Mechanism of Formation of Aryl Fluorides from Arenediazonium Fluoborates[1]

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Abstract: The Schiemann reaction (thermal decomposition of an arenediazonium fluoborate, $ArN_2^+BF_4^-$, to a fluoroarene and nitrogen) does not require dissociation of BF_4^- to F^-. The step that forms fluoroarene is a direct reaction of the BF_4^- ion. This is demonstrated by insensitivity to excess BF_3 concentration of the ratio of products, ArF/ArCl, from *p-tert*-butylbenzenediazonium fluoborate in methylene chloride solution at 25°. It contrasts with the previously demonstrated requirement of dissociation of ArN_2^+ to Ar^+ prior to the product-determining step.

As part of our mechanistic study of reactions of benzenediazonium salts in solution,[2-4] we sought to determine whether fluoborate ion, BF_4^-, reacts directly as such in the Schiemann reaction[5] or whether it first dissociates to fluoride anion. We have already excluded[2] direct reactions of arenediazonium ions (mechanism 1a and 1b) and shown

$$ArN_2^+ + BF_4^- \longrightarrow ArF + N_2 + BF_3 \qquad (1a)$$

$$ArN_2^+ + F^- \longrightarrow ArF + N_2 \qquad (1b)$$

that ArN_2^+ first dissociates to a singlet aryl cation (Ar^+) in the rate-determining step, leaving only the following possibilities (2a and 2b) for the step that forms fluoroarene.

$$Ar^+ + BF_4^- \longrightarrow ArF + BF_3 \qquad (2a)$$

$$BF_4^- \overset{K}{\rightleftharpoons} BF_3 + F^- \qquad (2b)$$

$$Ar^+ + F^- \longrightarrow ArF$$

Mechanism 2b requires a reciprocal dependence of the rate of formation of ArF from Ar^+ on the concentration of BF_3. The actual dependence cannot be discerned from rate measurements when ArF is the sole product because formation of Ar^+ is then the rate-determining step. However, it is discernible from experiments involving competition between ArF formation and a reaction of Ar^+ involving neither BF_4^- nor F^-.

For the present study, we chose the decomposition of *p-tert*-butylbenzenediazonium fluoborate [Ar = *p*-$(CH_3)_3CC_6H_4$] in a methylene chloride (CH_2Cl_2) solution at 25°. This diazonium salt is very soluble in CH_2Cl_2, whereas benzenediazonium fluoborate is almost insoluble. Gas-liquid chromatography showed that ArF and ArCl were the only aromatic products and accounted for all the diazonium salt decomposed. Methylene chloride does not react appreciably with BF_3 nor form a strong complex with it.

Table I shows that the product distribution is not affected by addition of excess BF_3 and thereby disproves mechanism 2b. Excess Br_2 was also added to the reaction mixture as a free radical trap in one experiment. Since no ArBr formed, radical reactions are improbable.

A slight increase in per cent ArF with increasing concentration of ArN_2^+ results from the increase in BF_4^-/CH_2Cl_2 ratio. Perhaps the ArF forms from ion pairs, while free ArN_2^+ ions in solution give ArCl.

In conclusion, our experiments prove that the source of F in the ArF is BF_4^- ion (mechanism 2a) and not F^- ion (mechanism 2b). It is not unreasonable that an intermediate (Ar^+) sufficiently electrophilic to be capable of attacking neutral CH_2Cl_2 should be capable of attacking BF_4^- ion without waiting for it to dissociate to F^- ion.

