Organosilicon Compounds. Part XII. Substituted 9-Fluorenyltrimethylsilanes.*

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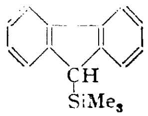
9-Trimethylsilylfluorene has been brominated in the 2-, 7-, and 9-position but nitration led to cleavage of the Si–C bond. The Si–C bond of 9-bromo-9-trimethylsilylfluorene was broken in reactions involving nucleophilic reagents but survived electrophilic attack on bromine. Some unusual Si–C bond cleavages are reported.

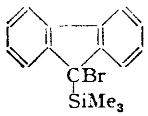
There has been little systematic study of organosilicon compounds in which the silicon is attached at a " reactive methylene " position, although they are of special interest in that the usual polarity $\overset{+}{\mathrm{Si}}-\overset{-}{\mathrm{C}}$ of the silicon–carbon bond is enhanced, with consequent increase in the reactivity of the bond. Sommer and Marans (*J. Amer. Chem. Soc.*, 1951, **73**, 5135) have studied trialkyl-1-indenylsilanes and we now describe the reactions of 9-trimethylsilylfluorene (I) and its derivatives.

Halogenation and Nitration.—With one equivalent of bromine in chloroform or two equivalents in carbon tetrachloride, the silane (I) gives, respectively, 2-bromo- and 2 : 7-dibromo-9-trimethylsilylfluorene. With *N*-bromosuccinimide, it gives 9-bromo-9-trimethylsilylfluorene (II), and di-9-fluorenyldimethylsilane gives di-(9-bromo-9-fluorenyl)dimethylsilane; with *N*-chlorosuccinimide the silane (I) gives 9-chloro-9-trimethylsilylfluorene.

(I)



(II)



Although nuclear bromination proceeds normally, nitration of 9-trimethylsilylfluorene

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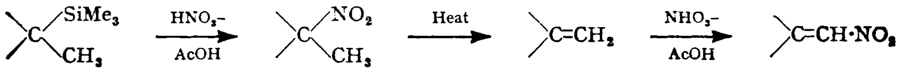
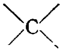
nitration, some 9-(nitromethylene)fluorene being formed. This may have been formed by the sequence :



(Here and below  represents the 9-carbon atom of fluorene.)

Since the Si–C cleavage in nitration involves electrophilic attack at position 9 it should be hindered by electron-withdrawing substituents on this carbon atom, and 9-bromo-9-trimethylsilylfluorene was successfully nitrated in position 2.

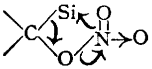
Reactions of 9-*Bromo*-9-*trimethylsilylfluorene* (II).—An α-trimethylsilyl group reduces the reactivity of alkyl halides markedly towards electrophilic reagents (Whitmore and Sommer, *J. Amer. Chem. Soc.*, 1946, **68**, 481 ; Sommer, Bailey, Whitmore, and Strong, *ibid.*, p. 1881) for reasons which are not clear, and less so towards nucleophilic reagents (Whitmore and Sommer, *loc. cit.*), probably from a combination of polar and steric influences. While steric hindrance by an α-trimethylsilyl group will be greater in the bromo-compound (II) than in primary halides, the large difference in rate of ethanolysis between it (less than 5% of which reacts in 50 minutes at 25°) and 9-bromo-9-methylfluorene [90% of which undergoes solvolysis under the same conditions (Bartlett and Cohen, *ibid.*, 1940, **62**, 1183)] is almost certainly because of inhibition of the S_N1 mechanism with the former compound.

No nucleophilic displacements of the bromine atom of the silane (II) occurred without cleavage of the C–Si bond. Reaction with sodium azide in aqueous methanol gave 9-azidofluorene (the nucleophile causing cleavage may not have been the azide ion, but hydroxide or alkoxide ions formed from it by solvolysis) and phenol gave 9-*p*-hydroxyphenylfluorene [which is formed from 9-bromofluorene under the same conditions (Wittig, Döser, and Lorenz, *Annalen*, 1949, **562**, 192)]. Probably in the latter case cleavage followed replacement of the bromine since the high stability of the 9-*p*-hydroxyphenylfluorenyl carbanion should lead to very ready cleavage.

Reaction between 9-bromo-9-trimethylsilylfluorene and sodium iodide in acetone was relatively slow as judged by the rate of precipitation of sodium bromide, and fluorenone was obtained in 80% yield. The fluorenone was probably produced by decomposition of initially formed 9-iodo-9-trimethylsilylfluorene, possibly through dissociation of the latter to the 9-trimethylsilylfluorenyl free radical which absorbed oxygen to give a peroxide which then broke down to fluorenone.

