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THE THIOLATE ANION AS A NUCLEOPHILE
PART X*. REACTIONS OF SOME NITROFLUOROAROMATICS

MAURICE E. LEBLANC, MICHAEL E. PEACH and HEATHER M. WINTER

Chemistry Department, Acadia University, Wolfville, Nova Scotia, BOP 1XO (Canada)

SUMMARY

The reactions of various nitrofluorobenzenes, $C_6H_xF_yNO_2$, with sodium methanethiolate have been studied in ethylene glycol/pyridine mixture as solvent. All the fluorine atoms, but not the nitrogroups, could be substituted by the methylthio group. The reactions have also been studied with the addition of a deactivating group, either methyl or amino, on the aromatic nucleus. Some of the methylthio groups in the products were oxidized to the corresponding sulfones. The new compounds isolated have been characterized and their spectra (IR, NMR and mass) examined.

INTRODUCTION

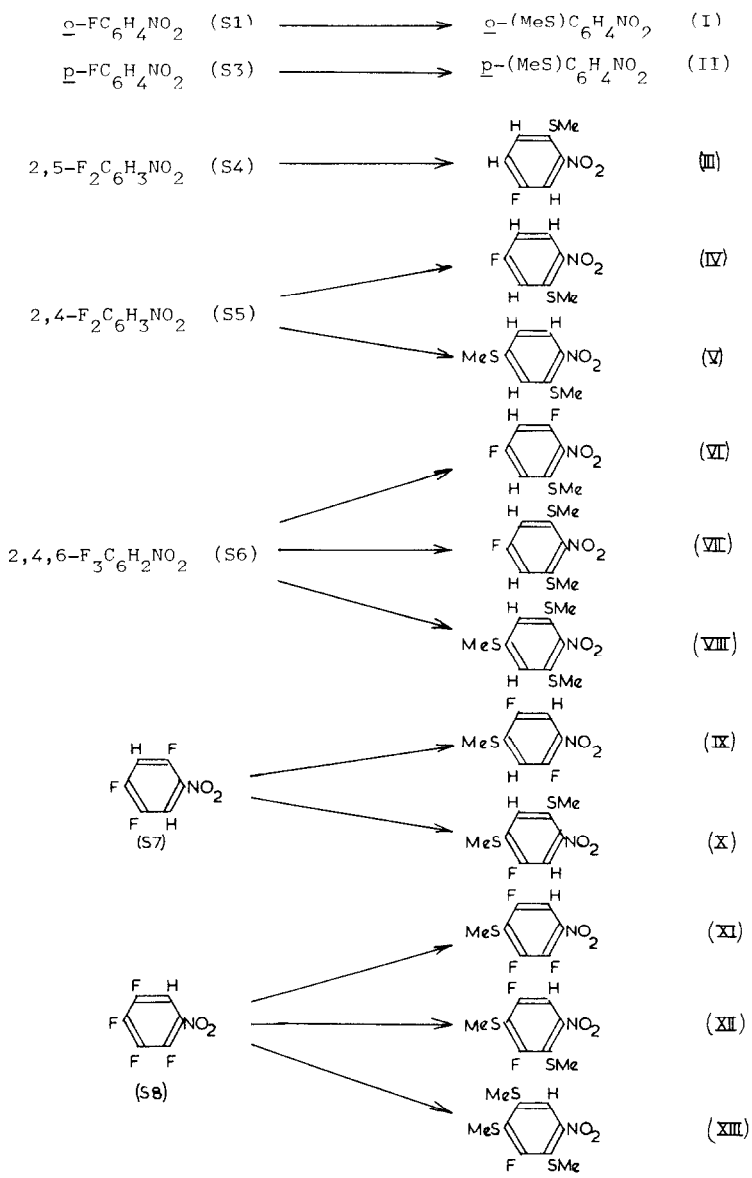
As a continuation of the study of the reactions of sodium methanethiolate with various substituted fluoroaromatics [1], the reactions of some nitrofluorobenzenes with sodium methanethiolate have been studied. The presence of the electron withdrawing nitro group on the aromatic ring should facilitate the nucleophilic replacement of fluorine and the reactions with the methanethiolate anion should be enhanced with respect to the simple fluorobenzenes, and considerably enhanced when compared with systems containing an electron donating group such as the aminofluorobenzenes.

