The Use of Arenediazonium Hexafluoro-antimonates and -arsenates in the Preparation of Aryl Fluorides

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Thermolysis of arenediazonium hexafluoroantimonates containing electron-withdrawing substituents (nitro- and carboxy-groups or fluorine) gives substantially better yields of the corresponding fluoro-compounds than the decomposition of diazonium salts of any other complex fluoro-acid so far reported. Arenediazonium hexafluoroarsenates with a free *para*-position when heated dry produce fluorine-substituted diarylarsonic acids; a mechanism is described for this reaction.

THE most widely used method for preparing ' lightly ' fluorinated aromatic or heteroaromatic compounds consists of heating dry diazonium tetrafluoroborates (Balz-Schiemann reaction).[1] However, certain substituents in the ring limit the scope of this reaction either by rendering the diazonium tetrafluoroborates water-soluble and hence difficult to prepare or by adversely affecting the conversion of the diazonium salt into its aryl fluoride. Foremost in the first category are the hydroxy- and carboxy-groups; the second includes the nitro-group and other electron-withdrawing substituents.

Diazonium salts of other complex fluoro-acids have been used as a substitute in the Schiemann reaction in an attempt to overcome these limitations. As early as 1930 Lange and Müller [2] prepared 4,4'-difluorobiphenyl and fluorobenzene by heating the appropriate diazonium hexafluorophosphates but only in low yield. More recently these diazonium compounds were investigated systematically [3] and shown to be better than the diazonium tetrafluoroborates for preparing fluorobenzoic acids and fluorophenols. Diazonium hexafluorosilicates [4] were found to be preferable to fluoroborates in the preparation of 2-fluoropyridine and *p*-fluorophenol; the latter could not be made directly by the Schiemann method.[5] However, all three fluorophenols have recently been obtained from the corresponding diazonium tetrafluoroborates by a slight modification [6] of the established procedure. The recently reported examples of aryl fluoride syntheses from diazonium hexafluorogermanates appear to offer no advantages over established reactions.[7]

As benzenediazonium hexafluoroantimonate had been shown to be insoluble and to yield fluorobenzene when heated, albeit in small yield,[8] we decided to study the pyrolysis of these diazonium salts. We found the preparation of the diazonium hexafluoroantimonates in general to be as practicable as that of the corresponding fluoro-borates or -phosphates (see Table), as they were insoluble and stable to light and air. Moreover, their decomposition points were invariably lower (see Table) than those of the corresponding fluoro-borates or -phosphates; this tempered the severity of the decomposition reaction. In fact, in most cases dilution of the diazonium compound with sand was not necessary. In general, electron-withdrawing groups did not reduce the yield. Consequently, the method proved particularly rewarding for the preparation of the three fluorobenzoic acids and *o*-fluoronitrobenzene (40% yield), a compound for which yields rarely exceed 10% in practice although

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[1] A. Roe, *Org. Reactions*, 1949, **5**, 193; H. Suschitzky, *Adv. Fluorine Chem.*, 1965, **4**, 1; Houben-Weyl, ' Methoden der organischen Chemie,' Georg Thieme, Stuttgart, 1962, vol. 5, p. 213.

[2] W. Lange and E. Müller, *Ber.*, 1930, **63**, 1058.

[3] K. G. Rutherford, W. A. Redmond, *J. Org. Chem.*, 1963, **28**, 568; K. G. Rutherford, W. A. Redmond, and J. Rigamonti, *ibid.*, 1961, **26**, 5149.

[4] R. D. Beaty and W. K. R. Musgrave, *J. Chem. Soc.*, 1952, 875.

[5] A. Roe, P. H. Cheek, and R. H. J. Wiley, *J. Amer. Chem. Soc.*, 1949, **71**, 1863.

[6] O. Danek, D. Snobl, I. Knizek, and F. Nouzova, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1642.

[7] L. G. Makarova and I. V. Polovyaniok, *Izvest. Akad. Nauk., S.S.S.R., Ser. khim.*, 1967, **12**, 2750.

