 d, J 1,5 Hz) (CCl_4)
$Ph_3SiCBr_2CH_2Br$	1,5	$Ph_3SiCBr{=}CHBr$	41	162—163 [c]	54.29 (54,07)	3,60 (3,63)	7,3—7,8; 7,2 (s, 1H) (CCl_4)
$Ph_3SiCBrMeCH_2Br$	22	$Ph_3SiCMe{=}CHBr$	45	174—175 [d]	66.49 (66,48)	5,04 (5,05)	7,2—7,8; 6.52 (q, J 1.5 Hz); 1,97 (d, J 1,5 Hz)
$Ph_3GeCHBrCH_2Br$	[e]	$Ph_3GeCBr{=}CH_2$	78	127—128 [d]	58,27 (58,61)	4,35 (5,18)	7,3—7,8; 6.70, 6,32 (AB, J 2 Hz)

[a] NMR spectra run in $CDCl_3$ unless otherwise noted. [b] Recrystallised from petroleum ether (b.p. 60—70° C). [c] Recrystallised from heptane and from methylene chloride/methanol. Stereochemistry not known. [d] Recrystallised from methylene chloride/methanol. [e] Reaction run in benzene with 2 equivalents of 1,5-diazabicyclo[4.2.0]nonane as dehydrohalogenating agent for 10 min.

1-bromovinyltriphenylgermane in good yield when 1,5-diazobicyclo[4,2,0]-nonane in refluxing benzene was employed.

It was also found possible to brominate 1-triphenylsilyl-2-phenylethane directly with various amounts of *N*-bromosuccinimide (NBS) and traces of peroxide. Monobromination occurred in reasonable yield at the benzylic carbon. Bromination with two equivalents of NBS gave a 1 : 2 mixture of the *erythro-* and *threo-*forms of 1,2-dibromo-1-triphenylsilyl-2-phenylethane, while bromination with three equivalents of NBS, during which copious evolution of hydrogen bromide was observed, gave a mixture of the 1,1,2-tribromide and (*Z*)-1-triphenylsilyl-1-bromo-2-phenylethene, the compound known to be formed from dehydrobromination of the 1,2-dibromide [1]. Further bromination of 1-triphenylsilyl-1,2-dibromoethane was not easily effected with NBS-peroxide in refluxing carbon tetrachloride, but in the presence of UV light a good yield of the α-bromination product, 1,1,2-tribromo-1-triphenylsilylethane was obtained. Thus these methods offer alternative routes for the preparation of brominated alkylsilanes.

Experimental

The source of ultraviolet light was a 100 W PAR 38 clear mercury lamp, ASA code H34-4GS. Reactions involving organolithium reagents were carried out under dry nitrogen. Vinyltriphenylsilane [6], 2-propenyltriphenylsilane [7], vinyltriphenylgermane [8] and the 1-triphenylsilyl-1-bromo-2-phenylethanes [1] were prepared by known methods. Microanalyses were performed by A.B. Gygli, Toronto.

Brominations with bromine in carbon tetrachloride.

The results of these reactions are given in Table 1. The following is a typical procedure. To a solution of 3.65 g (0.01 mol) of α-bromovinyltriphenylsilane in 40 ml of carbon tetrachloride was added 10 ml of a 1 *M* solution of bromine in carbon tetrachloride. The bromine colour persisted until the ultraviolet lamp was directed on the pyrex flask, when the colour faded over 2 min. The colourless solution was evaporated to dryness under reduced pressure, and the solid residue was recrystallized from ethanol to give 4.4 g (85%) of 1,1,2-tribromo-1-triphenylsilylethane.

Dehydrobromination with refluxing pyridine

Results are listed in Table 2: the following procedure is typical. A solution of 3.0 g (0.0065 mol) of 2-triphenylsilyl-1,2-dibromopropane in 50 ml of pyridine was refluxed for 22 h. The pyridine was then removed under reduced pressure, and the resulting black oil was worked up with ether and dilute hydrochloric acid. A sticky solid was recovered from the dried ether layer, which was crystallised from methylene chloride/methanol to give 1.10 g (45%) of fine white crystals.

Debromination and debromosilylation of 1-triphenylsilyl-1,1,2-tribromo-2-phenylethane

A solution of 0.20 g (0.33 mmol) of the tribromide in 10 ml of ether at —78°C was treated with 0.22 ml (0.35 mmol) of *n*-butyllithium. The solution,

TABLE 3

BROMINATION OF ALKYLSILANES WITH N-BROMOSUCCINIMIDE [a]

Alkylsilane	Equivalent of NBS	Time (h)	Product	Yield (%)	M.p. (°C)
$Ph_3SiCH_2CH_2Ph$	1	0.25	$Ph_3SiCH_2CHBrPh$ [b]	81	99—105 [c]
$Ph_3SiCH_2CH_2Ph$	2	2	$Ph_3SiCHBrCHBrPh$ [d]		
$Ph_3SiCH_2CH_2Ph$	3	2	$Ph_3SiCBr_2CHBrPh$	44	150—155 [e]
$Ph_3SiCHBrCH_2Br$	1	0.5 [f]	$Ph_3SiCBr_2CH_2Br$	86	166—167

[a] Reactions run in refluxing CCl_4 with a trace of benzoyl peroxide. [b] NMR (CCl_4): δ 7.0—7.7 (m, 22H): 5.32 (t, J 8 Hz, 1H); 2.73 (d(br), J 8 Hz, 2H) ppm. [c] Recrystallised from hexane (see text). [d] Crude product contained approximately 2 : 1 ratio of *threo*- and *erythro*-dibromides, isolated pure from hexane in 18% and 9% yields respectively after several recrystallisations. [e] Recrystallised once from petroleum ether (b.p. 60—70°C). Pure, m.p. 154—156°C. Also isolated was 28% (*Z*)-1-triphenylsilyl-1-bromo-2-phenylethene. [f] No reaction over 90 min under reflux. Reaction occurred when irradiated with ultraviolet lamp over next 30 min reflux.

after warming to room temperature, was worked up to give, after recrystallisation from methylene chloride/pentane, 0.13 g (88%) of (*Z*)-1-triphenylsilyl-1-bromo-2-phenylethane, m.p. 160—162°C, identified by comparison with an authentic sample. When 0.55 g of the tribromide was heated in a Kugelrohr tube at 140°C and 0.2 mmHg for 30 min, 0.21 g (88%) of β,β-dibromostyrene and 0.23 g (75%) of triphenylbromosilane were isolated after redistillation of the volatile material at 100°C/0.2 mmHg, and were identified by comparison with authentic samples.

Bromination of 1-triphenylsilyl-2-phenylethane with N-bromosuccinimide

To a refluxing mixture of 3.60 g (0.01 mol) of triphenylsilylphenylethane in 20 ml of carbon tetrachloride and 1.78 g (0.01 mol) of NBS was added a small crystal of benzoyl peroxide. After 15 min the suspension was cooled and filtered, and the filtrate, after removal of the solvent, gave a thick fuming oil. Crystallisation from dry hexane at —20°C gave 3.60 g (81%) of white solid, m.p. 86—100°C, judged to be almost pure 1-triphenylsilyl-2-bromo-2-phenylethane on the basis of its NMR spectrum. Recrystallisations from hexane raised the m.p. to 99—105°C, but failed to give an analytically pure sample, due to fairly rapid decomposition to triphenylbromosilane, styrene, and other unidentified products.

Similar procedures were followed using 2 and 3 equivalents of NBS, and the data are listed in Table 3.

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