125. *Aromatic Reactivity. Part XXVII.*[1] *Substituent Effects in Biphenyl and Fluorene.*

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We have measured the rates of cleavage (protodesilylation) of some 4′-substituted 4-trimethylsilylbiphenyls by sulphuric acid–acetic acid, and rates of detritiation of 3′- and 4′-substituted 4-tritiobiphenyls and 7-substituted 2-tritiofluorenes by trifluoroacetic acid. The effects of substituents in the 4′-position of biphenyl derivatives appear to be related in a fairly simple way to the effects of the same substituents in the *p*-position of benzene derivatives. The effects of 4′-substituents in detritiation of 4-tritiobiphenyl are similar to those of 7-substituents in detritiation of 2-tritiofluorene, and thus the non-coplanarity of the rings in biphenyl does not much affect the transmission of substituent effects.

In trifluoroacetic acid, for both 4′-X-4-tritiobiphenyls and 7-X-2-tritiofluorenes, the compounds with X = OMe are less reactive than those with X = Me, possibly because of interaction between the methoxyl group and the acid.

MOST papers in this series have been concerned with effects of substituents in a benzene ring on the ease of electrophilic substitution in the ring. Before much further progress can be made in the detailed analysis of effects of substituents, data must be obtained on the influence of substituents in other systems, as pointed out recently by Dewar and Grisdale.[2]

In order to obtain information about the transmission of substituent effects in biphenyl we have measured rates of cleavage (protodesilylation) of some 4′-X·C_6H_4·C_6H_4·$SiMe_3$-4 compounds by aqueous sulphuric acid in acetic acid (cf. ref. 3), and rates of detritiation of some 3′- and 4′-X·C_6H_4·C_6H_4·^3H-4 compounds by anhydrous trifluoroacetic acid (cf. refs. 4—8). To throw light on the importance of non-coplanarity of the benzene rings in biphenyl we have, for comparison, also measured the rates of detritiation of some 7-substituted 2-tritiofluorenes. The results are shown in Tables 1 and 2, as observed first-order rate constants k, and as values of k'_{rel}, the rates for the substituted compound relative to that of the parent compound in which X = H. Some comments are as follows.

TABLE 1.

Rates of cleavage of 4′-X·C_6H_4·C_6H_4·$SiMe_3$-4 compounds by acetic acid–sulphuric acid at 50·0°.

X	OMe	Me	$SiMe_3$	H	Cl	Cl	Br	CO_2Me	CO_2H	NO_2
[H_2SO_4] (M) *	7·6	7·6	7·6	7·6	7·6	9·6	9·6	9·6	9·6	9·6
10^3k (min.$^{-1}$)	167	95	70	53 †	29	183	163	73	64	31
k'^{Si}_{rel}	3·15	1·80	1·32	1·00	0·55	—	0·49	0·22	0·19	0·093

* Concn. of acid, 7·5 ml. of which was mixed with 10 ml. of a solution of the organosilane in acetic acid. † Under the same conditions, k for phenyltrimethylsilane = 18·5 × 10^{-3} min.$^{-1}$.

(*a*) We can consider from two different viewpoints effects of substituents in one ring of biphenyl on reactions at the other ring or in a side-chain attached to it. First, since the effect of a substituent is composed of a combination of inductive and tautomeric effects, the influences of which are likely to depend differently on the distance and number

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[1] Part XXVI, Eaborn and Walton, *J.*, 1963, 5626.
[2] Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539, 3548.
[3] Deans and Eaborn, *J.*, 1959, 2299.
[4] Eaborn and Taylor, *J.*, 1961, 247.
[5] Baker, Eaborn, and Taylor, *J.*, 1961, 4927.
[6] Baker and Eaborn, *J.*, 1961, 5077.
[7] Eaborn and Taylor, *J.*, 1961, 1012.
[8] Baker, Bott, and Eaborn, *J.*, 1963, 2136.

TABLE 2.

Rates of detritiation of substituted [4-^{3}H]biphenyls and [2-^{3}H]fluorenes in trifluoroacetic acid at 70·1°.

