Electrophilic Aromatic Substitution. Part 35.[1] Deviations from Additivity of Methyl Substituent Effects in Detritiation of Dimethylnaphthalenes: the Effect of Electron Supply on Bond Fixation

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Rate coefficients have been measured for protiodetritiation in anhydrous trifluoroacetic acid at 70 °C of all positions of 1,3-, 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, and 2,7-dimethylnaphthalenes. The derived partial rate factors show up to 10-fold departure from those calculated on the basis of additivity of the individual methyl substituent effects. Of the seventeen positions examined, all but three show reactivity which is greater than that calculated. The results point to a decrease in bond fixation in dimethylnaphthalenes compared to monomethylnaphthalenes, probably arising either from the increased electron supply in the former or from a sterically facilitated change in the shape of the naphthalene nucleus. Detritiation of 1,8-dimethylnaphthalene is accompanied by isomerisation to 1,7-dimethylnaphthalene due almost certainly to a sterically accelerated 1,2-methyl shift; this shift (which is the first observed during hydrogen exchange studies) accounts for discrepancies between previous measurements of the exchange rate of the (relatively unreactive) 3-position of 1,8-dimethylnaphthalene. The kinetics show that surface-catalysed protiodemethylation accompanies detritiation of 1,4-dimethylnaphthalene and this is aided by the high stability of the intermediate for this *ipso*-substitution.

Some years ago one of us measured the methyl substituent effects in protiodetritiation of naphthalene in anhydrous trifluoroacetic acid at 70 °C. The activating effects of a 1- or 2-methyl substituent upon each position of the naphthalene ring are shown in Figure 1 along with the corresponding values for benzene (in this latter case these values are the partial rate factors).[2] These data (supported by those for other substituents) showed very nicely the effect of bond fixation in naphthalene. Thus the naphthalene 1,2- and 2,3-bond orders are higher (1.756) and lower (1.570), respectively,[3] than that in benzene (1.667) and the corresponding *ortho*-methyl activating factors are 300, 3.59, and 219. Noticeable in these results (though attention has not been previously drawn to it) is the fact that although the differences between the benzene bond order and those of the 1,2- and 2,3-bonds is 0.089 and 0.097, respectively (*i.e.* closely similar), the increase in the bond order of the 1,2-bond relative to benzene produces only a modest increase in activating effect, whereas the corresponding decrease in the order of the 1,2-bond relative to that in benzene produces a large decrease in activating effect. We may therefore construct a simple picture of the effect of an electron-supplying substituent *vs.* bond order (Figure 2) where the point on the curve represents the benzene case, *i.e.* an increase in bond order relative to this produces a small increase in substituent activation whereas a comparable decrease in bond order produces a large decrease in activation. This analysis is crucial to interpretation of the results which we have obtained.

Our interest in dimethylnaphthalenes arose from the need to have accurate partial rate factors for exchange at the 2- and 4-position of 1,3-dimethylnaphthalene (I) in order to be able to analyse data for exchange in the cyclophanes (II), the main subject of our enquiry. The results showed that the reactivity of (I) was substantially different from that predicted on the basis of additivity of the methyl substituent effects. This prompted us to recall that the rates of deuteriation of a series of dimethylnaphthalenes had been determined by Dallinga *et al.*[4] (Table 1) but these results could not be properly analysed in terms of the rates of detritiation of monomethylnaphthalenes for reasons to which we previously drew attention.[5] These are as follows.

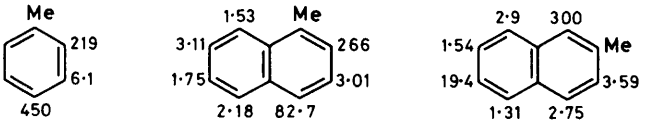


Figure 1. Activating effects of methyl substituents upon the rates of aromatic detritiation (anhydrous trifluoroacetic acid, 70 °C) at the positions indicated by the numbers

