Aromatic Reactivity. Part XXXVII.[1] Detritiation of Substituted 1- and 2-Tritionaphthalenes

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Rates of detritiation in trifluoroacetic acid have been measured for a series of X-1- and X-2-tritionaphthalenes. Rates at 70·0° (in some cases, shown italicized, obtained by extrapolation from measurements at other temperatures), relative to that of the parent 1- or -2-tritionaphthalene, are as follows: (*a*) 1-tritio-compounds: (X =) 2-Me *300*; 3-Me 2·75; 4-Me *83*; 5-Me 2·18; 6-Me 1·31; 7-Me 2·90; 8-Me 1·53; 2-OMe *2·2 × 10^4*; 4-OMe *8600*; 5-OMe 3·87; 4-Ph 15·9; 2-F 1·71; 4-F 4·6; 5-F 0·043; 8-F 0·053; 2-Cl 0·26; 3-Cl 0·0023; 4-Cl *0·265*; 5-Cl 0·028; 6-Cl 0·032; 7-Cl 0·138; 8-Cl 0·043; 2-Br 0·165; 4-Br *0·135*; 5-Br 0·025; 8-Br 0·047; 2-I 0·32; 4-I ~*0·18*; 8-I 0·066; (*b*) 2-tritio-compounds: (X =) 1-Me 270; 3-Me 3·59; 4-Me 2·99, 5-Me 1·76; 6-Me 19·4; 7-Me 1·59; 8-Me 3·11; 1-OMe *3·7 × 10^5*; 3-OMe 36; 4-OMe 1·58; 6-OMe 124; 1-F 0·54; 3-F *0·044*; 4-F *0·014*; 1-Cl *0·074*; 3-Cl *0·043*; 4-Cl *0·0103*; 5-Cl *0·0105*; 6-Cl 0·184; 7-Cl *0·029*; 8-Cl 0·0205; 1-Br *0·044*; 3-Br *0·029*; 4-Br *0·0096*; 8-Br *0·0136*; 1-I ~0·087; 3-I *0·048*; 4-I *0·0194*. The main features of the results are discussed, and in some cases are qualitatively interpreted theoretically.

ANALYSIS of the influence of substituents on the ease of electrophilic substitution in the benzene ring has contributed greatly to the present theories of substituent effects in organic chemistry,[2,3] but it seems likely that further effective development of these theories will require data for systems other than the benzene ring, and the most obvious extension is to naphthalene. The effects of methyl and methoxy-substituents in naphthalene have been measured for nitration of 1- and 2-methyl- and -methoxy-naphthalene in several media,[4,5] and we now describe the results for hydrogen-exchange of some methyl-, phenyl-, methoxy-, and halogeno-substituted 1- and 2-tritionaphthalenes in anhydrous trifluoroacetic acid. The advantages of this reaction in comparison with most electrophilic aromatic substitutions are that (*a*) there is no doubt about the position of reaction, and no analysis of isomeric products is involved, and (*b*) steric hindrance seems to be small or non-existent.[6]

Positional Reactivities.—In Tables 1 and 2 are shown the first-order rate constants, *k*, measured mainly at 70·0°, but in several instances measured at other temperatures, in which cases the calculated values at 70·0° are shown italicized. (For assumptions in the case of the halogen compounds, see below.) Also listed are the values, k_{rel}, of the rates relative to those of the parent 1- or 2-tritionaphthalene, and in Table 2 the approximate values, E_a, of the activation energies.

In Chart 1 the values of *k* are shown against the appropriate positions of the 1- or 2-substituted naphthalenes. From this it can be seen that the reactivities of the various positions of 1-methylnaphthalene fall in the order $4 > 2 > 5 > 8 > 7 \sim 3 > 6$. In the absence of serious steric effects, this should be the order of decreasing proportion of the possible isomers formed in common electrophilic substitutions of 1-methylnaphthalene, provided that the selectivity of the reagent is not too different from that of trifluoroacetic acid. The orders observed for nitration in some of the media used are as follows:[4]

HNO_3–$MeNO_2$	$4 > 5 > 2 \sim 8 > 3$ (>6 and 7)
HNO_3–$MeCO_2H$	$4 > 8 > 5 > 2 > 3$ (>6 and 7)
HNO_3–$(MeCO)_2O$	$4 > 2 > 8 > 5 > 3$ (>6 and 7)
NO_2BF_4–sulpholan	$4 \sim 2 > 8 > 5 > 3$ (>6 and 7)

The agreement with the order in detritiation is poor, presumably mainly because there is serious steric hindrance to nitration for all except the 3-, 6-, and 7-positions. When this hindrance is taken into account, the only surprising results in nitration are (*a*) the absence of 6- and 7-derivatives in spite of the formation of a

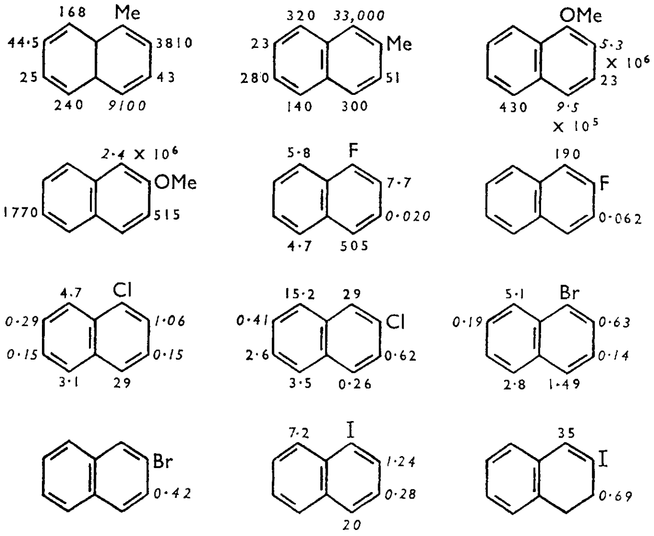

CHART 1

Values of 10^7k (sec.$^{-1}$) for detritiation at 70° at the positions indicated; italicized values were obtained by extrapolation from results at other temperatures

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[1] Part XXXVI, A. R. Butler and C. Eaborn, *J. Chem. Soc.* (*B*), 1968, 370.

[2] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, ch. VI.

[3] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965.

[4] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1377.

[5] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.*, 1965, **18**, 1391.

[6] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

few percent of 3-derivative, and (*b*) the formation of more 8- than 5-derivative in some media (since greater hindrance would be expected at the 8- than at the 5-position). It was estimated that less than 0·3% of 6- or 7-nitro-1-methylnaphthalene was formed,[4] but these isomers were not specifically sought in the gas–liquid chromatographic analysis, and the possibility was recognized that they might have had the same retention time as one of the other isomers. In view of the detritiation results, it seems possible that the retention times of the 6-, 7-, and 8-nitro-compounds were the same, so not only would the 6- and 7-isomers have escaped detection even if they formed a few per cent of the products, but also the reported proportion of 8-isomer would be correspondingly inflated. However, if this is not the case, there may exist to some extent in all the nitration media the undefined specific *peri*-activating effect which was suggested to give rise to the high yield of 8-nitro-derivative in acetic acid.[4]

Few results are available for other substitutions in 1-methylnaphthalene, but it is known that molecular bromination gives over 90% of the 4-bromo-derivative,[7] while molecular chlorination gives mainly the 4-chloro-derivative, but also at least one other isomer (which we should expect to be the 5-derivative).[8] Friedel–Crafts acetylation [9] and sulphonation at 40° [10] also give mainly the 4-derivatives, though some 5-derivative is also formed in the sulphonation. In view of the serious steric

TABLE 1

Rates of detritiation of X-1-tritionaphthalenes

X	Temp.	10^7k (sec.$^{-1}$)	$k_{rel.}$ (at 70°)	X	Temp.	10^7k (sec.$^{-1}$)	$k_{rel.}$ (at 70°)
H	70·0°	110[a]	1·00	5-OMe	70·0°	426	3·87
	100·7	1045	—	4-Ph	70·0	1750	15·9
	125·0	6030	—	2-F	70·0	188	1·71
2-Me	24·94	811	—	4-F	70·0	505	4·58
	35·04	1980	—	5-F	70·0	4·73	0·043
	45·05	4750	—	8-F	70·0	5·84	0·053
	70·0	*33,000*[b]	*300*[c]	2-Cl	70·0	29·1	0·26
3-Me	70·0	303	2·75	3-Cl	70·0	0·256	0·0023
4-Me	24·94	189	—	4-Cl	70·0	29·2[j]	0·265
	35·04	447	—	5-Cl	70·0	3·11	0·028
	45·05	1180	—	6-Cl	70·0	3·47	0·032
	70·0	*9100*[d]	*83*[d]	7-Cl	70·0	15·2	0·138
5-Me	70·0	240	2·18	8-Cl	70·0	4·70	0·043
6-Me	70·0	144	1·31	2-Br	70·0	18·2	0·165
7-Me	70·0	319	2·90	4-Br	70·0	14·9[k]	0·135
8-Me	70·0	168	1·53	5-Br	70·0	2·77	0·025
2-OMe	−11·95	11,000	—	8-Br	70·0	5·12	0·047
	−6·85	16,850	—	2-I	70·0	35·3	0·32
	−2·40	24,400	—	4-I	100·7	226	—
	70·0	*204*	2·2		70·0	*~20*	*~0·18*
		$\times 10^{6}$[f]	$\times 10^{4}$[g]	8-I	70·0	7·24	0·066
4-OMe	−11·70	5410	—				
	−6·20	8430	—				
	1·00	14,800	—				
	70·0	*9·5*	8600[i]				
		$\times 10^{-5}$[h]					

[a] E_a 18·8 kcal./mole. [b] ±3000. [c] ±30. [d] ±1000. [e] ±10. [f] $\pm 0{\cdot}6 \times 10^{6}$; E_a 11·8 kcal./mole. [g] $\pm 0{\cdot}6 \times 10^{4}$. [h] $\pm 1{\cdot}5 \times 10^{5}$; E_a = 11·2 kcal./mole. [i] ±1500. [j] From measurements at 100·7° and 125·0° (10^7k = 315 and 1600 sec.$^{-1}$); E_a = 19·8 kcal./mole. [k] From measurements at 100·7° and 125·0° (10^7k = 200 and 1190 sec.$^{-1}$); E_a = 21·8 kcal./mole.

