400. *Aromatic Reactivity. Part XXIV.*[1] *The Relative Reactivities of the 2- and the 4-Position of Biphenyl.*

By R. Baker, R. W. Bott, and C. Eaborn.

The rates of detritiation of 2- and 4-tritiobiphenyl by trifluoroacetic acid and heptafluorobutyric acid, when considered with those for hydrogen exchange for toluene, and for biphenyl in other media, suggest that the reactivity of the 2- relative to that of the 4-position of biphenyl falls, for electronic and not steric reasons, as the reactivity of the attacking acid decreases. Variations in *o*/*p* ratios in other electrophilic substitutions probably originate partly in similar effects.

The 2- and the 4-position of biphenyl were shown by Eaborn and Taylor[2] to be about equally reactive in detritiation by trifluoroacetic acid containing a little aqueous perchloric or sulphuric acid, but Shatenshtein and his co-workers[3] found that in dedeuteration by liquid hydrogen iodide or hydrogen bromide the 2- is distinctly less reactive than the 4-position. We have now measured the rates of detritiation of 2- and 4-tritiobiphenyl at 70·1° by anhydrous trifluoroacetic acid and heptafluorobutyric acid.

The Table summarises the results for the various media in terms of rate factors, f_o^{Ph} and f_p^{Ph}, for hydrogen exchange at the 2- and the 4-position of biphenyl relative to that at a single position of benzene, and of ratios derived from these factors; the ratios derived from the partial rate factors, f_o^{Me}, f_p^{Me}, $f_o^{\text{Bu}^t}$, and $f_p^{\text{Bu}^t}$, for hydrogen exchange at the *ortho*- and *para*-positions of toluene and t-butylbenzene are included for comparison.*

It will be seen that the ratios $f_o^{\text{Ph}}/f_p^{\text{Ph}}$ and (where available) $\log f_o^{\text{Ph}}/\log f_p^{\text{Ph}}$ vary in much the same way as the ratios $f_o^{\text{Me}}/f_p^{\text{Me}}$ and $\log f_o^{\text{Me}}/\log f_p^{\text{Me}}$. Since the ratios for toluene vary in the same way as corresponding ratios for t-butylbenzene, steric hindrance to *ortho*-substitution is unimportant in hydrogen-exchange in the media used,[4] and thus we suggest that the variations in the ratios for biphenyl are the result of electronic and not steric factors. For toluene, it was observed that the ratio $f_o^{\text{Me}}/f_p^{\text{Me}}$ falls as the reactivity of the catalysing acid decreases, and thus as the rate-determining transition state is further removed from the initial state towards the Wheland intermediate (or, in other words, as the proportion of positive charge on the aromatic ring in the transition state increases, and with it the "demand" on electron-release by substituents).[4] This is reasonable in the light of the recent demonstration that in the benzenium ion (a Wheland intermediate) the amount of positive charge is larger at the position *para* than at that *ortho* to the site of

Hydrogen exchange in biphenyl, toluene, and t-butylbenzene.

Medium	f_o^{Ph}	f_p^{Ph}	$\frac{f^{\text{Ph}}}{f_p^{\text{Ph}}}$	$\frac{\log f_o^{\text{Ph}}}{\log f_p^{\text{Ph}}}$	$\frac{f_o^{\text{Me}}}{f_p^{\text{Me}}}$	$\frac{\log f_o^{\text{Me}}}{\log f_p^{\text{Me}}}$	$\frac{f_o^{\text{Bu}^t}}{f_p^{\text{Bu}^t}}$	$\frac{\log f_o^{\text{Bu}^t}}{\log f_p^{\text{Bu}^t}}$
$CF_3\cdot CO_2H-H_2O-HClO_4$ (25°)	52 *	52 *	1·00	1·00	1·05 †	1·01	1·02 †	1·00
$CF_3\cdot CO_2H-H_2O-H_2SO_4$ (25°)	133 *	143 *	0·93	0·985	0·73 †	0·95	0·72 †	—
$CF_3\cdot CO_2H$ (70·1°)	98	163	0·60	0·90	0·49 †	0·88	0·45 †	0·87
n-$C_3F_7\cdot CO_2H$ (70·1°)	—	—	0·42	—	0·39 †	—	0·37 †	—
HI (25°) ‡	—	—	~0·25	—	~0·5	—	—	—
HBr (25°) §	520	2800	0·19	0·79	0·28	0·78	—	—

* Values from ref. 2. † Values from ref. 4. ‡ Ref. 3*a*. § Ref. 3*b*.

---

* There are some errors, as follows, in the Table of results[4] for toluene and t-butylbenzene; (i) Results for $CF_3\cdot CO_2H-H_2O-H_2SO_4$ refer to 24·84°, not 70·1°. (ii) For $CF_3\cdot CO_2H-H_2O-HClO_4$, figures listed as rate constants are actually partial rate factors at 25·0°.

