205. *Aromatic Reactivity. Part XV.*[1] *Biphenyl and Naphthalene in Detritiation.*

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We have measured the rates of detritiation of [2-, 3-, and 4-$^3H_1$]biphenyl and of [α- and β-$^3H_1$]naphthalene in trifluoroacetic acid containing aqueous sulphuric acid or aqueous perchloric acid. The 2- and the 4-position of biphenyl are about equally reactive in this hydrogen-exchange, and markedly more reactive than a single position in benzene, while the 3-position is somewhat less reactive than a single position in benzene. The α-position of naphthalene is more reactive than the β-position, which is about as reactive as the 4-position of biphenyl. The partial rate factors for the 4-position of biphenyl and the 2-position of naphthalene are compared with those in other electrophilic aromatic substitutions; it is shown that activation of these positions relative to activation of the *para*-position of toluene depends greatly on the electron-demand, but it is argued that there is nothing qualitatively abnormal about activation in biphenyl and naphthalene.

We have measured the rates of detritiation at 25·0° of monotritiated biphenyls and naphthalenes in media of the composition $CF_3\cdot CO_2H$ (95·31)–H_2O (2·21)–H_2SO_4 (2·48) and $CF_3\cdot CO_2H$ (92·04)–H_2O (5·45)–$HClO_4$ (2·51) (the figures denote mole-percentages) in which we previously studied detritiation of alkylbenzenes.[2] The values of the first-order rate constants, $k_{ex.}$, for the detritiation, are given in Table 1, along with the rates, f, relative to that for detritiation of [$^3H_1$]benzene, figures for [p-$^3H_1$]toluene being included for comparison. With the medium containing sulphuric acid, it was necessary to measure the rate of sulphonation, $k_{sulph.}$, of biphenyl and naphthalene, since sulphonation, whether

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[1] Part XIV, Eaborn and Waters, *J.*, 1961, 542.

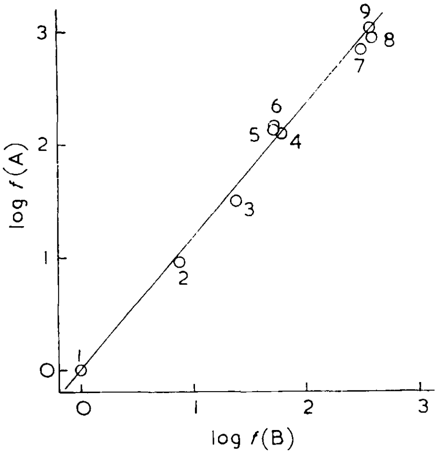
[2] Eaborn and Taylor, *J.*, 1961, 247.

at a tritiated position or not, results in a loss of tritium, and $k_{sulph.}$ must be subtracted from the apparent exchange rate, $k_{obs.}$, to give the value of $k_{ex.}$ (see refs. 2 and 3). Sulphonation accounts for about 9% of the apparent exchange rate with [2- and 4-$^3H_1$]biphenyl, and for about 3% with [α-$^3H_1$]naphthalene, but for about 19% with [β-$^3H_1$]naphthalene. [3-$^3H_1$]Biphenyl was not studied in this medium, but in a medium somewhat stronger in sulphuric acid [$CF_3{\cdot}CO_2H$ (85·08)–H_2O (6·42)–H_2SO_4 (8·50)] the value of $k_{sulph.}$ (341×10^{-7} sec.$^{-1}$) represented 97% of $k_{obs.}$ (353×10^{-7} sec.$^{-1}$), and the resulting figure for $k_{ex.}$ (12×10^{-7} sec.$^{-1}$) may be used only to conclude that exchange is slower than with [$^3H_1$]benzene (for which $k_{ex.} = 30 \times 10^{-7}$ sec.$^{-1}$), the value of f (0·4) possibly being in error by as much as ±100%. (In this medium $f_p^{Me} = ca.$ 540.) The exchanges in $CF_3{\cdot}CO_2H$–H_2O–$HClO_4$ were apparently free from interfering side-reactions.