(*i*) $X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}{}^3H$-4 *Compounds*

X	4′-Me	4′-OMe	H	4′-Cl	4′-Br	3′-Cl	4′-NO$_2$
10^7k (sec.$^{-1}$)	62	51	15·5 *	4·57	3·90	1·91	(0·57) †
$k'^{\mathrm{T}}_{\mathrm{rel}}$	4·0	3·3	1·00	0·29	0·25	0·12	(0·00097) ‡

(*ii*) 7-X-[2-^{3}H]*fluorenes*

X	Me	OMe	H	Cl	Br	CO$_2$H	NO$_2$
10^7k (sec.$^{-1}$)	6120	4820	1600 *	425	340	3·28	(23) †
$k'^{\mathrm{T}}_{\mathrm{rel}}$	3·8	3·0	1·00	0·27	0·21	0·002	(0·00038) ‡

* For [^{3}H]benzene at 70·1°, 10^7k = 0·095 sec.$^{-1}$. † At 110·15°, at which 10^7k for [^{3}H]benzene is 3·64 sec.$^{-1}$. ‡ Calculated by assuming that the ratio of rate for [^{3}H]benzene to that for [4-^{3}H]biphenyl or [2-^{3}H]fluorene is the same at 110° as at 70°.

of bonds between the substituent and the reaction centre (see, for example, ref. 2), no simple relation would be expected between the effects of substituents in the biphenyl system and those in the benzene system. On the other hand, if we regard the substituent X as influencing in the usual way the charge density at the 1′-position in the transition state, the effect then being relayed to the 1- and thus, say, to the 4-position in the other ring, we can see that the effects of a range of substituents, while weaker, might be quite simply related to those in the benzene system. Deviations from such a relationship could be expected, however, for substituents which have large polarizability relative to polarization effects in reactions which, in the benzene system, involve important conjugation between the substituents and the reaction centre (for example, for the methoxyl group in electrophilic aromatic substitutions of high electron demand).

(*b*) The effect of a group, X, in the 4′-position of biphenyl on the rate of substitution at the 4-position is much smaller than its effect, when in the 1-position of benzene, on the rate of substitution at the 4-position. (A similar conclusion was reached by Mizuno and Simamura in respect of the effect of the nitro-group in nitration,[9] and by de la Mare *et al.* concerning the effect of the methyl group in chlorination.[10,11]) For example, the 4′-methyl substituent activates the 4-position in biphenyl only 4·0 times in detritiation and 1·8 times in desilylation, whereas the 1-methyl substituent in benzene activates the 4-position 450 and 18 times in these respective reactions.[3,5] The effect of a 2-methyl substituent in fluorene on the rate of detritiation at the 7-position (namely a four-fold acceleration) is similarly small.

(*c*) The values of $k'^{\mathrm{Si}}_{\mathrm{rel}}$ for 4′-methyl- and 4′-chloro-4-trimethylsilylbiphenyl, namely 1·80 and 0·55, respectively, agree well with those (1·72 and 0·50) for cleavage by hydrochloric acid in acetic acid.[12]

(*d*) A plot of log $k'^{\mathrm{Si}}_{\mathrm{rel}}$ against the Hammett σ- constants [13] for *p*-X groups is a reasonably good straight line (not shown) except for the points for the carboxyl group (the σ-constant of which may not be appropriate for the cleavage medium), and the methoxyl group, which activates more than expected from its σ-constant. For groups for which substituent constants (for *p*-X) are accurately known,[13] a plot of log $k'^{\mathrm{Si}}_{\mathrm{rel}}$ against $[\sigma + r(\sigma^+ - \sigma)]$ (cf. refs. 14 and 15) is an excellent straight line when $r = 0{\cdot}2$ (Fig. 1). Thus,

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[9] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196; Mizuno and Simamura, *J.*, 1958, 3875.

[10] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths, London, 1959, p. 160.

[11] de la Mare, Hall, Harris, Hassan, Johnson, and Klassen, *J.*, 1962, 3784.

[12] Benkeser, Schroeder, and Thomas, *J. Amer. Chem. Soc.*, 1958, **80**, 2283.

[13] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420; Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[14] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[15] Eaborn and Pande, *J.*, 1961, 5082; Eaborn and Waters, *J.*, 1961, 542; Bott and Eaborn, *J.*, 1963, 2139.

while polarizability effects play only a small part, the mode of combination of polarization and polarizability effects is of the type common in electrophilic reactions in the benzene system (for example, $r = 0{\cdot}67$ in cleavage of $X{\cdot}C_6H_4{\cdot}SiMe_3$ compounds[15]).

