

for the optical absorption maxima of the electron in these solvents¹⁴ reflects the increasing stabilization of the electron by solvation. It is significant that the sequence of increasing dielectric constants is paralleled by increasing ρ values for the reaction. The greater sensitivity to substituent effects observed in solvents of larger static dielectric constant reflects an increasing energy of activation, and hence it is reasonable to conclude that the transition state for the substitution reaction in alcohols



is less stabilized by solvation than the electron.

The similarity between the ρ value in methanol and that found for the electron in water, 4.8,² is noteworthy and in accord with the previously noted⁷ agreement between the rate constants, determined by the pulse radiolysis technique, of benzyl chloride and oxygen in these two media. Hence the apparent correlation between the ρ value and dielectric constant observed in the two alcohols does not extend to reactions in water. Correspondingly, the correlation between the optical transition energy of the solvated electron and dielectric constant observed in five aliphatic alcohols (including methanol and 2-propanol)¹⁴ was also found to break down when extended to the hydrated electron.

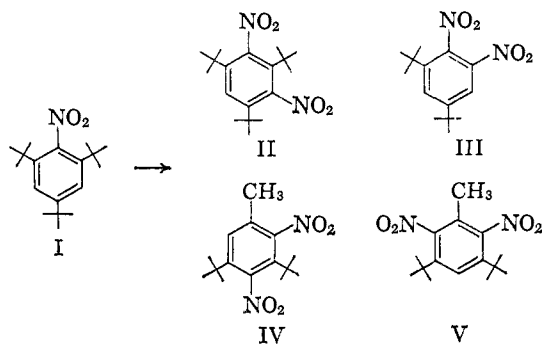
(14) M. C. Sauer, S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, **42**, 708 (1965).

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Reactions of Cyclohexadienyl Cations. Molecular Rearrangement Attendant Aromatic Nitration¹

Sir:

The products of nitration of 2,4,6-tri-*t*-butylnitrobenzene (I) dictate an unusual molecular rearrangement with important mechanistic implications. Reaction of I with 90% nitric acid at 0° affords four major products: 1,3-dinitro-2,4,6-tri-*t*-butylbenzene (II), 59%; 1,2-dinitro-3,5-di-*t*-butylbenzene (III), 5%; 2,4-dinitro-3,5-di-*t*-butyltoluene (IV), 34%; and 2,6-dinitro-3,5-di-*t*-butyltoluene (V), 2%. The same products but with different distribution are obtained by nitration of I with other nitrating agents, such as nitronium tetrafluoroborate.

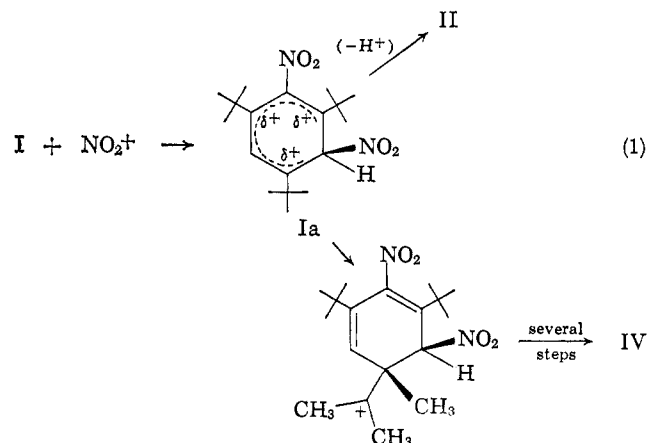


(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

The products III, IV, and V were isolated from the ethanol-soluble fraction of the crude nitration product and separated by a combination of column chromatography over alumina and preparative gas-liquid chromatography. Initial characterization of these compounds was effected by means of their definitive nmr spectra² and subsequently confirmed by mass spectral and elemental analyses. Syntheses of compounds identical in all respects with IV and V by stepwise nitration of 3,5-di-*t*-butyltoluene completed the proof of structure.³

III is almost certainly formed by direct nitrodealkylation. It is surprising perhaps that the amount of nitrodealkylation is so small.⁴

The transformation of I to IV and V appears to be without direct precedent. In the absence of any evidence of prior acid-catalyzed rearrangement of I, it is necessary to assume that IV and V are formed during nitration. A possible mechanism for the replacement of a *t*-butyl group by methyl which meets this condition is one involving a rearrangement of the intermediate alkylohexadienyl cation (Ia) followed by oxidative cleavage of the isopropyl moiety (eq 1).



