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CROWN-CATION COMPLEX EFFECTS. V.
REACTIONS OF ARYLDIAZONIUM IONS IN NONPOLAR MEDIA

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Aryldiazonium cations are well-known and widely studied species.[1] The preponderance of the literature on the subject, however, relates to reactions conducted in aqueous or other polar, hydroxylated media. Because aryldiazonium ions, particularly the chlorides, nitrates, and sulfates, are treacherous substances, they are most often generated in aqueous solution and used directly. The explosive proclivity of aryldiazonium salts can be controlled by utilizing either tetrafluoroborates or hexafluorophosphates as counter-ions.[2] Unfortunately, such salts are sparingly soluble in aqueous solution and virtually insoluble in lipophilic media. Crown ethers can be used to solubilize aryldiazonium tetrafluoroborates or hexafluorophosphate salts in such solvents as chloroform,[3] but the complexation phenomenon deactivates the substrate.[4,5] We present here an alternative method for solubilizing aryldiazonium cations in lipophilic media and demonstrate the utility of the method in a variety of transformations, particularly those involving aryl radicals generated under very mild conditions.

4-Chlorobenzenediazonium tetrafluoroborate (1) is insoluble in chloroform solution: after two weeks stirring at ambient temperature, filtration and treatment of the supernatant with an equivalent of N,N-dimethylaniline, no 4-chloro-4'-N,N-dimethylaminoazobenzene (2) was isolated, but the diazonium salt was recovered quantitatively.[6] In contrast, when 1 was stirred for 3 h at 0° C (see table) with chloroform and an equivalent of tetramethylammonium chloride,[7] filtered and the supernatant treated with an equivalent of N,N-dimethylaniline, an almost quantitative yield of 2 was obtained. Apparently, the diazonium tetrafluoroborate undergoes a metathetical gegenion exchange reaction according to equation 1. Under similar conditions, using the isolated yield of azo dye (equation 2) as a measure, we have found that 4-methoxy-, 4-methyl-, 4-bromo-, and 4-fluorobenzenediazonium ions are soluble to the extents of 50%, 67%, 66% and 51% respectively. The results of experiments using salts such as tetraethylammonium bromide, tetraethylammonium chloride and bromide and benzyltriethylammonium chloride suggest that yields may be improved by an appropriate choice of salts.

$$4\text{-X-}C_6H_4\text{-}N_2{}^+BF_4{}^- + Me_4N^+Cl^- \rightleftarrows 4\text{-X-}C_6H_4\text{-}N_2{}^+Cl^- + Me_4N^+BF_4{}^- \qquad \text{(eq. 1)}$$

$$4\text{-X-}C_6H_4\text{-}N_2{}^+Cl^- + C_6H_5\text{-}NMe_2 \rightarrow 4\text{-X-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}NMe_2 + HCl \qquad \text{(eq. 2)}$$

That the ionic aryldiazonium chloride[8] should be freely soluble in chloroform solution is somewhat surprising, but quantitative isolations of solid tetramethylammonium tetrafluoroborate by filtration (see equation 1) and silver chloride from the supernatant after treatment with alcoholic silver nitrate solution as well as Fourier transform infrared data[9] provide convincing evidence that it is the diazonium chloride in solution.

Appropriately *para*-substituted aryldiazonium ions undergo facile para-substitution reactions with certain nucleophiles.[5,10] In our own work,[5] it seems likely that the reactions involve the gegenion exchange phenomenon as a precursor to the exchange reaction. In the presence of acetate ion, either gegenion metathesis or *para*-substitution should occur. We see none of the latter when potassium acetate and a catalytic amount of 18-crown-6[11] are used as acetate source:[12] rather, in the absence of a radical scavenger (or in poorer yield in its presence), decomposition via the diazoanhydride occurs. 4-Bromobenzenediazonium tetrafluoroborate (at 20°C) in the presence of potassium acetate and crown ether yields bromobenzene or 4-deuteriobromobenzene in chloroform (H$^\cdot$ abstraction) or deuteriochloroform (D$^\cdot$ abstraction), *p*-dibromobenzene in bromotrichloromethane (Br$^\cdot$ abstraction) or 4-bromobiphenyl in benzene.[13] The yields for these four processes are 97%, 100%, 50% and 81% respectively.[14] The latter, in particular, is a general method for the high yield synthesis of unsymmetrical biphenyls and preparative conditions will be disclosed in a separate report.[15] The reaction of aryl radicals generated by this method with bromotrichloromethane constitutes an alternative to the Sandmeyer reaction.[16] In each of the reactions discussed above, we presume that the aryl radicals result from dissociation of the diazoanhydride according to the scheme. It is important to note that in the absence of 18-crown-6, under otherwise identical conditions, significantly lower yields were observed in all cases studied.

