Novel Reactions of Diazonium Salts: Direct Conversion of *o*- and *p*-Chlorobenzenediazonium Acetates into Hydroxybenzenediazonium Salts, of *o*-Acetoxybenzenediazonium Acetate into the Carbene, 2-Oxocyclohexa-3,5-dienylidene, and of *o*-Thioacetoxybenzenediazonium Acetate into 1,2,3-Benzothiadiazole

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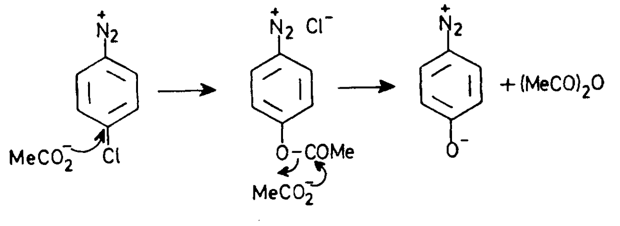
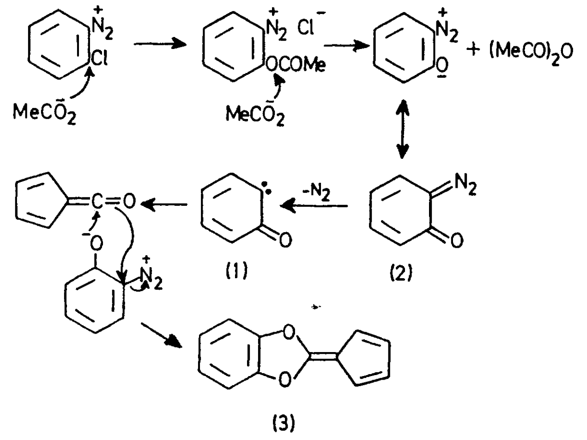
Summary The presence of 1,1-diphenylethene (1 equiv.) as a radical chain suppressor in decompositions of *o*- and *p*-chlorobenzenediazonium acetates formed *in situ* from the corresponding *N*-nitrosoacetanilides, in benzene at 50 °C, promotes previously unobserved ionic displacements of chloride by acetate, followed by deacetylation to give, for example, clean precipitation of *p*-hydroxybenzenediazonium chloride; extension of the reaction leads conveniently to the generation of 2-oxocyclohexa-3,5-dienylidene from *N*-nitroso-*o*-acetoxyacetanilide and of 1,2,3-benzothiadiazole from *N*-nitroso-*o*-thioacetoxyacetanilide.

1,1-DIPHENYLETHANE promotes ionic decomposition of benzenediazonium acetate to give benzyne at the expense of the competing radical mode which is dominant in the absence of the alkene.[1] We now report the promotion of previously inaccessible heterolytic displacements on *p*-chlorobenzenediazonium acetate leading directly to *p*-hydroxybenzenediazonium chloride and related reactions leading to the formation of the carbene (**1**) from *N*-nitroso-*o*-acetoxyacetanilide.



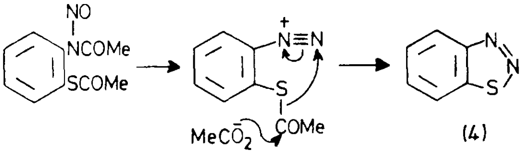
SCHEME 1

Thus, reaction of *p*-chlorobenzenediazonium acetate, formed *in situ* from *N*-nitroso-*p*-chloroacetanilide (1 mol) in an excess of benzene at 50 °C in the presence of 1,1-diphenylethene (1 mol) gave a precipitate of *p*-hydroxybenzenediazonium chloride (30%), produced so cleanly that the reaction has merit as a simple practical preparation. Also formed was acetic anhydride (34%). This points to reaction as in Scheme 1 whereby displacement of chloride *para*- to the activating diazonium group gives *p*-acetoxydiazonium chloride, which in turn is deacetylated by acetate ion to give the observed products. That such deacetylation is feasible follows from the observation that *p*-acetoxybenzenediazonium acetate in the presence of 1,1-diphenylethene (1 mol) in benzene at 50 °C gave acetic anhydride (80%) and only a trace of the radical derived product 4-acetoxybiphenyl. This acetate-induced displacement of chloride from *p*-chlorobenzenediazonium acetate appears to be unprecedented; indeed it has been stated not to occur[2] as a competing ionic reaction during homolysis of *p*-chlorobenzenediazonium acetate. Our experiments show that on suppression of the radical reaction this ionic displacement becomes predominant.



SCHEME 2

Corresponding reactions occur with *o*-chlorobenzenediazonium acetate. In this case *o*-chlorobenzenediazonium chloride (31%) is the least soluble salt, which precipitates out, and, again, deacetylation is shown by the appearance of acetic anhydride (31%). We have extended this reaction to produce what appears to be a convenient source of (**1**) *via* the intermediacy of the quinone-diazide (**2**). Thus *o*-acetoxybenzenediazonium acetate, formed *in situ* from readily prepared *N*-nitroso-*o*-acetoxyacetanilide, on thermolysis in boiling xylene gave the benzofulvalene (**3**) (22%) (Scheme 2). This is the oxocarbene-derived product and is identical with that obtained by thermolysis of (**2**).[3]



SCHEME 3

Finally, the foregoing suggests that the corresponding decomposition of *o*-thioacetoxybenzenediazonium acetate formed *in situ* from *N*-nitroso-*o*-thioacetoxyacetanilide should be a good route to 1,2,3-benzothiadiazole (**4**) (Scheme 3). This expectation was realised by the isolation of (**4**) in 70% yield (quantitative by g.l.c.) from the conversion carried out in benzene at 50 °C.

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[1] J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1976, 583.
[2] P. Miles and H. Suschitzky, *Tetrahedron*, 1962, **18**, 1369.
[3] R. Clinging, F. M. Dean, and G. H. Mitchell, *Tetrahedron*, 1974, **30**, 4065.