HYDROSILANE ADDITION OF PERFLUOROPHENYLSILANES TO SOME UNSATURATED SYSTEMS

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SUMMARY

The addition of (pentafluorophenyl)dimethylsilane (I), bis(pentafluorophenyl)-methylsilane (II) and tris(pentafluorophenyl)silane (III) to phenylacetylene catalyzed by hexachloroplatinic acid gave mixtures of α- and β-substituted styrenes in each case; the proportion of the α-isomer increased from (I)–(III).

Compound (I) underwent addition to the olefinic and carbonyl bonds of some representative compounds; addition did not occur under the conditions used with cyclohexene, furan, tetrakis(trimethylsilyl)allene nor with the azomethine, nitrile or azo linkages. The silane (I) added to benzalacetophenone to give the 1,4-adduct.

The addition of hydrosilanes to unsaturated compounds has, since its initial discovery[1], provided a direct and in many cases a preferred synthesis of functional organosilicon monomers*. Of the various catalysts which have been used to promote this reaction, that first used by Speier[3] (hexachloroplatinic acid) is generally very effective.

As an extension of our studies of functional organosilicon monomers and in particular those containing polyhalophenyl groups, we have investigated the addition reactions of (pentafluorophenyl)-dimethylsilane (I), bis(pentafluorophenyl)methyl-silane (II) and tris(pentafluorophenyl)silane (III) with a representative sample of unsaturated compounds, catalyzed by hexachloroplatinic acid. The results of the various reactions carried out are summarized in Table 1 and some representative experiments are described in the experimental section.

RESULTS AND DISCUSSION

(Pentafluorophenyl)dimethylsilane (I) underwent facile addition to phenyl-acetylene and those olefins which would be expected to undergo the hydrosilation reaction under the conditions used. Thus, addition occurred with phenylacetylene to give a mixture of isomeric substituted styrenes: dimethyl(pentafluorophenyl)-α-styrylsilane (IV) and dimethyl(pentafluorophenyl)-*trans*-β-styrylsilane (V) in the approximate ratio 1/6, respectively. The formation of an isomeric mixture can be

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* For a general account of the hydrosilation and related insertion reactions of Group IV-B elements, see ref. 2.

TABLE 1. ADDITION OF HYDROSILANES TO SOME UNSATURATED COMPOUNDS

Unsaturated compound (A)	Hydrosilane (B)	Molar ratio (A)/(B)	Solvent	Products	B.p. (°C/mm) n_D^{20}	Isomer ratio	Total yield (%)
$C_6H_5C{\equiv}CH$	$C_6F_5SiMe_2H$ (I)	2/1		$C_6H_5C(=CH_2)SiMe_2C_6F_5$ (IV) $C_6H_5CH=CHSiMe_2C_6F_5$ (V)	109/0.15 123/0.15 1.5290	IV/V=1/6	69
$C_6H_5C{\equiv}CH$	$(C_6F_5)_2SiMeH$ (II)	2/1		$C_6H_5C(=CH_2)SiMe(C_6F_5)_2$ (VI) $C_6H_5CH=CHSiMe(C_6F_5)_2$ (VII)	115–116/0.15 1.5250 130–134/0.15[a]	VI/VII=3/4	74
$C_6H_5C{\equiv}CH$	$(C_6F_5)_3SiH$ (III)	2.5/1	Benzene	$C_6H_5C(=CH_2)Si(C_6F_5)_3$ (VIII) $C_6H_5CH=CHSi(C_6F_5)_3$ (IX)	Mixture b.p. 170–175/0.1	VIII/IX=9/7	95
$Me_3SiCH_2CH=CH_2$	$C_6F_5SiMe_2H$ (I)	2/1		$C_6F_5SiMe_2(CH_2)_3SiMe_3$	69–70/0.15 1.4472		61.8
$C_6F_5CH_2CH=CH_2$	$C_6F_5SiMe_2H$	2/1		$C_6H_5(CH_2)_3SiMe_2C_6F_5$	96/0.1 1.4971		50.6
$C_6F_5CH_2CH=CH_2$	$C_6F_5SiMe_2H$	1/2		$C_6F_5SiMe_2(CH_2)_3C_6F_5$	96–98/0.5 1.4590		76.6
$C_6Cl_5CH_2CH=CH_2$	$C_6F_5SiMe_2H$	1/1.2	Benzene	$C_6Cl_5(CH_2)_3SiMe_2C_6F_5$	[b]		36.8
C_6H_5COMe	$C_6F_5SiMe_2H$	2/1		$C_6H_5CH(Me)OSiMe_2C_6F_5$	135/1.5 1.4998		63
$C_6H_5COC_6H_5$	$C_6F_5SiMe_2H$	1/1.2	Benzene	$C_6H_5CH(C_6H_5)OSiMe_2C_6F_5$	115/0.1		59.3
$C_6H_5CH=CHCOC_6H_5$	$C_6F_5SiMe_2H$	1/1	Benzene	$C_6H_5CH_2CH=C(C_6H_5)-OSiMe_2C_6F_5$	140/0.2 1.5440		82.5
$C_6H_5C{\equiv}CH$	HMe_2SiCl	1/2		$C_6H_5CH=CHSiMe_2Cl$	70/0.10		94
$C_6H_5C{\equiv}CH$	$HMeSiCl_2$	1/3		$C_6H_5CH=CHSiMeCl_2$	80/0.10		96
$C_6H_5C{\equiv}CH$	$HSiCl_3$	1/2.5		$C_6H_5CH=CHSiCl_3$	78–80/0.10		77.9