TABLE 2

Rates of detritiation of X-2-tritionaphthalenes

X	Temp.	10^7k (sec.$^{-1}$)	$k_{rel.}$ (at 70°)	E_a (kcal./mole)
H …………	70·0°	14·3	1·00	20·3
	100·7	159	—	—
	125·0	852	—	—
1-Me………	70·0	3810	267	—
3-Me………	70·0	15·4	3·59	—
4-Me………	70·0	42·8	2·99	—
5-Me………	70·0	25·2	1·76	—
6-Me………	70·0	277	19·4	—
7-Me………	70·0	22·8	1·59	—
8-Me………	70·0	44·5	3·11	—
1-OMe ……	−11·60	7120	—	14·4
	−5·70	13,300	—	—
	0·00	23,400	—	—
	70·0	*$5{\cdot}3 \times 10^{6}$*[a]	$3{\cdot}7 \times 10^{5}$[b]	—
3-OMe ……	70·0	515	35·9	—
4-OMe ……	70·0	22·6	1·58	—
6-OMe ……	70·0	1770	124	—
1-F ………	70·0	7·74	0·54	—
3-F ………	100·7	8·53	—	21·6
	125·0	50·1	—	—
	70·0	*0·062*	*0·044*	—
4-F ………	100·7	3·38	—	20·7
	125·0	18·4	—	—
	70·0	*0·020*	*0·014*	—
1-Cl ………	100·7	10·8	—	19·1
	125·0	51·8	—	—
	70·0	*1·06*	*0·074*	—
3-Cl ………	100·7	6·99	—	21·3
	125·0	40·0	—	—
	70·0	*0·62*	*0·043*	—
4-Cl ………	100·7	2·42	—	23·5
	125·0	16·6	—	—
	70·0	*0·146*	0·0103	—
5-Cl ………	100·7	2·64	—	23·4
	125·0	18·1	—	—
	70·0	*0·150*	*0·0105*	—
6-Cl ………	100·7	28·7	—	19·6
	125·0	143	—	—
	70·0	*2·63*	*0·184*	—
7-Cl ………	100·7	5·12	—	20·6
	125·0	28·9	—	—
	70·0	*0·414*	*0·029*	—
8-Cl ………	100·7	5·19		23·5
	125·0	35·7		
	70·0	*0·293*	*0·0205*	
1-Br ………	100·7	6·38	—	18·8
	125·0	29·8	—	—
	70·0	*0·63*	*0·044*	—
3-Br ………	100·7	5·65		21·1
	125·0	33·4		—
	70·0	*0·42*	*0·029*	—
4-Br ………	100·7	2·26	—	22·9
	125·0	15·0	—	—
	70·0	*0·137*	*0·0096*	—
8-Br ………	100·7	3·42	—	25·2
	125·0	27·0	—	
	70·0	*0·194*	*0·0136*	
1-I ………	100·7	12·6	—	—
	70·0	*~1·24*	*~0·087*	—
3-I ………	100·7	9·49	—	21·6
	125·0	56·0	—	—
	70·0	*0·69*	*0·048*	
4-I ………	100·7	4·58	—	22·8
	125·0	29·7	—	—
	70·0	*0·277*	*0·0194*	—

[a] $\pm 0{\cdot}8 \times 10^{6}$. [b] $\pm 0{\cdot}6 \times 10^{5}$.

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[7] R. D. Topsom and J. Vaughan, *J. Chem. Soc.*, 1957, 2842.

[8] G. Gum, P. B. D. de la Mare, and M. D. Johnson, *J. Chem. Soc.* (*C*), 1967, 1590.

[9] R. D. Haworth and C. R. Marvin, *J. Chem. Soc.*, 1932, 2720.

[10] G. T. Morgan and E. A. Coulson, *J. Soc. Chem. Ind.*, *Trans.*, 1934, **53**, 73.

hindrance to 2-substitution in these reactions, the clear dominance of 4-substitution is to be expected.

For 2-methylnaphthalene the order of reactivity of the various positions in detritiation is $1 \gg 8 > 4 > 6 > 5 > 3 > 7$. In nitration the orders observed were as follows:[4]

HNO_3–$MeNO_2$	$1 > 8 > 4 > 5 > 6$ (>3 and 7)
HNO_3–$MeCO_2H$	$1 > 8 > 4 > 5 > 6$ (>3 and 7)
HNO_3–$(MeCO)_2O$	$1 > 8 > 4 > 5 > 6 > 3$ (>7)
NO_2BF_4–sulpholan	$1 > 4 \sim 8 > 5 > 6 >$ (3 and 7)

Agreement is good, the only anomaly being the greater reactivity of the 5- than of the 6-position in nitration, it being remembered that some steric hindrance would be expected for 5-nitration.

Molecular chlorination and bromination of 2-methylnaphthalene give, as expected, mainly the 1-halogeno-derivative,[11] but sulphonation, in which steric hindrance at the 1-position is probably very serious, gives the 8-derivative in 80% yield at 40°.[12] Friedel–Crafts acetylation in nitrobenzene, which also seems to be subject to serious steric hindrance, gives mainly the 6-derivative;[13] since some 8-derivative was isolated, we should expect some 4-derivative to be present also.*

The detritiation results are less complete for 1- and 2-methoxynaphthalene, and their significance is limited by the fact that methoxy-groups are known to interact with the acidic medium in what we have called ' incipient protonation ' (probably involving hydrogen-bonding),[14] which decreases the electron release by the group. It seems safe to conclude, however, that, in the absence of serious steric hindrance, 2- and, to a lesser extent, 4-substitution should dominate for 1-methoxynaphthalene, and 1-substitution, possibly accompanied by a significant amount of 6-substitution, for 2-methoxynaphthalene.

Nitration of 1-methoxynaphthalene gives mainly the 4-, along with some 2- and a little 5-derivative,[5] steric hindrance presumably causing reversal of the order expected for the ease of 4- and 2-substitution. Bromination in acetic acid is said to give the 4-derivative above 80° but the 2-derivative at lower temperatures,[15] while Friedel–Crafts acetylation gives the 4-derivative.[16] Nitration of 2-methoxynaphthalene gives mainly 1- along with some 6- and 8-derivative.[5] Halogenation also gives the 1-derivative.[17] Friedel–Crafts acetylation in dichloroethane catalysed by ferric chloride gives 94% of 1-substitution.[18] Acetylation catalysed by aluminium chloride also gives mainly 1-substitution in carbon disulphide but mainly the 6-derivative in nitrobenzene or chloroform,[19] suggesting that steric hindrance is more serious in these solvents; the 6- and 7- are the only unhindered positions, and of these the 6- is expected to be markedly the more reactive.

From the detritiation results for the 1-halogenonaphthalenes, common electrophilic substitutions would be expected to occur very predominantly at the 4-position with the fluoro-compound, but, in the absence of serious steric hindrance, to give substantial amounts of 8- and 5-derivatives along with the dominant 4-derivative with the other halogeno-compounds. In agreement, nitration and bromination of 1-fluoronaphthalene gives the 4-derivatives in good yield,[20] while with 1-chloronaphthalene nitration gives up to 62% of the 4-, but also 36—41% of the 8-, and 1·5—19% of the 4-derivative.[21] (The proportion of 8-substitution is higher than would be expected from the detritiation results, particularly since some steric hindrance to 8-substitution would be expected. Possibly assistance to 8-substitution by interaction between the electrophile and the negative end of the C–Cl dipole in the 1-position, considered below, is greater for nitration than detritiation.) The proportion of 8-relative to that of 4-substitution should, in the absence of serious steric hindrance, be even larger for 1-bromonaphthalene. Sulphonations and chlorosulphonations of 1-halogenonaphthalenes occur mainly at the 4-position.[20]

The results are less complete for the 2-halogenobenzenes, but with 2-fluoronaphthalene it is unlikely that the reactivity of any position in the unsubstituted ring will approach that of the 1-position (which is actually activated in detritiation compared with the 1-position in naphthalene itself, as discussed below), and nitration gives the 1-derivative.[22] For 2-chloronaphthalene, in the absence of serious steric hindrance, substantial 8-substitution would be expected to accompany the dominant 1-substitution, and significant proportions of 5- and 6-substitution would also be expected. Halogenation occurs mainly in the 8-position,[20] which is compatible with the detritiation results in view of the dual hindrance to 1-substitution. 2-Chloronaphthalene also gives the 8-derivative on nitration in acetic acid, and the 1,8-dinitro-derivative on nitration in sulphuric acid.[23] Chlorosulphonation of 2-chloro- or 2-bromonaphthalene is said to give the 8-derivative in high yield, but sulphonation of 2-fluoronaphthalene at 110—130°

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* Dr. P. R. Wells informs us that some 4- and 1-derivative are indeed formed.

