

CROWN-CATION COMPLEX EFFECTS. IV. CROWN ETHER AND  
QUATERNARY ION MEDIATED DISPLACEMENTS IN ARYLDIAZONIUM COMPOUNDS

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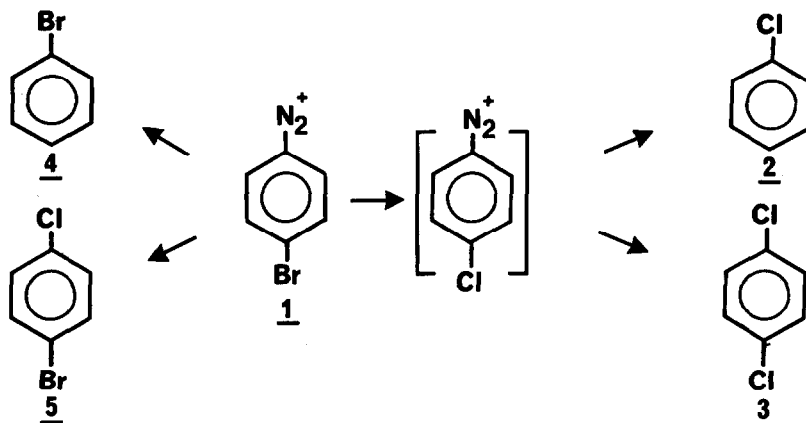
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Implicit in the high  $\sigma_p$  value reported for diazonio (1.8)<sup>1</sup> is the notion that facile nucleophilic aromatic substitution should be possible due exclusively to its electronic influence. That there is not a huge literature describing such processes is attributable largely to two factors: diazonio is itself a good leaving group and solvation by the aqueous medium (or other cation solvating solvent) attenuates the electronic effect. We have overcome these difficulties and achieved preparatively useful yields of nucleophilic aromatic substitution products by conducting the reactions in nonpolar media and utilizing nucleophiles which are ion-paired with quaternary ammonium cations or alkali metal-crown ether complexes.

Since Meldola and Streatfeild's first report in 1895,<sup>2</sup> a number of nucleophilic aromatic substitution reactions of aryldiazonium ions have been reported.<sup>3</sup> Although most of the work has been conducted in aqueous milieu, a variety of nucleophiles and ancillary substituents have been used and a wide variation in yield has been obtained. We have studied the halogen displacement reaction ( $Cl^-$  for  $Br^-$ ) of 4-bromobenzenediazonium tetrafluoroborate (1) in chloroform and dichloromethane at temperatures between 0° and 60°C. A chloroform solution of 1 (0.1 M)<sup>4</sup> and benzyltriethylammonium chloride (BTEAC, 0.5 M) when stirred for 24 h at 30.0 ± 0.2°C and then reduced<sup>5</sup> (7.5 eq. of 50% aq.  $H_3PO_2$  and catalytic  $Cu_2O$ ) yielded (glpc analysis<sup>6</sup>) chlorobenzene (2, 55%), p-dichlorobenzene (3, 14%), bromobenzene (4, 13%) and p-bromochlorobenzene (5, 17%). In the absence of BTEAC, even after 4 h reflux, no chlorinated products (>95% of 4) were obtained. Products 2 and 3 apparently arise from the intermediate 4-chlorobenzenediazonium ion by reduction and reaction with solvent or  $Cl^-$  ion respectively.<sup>7,8</sup> Products 4 and 5 arise similarly from residual 1. The presumed pathways are set forth in the scheme. Although it seemed an unlikely prospect that halogen exchange could occur under these conditions with 2, 3, 4 or 5, we have independently confirmed

## SCHEME



the absence of such processes. In dichloromethane solution at 30°C, the results were similar: compounds 2, 3, 4 and 5 were obtained in 51%, 19%, 3%, and 18% respectively. Likewise, when tetra-*n*-butylammonium chloride in chloroform solution was used instead of BTEAC, 52%, 13%, 14% and 21% yields of 2-5 were obtained. At 4°C, in a comparable period of time, similar results were obtained, but the conversion 1 → 2 + 3 had not gone as far.

It was anticipated that an appropriately sized macrocyclic (crown) polyether would complex the diazonio function.<sup>9</sup> To the extent that such a complexation occurs, the effective  $\sigma_p$  value for diazonio should be reduced. This remote substituent effect should be temperature and crown ether concentration dependent and should be reflected in the relative yields for the process 1 → 2. After 3 h at 30°C, 0.1 M 1 in CHCl<sub>3</sub> (in the presence of 5 equivalents of BTEAC) yielded a product mixture containing 55% of 2. In the presence of 18-crown-6<sup>10</sup> (1 eq.), only 30% of 2 was present, the difference being more 4. At 4°C, after 48 h, in the absence, presence of 1 eq. and 10 eq. of 18-crown-6 respectively, the yield of 2 was 30%, 6% and 0%. This dramatic reduction in yield is almost certainly due to attenuation of the positive charge at nitrogen by crown ether solvation of this activating group. As expected, this effect was not observed when the too small<sup>9a</sup> 12-crown-4<sup>11</sup> was substituted for 18-crown-6 or in the case of 2-bromobenzenediazonium tetrafluoroborate which undergoes facile halogen exchange.

Potassium chloride will also suffice as a chloride source when 18-crown-6, which apparently prefers to complex K<sup>+</sup> rather than -N<sub>2</sub><sup>+</sup>, is present. Thus, after 24 h at 30°C, 1 eq. each of KCl and 18-crown-6 converted 1 (0.1 M in CHCl<sub>3</sub>) to (inter alia) 2 in 57% yield. In the absence of crown, even with 5 eq. of KCl present, less than 10% of 2 was formed.

We are currently exploring the preparative utility of this transformation

and examining such obvious variables as crown ether, solvent, time, nucleophile, nucleofuge and concentration.<sup>12</sup>

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4. In the presence of >1.5 eq. of BTEAC (with or without crown) the normally insoluble **1** dissolves in chloroform or dichloromethane, due to anion exchange (see the following communication). 2-Bromobenzenediazonium tetrafluoroborate dissolved considerably more slowly.
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6. Yields determined by glpc analysis using 5' of 10' x 1/4" 10% SE-30 on NAW Chromosorb-P using an internal standard (corrected for detector response) are based on starting diazonium salt and represent two or more separate experiments (reproducibility: ±2% for each product). Products isolated by preparative glpc analysis were identified by retention time and either nmr or mass spectral analysis.
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8. Some 2 and 4 arise by in situ reduction prior to hypophosphorous acid addition. Thus partially deuterated 2 and 4 are isolated when the reaction is conducted in  $\text{CDCl}_3$  ( $\text{CBrCl}_3$  is isolated as a by-product).
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11. 12-Crown-4 was kindly provided by Professor H. D. Durst.
12. Dilution of the reaction mixture containing 5 eq. of BTEAC and 1 eq. of 1, from 0.1 M to 0.033 M increased the yield of 2 to 71% (while 4 decreased to 7%, 3 to 9%, and 5 to 13%).