[a] M.p. 81°. [b] M.p. 95–96°.

correlated with previous additions[4] of halohydrosilanes to this ethyne. The stereo-specific *cis*-addition which has been shown[5] to occur under catalysis by hexachloro-platinic acid leads to the *trans*-isomer. The terminal addition of the silicon-containing moiety to alkenes and alkynes which is generally observed would explain the pre-ponderance of the terminal *trans*-adduct. A similar result was obtained with phenyl-acetylene and bis(pentafluorophenyl)methylsilane (II); in this case, however, an appreciable amount of the α-styryl compound was also obtained (ratio $\alpha/\beta = 3/4$). In the addition of tris(pentafluorophenyl)silane (III) to phenylacetylene, the α-isomer was the major product; ratio $\alpha/\beta = 9/7$.

The *trans-β*-substituted styrenes obtained in these reactions were obtained independently by treatment of the appropriate *trans-β*-silylstyrene (resulting from the addition of chlorodimethylsilane, methyldichlorosilane[6] and trichlorosilane[6], res-pectively, to phenylacetylene catalyzed by hexachloroplatinic acid) with the stoi-chiometric amount of pentafluorophenyllithium:

$$C_6H_5CH=CHSiMe_xCl_{3-x} \xrightarrow{(3-x)\ C_6F_5Li} C_6H_5CH=CHSiMe_x(C_6F_5)_{3-x}$$

(*trans*)

$(x = 0–2)$

The addition of (pentafluorophenyl)dimethylsilane (I) to the terminal olefins, allyltrimethylsilane, 3-phenylpropene, 3-(pentafluorophenyl)propene and 3-(penta-chlorophenyl)propene gave the expected terminal addition products in each case.

The silane (I) underwent addition to the carbonyl groups of acetophenone and benzophenone. With benzalacetophenone, addition of (I) occurred in a 1,4-manner across the α,β-unsaturated ketone to give an alkenoxysilane (Table 1); the identity of the latter was confirmed by its IR and ^{1}H NMR spectra and by acidic hydrolysis to afford benzylacetophenone and bis(pentafluorophenyl)tetramethyldisiloxane:

$$C_6H_5CH_2CH=C(C_6H_5)OSiMe_2C_6F_5 \xrightarrow{H_3O^+}$$

$$[C_6H_5CH_2CH=C(C_6H_5)OH] + [C_6F_5SiMe_2OH]$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$C_6H_5CH_2CH_2COC_6H_5 + (C_6F_5SiMe_2)_2O$$

Such 1,4-addition of hydrosilanes and organotin monohydrides appears to be of general occurrence with α,β-unsaturated ketones[2,7]. Chlorogermanes, for example, chlorodiphenylgermane and phenyldichlorogermane have been shown[8] to add to the olefinic linkage of α,β-unsaturated ketones whereas the more sterically hindered triphenylgermane underwent addition to the carbonyl group of such compounds.

(Pentafluorophenyl)dimethylsilane (I) did not undergo reaction with cyclo-hexene, furan (in a sealed tube at 100°) or the allene system of tetrakis(trimethylsilyl)-allene[9] under catalysis by hexachloroplatinic acid. The azomethine, nitrile and azo linkages of benzophenone-anil, benzonitrile and azobenzene were also unaffected by (I) under the conditions of the hydrosilation reaction employed in the present in-vestigation. The moderate reactivity of silane (I) in the hydrosilation reaction is con-trasted by the behaviour of its chlorine analog, (pentachlorophenyl)dimethylsilane, under similar conditions. A preliminary examination of the interaction of (penta-chlorophenyl)dimethylsilane with some unsaturated substrates catalyzed by hexa-

chloroplatinic acid gave indefinite results and products which appeared to have a complex composition; these findings indicate that this silane is less reactive than (pentafluorophenyl)dimethylsilane (I) in Si–H addition reactions and possibly is more susceptible to side-reactions such as disproportionation.