[11] G. Gum, P. B. D. de la Mare, J. S. Lomas, and M. D. Johnson, *J. Chem. Soc.* (*B*), 1967, 244; D. M. Hall and R. K. Mitchell, *J. Chem. Soc.*, 1951, 1375.

[12] R. N. Shreve and J. H. Lux, *Ind. Eng. Chem.*, 1943, **35**, 306.

[13] G. A. R. Kon and W. T. Weller, *J. Chem. Soc.*, 1939, 792.

[14] R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 627.

[15] E. Fourneau, *Bull. Soc. chim. France*, 1928, **43**, 454.

[16] P. E. Popov, *Zhur. obshchei Khim.*, 1935, **5**, 986; J. G. Belton, N. V. Nowlon, and T. S. Wheeler, *Sci. Proc. Royal Dublin. Soc.*, 1949, **25**, 19.

[17] Elsevier's Encyclopaedia of Organic Chemistry, ed. F. Radt, series III, vol. 12B, 1948, pp. 1274—1277.

[18] I. N. Zemzina and I. P. Tsukervanic, *Zhur. obshchei Khim.*, 1963, **33**, 2605.

[19] R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, **181**, 518.

[20] Ref. 17, pp. 264—279.

[21] P. Ferrero and C. Caflisch, *Helv. Chim. Acta*, 1928, **11**, 795; H. F. Bassilos, *Bull. Soc. chim. France*, 1951, 651.

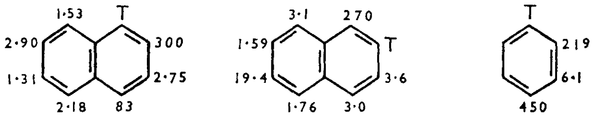
[22] G. Schiemann, W. Gueffroy, and W. Winkelmuller, *Annalen*, 1931, **487**, 270.

[23] H. E. Armstrong and W. P. Wynne, *Chem. News*, 1889, **59**, 225; K. Schied, *Ber.*, 1901, **34**, 813.

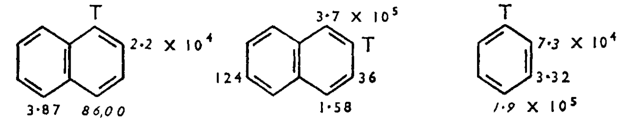
gives the 6-derivative.[18] Friedel–Crafts acetylation of 2-bromonaphthalene in carbon tetrachloride or chloroform gives mainly the 8- along with substantial quantities of the 6-derivative,[19] which is not surprising in view of the steric hindrance at the 1-position, but in nitrobenzene steric effects appear to be even more serious, and 6-dominates over 8-substitution. Since substantial quantities of 8-derivative are formed, we should also expect the 5-derivative to be produced in yields of a few per cent.

Substituent Effects.—The values of $k_{\rm rel.}$ at 70°, included in Tables 1 and 2, are also presented in Chart 2, in which the figure at each ring position represents the effect of the *substituent at that position* on the rate of substitution at the 1- or the 2-position of naphthalene, this being the most convenient form for use in the subsequent discussion. For comparison, corresponding values for the benzene system are also shown, but in the case of the halogenobenzenes these refer to exchange in $CF_3{\cdot}CO_2H–H_2O–H_2SO_4$ or $CF_3{\cdot}CO_2H–H_2O–HClO_4$ at 55°.[24] We shall use below the terms *x*,1- and *x*,2-interaction to denote the effect of a substituent at position *x* in naphthalene on reaction at the 1- and 2-position, respectively, and the terms *o*,1-, *m*,1-, and *p*,1-interaction to denote the effects of an *o*, *m*-, or *p*-substituent, respectively, on reaction in benzene.

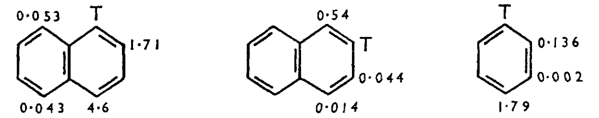
(a) Methyl substituents



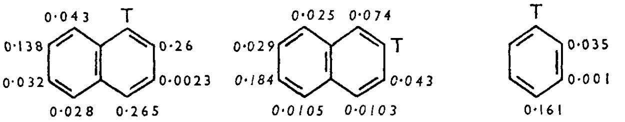
(b) Methoxy-substituents



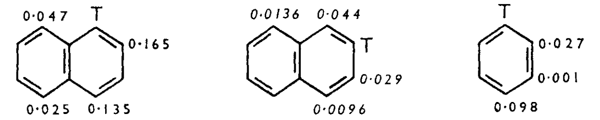
(c) Fluoro-substituents



(d) Chloro-substituents



(e) Bromo-substituents



(f) Iodo-substituents

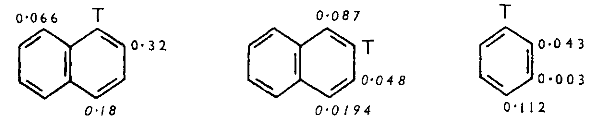


CHART 2

Rate factors representing the effects of the substituent at the position concerned on the rate of detritiation at the 1- or 2-position of naphthalene at 70°, with corresponding factors for benzene; italicized values were obtained by extrapolation from results at other temperatures

In attempts to rationalize the characteristics of the substituent effects in the detritiations we shall use the various theoretical quantities portrayed in Charts 3—5.

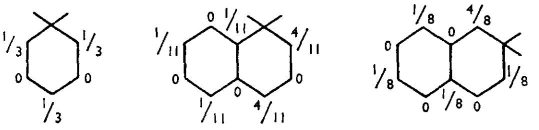


CHART 3

Proportion of positive charge at various positions of the Wheland intermediates

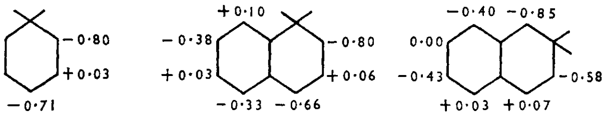


CHART 4

Values, ΔL_r^+ (in β-units) of the effect of a CH_2^- substituent at the position indicated on the localization energy for the 1- or 2-position of naphthalene or the 1-position of benzene

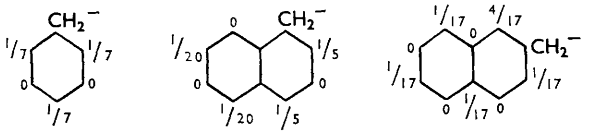


CHART 5

Proportion of negative charge on various ring positions in the naphthylmethyl and benzyl carbanions

Charts 3 and 4 present figures relevant to the Wheland intermediates; in Chart 3 are shown electron densities evaluated by the Longuet-Higgins method,[25] and in Chart 4 are shown the effects of a CH_2^- group on localization energies,[26] these being used as an indication of the effects of $+T$ groups generally on these energies. In Chart 5 are shown the charge distributions in the $ArCH_2^-$ anions,[27] and these are used below as a rough indication of the pattern of supply of electrons in the ground state of the aromatic systems through the resonance effects of $+T$ substituents.

(a) *The methyl group.* We first compare the effects of 1- and 2-methyl groups on the rates of detritiation at the various positions with the corresponding effects on the rates of nitration in acetic acid.[4] (The picture would be little changed if we considered the results for nitration in the other media used.[4]) There should be better correspondence between the sets of rate factors than

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[24] C. Eaborn and R. Taylor, *J. Chem. Soc.*, 1961, 2388.

[25] J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, 'Valence Theory,' Wiley, London, 1966, pp. 303, 324.

[26] A. Fischer, personal communication, 1967.

[27] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

between the sets of rates considered above, since the rate factors should not be influenced by steric hindrance to nitration in the α-position of naphthalene. The introduction of additional steric hindrance in positions adjacent or *peri* to the methyl group is not, however, taken into account in the factors.

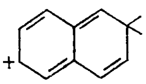
The order of activation of the various positions by a 1-methyl group in detritiation is $2 > 4 > 7 \sim 3 > 5 > 6 > 8$, compared with an order of $2 > 4 > 3 > 5 > 8$ (>6 and 7) in nitration. The only serious disagreement lies in the placing of the 6- and 7-positions, and we have noted above that the absence of nitration in these positions cannot be reconciled in any obvious way with the detritiation results. A puzzling feature is that, in nitration, activation of the 3-position by a 1-methyl group is only twice as small as that of the 4-position, and is markedly greater than activation of the *meta*-position in toluene, whereas in detritiation activation of the 3-position by a 1-methyl group is almost 30 times smaller than that of the 4-position, and only half that of the *meta*-position in toluene.

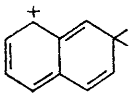
The main features of the effects of methyl groups, with comments, are as follows.

(*i*) The 3,1- and 4,2-interactions, which are roughly equal, are only half as large as the corresponding *m*,1-interaction in benzene.[*] [28] We can offer no satisfactory explanation of this. Insofar as the reactivity is determined by charge density at the attacked carbon atom in the ground state, we should expect much the same activation by 3,1- and 4,2- as by *m*,1-interactions, since inductive effects should be much the same in all three cases. Since the relative activations are more likely to be determined by stabilization of the transition state, it is tempting to associate the smallness of the pseudo-*meta*-interactions in naphthalene with the fact that the charge in this state is spread over two rings, so that the degree of charge in the attacked ring must be smaller than in benzene, but consideration of the detail of the charge distribution within the Wheland intermediate, taken as a model of the transition state, argues against this simple explanation. From Chart 3 we see that markedly less charge should lie adjacent to the 4-position for reaction at the 2-position in naphthalene than adjacent to the *meta*-position for reaction in benzene, and since the charges induced at the 4- and *m*-position should be correspondingly related, the 4,2- should be markedly smaller than the *m*,1-activation, as is observed, but by the same criterion the 3,1- should be slightly larger than the *m*,1-activation.