(*e*) Since two Me_3Si–Ar bonds are equally available for cleavage in 4,4′-bistrimethylsilylbiphenyl, the observed k'^{Si}_{rel} value of 1·32 must be halved if the effect of the 4′-Me_3Si group is to be compared with that of other 4′-X groups. Thus the 4′-Me_3Si group behaves as a slightly deactivating, electron-withdrawing substituent, whereas the *p*-Me_3Si group activates slightly in electrophilic substitutions in the benzene ring.[16]

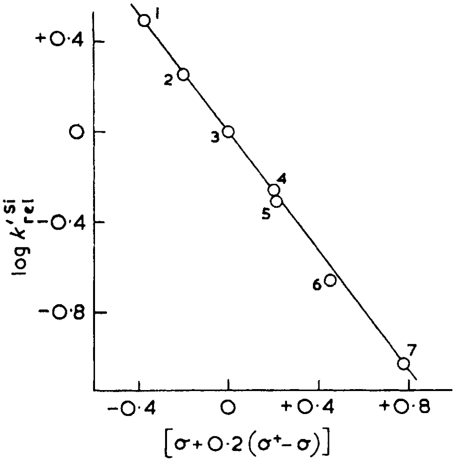

FIG. 1. Plot of log k'^{Si}_{rel} for the cleavage of 4′-X-4-trimethylsilylbiphenyls against $[\sigma + 0{\cdot}2(\sigma^+ - \sigma)]$.
1, OMe. 2, Me. 3, H. 4, Cl. 5, Br. 6, CO_2Me. 7, NO_2.

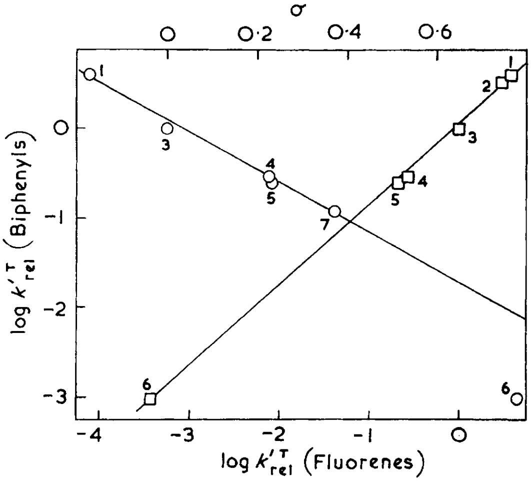

FIG. 2. Plot of log k'^{T}_{rel} for the detritiation of X-[4-^{3}H]biphenyls against log k'^{T}_{rel} for detritiation of 7-X-[2-^{3}H]fluorenes (□) or σ-constants (○).
1; 4′- or 2-Me. 2; 4′- or 2-OMe. 3; H. 4; 4′- or 2-Cl. 5; 4′- or 2-Br. 6; 4′- or 2-NO. 7; 3′-Cl.

(*f*) The result for the 4′-methoxyl compound in detritiation must be neglected in comparisons with reactions of biphenyl compounds in other media, because there seems to be serious interaction between the substituent and the trifluoroacetic acid (see below). When this compound is omitted, good straight lines result from plots of log k'^{T}_{rel} for the detritiation against log k'^{Si}_{rel} (not illustrated) or against σ-constants[13] (Fig. 2) (4′- and 3′-substituents being regarded as *p*- and *m*-, respectively),* except that the points for

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* For the substituents involved, values of σ are not significantly different from values of $[\sigma + r(\sigma^+ - \sigma)]$ when r is small.

[16] Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, p. 102.

the 4′-nitro-compound deviate seriously from the lines, by amounts corresponding to this compound's being some 7 times less reactive than expected. These points would not be expected to fall exactly on the lines, since the value of $k'^{\mathrm{T}}_{\mathrm{rel}}$ for the 4′-nitro-compound was deduced from its rate relative to that for [^{3}H]benzene at 110° instead of being measured at 70° at which the other compounds were studied, but this is unlikely to have led to an error as great as the observed deviations from the lines, and in any case would probably lead to deviations in the direction opposite to those observed (since the rate differences between two compounds normally decrease with increasing temperature). As discussed below, interaction between the nitro-group and the acid medium may be responsible for the abnormally low reactivity of the 4′-nitro-compound.