EXPERIMENTAL

Hexachloroplatinic acid was used as a 0.1 molar solution in isopropanol; in general, reaction mixtures were made 10^{-4}–10^{-5} molar in catalyst with respect to the olefin used.

(Pentafluorophenyl)dimethylsilane[10]   and   bis(pentafluorophenyl)methyl-silane[10] have been described previously; the method of preparation employed in this investigation is described. 3-(Pentafluorophenyl)propene was obtained from allyl-magnesium bromide and hexafluorobenzene by an analogous method to that described previously by Tamborski and coworkers[11].

VPC analyses were carried out with an F and M Model 500 Gas Chromatograph using an $18 \times \frac{1}{4}$ inch column packed with Silicone Gum Rubber SE30 on Chromosorb W (1/20). Isomer ratios were determined by comparison of peak areas (height at maximum × width at half maximum) of the relevant components on temperature-programmed gas chromatograms of the crude reaction product from the various hydrosilation reactions.

Petroleum ether used had b.p. 60–70°; ^{1}H NMR data are reported in τ values.

General procedure of the hydrosilation reaction

In general, the silicon hydride was added slowly to a heated mixture of the unsaturated substrate and added catalyst under a nitrogen atmosphere in the absence of a solvent. The temperature of the reaction mixture was initially kept at 70–100° depending on the reactants but normally rose higher as the exothermic reaction set in. When either of the reactants was a solid, the solvent employed was a minimum amount of benzene or acetonitrile, the temperature employed in such cases being the reflux temperature of the solvent. On completion of the hydrosilane addition, the resulting mixtures were heated for periods of 6–12 h to complete the reaction. The occurrence of an addition reaction was followed in some cases by periodic removal of aliquots of reaction mixtures and examination by VPC.

Preparation of (pentafluorophenyl)dimethylsilane (I)

Chlorodimethylsilane (37.80 g, 0.4 mole) in ether (30 ml) was added dropwise to pentafluorophenyllithium[11] (0.3 mole) in ether (300 ml) at −78°. After stirring the mixture at −78° overnight and allowing it to reach room temperature, Color Test I[12] was negative. Volatile solvents were removed by fractionation, the residue extracted from precipitated salts with petroleum ether and volatile solvents removed. Distillation of the residue gave (I), b.p. 85°/60 mm, n_D^{25} 1.4294 (56.3 g, 83%). (Reported[10] values: b.p. 61.8–62°/20 mm, n_D^{20} 1.4324.)

Preparation of bis(pentafluorophenyl)methylsilane (II)

Methyldichlorosilane (11.5 g, 0.1 mole) in ether (30 ml) was added slowly to pentafluorophenyllithium (0.2 mole) in ether (200 ml) at −78°. A procedure similar

to that described above gave (II), b.p. 70°/0.15 mm, n_D^{25} 1.4614 (28.8 g, 76.2%). (Reported[10] data: b.p. 94°/2 mm, n_D^{20} 1.4634.)

Preparation of tris(pentafluorophenyl)silane (III)

Trichlorosilane (7.0 g, 0.05 mole) in ether (30 ml) was added dropwise to pentafluorophenyllithium (0.15 mole) in ether (200 ml) at −78°. Work-up was similar to that described above except that the residue obtained on removal of volatile solvents was extracted with boiling benzene. The solid thus obtained was crystallized from petroleum ether to give tris(pentafluorophenyl)silane as a colorless, flocculent solid, m.p. and mixed m.p. 135–136.5° (18.6 g, 70.2%).

Preparation of 3-(pentachlorophenyl)propene

Pentachlorophenylmagnesium chloride[13] (0.3 mole) in THF (250 ml) was added to allyl bromide (60.5 g, 0.5 mole) in THF (50 ml) at 0°. The mixture was then allowed to reach 20° and heated at the reflux temperature overnight. Acidic hydrolysis, extraction of the hydrolysate with chloroform and removal of volatiles left a dark oil. Distillation of the latter gave 3-(pentachlorophenyl)propene, b.p. 140°/0.05 mm. m.p. 59–60° (60.8 g, 69.8%). (Found: C, 37.18; H, 1.84; mol.wt., 290. $C_9H_5Cl_5$ calcd.: C, 37.18; H, 1.72%; mol.wt., 290.5.)