The experimental results can be used to give a rough measure of the distribution of charge between the two rings in the transition state for substitution at the 1- or 2-position of naphthalene if, as a gross simplification, the logarithm of the activating effect of an *x*-Me group, which is a measure of the free energy of stabilization of the transition state relative to the ground state, is assumed to be proportional to the charge developed at the *x*-position.[†] On this basis, the ratio of charge wholly in the attacked ring to that wholly in the unattacked ring is 4·4 : 1 for 1-substitution [(log 300 + log 2·75 + log 83) : (log 2·18 + log 1·31 + log 2·90 + log 1·53)], and 1·6 : 1 for 2-substitution. The charge distributions in Chart 4 indicate that in the Wheland intermediate the ratio should be 4 : 1 for 1-substitution, in agreement with the value derived above, and 2·5 : 1 for 2-substitution, which is probably in as good agreement with the experimentally derived value as could be expected in view of the approximations involved.

(*ii*) The most striking feature for the methylnaphthalenes is the smallness of the 3,2-compared with the 1,2-interaction. This is nicely accounted for by the charge distribution, shown in Chart 3, in the Wheland intermediate for 2-substitution, which shows that 4 times as much charge should reside at the 1- as at the 3-position, whereas the ratio of the observed free energies of stabilization is 4·2 [given by (log 270)/(log 3·6)]. However, from the charge distributions of Chart 3, we should expect the 6,2- and 8,2-interactions to be the same as the 3,2-interactions, and while this is roughly true for the 8,2- it is untrue for the 6,2-interaction, which on a free energy basis is twice as large as the 3,2-interaction. A rationalization (not wholly satisfactory) of the difference between the 6,2- and 8,2-interaction can be found by comparing those Wheland intermediates, (I) and (II), for 2-substitution in which the charge is located at the 6- and the 8-position respectively. They differ only in the location of a double-bond, and (I), in which the 7,8-bond (which is of relatively high order in the ground state) appears as a double bond, is likely to be more stable than (II), in which not only has this bond become single but the 6,7-bond (which is of relatively low order in the ground state) has become double.


(I)


(II)

(*iii*) From the charge distributions of Chart 3 we should expect the 2,1- to be smaller than the 1,2-inter-

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[*] A factor we have considered is that, since the 2-position and, more especially, the 1-position, of naphthalene are more reactive than a single position of benzene, the transition state will be further removed from the Wheland intermediate, and the degree of positive charge on the rings in the transition state thus smaller in the naphthalene reactions. What little information is available on additivity of substituent influences in benzene, however, suggests that this effect will be small for the reactivity differences involved, and it is neglected in the subsequent discussion.

[†] If this assumption were wholly valid, the sum of logarithms of the rate factors for all the substituent positions should be the same for 1- as for 2-substitution (the sum of the charges on the carbon atoms common to both rings being reasonably assumed to be roughly equal in the two cases), since the total amount of charge developed must be the same. The sums are, in fact, identical (*viz.*, 5·9), though this exact agreement must be fortuitous. They should, however, also be only a little smaller than the corresponding sum for the five positions of benzene (the expected difference originating in the small amount of charge which resides on the carbon atoms common to both rings in naphthalene and in the greater proximity of the transition state to the Wheland intermediate in the case of benzene); the observed total for benzene is 8·9.

[28] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

action, whereas they are about the same, and both to be larger than the *o*,1-interaction in benzene, which is as observed. We should also expect, however, that the 4,1- should be the same as the 2,1-interaction, which is not the case, though the difference is small on a free energy basis, and that both should be larger than the *p*,1-interaction in benzene, which is clearly incorrect.

(*iv*) A guide to the influence of resonance effects from conjugated positions should be given by the values, shown in Chart 4, of the changes, ΔL_r^+, in the localisation energies for 1- and 2-substitution brought about by placing the methylene anion in the various ring positions. (The values can be used only for conjugated positions, since inductive effects will be too important for non-conjugated positions.) It we assume for simplicity that a methyl group at a conjugated position has only a resonance effect or, alternatively, that the proportionate contribution from inductive effects is roughly independent of the position, the values of ΔL_r^+ for 1-substitution indicate correctly that the 2,1- should be larger than the 4,1-interaction, that both should be markedly larger than the 5,1- and 7,1-interaction, and that the 7,1- should be slightly larger than the 5,1-interaction. However, they also suggest larger values for 5,1- and 7,1- relative to 4,1- and 2,1-interactions than are observed.

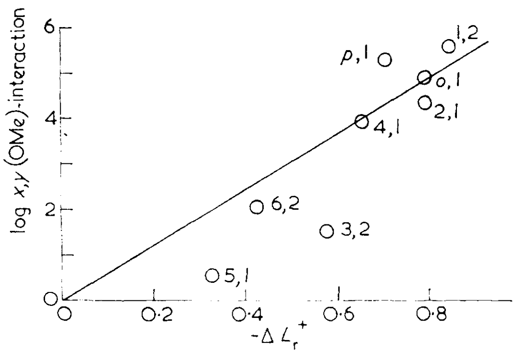

FIGURE 1 Plot of the logarithm of the *x*,*y*-interaction for a methoxy-substituent in naphthalene or benzene against the effect (in β-units), $-\Delta L_r^+$, of a methylene anion in position *x* on the localization energy at position *y*

For 2-substitution the ΔL_r^+ values correctly indicate that the 6,2- should be only about half as large (on a free energy basis) as the 1,2-interaction, but fail badly to indicate the smallness of the 3,2-interaction. They indicate correctly that the 8,2-, 7,1- and 5,1-interactions should be fairly similar to one another, with the last the smallest, but fail to predict the smallness of these interactions. (In a plot for methyl groups similar to that given in Figure 1 for methoxy-groups, the points for these interactions, and, more markedly, that for the 3,2-interaction lie well below the line through the origin.)

It is noteworthy that the rates of solvolysis of *x*-methoxy-1- and -2-bromomethylnaphthalenes [29] also indicate that the 6,2- is markedly larger than the 8,2-interaction, and distinctly larger also than the 7,1-interaction, as is the case with methyl substituents in detritiation. The solvolysis rates, however, show the 7,1- to be several times larger than the 5,1-interaction, whereas the difference is small for methyl groups in detritiation.

(b) *The methoxy-group.* The main features of the effects of the methoxy-group, shown in Chart 2, are mostly qualitatively in accord with those of the methyl group. Thus, (i) the 2,1- is clearly greater than 4,1-interaction, and the 4,1- is substantially smaller than the *p*,1-interaction in benzene, and (ii) the 3,2- is much smaller than the 1,2-, and also markedly smaller than the 6,2-interaction. Additional features of note are: (iii) the 4-OMe group facilitates substitution in the 2-position, even though these two centres are not conjugated, in accord with the fact that the *meta*-position in anisole is activated towards detritiation; (iv) the 1,2- is greater than the 2,1-interaction, (and this is not an artifact of the extrapolation of rates to 70°, since 1-MeO-2- and 2-MeO-1-tritionaphthalene have very similar rates at the temperatures of measurement, which means that at these temperatures the 1,2- must be some 10 times as great as the 2,1-activation). In view of the possibility of differential interaction of 1- and 2-OMe groups with the medium, this last effect cannot be regarded as very significant, although, from the charge distributions in the Wheland intermediates, shown in Chart 3, or from the ΔL_r^+ values for a group supplying electrons by a resonance effect, shown in Chart 4, the 1,2- would indeed be expected to be greater than the 2,1-interaction.

No very clear conclusions emerge from a comparison between the effects of the methoxy-group in nitration and those in detritiation, partly because steric hindrance influences some of the rate factors in nitration. It should be possible to obtain a measure of the influence in detritiation of the interaction of the methoxy-group with the trifluoroacetic acid by comparing the effect of this group with that of the methyl group in the two reactions. The value of the ratio of the logarithm of the rate factor for the methoxy-group to that for the methyl group is (*a*) for the 6,2-interaction, 1·62 in detritiation, and 2·41, 2·62, and 2·18 for nitration in nitromethane, acetic acid, and acetic anhydride, respectively, and (*b*) for the 4,1-interaction, 2·05 in detritiation, and 2·09, 2·69, and 3·01, respectively, for nitration in the same three media; these ratios suggest that interaction with the medium is reducing the effect of the methoxy-group in detritiation by at most a factor of 10.

A puzzling feature is that in nitration the 6,2- is within a factor of three of the 4,1-interaction,[5] the former possibly even being the larger in nitromethane, whereas in detritiation the 4,1- is some 70 times greater than the 6,2-interaction. The 5,1- is much smaller than the 6,2-activation in detritiation and nitration.