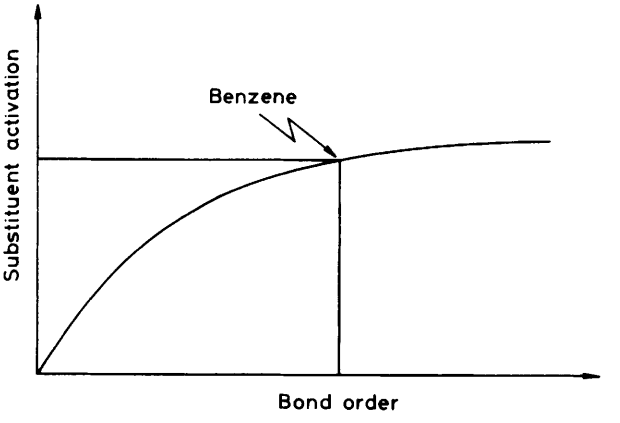
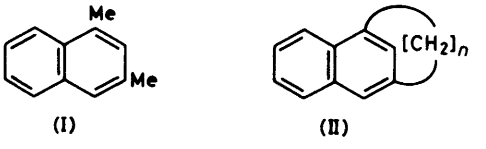


Figure 2. Variation of substituent activation with bond order



(i) The ρ factors for deuteriation and detritiation are not the same.

(ii) The rates of deuteriation were determined *via* mass spectrometry and involving a complicated procedure subject to considerable error.

Table 1. Rate data for deuteriation of dimethylnaphthalenes [a]

Compound	Position	$10^7 k/s^{-1}$	Activating effect of methyl groups	Observed [b] : calculated [c] effect of methyls
(Naphthalene)	1	9.0		
	2	1.19		
1,4-Dimethylnaphthalene	2	889	74	0.9
	5	83.3	9.85	2.8
	6	15.0	12.6	2.4
1,5-Dimethylnaphthalene	2	461	388	0.8
	3	18.6	15.6	1.7
	4	3 445	383	3.0
1,8-Dimethylnaphthalene	2	2 140	1 800	2.2
	3	7.5	6.3	1.2
	4	2 140	237	1.3
2,3-Dimethylnaphthalene	1	15 300	1 700	2.1
	5	483	54	2.1
	6	83.3	70	2.3
2,6-Dimethylnaphthalene	1	13 200	1 470	3.7
	3	86.1	72	13
	4	278	31	3.9
2,7-Dimethylnaphthalene	1	35 800	3 980	4.6
	3	411	345	5.0
	4	103	11	3.1

[a] Ref. 4. [b] In deuteriation. [c] Based on data for detritiation.

(iii) The medium used for deuteriation, *viz.* CH_3CO_2D–HPO_2F_2–CCl_4 at 20 °C is a unique condition for hydrogen exchange and no other data have been obtained using it. However, the exchange rates at the α- and β-position of naphthalene were determined under this condition which permitted calculation of the combined activation effects of the methyl substituents at each position and these are also given in Table 1. In the last column of Table 1 we give the ratios of these observed activations to those calculated on the basis of additivity of the monomethyl substituent effects in detritiation. There is a wide discrepancy in the values in this column which cannot be due to differences between the exchange reactions and conditions since if this were so an approximately constant discrepancy should result. The discrepancy must therefore be either real, or due to experimental error. First inspection suggests that the former cannot be the case since in the majority of cases, activation by the methyl substituent is greater than predicted. This is contrary to the general observation that the effects of activating substituents decrease the more reactive a substrate, because the transition state is nearer to the ground state. This has been best illustrated by the data for detritiation of polymethylbenzenes [6] where the effect of each additional methyl group decreases, the more reactive the substrate. On the other hand our data for 1,3-dimethylnaphthalene (a compound not investigated by Dallinga and his co-workers) suggested that there is indeed a real discrepancy in the results, and one of such novelty as to demand reinvestigation of exchange in dimethylnaphthalenes under the more rigorous conditions of detritiation. We therefore undertook this work and our results will show that whilst there is a substantial error in the data given in Table 1, there are indeed discrepancies of the kind indicated (though different in magnitude).