Addition of (pentafluorophenyl)dimethylsilane (I) to phenylacetylene

(Pentafluorophenyl)dimethylsilane (11.3 g, 0.05 mole) was added dropwise to a heated mixture (∼100°) of phenylacetylene (10.2 g, 0.1 mole) and hexachloroplatinic acid (0.1 ml of 0.1 molar solution in isopropanol). The resulting mixture was heated at 100–120° for 12 h. Analysis by VPC at the end of this time showed that all the silane had been consumed and that two products had been formed in an approximate ratio 6/1. Direct distillation of the reaction mixture using a spinning-band fractionating column gave recovered phenylacetylene (4.3 g) and (1) b.p. 190°/0.15 mm, (2.0 g); (2) b.p. 123°/0.15 mm (11.3 g).

The ^{1}H NMR spectrum of fraction (1) was consistent with the structure of the α-adduct: dimethyl(pentafluorophenyl)-α-styrylsilane (IV) [phenyl (2.93), olefinic (quartet, 4.06–4.35) and Si–Me (multiplet, 9.44–9.50) protons]. (Found: C, 58.70; H, 4.38; mol.wt., 328. $C_{16}H_{13}F_5Si$ calcd.: C, 58.53; H, 3.96%; mol.wt., 328.)

The ^{1}H NMR spectrum of fraction (2) indicated the trans-β-styryl isomer: dimethyl(pentafluorophenyl)-trans-β-styrylsilane (V) [phenyl (multiplet, 2.69–2.87), trans-olefinic (singlet, 3.18 and triplet, 3.36–3.41) and Si–Me (triplet, 9.43–9.50) protons]. (Found: C, 58.78; H, 4.33; mol.wt., 328. $C_{16}H_{13}F_5Si$ calcd.: C, 58.53; H, 3.96%; mol.wt., 328.)

Dimethyl(pentafluorophenyl)-trans-β-styrylsilane (V) from chlorodimethyl-trans-β-styrylsilane and pentafluorophenyllithium

A solution of chlorodimethyl-trans-β-styrylsilane (9.8 g, 0.05 mole) in ether (20 ml) was added to pentafluorophenyllithium (0.05 mole) in ether (100 ml) at −78°. Normal work-up gave an oil which on distillation gave (V), b.p. 125°/0.2 mm (11.4 g, 69.5%).

Addition of bis(pentafluorophenyl)methylsilane (II) to phenylacetylene

Interaction of phenylacetylene (12.24 g, 0.12 mole), the silane (II) (22.68 g, 0.06 mole) and hexachloroplatinic acid (0.12 ml) gave a mixture of two components, by VPC, in the approximate ratio 4/3. Fractionation of the mixture on a spinning-band column gave recovered phenylacetylene (5.6 g) and (*1*) b.p. 115–116°/0.15 mm (8.7 g); (*2*) b.p. 130–134°/0.15 mm, m.p. 80–81° (12.8 g).

The ^{1}H NMR spectrum of fraction (*1*) was indicative of the α-adduct: bis-(pentafluorophenyl)methyl-α-styrylsilane (VI) [phenyl (singlet, 2.70), olefinic (quartet, 3.67–4.13) and Si–Me (triplet, 8.94–8.99) protons]. (Found: C, 52.32; H, 2.14; mol.wt., 480. $C_{21}H_{10}F_{10}Si$ calcd.: C, 52.50; H, 2.08%; mol.wt., 480.)

The ^{1}H NMR spectrum of fraction (*2*) showed this to be the corresponding *trans-β*-isomer: bis(pentafluorophenyl)methyl-*trans-β*-styrylsilane (VII) [phenyl (complex multiplet, 2.51–2.80), *trans*-olefinic (singlet, 2.98; triplet, 3.05–3.13) and Si–Me (triplet, 8.93–9.00) protons]. (Found: C, 52.79; H, 2.22; mol.wt., 480. $C_{21}H_{10}F_{10}Si$ calcd.: C, 52.50; H, 2.08%; mol.wt., 480.)

