Organosilicon Compounds. Part LIII.[1] Base Cleavage of Substituted Fluoren-9-yltrimethylsilanes and Related Compounds

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The rates of cleavage of substituted fluoren-9-yltrimethylsilanes by methanol–aqueous base (5 : 1 v/v) relative to that of the unsubstituted compound expressed as 1000 are: (a) at 50°, 9-phenyl-, 140; 9-methyl-, 29; 9-ethyl-, 10; 9-trimethylsilyl-, 3·5; 2-trimethylsilyl-9-methyl-, 30; 9-*m*-chlorophenyl-, 560; 2-bromo-9-methyl-, 190; (b) at 30°, 9-chloro-, 44,000; 9-bromo-, 36,000; 2-bromo-, 5800; 2,7-dibromo-, 32,000. The factors at 30° for 1-trimethylsilylindene and 1,1-bis(trimethylsilyl)indene are 10,000 and 18, respectively. For fluoren-9-yltrimethylsilane and the 2-bromo- and 2,7-dibromo-fluoren-9-yl and inden-1-yl compounds, the reactivities are in accord with the acidities of the corresponding carbon acids, but for the other compounds, each of which carries an additional α-substituent, steric hindrance appears to reduce the reactivity. The reactivity of phenylethynyltrimethylsilane, which is cleaved three times as rapidly as fluoren-9-yltrimethylsilane at 30°, is much lower than would be expected from the kinetic acidity of phenylacetylene.

MUCH information has been accumulated on the cleavage of carbon–silicon and carbon–tin bonds by methanolic or aqueous methanolic alkali, but there are still uncertainties about the details of the mechanism.[2-4] Recently some previously puzzling facts have been explained by the demonstration that for cleavage of $R-SnMe_3$ bonds certainly, and possibly also for cleavage of $R-SiMe_3$ bonds, the leaving group R does not separate as a free carbanion, but acquires a proton from the solvent as the $R-MMe_3$ bond is broken.[4,5] For cleavage of $PhCH_2-MMe_3$ and aryl–$SnMe_3$ bonds, the evidence favours a reversible formation of a pentaco-ordinate intermediate in a fast step (1) followed by rate-determining attachment (2) of a proton from the solvent to the

$$XO^- + R{-}MMe_3 \rightleftharpoons [XOMMe_3R]^- \qquad (1)$$

$$[XOMMe_3R]^- + XOH \longrightarrow XOMMe_3 + RH + OX^- \qquad (2)$$

separating carbanion. It has been suggested that the large steric effects which are sometimes observed, especially in the more reactive systems (*e.g.* 9-trimethyl- is almost 1000 times as reactive as 9-triethyl-silylfluorene), may be associated with crowding in a transition state not very far removed from the pentaco-ordinate intermediate.[4]

Reliable information has become available in recent years on the kinetic and equilibrium acidities of the less acidic carbon acids.[6-8] We have now examined the base cleavage of a range of substituted fluoren-9-yltrimethylsilanes and of 1-trimethyl- and 1,1-bis(trimethyl-silyl)indene, in order to compare the pattern of reactivity with that of the kinetic and equilibrium acidities of the corresponding carbon acids. The rate of cleavage of phenylethynyltrimethylsilane, which was studied previously,[9] has also been compared directly with that for fluoren-9-yltrimethylsilane.

TABLE 1

Rates of cleavage of substituted fluoren-9-yltrimethylsilanes by methanol–aqueous sodium hydroxide (5 : 1 v/v) at 50·0°

Substituent(s)	[NaOH]/M [a]	λ/nm [b]	$10^{-4}k/s^{-1}$ [c]	k_{rel} [d]
None	0·02	290	24·5	1000
9-Me	0·50	234	17·8	29
9-Et	0·50	234	6·3	10
9-Ph	0·10 0·02	240	16·7 3·4	140
9-*m*-ClC_6H_4	0·02	240	13·7	560
2-Br-9-Me	0·20 0·02	234	46 4·6	190
9-Me_3Si	2·0	292	8·6	3·5
2-Me_3Si-9-Me	0·50 1·0	234	18·7 36	30

[a] Concentration of aqueous alkali, 1 vol of which was mixed with 5 vol of methanol. [b] Wavelength used to follow progress of reaction. [c] Observed first-order rate constant. [d] Relative rate, calculated by assuming the first-order rate constant to be proportional to the concentration of the aqueous alkali.