Results and Discussion

The rate coefficients for detritiation are given in Table 2. The data for naphthalene are from previous work as is the rate coefficient for exchange in mesitylene in 100% CF_3CO_2H.[6] This latter is 314.5 times greater than the rate coefficient for exchange in 50 v/v CF_3CO_2H in HOAc, and this factor was used to determine the otherwise inaccessible rate of exchange of the 4-position of 1,3-dimethylnaphthalene in 100% CF_3CO_2H from the value in the less acidic medium. The relative rates of exchange of the 2-position of 1,3-dimethylnaphthalene in 100% CF_3CO_2H at 70 and 30 °C was 27.95 and we used this value to determine the rate coefficients for exchange at the 1-position of 2,3-, 2,6-, and 2,7-dimethylnaphthalene at 70 °C from the data at 30 °C. (The correction factor will of course vary slightly according to the activation energies but the differences will be small. A previous determination of the relative exchange rates of the 5-position of acenaphthene at 70 and 30 °C gave a value of 28.8,[7] in close agreement with the value reported here).

From the exchange rate coefficients at 70 °C we obtain the partial rate factors by dividing with the rate coefficient for exchange of a position in benzene under the same conditions [8] (0.095×10^{-7} s^{-1}), and hence the σ^+-values, both parameters being given in Table 2. In Table 3 we show the activation of a given site by the methyl substituents *i.e.* the partial rate factors in Table 2 divided by the appropriate partial rate factors for the 1- or 2-position of naphthalene (1 150 and 151, respectively), and for comparison the activation calculated on the basis of additivity. The ratio of the former to the latter is given in Figure 3. Exchange in the 5- and 6-positions of 2,3-dimethylnaphthalene is predicted to be at approximately the same rate though one is found to be much slower than the other. Dallinga *et al.* assigned the slower exchange to the 6-position though their reason for doing so was unclear. To resolve the problem we partially deuteriated a sample by exchange with CF_3CO_2D and examined the n.m.r. spectrum (see Experimental) which confirmed that the slower exchange did indeed take place at the 6-position. Exchange in 1,8- and 1,4-dimethylnaphthalenes was accompanied by dealkylation which did not however significantly affect the rate data, and is described in detail below.

Our ratios of observed to calculated reactivities are on the whole consistent with the approximate values which could be deduced from the work of Dallinga *et al.*, though there are differences in relative reactivities in some molecules and in the

Table 2. Rate coefficients, partial rate factors, and σ^+-values for detritiation of dimethylnaphthalenes in trifluoroacetic acid

Compound no.	Substituents	Exchange position	T/°C	$10^7 k/s^{-1}$	f	σ^+
		1	70	110	1 150	−0.35
		2	70	14.3	151	−0.25
(1)	1,3-Me_2	2	30	959		
		2	70	26 800	282 000	−0.623
		4	70	3 480 [a]	11 500 000	−0.807
		5,7,8	70	1 300	(13 700)	
(2)	1,4-Me_2	2	70	4 760	50 100	−0.537
		5	70	659	6 940	−0.439
		6	70	205	2 160	−0.381
		b	70	~25		
(3)	1,5-Me_2	2	70	3 130	33 000	−0.516
		3	70	288	3 030	−0.398
		4	70	13 200	139 000	−0.588
(4)	1,8-Me_2	2	70	9 800	109 000	−0.576
		3	70	173	1 820	−0.373
		4	70	20 000	211 000	−0.608
(5)	2,3-Me_2	1	30	3 410	1 000 000	−0.686
		5	70	2 290	24 100	−0.501
		6	70	662	6 970	−0.439
(6)	2,6-Me_2	1	30	3 420	1 010 000	−0.686
		3	70	766	8 060	−0.446
		4	70	2 980	31 400	−0.514
(7)	2,7-Me_2	1	30	12 800	3 770 000	−0.752
		3	70	2 470	26 000	−0.505
		4	70	774	8 150	−0.447
	(Mesitylene)	1	70	674 500		
		1	70	2 145 [a]		

[a] Medium consisted of 50% v/v CF_3CO_2H in HOAc. [b] See text.