The intermediate role of cyclohexadienyl cations (σ complexes) in aromatic electrophilic substitution processes is well established. Energetically favorable

(2) The predominantly singlet spectra at 60 Mc in CCl_4 referenced to TMS (δ values) are as follows together with relative area and assignment: for I, 1.32 (9 H), *p-t*-Bu; 1.38 (18 H), *o-t*-Bu; 7.42 (2 H), ArH; for II, 1.39 (18 H), 4,6-*t*-Bu; 1.45 (9 H), 2-*t*-Bu; 7.72 (1 H), ArH; for III, 1.40 (9 H), 5-*t*-Bu; 1.43 (9 H), 3-*t*-Bu; 7.87 (2 H), AB quartet, $J = 2$ cps, ArH; for IV, 1.37 (9 H), 5-*t*-Bu; 1.43 (9 H), 3-*t*-Bu; 2.23 (3 H), doublet, $J = 0.6$ cps, 1-Me; 7.47 (1-H), quartet, $J \approx 0.6$ cps, ArH; for V 1.39 (18 H), 3,5-*t*-Bu; 2.05 (3 H), doublet, $J \approx 0.5$ cps, 1-Me; 7.57 (1-H), quartet, $J \approx 0.5$ cps, ArH.

(3) J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster *Rec. Trav. Chim.*, **75**, 305 (1956).

(4) Nitrodealkylation does not appear to be an important process in the nitration of either 1,3,5-triisopropylbenzene or 1,3,5-tri-*t*-butylbenzene. Although a report by Olah and Kuhn would indicate that both of these hydrocarbons undergo nitrodealkylation upon nitration with nitronium tetrafluoroborate in sulfolane, reinvestigation of these reactions shows that the normal nitration products are formed with no detectable (<1%) nitrodealkylation product.⁵ These results are quite similar to those obtained using more conventional nitration procedures.⁶ However, nitrodealkylation is an important process in the nitration of 2,4,6-tri-*t*-butylbromobenzene and 2,4,6-tri-*t*-butylfluorobenzene where 2-nitro-4,6-di-*t*-butylbromobenzene and 4-nitro-2,6-di-*t*-butylfluorobenzene are found to be the principal nitration products.

(5) (a) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **86**, 1067 (1964). (b) Professor Olah, in a private communication, has indicated that the results of this reinvestigation are correct and that the error in the initial study was due to the nature of the analytical method.

(6) (a) A. Newton, *J. Am. Chem. Soc.*, **65**, 2434 (1943); (b) P. D. Bartlett, M. Roha, and R. M. Stiles, *ibid.*, **76**, 2349 (1954); (c) B. M. Wepster, *et al.*, *Rec. Trav. Chim.*, **77**, 491 (1958); (d) P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960).

reaction paths of these ions are normally those which lead to aromatization by elimination of a cation, usually a proton. However, certain structural features or reaction conditions can permit other carbonium ion processes to become competitive with cation elimination. Addition reactions are known, particularly of the polycyclic aromatic hydrocarbons, and certain substitutions of benzene systems seem best explained in terms of addition-elimination reactions.⁷ In this context, IV and V can be considered products of complementary carbonium ion reactions, molecular rearrangements, which are open to alkylcyclohexadienyl cations provided a favorable balance of free energies of activation exists. The strong repulsion effects attending introduction of a second nitro group into this severely crowded system are undoubtedly the primary factors which permit successful competition of these two reactions, direct cation elimination and rearrangement followed by elimination.

That the methyl which replaces the *t*-butyl group comes from the replaced *t*-butyl group is substantiated by the observation that 2,4,6-tri-*t*-butylnitrobenzene-2,4,6- β -*t* undergoes reaction forming IV with loss of 23% of tritium activity. Theory predicts 22.2%.

The predominance of IV over V is not well understood, but it may reflect unsymmetrical charge distribution in Ia. If this is the case, the prediction is that the *p*-*t*-butyl group of I suffers rearrangement in preference to one of the *o*-*t*-butyl groups.

A further test of mechanism is clear. The proposed mechanism would strongly imply that the product distribution be altered by substitution of deuterium for aromatic hydrogen in I. Further, one would anticipate that this partitioning isotope effect would be larger than the observed kinetic isotope effect for the over-all nitration of I vs. I-3,5-*d*₂. The accompanying communication describes the results of these experiments.⁸

Acknowledgment. It is a pleasure to acknowledge the technical assistance of Terrill Rieger.