In Figure 1, the rate factors for the methoxy-substituents in positions conjugated with the reaction centre are plotted against the values of ΔL_r^+, points for the effects of *o*- and *p*-OMe substituents in anisole also being

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[29] K. C. Schreiber and R. G. Byers, *J. Amer. Chem. Soc.*, **1962**, **84**, 859.

included. With two exceptions the points lie well about a straight line, perhaps remarkably so in view of the fact that the methoxy-group has a substantial inductive effect in opposition to its electron-releasing resonance effect. The exceptions involve the point for the 5,1-interaction, and, more markedly, that for the 3,2-interaction. Similar deviations were noted qualitatively for the methyl compounds; indeed, for positions conjugated with the reaction centre, including those in anisole, there is a linear free energy relation (Figure 2) between the effects of the methoxy- and methyl groups which is remarkably good in view of the very different balance of inductive and resonance effects thought to exist in the two groups. The success of the correlation of the effects of the methoxy-groups with those of the methyl group and/or with theory suggest that interaction of the methoxy-group with the medium is much the same for 1- and 2-methoxynaphthalene and anisole.

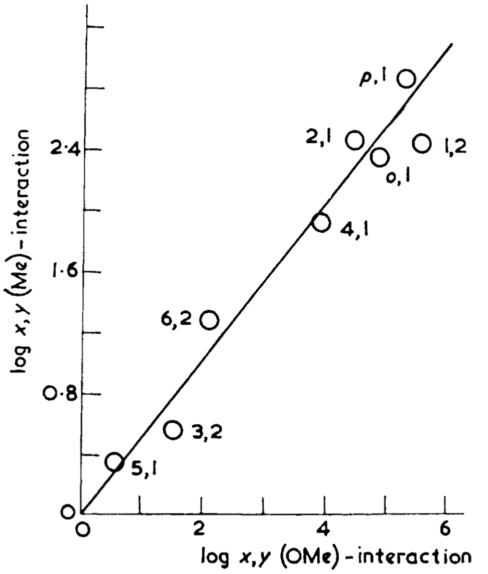

FIGURE 2 Plot of the logarithm of the x,y-interactions in methylnaphthalenes and toluene against the logarithm of the corresponding interactions in methoxynaphthalenes and anisole

(c) *The halogens.* As mentioned above, for some of the halogeno-compounds the values of the rates and rate factors at 70·0° are derived from measurements at 100·7° and 125·0°. In calculating such quantities, which are shown italicized in Charts 1–3, we have not used the observed value of the activation energy, E_a, for each compound because the variations in the values within a group of related compounds seem to us to be too large to be real; instead, we have used a single value of E_a within each such group in association with the observed rate constants at 100·7°. [The E_a values used are: (i) for the x-halogeno-2-tritionaphthalenes, 19·0 for $x = 1$, 21·5 for $x = 3$, 23·0 for $x = 4$, 23·5 for $x = 8$ and 5, 19·6 for $x = 6$, and 20·6 kcal./mole for $x = 7$, and (ii) for 4-halogeno-1-tritionaphthalenes, 20·0 kcal./mole.] The rate constants at 70·0° so calculated are, in fact, little different from those calculated by direct use of observed E_a values, and we estimate that the extrapolations introduce a maximum possible error of ±15%. A consequence of the procedure used is that, within each group of compounds, the rates relative to one another are shown to be the same at 70° as at 100·7°; within the results for 2-detritiation the observed values at 100·7° can, of course, be used directly in making comparisons, and this leads to no different conclusions. In the subsequent discussions we consider only differences in substituent effects which are either too large to be attributed to possible errors in the extrapolation or are clearly present in the rates observed directly at 100·7°.

Since the rate factors for the halogenobenzenes included in Charts 2 and 3 refer to a different medium, absolute (as distinct from free energy) comparisons with those for the halogenonaphthalenes are of limited significance. Some of the main features, with comments, of the effects of the halogens in the naphthalene compounds are as follows.

(*i*) Fluorine in the 2- activities the 1-position, but fluorine in the 1- slightly deactivates the 2-position; the large operation of resonance effects through the 1,2-bond, evident in the effects of methyl and methoxy-groups as noted above, is thus in one direction large enough to outweigh, and in the other direction almost to neutralize, the large inductive effect. If the inductive effect through the bond could be assumed to have the same influence in both directions, the results would indicate that the 2,1- is greater than the 1,2-resonance interaction, contrary to the uncertain indications given by the effects of the methoxy-group, and also, more significant, contrary to predictions from the charge distributions in Chart 3 and the values of ΔL_r^+ in Chart 4 (but in accord with the prediction from the charge distributions in the $C_{10}H_7CH_2^-$ anions, shown in Chart 5). The same effect is present with the other halogens; the 2,1- is 3—4 times as large as the 1,2-deactivation in all three cases, and the difference is too large to be attributed to any uncertainty in the extrapolation to 70°. We believe, however, that the influence of the inductive effect cannot, even as an approximation, be assumed to be the same in both directions, because, as indicated in Chart 3, a larger proportion of charge resides at the 1-position for 2-substitution than at the 2-position for 1-substitution, and thus the same inherent inductive withdrawal of electrons by a 1-halogen atom will result in a markedly larger rate decrease for 2-substitution than will that by a 2-halogen for 1-substitution. Consequently we cannot by inspection decide whether the inductive or the resonance effect is primarily responsible for the difference in the overall 2,1- and 1,2-interactions.

It is possible that there is a small but significant degree of electrostatic interaction between an α-halogen and a *peri*-hydrogen atom, of the nature of hydrogen-bonding, which slightly reduces the resonance supply of electrons by the halogen. Two facts argue against this explanation, *viz.*, (a) the 4-F substituent, which would be affected in this way, activates relatively strongly in 1-substitution, and (b) the reactivity order resulting from the 1,2-interaction, *viz.*, F > I > Cl > Br, is the same as that from the 2,1-interaction and also from the *o*,1-interaction in halogenobenzenes, suggesting that no new type of influence is operating.

(*ii*) In contrast with the influence of methyl and methoxy-groups, the halogens have larger effects (in this case deactivating) on 2-substitution from the 3- than from the 1-position, the difference being much greater for fluorine than for the other halogens. The reactivity order produced by the 3,2-interaction, *viz.*, I $>$ F $>$ Cl $>$ Br, differs from that produced by the 2,1-interaction in the relative positions of fluorine and iodine. The results are consistent with the assumption that resonance effects are markedly less important relative to inductive effects from the 3- than from the 1-position.

(*iii*) A 4-F substituent has a substantial activating effect on reaction at the 1-position. Because of the difference in media, we cannot be certain that this activation is greater than that of a *p*-F substituent in benzene, but it very probably is. A greater operation of electron-releasing resonance effects in 4,1- than in *p*,1-interactions would, indeed, be expected on the basis of the charge distributions shown in Chart 3 or Chart 5, but not on the basis of the localization energy effects noted in Chart 4. We have seen above that 4,1- are smaller than *p*,1-activations for methyl and methoxy-groups.

For the other halogens the 4,1- are very similar to the 2,1-interactions. The contrast with the benzene system, in which deactivation by *ortho*- is several times greater than that by the *para*-halogen, is to be attributed to the relatively large resonance contribution to the 2,1-interaction.

The reactivity order resulting from 4,1-interactions, *viz.*, F $>$ Cl $>$ I $>$ Br, coincides with that for *p*,1-interactions in benzene.

There is a satisfactory linear free energy relationship (not shown) between 4,1-interactions in detritiation and the effects of 1-halogens on molecular halogenation,[30] which takes place predominantly at the 4-position.

(*iv*) As far as they have been measured, the pseudo-*meta*-4,2-interactions are markedly smaller than the *m*,1-interactions, and the difference is too great to be attributed to the medium change; the same effect was noted with methyl compounds.

It is noteworthy that with chlorine the 3,1- appears to be a few times larger than the 4,2-deactivation, and the difference is unlikely to be wholly an artifact of the extrapolation procedure. The difference is consistent with the larger proportion of charge in the Wheland intermediate adjacent to the 3-position for 1-substitution than to the 4-position for 2-substitution (Chart 3). For chlorine the 5,2- is almost the same as 4,2-interaction. Since both 5- and 4-positions are unconjugated with the 2-position, inductive interactions should be mainly involved, and these should be smaller for the 5- than the nearer 4-position. The observed result is consistent with a significant resonance contribution, necessarily indirect, to the 4,2-interaction, and such a contribution would also account for the observed sequence of 4,2-deactivation by the various halogens, as it does for the same sequence of *m*,1-deactivation.[24]

(*v*) The pseudo-*meta*-8,1-interaction is smaller than the 3,1-interaction, and this is consistent with the indication (Chart 3) that less charge lies adjacent to the 8-position for 1-substitution than adjacent to the 3-position for 1-substitution. There is also the possibility, however, that a halogen atom in the 8-position may facilitate substitution at the 1-position by direct electrostatic interaction with the incoming proton in the transition state,* it being remembered that solvent molecules could not intervene between the halogen and hydrogen atoms to reduce such interaction. The fact that the reactivity order resulting from 8,1-interaction, *viz.*, I $>$ F $>$ Cl $\sim$ Br, is the same as that resulting from 4,2- or *m*,1-interaction argues against major contribution from such a specific effect. There is, in fact, an excellent linear free energy relationship (not shown) between the 8,1- and *m*,1-interaction.

It is noteworthy that the 8,1- is smaller than the 8,2-deactivation (the difference being too large to be attributable to the extrapolation procedure) even though (a) the substituent is nearer the reaction centre in the former case, and thus, on the simplest reasoning, will have a larger inductive influence, and (b) the $+T$ effect can operate to counteract the inductive effect in the latter but not the former case. We have seen above that the 8,2- seems to be markedly smaller than the 6,2-resonance interaction, for reasons which are not apparent, and the observed result could be attributed to the fact that development of charge at the 8-position is greater for 2- than 1-substitution, coupled with the fact that the inductive effect is more dominant in the 8,2-interaction than is usual for a conjugated interaction. It should be noted that there may be substantial interaction (in spite of unfavourable orientation of the C–Cl dipole) between the induced charge at the 8-carbon atom and the large charge developed at the 1-position during 2-substitution.

