307. *Organosilicon Compounds. Part XXVII.*[1] *The Reaction between Trichlorosilane and 4-Chlorophenylbut-1-enes.*

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Trichlorosilane reacts with 4-*m*- and 4-*p*-chlorophenylbut-1-ene in the presence of chloroplatinic acid to give benzylsilicon compounds, $Cl{\cdot}C_6H_4{\cdot}CH(SiCl_3){\cdot}[CH_2]_2{\cdot}CH_3$, in addition to the expected straight-chain compounds $Cl{\cdot}C_6H_4{\cdot}[CH_2]_4{\cdot}SiCl_3$.

From the addition of trichlorosilane to either 4-*m*- or 4-*p*-chlorophenylbut-1-ene in presence of chloroplatinic acid, we obtained two products of formula $Cl{\cdot}C_6H_4{\cdot}C_4H_8{\cdot}SiCl_3$. In each case, the major, higher-boiling product was shown to be the expected straight-chain compound, *m*- or *p*-$Cl{\cdot}C_6H_4{\cdot}[CH_2]_4{\cdot}SiCl_3$, and the minor product to be a benzyl-silicon compound, *m*- or *p*-$Cl{\cdot}C_6H_4{\cdot}CH(SiCl_3){\cdot}[CH_2]_2{\cdot}CH_3$. From 4-*o*-chlorophenylbut-1-ene, however, we obtained only the straight-chain product.

For ease of presentation the assigned structures will be assumed in the listing of evidence for the assignments, which was as follows:

(*a*) Table 1 lists the main features (maxima wavelengths, $\lambda_{max.}$, and the associated extinction coefficients, $\varepsilon_{max.}$) of the ultraviolet spectra above 245 mμ for the $Me_3Si{\cdot}C_6H_4{\cdot}C_4H_8{\cdot}SiMe_3$ compounds derived from the products of the additions, and of $Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_n{\cdot}SiMe_3$ compounds, in which $n = 2$ or 3, made by unambiguous routes.

Table 1.

Ultraviolet spectra in methanol.

(i) $R{\cdot}C_6H_4{\cdot}[CH_2]_n{\cdot}SiMe_3$ compounds

	$n = 2$		$n = 3$		$n = 4$	
R	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
p-Me_3Si	2580	230	2575	220	2575	220
	2635	270	2630	260	2630	260
	2695	195	2690	190	2690	190
m-Me_3Si	2675	410	2675	390	2675	390
	2750	350	2745	335	2745	340
o-Me_3Si	2685	475	2680	425	2680	410
	2755	410	2750	370	2750	360

(ii) $R{\cdot}C_6H_4{\cdot}CHY{\cdot}SiMe_3$ compounds

	Y = H		Y = Pr^n	
R	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
p-Me_3Si	2620	540	2620	490
	2685	565	2685	470
	2775	325	—	—
m-Me_3Si	(2795) *	(560) *	(2795) *	(465) *
	(2660) *	(475) *	(2660) *	(425) *
	2735	685	2735	580
	2810	600	2810	480
o-Me_3Si	(2650) *	(725) *	—	—
	2750	1010	—	—
	2815	875	—	—
H	2615	355	2610	365
	2675	440	2680	420
	2745	355	2750	310

* Denotes inflexion.

The spectra of the (assumed) *o*-, *m*-, and *p*-$Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_4{\cdot}SiMe_3$ compounds are seen to be closely similar to those of the corresponding *o*-, *m*-, and *p*-$Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_n{\cdot}SiMe_3$

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[1] Part XXVI, Eaborn, Jaura, and Walton, *J.* 1964, 1198.

compounds with $n = 2$ or 3. The spectra of the (assumed) *m*- and *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}CH(SiMe_3){\cdot}[CH_2]_2{\cdot}CH_3}$ compounds are different [which those of the corresponding isomeric $\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CH(SiMe_3){\cdot}CH_3}$ compounds would not be], and closely resemble those of the appropriate $\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3}$ compounds.