Cleavage of the Si–C bond without destruction of the C–Br bond occurred when the bromo-compound (II) was heated with potassium permanganate in acetone (giving 9 : 9′-dibromo-9 : 9′-difluorenyl), and also when it was boiled with aqueous acetone (giving some 9-bromofluorene).

Primary and secondary carbonium ions with α-trimethylsilyl substituents rearrange to siliconium ions (Whitmore, Sommer, and Gold, *J. Amer. Chem. Soc.*, 1947, **69**, 1976; Sommer, Bailey, Gould, and Whitmore, *ibid.*, 1954, **76**, 801 ; Sommer and Evans, *ibid.*, p. 1186). Rearrangement of the 9-trimethylsilylfluorenyl 9-carbonium ion is unlikely since it is stabilised by resonance and, as expected, the silane (II) was unaffected by aluminium bromide in ether. Reactions through electrophilic attack on bromine might thus be expected to lead to simple replacement of the bromine atom in this compound without Si–C bond cleavage. With silver nitrate in ethanol, the bromo-compound gave 9-ethoxy-9-trimethylsilylfluorene and some fluorenone, but only fluorenone in high yield was obtained from it by treatment with silver nitrate in aqueous acetone. Since 9-hydroxy-9-trimethylsilylfluorene was obtained without fluorenone formation on treatment with silver acetate in aqueous acetone, the fluorenone formed in the silver nitrate reaction probably came from decomposition of 9-trimethylsilyl-9-fluorenyl nitrate initially formed. The decomposition could be by either an intermolecular process,  $NO_3^-\ Si—C—O—NO_2$ [analogous to Baker and Easty's $E_{Co}2$ mechanism (*J.*, 1952, 1193)] or, more likely, by an intramolecular process (*A*) [the thermal



(*A*)

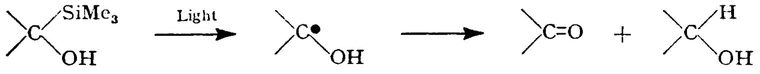
decomposition of diphenylmethyl nitrate to benzophenone (Cheeseman, *Chem. and Ind.*, 1954, 281) could have an analogous mechanism].

It is probable that 9-ethoxy- and 9-hydroxy-9-trimethylsilylfluorene were formed by interaction of the carbonium ion with the solvents, but they could have come from solvolysis of initially formed nitrate and acetate. (9-Fluorenyl nitrate is converted into ethyl 9-fluorenyl ether by ethanol.) In either case the Si–C bond seems to survive formation and reaction of the carbonium ion.

Metallation of 9-*Trimethylsilylfluorene* (I).—The Si–C bond also survives carbanion formation. By cross-metallation of the silane (I) (cf. Gilman, Benkeser and Dunn, *ibid.*, 1950, **72**, 1689) we have prepared the 9-lithio-derivative, and this with chloro-trimethylsilane and methyl iodide gives 9 : 9-bistrimethylsilylfluorene and 9-methyl-9-trimethylsilylfluorene, respectively.

Cleavage of the Si–C *Bond.*—Alkali readily cleaves the silane (I) but aqueous or acidic ethanol is ineffective. Cleavage is facilitated by electron-withdrawing substituents in the 9-position [see the reactions of the bromo-compound (II) above and of 9-ethoxy-9-trimethylsilylfluorene] and in the aromatic rings; 2-bromo- and 2 : 7-dibromo-9-trimethylsilylfluorene were completely cleaved even by boiling 95% aqueous ethanol in less than 18 and 1½ hours, respectively, while 9-bromo-2-nitro-9-trimethylsilylfluorene was completely cleaved by aqueous acetone in ½ hour at room temperature. 9-Ethoxy-9-trimethylsilylfluorene, which is readily cleaved by alkali, is stable to neutral aqueous ethanol but is cleaved by aqueous-ethanolic hydrochloric acid. The acidic cleavage probably involves initial attachment of a proton to the ethereal oxygen atom, to give a positively charged entity in which the silicon atom will be particularly susceptible to nucleophilic attack by the solvent.

An unusual cleavage occurred with 9-hydroxy-9-trimethylsilylfluorene, which decomposed in daylight to give a mixture from which fluorenone and 9-fluorenol were isolated in roughly equal amounts. Probably a free radical was formed and underwent disproportionation :



The 9-hydroxyfluorenyl radical has been proposed as an intermediate in the photochemical decomposition of " fluorenopinacol " in acetone to fluorenone and *iso*propyl alcohol (Schönberg and Mustafa, *J.*, 1944, 67).