[1] Part XXIII, Bott, Eaborn, and Waters, *J.*, 1963, 681.

[2] Eaborn and Taylor, *J.*, 1961, 1012.

[3] (*a*) Shatenshtein and Alikhanov, *Zhur. obshchei Khim.*, 1960, **30**, 992; (*b*) Yurygina, Alikhanov Izrailevich, Manochkina, and Shatenshtein, *Zhur. fiz. Khim.*, 1960, **34**, 587.

[4] Baker, Eaborn, and Taylor, *J.*, 1961, 4927.

protonation,[5] for a methyl group will clearly stabilize the ion more if attached to the *para*- than to the *ortho*-position. The same explanation applies to the greater stabilization by a *p*-Ph than by an *o*-Ph substituent as the transition state becomes closer to the Wheland intermediate.

For toluene, the greater reactivity of the *ortho*- than of the *para*-position in transition states closer to the initial state can be explained in terms of a higher electron-density at the *ortho*-position caused by the inductive effect's operating more strongly to a nearer position. An analogous explanation cannot apply to biphenyl because the phenyl group has an electron-withdrawing inductive effect, but the greater reactivity of the 2- than of the 4-position for transition states close to the initial state accords with the higher free valence number [6] of the 2-position.

Discussions of the *ortho*/*para* ratio in electrophilic substitutions in biphenyl, which are usually conducted in terms of steric effects at the *ortho*-position, must take into account our observation that $f_o^{\mathrm{Ph}}/f_p^{\mathrm{Ph}}$ and $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratios fall with decreasing reactivity of the reagent. Thus, for example, the fall from the high $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratio for nitration in acetic anhydride (1·02) [7] to that for molecular chlorination in acetic acid [8] (0·92),* and, again, to that for molecular bromination in acetic acid (0·45),[12] is in accord with expectation, though there may also be steric effects; indeed, since the overall electron-demand, as measured roughly by f_p^{Me}, is smaller in molecular bromination than in dedeuteration by liquid hydrogen bromide, the low value of $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ in the bromination suggests that there is marked steric hindrance to *ortho*-halogenation.

Weingarten [9] noted that the 0·5*o*/*p* ratio in chlorination decreased with decreasing reactivity of the attacking species, but he attributed this to increasing steric hindrance to *ortho*-substitution resulting from the decreasing length of the forming C–Cl bond in the transition state. He believed that steric effects were responsible because a plot of the 0·5*o*/*p* ratio against the 0·5*m*/*p* ratio rose sharply with increase in the latter ratio before levelling off towards an 0·5*o*/*p* ratio of slightly less than unity, but this is what would be expected if a linear free-energy relationship holds even roughly, and if $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ is somewhat less than unity while $\log f_m^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ is small (see ref. 13). (The variation in the $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratio which we have observed means that the linear free energy relationship does not hold exactly, and that the plot of 0·5*o*/*p* against 0·5*m*/*p* will be more sharply curved than expected from such a relationship.) While Weingarten's results thus do not, in our opinion, demonstrate the existence of steric effects, we do not assert that these are absent. However, while, for example, the 0·5*o*/*p* ratio for chlorination in acetic acid (0·27) [9] looks small, use of this ratio along with rates measured for this reaction by de la Mare *et al.*,[8] Mason,[10] or Dewar and Mole [11] leads to $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratios of 0·80, 0·82, and 0·83, respectively, which are not particularly low, while the partial rate factors obtained by de la Mare and his colleagues [8] correspond with a larger $\log f_o^{\mathrm{Ph}}/\log f_p^{\mathrm{Ph}}$ ratio of 0·92.

The reactivity of the 4-position of biphenyl has been discussed recently by Brown and Stock.[12,14] Since a plot of $\log f_p^{\mathrm{Ph}}$ against $\log f_p^{\mathrm{Me}}$ curves markedly, and more than does a plot of $\log f_2^{\mathrm{Fl}}$ against f_p^{Me} (where f_2^{Fl} refers to the 2-position of fluorene), they concluded that the activating effect of the *p*-Ph group increases with increasing electron-demand, as

---

* There is disagreement about the isomer proportions [8, 9] and the relative rates [8, 10, 11] in this reaction (see below).

[5] MacLean and Mackor, *Mol. Phys.*, 1961, **4**, 241; *J. Chem. Phys.*, 1961, **34**, 2208.

[6] Streitwieser, " Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, 1961, p. 330.

[7] Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196.

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

[9] Weingarten, *J. Org. Chem.*, 1961, **26**, 4347.

[10] Mason, *J.*, 1959, 1233.

[11] Dewar and Mole, *J.*, 1957, 342.

[12] Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 1238.

[13] Smith and Taylor, *Tetrahedron*, 1963, in the press.

