460. *Aromatic Reactivity. Part XXII.*[1] *The 2-Position of Fluorene and of its 9-Methyl and 9,9-Dimethyl Derivative.*

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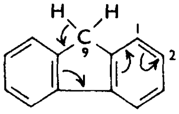
We have measured the rates of cleavage of 2-trimethylsilylfluorene and its 9-methyl and 9,9-dimethyl derivative by aqueous-methanolic perchloric acid, and the rates of detritiation of [2-^{3}H]fluorene and its 9-methyl and 9,9-dimethyl derivative by anhydrous trifluoroacetic acid, trifluoroacetic acid containing a little aqueous perchloric acid, and acetic acid containing aqueous sulphuric acid.

An analogy exists between the relative reactivities of the *para*-positions in toluene and t-butylbenzene and of the 2-positions in fluorene and 9,9-dimethylfluorene.

DE LA MARE, HALL, HARRIS, and HASSAN[2] have shown that fluorene undergoes molecular chlorination faster than 9,9-dimethylfluorene, and have tentatively suggested the existence in fluorene of hyperconjugation involving the methylene group. Such hyperconjugation would increase the electron supply to the 2-position (at which chlorination presumably mainly occurs) by process (I), so that the methylene group, which is most simply regarded as *meta* to the 2-position, would influence this position in the same way as the methyl group of toluene influences the *para*-position, and an analogy could be drawn between relative activation of the 2-position of fluorene or 9,9-dimethylfluorene on the one hand and of the *para*-position of toluene or t-butylbenzene on the other (the *para*-position of toluene being more reactive in molecular chlorination than that of t-butylbenzene).



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[1] Part XXI, Eaborn and Pande, *J.*, 1961, 5082.

[2] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.

We have measured the rates of cleavage (protodetrimethylsilylation) of 2-trimethylsilylfluorene and its 9-methyl and 9,9-dimethyl derivative by a mixture of methanol (5 vol.) and 9·45M-aqueous perchloric acid (2 vol.) at 50·0° (cf. refs. 3 and 4), and the rates of detritiation of 2-tritiofluorene and its 9-methyl and 9,9-dimethyl derivative in (*a*) acetic acid containing aqueous sulphuric acid at 25·0° (molar composition: $CH_3{\cdot}CO_2H$, 20·83; H_2O, 34·43; H_2SO_4, 44·74%), (*b*) trifluoroacetic acid containing aqueous perchloric acid at 25·0° (molar composition: $CF_3{\cdot}CO_2H$, 99·962; H_2O, 0·0278; $HClO_4$, 0·0102%), and (*c*) anhydrous trifluoroacetic acid at 70·1°; the results appear in the Table as observed first-order rate constants, *k*, and as rates, k_{rel}, relative to those for phenyltrimethylsilane or tritiobenzene.

Rates of reaction of 2-trimethylsilyl- and 2-tritio-fluorenes in acids.

	Desilylation				Detritiation			
	$MeOH-H_2O-HClO_4$ (50·0°)		$CH_3{\cdot}CO_2H-H_2O-H_2SO_4$ (25·0°)		$CF_3{\cdot}CO_2H-H_2O-HClO_4$ (25·0°)		$CF_3{\cdot}CO_2H$ (70·1°)	
Compound	10^7k (sec.$^{-1}$)	k_{rel}	10^7k (sec.$^{-1}$)	k_{rel}	10^7k (sec.$^{-1}$)	k_{rel}	10^7k (sec.$^{-1}$)	k_{rel}
2-X-Fluorene	14,600	45·6	3900	2100	2950	3610	1600	16,800
2-X-9-Methylfluorene	13,500	42·2	3790	2040	3110	3800	1660	17,500
2-X-9,9-Dimethylfluorene	11,400	35·6	3580	1930	3980	4870	1900	20,000
p-X-Toluene	6400	20·0	581	313 *	256	313 †	42·7	450
X-Benzene	320	1	—	1	—	1	0·095	1

* Value previously obtained [5] in slightly different medium. † Value obtained in slightly different medium, *viz.*, $CF_3{\cdot}CO_2H$ (99·79)–H_2O (0·065)–$HClO_4$ (0·145).

It will be seen that in desilylation and in detritiation in $CH_3{\cdot}CO_2H-H_2O-H_2SO_4$, in both of which the *para*-position of toluene is more reactive than that of t-butylbenzene,[3,5] the 2-position of fluorene is more reactive than that of 9,9-dimethylfluorene (with that of 9-methylfluorene intermediate in reactivity). But in detritiation by $CF_3{\cdot}CO_2H-H_2O-HClO_4$ or anhydrous trifluoroacetic acid, in which the relative reactivities of the *para*-positions of toluene and t-butylbenzene are reversed,[1,5] so also those of the 2-position of fluorene and 9,9-dimethylfluorene are reversed (with the 9-methyl derivative again intermediate in reactivity). Since in detritiation in all the media the *meta*-position of toluene is markedly less reactive than that of t-butylbenzene (the difference is in the same direction but smaller for the desilylation), the results confirm the analogy between the effect on the 2-position of the methylene group of fluorene and the effect on the *para*-position of the methyl group of toluene.