EXPERIMENTAL

Cleavage Reactions.—Unless otherwise stated, reaction mixtures were added to water and the solid was either filtered off or taken up in ether and recovered. When the rate of cleavage was of interest samples of the mixture were withdrawn at intervals and added to water, and the m. p. (after drying) of the solid was found; this procedure is denoted below by " method A."

In " x% aqueous ethanol " and similar phrases, x denotes the vol.-% of organic solvent.

9-*Trimethylsilylfluorene* (I).—This, m. p. 97·5° (from ethanol), was prepared in *ca.* 60% yields by interaction of chlorotrimethylsilane with 9-fluorenyl-lithium in ether or 9-fluorenylsodium in light petroleum.

Over 95% recoveries, with no evidence of cleavage, were made when the silane was boiled with 90% aqueous ethanol for 18 hr., with 70% aqueous ethanol containing 10% of hydrochloric acid for 3 hr., and with silver nitrate (3%) in 92% aqueous acetone for 3 hr., and when its solution in glacial acetic acid was kept at room temperature for 24 hr. In ¼ hr., with boiling 90% aqueous ethanol containing 10% potassium hydroxide, it gave fluorene in 94% yield.

" Method A " showed cleavage to be complete in 6 hr. when the silane was boiled with a saturated solution of sodium azide in 90% aqueous methanol, and fluorene (97%) was obtained.

Di-9-fluorenyldimethylsilane.—To 9-fluorenylsodium, prepared from sodamide (10 g.) and fluorene (56 g.) in decalin and washed with light petroleum, benzene (100 ml.) was added, followed by a solution of chlorotrimethylsilane (18 g.) in light petroleum (b. p. 40—60°). The mixture was boiled for 12 hr., and then filtered. Evaporation left an oil which solidified on addition of moist acetone. Fractional crystallization from acetone and *cyclo*hexane gave the readily soluble *di-9-fluorenyldimethylsilane*, m. p. 178—179° (1·7 g., 3%) (Found : C, 86·1; H, 6·25. $C_{28}H_{24}Si$ requires C, 86·6; H, 6·2%), and the sparingly soluble s-*di-9-fluorenyltetramethyldisiloxane*, m. p. 216—217° (0·52 g., 0·7%) (Found : C, 77·5; H, 6·4%; *M*, *ca.* 400.

$C_{30}H_{30}OSi_2$ requires C, 77·9; H, 6·5%; *M*, 450). Both products gave fluorene in ~90% yield on alkaline cleavage, the former after 1 hr. in boiling 97% aqueous ethanol containing 3% of potassium hydroxide and the latter after 3 hr. in 98% aqueous acetone containing 0·8% of potassium hydroxide.

9 : 9-*Bistrimethylsilylfluorene*.—A solution of the silane (I) (7·9 g.) in ether (100 ml.) was added to *n*-butyl-lithium [from lithium (1 g.) and *n*-butyl bromide (5·5 g.)] in ether (35 ml.) and the mixture was boiled for 3 hr. Chlorotrimethylsilane (4·5 g.) in ether (20 ml.) was added dropwise, and the mixture was set aside overnight and then filtered. The filtrate was evaporated, and the organic matter was extracted from the residue with chloroform and then recovered. Recrystallization from ethanol and acetone gave 9 : 9-*bistrimethylsilylfluorene*, m. p. 110° (1·76 g., 17%) (Found : C, 73·2; H, 8·5. $C_{19}H_{26}Si_2$ requires C, 73·5; H, 8·4%). (The remaining product had m. p. 60—90° and was probably a mixture of the initial and the final silane, since it gave pure fluorene with alcoholic alkali.)

Boiling for 24 hr. with 90% aqueous ethanol did not affect 9 : 9-bistrimethylsilylfluorene, but boiling for ¼ hr. with this solvent containing 10% of potassium hydroxide gave a 90% yield of fluorene.

9-*Methyl*-9-*trimethylsilylfluorene*.—Metallation of the silane (I) (8·7 g.) in ether with *n*-butyl-lithium was followed by addition of methyl iodide (20 g.) in ether. The mixture was boiled for 4 hr. and then worked up as in the previous experiment, but with recrystallization from ethanol, to give 9-*methyl*-9-*trimethylsilylfluorene*, m. p. 118° (2·86 g., 31%) (Found : C, 80·5; H, 7·5. $C_{17}H_{20}Si$ requires C, 80·9; H, 8·0%). This compound gave 9-methylfluorene, m. p. and mixed m. p. 45—47° in 91% yield when boiled for ¼ hr. with 90% aqueous ethanol containing 10% of potassium hydroxide.