(*vi*) The relatively large 6,2-resonance interaction, noted for the methyl and methoxy-substituents, operates to make 6- several times more reactive than 5- or 7-chloro-2-tritionaphthalene. A related, though smaller, effect shows up in the reactivity of 7- compared with 8- and 6-chloro-1-tritionaphthalene.

(d) *The* 4-*phenyl group*. The feature of interest in the 4,1-interaction for the phenyl group is that the activation is about three times smaller than would be expected by comparison with the corresponding *p*,1-interaction in benzene. (Thus, the ratio of the logarithms of the *p*,1-activations by Me and Ph in benzene is 1·20, whereas the corresponding ratio for 4,1-interactions in naphthalene is 1·60.) This can be mainly attributed to the fact

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* There would necessarily, of course, be similar interaction with the leaving proton. For simplicity we write throughout this paper as though the formation of the Wheland intermediates is rate-determining, whereas in fact both its formation and destruction determine the rate. No significant error is introduced by this simplification.

[30] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 1948, 100.

that the *peri*-hydrogen atom prevents the 4-phenyl group from becoming coplanar with the naphthalene nucleus, which it must do for maximum conjugation. It is surprising that there is so little supression of the conjugative effect, but the ultraviolet spectrum of 1-phenylnaphthalene is said to indicate that there are, in spite of strong steric hindrance to coplanarity, ' appreciable contributions from coplanar resonance '.[31]

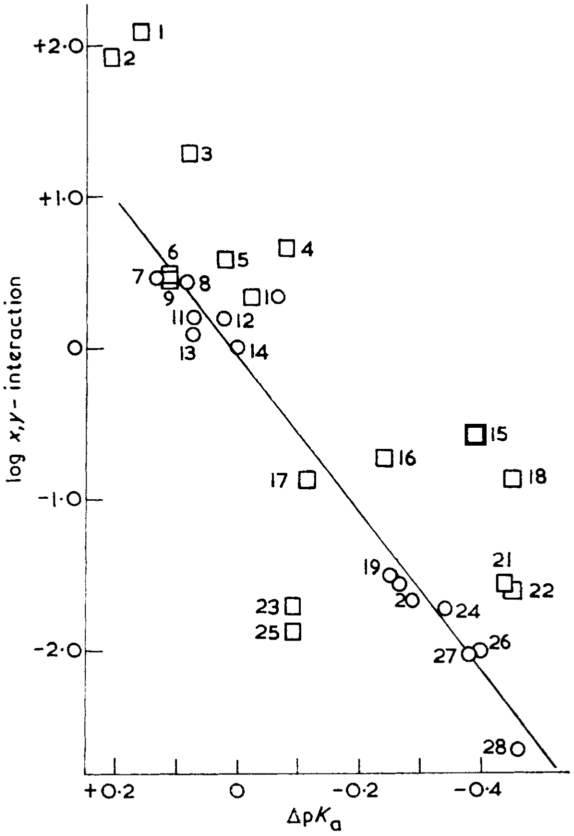

FIGURE 3 Plot of the logarithm of the x,y-interaction for detritiation in substituted naphthalenes against the corresponding effects, ΔpK_a, of the substituents on the pK_a of 1- or 2-naphthoic acid; conjugated interactions are denoted by squares, and non-conjugated interactions by circles

Key: 1, 6,2(OMe); 2, 4,1(Me); 3, 6,2(Me); 4, 4,1(F); 5, 5,1(OMe); 6, 8,2(Me); 7, 4,2(Me); 8, 3,1(Me); 9, 7,1(Me); 10, 5,1(Me); 11, 7,2(Me); 12, 4,2(OMe); 13, 6,1(Me); 14, H; 15, 4,1(Cl); 16, 6,2(Cl); 17, 7,1(Cl); 18, 4,1(Br); 19, 6,1(Cl); 20, 7,2(Cl); 21, 5,1(Cl); 22, 5,1(Br); 23, 8,2(Cl); 24, 4,2(I); 25, 8,2(Br); 26, 4,2(Cl); 27, 4,2(Br); 28, 3,1(Cl)

(e) *Comparison with effects of substituents on the strengths of naphthoic acids.* It is instructive to compare the effects of substituents on the rates of detritiation with those on the strengths of 1- and 2-naphthoic acid in 50% ethanol at 25°,[32,33] and this is best done by means of plot (see Figure 3) of the logarithms of the rate factors in detritiation against the effects, ΔpK, of the substituents on the pK_a of the acids. The line shown is drawn, by visual inspection, between the points for interactions between non-conjugated centres and that for the origin, and it will be seen that all such points lie reasonably near this line. As would be expected, most of the points for conjugated interactions deviate seriously from the line. The very large deviations with the halogens for 4,1-interactions are in line with the expected large contribution of $+T$ effects, which are apparent also in *p*,1-interactions in benzene. [The point for the MeO(4,1)-interaction, which is not included in Figure 3 because it lies inconveniently far from the other points, shows a similar large deviation.] The same kind of deviations occur for Cl(5,1)-, Cl(6,2)-, Me(5,1)-, and MeO(5,1)-interactions, but are markedly smaller, indicating that resonance effects are less important from the unattacked ring, although there is a large deviation for the MeO(6,2)-interaction.* The points for the Cl(7,1)- and Me(7,1)-interactions lie close to the line, indicating that resonance interactions are small between the positions concerned.†

The most interesting deviations are those for the halogen (8,2)-interactions, because they are not only very large, but also in the opposite direction to that expected for contribution from resonance effects in the detritiation, and thus to that observed for the analogous 6,2-interaction. A combination of two effects may be responsible for this; first, the acid-strengthening inductive effect of the halogen atom in a 8-halogen-2-naphthoic acid is probably unusually small because of the unfavourable orientation of the C–Hal dipole with respect to the carboxyl group,[34] and secondly the influence of the inductive effects of 8-halogens in 2-detritiation, relative to that in acid dissociation, may be very large because of the large degree of positive charge developed at the 8- and the nearby 1-position in the transition state, as discussed above.

EXPERIMENTAL

Preparation of Tritiated Naphthalenes.—2-Naphthylamine was used in some of the earlier preparations, but its use was abandoned when the seriousness of the toxicological risk was appreciated. Some syntheses described below were much more complex than they would have been if we had continued to use this compound. The literature values given alongside observed physical constants for substituted [^{3}H]naphthalenes refer to the untritiated compounds.

4-*Fluoro*[1-^{3}H]*naphthalene.* 1-Amino-4-bromo-,[35] made from 1-acetamido-4-bromo-,[36] was converted through the

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* It is noteworthy that the relatively large electron supply to the 2-position from a 6-methoxy-group is not to be entirely associated with the requirements of an electron-deficient transition state, since it is evident also in the ^{19}F chemical shift of 2-fluoro-6-methoxynaphthalene.[33]

† Since the pK_a of 7-chloro-1-naphthoic acid is not available, the value has been assumed to be the same as that of the corresponding bromo-compound.[34]

[31] R. A. Friedel, M. Orchin, and L. Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 159.

[32] M. J. S. Dewar and P. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3546.

[33] W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1967, **89**, 379.

[34] P. R. Wells and W. Adcock, *Austral. J. Chem.*, 1965, **18**, 1365.

[35] L. F. Fieser and V. Desreux, *J. Amer. Chem. Soc.*, 1938, **60**, 2255.

[36] H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 1943, 321.

diazonium fluoroborate into 1-bromo-4-fluoronaphthalene, m.p. 36° (lit.,[37] 37°). The Grignard reagent made from the latter in ether was treated with tritiated water to give 4-fluoro[1-^{3}H]naphthalene, b.p. 81°/9 mm., n_D^{25} 1·5913 (lit.,[37] b.p. 80°/11 mm., $n_D^{19\cdot5}$ 1·5939).

4-*Chloro- and* 4-*bromo*-[1-^{3}H]*naphthalene*. 1-Amino-4-bromo- was converted, through the diazonium mercurichloride, into 1-bromo-4-chloronaphthalene, m.p. 66—67° (lit.,[35] 67·5°). The Grignard reagent made from the latter in ether was converted into 4-chloro[1-^{3}H]naphthalene, b.p. 124—126°/14 mm., n_D^{25} 1·6310 (lit.,[37,38] b.p. 111°/12 mm., 127·8°/15 mm., n_D^{20} 1·6322). 4-Bromo[1-^{3}H]-naphthalene, b.p. 118°/4·5 mm., n_D^{25} 1·6550 (lit.,[37,38] b.p. 143·9°/15 mm., n_D^{20} 1·6583), was made analogously through 1,4-dibromonaphthalene, m.p. 83° (lit.,[38] 82—83°).

2-*Amino*[1-^{3}H]*naphthalene*. 2-Acetamidonaphthalene was converted into 2-amino-1-bromonaphthalene,[39] m.p. 63° (lit.,[38] 63—64°). An ether solution of the latter was added, dropwise but fairly rapidly, to a solution of 3·4 equiv. of n-butyl-lithium in ether at 0°. When the spontaneous refluxing had finished, the mixture was cooled and treated with tritiated water, to give 2-amino[1-^{3}H]-naphthalene, m.p. 112·5° (from light petroleum) (lit.,[37] 112°).