(*b*) The proton magnetic resonance spectra of the *m*- and *p*-$\mathrm{Cl{\cdot}C_6H_4{\cdot}C_4H_8{\cdot}SiMe_3}$ derivatives of the addition products were recorded, as were, for comparison, those of the compounds *o*- and *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3}$ and *o*- and *p*-$\mathrm{Cl{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}SiMe_3}$. The (assumed) straight-chain products *m*- and *p*-$\mathrm{Cl{\cdot}C_6H_4{\cdot}[CH_2]_4{\cdot}SiMe_3}$ have a triplet at $\tau = 7{\cdot}3$ and 7·5 p.p.m., respectively, a triplet at $\tau = 9{\cdot}5$ and a complex resonance at 8·2—9·1 p.p.m., in addition to peaks attributable to the aromatic protons and the protons of the trimethylsilyl groups. The triplet in the region of $\tau = 7{\cdot}4$ p.p.m., can be assigned to the methylene group adjacent to the aromatic ring. (The $\mathrm{Ar{\cdot}CH_2{\cdot}CH_2{\cdot}SiMe_3}$ compounds have a quintuplet in this region; a triplet was expected, but it seems there is restricted rotation about the $\mathrm{CH_2{-}CH_2}$ bond.) The triplet at $\tau = 9{\cdot}5$ p.p.m. can be assigned to the methylene group adjacent to the silicon atom (the $\mathrm{Ar{\cdot}CH_2{\cdot}CH_2SiMe_3}$ compounds have a quintuplet in this region), and the resonance at $\tau = 8{\cdot}2$—$9{\cdot}1$ p.p.m. to the two remaining methylene groups.

The (assumed) *m*- and *p*-$\mathrm{ClC_6H_4{\cdot}CH(SiMe_3){\cdot}Pr^n}$ compounds showed no resonance in the $\tau = 7{\cdot}4$ p.p.m. region, in which the isomeric $\mathrm{ClC_6H_4{\cdot}[CH_2]_2{\cdot}CH(SiMe_3){\cdot}CH_3}$ compounds should show a triplet.

(*c*) The strongest support for the assignment of structures came from measurements of the rates of cleavage of the derived *m*- and *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}C_4H_8{\cdot}SiMe_3}$ compounds by aqueous methanolic perchloric acid (cf. ref. 2). The rates, along with those for *m*- and *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_{\mathit{n}}{\cdot}SiMe_3}$ compounds where $n = 1$—3, and for trimethyl-*m*- and -*p*-tolylsilane, are shown in Table 2 as values of k_{rel}, the rate relative to that for trimethylphenylsilane.* The high reactivity of the branched-chain compounds clearly shows them to have a trimethylsilyl group separated from the ring by only one carbon atom; the reactivities of the isomers *m*- or *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CH(SiMe_3){\cdot}CH_3}$ structures would be smaller, and very similar to those of the corresponding straight-chain compounds, *m*- or *p*-$\mathrm{Me_3Si{\cdot}C_6H_4{\cdot}[CH_2]_{\mathit{n}}{\cdot}SiMe_3}$ with $n > 1$, since the silicon atom has little effect when separated from the ring by more than one carbon atom.

TABLE 2.

Relative rates of cleavage of $\mathrm{RC_6H_4{\cdot}SiMe_3}$ compounds by aqueous methanolic perchloric acid at 50·1°.

R	k_{rel}	R	k_{rel}	R	k_{rel}	R	k_{rel}
m-$\mathrm{CH_3}$	2·5	*m*-$\mathrm{Me_3Si[CH_2]_2}$	3·5	*p*-$\mathrm{CH_3}$	20·5	*p*-$\mathrm{Me_3Si[CH_2]_2}$	27·5
m-$\mathrm{Me_3Si{\cdot}CH_2}$	6·4	*m*-$\mathrm{Me_3Si[CH_2]_3}$	3·7	*p*-$\mathrm{Me_3Si{\cdot}CH_2}$	270	*p*-$\mathrm{Me_3Si[CH_2]_3}$	21
m-$\mathrm{Me_3Si(Pr^n)CH}$	7·9	*m*-$\mathrm{Me_3Si[CH_2]_4}$	3·4	*p*-$\mathrm{Me_3Si(Pr^n)CH}$	260	*p*-$\mathrm{Me_3Si[CH_2]_4}$	23