Halogenation.—(i) A solution of bromine (1·18 g.) in chloroform (5 ml.) was added to a solution of the silane (I) (1·78 g.) in chloroform (20 ml.) during 45 min.; the mixture was boiled for 2 hr. and then decolorized with charcoal. Evaporation left a residue which was recrystallized from acetone, to give 2-*bromo*-9-*trimethylsilylfluorene*, m. p. 116·5° (0·9 g., 23%) (Found : C, 60·8; H, 5·3. $C_{16}H_{17}BrSi$ requires C, 60·6; H, 5·4%). When the product was boiled with 90% aqueous alcohol cleavage was complete in 18 hr. (method A), and 2-bromofluorene, m. p. and mixed m. p. 110·5—111·5°, was obtained in 90% yield.

Similarly, from bromine (3·5 ml.) and the silane (I) (5·15 g.) in chloroform, but with 3 hr. at 0° instead of the b. p., there was obtained 2 : 7-*dibromo*-9-*trimethylsilylfluorene*, m. p. 149° (3·93 g., 46%) (Found : C, 47·8; H, 3·9. $C_{16}H_{16}Br_2Si$ requires C, 48·5; H, 4·1%).

When the product was boiled with 90% aqueous alcohol cleavage was complete in 1½ hr. (method A) and 2 : 7-dibromofluorene, m. p. and mixed m. p. 163—164°, was obtained in 90% yield.

(ii) Boiling the silane (I) (50 g.) with *N*-bromosuccinimide (41·5 g.) in carbon tetrachloride for 11 hr. followed by filtration and concentration of the solution gave 9-*bromo*-9-*trimethylsilylfluorene* (II), m. p. 134·5° (65 g., 98%) (Found : C, 60·4; H, 5·6; Br, 25·2. $C_{16}H_{17}BrSi$ requires C, 60·6; H, 5·4; Br, 25·2%).

Similarly di-9-fluorenyldimethylsilane (0·88 g.) and *N*-bromosuccimide (1·0 g.) gave *di*-(9-*bromo*-9-*fluorenyl*)*dimethylsilane*, m. p. 220—230° (with decomp. above 200° and formation of a deep red liquid) (from ethanol) (0·45 g., 36%) (Found : C, 61·4; H, 4·3. $C_{28}H_{22}Br_2Si$ requires C, 61·5; H, 4·1%).

(iii) A mixture of *N*-chlorosuccinimide (2·3 g.), benzoyl peroxide (0·2 g.), and the silane (I) (3·8 g.) in carbon tetrachloride (20 ml.) was boiled for 3 hr., under illumination from a 150-w lamp, to give 9-*chloro*-9-*trimethylsilylfluorene*, m. p. 122° (from acetone) (1·16 g., 27%) (Found : C, 69·6; H, 6·3. $C_{16}H_{17}ClSi$ requires C, 70·4; H, 6·3%).

Nitration.—(i) Nitric acid (*d*, 1·4) (4·5 ml.) was added during 15 min. to the silane (I) (5 g.) dissolved in glacial acetic acid (42 ml.). The temperature of the mixture was raised to 80° and then allowed to fall slowly. The solid which separated was washed with acetic acid and water and recrystallized from benzene to give 2 : 9-dinitrofluorene, m. p. and mixed m. p. 136—137° (2·4 g., 41%) (Found : C, 61·0; H, 3·1; N, 11·2. Calc. for $C_{13}H_8O_4N_2$: C, 60·9; H, 3·15; N, 10·9%).

(ii) Nitration of 9-methyl-9-trimethylsilylfluorene was similarly performed, but exothermic reaction caused the temperature to rise above 100°. The mixture was poured into water, and the organic matter was extracted with ether. The solvent was removed, to leave a residue which on recrystallization from acetone gave orange-red 9-nitromethylenefluorene, m. p. and mixed m. p. 133·5—134° (Found : C, 75·3; H, 4·1; N, 6·6. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·1; N, 6·3%). Its ultraviolet absorption spectrum was identical with that of an authentic sample (prepared by boiling together 9-iminofluorene and nitromethane for 3½ hr., removing the solvent, and purifying the residue by chromatography on alumina).