Table 3. Observed and calculated activation by dimethyl substituents in naphthalene

Substituents	Position	Activating effect: Observed	Activating effect: Calculated	Observed : calculated activation
1,3-Me_2	2	1 870	955	1.96
	4	10 000	24 800	0.403
	(5,7,8)	(37.7) [c]	(27.2) [a]	1.39
1,4-Me_2	2	332	801	0.414
	5	6.03	3.34	1.81
	6	14.3	5.44	2.63
1,5-Me_2	2	219	466	0.47
	3	20.1	9.36	2.15
	4	121	127	0.95
1,8-Me_2	2	722	827	0.873
	3	12.1	5.27	2.30
	4	184	180	1.02
2,3-Me_2	1	870	825	1.05
	5	21.0	3.80	5.53
	6	46.2	29.9	1.55
2,6-Me_2	1	878	393	2.23
	3	53.4	5.53	9.67
	4	27.3	7.98	3.42
2,7-Me_2	1	3 280	870	3.77
	3	172	69.6	2.47
	4	7.09	3.60	1.97

[a] Average value.

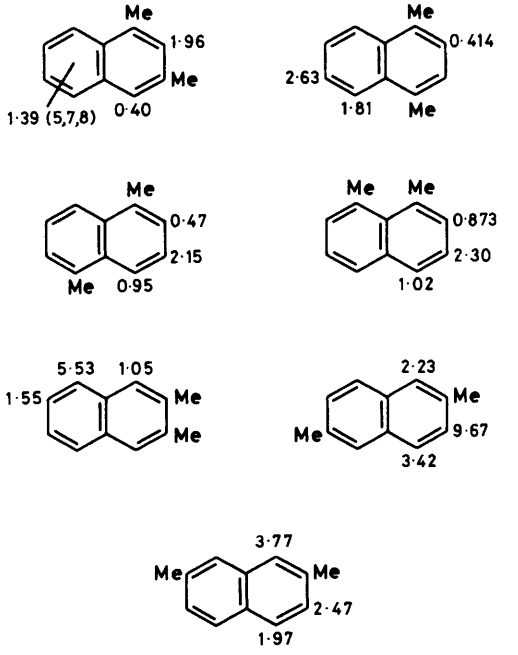
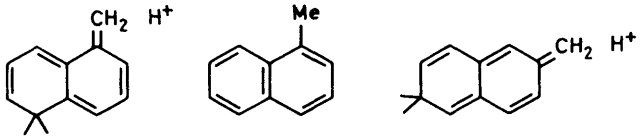


Figure 3. Ratio of observed to calculated reactivities at the positions indicated

rate differences overall, as we had anticipated in view of the inaccuracies inherent in the deuteriation method. Before discussing our results it is appropriate to recall the main features evident from exchange in monomethylnaphthalenes, as follows.

(i) Because of bond order differences and the shape of Figure 1, two *ortho*-methyl substituents *i.e.* at positions 1 and 3 in naphthalene will collectively activate *much* less than two *ortho*-methyl substituents in benzene *viz.* by a factor of 44. Any tendency to reduce bond fixation will increase the reactivity of a site activated in this way.

(ii) The activation of non-conjugated positions in methylnaphthalene is low relative to that of a *meta* site in toluene,



(III) (IV) (V)

probably as a result of intervening bonds of low bond-order being the limiting factor governing transmission of electronic effects. A reduction in bond fixation should therefore increase the activation of non-conjugated positions.

(iii) Bond fixation causes very poor conjugation between one ring and another. This is evident for example in the data for 1-methylnaphthalene (Figure 1) where conjugated positions in the unmethylated ring are barely more activated than the conjugated positions. This is because conjugation requires structures such as (III) in which the double bonds are unfavourably located relative to the ground state (IV).[9] It follows therefore that if bond fixation is diminished then structures such as (III) do not become so unfavourable.

(iv) The exception to (iii) is the 2,6-interaction (V) which is quite strong because structure (V) is relatively stable.[10] This interaction also has a fairly high substituent activation factor A_f, itself a measure of the effect of bond fixation.[11] Consequently any decrease in bond fixation will tend to reduce the 2,6-interaction.

With these factors in mind we can now consider the dimethylnaphthalene results.