TABLE 1. *Detritiation at 25·0°.*[a]

	$CF_3{\cdot}CO_2H$–H_2O–H_2SO_4[b] (95·31 : 2·21 : 2·48)				$CF_3{\cdot}CO_2H$–H_2O–$HClO_4$ (92·04 : 5·45 : 2·51)	
	$10^7k_{obs.}$	$10^7k_{sulph.}$	$10^7k_{ex.}$	f	$10^7k_{ex.}$	f
[$^3H_1$]Benzene[b]	3·74	<0·15	3·6	1	14·3	1
[p-$^3H_1$]Toluene[b]	2552	26	2526	702	4480	313
[2-$^3H_1$]Biphenyl	525	48	477	133	748	52
[3-$^3H_1$]Biphenyl	—	—	—	—	9·8	0·68
[4-$^3H_1$]Biphenyl	563	48	515	143	748	52
[α-$^3H_1$]Naphthalene	3990	104	3886	1079	5300	370
[β-$^3H_1$]Naphthalene	560	104	456	127	885	62

[a] Rate constants in sec.$^{-1}$. [b] See ref. 2.



Plot of (A) log f *in* $CF_3{\cdot}CO_2H$–H_2O–H_2SO_4 *against* (B) log f *in* $CF_3{\cdot}CO_2H$–H_2O–$HClO_4$.

Points:

1, [$^3H_1$]C_6H_5.
2, [m-$^3H_1$]C_6H_4Me.
3, [m-$^3H_1$]$C_6H_4Bu^t$.
4, [β-$^3H_1$]$C_{10}H_7$.
5, [2-$^3H_1$]$C_{12}H_9$.
6, [4-$^3H_1$]$C_{12}H_9$.
7, [p-$^3H_1$]C_6H_4Me.
8, [p-$^3H_1$]$C_6H_4Bu^t$.
9, [α-$^3H_1$]$C_{10}H_7$.

The results constitute the first reports of accurate partial rate factors for hydrogen-exchange at the several positions in biphenyl and naphthalene. The reactivities of the positions relative to one another have been measured for deuteration in $CF_3{\cdot}CO_2D$–CCl_4–D_2SO_4,[4] and the results are consistent with ours. (Rates relative to a single position in benzene can only be obtained from the deuteration results[4] by unsatisfactory extrapolations based on assumed dependences of rate on acidity function, and may be considerably in error.) The main features of our results are as follows:

(i) The spread of rates depends markedly on the medium, as with alkylbenzenes.[2,3,5] There is an approximate linear free-energy relation between the results in the two media (see Figure). (The line is drawn to pass between all the points. A good straight line

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[3] Eaborn and Taylor, *J.*, 1960, 3301.

[4] Dallinga, Verrijn Stuart, Smit, and Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.

[5] Eaborn and Taylor, *Chem. and Ind.*, 1959, 949.

may be drawn to pass through the origin and the points for the alkylbenzenes, and the points for the naphthalene and biphenyl systems then fall to the left. This is what would be expected if the naphthalene and biphenyl systems respond more effectively to the increased electron-demand in $CF_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$ which is indicated by the greater spread of rates in the medium. Discussion below is relevant to this point.)

(ii) The 2- and the 4-position of biphenyl are equally reactive. Since primary steric effects are unimportant in detritiation,[6] this result is probably a true reflection of the relative electronic activation at the positions, and is in agreement with Dewar's simple estimates of localization energies,[7,8] but not with more complicated calculations of localization energies,[9–11] with calculations by the self-consistent-field method of the energies required to convert the hydrocarbon ArH into the ion ArH_2^+,[4] or with free-valence numbers,[9] all of which assign a distinctly higher reactivity to the 2-position. The small deactivation of the 3-position disagrees with some calculations,[4,12] but agrees with others,[9] and also with experimental results in protodesilylation,[13] mercuridesilylation,[13] bromodesilylation,[13] and ionic bromination.[14]