(*g*) Although the reactivity of the 2-position of fluorene in detritiation is much greater than that of the 4-position of biphenyl, the effects of analogously placed substituents are remarkably similar in the two cases; thus, the 4′-methyl group in biphenyl activates 4·0 times and the 7-methyl group in fluorene 3·8 times, while the 4′-chloro-substituent deactivates 3·4 times and the 7-chloro-substituent 3·7 times. Furthermore, a plot of log $k'^{\mathrm{T}}_{\mathrm{rel}}$ for the biphenyl compounds against that for the corresponding fluorene compounds is an excellent straight line (Fig. 2). (This line can be drawn with unit slope if not required to pass through the point for the nitro-group, which may be affected by interaction with the medium. That the point for the methoxyl group lies on the line means that any interaction between this group and the medium is similar in both the biphenyl and fluorene compounds; 2-hydroxyfluorene and 4-hydroxybiphenyl have very similar acid strengths,[17] and thus 2-methoxyfluorene and 4-methoxybiphenyl could reasonably be expected to have similar base strengths.) Since the substituent effects are so similar in the two sets of compounds, we conclude that the non-coplanarity of the rings in biphenyl does not have an important influence on the effect of 4′-substituents. This is not surprising, since even if non-coplanarity causes biphenyl to be less reactive than fluorene in electrophilic substitution, as has been suggested [18] (cf. ref. 8), the effects of substituents on the transition state are likely to be much more important than those on the initial state, and the two rings are probably near coplanarity in the transition state. It is noteworthy that Kreiter, Bonner, and Eastman [17] concluded, from measurements of strengths of analogously substituted hydroxy-biphenyls and -fluorenes, that lack of planarity in biphenyl did not influence transmission of substituent effects in unexcited states (although Grantham, Weisburger, and Weisburger [19] assert the contrary, but without, we believe, any direct evidence).

(*h*) Dewar and Grisdale have recently calculated, from the Hammett σ-constants applicable to the benzene derivatives, constants $\sigma_{4'4}$ and $\sigma_{3'4}$ which should indicate the effects of substituents in the 4′- and 3′-position, respectively, of biphenyl on appropriate reactions at the 4-position or in a side-chain attached to that position.[2] Our results are not sufficiently extensive, particularly in view of the complications with the methoxy- and nitro-substituents, to provide tests of these constants, but we note that plots of the logarithms of the appropriate rate or dissociation constants for dissociation of $\mathrm{X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO_2H\text{-}4}$ compounds,[20] hydrolysis of $\mathrm{X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO_2Et\text{-}4}$ compounds,[21] cleavage of $\mathrm{X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SiMe_3\text{-}4}$ compounds, and detritiation of $\mathrm{X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}{}^3H\text{-}4}$ compounds (the methoxyl substituent being omitted in this case) against Hammett σ-constants (4′- and 3′-substituents being treated as *p*- and *m*-substituents, respectively) are very much better straight lines than corresponding plots against the Dewar–Grisdale constants. The existence of even rough linear free-energy correlations between substituent effects in the biphenyl and benzene system would not be expected on the basis of the Dewar–Grisdale proposals, and the excellent correlation, in terms of the Yukawa–Tsuno equation,[14]

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[17] Kreiter, Bonner, and Eastman, *J. Amer. Chem. Soc.*, 1954, **76**, 5770.
[18] Ref. 10, pp. 158—160; Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 1238, 1242.
[19] Grantham, Weisburger, and Weisburger, *J. Org. Chem.*, 1961, **26**, 1008.
[20] Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479.
[21] Berliner and Liu, *J. Amer. Chem. Soc.*, 1953, **75**, 2417.

of substituent effects in the biphenyl system with substituent constants applicable to the benzene system (see above and ref. 22) indicates that the balance of polarization and polarizability effects of groups differs less in the two systems than the Dewar–Grisdale picture would imply.

