Tetrahedron Letters No. 52, pp 4685 - 4688, 1975. Pergamon Press. Printed in Great Britain.

SPECTROSCOPIC OBSERVATION OF THE INTERMEDIATES IN THE OXIDATION OF METHYL BENZENES

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(Received in UK 6 November 1975; accepted for publication 13 November 1975)

Although it has been established that anodic oxidation of durene in wet acetonitrile gives 2,4,5-trimethylbenzylacetamide by side chain attack but similar oxidation of mesitylene in high concentration gives mainly 2,4,6,2',4',6'-hexamethylbiphenyl, no intermediates have been observed spectroscopically. We now report the observation of ion radical intermediates in the oxidation of mesitylene in addition to the carbonium ion seen from both durene and mesitylene, and with further evidence from cyclic voltammetry and rotating disc experiments we contrast the behaviour of mesitylene with durene.

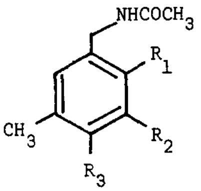
Our controlled potential electrolysis experiments gave results as in Table 1, and these are basically in agreement with Nyberg[1,2], the differences in absolute yield being dependent on the absolute concentration of aromatic and the relative concentration of water.

Studies of the kinetics of the reaction using cyclic voltammetry over a wide range of sweep speeds show that the first (lowest potential) anodic process is irreversible for both hydrocarbons. Use of a rotating disc electrode to control the rate of transport of intermediate species away from the electrode surface does, however, show an interesting distinction. At low rotation speeds both compounds show about the same value for the limiting anodic current but at high rotation speeds the ratio of the limiting currents approaches a value of two, the value for mesitylene being the smaller of the two. A comparison of these currents with those obtained for 2,4,6,2',4',6'-hexamethoxydiphenylmethylamine which is known to undergo a well-behaved, one electron, reversible oxidation shows that mesitylene oxidises in a one electron process at high rotation speeds whereas durene undergoes two-electron oxidation. The inference that mesitylene, but not durene, forms a relatively stable ion radical intermediate was confirmed using Specular Reflectance Spectroscopy (SRS)[3]. This _in situ_ technique enables the uv-visible spectra of short lived intermediates to be obtained. In the case of durene, the optical measurements show the appearance of absorption peaks at 250, 298 and 450 nm when oxidation is carried out at potentials in the first anodic wave. These are in good accord with published spectral data[4] for carbonium ions prepared from the appropriate alcohol in strongly acidic media and we attribute them, therefore, to a transient carbonium ion species. In the case of mesitylene, however, in addition to similar absorption peaks from the carbonium ion, we observe new, broad spectral features in the region of 800 nm and 1100 nm. These additional peaks are similar to those obtained by Badger and Brocklehurst[5] and assigned to the dimer cation radical (e.g. 4a) in studies of the cation radicals produced by γ-radiolysis of a series of substituted benzenes. Interestingly, we have no clear evidence for the primary cation radical (3a).

TABLE 1

OXIDATION PRODUCTS FROM MESITYLENE AND DURENE IN ACETONITRILE

Electrolysis Solution	Potential of Oxidation (vs Ag/Ag^+ 0.01M)	Products and Yields	
Mesitylene (.02M), H_2O (0.1M), $Bu^n{}_4NBF_4$ (0.1M)	2.1V	5a(20%),6(4%),7(1%)	This work
Durene (.083M), H_2O (0.2M) Bu^nNBF_4 (0.39 M)	1.4V	5b(70%),8(5%)	This work
Durene (.08M) (no H_2O) $Bu^n{}_4NBF_4$ (0.39M)	1.4V	8(5%),5b(trace), polymer	This work
Mesitylene (0.2M)(no added H_2O)	1.9V (vs S.C.E.)	6(3%)	Ref.1
Mesitylene (2M) (no added H_2O)	1.9V (vs S.C.E.)	6(71%), trimer	Ref.1
Durene (0.2M), H_2O (0.1M)	1.0V (vs S.C.E.)	5b(38%)	Ref. 2,6



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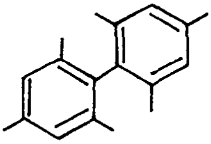

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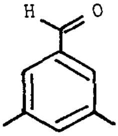

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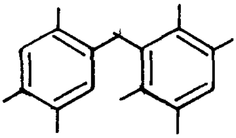

