On the Formation of Benzenediazonium Chloride in Gomberg–Hey Type Reactions of Diazonium Salts with Bromotrichloromethane, Carbon Tetrachloride, and Chloroform. The Solution of a Long-standing Mechanistic Puzzle

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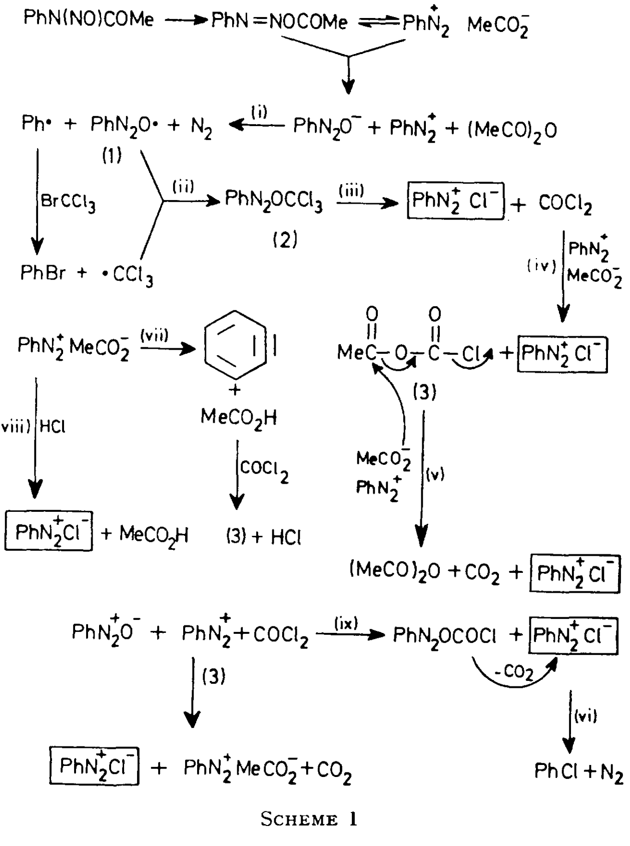
Summary A mechanism is offered for the formation of benzenediazonium chloride from the diazonium acetate in bromotrichloromethane and other polyhalogenomethanes, and of 'anomalous' halogen abstractions involving diazonium salts in general, based on the transient intermediacy of radical-derived trichloromethyl benzenediazoate ($PhN{=}NOCCl_3$) which decomposes into the diazonium chloride and phosgene, which in turn reacts with unchanged diazonium acetate to give the diazonium chloride, acetic anhydride, and carbon dioxide.

Despite many attempts,[1] an explanation of the conversion of benzenediazonium acetate, formed *in situ* from *N*-nitrosoacetanilide (NNA), into benzenediazonium chloride,[2] on reaction with carbon tetrachloride, has eluded chemists for 42 years. Also unexplained are the observations that decompositions of diazonium precursors *via* NNA,[3] the Gomberg reaction,[3] and pentyl nitrite–aniline,[4] normally good sources of phenyl radicals, gave, in chloroform, significant amounts of chlorobenzene as well as benzene but no hexachloroethane, whereas other established sources of phenyl radicals gave only benzene and hexachloroethane as expected. Similar unexplained anomalies occur in reactions of diazonium salts with bromoform[3,4] and with bromotrichloromethane,[2] the latter giving, for example, chlorobenzene as well as the expected bromobenzene.

We now offer an explanation. First, in the case of bromotrichloromethane with NNA, we invoke the accepted[1a,5] genesis of a phenyl radical [Scheme 1, reaction (i)] which abstracts bromine from bromotrichloromethane to give bromobenzene and a trichloromethyl radical, which in turn is scavenged [reaction (ii)] by the persistent phenyldiazoxyl radical (**1**) also formed in (i). This accounts for the absence of hexachloroethane. Decomposition of the resulting trichloromethyl benzenediazoate (**2**) then gives the observed benzenediazonium chloride and phosgene [reaction (iii)]. Reaction (iv) of another equivalent of benzenediazonium acetate with phosgene gives a second equivalent of the

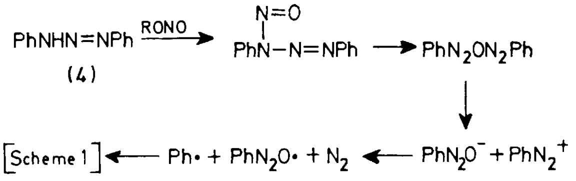


Scheme 1

diazonium chloride and the chlorocarbonyl anhydride (**3**), which in turn gives a third equivalent of the diazonium chloride together with acetic anhydride and carbon dioxide on reaction (v) with a further equivalent of the diazonium acetate. At room temperature the insoluble diazonium chloride appears as a precipitate but at higher temperatures thermolysis to chlorobenzene occurs (reaction vi), as established by control experiments, thus accounting for the hitherto puzzling appearance of both chloro- and bromobenzene.[1b]

Benzenediazonium chloride and hence chlorobenzene may also be formed by three further routes, *via* reactions (vii)[1] and (viii)[6] based on known chemistry, and reaction (ix) for which we present evidence below.

The following observations further support Scheme 1. (a) Benzenediazonium acetate, from NNA, in an excess of bromotrichloromethane at room temperature, gave a precipitate of a mixture of benzenediazonium-chloride (28·5 mol. equiv./100 mol. equiv. NNA) and -acetate (6 mol. equiv.), the bromide being absent. Also formed were carbon dioxide (23 mol. equiv.), chlorobenzene (3 mol. equiv.), bromobenzene (22 mol. equiv.), phenyl acetate (3 mol. equiv.), and acetic anhydride (15 mol. equiv.). Methyl bromide was not formed, thus ruling out the process $CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$. Separate experiments established the presence of acetic acid (50 mol. equiv.) and benzyne (25 mol. equiv.), trapped with tetraphenylcyclopentadienone. (b) Rapid formation of carbon dioxide and acetic anhydride from acetate and phosgene is a known reaction[7] confirmed by us. (c) Formation of trichloromethyl benzenediazoate (**2**), which should decompose instantly to give phosgene and benzenediazonium chloride according to reaction (iii), from silver benzenediazoate and bromotrichloromethane was very slow as a result of heterogeneity. Nevertheless the little reaction (2%) which occurred after 4 days at 20 °C gave benzenediazonium chloride as expected. (d) Addition of a further radical trap, 1,1-diphenylethene (1 equiv.),[8] led to the almost complete suppression of the formation of benzenediazonium chloride *via* (**2**) and hence to chlorobenzene (2%). Also formed were bromobenzene (39%) and phenyl acetate (15%). (e) Also in accord with Scheme 1 are our previously unreported experiments with 1,3-diphenyltriazene (**4**) with pentyl nitrite which in benzene, say, gives biphenyl (114 mol. equiv./100 mol. equiv. triazene) *via* phenyl radicals (Scheme 2),[9] other substituted triazenes behaving similarly. In an excess of bromotrichloromethane at 20 °C the triazene (1 mol) and pentyl nitrite (1·5 mol.) gave benzenediazonium chloride in high yield (85 mol. equiv./100 mol. equiv. triazene) together with chlorobenzene (21 mol. equiv.) and bromobenzene (33 mol. equiv.), thus pointing to the reality of reaction (ix), Scheme 1.



Scheme 2

Similar mechanistic explanations can be applied to decompositions in carbon tetrachloride, chloroform, and bromoform.

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