The major product in the reaction of 4-*m*- and 4-*p*-chlorophenylbut-1-ene with trichlorosilane is then the expected straight-chain compound, $\mathrm{Cl{\cdot}C_6H_4{\cdot}[CH_2]_4{\cdot}SiCl_3}$, while the minor product is the benzyl-silicon compound, $\mathrm{Cl{\cdot}C_6H_4{\cdot}CH(SiCl_3){\cdot}Pr^n}$, the formation of which is reasonable in view of the several reported examples of rearrangements during chloroplatinic acid-catalysed additions of silicon hydrides to olefins.[3-5] For example, addition of trichloro-, dichloromethyl-, or chlorodimethyl-silane to hept-3-ene in presence of chloroplatinic acid gives n-heptyl-silicon compounds exclusively, and Saam and Speier [5] have presented evidence that such addition of a silicon hydride to an olefin involves initial

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* These rates will be discussed fully in a later paper.

[2] Eaborn, *J.*, 1956, 4858; Bott, Eaborn, Pande, and Swaddle, *J.*, 1962, 1217.

[3] Speier, Webster, and Barnes, *J. Amer. Chem. Soc.*, 1957, **79**, 974; Smith, Ryan, and Speier, *J. Org. Chem.*, 1962, **27**, 2183.

[4] Saam and Speier, *J. Amer. Chem. Soc.*, 1958, **80**, 4104.

[5] Saam and Speier, *J. Amer. Chem. Soc.*, 1961, **83**, 1351.

transfer of a hydride ion to give a carbanion, which can then acquire a $\equiv Si^+$ fragment or, in suitable cases, rearrange to a more stable carbanion which then either acquires a $\equiv Si^+$ fragment or loses a hydride ion to form a new olefin; n-heptyl-silicon compounds are formed in this way from hept-3-ene because the primary n-heptyl carbanion is more stable than the initially-formed secondary carbanion.[4,5] In reactions involving an olefin of the type $Ar{\cdot}[CH_2]_n{\cdot}CH{=}CH_2$ (where n can be 0), the initially-formed primary carbanion, $Ar{\cdot}(CH_2)_n{\cdot}CH_2{\cdot}CH_2^-$, can be expected to undergo some rearrangement to give the secondary carbanion $Ar{\cdot}{}^-CH{\cdot}[CH_2]_n{\cdot}CH_3$, which is stabilised by resonance involving the aryl group.

Our results contrast with those described by Petrov and his co-workers,[6] who obtained only the expected straight-chain product from addition of trichlorosilane to the alkenylbenzenes, $Ph{\cdot}[CH_2]_n{\cdot}CH{=}CH_2$, where $n = 0$—2; they did obtain branched-chain isomers as minor products in addition of ethyl- and methyl-dichlorosilane to these olefins, but concluded from Raman spectral studies that these isomers had the structure $Ph{\cdot}[CH_2]_n{\cdot}CH(SiRCl_2){\cdot}CH_3$. Our results suggest that their minor products were, in fact, benzyl-silicon compounds, $Ph{\cdot}CH(SiCl_2R){\cdot}[CH_2]_n{\cdot}CH_3$.*

We obtained only the straight-chain product from the reaction between trichlorosilane and 4-*o*-chlorophenylbut-1-ene, its identity being confirmed by the methods indicated above. There would be some steric hindrance to formation of the benzyl-silicon type of product, but we think there must be an additional factor operating. The proportion of rearrangement during this type of reaction depends greatly on conditions,[7] and possibly the *ortho*-olefin would give some rearranged product under only slightly different conditions.