(i) Reaction at the 2-positions of compounds (1), (2), (3), and (4), all of which have a 1-methyl substituent. The reactivity in the latter three compounds is less than predicted which would arise if the order of the 1,2-bond is decreased. The 2-position of compounds (2) and (3) is also non-conjugated with respect to the other methyl substituent and so there should be some compensation of the first effect, but evidently not enough to outweigh it. In compound (4) the 2-position is conjugated with the second methyl group and this conjugation should increase as bond fixation decreases. The overall reactivity then turns out to be almost exactly that predicted. Comparison of the results for compounds (3) and (4) shows that the conjugative inter-ring interaction is improved more than the non-conjugative interaction by a decrease in bond fixation, and this feature manifests itself in two other results (below).

The 2-position of compound (1) is *more* reactive than predicted, and this is because it is *ortho* to two methyl groups and the consequences of decreased bond fixation, as described above.

(ii) Reaction at the 4-position of compounds (1), (3), and (4). There is good conjugation between the 1- and 4-positions (high substituent activation factor A_f)[11] therefore this interaction should be less favourable if bond fixation decreases, consequently each position should be less reactive as a result of this effect. In compound (1) in addition, position 4 has an adjacent 3-methyl group so there is a 1,2-interaction which should decrease if bond fixation decreases. Both effects combine therefore to make the 4-position of compound (1) less reactive than predicted.

For compounds (3) and (4) there is a 1,5- (conjugated) and a 1,8- (non-conjugated) interaction between the 4-position and methyl in the other ring. These interactions should be increased by a decrease in bond fixation, compensating for the reduced 1,4-interaction so that the overall observed reactivity is close to that predicted. It is again noticeable that the increase in reactivity is higher in compound (4) which has the conjugative inter-ring interaction [*cf.* (i) above].

(iii) Reaction at the 3-position of compounds (3) and (4), the 1-position of compound (5), and the 4-position of compounds (6) and (7). In each of these, reaction takes place *meta* to methyl in the same ring so that the observed reactivity should be higher than predicted if bond fixation is diminished; this is found to be the case. However in compound (5) the 1-position is adjacent to a 2-methyl substituent and the 1,2-interaction will be reduced by less bond fixation, so the two effects compensate giving an overall reactivity only slightly greater than predicted. For the remaining positions the reactivity should be enhanced by increased interaction from the methyl substituent in the other ring so that the overall increase in reactivity is quite substantiated. Once again it is evident that in the compound with the greatest increase in reactivity [compound (6)] the reaction site is conjugated with methyl in the other ring.

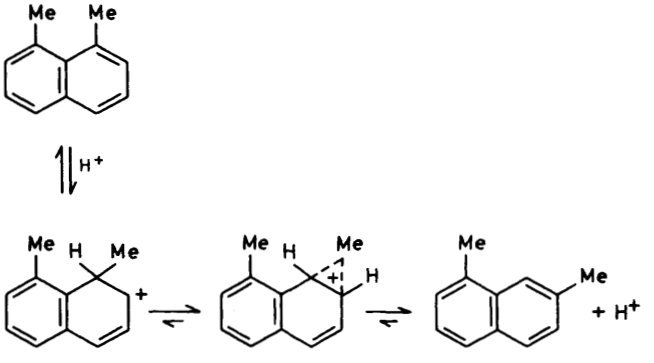
(iv) Reaction at the 3-position of compounds (6) and (7). In these there is a 2-methyl substituent and if bond fixation decreases, then the observed reactivity should be substantially greater than predicted, which is the case. There is a marked difference between the two compounds in the magnitude of the deviation and this follows because the second methyl substituent in compound (7) has a 2,6-relationship with the reaction site, and this interaction should decrease significantly.

(v) Reaction at the 5—8-positions of compound (1), the 5- and 6-positions of compound (2), and the 5- and 6-positions of compound (5). All these positions show exalted reactivity because the transmission of electronic effects between the rings will be increased by a decrease in bond fixation. In compound (5) the 6-position shows much less increase in reactivity than does the 5-position and this follows from the diminished 2,6-interaction adversely affecting the former position.