The results are presented in Tables 1 and 2. Table 1 refers to cleavages at 50° in methanol–aqueous sodium

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[1] Part LII, B. Bøe, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1974, **82**, 327.

[2] C. Eaborn and R. W. Bott, in 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Dekker, New York, 1968, vol. 1, part 1, pp. 358—435.

[3] I. P. Beletskaya, K. P. Butin, and O. A. Reutov, *Organometallic Chem. Rev.*, 1971, **7A**, 51.

[4] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 490.

[5] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 304.

[6] J. R. Jones, 'The Ionisation of Carbon Acids,' Academic Press, London, 1973; *Progr. Phys. Org. Chem.*, 1972, **9**, 241.

[7] A. Streitwieser, jun., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 1965, **3**, 41.

[8] A. Streitwieser, jun., M. R. Granger, F. Mares, and R. A. Wolf, *J. Amer. Chem. Soc.*, 1973, **95**, 4257, and earlier papers in the series.

[9] C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.* 1965, **4**, 217.

hydroxide (5 : 1 v/v). Table 2 refers to reactions at 30° in the same medium or in methanol–aqueous 1 : 1 potassium carbonate–potassium hydrogen carbonate (5 : 1 v/v); the latter medium gives more reproducible results at the low base concentrations needed for the most reactive compounds. Table 3 presents values of the rate constants, k_{rel}, relative to those for fluoren-9-yltrimethylsilane along with the relevant p*K* values. In deriving the k_{rel} values, the observed first-order rate constants are assumed to be proportional to the concentration of base or of K_2CO_3–$KHCO_3$; this is in accord with previous experience [9-11] and with the results in Tables 1 and 2, and certainly any errors thus introduced are unimportant for the present purposes. The main features of the results are discussed in (*a*)—(*h*) below.

TABLE 2

Rates of cleavage at 30·0° of some R–$SiMe_3$ compounds by methanol (5 vol) and either (*a*) aqueous sodium hydroxide (1 vol), or (*b*) aqueous 1 : 1 potassium carbonate–potassium hydrogen carbonate (1 vol)

R	[NaOH]/ M [a]	[K_2CO_3]/ M [b]	λ/ nm [c]	10^4k/ s^{-1} [d]	k_{rel} [e]
Fluoren-9-yl	0·020		290	5·4	1000
		0·050		12·0	
		0·010		2·45	
9-Methyl-fluoren-9-yl	1·00		234	5·9	22
Inden-1-yl	0·010		281	27·5	10,200
1-Trimethyl-silylinden-1-yl	1·00		265	4·9	18
9-Chloro-		0·0050	236	57	44,000
fluoren-9-yl		0·0020		22·5	
9-Bromo-		0·0050	240	47	36,000
fluoren-9-yl		0·0020		18·0	
2-Bromo-		0·0050	234	7·3	5800
fluoren-9-yl		0·010		15·4	
2,7-Dibromo-fluoren-9-yl)		0·005	234	41	32,000
Phenylethynyl		0·050	258	36	3000

[a] Concentration of aqueous alkali, 1 vol of which was mixed with 5 vol of methanol. [b] Concentration of the potassium carbonate and also of the potassium hydrogen carbonate in the aqueous solution, 1 vol of which was mixed with 5 vol of methanol. [c] Wavelength used. [d] Observed first-order rate constant. [e] Relative rates are calculated by assuming that the rate is proportional to the concentration of the added aqueous alkali or aqueous carbonate–hydrogen carbonate.