[8] W. Lange and K. Askitopoulos, *Z. anorg. Chem.*, 1935, **223**, 369.

claims for higher yields have been made in the literature. Also 1,2,3-trifluorobenzene was produced in over 30% yield from the 2,3- and the 2,6-difluorobenzenediazonium hexafluoroantimonates. This again is a substantial increase over the yield (<10%) reported for these preparations from diazonium fluoroborates.[9] Some improvement was also observed in the synthesis of 2-fluoropyridine (see Table).

Yields of arenediazonium salts and of aryl fluorides obtained from their decomposition (all yields based on parent amine)

Aromatic amine	$ArN_2^+SbF_6^-$ Yield (%) Method *A*				$ArN_2^+AsF_6^-$ Yield (%) Method *A*				$ArN_2^+BF_4^-$ Yield [1] (%)			$ArN_2^+PF_6^-$ Yield [3] (%)		
	A	*B*	Decomp. temp.	ArF Yield (%)	*A*	*B*	Decomp. temp.	ArF Yield (%)	Yield [1] (%)	Decomp. temp.	ArF Yield [1] (%)	Yield [3] (%)	Decomp. temp.	ArF Yield [3] (%)
Aniline	90		69°	50		93	79°	0 [a]	56—97	121°	51—90			
o-Toluidine	Quant.		70	21		97	101	0 [b]	59—90	106	45—65	97	110	58
m-Toluidine	90		96	30	Quant.		80	Trace [c]	79—90	108	69—87	Quant.	110	57
p-Toluidine	Quant.		102	47		93	104	2 [b]	67—90	114	70	97	112	71
o-Aminobenzoic acid	87 [d]		107	62		67	137	0	0—46	125	9	79	129	60
m-Aminobenzoic acid		87 [d]	105	77	83		129	0	31	155	5			
p-Aminobenzoic acid		93	108	76	69		134	0	76—84	140	40	77	150	49
o-Nitroaniline	95		130	40	90		140	31	63—92	135	9—17	97	161	10—20
m-Nitroaniline	94		129	60	96		132	51	79—99	178	43—54	Quant.		58
p-Nitroaniline	97		135	60	96		135	0	80—100	156	40—58	Quant.	170	63
p-Aminophenol	54		109	Trace					*e*		*e*	77	130	10—20
o-Anisidine		94	135	37	93		148	0	52—91	125	54—67	Quant.	120	60
2,3-Difluoroaniline	70		150	33					*f*		*f*			
2,6-Difluoroaniline	Quant.		150	35					*f*		*f*			
2-Aminopyridine	*g*			50					*g*		34			
3-Aminopyridine	*g*			35					*g*		48			

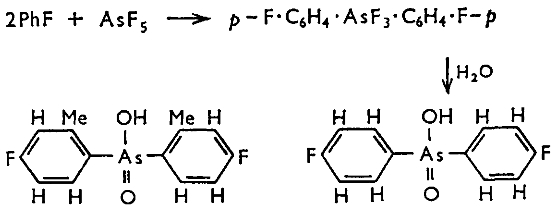
[a] 4,4′-Difluorodiphenylarsonic acid (86·5%) was the product. [b] A glassy arsenic-containing mixture was obtained. [c] The main product was the corresponding arsonic acid (cf. Experimental section). [d] This diazonium salt was washed with chloroform because of its solubility in water. [e] Cf. ref. 6 for a recent preparation from $ArN_2^+BF_4^-$. [f] This preparation has been reported (ref. 9) to give a very small yield. [g] Diazonium salt too unstable for isolation.

The decomposition of the arenediazonium hexafluoroarsenates took an unexpected course. For instance, when benzenediazonium hexafluoroarsenate was pyrolysed, no fluorobenzene distilled over. Instead a deliquescent solid was obtained which reacted with water to give 4,4′-difluorodiphenylarsonic acid. In view of the yield (87%) and convenience this appears to be by far the best preparation of this compound, which has been made from more inaccessible starting materials in unstated yield.[10] Also, the general procedures for making diarylarsonic acids [11] require several steps and yields are comparatively poor.