(iii) The α-position of naphthalene is considerably more activated than the β-position, in agreement with calculations.[4,7–10] The β-position is roughly as reactive as the 4-position of biphenyl, being slightly more or less reactive depending on the medium. Calculations indicate that the β-position should be less reactive than the 4-position of biphenyl,[4,8–10] and this is the case in protodesilylation,[15] mercuridesilylation,[15] and protodegermylation [16] (all reactions which seem to make relatively small demands on electromeric effects of substituents), but in bromodesilylation the positions are equally reactive; [15] in nitration the β-position of naphthalene may be more reactive than the 4-position of biphenyl,[8] though there is conflicting experimental information on the partial rate factors for biphenyl in this reaction.[17]

(iv) The values of $(\log f_p^{\mathrm{Me}})/(\log f_p^{\mathrm{Ph}})$ are in line with the observation that this ratio shows a general tendency to fall from reaction to reaction as f_p^{Me} rises,[13] probably as the electron-demand rises and calls forth increasingly the $+E$ effect of the *p*-Ph group.[13,14]

TABLE 2.

Reaction	f_p^{Me}	$\log f_p^{\mathrm{Me}}/\log f_p^{\mathrm{Ph}}$	Reaction	f_p^{Me}	$\log f_p^{\mathrm{Me}}/\log f_p^{\mathrm{Ph}}$
Protodestannylation [1] ...	5·6	3·0	Ionic bromination [14]	59	1·48
Protodegermylation [16] ...	14	2·66	Detritiation	313	1·45
Protodesilylation [13]	18	2·82	Detritiation	702	1·32
Mercuridesilylation [15] ...	17·5	2·40	Molec. chlorination [18, 19] ...	820	1·05
Nitration [8, 14]	58	1·70			

Table 2 illustrates this. The results confirm the observation [13] that no single substituent constant can satisfactorily represent the effect of a *p*-Ph group in electrophilic aromatic substitution.*

(v) The values of the ratio $(\log f_p^{\mathrm{Me}})/(\log f_{3,4}^{C_4H_4})$ are lower than for the other reactions

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* The absolute deviation of the *p*-Ph group from a $(\log f){-}\sigma^+$ plot may be no greater than for many other substituents, but the deviation relative to the value of σ^+, which is important in a detailed analysis of the effect of a group, is abnormally large, as discussed below.

[6] R. Baker, unpublished work.
[7] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3337.
[8] Dewar, Mole, and Warford, *J.*, 1956, 3581.
[9] Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.
[10] Mason, *J.*, 1959, 1233.
[11] R. D. Brown, *Experientia*, 1950, **6**, 376; *J. Amer. Chem. Soc.*, 1953, **75**, 4077.
[12] Dewar, *J.*, 1952, 3544.
[13] Deans, Eaborn, and Webster, *J.*, 1959, 3031.
[14] de la Mare and Hassan, *J.*, 1957, 3004.
[15] Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.
[16] Eaborn and Pande, *J.*, 1961, 297.
[17] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.
[18] de la Mare, Hall, Harris, and Hassan, *J.*, 1958, 1086.
[19] H. C. Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 5175.

for which it is known, with the exception of nitration,[8] the data for which appear anomalous.† Apart from this, the value of the ratio tends generally to fall as f_p^{Me} rises (Table 3), indicating that electron-release by the activating ring is called forth more strongly as the general electron-demand rises. The way in which this ratio varies suggests that there is no qualitative difference between the type of response of biphenyl and of naphthalene systems to electron-demand; a difference would not have been surprising in view of the fact that the two rings are coplanar in naphthalene but not in biphenyl.

TABLE 3.

Reaction	f_p^{Me}	$\log f_p^{\mathrm{Me}}/\log f_{3,4}^{\mathrm{C_4H_4}}$	Reaction	f_p^{Me}	$\log f_p^{\mathrm{Me}}/\log f_{3,4}^{\mathrm{C_4H_4}}$
Protodegermylation [16]	14	4·54	Detritiation	313	1·39
Protodesilylation [15] ...	21	3·96	Detritiation	702	1·32
Mercuridesilylation [15]...	17·5	2·69	Nitration [8]	58	1·02

The results confirm the observation [15] that no single substituent constant can satisfactorily represent the effect of the 3,4-C_4H_4 system in electrophilic aromatic substitution.