TABLE 3

Relative rates of cleavage of some R–$SiMe_3$ compounds and p*K* values of the corresponding carbon acids, RH

R	Relative rates	p*K* [a]
Fluoren-9-yl	1·0	22·74
Inden-1-yl	10·1 [b]	19·93
2-Bromofluoren-9-yl	5·8	21·2 [c]
2,7-Dibromofluoren-9-yl	32	19·6 [d]
9-Phenylfluoren-9-yl	0·14	18·49
9-Methylfluoren-9-yl	0·029	22·33
9-Ethylfluoren-9-yl	0·010	22·60
9-Phenylethynyl	3·0	23·2 [e]

[a] In cyclohexylamine–caesium cyclohexylamide.[14] [b] The experimental value has been halved to take account of the availability of two C–$SiMe_3$ bonds. [c] The p*K* difference of 1·54 units between fluorene and 9-bromofluorene, observed for water–dimethyl sulphoxide solutions [K. Bowden, A. F. Cockerill, and J. R. Gilbert, *J. Chem. Soc.* (*B*), 1970, 179], is assumed to apply. [d] Calculated by assuming additivity of the effects of the 2-bromo-substituents. [e] In cyclohexylamine–lithium cyclohexylamide.

(*a*) In the absence of any additional substituents at the carbon atom bearing the trimethylsilyl group (referred to below as the α-carbon atom), the pattern of reactivities is consistent with the pattern of acidities of the corresponding carbon acid, RH.

(*b*) A 2-bromo-substituent activates 5·8 times in the cleavage at 30°, and introduction of the second analogously placed bromine atom, in the 2,7-dibromo-compound, causes a further similar rate acceleration. A 2-bromo-substituent causes a 22-fold rate acceleration in hydrogen exchange in methanolic sodium methoxide at 45°,[12] and this, along with the somewhat larger rate factor on going from the fluorene to the indene system in the exchange (*viz.* 16) compared with that (*viz.* 10) in the cleavage, indicates that the rates show a larger variation with acidity in the exchange. Based solely on the data for the indene and fluorene systems, the Brønsted slope, α, is 0·38 for the exchange and 0·32 for the cleavage.

(*c*) A very clear steric effect is revealed by the low reactivity of 9-phenylfluoren-9-yltrimethylsilane, which is some 7 times less reactive than fluoren-9-yltrimethylsilane, even though 9-phenylfluorene is 4·5 p*K* units more acidic than fluorene and undergoes hydrogen-exchange 44 times as rapidly in methanolic sodium methoxide.[7,12] With the Brønsted slope α of 0·32 noted above, the 9-phenyl derivative would be expected to be 14 times more reactive than the fluoren-9-yl compound itself, so the steric hindrance is equivalent to a rate factor of *ca.* 100. Use of kinetic acidity results, as in (*e*) below, indicates that the 9-phenyl derivative should be *ca.* 9 times as reactive as fluoren-9-yltrimethylsilane, so that the steric hindrance would correspond with a factor of 60.

The question arises whether the hindrance arises directly from serious compression in the transition state, or is a secondary effect associated with additional inhibition of resonance delocalisation of the negative charge by the phenyl group over and above that present [13] in the carbanion. The 4-fold activation (at 50°) by the *m*-Cl substituent in 9-*m*-chlorophenylfluoren-9-yltrimethylsilane, which compares with the 5·8-fold activation (at 30°) by the 2-bromo-substituent in the 2-bromofluoren-9-yl compound, indicates that a substantial proportion of the delocalised charge does reside in the phenyl group at the transition state, and so the low reactivity of the 9-phenyl compound appears to arise mainly from direct steric compression.

(*d*) A similar, if smaller, steric effect probably operates

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[10] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126; R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 448.

[11] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Organometallic Chem.*, 1963, 2342.

[12] A. Streitwieser, jun., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubinstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

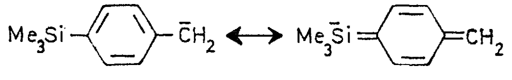
[13] A. F. Cockerill and J. E. Lamper, *J. Chem. Soc.* (*B*), 1971, 503.

in the case of 9-methylfluoren-9-yltrimethylsilane, which is 34 times less reactive than the fluoren-9-yl compound. While the equilibrium acidity of 9-methylfluorene is slightly greater than that of fluorene,[14] the kinetic acidities, as revealed by the rates of hydrogen exchange in methanolic sodium methoxide, are in the opposite order, and this has been attributed to the fact that the stabilising effect of an α-Me group can only operate effectively in a fully developed, planar carbanion.[15] However, the deactivating influence is much larger in the desilylation than in the exchange (in which[15] the factor is *ca.* 4 at 45°), even though the latter reaction is, as we have seen, slightly more sensitive to electronic effects, and it seems likely that steric hindrance is responsible for a *ca.* 10-fold deactivation in the cleavage.