EXPERIMENTAL

3-x-*Chlorophenylpropan*-1-*ol*.—Ethylene oxide (100 g., 2·27 mole) in ether (250 ml.), cooled to −30°, was added dropwise to the Grignard reagent formed from *p*-chlorobenzyl chloride (204 g., 1·25 mole) and magnesium (36·5 g., 1·5 g.-atom) in ether (750 ml.), the temperature being kept below 10°. The mixture was allowed to warm to room temperature, and was then treated with an excess of 10% sulphuric acid. The usual working-up, followed by fractionation, gave 3-p-*chlorophenylpropan*-1-*ol* (160 g., 75%), b. p. 113—114°/1·5 ± 0·2 mm., n_D^{25} 1·5404 (Found: C, 63·6; H, 6·7. $C_9H_{11}ClO$ requires C, 63·3; H, 6·5%).

The *ortho*-isomer, b. p. 104—107°/1·5 ± 0·2 mm., n_D^{25} 1·5420 (lit.,[8] b. p. 100—101°/2 mm., n_D^{25} 1·5390), was similarly prepared in 70% yield. The meta-*isomer*, b. p. 106—107°/1·0 ± 0·2 mm., n_D^{25} 1·5412, was prepared analogously in 66% yield from *m*-chlorobenzyl bromide (Found: C, 63·1; H, 6·5%).

1-*Bromo*-3-x-*chlorophenylpropane*.—A mixture of 3-*p*-chlorophenylpropan-1-ol (155 g., 0·91 mole) and 48% hydrobromic acid (470 g., 2·80 mole) was refluxed for 6 hr., then cooled, and diluted with water. Ether extraction, followed by washing of the extract with aqueous sodium hydrogen carbonate and then water, and fractionation, gave impure 1-bromo-3-*p*-chlorophenylpropane (172 g., 80%), b. p. 100—103°/1·0 mm.

The impure *ortho*-, b. p. 91—93°/1·0 ± 0·2 mm., and *meta*-isomer, b. p. 96—98°/0·7—1·0 mm., were similarly prepared.

3-x-*Chlorophenyl*-1-*iodopropane*.—A mixture of the impure 1-bromo-3-*p*-chlorophenylpropane (89·5 g., 0·38 mole), anhydrous sodium iodide (97 g., 0·65 mole), and acetone (1·25 l.) was refluxed for 48 hr., and the acetone was then distilled off. Water was added to the residue, and ether-extraction, followed by washing, drying, and fractionation of the extract gave 3-p-*chlorophenyl*-1-*iodopropane* (60 g., 56%), b. p. 95—97°/0·2 — 0·4 mm., n_D^{25} 1·5919 (Found: C, 38·8; H, 3·6. $C_9H_{10}ClI$ requires C, 38·5; H, 3·6%).

The ortho-, b. p. 99—101°/0·4—0·6 mm., n_D^{25} 1·5935 (Found: C, 38·4; H, 3·7%) and meta-*isomer*, b. p. 102—105°/0·4—0·6 mm., n_D^{25} 1·5924 (Found: C, 38·4; H, 3·5%), were similarly prepared in 72 and 81% yields, respectively.

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* Addition of trichlorosilane to allylbenzene in presence of chloroplatinic acid gives the compounds $Ph{\cdot}[CH_2]_3{\cdot}SiCl_3$ and $Ph{\cdot}CH(SiCl_3){\cdot}CH_2{\cdot}CH_3$.[7]

[6] Petrov, Chernyshev, Dolgaya, Egorov, and Leites, *Zhur. obshchei Khim.*, 1960, **30**, 376.

[7] Speier and Usloff, personal communication.

[8] Baddar, El-Assal, and Doss, *J.*, 1959, 1027.

3-x-*Chlorophenylpropyltrimethylsilane.*—Chlorotrimethylsilane (32·5 g., 0·30 mole) was added dropwise to the Grignard reagent from 3-*p*-chlorophenyl-1-iodopropane (56 g., 0·20 mole) and magnesium (6·1 g., 0·25 g.-atom) in ether (200 ml.), and the mixture was then refluxed for 24 hr. Treatment with dilute acid, followed by the usual working-up and fractionation, gave 3-p-*chlorophenylpropyltrimethylsilane* (20·1 g., 44%), b. p. 117—118°/5·0 ± 0·5 mm., n_{D}^{25} 1·4978 (Found: C, 64·0; H, 8·5. $C_{12}H_{19}ClSi$ requires C, 63·5; H, 8·4%).