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SCHEME

$4\text{-Br-}C_6H_4\text{-}N_2{}^+BF_4{}^- \xrightarrow{AcO^-} 4\text{-Br-}C_6H_4\text{-N=N-OAc}$

$4\text{-Br-}C_6H_4\text{-N=N-OAc} + AcO^- \longrightarrow 4\text{-Br-}C_6H_4\text{-N=N-O}^- + Ac_2O$

$4\text{-Br-}C_6H_4\text{-N=N-O}^- + 4\text{-Br-}C_6H_4\text{-}N_2{}^+ \longrightarrow (4\text{-Br-}C_6H_4\text{-N=N-})_2O$

$(4\text{-Br-}C_6H_4\text{-N=N-})_2O \longrightarrow 4\text{-Br-}C_6H_4\text{-N=N-O}^\cdot + N_2 + 4\text{-Br-}C_6H_4{}^\cdot$

$4\text{-Br-}C_6H_4{}^\cdot \xrightarrow{CHCl_3} C_6H_5\text{-Br}\ (97\%)$

$4\text{-Br-}C_6H_4{}^\cdot \xrightarrow{BrCCl_3} 4\text{-Br-}C_6H_4\text{-Br}\ (50\%)$

$4\text{-Br-}C_6H_4{}^\cdot \xrightarrow{C_6H_6} 4\text{-Br-}C_6H_4\text{-}C_6H_5\ (81\%)$

TABLE

Reactions of Aryldiazonium Ions[a,b]

X[a]	Reagent (Equiv.)	Solvent	Conditions[c]	Product (% Yield)[d]	
Cl	$Me_4N^+Cl^-$ (1)	$CHCl_3$	0°C, 3 h	$4\text{-Cl-}C_6H_4\text{-N=N-}C_6H_4\text{-NMe}_2$	(93)
MeO	$Me_4N^+Cl^-$ (2)	$CHCl_3$	0°C, 3 h	$4\text{-MeO-}C_6H_4\text{-N=N-}C_6H_4\text{-NMe}_2$	(50)
Me	$Me_4N^+Cl^-$ (2)	$CHCl_3$	0°C, 3 h	$4\text{-Me-}C_6H_4\text{-N=N-}C_6H_4\text{-NMe}_2$	(67)
Br	$Et_4N^+Br^-$ (2)	$CHCl_3$	0°C, 3 h	$4\text{-Br-}C_6H_4\text{-N=N-}C_6H_4\text{-NMe}_2$	(66)
F	$Me_4N^+Cl^-$ (2)	$CHCl_3$	0°C, 3 h	$4\text{-F-}C_6H_4\text{-N=N-}C_6H_4\text{-NMe}_2$	(51)
Cl	$Me_4N^+Cl^-$ (1)	$CHCl_3$	0°C, 3 h	---[e]	
Br	KOAc (2)/18-C-6 (0.05)	C_6H_6	20°C, 1 h	$4\text{-Br-}C_6H_4\text{-}C_6H_5$	(81)
Br	KOAc (2)/18-C-6 (0.05)	$CDCl_3$	20°C, 1 h	$4\text{-Br-}C_6H_4\text{-D}$	(100)[f]
Br	KOAc (2)/18-C-6 (0.05)	$CHCl_3$	20°C, 1 h	$Br\text{-}C_6H_5$	(97)[f]
Cl	KOAc (2)/18-C-6 (0.05)	--[g]	20°C, 1 h	$4\text{-Cl-}C_6H_4\text{-Br}$	(93)[f]
Br	KOAc (2)/18-C-6 (0.05)	--[g]	20°C, 1 h	$4\text{-Br-}C_6H_4\text{-Br}$	(50)[f]

a) According to equation 1. b) All reactions were carried out under nitrogen at a diazonium concentration of 0.1 molar. c) Reactions at shorter reaction times and higher temperatures gave lower yields. d) Isolated yields on compounds which were >99% pure by spectroscopic analyses and/or comparison with an authentic sample. e) In this case, a quantitative yield of tetramethylammonium tetrafluoroborate was isolated by filtration and 98% yield of AgCl was isolated by treatment of the supernatant with silver nitrate solution. f) See reference 13. g) The solvent was 1/1 (v/v) $BrCCl_3/HCCl_3$.

NOTES AND REFERENCES

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