(vi) Reaction at the 1-position of compounds (6) and (7). In the latter the reaction site is conjugated with methyl in the other ring so here again the reactivity is enhanced more than is the case for compound (6) where there is no conjugation. However we would have expected that the dominant factor would have been the decreased bond order of the 1,2-bond so that overall both 1-positions would have been less reactive than predicted [*cf.* the reactivities of the 2-positions of compounds (2) and (3)]. Evidently there is an additional factor operating but at present we are unable to suggest what this might be.

The question arises as to why the introduction of a second methyl substituent causes a change in bond order (if indeed this is what happens). One strong possibility must be that steric interactions cause changes in the shapes of the molecules with corresponding changes in bond lengths. It may also be that the increased electron supply into the naphthalene nucleus produces a levelling of the bond orders.

Side Reactions.—(i) 1,8-*Dimethylnaphthalenes.* Our method for preparatively incorporating tritium into the dimethylnaphthalenes involved heating a sample with tritiated water and trifluoroacetic acid at 70 °C for a time calculated (on the basis of additivity of the individual methyl substituent effects) to give > 95% incorporation into the least reactive position. The ampoules were then cooled, opened, neutralized, and extracted to give the tritiated dimethylnaphthalenes. The purity of each was checked by g.l.c. whence it was discovered that the product from tritiation of 1,8-dimethylnaphthalene consisted of 30% of this isomer and 70% of another, identified by n.m.r. as the 1,7-isomer. Koptyug and co-workers,[12] and Lammertsma and Cerfontain [13] have both recently reported that 1,8-dimethylnaphthalene isomerises to 1,7-dimethylnaphthalene in the presence of superacids, but there has been no report of this occurring under the mild conditions that we used. Indeed this is the first observation of a 1,2-methyl shift (VI) accompanying hydrogen exchange and is clearly aided by



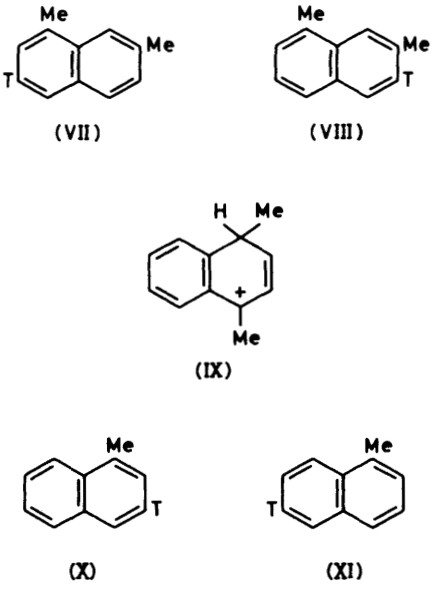
(IV)

both steric acceleration, and the high reactivity of the 1-position of naphthalene towards electrophilic substitution. 2,3-Dimethylnaphthalene does not undergo a similar reaction because the steric interaction is reduced by the unusually long 2,3-bond, and the 2-position is much less reactive towards electrophilic substitution. Under more drastic conditions (CF_3CO_2H containing 2.3 mol % CF_3SO_3H, 70 °C, 28 days) all of the 1,8-dimethylnaphthalene was converted into 1,7-dimethylnaphthalene and other isomers, which we did not identify but assume that the 2,7-isomer would be a major component.

There have been two previous kinetic studies of hydrogen exchange in 1,8-dimethylnaphthalene, and one of these involved detritiation of the specifically labelled isomers in CF_3CO_2H at 30 °C.[14] We previously calculated the rate coefficients ($10^7k/s^{-1}$) at 70 °C from these results by using the activation energy for detritiation of acenaphthalene which is of comparable reactivity, and obtained the values: 124 000 (exchange position 2); 1 825 (3); 230 000 (4).[7] This compound was re-examined in the present work merely to confirm the extrapolation and the results in Table 2 show that there is close agreement between the two sets of data. In our earlier report we drew attention to the fact that there was marked disagreement in the positional reactivity ratios (especially the reactivity of the 3-isomer relative to the others) obtained in detritiation in trifluoroacetic acid,[14] and deuteriation in CH_3CO_2D–HPO_2F_2–CCl_4,[4] a more acidic medium. It now seems very probable that the discrepancy arises because of the accompanying rearrangement which would be more serious under the deuteriation conditions and would of course be most likely to affect the observed exchange rate of the slowest isomer. Rearrangement of this would give (VII) and (VIII); the former should be substantially more reactive than [3-^{3}H]-1,8-dimethylnaphthalene whereas the latter should be of comparable reactivity.