Similar considerations apply to the effects of the 9-ethyl substituent, which deactivates by a factor of *ca.* 100 in the desilylation and of 5·5 in the hydrogen exchange.[15]

(*e*) The halogeno-substituents in 9-bromo- and 9-chloro-fluoren-9-yltrimethylsilane have substantial activating influences, in line with the enhanced kinetic acidities of the corresponding 9-halogenofluorenes relative to fluorene. In detritiation in methanolic sodium methoxide at 45°, 9-bromo- and 9-chloro-fluorene are, respectively, 7×10^2 and 4×10^2 times as reactive as fluorene;[16] 2-bromofluorene is 22 times as reactive in the exchange as fluorene,[7] while 2-bromofluoren-9-yl- is 5·8 times as reactive as fluoren-9-yl-trimethylsilane, and on assumption of a linear free energy relationship, 9-bromo- and 9-chloro-fluoren-9-yltrimethylsilane should be *ca.* 40 and 30 times, respectively, as reactive as fluoren-9-yltrimethylsilane. These values are close enough to the observed factors of 35 and 44 as to suggest that steric hindrance by these 9-substituents is not large; the reversal of the activation order for the chloro- and bromo-compounds could be due to a small amount of hindrance, but the relative effects of α-halogeno-substituents are very dependent on the degree of carbanion formation.[15-17]

(*f*) The presence of a second Me$_3$Si group on the α-carbon greatly lowers the ease of cleavage in both the fluoren-9-yl and inden-1-yl compounds. {The low reactivity of 2-[bis(trimethylsilyl)methyl]- compared with 2-(trimethylsilylmethyl)-pyridine was noted some years ago.[18]} Allowing for the availability of two equivalent C–Si bonds in the bis(trimethylsilyl) compounds the deactivation involves a factor of *ca.* 570 for the fluorene and *ca.* 1100 for the indene derivatives. From a consideration of electronic effects, the additional α-Me$_3$Si groups might have been expected to activate, with $(p \longrightarrow d)_\pi$ delocalisation of the carbanionic negative charge more than balancing out any inductive release of electrons towards carbon by the silicon atom; thus compared with simple alkanes, tetramethylsilane, and tris(trimethylsilyl)methane are relatively readily metallated [to give the species Me$_3$SiCH$_2$Li[19] and (Me$_3$Si)$_3$CLi[20]], and this has been attributed to $(p \longrightarrow d)_\pi$ bonding, as, in terms of structure (Ib), has the 10-fold rate increase brought about by the *p*-Me$_3$Si group in base cleavage of the *p*-Me$_3$SiC$_6$H$_4$CH$_2$–SiMe$_3$ bond.[10]


(Ia) (Ib)

The much reduced reactivities of 9,9-bis(trimethylsilyl)fluorene and 1,1-bis(trimethylsilyl)indene are thus probably due to steric hindrance, which, as we have seen, can be especially large for the better carbanionic leaving groups.[4] Additional α-Me$_3$Si groups also cause very marked deactivation in cleavage of PhCH$_x$(SiMe$_3$)$_{3-x}$ compounds by a dimethyl sulphoxide–aqueous sodium hydroxide (6 : 1 v/v), the relative reactivities at 30—50° being roughly 1000 : 50 : 1 for $x = 0 : 1 : 2$, after correction for the number of equivalent C–SiMe$_3$ bonds.[21] The smaller effect of the first additional α-Me$_3$Si group compared with that in the fluorene and indene derivatives is consistent with the fact that the Et$_3$Si : Me$_3$Si ratio (which we regard as one measure of the sensitivity to steric hindrance), is much smaller for R$_3$SiCH$_2$C$_6$H$_4$CO$_2{}^-$-*p* compounds,[22] *viz.* 5, than that, *viz.* 960, for the 9-trialkylsilylfluorenes,[11] cleavage in aqueous methanolic alkali being involved in each case.