(vi) The ratio ($\log f_{2,3}^{\mathrm{C_4H_4}})/\log f_{3,4}^{\mathrm{C_4H_4}}$) has values of 1·44 and 1·43 in the detritiations. These are lower than the values in desilylations,[15] in which steric effects occur.

(vii) " Reactivity numbers," [8] Hückel localization energies,[10] and energies calculated for formation of the ions ArH_2^+ from the hydrocarbons ArH,[4] are all quantitatively inconsistent with the observed reactivities, in that plots of $\log f$ for the single positions of benzene, biphenyl, and naphthalene against the various sets of energies are far from linear.

Activation in Biphenyl and Naphthalene.—We conclude with a brief general comment on the nature of the activating influences of the *p*-Ph group and the 3,4-C_4H_4 system in electrophilic aromatic substitution. We have shown that the effects of these substituents relative to that of a *p*-Me group, vary markedly with the electron-demand, but we wish to stress that there is nothing abnormal about the substituents. Any apparent abnormality is largely a consequence of calculating partial rate factors relative to a single position in benzene, which is logical (since, by definition, polar effects are absent at such a position) but not essential; if, for example, we calculated rate factors, f', relative to the *meta*-position in chlorobenzene, there would be fairly small variation in $(\log f'^{\mathrm{Me}}_p)/(\log f'^{\mathrm{Ph}}_p)$ ratios.

It is instructive to use Yukawa and Tsuno's approach [20] to analysis of substituent effects in electrophilic substitutions.‡ These authors point out that the quantity σ_R, which is equal to $(\sigma^+ - \sigma)$, is a measure of the potential ability of a substituent to stabilize, by resonance effects, a centre of excess positive charge with which it is conjugated. (The values of σ^+ are those derived from solvolysis of αα-dimethylbenzyl chlorides in 90% aqueous acetone,[23] and values of σ are those derived from ionization of benzoic acids in water at 25°.[24]) They further point out that the extent to which resonance effects operate varies from reaction to reaction, and show that for a number of electrophilic reactions the relation $\log f = \rho(\sigma + r\sigma_R)$ is more satisfactory than either of the relations $\log f = \rho\sigma$ and $\log f = \rho\sigma^+$.[20] The value of r, which is a measure of the extent to which electromeric and possibly inductomeric effects of substituents are brought into play, has, by definition, a value of 1 for solvolysis of αα-dimethylbenzyl chlorides and of 0 for ionization of benzoic acids in water, and can have a range of values above zero in electrophilic reactions; for

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† The factors $f_{3,4}^{\mathrm{C_4H_4}}$ and $f_{2,3}^{\mathrm{C_4H_4}}$ refer respectively to the 2- and the 1-position of naphthalene.

‡ An equivalent approach will be found in ref. 21. A related procedure, but applicable to reactions in which loss of resonance occurs on going from initial state to transition state, has been outlined by Dickinson and Eaborn.[22]

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

[21] Bekhum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[22] Dickinson and Eaborn, *J.*, 1959, 3036.

[23] H. C. Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[24] McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

example, 2·29 in brominolysis of benzeneboronic acids,[20] 1·66 in molecular chlorination in acetic acid,[20] 0·90 for nitration in nitromethane or acetic acid,[20] 0·7 in protodesilylation,[1] and 0·4 in protodestannylation.[1]

