1005. *Aromatic Reactivity. Part XX.*[1] *Diphenyl Ether, Diphenyl Sulphide, Dibenzofuran, and Dibenzothiophen in Detritiation.*

By R. Baker and C. Eaborn.

We have measured the rates of detritiation of [2- and 4-$^{3}\text{H}_1$]-diphenyl ether and -diphenyl sulphide, and of [1-, 2-, 3-, and 4-$^{3}\text{H}_1$]-dibenzofuran and -dibenzothiophen in anhydrous trifluoroacetic acid at 70·1°. The 2- and 4-positions of diphenyl ether are more reactive than those of diphenyl sulphide. The order of reactivity of the several positions of dibenzo-furan and -thiophen is $2 > 3 > 4 > 1$, the 2-position being more, and the other positions less reactive in the oxygen than in the sulphur compound. Positions *ortho* and *para* to the hetero-atom are less reactive in the cyclic than in the open-chain compounds, the difference being greater with the oxygen compounds, but positions *meta* to the hetero-atom are more reactive in the cyclic compounds.

We have measured the rates of detritiation of [2- and 4-$^{3}\text{H}_1$]-diphenyl ether and -diphenyl sulphide, and of [1-, 2-, 3-, and 4-$^{3}\text{H}_1$]-dibenzofuran and -dibenzothiophen by trifluoroacetic acid at 70·1°, and the results are shown in the Table. We have also measured the rate of detritiation of [$^{3}\text{H}_1$]benzene under these conditions in order to derive rate factors, f, for the reactivities of the separate positions of the oxygen and sulphur compounds relative to the reactivity of a single position in benzene. These factors must be regarded as approximate because only 10% of reaction occurs with benzene in three months, but we have no reason to believe that the measured rate for benzene is in error by more than ±5%. (The reactivities of the separate positions of the oxygen and sulphur compounds relative to one another are, of course, unaffected by this uncertainty.) The factors are set out in the diagram below, some figures for toluene being included for comparison.

Rates of detritiation in trifluoroacetic acid at 70·1°.

Aromatic compound	Posn. of ^{3}H	10^6k (sec.$^{-1}$)	Aromatic compound	Posn. of ^{3}H	10^6k (sec.$^{-1}$)	Aromatic compound	Posn. of ^{3}H	10^6k (sec.$^{-1}$)
Diphenyl ether	2	65·8	Dibenzofuran	1	1·28	Dibenzothiophen	1	2·58
	4	293		2	34·9		2	17·4
Diphenyl sulphide	2	31·6		3	2·97		3	4·08
	4	93·4		4	1·52		4	3·44
						Benzene	1	0·0095

The main features of the results are as follows:

(i) There is a large spread of rates in detritiation in trifluoroacetic acid, and thus probably also a large demand on polarizability effects in the aromatic systems concerned. For example, the rate factor, f, for the *para*-position of toluene, *viz.*, 450, is markedly greater than that in protodesilylation ($f = 20$) [2] or nitration ($f = 58$),[3] but less than that in molecular bromination ($f = 2420$) or chlorination ($f = 820$).[4] The values of f in

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[1] Part XIX, Baker, Eaborn, and Taylor, *J.*, 1961, 4927.

[2] Eaborn, *J.*, 1956, 4858.

[3] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291; cf. Knowles, Norman, and Radda, *J.*, 1960, 4885.

[4] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421, 5175.

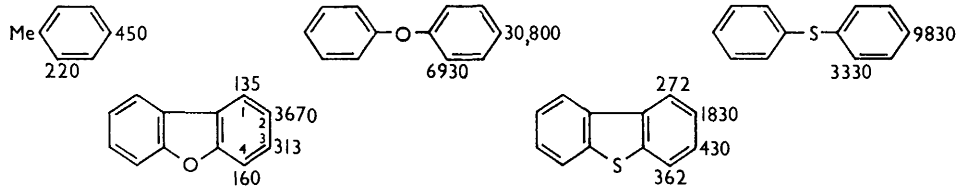
nitration for the 2- and 4-positions of diphenyl ether (117 and 234, respectively) and for the 1-, 2-, 3-, and 4-positions of dibenzofuran (47, 94, 94, and 0, respectively[6]) are all several times smaller than in detritiation.

(ii) The 2- and 4-positions of diphenyl ether are more reactive than the corresponding positions of diphenyl sulphide, in agreement with the smaller $+T$ effect of a sulphur than of an oxygen atom. The same result is found in protodesilylation,[7] but the differences are greater in that reaction; for example, the 4-position of diphenyl ether is 8 times more reactive than the 4-position of diphenyl sulphide in protodesilylation, but only 3 times in detritiation, in spite of the much greater spread of rates normally associated with detritiation.