Explaining the results for the fluorene compounds in terms of hyperconjugation is as difficult as explaining the relative reactivities of the *para*-position of toluene and t-butylbenzene; [5] in particular, it is difficult to understand the change from the hyperconjugative order of activation to the inductive order when the medium is changed (*viz.*, from $CH_3{\cdot}CO_2H-H_2O-H_2SO_4$ to trifluoroacetic acid) in such a way that the overall electron demand, as measured by the rate factor for the *para*-position of toluene (*viz.*, 313 and 450 respectively), is increased. A special difficulty with fluorene compounds is that process (I) seems unlikely to be of major importance in view of the recent observation [6] that there is insignificant conjugation between a 2-methoxy-group and a carbonium ion forming at the 9-position in the S_N1 hydrolysis of 9-chloro-2-methoxy-9-phenylfluorene. However, there may be a greater general hyperconjugative release from the methylene group into the 5-membered ring of fluorene than from the methyl group into the ring of toluene (the shorter length of the bond between the 9-carbon atom and the aromatic rings in fluorene,

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[3] Eaborn, *J.*, 1956, 4858.
[4] Eaborn and Sperry, *J.*, 1961, 4921.
[5] Eaborn and Taylor, *J.*, 1961, 247.
[6] Eaborn, Golesworthy, and Lilly, *J.*, 1961, 3052.

viz., 1·47 Å,[7] compared with that of the bond between the methyl group and the ring in toluene, *viz.*, 1·52 Å,[8] is consistent with this), and this would result in increased availability of electrons at all the aromatic positions of fluorene.

Interpretation of the results for fluorene compounds in terms of steric hindrance to solvation of the transition state, which is an explanation often offered for the smaller activation of a *para*-position by a t-butyl than by a methyl group (for leading references see ref. 5) is even more difficult. With toluene or t-butylbenzene a large proportion of the excess of positive charge in the transition state of an electrophilic substitution at the *para*-position resides on the ring carbon atom bearing the alkyl group, but with fluorene this charge will be more dispersed, the parts residing on the 1-, 3-, 5-, and 7-carbon atoms being at least as great as that on one of the two ring carbon atoms joined to the methylene group (the other such carbon atom will carry a smaller amount of charge, similar to that at the 4-position), and steric hindrance to solvation of charge by methyl groups in the 9-position must be fairly unimportant. Indeed, the similarity between the detritiation results for the fluorenes and those for the alkylbenzenes is a strong argument against attributing the hyperconjugative order in alkylbenzenes to steric hindrance to solvation by the t-butyl group.

The reactivity of the 2-position of fluorene relative to that of the *para*-position of biphenyl, as measured by the ratio $(\log f^{2-\mathrm{Fl}})/(\log f_{\mathrm{p}}^{\mathrm{Ph}})$, falls with increasing electron demand, as indicated by the partial rate factor, $f_{\mathrm{p}}^{\mathrm{Me}}$, for the *para*-position of toluene, the values of the ratio being 3·02 in protodetrimethylsilylation ($f_{\mathrm{p}}^{\mathrm{Me}} = 20$), 1·91 in detritiation in trifluoroacetic acid ($f_{\mathrm{p}}^{\mathrm{Me}} = 450$), and 1·82 in molecular chlorination in acetic acid ($f_{\mathrm{p}}^{\mathrm{Me}} = 820$). (In deriving the last ratio we used the approximate value of 600 for $f_{\mathrm{p}}^{\mathrm{Ph}}$,[9] and assumed that chlorination of fluorene occurs exclusively in the 2-position.) It seems that, as might have been expected in view of the contribution of the methylene group in fluorene, polarizability effects are less important relative to polarization effects in fluorene than in biphenyl.

An interesting incidental observation was that when [2-^{3}H]fluorene was made by hydrolyzing with tritiated water the Grignard reagent prepared from 2-bromofluorene by the entrainment method, about 8% of the activity introduced was in the 9-position, indicating that metallation had taken place there.

EXPERIMENTAL

2-Trimethylsilylfluorene.—Benzene (200 ml.) and chlorotrimethylsilane (38 g., 0·35 mole) were added to the Grignard reagent made from 2-bromofluorene (80 g., 0·33 mole) in ether (200 ml.) by the entrainment method utilizing ethylene dibromide.[10] The mixture was refluxed for 20 hr., and the usual working-up followed by fractional distillation gave *2-trimethylsilylfluorene* (20 g., 25%), b. p. 160—170°/2—3 mm., m. p. 127° (from MeOH) (Found: C, 80·7; H, 7·7. $C_{16}H_{18}Si$ requires C, 80·6; H, 7·6%).

9-Methyl-2-trimethylsilylfluorene.—From 2-bromo-9-methylfluorene, by the method described in the previous paragraph, was prepared *9-methyl-2-trimethylsilylfluorene* (31%), b. p. 151—153°/1—2 mm., m. p. 59° (from MeOH) (Found: C, 81·1; H, 7·8. $C_{17}H_{20}Si$ requires C, 80·9; H, 8·0%).