(7) (a) C. C. Price and C. T. Arntzen, *J. Am. Chem. Soc.*, **60**, 2835 (1938); (b) F. R. Mayo and W. B. Hardy, *ibid.*, **74**, 911 (1952); (c) P. B. D. de la Mare, M. Hassan, E. A. Johnson, and N. V. Klassen, *J. Chem. Soc.*, 2749 (1961); (d) P. B. D. de la Mare, R. Koenigsburger, J. S. Lomas, V. Sanchez de Olma, and A. Saxton, *Rec. Trav. Chim.*, **84**, 109 (1965); (e) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levinsky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965); (f) P. C. Myhre and G. S. Owen, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 48S.

(8) P. C. Myhre and M. Bueg, *J. Am. Chem. Soc.*, **88**, 1569 (1966).

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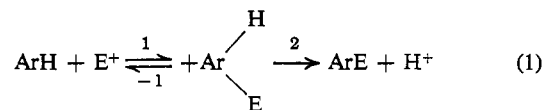
A Slow Proton Transfer in Aromatic Nitration¹

Sir:

Steric effects are powerful factors in the determination of the relative velocity ratio, v_2/v_{-1} , in aromatic electrophilic substitution reactions (eq 1).² The es-

(1) Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) (a) H. Zollinger, *Helv. Chim. Acta*, **38**, 1597, 1608, 1617, 1624 (1955); (b) W. M. Schubert and P. C. Myhre, *J. Am. Chem. Soc.*, **80** 1755 (1958); (c) P. C. Myhre, *Acta Chem. Scand.*, **14**, 219 (1960); (d) P. G. Farrell and S. F. Mason, *Nature*, **183**, 250 (1959); **197**, 590 (1963); (e) J. E. Dubois and R. Uzan, *Tetrahedron Letters*, **1965**, 309.



sential argument is that nonbonded repulsion energy increases as a large electrophile replaces hydrogen at a confined or sterically crowded site, and that this increasing repulsion energy will manifest itself more strongly in step 2, since it is at this stage that the electrophile starts assuming product configuration.³ It is suggested that the susceptibility of aromatic substitution reactions to steric effects represents a presently crude but useful means of ascertaining free-energy differences between steps -1 and 2 for different kinds of aromatic substitution reactions. As shown in Figure 1

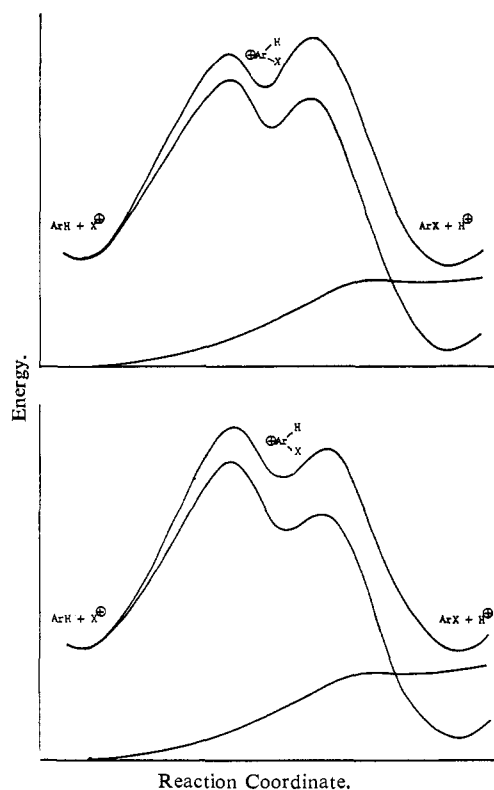


Figure 1. Energy profiles for two aromatic electrophilic substitution reactions showing the effect of imposed steric hindrance (lowest curves) on "normal" energy profile. In each case the resultant energy profile is taken as the sum of the lower curves.

the superposition of the same increasing repulsion energy term on energy profiles of "normal" aromatic substitution reactions may or may not lead to an alteration in the rate-determining step depending upon the "normal" velocity ratios, v_2/v_{-1} .

The absence of an isotope effect in nitration of the very hindered 1,3,5-tri-*t*-butylbenzene, but the presence of a strong isotope effect in the positive bromination of the same hydrocarbon, indicates that these two reactions with very similar ρ values (-6.0 and -6.2) and about equivalently sized electrophiles have rather different velocity ratios.^{2c} The question of importance to the construct is whether the rate ratio, v_2/v_{-1} ,

(3) Considerations of the effect of structure on the rate of proton transfer from the intermediate to solvent bases are also important.^{2a,b}