Its infrared spectrum had maxima at 1656, 1613, 1572, 1522, 1473, 1397, 1346, 1117, 1004, 958, 917, 852, 788, 749, and 732 cm.$^{-1}$, indicating the absence of an exocyclic methylene group which has a maximum at 890 cm.$^{-1}$.

(iii) Nitric acid (2 ml.; *d* 1·52) in acetic anhydride (10 ml.) was added slowly to a suspension of the bromo-silane (II) (6·4 g.) in acetic anhydride (25 ml.). The mixture was stirred for 2 hr. and then cooled to 0°. The precipitate was recrystallised from acetone, to give pale yellow 9-*bromo*-2-*nitro*-9-*trimethylsilylfluorene*, m. p. 160° (4·06 g., 56%) (Found: C, 53·1; H, 4·1; N, 4·1. $C_{16}H_{16}O_2NBrSi$ requires C, 53·0; H, 4·45; N, 3·9%).

Cleavage by 90% aqueous acetone for 1 hr. at *ca.* 18° gave a 90% yield of 9-bromo-2-nitrofluorene, m. p. and mixed m. p. 144°. The solution contained no bromide ion.

Interaction of the Silane (II) *and Silver Salts.*—(i) A precipitate formed immediately when a boiling solution of silver nitrate (2·63 g.) in ethanol (100 ml.) was added to a boiling solution of the silane (II) (4·91 g.) in ethanol (50 ml.). The mixture was boiled for 10 min. and filtered, to give silver bromide (2·80 g., 96%). Evaporation of the filtrate left a residue which was taken up in chloroform, and the solution was filtered and evaporated. Fractional crystallization of the residue from aqueous ethanol gave 9-*ethoxy*-9-*trimethylsilylfluorene*, m. p. 76° (from aqueous ethanol, acetone, or light petroleum) (1·46 g., 33%) (Found: C, 76·6; H, 7·7. $C_{18}H_{22}OSi$ requires C, 76·55; H, 7·9%), and fluorenone (0·23 g., 8%), m. p. and mixed m. p. 82—83°.

There was no detectable cleavage when the former product was boiled with 90% aqueous ethanol for 6 hr. Method A showed cleavage to be complete in 18 hr. in boiling 75% aqueous ethanol containing hydrochloric acid (3N), and ethyl 9-fluorenyl ether, m. p. and mixed m. p. 50—52°, was obtained in 80% yield.

Cleavage with 90% aqueous ethanol containing 10% of potassium hydroxide for ¼ hr. gave ethyl 9-fluorenyl ether, m. p. and mixed m. p. 52—54°, in 82% yield and no unchanged material.

(ii) When the solution of the silane (II) (3·9 g.) in acetone (50 ml.) was added to a solution of silver nitrate (2·1 g.) in 20% aqueous acetone (25 ml.) a precipitate formed immediately and the liquid became deep yellow. After ½ hr. the silver bromide (2·28 g., 98%) was filtered off, and the solvent was removed from the filtrate at reduced pressure. The residue was recrystallized from light petroleum, to give fluorenone, m. p. and mixed m. p. 83—84° (1·88 g., 85%); the phenylhydrazone had m. p. and mixed m. p. 149—150°.

(iii) A solution of the silane (II) (7·63 g.) in boiling acetone (250 ml.) was added to one of silver acetate (4·0 g.) in boiling water. The mixture was boiled for ¼ hr. and then filtered, and the filtrate added to water. Ether-extraction followed by drying (Na_2SO_4) and evaporation of the extract left a residue which recrystallized from light petroleum, to give 9-*hydroxy*-9-*trimethylsilylfluorene*, m. p. 92° (2·08 g., 34%) (Found: C, 75·8; H, 7·5. $C_{16}H_{18}OSi$ requires C, 75·6; H, 7·1%).

The compound decomposed slowly in a corked tube in the dark. A sample exposed to daylight in an open dish quickly became yellow and moist but had a dry appearance again after a week. Chromatography on alumina gave fluorenone (0·11 g.) and 9-fluorenol (0·09 g.) and a small amount of a substance of m. p. >300°.

9-*Fluorenyl Nitrate.*—A solution of 9-bromofluorene (5·3 g.) in acetonitrile (55 ml.) was added to one of silver nitrate (3·7 g.) in acetonitrile (10 ml.) and after 2 hr. silver bromide was filtered off (4·0 g., 98%). The filtrate was decolorized with charcoal, the solvent was removed, and the residue recrystallized from light petroleum to give 9-*fluorenyl nitrate*, m. p. 89° (3·0 g., 61%) (Found: C, 69·1; H, 4·1; N, 5·9. $C_{13}H_9O_3N$ requires C, 68·7; H, 4·0; N, 6·2%).