The ortho-, b. p. 112—114°/5·0 ± 0·5 mm., n_{D}^{25} 1·4998 (Found: C, 63·8; H, 8·1%), and meta-*isomer*, b. p. 114—117°/5·0 ± 0·5 mm., n_{D}^{25} 1·4982 (Found: C, 63·6; H, 8·4%), were prepared analogously in 20 and 28% yield, respectively.

Trimethyl-3-x-*trimethylsilylphenylpropylsilane.*—A mixture of 3-*p*-chlorophenylpropyltrimethylsilane (18·2 g., 0·08 mole) and chlorotrimethylsilane (10·8 g., 0·10 mole) was added dropwise to sodium (4·6 g., 0·2 g.-atom) in refluxing toluene (75 ml.). The mixture was subsequently refluxed for 5 hr., then cooled and filtered, and the filtrate was fractionated to give *trimethyl*-3-p-*trimethylsilylphenylpropylsilane* (15·0 g., 71%), b. p. 133°/5·0 ± 0·5 mm., n_{D}^{25} 1·4852 (Found: C, 68·0; H, 10·5. $C_{15}H_{28}Si_2$ requires C, 68·1; H, 10·7%).

The ortho-, b. p. 129—130°/5·0 ± 0·5 mm., n_{D}^{25} 1·4912 (Found: C, 68·3; H, 10·3%) and meta-*isomer*, b. p. 127°/5·0 ± 0·5 mm., n_{D}^{25} 1·4832 (Found: C, 68·4; H, 10·6%), were prepared analogously in 34 and 40% yield, respectively.

2-m- *and* 2-p-*Chlorophenylethanol.*—Reaction between ethylene oxide (100 ml., 2·05 mole) and the Grignard reagent from *m*-bromochlorobenzene (192 g., 1·00 mole) and magnesium 30·4., 1·25 g.-atom), followed by the usual working-up gave 2-m-*chlorophenylethanol* (91 g., 58%), b. p. 92—95°/1·0 ± 0·2 mm., n_{D}^{25} 1·5489 (Found: C, 61·7; H, 5·75%. C_8H_9ClO requires C, 61·4; H, 5·75%).

The *para*-isomer, b. p. 99—100°/1·0 ± 0·1 mm., n_{D}^{25} 1·5472 (lit.,[9] b. p. 77—78°/0·5 mm., n_{D}^{25} 1·5482), was prepared analogously in 64% yield.

2-m- *and* 2-p-*Chlorophenylethyl Iodide.*—2-*p*-Chlorophenylethanol was heated with 48% hydrobromic acid to give 2-*p*-chlorophenylethyl bromide (85%), b. p. 85°/1·0 ± 0·2 mm., n_{D}^{25} 1·5690 (lit.,[9] b. p. 86·5°/1·6 mm., n_{D}^{25} 1·5697). The *meta*-isomer, b. p. 107—109°/5·0 ± 0·5 mm., n_{D}^{25} 1·5680, was prepared analogously in 86% yield.

The bromides were treated with sodium iodide in acetone, and the usual working-up and fractionation gave 2-m-*chlorophenylethyl iodide*, b. p. 105—106°/1·0 ± 0·1 mm., n_{D}^{25} 1·6084 (Found: C, 36·2; H, 3·0. C_8H_8ClI requires C, 36·1; H, 3·0%), and its *para*-isomer, b. p. 91—94°/0·6—0·7 mm. (lit.,[10] b. p. 115—117°/1 mm.), n_{D}^{25} 1·6093 (Found: C, 36·1; H, 3·0%).