Table I. Products from *p-tert*-Butylbenzenediazonium Fluoborate in Methylene Chloride Solution at 25°

$[ArN_2BF_4]_0$, *M*	$[BF_3]_0$, *M*	% ArF	% ArCl
0.0018	0.00	41	56
0.0045	0.00	52	48
0.0062	0.00	58	42
0.0080	0.00	60	40
0.0144	0.00	65	35
0.0291	0.00	68	32
0.0361	0.00	70	30
0.0723	0.00	73	27
0.0107	0.09	62	38
0.0262	0.09	65	35
0.0728	0.09	75	25
0.0107	0.00	63	37
0.0107	0.02	61	39
0.0107	0.04	64	36
0.0546	0.00[a]	70[a]	30[a]

[a] 0.101 *M* Br_2 present, no ArBr formed.

Experimental Section

CH_2Cl_2 (Fisher reagent), 2 l., was stirred thrice with 400-ml portions of concentrated H_2SO_4 for 2 hr each, washed with 1 l. of water, 1 l. of 0.1 *M* NaOH, and three 1-l. portions of water, dried over Drierite, and distilled, bp 40.1°.

p-tert-Butylbenzenediazonium fluoborate was prepared as follows. *tert*-Butylbenzene (Aldrich), 125 ml, was nitrated[6] with 83 g of 16 *M* HNO_3 and 125 g of 18 *M* H_2SO_4 at 30-40° for 3 hr. The reaction mixture was poured into ice and extracted with ether. The mixture of isomers (o/p = ¼), bp 161-170° (43 mm), was reduced by shaking 50 g with 89 g of Sn and 250 ml of 12 *M* HCl for 1 hr. Neutralization with NaOH and steam distillation afforded a mixture of *tert*-butylanilines (o/p = ⅕). After treatment with Ac_2O for 30 min. and cooling, the *p-tert*-butylacetanilide precipitated. It was recrystallized from ether-hexane, mp 170-171° (lit.[7] 171-172°), hydrolyzed with 15% HCl, neutralized, extracted with ether, and distilled, bp 93-95° (1 mm) [lit.[6] 89-90° (1 mm)]. The amine (5 g) was added to HBF_4 (17.5 ml, Baker 48%), cooled to 0°, and diazotized by dropwise addition of a solution of 3 g of $NaNO_2$ in 6 ml of water. The crystals of diazonium salt were collected and washed with ether. They were then dissolved in CH_2Cl_2, sufficient pentane was added to precipitate a small amount of the salt, and the solution was cooled to −30°. The crystals were collected, and the procedure was repeated twice more, yielding 3 g (36%) of white crystals, mp 99-102° dec, stored under vacuum in a desiccator at −30°: nmr (D_2O) δ 1.40 (9 H, s), 8.05 (2 H, d), 8.61 (2 H, d); ir (KBr) 2980, 2270, 1580, and 1150-1000 (BF_4^-) cm^{-1}.

A 0.0089 *M* solution in CH_2Cl_2 was allowed to stand for 10 days at 25°. At the end of this time, the products were analyzed by glc. The columns used were either 6-ft XE60 on Diatoport S at 70° or 3-ft 10% Corning vacuum grease on Chromosorb W at 140°. For the first column, dodecane was used as the internal standard, and for the second, anisole was used. All runs showed *p-tert*-butylfluorobenzene and *p-tert*-butylchlorobenzene as the only aromatic products, and all runs that were checked showed that these compounds accounted for all the initial diazonium salt.

For runs with excess BF_3, a solution of the diazonium salt was prepared as above and placed in a bubble tube equipped with stopcocks at both ends. BF_3 was bubbled through the tube for several minutes, and then the stopcocks were closed, sealing the tube. At the end of 10 days, the tube was opened and 1 ml of the solution was pipetted into water to hydrolyze the BF_3. The H_3BO_3 thus produced was titrated by standard methods. The rest of the solution was analyzed for products as above. In the runs with excess Br_2, Br_2 concentration was determined by $Na_2S_2O_3$ titration of I_2 liberated from KI.

p-tert-Butylhalobenzenes which were used as standards to calibrate the glc were prepared by reaction of the appropriate halobenzene with *tert*-butyl chloride in the presence of $FeCl_3$. The literature procedure for chlorobenzene[8] was also used for fluoro- and bromobenzene.

