Nitration of Triptycene in Acetic Anhydride

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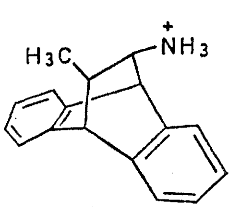
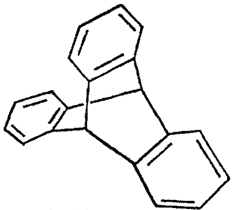
Nitration in acetic anhydride of one ring of triptycene deactivates nitration in either of the other rings by a factor of 5.5. For triptycene, the β-partial rate factor is 67, whilst that for the α-position is 1.6. It is shown that, as in acid-catalysed detritiation, (i) transannular resonance effects are not important and (ii) the decrease in bond order from 1.5 in the ground state to *ca.* 1.3 in the transition state for the bond fusing the aromatic and aliphatic rings makes a significant contribution in determining reactivity at the β-position.

HYDROGEN isotope exchange in the ion (I) has recently been studied[1] in order to examine whether aromatic reactivity depends upon the distance between the nitrogen pole and each aromatic ring. We had originally intended to report on the nitration of this ion, but were unable to complete this investigation; a large number of mono- and di-nitrated derivatives formed which we were unable to separate satisfactorily.



(I)



(II)

In hydrogen isotope exchange, substitution in one ring of (I) should not affect the reactivity of the other, but this will not be true for nitration. Two aromatic rings in triptycene (II) occupy almost the same position in space as the aromatic rings of (I) and are linked in the same way. Klanderman and Perkins[2] have estimated that mononitration of one ring of (II) deactivates nitration in acetic anhydride of either of the other two by a factor of 4.8. This value is corrected for statistical effects and is the average of widely differing results obtained by the competition and kinetic methods (6.0 and 3.6 respectively). Mononitration occurs mainly in the β-positions (97.7%), and α-positions being *ca.* 40 times less reactive. Further nitration leads to the formation of almost equal amounts of the two ββ′-dinitrotriptycenes.[2]

Klanderman and Perkins' kinetic analysis[2] is unsatisfactory, for they assumed the reactions to be first order in the stoicheiometric concentration of nitric acid,‡ $[HNO_3]_0$, whereas, since unpurified acetic anhydride was used, they were probably third order.[3] Their rate coefficients typically varied by a factor of *ca.* 1.5 during a run and were determined from just 10—20% reaction.

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‡ In acetic anhydride, nitric acid is present mainly as acetyl nitrate: $HNO_3 + Ac_2O \rightleftharpoons AcONO_2 + AcOH$.

[1] J. H. Rees and J. H. Ridd, *J.C.S. Chem. Comm.*, 1974, 518

[2] B. H. Klanderman and W. C. Perkins, *J. Org. Chem.*, 1969, **34**, 630.

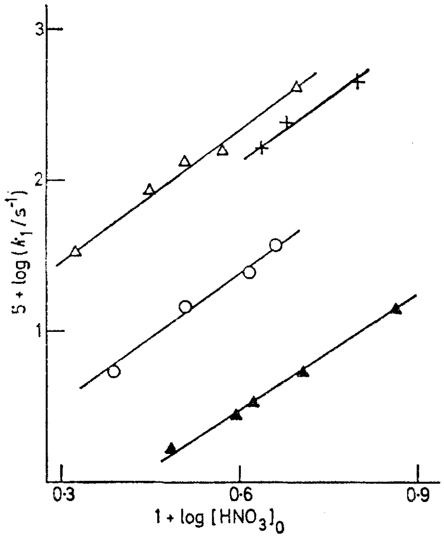
[3] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 1256.

In order to study the nitration of the ion (I), it was first necessary to re-examine the nitration of triptycene in order to obtain a more reliable factor by which nitration of one aromatic ring in (I) deactivates substitution in the other.