2-x-*Chlorophenylethyltrimethylsilane.*—Chlorotrimethylsilane (54 g., 0·50 mole) in ether (100 ml.) was added dropwise to the Grignard reagent formed from 2-*p*-chlorophenylethyl iodide (93·4 g., 0·35 mole) and magnesium (9·73 g., 0·40 g.-atom) in ether (200 ml.), and the mixture was subsequently refluxed for 1 hr. The ether was then distilled off and simultaneously replaced by benzene, and the mixture was refluxed for 48 hr. more. The usual working-up and fractionation gave 2-p-*chlorophenylethyltrimethylsilane* (12·4 g., 16%), b. p. 104—105°/5·0 ± 0·5 mm., n_{D}^{25} 1·4998 (Found: C, 62·2; H, 7·8. $C_{11}H_{17}ClSi$ requires C, 62·1; H, 8·1%).

The meta-*isomer*, b. p. 105—106°/5·0 ± 0·5 mm., n_{D}^{25} 1·4998, was prepared analogously in 15% yield (Found: C, 62·1; H, 7·9%).

2-m- *and* 2-p-*Trimethylsilylphenylethyltrimethylsilane.*—Reaction between 2-*m*-chlorophenylethyltrimethylsilane (11·0 g., 0·052 mole), chlorotrimethylsilane (6·0 g., 0·055 mole), and sodium (4·0 g., 0·15 g.-atom) in toluene (75 ml.) gave 2-m-*trimethylsilylphenylethyltrimethylsilane* (7·0 g., 53%), b. p. 113—114°/5·0 ± 0·5 mm., n_{D}^{25} 1·4843 (Found: C, 67·2; H, 10·0. $C_{14}H_{26}Si_2$ requires C, 67·1; H, 10·5%).

The *para*-isomer, b. p. 120—122°/5·0 ± 0·5 mm., n_{D}^{25} 1·4850 (lit.,[11] b. p. 110—112°/5 mm., n_{D}^{25} 1·4788), was prepared analogously (Found: C, 67·0; H, 10·4%).

2-o-*Chlorophenylethyltrimethylsilane.*—o-Chlorostyrene (65 g., 0·47 mole) was refluxed for 5 hr. with trichlorosilane (75 g., 0·55 mole) in presence of chloroplatinic acid (2 ml. of an 0·1M solution in isopropyl alcohol). Fractionation gave 2-o-*chlorophenylethyltrichlorosilane* (98 g., 76%), b. p. 87—89°/1·0 ± 0·2 mm., n_{D}^{25} 1·5281 (Found: hydrolysable Cl, 38·3. $C_8H_8Cl_4Si$ requires hydrolysable Cl, 38·8%).

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[9] Saunders and Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712.

[10] DePuy and Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710.

[11] Egorov, Leites, Tolstikova, and Chernyshev, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 445.

The chloride (90 g., 0·33 mole) was treated with the Grignard reagent from methyl bromide (178 g., 1·82 mole) and magnesium (48·6 g., 2·00 g.-atom) in ether, and the usual working-up and fractionation gave 2-o-*chlorophenylethyltrimethylsilane*, b. p. 99—100°/5·0 ± 0·5 mm., n_D^{25} 1·5005 (Found: C, 62·2; H, 7·8. $C_{11}H_{17}ClSi$ requires C, 62·1; H, 8·1%).

Trimethyl-2-o-*trimethylsilylphenylethylsilane.*—Treatment of 2-*o*-chlorophenylethyltrimethylsilane (63·3 g., 0·25 mole) and chlorotrimethylsilane (29·7 g., 0·28 mole) with sodium (13·8 g., 0·60 g.-atom) in toluene (350 ml.) gave, after fractionation, *trimethyl*-2-o-*trimethylsilylphenylethylsilane* (27·3 g., 43%), m. p. 117—118°/5·0 ± 0·5 mm., n_D^{25} 1·4912 (Found: C, 67·3; H, 10·1. $C_{14}H_{26}Si_2$ requires C, 67·1; H, 10·5%).

m- *and* p-*Chlorobenzyltrimethylsilane.*—Reaction between chlorotrimethylsilane and the Grignard reagent from *m*-chlorobenzyl bromide or *p*-chlorobenzyl chloride in ether gave *m*-, b. p. 225°/748 mm., n_D^{20} 1·5099 (lit.,[12] b. p. 228—229°, n_D^{20} 1·5108), and *p*-chlorobenzyltrimethylsilane, b. p. 229°/755 mm., n_D^{20} 1·5113 (lit.,[12] b. p. 231—232°, n_D^{12} 1·5154).

