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A NEW 1,2-SHIFT IN THE OXIDATION OF AROMATIC RINGS

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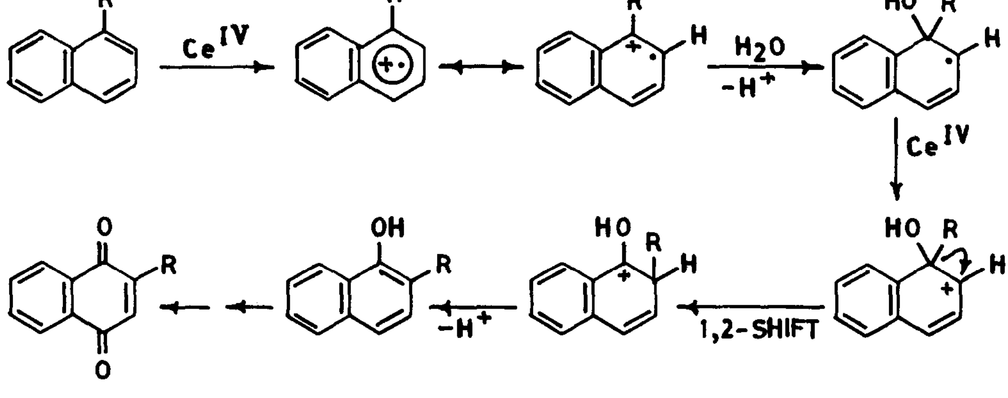
Although ceric ammonium nitrate, $(NH_4)_2[Ce(NO_3)_6]$, is the most widely used oxidant among ceric salts[1], we have found ceric ammonium sulphate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, is a superior reagent for oxidation of aromatic rings[2]. While continuing our studies[3-6] on kinetics and mechanisms of oxidation of aromatic rings, we have observed a new type of 1,2-shift in cerium IV oxidation of naphthalene and its substituted derivatives. This 1,2-shift which does not involve an arene oxide intermediate, is different from the well known NIH-shift[7]. We had previously observed a NIH-shift in the oxidation of naphthalene-1,4-D_2 by chromic acid in acetic acid medium[5]. Whereas chromic acid and its derivatives being oxotransition metal oxidants oxidise the aromatic rings by ligand transfer mechanism leading to an arene oxide intermediate[8] no such possibility exists with ceric ammonium sulphate, a single electron oxidant which functions by electron transfer mechanism. A tentative mechanistic proposal consistent with our observations is shown in Scheme 1.

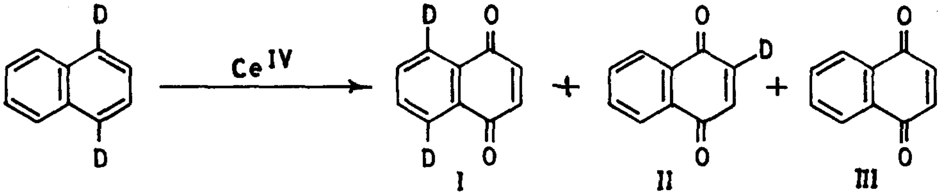
Scheme 1



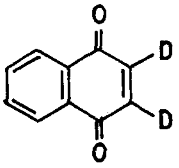
R=D,Br,Ph

Napthoquinone, obtained by ceric ammonium sulphate oxidation of naphthalene-1,4-D_2 showed the intensity of peaks in the NMR spectrum for α:β:quinonoid hydrogens = 2:4:3 (instead of 2:4:4 expected for equimolecular mixture of I and III in Scheme 2[9]). Clearly, the hydrogens of quinonoid moiety were partly substituted with deuterium. This view was confirmed by mass spectrum which showed the M^+ peaks corresponding to I, II and III at m/e 160, 159 and 158 respectively.

Scheme 2



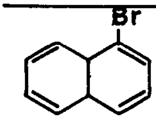
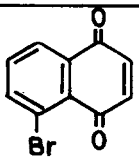
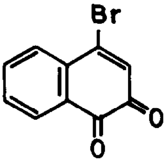
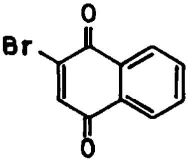
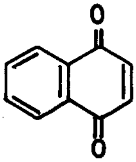
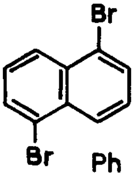
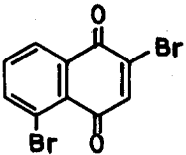
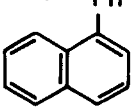
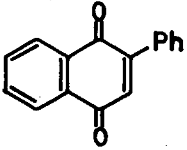
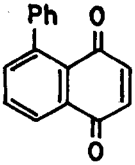
The fragmentation patterns m/e 130, 131 and 132 (M^+ -CO), 102, 103 and 104 (M^+ -2CO), 104 and 106 (130 and 132-C_2H_2 and 131-C_2HD), and 76 & 78 (benzyne and benzyne-D_2), convincingly showed evidence for I, II and III. On the basis of our data we cannot rule out the formation of IV which gives a fragmentation pattern indistinguishable from that of I. Thus the spectral data of the 1,4-naphthoquinone obtained in the oxidation of naphthalene-1,4-D_2 indicate the migration of deuterium from 1 to 2 position.



IV

We observed similar migrations of bromine and phenyl group in ceric ammonium sulphate oxidation of the corresponding substituted naphthalenes as shown in Table I.

Table I. Ceric Ammonium Sulphate Oxidation of Substituted Naphthalenes

Substrate[a]	Reaction conditions		Product[b]	Yield (%)	mp (°C)	Lit.mp (°C)Lit
	Temperature (°C)	Time (hr)				
	50	5		15	159-160	160-161[10]
				30	153-154	154[11]
				10	129-130	130-131[12]
				18	124-125	123-125[13]
	60	5		66	68-70	
	50	4		24	110-111	111-112[14]
				28	150-152	

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[a] Oxidations were carried out in acetonitrile and dilute sulphuric acid (4N) mixture as described in our previous communication[2].

[b] The products were isolated by preparative TLC (silica gel/benzene) and identified on the basis of their IR and NMR spectra.

In a previous communication[2] we reported that ceric ammonium sulphate oxidation of 1-methylnaphthalene furnished 1-naphthaldehyde and 1,4-naphthoquinone but no methylnaphthoquinone could be isolated. It has been further established that 1,4-naphthoquinone is formed in the ceric ammonium sulphate oxidation of 1-naphthaldehyde and 1-naphthoic acid. We believe that in the case of 1-methylnaphthalene the side chain oxidation followed by oxidative decarboxylation is favoured over the direct oxidation of the aromatic ring.

We have also found that slow addition of dilute solution (0.01M) of 1-naphthol (1 mmol) in acetonitrile to ceric ammonium sulphate (4 mmol) in 4N sulphuric acid (50 ml) at 50°C gives 1,4-naphthoquinone (20% yield) besides oxidatively coupled products. This result implies that 1-naphthol may be an intermediate in the oxidation of naphthalene to 1,4-naphthoquinone as shown in Scheme 1.

References and Notes

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