One curious feature which we are unable to explain arose during the preparative tritiation of 1,2-dimethylnaphthalene which involved heating the inactive material with T_2O–CF_3CO_2H at 70 °C during 1.5 h. After this time there should have been *ca.* 99% of theoretical incorporation into the 2- and 4-positions and *ca.* 9% in the 3-position. However the kinetics indicated that 25% of the tritium was in the 3-position which could only arise if the tritium migrated around the ring in which case anomalous kinetics should have been observed in detritiation of the specifically labelled 2- and 4-tritiated isomers; none was reported however.[14]

(ii) 1,4-*Dimethylnaphthalene*. The kinetic studies with this compound revealed four separate rate coefficients (Table 2)



(VII) (VIII) (IX) (X) (XI)

the lowest of which was much too small to be due to exchange in a dimethylnaphthalene. The probability that tritium could have been incorporated into the methyl groups during tritiation, as a result of side-chain exchange (as would be the subsequent detritiation) was discounted by heating with ethanolic sodium ethoxide during 7 days, but no change in specific activity was observed. Side-chain exchange was further disproved by the observation that the proportion of the total exchange due to the slow reaction was not constant, but varied inversely as the concentration of the aromatic. Thus after 150 h (at which time the three fast exchanges had effectively ceased) the activity due to the slow-reacting species as a percentage of the initial activity was 2.2, 4.0, and 6.3% for 0.056, 0.044, and 0.28% solutions of aromatic in trifluoroacetic acid. We have observed similar phenomena before in detritiation of alkylbenzenes possessing bulky alkyl groups, where there is steric acceleration towards protiodealkylation, which is surface catalysed.[15]

To examine this reaction further, 1,4-dimethylnaphthalene (and also the 1,5-isomer for comparison) was allowed to react with CF_3SO_3H in CF_3CO_2H as described above for the 1,8-isomer. Whereas the 1,5-compound was completely stable, the 1,4-isomer had completely protiodealkylated to give 1-methylnaphthalene (and some other dimethylnaphthalenes), a reaction obviously aided by the high stability of the intermediate (IX); this protonated species was observed in superacid by Lammertsma and Cerfontain,[13] and the corresponding reaction occurs in nitration [16] and bromination.[17]

Because the dealkylation is slow relative to the two fastest exchanges (shown by the amount of the original tritium content involved in the slow exchange) then before appreciable dealkylation has occurred, tritium has exchanged out of the 2- and 5-positions. Thus dealkylation is effectively of [6-^{3}H]-1,4-dimethylnaphthalene which would give either (X) or (XI), the rate coefficients for exchange of which are 43×10^{-7} s^{-1} and 25×10^{-7} s^{-1}, respectively. These values are in close agreement with that which we observe, itself rather inaccurate because surface-catalysed dealkylation always produces scattered kinetic plots.

Experimental

All the dimethylnaphthalenes (except the 2,7-isomers) were commercial samples recrystallised before use. The 2,7-isomer

was prepared in 5% overall yield from *m*-xylene by the literature method.[18] Tritium was incorporated by heating the dimethylnaphthalene (1 g, 0.0064 mol), trifluoroacetic acid (10 ml, 0.135 mol), and tritiated water (0.1 ml of 100 mCi g^{-1} activity, 0.0056 mol) in a sealed ampoule at 70 °C for at least five times the half-life of the estimated slowest exchange rate within the given aromatic. In some cases further batches were heated for substantially shorter times to reduce incorporation into the slowest site in order to simplify the kinetics. The ampoules were cooled, opened, neutralized, and the dimethylnaphthalene was extracted and purified either by fractional distillation for the liquids and recrystallization (twice) from methanol for the solids. The products had between 0.5 and 1.5 mCi g^{-1} specific activity.

