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SOME UNEXPECTED PRODUCTS FROM ATTEMPTED HALOGEN EXCHANGE IN 2-NITROHALOAROMATIC SYSTEMS

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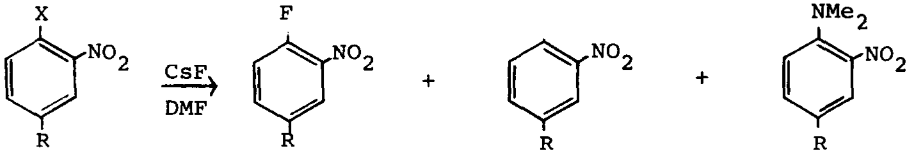
We wish to report some novel reactions in the attempted halogen exchange of activated haloaromatics (I) using CsF in dipolar aprotic solvents (Scheme 1 and Table).

SCHEME 1



I II III IV

The data in the Table shows that three competing reactions are occurring. Only in the cases of X=Cl are substantial quantities of the anticipated products (II) observed. When X=Br or I, dehalogenation or nucleophilic substitution of X by dimethylamine compete for I. The ratio of these products is directed by the electronic nature of the 4-substituent (R). For electron withdrawing substituents (Compounds 6-9) formation of the dimethylamino[1] compound IV is favoured.

TABLE

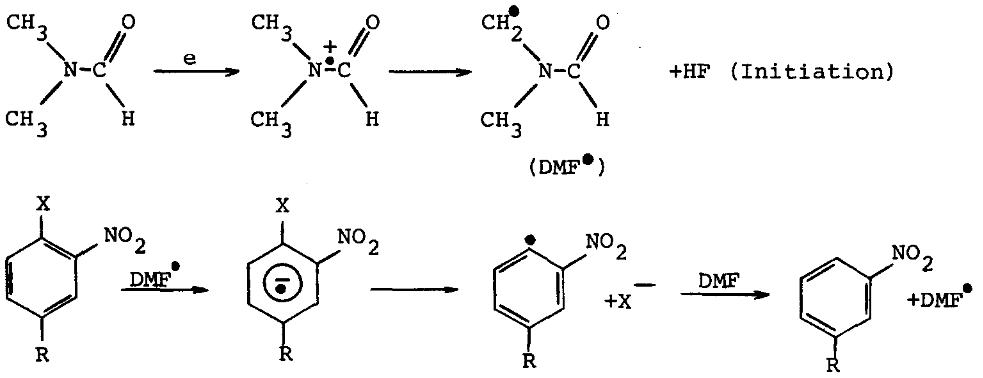
Starting Material (I)			Reaction Time (hr.)	Product Distribution (GLC-Mass Spectrometry)			
		R		I	II	III	IV
1.	X=Cl	Me	48	39	19	4	23
2.		H	40	20	49	0	29
3.	X=Br	NMe_2	48	17	0	77	0
4.		OMe	48	3	0	61	0
5.		Me	50	10	<1	53	16
6.		H	40	10	7	27	47
7.		Br	48	26	0	0	40
8.		CO_2H	48	43	0	0	23
9.		NO_2	48	0	0	0	100
10.	X=I	Me	48	25	0	60	5
11.		H	48	9	0	50	17

Standard conditions employed were: CsF (1 mmol) and the halonitroaromatic (I, 1 mmol) in refluxing DMF (15 ml).

Other Cs salts were evaluated and the debromination yields were in the order $CsF \simeq Cs_2CO_3 \gg CsCl > CsBr > CsNO_3$. A little debromination occurred with RbF but none with KF or NaF. The source of the introduced hydrogen was clearly identified using d_7-DMF as solvent (greater than 95% incorporation of one deuterium atom indicated by mass spectrometry). The novel debromination reaction was also observed in DMSO and in dimethylacetamide.

We rationalise the formation of the debrominated product as proceding by fragmentation of a radical anion[2] derived from the halonitroaromatic initiating species (Scheme 2). Experimental support is given by the threefold decrease in debromination rate upon addition of the radical anion traps[3] galvinoxyl or p-dinitrobenzene (10 mole %).

SCHEME 2



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