Reactions of the Bromo-compound (II).—(i) After 1 hr. at *ca.* 18° a solution of this compound (1·07 g.) in ethanol (75 ml.) was poured into water, and the precipitate was filtered off and dried, to give unchanged material (1·02 g., 95%), m. p. and mixed m. p. 133—134°. There was no bromide ion in the filtrate.

(ii) A solution of the bromide (II) (1·62 g.) in 95% aqueous acetone (50 ml.) was boiled for 3 hr. and then concentrated and cooled, to give unchanged material (0·99 g., 61%), m. p. and mixed m. p. 132—134°. The mother-liquor was evaporated to dryness and the residue, recrystallized from acetone and light petroleum, gave 9-bromofluorene (0·06 g., 5%), m. p. and mixed m. p. 102—103·5°.

(iii) A solution of the compound (II) (3·11 g.) in methanol (50 ml.) was boiled with excess of sodium azide (2 g.) for 1½ hr. and then added to water. The precipitated oil was taken up in ether, recovered, and dissolved in hot aqueous ethanol. The solution was quickly cooled in ice, to give 9-azidofluorene, m. p. and mixed m. p. 42—44° (1·72 g., 85%).

(iv) A solution of the compound (II) (1·84 g.) and sodium iodide (1·5 g.) in acetone (65 ml.) was stored in the dark for 3 days, during which a solid was slowly deposited and a deep iodine colour appeared. The solid was filtered off and identified as sodium bromide (0·36 g., 60%). The filtrate was diluted with ether and iodine was removed with aqueous sodium thiosulphate. Evaporation left a deep yellow solid, which was recrystallized from ether–light petroleum to give fluorenone, m. p. and mixed m. p. 82—83° (0·82 g., 79%).

(v) A mixture of phenol (7 g.) and the compound (II) (3·75 g.) was kept at 55° for 3½ hr., after which evolution of hydrogen bromide had stopped. *cyclo*Hexane (15 ml.) was added, and the solution was boiled for 5 min. and then allowed to cool. The solid which separated was recrystallised from *cyclo*hexane, to give 9-*p*-hydroxyphenylfluorene, m. p. and mixed m. p. 178—179° (2·62 g., 85%).

(vi) A mixture of potassium permanganate (0·98 g.) and the silane (II) (3·0 g.) and acetone (100 ml.) was boiled for 2 hr. then filtered. Evaporation left a residue which, recrystallised from benzene, gave 9 : 9′-dibromo-9 : 9′-difluorenyl, m. p. 243—244° (decomp. to a deep red liquid) (Found : C, 64·0; H, 3·4; Br, 32·3. Calc. for $C_{26}H_{16}Br_2$; C, 63·9; H, 3·3; Br, 32·8%). Ingold and Jessop (*J.*, 1929, 2360) report m. p. 236° (decomp.).

Spectra.—The ultraviolet absorption spectra of many compounds referred to above have been previously reported (Eaborn and Shaw, *J.*, 1954, 2027; on the log ε axes on p. 2028 of that paper 4·0, 4·4, and 4·8, should be replaced by 3·4, 4·0, and 4·6, respectively). The following additional data were obtained (values of $\lambda_{max.}$ in mμ with log ε in parentheses; * denotes inflexion) : 9-fluorenyl nitrate, 221 (4·40), 227·5 (4·48), 235 (4·46), 273·5 (4·14), 281·5* (4·07); *n*-butyldi-9-fluorenylamine, 230·5 (4·35), 262·5 (4·51), 296 (3·75), 307·5 (3·76); *s*-di-9-fluorenyltetramethyldisiloxane, 259·5 (4·50), 264·5 (4·49), 278* (4·06), 290 (4·23), 299·5 (4·37); 9-iodo-9-nitrofluorene, 244 (4·43); 9-iminofluorene, 217·5* (4·22), 245·5 (4·72), 254 (4·86), 290·5 (3·72), 297 (3·58), 309* (3·03), 354 (2·45), 373* (2·33); potassium 9-*aci*-nitrofluorene, 246 (4·70), 311 (3·72), 372 (4·20); 9-nitromethylenefluorene, 267·5 (4·53), 288 (3·91), 345 (4·03). The last two compounds were examined in 95% aqueous ethanol and the others in *n*-hexane.

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