Interaction between Solvent and Substituents.—As noted above, in relation to its effects in other reactions, the 4-methoxyl group appears to have a normal influence on the 4′-position in protodesilylation; certainly it has an activating effect markedly greater than that of the 4-methyl group. In detritiation, however, its activating effect is less than that of the 4-methyl group, and viewed in isolation this could be taken to indicate that in a reaction of high electron-demand, suppression of the influence of the $+E$ effect of the 4-methoxyl group by the non-coplanarity of the rings in biphenyl renders the group less electron-supplying than the 4-methyl group. An explanation in terms of non-coplanarity of the rings of biphenyl was discounted, however, when 7-methoxy- was found to be less reactive than 7-methyl-2-tritiofluorene in detritiation. It seemed that the activation order 4-Me $>$ 4-OMe in detritiation might arise from interaction between the trifluoroacetic acid (which is a markedly more strongly acidic medium than that used in desilylation) and the weakly basic oxygen atom of the ether, and that this is indeed the case is shown by the change to the normal activation order, 4-Me $<$ 4-OMe, when the acidity of the detritiation medium is lowered by addition of acetic acid (Table 3).

The interaction between the trifluoroacetic acid and the methoxyl group is not a simple protonation of the group, to give the conjugate acid, since a considerable proportion of the ether would have to be so protonated to give rise to the observed results, and this needs much higher acidities (cf. ref. 23). Furthermore, such protonation shows up in a complete change in the ultraviolet absorption spectrum of the ether,[23] whereas the spectrum of 4-methoxybiphenyl in trifluoroacetic acid is very similar to that in methanol. The interaction, which we refer to, for convenience, as " incipient protonation," may be hydrogen-bonding. It is clearly sensitive to change in the acidity of the medium, and is apparently unimportant in the acetic acid–sulphuric acid media used for desilylation. The possibility of this incipient protonation must be taken into account when results for other electrophilic substitutions involving anisole or other ethers in strongly acidic media are being analysed, and results for detritiation of diphenyl ether and dibenzofuran [6] may have to be reconsidered.

TABLE 3.

Rates of detritiation of 4′-X-4-tritiobiphenyl and 7-X-2-tritiofluorene in mixtures of trifluoroacetic acid and acetic acid at 70·1°.

Wt.-% of acetic acid		10^7k (sec.$^{-1}$)			
	(X =)	4′-OMe	4′-Me	7-OMe	7-Me
0		51	62	4820	6120
1·68		43	50	—	—
13·2		30	23	2370	1800
22·8		8·15	4·9	780	490

If, as we suggest, there is incipient protonation of a methoxyl group in trifluoroacetic acid, a similar effect would be expected with the nitro-group, and the considerable deviation of the point for 4′-nitro-4-tritiobiphenyl from the linear free-energy plots, as noted above, could be the result of such interaction. If this is so, then such incipient protonation would be much greater in nitration of nitro-aromatic compounds in concentrated sulphuric acid, even at concentrations well below those at which the conjugate

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[22] Inukai, *Bull. Chem. Soc. Japan*, 1962, **35**, 400.

[23] Arnett and Wu, *J. Amer. Chem. Soc.*, 1960, **82**, 5660.

acid of the nitro-compound is detectable; the probability that hydrogen-bonded complexes between nitro-compounds and sulphuric acid do participate in nitration in aqueous sulphuric acid has been discussed by Gillespie and Millen.[24]

EXPERIMENTAL

Preparation of Materials.—(*a*) *Substituted bromobiphenyls.* The following 4-Br•C_6H_4•C_6H_4•X-4′ compounds were made by bromination of 4-X-biphenyls: (X =) Br, m. p. 166°; [25] Cl, m. p. 157°; [26] Me, m. p. 133°; OMe, m. p. 144°.[27]

(*b*) *Substituted trimethylsilylbiphenyls.* A solution of n-butyl-lithium (1 mol.) in ether was added with stirring to a solution of the 4-Br•C_6H_4•C_6H_4•X-4′ compound (1 mol.) in benzene. The mixture was stirred for 1 hr. at room temperature, chlorotrimethylsilane (1 mol.) in ether was added, and the mixture was set aside for 18 hr. The solution was filtered and the filtrate was shaken with dilute acid, washed, and dried (Na_2SO_4). The solvent was removed, and the residue was recrystallized from methanol to give 4′-X-4-trimethylsilylbiphenyls as follows: (X =) H, m. p. 55°; Br, m. p. 103° (43%) (Found: C, 58·7; H, 5·6. $C_{15}H_{17}BrSi$ requires C, 59·0; H, 5·6%); Cl, m. p. 117·5° (80%); [12] Me, m. p. 67° (78%); [12] OMe, m. p. 125·5° (43%) (Found: C, 75·1; H, 7·85. $C_{16}H_{20}OSi$ requires C, 74·95; H, 7·9%).

