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CONVERSION OF ARENEDIAZONIUM TETRAFLUOROBORATES INTO UNSYMMETRICAL BIARYLS USING CATALYSTS OTHER THAN POLYETHERS[1]

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Abstract In addition to crown ethers and glymes which catalyze the phase transfer Gomberg-Bachmann reaction, quaternary salts, carboxylate anions, and acetonitrile cosolvent are all shown to be effective in this system

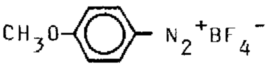
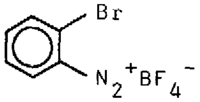
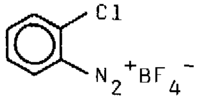
The chemistry of arenediazonium cations has been a subject of academic interest and commercial importance for more than a century [3] This chemistry has been amply reviewed.[4] Cram's observation[5] that otherwise insoluble arenediazonium tetra fluoroborates can be solubilized in nonpolar media has enhanced interest in the chemistry of arenediazonium salts in general and particularly in the stable BF_4^- and PF_6^- species Doyle[6] and Cadogan[7] have examined in situ reactions while we,[8] and Bartsch[9] and others[10] have utilized crowns[11] and glymes[12] as catalysts for various reactions. We have reported that gegenion metathesis involving quaternary ammonium salts[13] may be used to solubilize diazonium compounds and Butler and Shepherd[14] have demonstrated crown catalyzed azo-coupling of 4-methoxybenzenediazonium tetrafluoroborate with N-methylpyrrole in $CHCl_3$. Recently, Ellwood, Griffiths, and Gregory have claimed the "first examples of phase transfer catalysis in electrophilic substitution reactions" accelerating the azo-coupling reaction by addition of sundry soaps.[15] The latter work prompts us to disclose our own attempts to catalyze arenediazonium salt reactions using quaternary ammonium compounds, carboxylate salts, and dipolar aprotic solvents

The results reported here are for the phase transfer variant[16] of the classical Gomberg-Bachmann arylation reaction[17] since we believe that this is one of the most synthetically useful of the arenediazonium cation transformations. The conversion is illustrated in equation 1. In a previous report[18] we demonstrated

$$Ar\text{-}N_2^+BF_4^- + KOAc + Ar'\text{-}H(solvent) \xrightarrow[\text{rt, 1 5 h}]{\text{catalyst}} Ar\text{-}Ar' \qquad (1)$$

that the reaction could be carried out much more easily, quickly, and in generally

Table. Synthesis of Monosubstituted Biaryls from Arenediazonium Salts and Benzene[a]

Arenediazonium Salt	Catalyst	Mol-%[b]	Eq. KOAc[b]	Yield(%) after 1.5 h[c]	24 h[d]
	none	-	2	4	--
	18-crown-6	5	2	80[d]	80
	$PhCH_2N^+(C_2H_5)_3Cl^-$	5	2	49	60
	$(C_4H_9)_4N^+HSO_4^-$	5	2	54	87
	Aliquat 336[e]	5	2	79	71
	$K^{+-}O_2C(CH_2)_4CH_3$	200	0	75	68
	$K^{+-}O_2C(CH_2)_{14}CH_3$	200	0	53	67
	CH_3CN	5[f]	2	68	76
	CH_3CN	10[f]	2	72	69
	18-crown-6	5	2	81	--
	$(C_4H_9)_4N^+HSO_4^-$	5	2	--	51
	18-crown-6	5	2	73	--
	$(C_4H_9)_4N^+HSO_4^-$	5	2	60[d]	--
	$K^{+-}O_2C(CH_2)_4CH_3$	200	0	23	26
	$K^{+-}O_2C(CH_2)_{14}CH_3$	200	0	44	42
	none	-	2	30[d]	--

a. The solid diazonium salt (0.01 mol) and KOAc (0.02 mol) were stirred in benzene (100 mL) at ambient temperature in the presence of the specified additive for the indicated time period as described in eq. 1 and ref 18. b. Mol-% of additive relative to arenediazonium salt. c. Yield determined by gas chromatographic analysis unless otherwise specified. d. Yield is for isolated, pure material. e. Aliquat 336 is a mixture of $(C_8H_{18}\text{-}C_{10}H_{22})_3NCH_3{}^+Cl^-$ f. Volume-% of acetonitrile cosolvent in benzene; no catalyst per se added.

higher yield than was possible using classical conditions. In considering the mechanism of this reaction,[19] it occurred to us that if crown ether complexation[5] of the arenediazonium cation was required for reaction, some slowing[9] of the inherent reaction rate must be occurring and yields for the poorly complexed, ortho-substituted arenediazonium cations should be inferior. In the phase transfer Gomberg-Bachmann (ptGB) reaction,[8] this does not appear to be the case. This further suggested to us that such species as quaternary salts, already known to be capable of facilitating solubilization[13] and even long-chain alkali metal carboxylates might be useful catalysts for this reaction The success of these various species is apparent from a perusal of the table Note that in this study, the three diazonium salts chosen were all coupled with benzene. This was done in an effort to ensure comparability, and studies with other solvents and other salts will be disclosed in the full report of this work.

In essentially all of the cases examined, crown ether catalysis of the ptGB reaction was superior to non-crown catalysis, but in some instances it was only marginally so The quaternary salts tetrabutylammonium bisulfate and benzyltriethylammonium chloride were effective but rates were slow. Aliquat 336 appeared to be as useful as crown. Most useful of all, however, was adding a small amount of acetonitrile as a cosolvent The yields were only slightly inferior to the crown and quaternary salt reactions and they were extremely convenient to conduct

The potassium hexanoate and hexadecanoate salts are interesting in that they serve two functions in this reaction First, each presumably acts as a phase transfer agent by forming a soluble diazoester, Ar-N=N-O-CO-R This can then react with another equivalent of acid salt to form the required[19] diazoanhydride One would predict from this analysis that palmitate would be a better catalyst than caproate as is observed for the 2-chlorobenzenediazonium salt The result is different, however, for the 4-methoxybenzenediazonium salt and this variation likely reflects a difference in lattice energies between the starting materials It now seems clear that phase transfer processes involving arenediazonium salts are influenced by rather subtle solubility factors and the latter is but one example of this phenomenon.

Use of acetonitrile as a cosolvent enhances the convenience of this reaction, reduces the expense and facilitates workup We are currently assessing its generality in replacing other pt-catalysts in this and related reactions.

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