The values of σ_R for the *p*-Ph group (—0·17) and the 3,4-C_4H_4 system (—0·177) are not particularly large (cf. —0·141 for *p*-Me and —0·510 for *p*-OMe), but because σ is so small in both cases the value of the sum ($\sigma + r\sigma_R$) rises steeply with r as the following Table shows:

r	0	0·2	0·4	0·6	0·8	1·0	1·5
$\sigma + r\sigma_R$ for *p*-Ph	—0·01	—0·04	—0·078	—0·11	—0·15	—0·179	—0·26
$\sigma + r\sigma_R$ for 3,4-C_4H_4	+0·042	+0·007	—0·029	—0·064	—0·100	—0·135	—0·223
$\sigma + r\sigma_R$ for *p*-Me	—0·170	—0·198	—0·226	—0·255	—0·283	—0·311	—0·381

If the Yukawa–Tsuno equation applied exactly, then as r varied from 0·2, to 0·6, to 1, to 2, the value of the ratio ($\log f_p^{Me}$)/($\log f_p^{Ph}$) would fall from 5, to 2·3, to 1·7, to 1·3. [If we reckoned rate factors relative to the *meta*-position of chlorobenzene, this would be equivalent to adding *ca.* —0·38 to each value of the sum ($\sigma + r\sigma_R$), and the new sum would then appear less variable with r.] The effect of the 3,4-C_4H_4 system falls into the same pattern; the value of σ_R is rather similar to that for *p*-Ph, and if it is slightly greater, as it may be, then the sum ($\sigma + r\sigma_R$) for 3,4-C_4H_4 can overtake that for *p*-Ph at high values of r. We do not suggest, of course, that the Yukawa–Tsuno approach to substituent effects has fundamental significance in its present state of refinement, or that wholly quantitative analysis of effects on individual groups is possible by its use, but it serves to interpret semi-quantitatively the variability of effects of *p*-Ph and 3,4-C_4H_4 substituents noted in Tables 2 and 3, and to illustrate that the response of these substituents to electron-demand is not, in absolute terms, abnormal.

EXPERIMENTAL

Materials.—Monotritiated biphenyls and naphthalenes were made by the usual method from 2-iodo-, 3-bromo, or 4-bromo-biphenyl or from α-bromo- or β-chloro-naphthalene; [2,3] the Grignard reagent from the last compound was prepared in tetrahydrofuran. Maximum activities (theoretical use of the tritiated water being assumed; see ref. 3) were 2 and 3 mc./g. for [α- and β-$^3H_1$]naphthalene, respectively, 5 mc./g. for the [$^3H_1$]biphenyls. (Actual activities might have been only one-quarter of these values.)

Exchange Measurements.—The media and general method for rate measurements were as previously described,[2,3] except that for the naphthalene compounds only 5 ml. of toluene were used in the extraction in order to give a more active extract. About 0·02—0·03 g. of the tritiated aromatic compound was used in about 7·5 g. of the reaction medium, the solution obtained being sufficient for 5 samples in sealed tubes.[2] In calculating " equilibrium " deflections, it was assumed that four positions were available for tritiation with [α-$^3H_1$]-naphthalene, 8 with the β-isomer, 6 with [2- and 4-$^3H_1$]biphenyl, and 10 with the 3-isomer (cf. ref. 2). (In all cases the " equilibrium " deflection would correspond to less than 3% of the tritium's remaining in the aromatic compound.)

Sulphonation.—The rates of sulphonation of biphenyl and naphthalene in $CF_3 \cdot CO_2H$–H_2O–H_2SO_4 were measured by partition of the hydrocarbon and its sulphonic acid between hexane and water, followed by spectrophotometric determination of the concentration of the hydrocarbon in the hexane.[2] Wavelengths of 247, 255, 265, and 280 mμ were used for biphenyl, and of 266, 276, 290, and 295 mμ for naphthalene. The first-order rate constants for sulphonation fell slightly as reaction proceeded (as sulphuric acid was removed and water formed; cf. ref. 2), and initial rates are given in Table 1. The rates determined at the several wavelengths agreed to within ±4%.

We thank the Department of Scientific and Industrial Research for financial support, and the Chemical Society for a grant from the Research Fund.

THE UNIVERSITY, LEICESTER. [*Received, September 9th,* 1960.]