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AROMATIC DETRITIATION V.[1]

ON THE DETRITIATION OF 1, 8-DIMETHYLNAPHTHALENE, ACENAPHTHENE, AND PERINAPHTHANE.

By H.V. Ansell and R. Taylor

School of Molecular Sciences, University of Sussex,

Brighton BN1 9QJ, Sussex, England.

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The observation by Mackor *et al.*[2] that acenaphthene is more reactive than 1, 8-dimethylnaphthalene at each nuclear position in hydrogen exchange has recently been confirmed by Opie *et al.*[3], who studied detritiation in anhydrous trifluoroacetic acid, *cf.* deuteration in trifluoroacetic acid-difluorohypophosphorous acid-carbon tetrachloride used by the former workers. Both sets of work are in good quantitative agreement in giving an *ortho*:*para*-ratio of *ca.* 0·4 for acenaphthene and a 20-fold increase in reactivity of the *para*-position in acenaphthene over the corresponding position in 1, 8-dimethylnaphthalene.

We too have measured rates of protiodetritiation of the *para*-position of acenaphthene in anhydrous trifluoroacetic acid, and our rates (10^7k) at 0·18° (672), 15·0° (3, 371), and 25° (9, 518) yield a good Arrhenius plot ($E_{act.}$ = 17·1 kcal/mole) and a predicted rate at 30° of 14, 900 which is in satisfactory agreement with that (13, 800) given in ref. 3, bearing in mind the small differences in rates often obtained by different workers using this medium[4].

In analysing their results, Opie *et al.*[3] have unfortunately made an error in calculating the predicted partial rate factors for 1, 8-dimethylnaphthalene (based on our earlier results on methyl naphthalenes[5] and the additivity principle), and which vitiates much of their discussion. We therefore offer our interpretation of the rate data because we believe that these when taken along with other data in the literature, provide the first example of steric enhancement of hyperconjugation in electrophilic aromatic substitution. For simplification we express all of their rates in terms of partial rate factors (relative to a single position in benzene) calculated at 70° for consistency with all previous work with this medium; in doing so we have extrapolated our rate for acenaphthene to 70°, and likewise treated their data using our activation energy for the 5-acenaphthene position. This may introduce a slight error for the other positions but this will be of inconsequential magnitude as far as this analysis is concerned. The observed partial rate factors together with those correctly calculated on the basis of the additivity principle from the previous data[5], are given in the Table, from which it is clear that, contrary to the beliefs of Opie *et al.*[3], their experimentally observed rate factors for the *ortho*- and *para*-positions of 1, 8-dimethylnaphthalene are in *excellent* agreement with those predicted. Consequently the mode of operation of electronic effects in 1, 8-dimethylnaphthalene is not different from that in the monomethylnaphthalenes. (The less satisfactory agreement for the *meta*-position may reflect greater experimental error in measuring the rate of this position which is unreactive relative to the possible isomeric impurities and in this connexion it may be significant that Opie *et al*. obtained a ratio of *meta*:*ortho*-substitution of 0·0147 *cf.* 0·0085 by Mackor *et al.*[2] and 0·0064 predicted.)

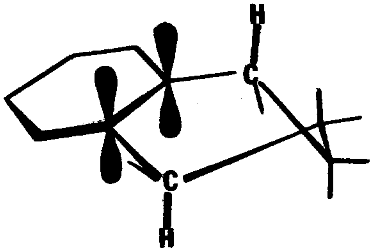
TABLE

Partial rate factors for protodetritiation (70°)

Position	f(obs.)	f(calc.)
[2-^{3}H]-1, 8-Dimethylnaphthalene	124,000	125,000
[3-^{3}H]- "	1,825	795
[4-^{3}H]- "	230,000	210,000
[3-^{3}H]-Acenaphthene	1,680,000	
[4-^{3}H]- "	3,100	
[5-^{3}H] "	4,520,000	
[4-^{3}H]-Perinaphthane	309,000	
[5-^{3}H]- "	1,365	
[6-^{3}H]- "	895,000	

Now since there is no evidence whatsoever of any steric hindrance to hydrogen exchange of the monomethylnaphthalenes, the truly excellent agreement of the predicted and observed reactivities at the *ortho*- and *para*-positions of 1, 8-dimethylnaphthalene shows that *there cannot be any significant hindrance to exchange at these positions either*. The rate enhancement observed in hydrogen exchange of acenaphthene does *not* therefore arise from a more sterically favourably environment for the electrophile, (and it is therefore probable that the enhanced rate of nitration[6] and bromination[7] of acenaphthene over that of 1, 8-dimethylnaphthalene derives largely or entirely from electronic origins). We also do not believe that bond-order-strain theories can be satisfactorily applied to account for the enhanced *meta*-reactivity of acenaphthene (as proposed by Opie *et al.*[3]) and we propose therefore that the rate enhancement at all three positions is *entirely electronic in origin*. We suggest that the carbons in the strained ethylene bridge adopt a hybridisation tending towards sp^2 (as they do for example in cyclopropane and cyclobutane[8]) and this produces an enhanced conjugative electron release. Consequently we should expect a larger rate enhancement at the *ortho*- and *para*-positions than at the *meta*, exactly as observed. It should also be noted that whereas it appears that the relative reactivities at the *ortho*- and *para*-positions in 1, 8-dimethylnaphthalene and acenaphthene are different, this is illusory and derives from the failure to use a linear free energy analysis. In fact, $\log f_o : \log f_p$ is exactly the same (0·95) for both molecules. (For a discussion of the general principles involved here, see ref. 9).

The greater reactivity of perinaphthane relative to 1, 8-dimethylnaphthalene has a precedent to which we have previously drawn attention, namely the greater reactivity of tetralin relative to *o*-xylene[10], and, as in the presence case, the greater activation by the cyclic substituent cannot be reasonably attributed to strain effects. Significantly, the difference in rate between tetralin and *o*-xylene (*ca*. 2) is similar to, and slightly less than, the present use. We suggested that for these two molecules the difference might stem from the fact that the inductive order of alkyl group activation is obtained in hydrogen exchange in trifluoroacetic acid (since the cyclic substituent contains extra carbon atoms[10, 11]). We now suggest a further contributory and probably decisive factor. In the lowest energy conformers of both tetralin (I) and perinaphthane (II) the side chain α-carbon atoms are so constrained such that one of the C-H bonds is favourably aligned for stabilisation of the empty *p*-orbital of the adjacent ring carbon by hyperconjugation (see Figure); the alignment is perfect for perinaphthane and slightly less so for tetralin which



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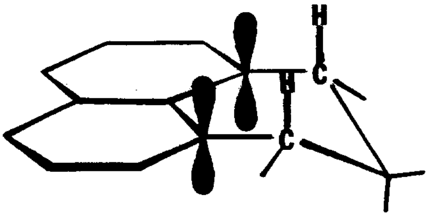

II

accords precisely with the order of experimental enhancement. Such effects will be less important in reactions with less demand for resonance stabilisation of transition states and consequently the marginal greater reactivity of tetralin over o-xylene in protodesilylation[10, 12] follows; we predict therefore that the reactivity of the para- position of perinaphthane and 1,8-dimethylnaphthalene will be closely similar in protodesilylation. It also follows that rate enhancement of perinaphthane over that of 1,8-dimethylnaphthalene should be found at the ortho- and para-positions rather than at the meta. This is also the experimental observation.

Further experiments are in hand to test the validity of the concept of steric enhancement of hyperconjugation in electrophilic substitution.

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