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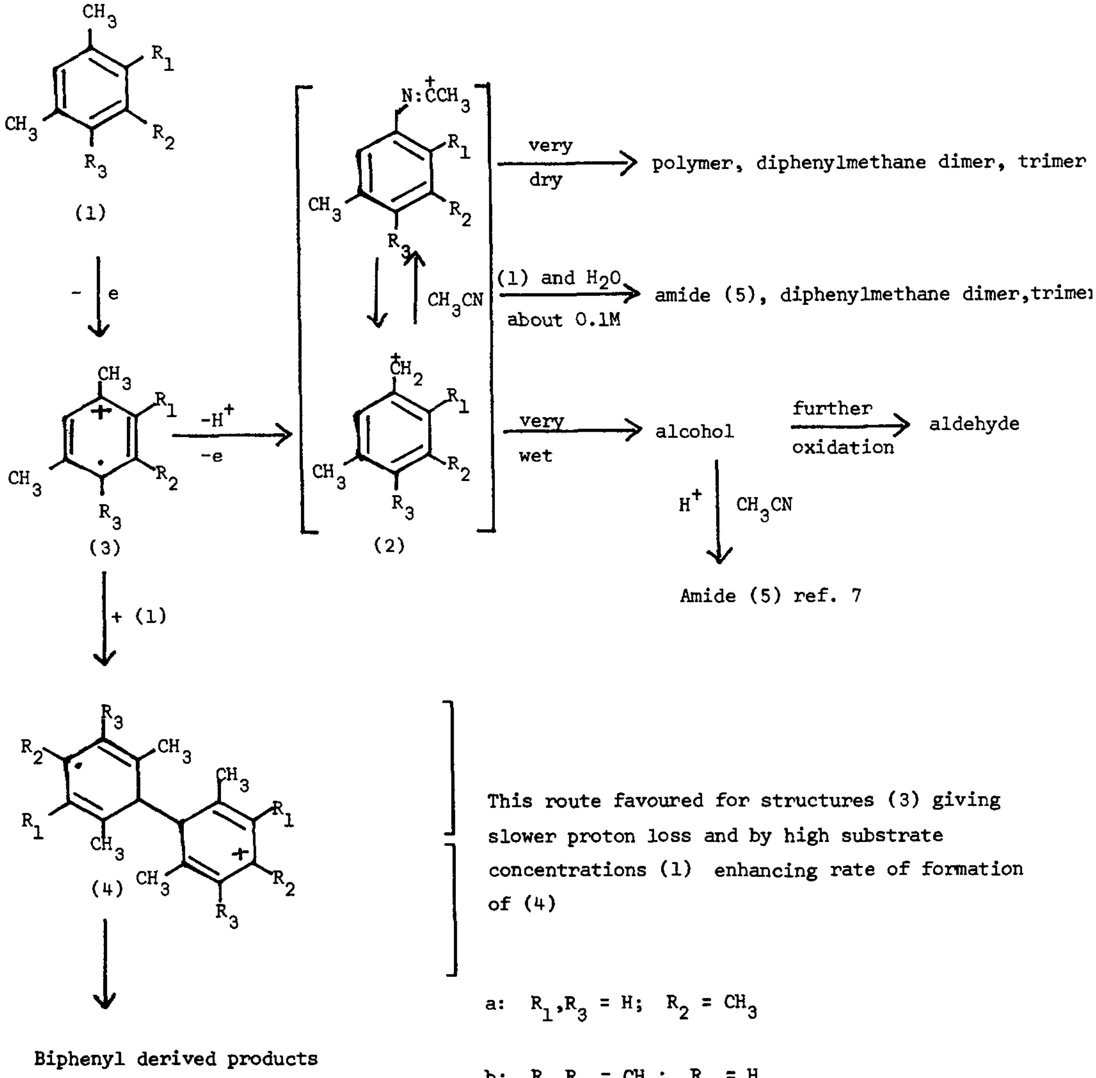
a: R_1,R_3 = H; R_2 = CH_3

b: R_1,R_3 = CH_3; R_2 = H

These observations permit us to propose the mechanism of Scheme 1. The cation radical of mesitylene (3a) has sufficient stability to avoid very rapid proton loss. As a result reaction to form the dimer is possible and this can become dominant at high concentrations of mesitylene. The SRS results show that at a mesitylene concentration of 11mM both the dimer cation radical and the carbonium ion (in equilibrium with the corresponding nitrilium ion) are observed and both reaction routes are important. The results obtained at the rotating disc electrode confirm the stability of the cation radical; at high rotation speeds it is removed

SCHEME 1



This route favoured for structures (3) giving slower proton loss and by high substrate concentrations (1) enhancing rate of formation of (4)

a: R_1,R_3 = H; R_2 = CH_3

b: R_1,R_3 = CH_3; R_2 = H

from the electrode surface before it has time to lose a proton and undergo further oxidation to the carbonium ion (2a). Durene cation radical undergoes proton loss much more rapidly and hence only the carbonium ion route is observed, and the only intermediate seen in SRS is the carbonium ion (in equilibrium with the nitrilium ion). The table also shows the significance of water in the absolute yields of the various products. The stability of the cation radical depends both upon its acid strength and its electrophilicity, a higher acid strength favouring carbonium ion formation and a higher electrophilicity favouring attack on a substrate molecule at a free ring position. Calculations, supported by ESR measurements,[8,9] of the distribution of unpaired electron density and positive charge in the cation radicals of a series of methyl benzenes show that durene cation radical should be both a stronger acid and a weaker electrophile than mesitylene cation radical at the free ring positions. The implications of the present results to the discussion of the electron donor/acceptor properties of methyl groups[10] will be given in more detail in a full paper.

Nyberg[1] also postulated the dimer cation radical as the intermediate which leads to the biphenyl product; he found that mixed biphenyls were produced from the oxidation of a mixture of mesitylene and benzene (in the region where benzene itself does not oxidise), and this can only arise if a mesitylene cation radical attacks a neutral benzene molecule.

Our work shows the benefit of SRS for studying electroorganic systems in that in situ observation of the intermediates by spectroscopy can be accomplished. At present we are using SRS for studying intermediates in the oxidation of durene and hexamethylbenzene at higher anodic potentials.

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