RESULTS

Rates of nitration were determined by observing the changes in the u.v. spectrum of each reaction at a suitable wavelength. A large excess of nitric acid over substrate was employed, and nitrations were first order in the concentration of aromatic compound. The Figure shows rate profiles for the mononitration of both triptycene and mononitrotriptycene; plots for benzene and toluene are included. The lines are parallel, with slopes of *ca.* 2.5; triptycene is 70 times more reactive than benzene (23 times per ring) and 8.8 times more reactive than mononitrotriptycene (5.5 times per ring). This last value is 55% higher than that from the previous kinetic analysis.[2]

Toluene is 48 times more reactive than benzene, a result agreeing well with that previously obtained by Hartshorn *et al.*[3] However, the form of the rate profiles shown in the Figure differs somewhat from that observed by Hartshorn *et al.*, and a detailed discussion of this will appear later.[4]

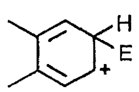


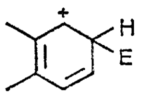
Rate profiles for the nitration of some aromatic compounds in purified acetic anhydride at 25°: △, triptycene (mononitration); ○, mononitrotriptycene; +, toluene; ▲, benzene

DISCUSSION

The results reported here, together with the isomer distribution obtained by Klanderman and Perkins,[2] show that the β-partial rate factor for the nitration of triptycene is 67, whilst the α-partial rate factor is 1.6. For the nitration of toluene in acetic anhydride, 35% of the substitution occurs in the *para*-position;[3] the partial rate factor for this position is therefore 101. The reactivity of this position is similar to that of the β-position in triptycene, the ratio log f_{para} (toluene) : log f_β (triptycene) being 1.10; similar selectivity is observed for detritiation in anhydrous trifluoroacetic acid at 70°, where this ratio has a value of 1.04.[5]

The activation of the β-positions observed for electrophilic substitution in substrates in which the aromatic ring is fused to a strained aliphatic ring (*e.g.* triptycene and biphenylene) is usually ascribed to the decrease in strain in the aliphatic ring on going to the transition state.[6,7] If the transition state is assumed to resemble a σ-complex then, from the three canonical structures (III)—(V), it can be seen that the order of the bond common to the aromatic and aliphatic rings is decreased from


(III)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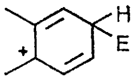
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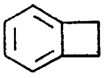
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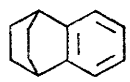
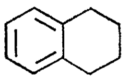

(VII)


(VIII)

1.5 in the ground state to *ca.* 1.3 in the transition state. In contrast, α-substitution leads to a bond-order of *ca.* 1.7 in the transition state, thus increasing the strain in the aliphatic ring.

Streitweiser *et al.* have found that the α- and β-protons in triptycene have greater acidity than the protons of benzene; to explain this, it was suggested that the strained bridgehead carbon atoms have increased electronegativity.[8] Clearly such an electronegativity effect does not outweigh the bond-order effects for β-nitration in triptycene, though on the basis of these results it is not possible to assess accurately its importance. An examination of detritiation in triptycene[5] concluded that the observed reactivities at the α- and β-positions could be satisfactorily explained in terms of bond-order effects alone, as the α-position was less reactive than predicted from data on unstrained systems whilst the β-position was more reactive.

For detritiation in anhydrous trifluoroacetic acid, the α-reactivity is *ca.* 5 times lower than the β-reactivity;[5] as nitration is a less selective electrophilic substitution than hydrogen isotope exchange, it would be expected that this factor should be smaller for nitration, rather than the value of *ca.* 40 observed. The ratio log f_β : log f_α is 1.5 for detritiation and 8.9 for nitration. It is possible that, because the transition state for nitration is closer to the initial state than it is for detritiation, electronegativity (and therefore inductive) effects are more important for α-substitution in the former than in the latter. However, for protodesilylation in 1,2-dihydrobenzocyclobutene (VI), log f_β/log f_α is 2.3;[9] protodesilylation is a less selective electrophilic substitution than

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[4] N. C. Marziano, J. H. Rees, and J. H. Ridd, unpublished observations.

[5] A. J. Holmes, R. Taylor, and G. J. Wright, *J. Chem. Soc.* (*B*), 1967, 780.

