Nitration of Mesitylene: Comparison with Reactions of the Cation-radical $C_6H_3Me_3^{+\cdot}$

By MARK R. DRAPER and JOHN H. RIDD*
(*Chemistry Department, University College, 20 Gordon Street, London* WC1H 0AJ)

Summary The product composition from reactions of the cation radical of mesitylene differs from that found in direct nitration even when the cation radical is generated by ceric ammonium nitrate in the nitrating medium and in the presence of added dinitrogen tetroxide.

IN recent years,[1-3] several authors have suggested that the nitration of the more reactive aromatic compounds by the nitronium ion occurs through a preliminary electron transfer to form an aromatic cation radical and nitrogen dioxide followed by the recombination of these species either before[3] or after[1] separation from the radical pair. The evidence for this reaction path comes partly from the detection of cation radicals by e.s.r. spectroscopy,[1] partly from arguments concerning ionisation potentials,[3] and partly from the apparent consistency of the product composition obtained from nitration with that expected or obtained from reactions of the corresponding cation radical with nitrogen dioxide.[3]

In general, these arguments in favour of intermediate cation radicals are permissive rather than compelling and so, to provide a more stringent test, we have compared the products from nitration and from reaction through the cation radical under the same conditions using a substrate capable of more than one type of reaction. The results for the reactions of mesitylene in acetonitrile are in the Table.

TABLE. Product compositions from the reactions of mesitylene (0·20—0·21 mol dm^{-3}) with nitric acid and ceric ammonium nitrate (CAN) in acetonitrile at 65 °C.

					% Composition[b]	
Time/min	[HNO_3]/ mol dm^{-3}	[CAN]/ mol dm^{-3}	[N_2O_4]/ mol dm^{-3}	% Yield[a,b]	$ArNO_2$	$ArCH_2ONO_2$
100	3·05	—	—	100	100	—
60	—	0·26	—	35	—	100
30	—	0·26	0·19	5	74	26
30	0·80	0·26	—	27	67[c]	33[c]
30	0·80	0·26	0·22	38	90	10

[a] Total yield relative to the initial amount of mesitylene. [b] Determined from the n.m.r. spectrum of the extracted product: errors *ca.* ±3%. [c] The composition of this product varies with the extent of reaction.

The nitration of mesitylene under these conditions gives only the ring-substituted product. The reaction of mesitylene with ceric ammonium nitrate in acetonitrile gives only 3,5-dimethylbenzyl nitrate. By analogy with the related reactions in acetic acid as solvent,[4] we consider this nitrate to be formed through the intermediate formation of the cation radical as shown in equation (1). In the presence of an approximately equivalent amount of nitrogen dioxide, the greater part of the product is that from ring-substitution (presumably as a result of the capture of the cation radical by NO_2)† but *ca.* 25% of 3,5-dimethylbenzyl nitrate is still formed. By a suitable choice of conditions, the nitration and the reaction with ceric ammonium nitrate can be made to occur in the same solution to give approximately equal amounts of nitromesitylene and 3,5-dimethylbenzyl nitrate. The reactions appear to be independent for only the ring substitution is suppressed by the addition of water. In the presence of added dinitrogen tetroxide the yield of 3,5-dimethylbenzyl nitrate is reduced but still remains significant.

$$ArCH_3 \xrightarrow{Ce^{IV}} ArCH_3^{+\cdot} \xrightarrow{-H^+} ArCH_2\cdot \xrightarrow{fast} Products \qquad (1)$$

These results imply that the reactions of the cation radical leading to side-chain substitution compete with the addition of NO_2 even when the cation radical is formed in the nitrating medium and when a high concentration of dinitrogen tetroxide is present. Since substitution in the side-chain is not observed in the reaction of mesitylene with nitric acid, then either this reaction does not involve the cation radical or the life-time of the cation radical when formed by electron transfer to the nitronium ion is too short to show the normal reactions of this species. This argument does not rule out the transient formation of the cation radical on the reaction path leading to the Wheland intermediate but it is very difficult to distinguish between this hypothesis and the one-stage formation of the Wheland intermediate through a transition state involving some charge transfer.[5] The argument does show that the products of nitration are not necessarily those obtained from the cation radical when this species is generated independently in the same solution.

One of us (M.R.D.) thanks the S.R.C. for a studentship.

(*Received, 6th March* 1978; *Com.* 239.)

---

† The rate of reaction of mesitylene under these conditions with dinitrogen tetroxide is negligible.

[1] V. D. Pokhodenko, V. A. Khizhnyi, V. G. Koshechko, and O. I. Shkrebtii, *Zhur. Org. Khim.*, 1975, **11**, 1873.

[2] J. K. Kochi, *Tetrahedron Letters*, 1975, 41.

[3] C. L. Perrin, *J. Amer. Chem. Soc.*, 1977, **99**, 5516.

[4] E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Letters*, **1976**, 3343.

[5] For a discussion of the amount of electron transfer involved see T. Takabe, K. Takenaka, K. Yamaguchi, and T. Fueno, *Chem. Phys. Letters*, 1976, **44**, 65.