References and Notes

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Reactions of the Zwitterions from Trisubstituted Electron-Deficient Ethylenes and Electron-Rich Olefins

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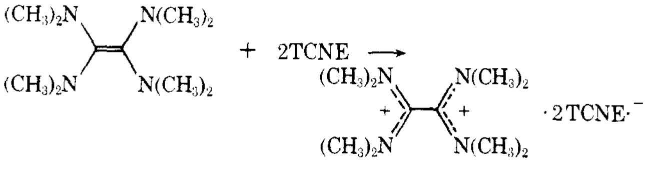
Abstract: Reactions of a series of electrophilic trisubstituted olefins (**1–4**) with a series of electron-rich olefins (**5–10**) were studied. The reactivities increased sharply with the degree of electrophilic and nucleophilic character, respectively; however, steric effects of β substituents prevented a 1:1 correspondence. The kinetically favored products were cyclobutanes in almost all cases. In polar solvents or on heating, they isomerized to olefinic adducts *via* hydrogen shift or underwent cycloreversion. All this behavior could be understood in the context of a zwitterionic intermediates, as described by earlier investigators in related systems. However, formation of 2-*N,N*-dimethylamino-1,1-dicyanoethylene (**11**) from reactions of tricyanoethylene with *N,N*-dimethylvinyl- or -isobutenylamines appeared to occur by a concerted cleavage of an unstable cyclobutane. Facile olefin metathesis occurs in the region between cyclobutane formation and direct electron transfer.

Reactions of electrophilic olefins with nucleophilic olefins comprise an interesting and versatile chapter of organic chemistry. Electrophilic olefins containing a single electron-withdrawing group (acrylonitrile, methyl acrylate) or two such substituents in the 1,2 positions (fumaronitrile, diethyl fumarate) require elevated temperatures to bring about reaction with even the extremely nucleophilic aliphatic enamines, although enamines containing β hydrogens react under milder conditions.[1]

At the other extreme of electrophilic character, tetracyanoethylene reacts readily at room temperature with a wide variety of moderately electron-rich olefins.[2] Other extremely electrophilic tetrasubstituted ethylenes including 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene[3] and the isomeric 1,2-bis(trifluoromethyl)-1,2-dicyanoethylenes[2] behave similarly. With aggressive electrophiles such as these, the activating substituent in the electron-rich partner can be nonbasic nitrogen (*N*-vinylamides, *N*-vinylsulfonamides, *N*-vinylcarbazole), oxygen (vinyl ethers), sulfur (vinyl sulfides), or carbon (*p*-methoxystyrene, cyclopropylethylene[2b,c]). Under very mild conditions, enamines reacted with the very active TCNE to give 1,1,2-tricyano-3-alkyl-4-*N,N*-dialkylaminobutadienes.[4] Wiberg[5] showed that, in the extreme case, tetrakis(dimethylamino)ethylene reacted with tetracyanoethylene in a redox manner:



With the exception of this last unusual reaction, all the reactions cited involved formation of a zwitterion intermediate in the rate-determining step. Detailed mechanistic studies on the cycloaddition of TCNE to vinyl ether have been carried out by Huisgen and his collaborators.[6] Large solvent effects on the rate constant were observed. Particularly in the more polar solvents, the zwitterion was sufficiently long-lived to permit conformational rotation and loss of stereochemistry. A study[7] of the effect of pressure on these reactions lent further support to the presence of a zwitterion intermediate.

In the reactions of para-substituted styrenes with TCNE, the ρ value was -7.2,[8] and enormous solvent effects on the rate constants were observed. All these observations strongly point toward rate-determining zwitterion formation in these reactions also.

The zwitterion proceeds to products in a variety of ways (Scheme I). The cyclobutane is usually the kinetically favored product. However, owing to ring strain and substitu-

Scheme I