9,9-Dimethyl-2-trimethylsilylfluorene.—A mixture of n-butyl-lithium (0·24 mole) and 2-bromo-9,9-dimethylfluorene (62 g., 0·23 mole) in ether was stirred for 5 hr. at room temperature. Chlorotrimethylsilane (26 g., 0·24 mole) was added, and the mixture was refluxed for 2 hr. and set aside for 18 hr. The usual working-up, followed by distillation and recrystallization from

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[7] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, London, 1958, p. M214.

[8] Ref. 7, p. M237.

[9] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, p. 157.

[10] Pearson, Cowan and Beckler, *J. Org. Chem.*, 1959, **24**, 504.

methanol, gave 9,9-*dimethyl-2-trimethylsilylfluorene* (41 g., 68%), m. p. 49° (Found: C, 81·3; H, 8·6. $C_{18}H_{22}Si$ requires C, 81·1; H, 8·3%).

[2-^{3}H]*Fluorene*.—To the Grignard reagent made from 2-bromofluorene (80 g., 0·30 mole) in ether (300 ml.) by the entrainment method[10] was added tritiated water (7 ml.; activity 100 mc/ml.) and then an excess of ordinary water. Treatment with aqueous ammonium chloride, followed by the usual working-up, fractionation, crystallization, and sublimation, gave tritiated fluorene, m. p. 116°.

When this material was used in the exchange in $CH_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$, it was found that about 8% of the tritium remained in the molecule after 10 and 15 times the approximate half-life of the exchange in the 2-position. With the 9-methyl derivative made from this material by the method described below, about 5% of the tritium similarly remained unexchanged, but none with the 9,9-dimethyl derivative. It was concluded that some tritium had entered the 9-position when the Grignard reagent from the 2-bromofluorene was hydrolyzed, and, in agreement, it was found that after the tritio-fluorene and -9-methylfluorene had been boiled with 10% aqueous-ethanolic alkali for 2 hr., the recovered samples retained no activity in acid exchange. These samples were used in measurement of the reported rate constants.

Methyl- and 9,9-*Dimethyl*-[2-^{3}H]*fluorene*.—Metallation of [2-^{3}H]fluorene with n-butyllithium in ether, followed by treatment with methyl iodide gave, after the usual working-up, 9-methyl[2-^{3}H]fluorene, b. p. 159—162°/17 mm., m. p. 48° (from MeOH).

Similarly from 9-methyl[2-^{3}H]fluorene was prepared 9,9-dimethyl[2-^{3}H]fluorene, b. p. 147°/10 mm., m. p. 96°.

Reaction Media.—The $CH_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$ medium was a mixture of 4713 g. of 97·60% sulphuric acid, 526 g. of water, and 1320 g. of 99·2% acetic acid.

The $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$ medium was a mixture of 0·0180 g. of 72·02% perchloric acid and 159·05 g. of anhydrous trifluoroacetic acid.

Anhydrous trifluoroacetic acid was purified as previously described.[11]

Rate Measurements.—The desilylations were studied spectrophotometrically,[3] at a wavelength of 306 mμ in the case of 2-trimethylsilylfluorene and its 9-methyl derivative and of 307 mμ in the case of the 9,9-dimethyl derivative.

The detritiations were studied by the techniques previously described.[5,12] The 1 ml. samples, containing *ca.* 0·003 g. of the tritiated compound, used with $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$ and $CF_3{\cdot}CO_2H$ media were contained in sealed tubes, and it was assumed that 3 positions of each fluorene compound were available for tritium at 10 times the half-life of the exchange (cf. ref. 5). Larger samples (50 ml., containing *ca.* 0·01 g. of tritiated compound) were used with $CH_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$, and negligible activity would be present in the fluorene compound at equilibrium.

In desilylations, individual rate constants during a run varied from the mean by less than ±1%, and the mean rate constants (determined graphically) were reproducible to within ±1%. In detritiations, the corresponding limits were ±1·5% and ±1·5%, respectively. These deviations were of the same magnitude as in previous parts of the series.

Side Reactions.—There was no decrease in activity when [9-^{3}H]fluorene was kept in the $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$ medium for a time comparable with that used for the 2-tritio-compounds, indicating that no exchange or oxidation took place at the 9-position.

In the $CH_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$ medium, tritium-loss did occur with [9-^{3}H]fluorene ($k = 100 \times 10^{-7}$ sec.$^{-1}$), probably because of sulphonation (cf. refs. 5, 12, 13). This is unimportant compared with exchange at the 2-position, and no correction was applied to the rates of tritium-loss observed for the 2-tritio-compounds.

Part of this research was supported by the U.S. Army through its European Research Office. We thank the Department of Scientific and Industrial Research for a maintenance grant (to R. B.), and the Royal Society for the loan of apparatus.

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[*Received, October* 12*th*, 1961.]

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[11] Baker, Eaborn, and Taylor, *J.*, 1961, 4927.
[12] Eaborn and Taylor, *J.*, 1960, 3301.
[13] Eaborn and Taylor, *J.*, 1960, 1480.