A reasonable mechanism (see Scheme) for the formation of the arsonic acid from diazonium hexafluoroarsenates involves the initial formation of fluorobenzene as in a normal Schiemann-type reaction. The liberated arsenic pentafluoride then combines with two molecules of fluorobenzene in the *para*-position, owing to the influence of the strongly *para*-directing fluorine, to give a trifluoro-compound which is subsequently hydrolysed to the arsonic acid. Support for this Scheme was

$$[PhN_2]^+AsF_6^- \longrightarrow PhF + AsF_5 + N_2$$

obtained by passing arsenic pentafluoride (prepared by decomposing *m*-nitrobenzenediazonium hexafluoroarsenate) through boiling fluorobenzene. Treatment of this reaction mixture with water gave the difluorodiarylarsonic acid as before. No products were obtained from the reaction of arsenic trifluoride with fluorobenzene.



(II) (I)

SCHEME

When the *para*-position was blocked, however, as in *p*-toluene-diazonium hexafluoroarsenate, only a glassy mixture of products containing arsenic was obtained, which could not be purified. This is understandable, since arsenic pentafluoride will attack the intermediate *p*-fluorotoluene in more than one position. When the reaction was applied to the toluene-*m*-diazonium compound the expected diarylarsonic acid (II) was obtained, although in lower yield (24%). It thus appears that the intermediate fluorine compound must have a vacant position *para* to the halogen if the reaction is to be practicable. Also, since attack of the arsenic fluoride on the ring is electrophilic, it was not surprising that the presence of a nitro-group prevented formation of the arsonic acid. Thus decomposition of *o*- or *m*-nitrobenzenediazonium hexafluoroarsenate proceeded in a similar manner to that of the hexafluoroantimonate analogues, to yield the corresponding fluoronitro-compounds (see Table). Again, a yellowish deliquescent sublimate was observed which appeared to be an addition compound of arsenic pentafluoride and fluoronitro-

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[9] A. Roe, R. A. Burton, and D. R. Reavill, *Chem. Comm.*, 1965, 582; A. Roe, private communication.

[10] O. A. Zeide, S. M. Sherlin, and A. B. Brucker, *Zhur. obshchei Khim.*, 1958, **28**, 2404.

[11] H. Bart, *Annalen.*, 1922, **429**, 55; G. O. Doak and L. D. Freedman, U.S.P. 2,653,160/1953.

benzene, since addition of water produced fumes of hydrofluoric acid and the requisite fluoronitro-compound.

EXPERIMENTAL

As hexafluoro-antimonic and -arsenic acids attack glass, polythene beakers were used in the preparation of diazonium compounds.

Preparation of Arenediazonium Hexafluoroantimonates.—*Method A*. In a typical preparation a solution of *p*-toluidine (7·0 g.) in water (5 ml.) and hydrochloric acid (*d* 1·18; 15 ml.) was diazotised at −5° by addition of powdered sodium nitrite (4·52 g.). Hexafluoroantimonic acid (65%; 24 ml.) was added dropwise with stirring to the cold reaction mixture. The precipitate of diazonium salt was filtered off, washed with ice-cold water and then with ether, and finally dried in air or *in vacuo*. For details of this and other preparations see Table.

Method B. Hexafluoroantimonic acid was used for both the diazotisation and precipitation; otherwise the procedure was as under (*A*).

Preparation of Arenediazonium Hexafluoroarsenates.—Methods *A* and *B* as described for the hexafluoroantimonates were used (see Table).