[14] Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 1242.

the two rings, which are not coplanar in the initial state, tend more and more towards coplanarity in the transition state. They acknowledge that Eaborn and Taylor[2] had previously noted the considerable variation in the $\log f_p^{\mathrm{Ph}}/\log f_p^{\mathrm{Me}}$ ratio (which increases with f_p^{Me}), but seem to have overlooked their demonstration that the corresponding ratio for the 2-position of naphthalene, $\log f_{3,4}^{\mathrm{C_4H_4}}/\log f_p^{\mathrm{Me}}$, varies even more seriously, and thus that the apparently abnormal behaviour of the *p*-Ph substituent is not to be attributed to the non-coplanarity of the rings in biphenyl. Eaborn and Taylor indeed showed that the variations in the reactivity of the 4-position of biphenyl and the 2-position of naphthalene can be interpreted in terms of the Yukawa–Tsuno treatment of substituent effects,[15] and that such variations are to be expected for any position at which a large polarizability is superimposed on a small polarization. Neuman[16] has shown that a plot of $\log f_2^{\mathrm{Fl}}$ against $\log f_p^{\mathrm{Ph}}$ is closer to a straight line than is a plot of $\log f_2^{\mathrm{Fl}}$ against $\log f_p^{\mathrm{Me}}$, and that there is no abnormal effect in activation at the 4-position of biphenyl which is absent in activation of the 2-position of fluorene.

Although we believe the variability of the $\log f_p^{\mathrm{Ph}}/\log f_p^{\mathrm{Me}}$ ratio is not to be associated with the non-coplanarity of the rings in biphenyl, we have no grounds for doubting that the much greater reactivity of the 2-position of fluorene than of the 4-position of biphenyl originates in the coplanarity of the rings in fluorene, as suggested by de la Mare and his colleagues[8,17] and again by Brown and Stock.[12,14] It is, however, unsafe to regard, as do Brown and Stock, the activating effect of the methylene group in fluorene as similar to that of the combined effects of a *m*-methyl and an *o*-tolyl group on benzene, for the bond between the methylene group and the aromatic rings in fluorene is much shorter than that between the methyl group and the ring in toluene, which implies a different interaction between the groups and the ring in the two cases;[18] there may, for example, be considerable activation in fluorene by hyperconjugation with the methylene group.[8] Furthermore, in some respects, at least, the methylene group in fluorene shows more analogy to a *para-* than to a *meta*-methyl group in toluene.[4,8,18]

EXPERIMENTAL

Materials.—The preparation of tritiated biphenyls[2] and the purification of trifluoroacetic acid and heptafluorobutyric acid[4] have been described.

Rate Measurements.—The techniques were as previously described.[19]

The following specimen run refers to [4-^{3}H]biphenyl in heptafluorobutyric acid at 70·1°; the symbols have the meanings previously noted.[19] The biphenyl (0·0212 g.) was dissolved in the acid (10·1985 g.) and five aliquot parts (1 ml.) were transferred to small tubes which were then sealed and placed in the thermostat-bath. (The residual solution weighed 1·5217 g., so that each tube contained 0·0036 g. of the biphenyl, and since the biphenyl gave a deflection of 420 mm./0·0040 g., the tritium remaining in the biphenyl at ten times the half-life of the exchange would give a deflection of *ca.* 7 mm., it being assumed that the equivalent of approximately 4 positions of the aromatic would be available for tritium after this time.) Samples were removed at appropriate times and broken under a mixture of toluene (10 ml.) and 3% aqueous sodium hydroxide (100 ml.); subsequent procedure was as before.[19]

t (hr.)	0	335	672	1006	1336	∞
D (mm.)	420	252	151·5	92	55	(7)
10^9k (sec.$^{-1}$)	—	433	434	438	446	—

The rate constants at 70·1° obtained for the [x-^{3}H]biphenyls were: (i) In $CF_3{\cdot}CO_2H$: $x = 2$, $k = 9{\cdot}3 \times 10^{-7}$; $x = 4$, $k = 15{\cdot}5 \times 10^{-7}$ sec.$^{-1}$. (ii) In n-$C_3F_7{\cdot}CO_2H$: $x = 2$, $k = 1{\cdot}82 \times 10^{-7}$; $x = 4$, $k = 4{\cdot}35 \times 10^{-7}$ sec.$^{-1}$.

---

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

[16] Neuman, *J. Amer. Chem. Soc.*, 1962, **84**, 3025.

[17] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., 1959, pp. 158—160.

[18] Baker, Eaborn, and Sperry, *J.*, 1962, 2382.

[19] Eaborn and Taylor, *J.*, 1960, 3301; 1961, 247; Baker and Eaborn, *J.*, 1961, 5077.

We thank The Royal Society for the loan of apparatus, and the Department of Scientific and Industrial Research for a maintenance grant to one of us (R. B.).

DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, LEICESTER.

[*Received, September* 14*th*, 1962.]