4-x-*Chlorophenylbut*-1-*ene.*—Allyl bromide (181·5 g., 1·50 mole) was added dropwise to the Grignard reagent from *p*-chlorobenzyl chloride (204 g., 1·25 mole) and magnesium (36·5 g., 1·50 g.-atom) in ether (300 ml.), and the mixture was refluxed for 20 hr. Treatment with dilute acid followed by the usual working-up and fractionation gave 4-p-*chlorophenylbut*-1-*ene* (155 g., 74%), b. p. 92—93°/9—10 mm., n_D^{25} 1·5239 (Found: C, 72·0; H, 7·0. $C_{10}H_{11}Cl$ requires C, 72·0; H, 6·65%).

The meta-, b. p. 93—94°/10 mm., n_D^{25} 1·5240 (Found: C, 72·3; H, 6·7%) and ortho-*isomer*, b. p. 86—88°/10 mm., n_D^{25} 1·5253 (Found: C, 71·6; H, 6·6%), were prepared analogously in 72 and 68% yield, respectively, from *m*-chlorobenzyl bromide and *o*-chlorobenzyl chloride.

Reaction of Trichlorosilane with 4-p-*Chlorophenylbut*-1-*ene.*—A mixture of trichlorosilane (135·5 g., 1·0 mole) with chloroplatinic acid (2 ml. of an 0·1M solution in isopropyl alcohol) was refluxed briefly, and 4-*p*-chlorophenyl-but-1-ene (143 g., 0·86 mole) was then added dropwise. The temperature of the mixture rose to 80° during the addition. The mixture was refluxed for 5 hr., the excess of trichlorosilane was removed by distillation, and the residue fractionated to give 1-p-*chlorophenyl*-1-*trichlorosilylbutane* (38·6 g., 14·8%), b. p. 122—126°/2·5 ± 0·5 mm., n_D^{25} 1·5291 (Found: hydrolysable Cl, 35·2. $C_{10}H_{12}Cl_4Si$ requires hydrolysable Cl, 35·4%), and *trichloro*-4-p-*chlorophenylbutylsilane* (159 g., 61%), b. p. 140—142°/2·0 ± 0·5 mm., n_D^{25} 1·5228 (Found: hydrolysable Cl, 35·2%).

Under identical conditions, from 4-*m*-chlorophenylbut-1-ene, were obtained 1-m-*chlorophenyl*-1-*trichlorosilylbutane* (29·2 g., 11%), b. p. 128—130°/5·0 ± 0·5 mm., n_D^{25} 1·5286 (Found; hydrolysable Cl, 35·2%), and *trichloro*-4-m-*chlorophenylbutylsilane* (168·9, 62%), b. p. 129—131°/1·0 ± 0·2 mm., n_D^{25} 1·5230 (Found: hydrolysable Cl, 35·2%).

From 4-*o*-chlorophenylbut-1-ene, under identical conditions, except that only 0·79 mole of the olefin was taken, was obtained *trichloro*-4-o-*chlorophenylbutylsilane* (183 g., 76%), b. p. 119—121°/1·0 ± 0·2 mm., n_D^{25} 1·5236 (Found: hydrolysable Cl, 35·2%). (We think that we would have isolated some of the branched-chain isomer if it had been formed in more than 2% yield.)

4-x-*Chlorophenylbutyltrimethylsilane.*—Trichloro-4-*o*-chlorophenylbutylsilane (168·2 g., 0·56 mole) was added to the Grignard reagent from methyl bromide (207 g., 2·18 mole) and magnesium (54 g., 2·25 g.-atom) in ether (900 ml.), and the mixture was refluxed for 16 hr. The usual working-up followed by fractionation gave 4-o-*chlorophenylbutyltrimethylsilane* (100 g., 75%), b. p. 124—126°/5·0 ± 0·5 mm., n_D^{25} 1·4963 (Found: C, 65·0; H, 8·9. $C_{13}H_{21}ClSi$ requires C, 64·8; H, 8·8%).