The 2-Me$_3$Si group in 2,9-bis(trimethylsilyl)fluorene has very little effect on the reactivity; it possibly activates slightly, in line with the small activation by the *m*-Me$_3$Si group in *m*-trimethylsilylbenzyltrimethylsilane.[10]

(*h*) Phenylethynyltrimethylsilane is cleaved *ca.* 3·0 times as rapidly as fluoren-9-yltrimethylsilane at 30°. This is *ca.* 10 times as rapidly as would be expected on the basis of the p*K* values in Table 3, but the reactivity of phenylethynyltrimethylsilane cannot be satisfactorily related to the equilibrium acidity of phenylacetylene because the latter is so dependent upon the medium. (*E.g.*, the pK_a of phenylacetylene is thought to be about equal to that of 9-phenylfluorene in ether,[23] but to be *ca.* 6 units higher than that of fluorene in CH$_3$SOCH$_3$–CH$_3$SOCH$_2$K.[24]) The rate of cleavage of phenylethynyltrimethylsilane is, however, wholly out of keeping with the kinetic acidity of phenylacetylene,

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[14] A. Streitwieser, jun., E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, 1967, **89**, 63; A. Streitwieser, jun., C. J. Chang, and D. M. E. Reuben, *ibid.*, 1972, **94**, 5730.

[15] A. Streitwieser, jun., A. P. Marchand, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1967, **89**, 693.

[16] A. Streitwieser, jun., and F. Mares, *J. Amer. Chem. Soc.*, 1968, **90**, 2444.

[17] E. C. Buncel, 'Carbanions. Mechanistic and Isotopic Aspects,' Elsevier, Amsterdam, 1975, pp. 48—50.

[18] C. Eaborn and R. A. Shaw, *J. Chem. Soc.*, 1955, 3306.

[19] D. J. Peterson, *J. Organometallic Chem.*, 1967, **9**, 373.

[20] M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 529.

[21] M. J. Spillett, personal communication.

[22] Ref. 2, p. 404.

[23] J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212; W. K. McEwen, *ibid.*, 1936, **58**, 1124.

[24] F. G. Bordwell and W. S. Matthews, *J. Amer. Chem. Soc.*, 1974, **96**, 1214.

which undergoes detritiation[9] in buffered 20% MeOH–H_2O *ca.* 10^6 times as readily as does fluorene in methanolic sodium methoxide.[12] It has been previously noted that phenylacetylene is ionised by hydroxide ion in water 50—500 times faster than nitroethane, which is at least 10^{11} pK units more acidic, and this anomalously high reactivity has been attributed to the fact that there is little delocalisation of charge in the carbanion, and thus little reorganisation of the rest of the molecule is necessary when the proton leaves.[25] If this is a correct explanation, it is difficult to see why the same factors should not operate in the cleavage of phenylethynyltrimethylsilane, which appears to occur at a rate reasonably consistent with the pK range of phenylacetylene.

The anomaly can be seen in another light, *viz.* that phenylacetylene is more reactive towards base than phenylethynyltrimethylsilane by a factor in the region of 10^3 (a difference between the water contents of the aqueous methanolic media being neglected) whereas fluoren-9-yltrimethylsilane is *ca.* 3×10^3 times more reactive than fluorene at 30° if the data for the cleavage in aqueous methanolic alkali in Table 1 are compared with those for the hydrogen exchange in methanolic sodium methoxide. The alkynyl systems still, in fact, represent the only known cases in which the R–H bond, where R is an organic group, is more readily cleaved by base than the corresponding R–$SiMe_3$ bond. (It is noteworthy, however, in view of the analogy between the C≡C and C≡N systems, that the NC–H bond is more reactive towards base than the NC–$SiMe_3$ bond.) If we consider this in isolation (*i.e.*, neglecting the indication above that it may be the hydrogen exchange of phenylacetylene which is anomalously fast, not the cleavage of phenylethynyltrimethylsilane which is anomalously slow), the most plausible explanation is to be found in steric hindrance in the cleavage, probably mainly towards solvation of the separating carbanion, which is especially serious because at the transition state the developing charge is concentrated in the line of the breaking C–Si bond.[9]