Carbonation of the aryl-lithium, made from 4′-bromo-4-trimethylsilylbiphenyl by the method described above, gave *4′-carboxy-4-trimethylsilylbiphenyl*, m. p. 258° (40%) (Found: C, 71·4; H, 6·5. $C_{16}H_{18}O_2Si$ requires C, 71·1; H, 6·7%). Treatment of this acid with an excess of diazomethane in ether gave *4′-methoxycarbonyl-4-trimethylsilylbiphenyl* (95%), m. p. 106·5° (from methanol) (Found: C, 71·8; H, 7·0. $C_{17}H_{20}O_2Si$ requires C, 71·8; H, 7·1%).

Treatment of 4-bromo-4′-trimethylsilylbiphenyl with chlorotrimethylsilane and sodium in boiling toluene gave *4,4′-bis(trimethylsilyl)biphenyl* (80%), m. p. 88° (Found: C, 72·4; H, 8·9. $C_{18}H_{26}Si_2$ requires C, 72·6; H, 9·0%).

(*c*) *Tritiated biphenyls.* (i) *Some 4′-substituted-4-tritiobiphenyls.* A solution of n-butyl-lithium (0·065 mole) in ether was added to a solution of 4-bromo-4′-methylbiphenyl in benzene. The mixture was stirred for 1 hr. at room temperature, then treated with tritiated water (1·5 ml.; 100 mc/ml.), followed by an excess of aqueous ammonium chloride. The usual working-up gave 4′-methyl-4-tritiobiphenyl (8 g., 70%), b. p. 124°/2 mm., m. p. 46° (from ethanol), having an estimated activity (cf. ref. 28) of *ca.* 6 mc/g.

The following 4′-X-4-tritiobiphenyls (*ca.* 4—8 mc/g.) were made analogously: (X =) OMe, m. p. 89°; Br, m. p. 90°; Cl, m. p. 77°; $SiMe_3$, m. p. 55°.

(ii) *4-Bromo-3′-chlorobiphenyl and 3′-chloro-4-tritiobiphenyl.* 3′-Amino-4-bromobiphenyl, m. p. 105° (after six recrystallizations from ethanol), was made by reduction of the corresponding nitro-compound. Diazotization, treatment of the diazo-compound with aqueous cuprous chloride, and the usual working-up gave *4-bromo-3′-chlorobiphenyl* (32%), b. p. 140°/1 mm., n_D^{25} 1·6496 (Found: C, 54·4; H, 3·2. $C_{12}H_8BrCl$ requires C, 53·9; H, 3·0%). The product (0·037 mole) was refluxed for 2 hr. with magnesium (0·04 g.-atom) in tetrahydrofuran, and tritiated water (0·8 ml.; 100 mc/ml.) was added. The usual working-up, ending in a fractional distillation, gave 3′-chloro-4-tritiobiphenyl (5 g., 71%), b. p. 155°/6 mm. (activity, *ca.* 6 mc/g.).

(iii) *4′-Carboxy-4-tritiobiphenyl.* This acid, m. p. 228° (*ca.* 4 mc/g.), was made by carbonation of the organo-lithium prepared from the 4′-bromo-compound (8 mc/g.) by the method described above.

(iv) *4′-Nitro-4-tritiobiphenyl* (Prepared by Mr. K. LEYSHON). To acetic anhydride (25 g.) was added dropwise, with stirring, nitric acid (6·75 g., 0·075 mole, 70 wt.-%), the temperature being maintained at 20—25°. The mixture was then added dropwise to a solution of 4′-trimethylsilyl-4-tritiobiphenyl (7·3 g., 0·032 mole) in acetic anhydride (45 g.), the temperature being maintained at 100°. The mixture was subsequently kept at 100° for 2 hr., then cooled and added to ice-cooled aqueous sodium hydroxide (70 g. in 300 ml.). Ether extraction, followed by separation, washing, and drying of the ethereal solution, removal of the solvent,

[24] Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.
[25] Fittig, *Annalen*, 1864, **132**, 204.
[26] Shaw and Turner, *J.*, 1932, 285.
[27] Abernethy and Pollock, *J. Amer. Chem. Soc.*, 1951, **73**, 1351.
[28] Eaborn and Taylor, *J.*, 1960, 3301.

and fractional distillation gave 4′-nitro-4-tritiobiphenyl (5·0 g., 78%), m. p. 114—114·5° (from ethanol), having a specific activity only slightly smaller than that of the starting material.