The meta-, b. p. 128—130°/5·0 ± 0·5 mm., n_D^{25} 1·4949 (Found: C, 65·1; H, 9·0%), and para-*isomer*, b. p. 113—115°/2·0—2·5 mm., n_D^{25} 1·4957 (Found: C, 64·6; H, 8·8%), were prepared analogously in 82% yield.

1-x-*Chlorophenyl*-1-*trimethylsilylbutane.*—Reaction (with 16 hours' refluxing) between 1-*p*-chlorophenyl-1-trichlorosilylbutane (33·5 g., 0·11 mole) and the Grignard reagent from methyl bromide (34·0 g., 0·36 mole) and magnesium (9·7 g., 0·40 g.-atom) in ether (200 ml.), followed by the usual working-up and fractionation, gave 1-p-*chlorophenyl*-1-*trimethylsilylbutane* (18·5 g., 69%), b. p. 114—115°/5·0 ± 0·5 mm., n_D^{25} 1·5074 (Found: C, 64·6; H, 8·7. $C_{13}H_{21}ClSi$ requires C, 64·8; H, 8·8%).

The meta-*isomer*, b. p. 111—112°/5·0 ± 0·5 mm., n_D^{25} 1·5070 (Found: C, 65·1; H, 8·9%), was prepared analogously in 85% yield.

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[12] Eaborn and Parker, *J.*, 1954, 939.

Trimethyl-4-x-*trimethylsilylphenylbutylsilane.*—Chlorotrimethylsilane (*ca.* 2 g.) was added to sodium (19·6 g., 0·85 g.-atom) in refluxing toluene (400 ml.), and a mixture of 4-*o*-chlorophenylbutyltrimethylsilane (94 g., 0·39 mole) and the remaining chlorotrimethylsilane (total 48·6 g., 0·45 mole) was then added dropwise at such a rate as to maintain boiling without external heating. After the addition the mixture was refluxed for 1·5 hr., then cooled and filtered through a sintered-glass disc, and the filtrate was fractionated to give *trimethyl*-4-o-*trimethylsilylphenylbutylsilane* (63 g., 58%), b. p. 140—142°/5·0 ± 0·5 mm., n_D^{25} 1·4897 (Found: C, 68·6; H, 10·6. $C_{16}H_{30}Si_2$ requires C, 69·0; H, 10·9%).

The meta-, b. p. 138—139°/5·0 ± 0·5 mm., n_D^{25} 1·4823 (Found: C, 68·9; H, 10·4%), and para-*isomer*, b. p. 144—146°/5·0 ± 0·5 mm., n_D^{25} 1·4837 (Found: C, 68·9; H, 10·6%), were prepared analogously in 58% yield.

1-*Trimethylsilyl*-1-x-*trimethylsilylphenylbutane.*—From 1-*p*-chlorophenyl-1-trimethylsilylbutane (15·7 g., 0·065 mole), chlorotrimethylsilane (8·6 g., 0·080 mole), and sodium (4·2 g., 0·18 g.-atom) in toluene (75 ml.), by the method described above, was made 1-*trimethylsilyl*-1-p-*trimethylsilylphenylbutane* (9·4 g., 52%), b. p. 128—129°/5·0 ± 0·5 mm., n_D^{25} 1·4921 (Found: C, 69·1; H, 10·6. $C_{16}H_{30}Si_2$ requires C, 69·0; H, 10·9%).

The meta-*isomer*, b. p. 119—121°/5·0 ± 0·5 mm., n_D^{25} 1·4862, was prepared similarly in 67% yield (Found: C, 68·6; H, 10·4%).

Spectra.—Proton magnetic resonance spectra were recorded in carbon tetrachloride solutions with a Varian A60 spectrometer. A Unicam S.P. 500 spectrophotometer was used for the ultraviolet spectra.

Cleavage Rates.—The medium for the cleavages was a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol.).[2] Details will be given in a separate paper.

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