2-*Halogeno*[1-^{3}H]*naphthalenes*. The diazonium salt made from 2-amino[1-^{3}H]naphthalene in 6% sulphuric acid was treated with potassium iodide, to give 2-iodo[1-^{3}H]naphthalene, b.p. 138°/9 mm., n_D^{20} 1·7024 (lit.,[38] b.p. 161—162°/15 mm., n_D^{20} 1·7026).

2-Fluoro-, m.p. 61° (after sublimation) (lit.,[22,38] 61°), was prepared from the amine through the diazonium fluoroborate, 2-chloro-, m.p. 59° (after sublimation) (lit.,[38] 59—60°), through the diazonium mercurichloride, and 2-bromo-[1-^{3}H]naphthalene, m.p. 60° (after sublimation) (lit.,[37] 56—57°, 59°, 62°), through the diazonium mercuribromide.

3-*Chloro*[1-^{3}H]*naphthalene*. 1-Acetamido-4-bromo- was converted into 1-bromo-3-chloro-naphthalene,[40] m.p. 56·5° (lit.,[40] 56·5°). The Grignard reagent prepared from the latter in ether was treated with tritiated water, to give 3-chloro[1-^{3}H]naphthalene, m.p. 59°.

5-*Fluoro*[1-^{3}H]*naphthalene*. 1-Amino-5-bromonaphthalene,[41] m.p. 68°, was converted into the diazonium fluoroborate. The residue from thermal decomposition of the latter was extracted with light petroleum, and the extract was passed through a column of alumina and concentrated, to give material of m.p. 25—27°, which was fractionally distilled, to give 1-*bromo*-5-*fluoronaphthalene* (65%), m.p. 30° (Found: C, 52·9; H, 2·7; Br, 35·5; F, 8·4. $C_{10}H_6BrF$ requires C, 53·3; H, 2·7; Br, 35·5; F, 8·4%). The Grignard reagent prepared from the latter in ether gave 5-fluoro-[1-^{3}H]naphthalene, b.p. 92°/13—14 mm., n_D^{25} 1·5913 (lit.,[38] b.p. 91°/13 mm., n_D^{20} 1·5939).

5-*Chloro*[1-^{3}H]*naphthalene*. 1-Amino-5-bromo- was converted through the diazonium mercurichloride into 1-bromo-5-chloro-naphthalene, m.p. 115—116° (lit.,[42] 115—116°). The Grignard reagent from the latter was converted into 5-chloro[1-^{3}H]naphthalene, b.p. 101°/5 mm., n_D^{25} 1·6310.

5-*Bromo*[1-^{3}H]*naphthalene*. 1-Amino-5-bromo- was converted through the diazonium mercuribromide into 1,5-dibromo-naphthalene, m.p. 131° (lit.,[38] 131°). A solution of the latter (0·05 mole) in benzene (150 ml.) was added during 5 min. to n-butyl-lithium (0·025 mole) in ether at 0°. Treatment with tritiated water followed by excess of ordinary water gave, after the usual work-up, 5-bromo[1-^{3}H]-naphthalene (5·2 g., 50%), b.p. 132—134°/7 mm., n_D^{25} 1·6550, and unchanged 1,5-dibromonaphthalene (7 g., 48%).

6-*Chloro*[1-^{3}H]*naphthalene*. 6-Aminonaphthalene-1-sulphonic acid was converted by the Sandmeyer method (cf. ref. 43) into 6-chloronaphthalene-1-sulphonic acid, which was converted into the sulphonyl chloride, m.p. 70°, and hence into the sulphinic acid,[44] m.p. 129°. The latter was converted into 6-chloronaphthalene-1-mercurichloride,[44,45] m.p. 306°, and hence into 6-chloro-1-iodonaphthalene,[46] m.p. 57°. The Grignard reagent made from the latter in ether was converted in the usual way into 6-chloro[1-^{3}H]naphthalene, m.p. 59·5°.

7-*Chloro*[1-^{3}H]*naphthalene*. 1-Amino-7-nitro-, m.p. 132—133°,[47] was converted through the diazonium mercuribromide into 1-bromo-7-nitro-naphthalene, m.p. 134° (lit.,[38] 135°). The latter was reduced with iron powder and ferrous sulphate in water, to give 7-amino-1-bromonaphthalene, m.p. 74° (lit.,[38] 74°), which was converted through the diazonium mercurichloride into 1-bromo-7-chloronaphthalene, m.p. 69° (lit.,[48,49] 69°). The Grignard reagent from the latter gave 7-chloro[1-^{3}H]naphthalene, m.p. 59°.

8-*Halogeno*[1-^{3}H]*naphthalenes*. The preparations of 8-chloro- and 8-fluoro-[1-^{3}H]naphthalene from 8-amino-[1-^{3}H]naphthalene have been described.[50] The amine was also diazotized in 6% sulphuric acid and converted (*i*) by treatment with cuprous bromide into 8-bromo[1-^{3}H]-naphthalene, b.p. 121°/8 mm., n_D^{20} 1·6583, and (*ii*) by treatment with potassium iodide into 8-iodo[1-^{3}H]naphthalene, b.p. 150°/12 mm., n_D^{20} 1·7024 (lit.,[38] b.p. 161—162°/15 mm., n_D^{20} 1·7026).

Methyl[1-^{3}H]*naphthalenes*. 1-Bromo-2-methyl-,[50] b.p. 125—126°/2 mm., was converted through the Grignard reagent into 2-methyl[1-^{3}H]naphthalene, m.p. 35—36° (lit.,[38] 35—36°). Sublimation removed a coloured impurity without changing the m.p. 1-Bromo-3-,[40] b.p. 130°/4 mm., and 1-bromo-4-methylnaphthalene,[7] b.p. 124—126°/2 mm., were likewise respectively converted into 3-, m.p. 35—36° (after sublimation), and 4-methyl[1-^{3}H]naphthalene, b.p. 109°/9—10 mm., n_D^{25} 1·6148 (lit.,[38] b.p. 111°/12 mm., n_D^{25} 1·6147).

1,5-Dibromonaphthalene (0·066 mole) in benzene (200 ml.) was added to n-butyl-lithium (0·5 mole) in ether (150 ml.) at −25°. Methyl iodide (21·6 g., 0·15 mole) was added, the temperature being kept below 0°, and the solution was subsequently stirred for 40 min. and refluxed for 2 hr. The

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usual work-up gave 5-bromo-1-methylnaphthalene (95%), m.p. 64° (lit.,[37] 63—64°), which was converted through the Grignard reagent into 5-methyl[1-^{3}H]naphthalene, b.p. 110°/11—12 mm., n_D^{25} 1·6147.

The Grignard reagent prepared from 6-chloro[1-^{3}H]naphthalene in tetrahydrofuran was treated with dimethyl sulphate, to give 6-methyl[1-^{3}H]naphthalene (33%), m.p. 35°.

1,1,1,3-Tetrachloro-4-*p*-tolylbutane [51] was converted into 7-chloro-1-methylnaphthalene,[52] b.p. 121°/2·5 mm., n_D^{25} 1·6097 (lit.,[52] b.p. 137—138°/12 mm., n_D^{16} 1·6148). The Grignard reagent made from the latter in tetrahydrofuran was treated in the usual way, to give 7-methyl[1-^{3}H]naphthalene, m.p. 35°.

The preparation of 8-methyl[1-^{3}H]naphthalene has been described.[50]

Methoxy[1-^{3}H]*naphthalenes*. Bromination of 2-naphthol in acetic acid gave 1-bromo-2-naphthol, m.p. 84°, which was treated with dimethyl sulphate and aqueous sodium hydroxide to give 1-bromo-2-methoxynaphthalene, m.p. 85° (lit.,[38] 85°). The latter was converted through the Grignard reagent into 2-methoxy[1-^{3}H]naphthalene, m.p. 72·5° (after crystallization from ethanol and sublimation) (lit.,[38] 72·5—73°).

Treatment of 1-naphthol in acetic acid with bromine in the presence of iodine [35] gave 4-bromo-1-naphthol, m.p. 127° (lit.,[37] 128°), which was treated with dimethyl sulphate in anhydrous acetone in the presence of potassium carbonate, to give 4-bromo-1-methoxynaphthalene, b.p. 142—144°/2—3 mm. (lit.,[35] 182°/15 mm.). This was converted through the Grignard reagent into 4-methoxy[1-^{3}H]naphthalene, b.p. 122—124°/8 mm., n_D^{25} 1·6179 (lit.,[37] b.p. 265—266°, $n_D^{13\cdot9}$ 1·6232).

5-Bromo-1-naphthol,[53] m.p. 131°, was converted into 5-bromo-1-methoxynaphthalene,[54] m.p. 68°, which was converted through the Grignard reagent into 5-methoxy[1-^{3}H]naphthalene, b.p. 122—124°/8 mm., n_D^{25} 1·6177.

4-*Phenyl*[1-^{3}H]*naphthalene*. 4-Bromo-1-phenylnaphthalene,[55] m.p. 78°, was converted through the Grignard reagent into 4-phenyl[1-^{3}H]naphthalene, b.p. 147°/1 mm. (lit.,[38] 137—154°/1—1·2 mm.).

4-*Halogeno*[2-^{3}H]*naphthalenes*. 4-Amino-1-nitro-,[56] m.p. 195°, was converted into 4-amino-3-bromo-,[57] m.p. 250°, and hence into 3-bromo-1-nitro-,[57,58] which was reduced by Feynes' method [59] to 1-amino-3-bromo-naphthalene, m.p. 70° (lit.,[58] 70°). This was converted through the diazonium fluoroborate into 1-fluoro-3-bromonaphthalene, m.p. 25° (lit.,[58] 24·5°), and hence, through the Grignard reagent, into 4-fluoro[2-^{3}H]naphthalene, b.p. 73—74°/4·5 mm., n_D^{20} 1·5937.