[6] J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 166.

[7] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 536.

[8] A. Streitweiser, jun., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

[9] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12.

nitration, and the four-membered ring of (VI) is more strained than the aliphatic rings of triptycene. On the basis of the above argument, $\log f_\beta/\log f_\alpha$ for (IV) should be >8.9.

Tanida and Muneyuki[10] accounted for the relatively low reactivity in nitration of the α-positions of benzobicyclo[2.2.2]octene [(VII); f_β/f_α *ca.* 25] in terms of steric effects. As in triptycene, the bridgehead protons in this rigid molecule lie sufficiently close to the α-positions (*ca.* 2.5 Å from the α-carbon atoms) for this to be reasonable. The β-reactivity of indane (VIII) is about the same as that of (VII) in nitration; the ratio $f_\beta : f_\alpha$ for the former is 1.0, and the flexible aliphatic ring of indane can deform so as to minimise steric hindrance.[10]

The work of Taylor *et al.* on detritiation in *o*-xylene, 9,10-dihydroanthracene, and triptycene[5] clearly indicated that the transition state for substitution in the latter is not stabilised by donation of π-electron density from the rings not undergoing reaction (transannular resonance). This conclusion can now be extended to nitration, because triptycene has the reactivity predicted from the data on proton exchange.[6] The factor of 5.5 by which nitration of one ring in triptycene deactivates substitution in one other can thus with some confidence be applied to a study of the nitration of the ion (I).

EXPERIMENTAL

Materials.—Triptycene (Aldrich) was recrystallised from cyclohexane, m.p. 249—250° (lit., 247—248,[11] 249—250°[12]).

The isolation of mono- and di-nitrotriptycene from preparative nitrations of triptycene in acetic anhydride is fully described in ref. 13. Both were recrystallised from ethanol, the former having m.p. 261—263° (lit.,[2] 268—271°) (Found: C, 79.8; H, 4.6; N, 4.35. Calc. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.35; N, 4.7%). The latter had m.p. 245—246° (Found: C, 69.35; H, 3.6; N, 7.75. $C_{20}H_{12}N_2O_4$ requires C, 69.8; H, 3.5; N, 8.15%). AnalaR benzene was used without further purification; laboratory reagent toluene was purified by distillation. The preparation of pure nitric acid and the purification of acetic anhydride using sodium have been previously described.[14]

Kinetic Methods.—Existing techniques were used to measure the rates of nitration of toluene[3] and benzene,[15] satisfactory first-order kinetics being obtained.

The method used for toluene was also employed to follow the mononitration of triptycene at 345 nm. This was possible because mononitrotriptycene has the same extinction coefficient in acetic anhydride at this wavelength ($-\varepsilon\ 2.39 \mp 0.06 \times 10^3$ l mol^{-1} cm^{-1}) as the dinitro-derivative ($2.64 \mp 0.04 \times 10^3$ l mol^{-1} cm^{-1}).

Only at wavelengths below 345 nm does dinitrotriptycene have an appreciably higher extinction coefficient than mononitrotriptycene; at 300 nm these values are $1.26 \mp 0.02 \times 10^4$ and $6.23 \mp 0.07 \times 10^3$ l mol^{-1} cm^{-1}, respectively. However, in this spectral region the nitrating solutions absorb too strongly for direct measurement of changes in absorbance during reaction, and so a quenching technique was used to measure the rate of nitration of mononitrotriptycene.[13]

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[5/030 *Received, 7th January,* 1975]

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[10] H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, 1965, **87**, 4794.

[11] U. Berger-Brose, K. H. Beyer, and W. Theilacker, *Chem. Ber.*, 1960, **93**, 1658.

[12] K. Bowden, J. G. Irving, and M. J. Price, *Canad. J. Chem.*, 1968, **46**, 3903.

[13] J. H. Rees, Ph.D. Thesis, London, 1973.

[14] N. C Marziano, J. H. Rees, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 600.

[15] M. A. Paul, *J. Amer. Chem. Soc.*, 1958, **80**, 5329.