The reactivity of the 4- relative to that of the 2-position of diphenyl ether ($\log f_4/\log f_2 = 1{\cdot}17$) agrees with that in nitration ($\log f_4/\log f_2 = 1{\cdot}14$),[5] but is much smaller than that in protodesilylation ($\log f_4/\log f_2 = 2{\cdot}07$),[7] and the difference between detritiation and protodesilylation in this respect is even more marked for diphenyl sulphide. The differences cannot reasonably be ascribed to steric influences at the 2-position, since primary steric effects are believed to be very small in hydrogen-exchange,[1] while steric interference from *ortho*-substituents normally results in acceleration of protodesilylation.[8]

The ratio of the reactivities of the 4- and 2-positions of diphenyl ether, *viz.*, 4·4, is somewhat greater than that for the 4- and 2-positions of anisole in dedeuteration, *viz.*, 2·4 in aqueous sulphuric acid at 25°[9] and 3·0 in sulphuric acid–acetic acid at 80°.[10]

(iii) Closure of the five-membered rings on going from diphenyl ether to dibenzofuran or from diphenyl sulphide to dibenzothiophen, is associated with a large reduction in reactivity of the positions *ortho* and *para* to the heteroatoms (cf. ref. 5), the reduction being much greater for those *ortho* than for those *para* to those atoms, and being greater for the oxygen than for the sulphur compounds. The effect is so large for positions *ortho* to the oxygen atom that the 4-position of dibenzofuran is less than half as reactive as the 4-position of dibenzothiophen, even though the corresponding 2-position of diphenyl ether is more than twice as reactive as that in diphenyl sulphide.



The reduction of reactivity on ring-closure is to be attributed mainly to the engagement of the lone-pair of the oxygen and sulphur atoms in giving aromatic character to the five-membered rings, the $+T$ effects of those atoms being made available to the 4- and 2-positions of the heterocyclic compounds only at the expense of this aromatic character.

Positions *meta* to the hetero-atoms are very greatly increased in reactivity by the ring closure. The values of f for the 3-positions of diphenyl ether and sulphide are probably less than 1 (preliminary measurements indicate this to be the case for diphenyl ether), while the values for the 3-position of dibenzo-furan and -thiophen are 313 and 430, respectively, and for the 1-position are 135 and 272. The activation of the 1- and 3-positions is presumably to be attributed to the $+T$ effect of the substituted-phenyl group

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[5] Dewar and Urch, *J.*, 1958, 3079.

[6] Dewar and Urch, *J.*, 1957, 345.

[7] Eaborn and Sperry, *J.*, 1961, 4921.

[8] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; Benkeser, Hickner, Hoke, and Thomas, *ibid.*, 1958, **80**, 5289; Eaborn and Moore, *J.*, 1959, 3640; Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.

[9] Satchell, *J.*, 1956, 3911.

[10] Lauer and Day, *J. Amer. Chem. Soc.*, 1955, **77**, 1904.

ortho and *para* to these positions, respectively (the 2- and 4-positions of biphenyl are activated 133 and 143 times, respectively, in detritiation in trifluoroacetic acid containing aqueous sulphuric acid,[11] and greater activation is to be expected when the two benzene rings are held co-planar [12]).

(iv) The 1-, 3-, and 4-positions are more reactive in dibenzothiophen than in dibenzofuran. In protodesilylation the 3-position of the oxygen compound is slightly the more reactive.[7] (In the latter reaction the reactivities of the 1-positions are influenced by steric effects.)

(v) In both dibenzofuran and dibenzothiophen the order of reactivity of the positions in detritiation is $2 > 3 > 4 > 1$.

(vi) The reactivity of the 2-position of dibenzothiophen represents 64% of the total reactivity of the 1-, 2-, 3-, and 4-positions. Thus in other electrophilic aromatic substitutions we should expect predominant but certainly not exclusive 2-substitution, though the substitution in the other positions might be too small to detect easily in a highly selective reaction such as molecular bromination. It is usually said that only 2-substitution occurs, but the experimental evidence available does not support this. All that can be said is that (except for the isolation of a little 4-derivative in acetylation [14]) only the 2-substituted product has been obtained pure from each reaction. From bromination the 2-bromo-compound is obtained in about 80% yield,[13] but other isomers could also be present. From nitration in acetic acid, Cullinane, Davies, and Davies isolated the 2-nitro-derivative in 40% yield along with an equal amount of dibenzothiophen 5-oxide,[13] but Gilman and Nobis could obtain the 2-nitro-derivative in only 28% yield.[14] Sulphonation is said to lead to 2-substitution, but no details are given.[15] Acetylation gives predominant 2-substitution, but Gilman and Nobis isolated the pure 2-acetyl derivative in only 41% yield,[14] while Burger, Wartman, and Lutz reported that a mixture is formed, and isolated only 25% of the 2-, along with a very small amount of the 4-acetyl derivative.[16]