Decomposition of Diazonium Hexafluoroantimonates.—The dry diazonium salts were thermally decomposed as described previously.[12] Addition of an equal volume of sand was only necessary with the nitro-compounds. The reaction mixture was steam-distilled and the product if volatile was extracted from the distillate or if non-volatile from residue with chloroform or ether. The identity of all compounds was confirmed by i.r. or mixed m.p. comparison with an authentic sample. For yields of fluoro-compounds see Table.

Decomposition of the 2- and the 4-pyridinediazonium hexafluoroantimonates occurred spontaneously during the diazotisation and the respective products [2-fluoropyridine and *N*-(4-pyridyl)-4-pyridone] were obtained by working up the reaction mixture as described.[13] The n.m.r. spectrum of the pyridylpyridone (deuterium oxide) showed two overlapping quartets at τ 1·42 and 2·45 (2- and 3-H of pyridone ring), *J* 6·5 c./sec., and 1·92 and 3·48 (2- and 3-H of pyridyl ring), *J* 8 c./sec.

Pyridine-3-diazonium hexafluoroantimonate was obtained as an unstable solid and decomposed by stirring a suspension in ether overnight. The ethereal solution was saturated with dry hydrogen chloride gas and 3-fluoropyridine hydrochloride was filtered off. The salt was treated with a calculated amount of dimethylaniline for exact neutralisation and the liberated 3-fluoropyridine was distilled off.

Decomposition of Diazonium Hexafluoroarsenates.—(*a*) Benzenediazonium hexafluoroarsenate (14·8g.) was thermally decomposed in the usual way. The product which condensed and solidified on the cooler parts of the apparatus was dissolved in dil. aqueous sodium hydroxide and the solution was filtered. Addition of hydrochloric acid to the filtrate precipitated a white solid which was extracted with chloroform. Removal of the solvent left 4,4′-difluorodiphenylarsonic acid (I) (6·5 g., 86·5%), m.p. 138° (from light petroleum) (lit.,[10] 136—138°), τ ($CDCl_3$) 1·8 (1H, exchanged in D_2O), 2·83 (4H, t, $J_{2,3} = J_{HF} =$ 8·5 c./sec., *m*-protons), and 2·18 (4H, q, $J_{2,3}$ 8·5, J_{HF} 5·5 c./sec., *o*-protons).

(*b*) Other diazonium arsenates were decomposed similarly and results are given in the Table.

(*c*) Toluene-*m*-diazonium hexafluoroarsenate yielded *2,2′-dimethyl-4,4′-difluorodiphenylarsonic acid* (II) (24%), m.p. 195° (Found: C, 52·6; H, 4·0; F, 12·0. $C_{14}H_{13}AsF_2O_2$ requires C, 52·8; H, 4·1; F, 12·3%), τ ($CDCl_3$) 0·6 (1H, exchangeable in D_2O, OH), 7·58 (Me), 2·05 (2H, q, $J_{5,6}$ 9·5, J_{HF} 6 c./sec., *o*-protons), and 2·8—3·2 (complex, *m*-protons).

Reaction of Arsenic Fluorides with Fluorobenzene.—(*a*) Arsenic trifluoride[14] (6 g.) and fluorobenzene (2 g.) were heated under reflux but no reaction occurred.

(*b*) Arsenic pentafluoride was liberated by decomposition of *m*-nitrobenzenediazonium hexafluoroarsenate (12·3 g.) and passed through a reflux condenser to remove any volatile organic compounds. It was then passed through boiling fluorobenzene (5 ml.). The excess of fluorobenzene was distilled off and the residue was dissolved in dil. aqueous sodium hydroxide. The solution was filtered, acidified (hydrochloric acid), and then extracted with chloroform to yield 4,4′-difluorodiphenylarsonic acid (0·4 g.), m.p. and mixed m.p. 138°.

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[12] H. Suschitzky, *J. Chem. Soc.*, 1953, 3042.

[13] A. Roe and G. F. J. Hawkins, *J. Amer. Chem. Soc.*, 1947, **69**, 2443.

[14] C. J. Hoffmann, *Inorg. Synth.*, 1953, **4**, 150.