The diazonium mercurichloride from 1-amino-3-bromo- was decomposed to give 1-chloro-3-bromo-naphthalene, m.p. 59° (lit.,[60] 60°), which was converted through the Grignard reagent, prepared in ether, into 4-chloro[2-^{3}H]naphthalene, b.p. 90°/4·7 mm., n_D^{20} 1·6320.

1-Amino-3-bromonaphthalene was converted, by the method used for 2-amino[1-^{3}H]naphthalene, into 4-amino[2-^{3}H]naphthalene, m.p. 50° (lit.,[61] 50°). The latter was converted through the diazonium mercuribromide into 4-bromo[2-^{3}H]naphthalene, b.p. 128°/6 mm., n_D^{20} 1·6581.

4-Amino[2-^{3}H]naphthalene was diazotized in 6% sulphuric acid, and the solution was treated with potassium iodide, to give 4-iodo[2-^{3}H]naphthalene, b.p. 141—142°/10 mm., n_D^{20} 1·7025.

3-*Halogeno*[2-^{3}H]*naphthalenes*. 3-Amino-2-bromonaphthalene,[59] m.p. 168°, was metallated with 3·5 equiv. of n-butyl-lithium in ether, and the resulting mixture was treated with tritiated water, to give 3-amino[2-^{3}H]naphthalene (31%), m.p. and mixed m.p. 112·5°. The amine was converted through the diazonium fluoroborate into 3-fluoro[2-^{3}H]naphthalene, m.p. 60° (after sublimation).

3-Amino-2-bromonaphthalene was diazotized in 20% hydrochloric acid, and the solution was treated with cuprous chloride to give 2-bromo-3-chloro-, m.p. 126·5° (lit.,[62] 127°), or with potassium iodide to give 2-bromo-3-iodo-naphthalene, m.p. 119·5° (lit.,[63] 120°). The bromo-chloro-compound was converted, through its Grignard reagent prepared in ether, into 3-chloro[2-^{3}H]naphthalene, m.p. 60°. The bromo-iodo-compound was converted into a Grignard reagent by treatment with 1 mol. of magnesium in ether. Hydrolysis with tritiated water, followed by addition of 2-bromo- and 2-iodo-naphthalene to facilitate work-up and fractionation, gave 3-bromo-, b.p. 135°/10 mm., m.p. 61·5°, and 3-iodo[2-^{3}H]naphthalene, b.p. 146°/10 mm., m.p. 55° (lit.,[38] 54·5°).

4-*Halogeno*[1- *and* -3-^{3}H]*naphthalenes*. 1-Amino-2,4-dibromonaphthalene,[64] m.p. 116—117°, was converted into a mixture of 1-amino[2- and -4-^{3}H]naphthalene, m.p. and mixed m.p. 49·5°, by use of the method described for 2-amino[1-^{3}H]naphthalene. The usual methods, utilizing diazonium derivatives as described above, then gave mixed 4-fluoro[1- and -3-^{3}H]naphthalene, b.p. 78°/10 mm., n_D^{20} 1·5940, mixed 4-chloro[1- and -3-^{3}H]naphthalene, b.p. 120°/10 mm., n_D^{20} 1·6321, mixed 4-bromo[1- and -3-^{3}H]naphthalene, b.p. 137°/10 mm., n_D^{20} 1·6585, and mixed 4-iodo[1- and -3-^{3}H]naphthalene, b.p. 148°/10 mm., n_D^{20} 1·7024.

5-, 6-, *and* 7-*Chloro*[2-^{3}H]*naphthalenes*. By methods analogous to those used in the preparation of 6-chloro[1-^{3}H]naphthalene, described above, 5-chloro[2-^{3}H]naphthalene, b.p. 106°/10 mm., n_D^{25} 1·6313, was prepared through 5-aminonaphthalene-2-sulphonic acid, potassium 5-chloronaphthalene-2-sulphonate, 5-chloronaphthalene-2-sulphonyl chloride, m.p. 113°, 5-chloronaphthalene-2-sulphonic acid, m.p. 132°, 5-chloronaphthalene-2-mercuric chloride, m.p. 271°, and 5-chloro-2-iodonaphthalene, m.p. 132° (lit.,[46] 132°).

6-Chloro[2-^{3}H]naphthalene, m.p. 59·5°, was prepared analogously from 6-aminonaphthalene-2-sulphonic acid. The intermediate 6-chloro-2-iodonaphthalene had m.p. 141° (lit.,[46] 141°).

7-Chloro[2-^{3}H]naphthalene, m.p. 59·5°, was likewise prepared from 7-aminonaphthalene-2-sulphonic acid. The

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intermediate 7-chloro-2-iodonaphthalene had m.p. 128·5° (lit.,[46] 129°).

8-*Chloro*[2-^{3}H]*naphthalene*.[47] 1,2,3,4-Tetrahydro-7-nitro-1-oxonaphthalene oxime (30 g.), m.p. 167—169°, in acetic acid (150 ml.), was treated with acetic anhydride (15 ml.). The mixture was heated on a steam-bath for 15 min., then dry hydrogen chloride was passed into the rapidly stirred solution for 70 min. The crude 1-amino-7-nitronaphthalene hydrochloride which separated as a brown solid on cooling was washed with a little acetic acid, then suspended in ice–water and treated with aqueous ammonia (*d* 0·880). The solid obtained was recrystallized from ethanol, to give 1-amino-7-nitronaphthalene (45%), m.p. 132—133° (lit.,[47] 132—133°). The amine was converted by the Sandmeyer method into 7-chloro-nitro-, m.p. 140°, which was reduced [59] to 7-amino-1-chloro-naphthalene, m.p. 69·5° (lit.,[38] 69—70°). This was converted by the Sandmeyer method into 7-bromo-1-chloronaphthalene, m.p. 64° (lit.,[65] 65°), and the Grignard reagent made from the latter in ether was treated with tritiated water, to give 8-chloro[2-^{3}H]naphthalene, b.p. 108°/11 mm., n_D^{20} 1·6320.

8-*Bromo*[2-^{3}H]*naphthalene*. 1-Amino-7-nitro- was converted, through the diazonium mercuribromide, into 1-bromo-7-nitro-naphthalene, m.p. 134°, which was reduced with iron powder, ferrous sulphate, and water, to give 7-amino-1-bromonaphthalene, m.p. 74°. The diazonium salt from the latter was treated with potassium iodide, to give 1-bromo-7-iodonaphthalene, m.p. 50°, which was converted through the Grignard reagent, made by use of 1 equiv. of magnesium in ether, into 8-bromo[2-^{3}H]naphthalene, b.p. 131°/7 mm., n_D^{20} 1·6584.

Methyl[2-^{3}H]*naphthalenes*. The appropriate chloro-[2-^{3}H]naphthalenes were converted, by the method described above for the 6-methyl[1-^{3}H]isomer, into 4-, b.p. 94°/6·8 mm., n_D^{25} 1·6145, 5-, b.p. 107°/10 mm., n_D^{25} 1·6146, 6-, m.p. 34·5°, and 7-methyl[2-^{3}H]naphthalene, m.p. 35°. Likewise, 3- and 8-bromo[2-^{3}H]naphthalene were converted into 3-, m.p. 35°, and 8-methyl[2-^{3}H]naphthalene, b.p. 105°/10 mm., n_D^{25} 1·6147.

Methoxy[2-^{3}H]*naphthalenes*. 2-Bromo-1-methoxynaphthalene,[66] m.p. 59°, was converted through the Grignard reagent into 1-methoxy[2-^{3}H]naphthalene, b.p. 121°/4·7 mm., n_D^{25} 1·6174 (lit.,[37] b.p. 265—266° $n_D^{13\cdot7}$ 1·6232).

3-Bromo-1-, m.p. 73° (lit.,[67] 74°), and 6-bromo-2-methoxynaphthalene, m.p. 108° (lit.,[68] 108°), prepared from the corresponding naphthols,[58,69] were similarly converted into 4-, b.p. 125/6·9 mm., n_D^{25} 1·6174, and 6-methoxy[2-^{3}H]-naphthalene, m.p. 72·5°.

2-Methoxynaphthalene, m.p. 72°, was metallated with n-butyl-lithium.[70] Treatment with tritiated water gave 3-methoxy[2-^{3}H]naphthalene, m.p. 72·5°.

Rate Measurements.—Rates of detritiation in anhydrous trifluoroacetic acid were determined as previously described.[1,71] With the mixtures of 4-halogeno[1- and 4-halogeno[3-^{3}H]naphthalenes, the first-order plot showed two distinct linear positions. The first gave the rate constants for the 4-X-[1-^{3}H]-compound, and for X = F, Cl, and Br these were identical within experimental error (±2%) with those obtained with separately prepared authentic samples of the 4-X-[1-^{3}H]naphthalenes. The second linear position gave the rate for the 4-X-[3-^{3}H]naphthalenes (*i.e.*, the 1-X-[2-^{3}H]naphthalenes). (This type of dual rate constant measurement has been used previously with, for example, detritiation of [1- and 2-^{3}H]biphenylene.[72]) The runs were less satisfactory for the 4-I-[1-^{3}H]- and 1-I-[2-^{3}H]-naphthalenes, and the results of these compounds in Tables 1 and 2 must be regarded as approximate.

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