(vii) In dibenzofuran the reactivity of the 2-position represents about 86% of the total reactivity of the 1-, 2-, 3-, and 4-positions in detritiation, and thus we should expect to find greater predominance of 2-substitution in other reactions than for dibenzothiophen. This should be particularly true for reactions of high selectivity, and only the 2-bromo-derivative has been isolated after molecular bromination, in about 80% yield.[17] Sulphonation is said to give exclusive 2-substitution,[18] but the facts are that 89% of a sodium salt was isolated, with no evidence that it was a single substance and, from this, pure 2-dibenzothiophensulphonyl chloride was obtained in 85% yield, so that at least 76% of 2-sulphonation must occur. In benzoylation the 2-derivative was isolated exclusively, but only in 40% yield.[19]

The results of mercuration and nitration are quite anomalous. Mercuration is said to give only 4-substitution; [20] although only 38% of the pure 4-derivative was isolated, even this amount is out of accord with the results in other substitutions. Possibly the acetoxymercuric group is attached first to the oxygen atom of dibenzofuran and then migrates to the adjacent 4-position, but anisole under comparable conditions gives mainly the *para*-derivative. (However, such attachment to oxygen might be less sterically hindered in the cyclic compound than in anisole.)

From nitration in acetic acid, up to 80% of 3-nitrodibenzofuran has been isolated,

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

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

[13] Cullinane, Davies, and Davies, *J.*, 1936, 1435.

[14] Gilman and Nobis, *J. Amer. Chem. Soc.*, 1949, **71**, 274.

[15] Courtot, *Compt. rend.*, 1934, **198**, 2260.

[16] Burger, Wartman, and Lutz, *J. Amer. Chem. Soc.*, 1938, **60**, 2628.

[17] Mayer and Krieger, *Ber.*, 1922, **55**, 1659.

[18] Gilman, Smith, and Oatfield, *J. Amer. Chem. Soc.*, 1934, **56**, 1412.

[19] Johnson, Willis, and Gilman, *J. Amer. Chem. Soc.*, 1954, **76**, 6407.

[20] Gilman and Young, *J. Amer. Chem. Soc.*, 1934, **56**, 1415.

along with a little of the 2- and possibly some of the 1-isomer.[21] Nitration in acetic anhydride is said to give 40% of 2- and of 3-, and 20% of 1-nitration.[6] These results seem to be inexplicable at present in terms of the concepts which serve to interpret reactivities of monosubstituted benzenes in common electrophilic substitutions. A suggestion [22] that the 3-nitration of dibenzofuran results from prior protonation of the oxygen atom is untenable.[7]

It must be stressed that (even when steric effects are ignored) change in the position of maximum reactivity of a complex aromatic compound from reaction to reaction is not in itself surprising, since the balance of polarization and polarizability factors differ from reagent to reagent. Towards a reagent of low electron demand a position of high electron density in the initial state may well be the point of maximum reactivity, whereas towards a reagent of high electron demand a position to which electromeric effects can operate most strongly is likely to be the most reactive. Compared with halogenation, deuteration, and sulphonation (see ref. 23), nitration has a low electron demand, and thus might bring about most substitution at a different position. However, not only is there no evidence of 3-nitration in dibenzothiophen (for which in detritiation, the 2- and 3-positions are less separated in reactivity than they are in dibenzofuran), but also in protodesilylation, which is a reaction of markedly lower electron demand than nitration, the 2-position of dibenzofuran is 8 times more reactive than the 3-position.[7]

It may be relevant that nitration of anisole by acetyl nitrate is also " anomalous " in that an abnormally high proportion of *ortho*-substitution occurs, and de la Mare and Ridd [24] (and later Norman and Radda [25]) have suggested that the nitrating species becomes initially attached to the oxygen atom, a rearrangement subsequently occurring. A similar initial step might be postulated for nitration of dibenzofuran (although an electrophile can be attached at oxygen only by destroying the aromatic character of the five-membered ring), but one is left with the difficulty of explaining why the rearrangement should give the 3-isomer.

Recent calculations of π-electron density in dibenzofuran and related heterocyclic compounds are said to " account fully for all observations on electrophilic substitution " in these compounds,[26] but for dibenzofuran it seems to have been assumed that the order of reactivity of the positions observed in nitration in acetic anhydride,[6] *viz.*, $2 = 3 > 1 > 4$, is general for all such substitutions, whereas it is clearly anomalous. It is evident that a theory which relates the reactivities of the several positions only to the π-electron densities in the initial aromatic molecule cannot hope to explain the different reactivity orders observed in different reactions.