Kinetic Studies.—These were carried out in the usual way [19] and because each compound had a number of different exchangeable hydrogens, non-linear kinetic plots of log (c.p.s.) *vs.* time were obtained. These were separated into the first-order components in the standard way, *i.e.* the plots were followed until they assumed a linear form, due to exchange at the slowest position. This was generally followed to at least 90% of total exchange to confirm that no deviation from this linearity occurred. The linear portion gave the rate coefficient for the slow exchange from which the activities due to the faster isomer at various times could be calculated. These in turn then gave a linear first-order plot in most cases, because one isomer was so much more reactive than the other that it had already exchanged at 70 °C before the first measurement could be made; these fast rates were therefore measured at lower temperature and corrected to those at 70 °C as described in the Results. If however a non-linear plot was obtained, then the analytical process described above was repeated to separate the two rates. Because of this method of analysis, some thirty or more points were used in each kinetic run. The kinetic data (accurate to ±2%) are given in Table 2.

Because in each molecule the predicted reactivities of each position differ widely there was no difficulty in assigning exchange rates to position, except in the case of the 5- and 6-positions of 2,3-dimethylnaphthalene, which are predicted positions of 2,3-dimethylnaphthalene, which are predicted to be closely similar. Dallinga *et al.* assigned the slowest rate to the 6-position but gave no reason for doing so. The n.m.r. spectrum of 2,3-dimethylnaphthalene shows three groups of aromatic protons, τ(CCl_4) 2.39 (m), 2.51 (s), and 2.72 (m). Since the benzo-substituent has a $-I$ effect then the α-protons of naphthalene appear more downfield than the β-protons. Taking into account the $+I$ effect of the methyl groups and the splitting, the above peaks may be assigned to the 5-, 1-, and 6-protons respectively. We allowed 2,3-dimethylnaphthalene to react with deuteriated trifluoroacetic acid for a time sufficient to produce *ca.* 40% exchange. After this time the integrated peak areas showed deuterium to have entered the positions in the order $1 > 5 > 6$, so that the assignment of rates given by Dallinga *et al.* was correct.

References

1 Part 34, W. J. Archer, R. Cook, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1983, 813.
2 C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc., B*, 1968, 1112.
3 O. W. Adams and R. L. Miller, *J. Am. Chem. Soc.*, 1966, **88**, 404.
4 G. Dallinga, P. J. Smit, and E. L. Mackor, *Mol. Phys.*, 1960, **3**, 130.
5 R. Taylor, *Comprehensive Chem. Kinet.*, 1972, **13**, 258.
6 See R. Taylor, 'Aromatic and Heteroaromatic Chemistry,' (Specialist Periodical Report), The Chemical Society, London, 1974, vol. 2, p. 226 for data and references.
7 H. V. Ansell and R. Taylor, *Tetrahedron Lett.*, 1971, 4915.
8 H. V. Ansell and R. Taylor, *J. Chem. Soc., Chem. Commun.*, 1973, 952.
9 E. Glyde and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1783.
10 H. G. Benson and J. N. Murrell, *J. Chem. Soc., Faraday Trans. 2*, 1972, 129.
11 W. J. Archer and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1153.
12 V. I. Rodionov, M. M. Shakirov, I. S. Isaev, and V. A. Koptyug, *J. Org. Chem. U.S.S.R.*, 1979, **16**, 1303.
13 K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.*, 1979, **101**, 3618.
14 M. C. A. Opie, G. J. Wright, and J. Vaughan, *Aust. J. Chem.*, 1971, **24**, 1205.
15 M. M. J. Le Guen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1976, 559.
16 A. Fischer and A. L. Wilkinson, *Can. J. Chem.*, 1972, **50**, 3988.
17 E. Berliner, J. B. Kim, and M. Link, *J. Org. Chem.*, 1968, **33**, 1160.
18 J. W. Mocydlarz, P. Cononne, and L. C. Leitch, *Synthesis*, 1974, **8**, 566.
19 J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 1964, 4641.

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