EXPERIMENTAL

Preparations.—9-*Ethyl*-9-*trimethylsilylfluorene*. A solution of 9-trimethylsilylfluorene (30 g, 0·12 mol) in ether (200 ml) was added dropwise with stirring, to n-butyllithium (0·15 mol) in ether (100 ml), and the mixture was boiled under reflux for 3 h. To the yellow solution, after cooling, ethyl bromide (27 g, 0·25 mol) was added dropwise and the mixture was boiled under reflux for 12 h. Addition of aqueous ammonium chloride, was followed by separation, washing, and drying (Na_2SO_4) of the ethereal layer, and removal of the solvent, and the residue was recrystallised from ethanol to give needles of 9-*ethyl*-9-*trimethylsilylfluorene* (20 g, 64%), m.p. 62·5° (Found: C, 81·4; H, 8·4. $C_{18}H_{22}Si$ requires C, 81·1; H, 8·3%), τ ($CDCl_3$) 2·47 (m, aromatic), 7·62 (q, CH_2), 9·64 (t, CH_2CH_3), and 10·22 (s, $SiMe_3$), *m*/*e* 266 (M^+).

9-*Phenyl*-9-*trimethylsilylfluorene*. n-Butyl-lithium (0·018 mol) in ether (30 ml) was added with stirring to a solution of 9-phenylfluorene (4·0 g, 0·016 mol) in ether (150 ml). The reddish orange mixture was refluxed for 24 h, then cooled in ice, and chlorotrimethylsilane (2·06 g, 0·019 mol) in ether (50 ml) was added dropwise with stirring, and the orange-yellow mixture was refluxed for 5 h. The usual work-up left an oil, which after distillation (b.p. 134—136° at *ca.* 0·001 mmHg) slowly crystallised. Recrystallisation from ethanol gave 9-*phenyl*-9-*trimethylsilylfluorene* (2·5 g, 50%), m.p. 111·5° (Found: C, 84·2; H, 7·0. $C_{22}H_{22}Si$ requires C, 84·0; H, 7·05%), τ ($CDCl_3$) 2·53 (m, aromatic) and 10·12 (s, $SiMe_3$), *m*/*e* 314 (M^+).

2-*Bromo*-9-*methyl*-9-*trimethylsilylfluorene*. A solution of bromine (31·9 g, 0·20 mol) in chloroform (100 ml) was added with stirring during 45 min to 9-methyl-9-trimethylsilylfluorene (50 g, 0·20 mol) in chloroform (550 ml). The mixture was set aside overnight, boiled under reflux for 2 h, then decolourised with charcoal. The solvent was taken off, and the residue recrystallised several times from acetone to give 2-*bromo*-9-*methyl*-9-*trimethylsilylfluorene* (35 g, 53%), m.p. 99—100° (Found: C, 61·5; H, 5·8; Br, 24·2. $C_{17}H_{19}BrSi$ requires C, 61·6; H, 5·8; Br, 24·1%), τ 2·47 (m, aromatic), 8·36 (s, 9-Me), and 10·20 (s, $SiMe_3$), *m*/*e* 331 (M^+).

9-*Methyl*-2,9-*bis*(*trimethylsilyl*)*fluorene*. Chlorotrimethylsilane (8·6 g, 0·080 mol) was added with stirring to the Grignard reagent from 2-bromo-9-methyl-9-trimethylsilylfluorene (26·5 g, 0·080 mol) and magnesium (2·90 g, 0·12 g atom) in tetrahydrofuran (100 ml). The mixture was boiled under reflux for 12 h, and the usual work-up left an oil, which solidified after distillation (b.p. 113° at *ca.* 0·01 mmHg). Recrystallisation from methanol gave 9-*methyl*-2,9-*bis*(*trimethylsilyl*)*fluorene* (16 g, 64%), m.p. 51—52° (Found: C, 74·3; H, 8·7. $C_{20}H_{28}Si_2$ requires C, 74·0; H, 8·7%), τ (neat) 2·47 (m, aromatic), 8·26 (s, 9-Me), 9·62 (s, 9-$SiMe_3$), and 10·20 (s, 2-$SiMe_3$), *m*/*e* 324 (M^+).