EXPERIMENTAL

Preparation of Materials.—Monotritiated compounds, having calculated activity (see ref. 27) of *ca.* 8 mc/g., were prepared by hydrolysing the appropriate arylmetal derivative with a 20—50% excess of tritiated water (100 mc/ml.) before an excess of ordinary water was added.[27] The arylmetal derivative was made in each case as described for preparation of trimethylsilyl derivatives.[7] Yields of [X-$^3H_1$] aromatic compounds were as follows:

(i) Diphenyl ether: 2-, 85%; 4-, 83% (m. p. in both cases, 28·0°). (ii) Diphenyl sulphide: 2, 86% (b. p. 145°/11 mm., n_D^{20} 1·6346); 4-, 63% (b. p. 152°/18 mm., n_D^{20} 1·6345). (iii)

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[21] Cullinane, *J.*, 1930, 2267; Gilman and Swiss, *J. Amer. Chem. Soc.*, 1944, **66**, 1884.

[22] Hartough and Meisel, " Compounds with Condensed Thiophene Rings," Interscience Publ., Inc., New York, 1954, p. 12.

[23] Eaborn and Taylor, *J.*, 1960, 1480; Cerfontain, Kaandorp, and Sixma, *Rec. Trav. chim.*, 1960, **79**, 935.

[24] Ref. 12, p. 76.

[25] Norman and Radda, *Proc. Chem. Soc.*, 1960, 423.

[26] Brown and Coller, *Austral. J. Chem.*, 1959, **12**, 152.

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

Dibenzofuran: 1-, 48%; 2-, 78%; 3-, 66%; 4-, 90% (m. p. in each case, 86·0°). (iv) Dibenzothiophen: 1-, 60%; 2-, 88%; 3-, 70%; 4-, 92% (m. p. in each case, 99°).

Rate Measurements.—The general methods have been described.[11,27,28] Relative tritium activities were measured as galvanometer deflections by the Matsukawa and Eaborn's method.[29] All reactions were carried out in sealed tubes.

In calculation of " equilibrium " deflections [28] it was assumed that the following number of ring positions would be available for tritium at ten times the half-life of the exchange: [2-$^3H_1$]diphenyl ether and sulphide, 6; [4-$^3H_1$]diphenyl ether, [4-$^3H_1$]diphenyl sulphide, [2-$^3H_1$]dibenzo-furan and -thiophen, 2·5; [3-$^3H_1$]dibenzo-furan and -thiophen, 7; [1-$^3H_1$]- and [4-$^3H_1$]-dibenzo-furan and -thiophen, 8. Any errors introduced by the assumptions would be very small.

The following specimen run refers to [1-$^3H_1$]dibenzothiophen.

Five 1 ml. portions were transferred to tubes from a solution of the tritiated compound (0·0149 g.) in trifluoroacetic acid (7·8366 g.), and the residue weighed 0·429 g. There was thus 0·0028 g. of the [1-$^3H_1$]dibenzothiophen in each tube, and separate measurement showed that this amount, when dissolved in 10 ml. of toluene, gave, under our standard conditions of measurement, a deflection of 76·2 mm. On the assumption that one position of trifluoroacetic acid and eight of dibenzothiophen are equally available for tritium, at ten times the half-life of the exchange 0·9% of the tritium will be in the aromatic compound, and 8·8 g. of toluene extract will give a deflection, D_∞, of 0·7 mm.

In the following Table, D_t is the deflection for 8·8 g. of toluene extract at a time, t, measured from the time of removal of the first tube from the bath. If D_0 is the deflection resulting from this first sample, the *pseudo*-first-order rate constant, k, is given by

$$kt = 2{\cdot}303 \log [(D_0 - D_\infty)/(D_t - D_\infty)]$$

t (hr.)	0·0	30·2	70·7	95·4	142·85
D_t (mm.)	55·2	41·8	28·5	22·6	14·6
10^7k (sec.$^{-1}$)	—	25·6	26·0	26·0	25·9

Mean rate constants, usually obtained graphically, could be duplicated to within ±1·5%.

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 purchased through the Government Grant-in-Aid.

THE UNIVERSITY, LEICESTER. [*Received, June 12th,* 1961.]

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

[29] Matsukawa and Eaborn, *Research* (Correspondence), 1956, **9**, S37; Eaborn, Matsukawa, and Taylor, *Rev. Sci. Instr.*, 1957, **28**, 725.