Bis(pentafluorophenyl)methyl-trans-β-styrylsilane (VII) from methyldichloro-trans-β-styrylsilane and pentafluorophenyllithium

A solution of *trans*-methyldichloro-β-styrylsilane (10.85 g, 0.05 mole) in ether (20 ml) was added to pentafluorophenyllithium (0.1 mole) in ether (150 ml) at −78°. The normal procedure gave a solid which was crystallized from petroleum ether to give (VII), m.p. and mixed m.p. 79–80° (11.0 g, 45.8%).

Tris(pentafluorophenyl)-trans-β-styrylsilane (IX) from trans-β-styryltrichlorosilane and pentafluorophenyllithium

A solution of *trans*-β-styryltrichlorosilane (11.88 g, 0.05 mole) in ether (30 ml) was added to pentafluorophenyllithium (0.15 mole) in ether (200 ml) at −78°. Normal work-up gave a solid which was crystallized from petroleum ether to afford (IX), m.p. 70–71° (12.1 g, 38.3%). (Found: C, 49.73; H, 1.43. $C_{26}H_7F_{15}Si$ calcd.: C, 49.38; H, 1.11%.)

Addition of tris(pentafluorophenyl)silane (III) to phenylacetylene

A solution of (III) (10.6 g, 0.02 mole) in benzene (50 ml) was added to a heated mixture (∼100°) of phenylacetylene (5.1 g, 0.05 mole) and hexachloroplatinic acid solution (0.05 ml). After heating the reaction mixture at reflux for 12 h, analysis by VPC indicated that two products were present in the approximate ratio 9/7. The minor component corresponded in retention time to tris(pentafluorophenyl)-*trans-β*-styrylsilane (IX) described above. The mixture could not be resolved into its components by distillation.

Addition of (pentafluorophenyl)dimethylsilane (I) to benzalacetophenone

The silane (I) (11.3 g, 0.05 mole) was added to a solution of benzalacetophenone (10.4 g, 0.05 mole) and hexachloroplatinic acid (0.05 ml) in refluxing benzene (40 ml). After heating at reflux for 8 h, removal of the solvent left an oil. Examination by VPC indicated that only one component was present. Direct distillation of the product gave the 1,4-addition product (Table 1), b.p. 140–142°/0.2 mm (17.9 g, 82.5%). The IR spectrum of this product showed bands[14] ascribed to Si–C_6F_5 (1460, 1515 and 1640

cm^{-1}) and Si–O–C (1085 cm^{-1}); no carbonyl band was present. The ^{1}H NMR spectrum gave confirmatory evidence for the 1,4-adduct: phenyl (multiplet, 2.48–2.69); olefinic (triplet, 4.29, 4.42, 4.54), methylene (doublet, 6.24, 6.34) and Si–Me (triplet, 9.24–9.52) protons in the integrated ratio 10.2/1/2/6.3, respectively (required ratio, 10/1/2/6). (Found: C, 63.85; H, 4.83. $C_{23}H_{19}F_5OSi$ calcd.: C, 63.59; H, 4.38%.)

Acidic hydrolysis of above 1,4-adduct. Aqueous hydrochloric acid (30 ml of 2 N solution) was added to a solution of the 1,4-adduct (13.9 g, 0.03 mole) in THF (30 ml) and the homogeneous solution heated at reflux for 3 h. Normal work-up gave an oil which showed two components by VPC. Distillation of the product gave: (*1*) b.p. 115°/1.5 mm, m.p. 41°, mixed m.p. with bis(pentafluorophenyl)tetramethyldisiloxane[15], 40–41° (4.3 g, 57.6%); (*2*) b.p. 155°/1.5 mm, m.p. 69–70°, mixed m.p. with benzylacetophenone, 68–70° (4.1 g, 61%).

Products of the various hydrosilation reactions described in Table 1 which gave satisfactory elemental analyses and which are not described in the Experimental Section, are listed, together with the relevant data, in Table 2.

TABLE 2

Compound	Calcd. (%)		Found (%)	
	C	H	C	H
$C_6F_5SiMe_2(CH_2)_3SiMe_3$	49.41	6.18	49.42	6.40
$C_6H_5(CH_2)_3SiMe_2C_6F_5$	59.29	4.94	59.26	4.97
$C_6F_5SiMe_2(CH_2)_3C_6F_5$	47.00	2.77	47.09	2.60
$C_6Cl_5(CH_2)_3SiMe_2C_6F_5$	39.50	2.32	40.05	2.39
$C_6H_5CH(CH_3)OSiMe_2C_6F_5$	55.49	4.34	55.24	4.30
$C_6H_5CH(C_6H_5)OSiMe_2C_6F_5$	61.76	4.17	61.51	3.96

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