(*d*) *Tritiated fluorenes.* (i) 2-Tritiofluorene, m. p. 115° (*ca.* 10 mc/g.), was made as previously described.[29] It was brominated to give 7-bromo-2-tritiofluorene, m. p. 112° (which, as expected, had approximately half the specific activity of the starting material), and nitrated [30] to give 7-nitro-2-tritiofluorene, m. p. 156° (which had markedly less than the expected activity, some hydrogen-exchange apparently having occurred).

(ii) The Grignard reagent prepared in ether from 7-bromo-2-tritiofluorene by the ethylene dibromide entrainment method [31] was carbonated to give 7-carboxy-2-tritiofluorene of the expected activity.

(iii) The Grignard reagent prepared in ether from 2-bromo-7-methoxyfluorene (0·009 mole) by the ethylene dibromide entrainment method was treated with tritiated water (0·3 ml.; 100 mc/ml.) and then an excess of aqueous ammonium chloride. The usual working-up gave 7-methoxy-2-tritiofluorene, m. p. 108°.

Analogously, 7-chloro-2-tritiofluorene, m. p. 96°, was prepared from 7-bromo-2-chlorofluorene (which was made by Bachmann and Boatner's method [32]), and 7-methyl-2-tritiofluorene, m. p. 104°, was made from 2-bromo-7-methylfluorene (obtained by the route: 2-acetyl- → 2-methyl- [33] → 2-methyl-7-nitro- [34] → 7-amino-2-methyl- [34] → 7-bromo-2-methylfluorene [32]).

(Originally, 7-methyl-2-tritiofluorene was made by decarboxylation of 7-carboxymethyl-2-tritiofluorene, itself made by the Willgerodt–Kindler conversion from 7-acetyl-2-tritiofluorene,[33,35] which was made by Friedel–Crafts acetylation of 2-tritiofluorene,[36] but the final product contained a fairly large proportion of tritium which did not readily exchange with acid. Separate experiments showed that tritium is incorporated in the acetyl group during the acetylation.)

Rate Measurements.—(*a*) *Protodesilylation.* A solution (10 ml.) of the $4'\text{-X}\cdot C_6H_4\cdot C_6H_4\cdot SiMe_3\text{-}4$ compound in anhydrous acetic acid was added to sulphuric acid (7·5 ml.) of the appropriate strength (as listed in Table 1) contained in a stoppered flask which was cooled in an ethanol–solid carbon dioxide bath. The mixture was allowed to warm and was well shaken, and some was transferred to a 1-cm. stoppered quartz cell, which was then placed in a thermostatted holder kept at 50·00° ± 0·03°, in a Unicam S.P. 500 spectrophotometer. Rate constants were calculated, as previously described,[3,37] from measurements of the optical density relative to water at an appropriate wavelength, which (in mμ) was as follows: (X =) H, 289; Me, $SiMe_3$; 290; Cl, Br, 292; OMe, 301; CO_2H, 317; CO_2Me, 315; NO_2, 355.

(*b*) *Detritiation.* The general methods have been described.[4–8] In calculation of the "equilibrium deflection" (cf. refs. 4, 5, and 28), the following number of aromatic positions were assumed to be available for tritium after 10 half-lives. (i) X-4-Tritiobiphenyl compounds: (X =) H, 6; 4-Me, -Cl, -Br, -OMe, $-NO_2$, 4; 3-Cl, 7. (ii) 7-X-2-Tritiofluorenes: (X =) H, 3; Br, 4; CO_2H, NO_2, 5; for X = Me, OMe, or Cl, the "equilibrium deflection" was determined experimentally after 10 half-lives.

Mixtures of trifluoroacetic acid and acetic acid were made up by weight.

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