9-m-*Chlorophenyl*-9-*trimethylsilylfluorene*. A solution of 9-*m*-chlorophenylfluorene (8·4 g, 0·030 mol) in ether (150 ml) was added to n-butyl-lithium (0·32 mol) in ether (50 ml). The mixture was boiled under reflux for 3 h, and to the orange-yellow solution chlorotrimethylsilane (3·5 g, 0·032 mol) in ether (20 ml) was added dropwise with stirring. The mixture was boiled under reflux for 5 h, then the usual work-up gave a solid residue which was recrystallised several times from light petroleum (b.p. 40—60°) to give 9-m-*chlorophenyl*-9-*trimethylsilylfluorene* (4·3 g, 41%), m.p. 103° (Found: C, 75·6; H, 6·5; Cl, 10·2. $C_{22}H_{21}ClSi$ requires C, 75·7; H, 6·1; Cl, 10·2%), τ ($CDCl_3$) 2·53 (m, aromatic) and 10·12 (s, $SiMe_3$), *m*/*e* 348 (M^+).

Other compounds. 9-Trimethylsilylfluorene, m.p. 97°, was prepared by a standard method.[26] 9,9-Bis(trimethylsilyl)fluorene and the other substituted 9-trimethylsilylfluorenes were prepared as described earlier, and the m.p.s agreed well with those recorded previously.[27] 1-Trimethylsilyl-, b.p. 82—84° at 4 mmHg, n_D^{20} 1·5423 (lit.,[28] b.p. 87° at 4 mmHg, n_D^{20} 1·5426) and 1,1-bis(trimethylsilyl)-indene, b.p. 94° at 2·5 mmHg, n_D^{20} 1·5307 (lit.,[28] b.p. 106° at 3 mmHg, n_D^{20} 1·5300) were prepared by known methods.[28] G.l.c. analysis of the 1,1-bis(trimethylsilyl)-indene revealed the presence of a few percent of an impurity of very similar retention time, probably an isomer, such as

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[25] J. Hine, *J. Org. Chem.*, 1966, **31**, 1236.

[26] H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Amer. Chem. Soc.*, 1950, **72**, 1689.

[27] C. Eaborn and R. A. Shaw, *J. Chem. Soc.*, 1955, 1420.

[28] L. H. Sommer and N. S. Marans, *J. Amer. Chem. Soc.*, 1951, **73**, 5135.

the 1,3-compound,[29] and the kinetic studies were consistent with this (see below). The separation of the peaks was not sufficient to permit purification by g.l.c.

Rate Measurements.—For the rate studies, 1 vol of aqueous base was added to 5 vol of a solution of the organosilane in methanol. The aqueous base contained either sodium hydroxide or an equimolar mixture of potassium carbonate and potassium hydrogen carbonate. Rate constants were determined spectrophotometrically as previously described.[11]

Good first-order plots were obtained for at least 90% completion of the reaction, and the spectra after 10 half-lives agreed with those of the expected cleavage product. In the case of 9-bromo-9-trimethylsilylfluorene, use of 1·0M added sodium hydroxide at 50° (conditions under which the cleavage is effectively complete within a few minutes) caused an optical density change at 241 nm corresponding to a first-order rate constant of $8{\cdot}0 \times 10^{-4}\ s^{-1}$, in satisfactory agreement with the value of $7{\cdot}8 \times 10^{-4}\ s^{-1}$ for an authentic sample of 9-bromofluorene. The corresponding rate constants for the 9-chloro-9-trimethylsilylfluorene (at 236 nm) with 2·0M added alkali was $0{\cdot}79 \times 10^{-4}\ s^{-1}$.

With the sample of 1,1-bis(trimethylsilyl)indene used, an optical density change occurred at 281 nm with 0·01M added alkali at 30° at a rate (k $28 \times 10^{-4}\ s^{-1}$) virtually identical with that for 1-trimethylsilylindene; it is thought to arise from the presence of the impurity.

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[29] Yu. A. Ustynyuk, A. V. Kisin, I. M. Pribytkova, A. A. Zenkin, and N. D. Antonova, *J. Organometallic Chem.*, 1972, **42**, 47.