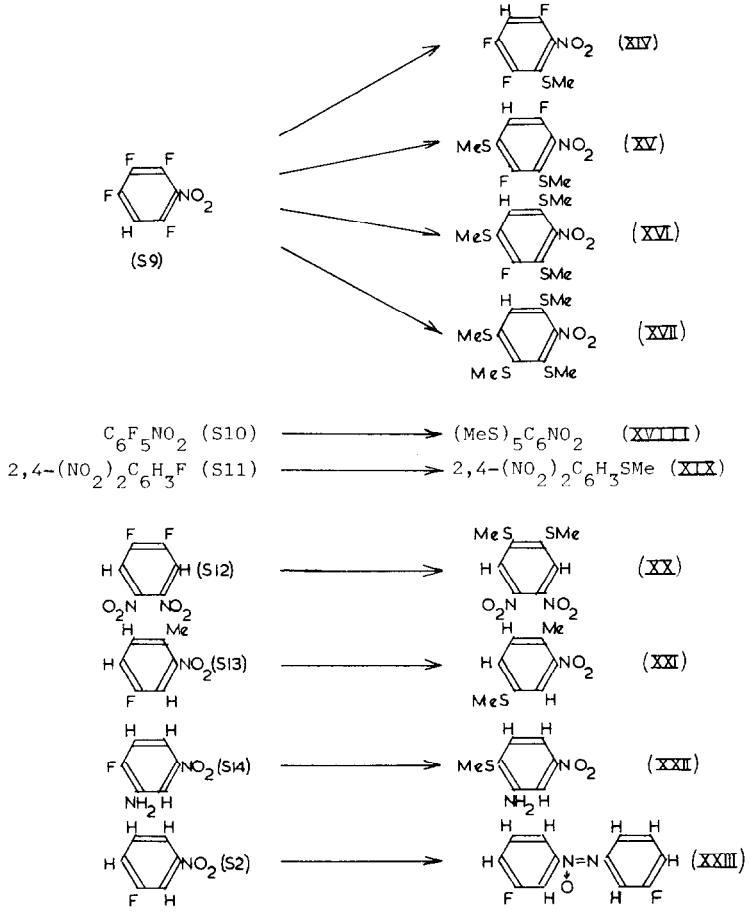
The reactions of pentafluoronitrobenzene with the methanethiolate anion have been examined previously [2]. The results show that using an

$$C_6F_5NO_2 \xrightarrow{SMe^-} O_2NC_6F_4SMe,\ O_2NC_6F_3(SMe)_2,\ O_2NC_6F_2(SMe)_3$$

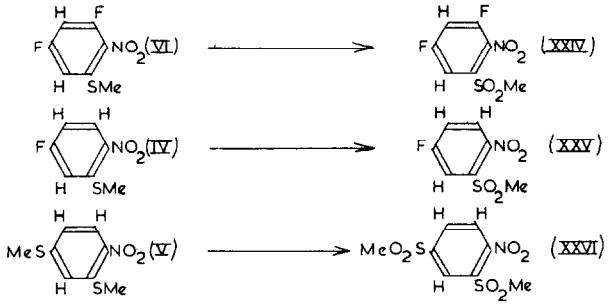
*For Part IX, see ref. 1

ethylene glycol/pyridine mixture as a solvent partial replacement of the fluorine atoms occurred. These reactions have been extended to several fluoronitrobenzenes, $C_6F_xH_yNO_2$, $C_6F_xH_y(NO_2)_2$, 4-fluoro-2-nitrotoluene and 2-fluoro-5-nitroaniline. The reactions observed are summarized below.





The methylthio groups in some of the products were oxidized to the corresponding sulfones, summarized below.



RESULTS AND DISCUSSION

The kinetics of the nucleophilic substitution of the fluorine on 2,4-dinitrofluorobenzene and p-fluoronitrobenzene have been extensively studied in methanol [3,4,5,6] . The reactions probably proceed through the formation of a Meisenheimer complex, such as

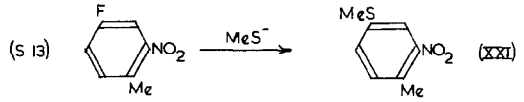
In other solvent systems such as DMF replacement of the nitro group can also be observed [7]. For example, hexakis(methylthio)benzene can be prepared from 1,3,4,5-tetrachloro-2,6-dinitrobenzene in DMF [8]. In some cases stepwise nucleophilic substitution can occur. The chlorine in 4-chloro-3,5-dinitrobenzotrifluoride can be substituted by the methylthio group in aqueous methanol, and then the nitro groups in the intermediate product substituted by the methylthio group in DMF [8]. In the present study a mixture of ethylene glycol and pyridine (volume ratio 1·2) was used as a solvent and exclusive replacement of the fluorine occurred. Only the major products of each reaction were isolated.

The activating effects of the nitro group are apparent as these reactions in ethylene glycol/pyridine solvent proceeded at ice-bath temperature, rather than refluxing conditions used for other fluoroaromatics [2,3,9]. Stepwise replacement of the fluorine could be observed. Tars tended to be formed if the reactions were studied in a refluxing solvent. In most cases all the aromatic fluorine atoms were readily replaced. This is in marked contrast to observations on the substitution of various simple fluorobenzenes and fluoroanilines in the same solvent system where at least two fluorine atoms, usually para to each other, remained on the aromatic ring [2,10] . However, if DMF is used as a solvent complete replacement of fluorine in fluorobenzenes with the methanethiolate anion occurred [1], in marked contrast to the reactions in ethylene glycol/pyridine as solvent [9] .

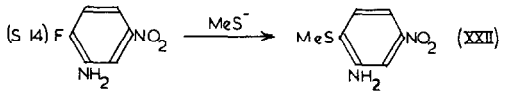
Initial substitution, where possible, occurred ortho or para to the nitro group. Subsequently the remaining fluorines ortho and para to the nitro group were then substituted. It is difficult to assess the effects of the other substituents, H, F and MeS on the position of substitution. The difficulty of replacing fluorine meta to the nitro group is apparent. It is however noteworthy that in the conversion of XVI to XVII substitution was para to a methylthio group, whereas the fluorine in X could not be substituted.

The only example of the reducing properties of the methanethiolate anion occurred with S2 where again the fluorine is meta to the nitro group.

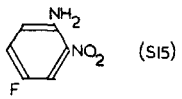
The effect of the other functional groups on the ease of substitution is also shown in the reaction of 4-fluoro-2-nitrotoluene(S13). The nitro



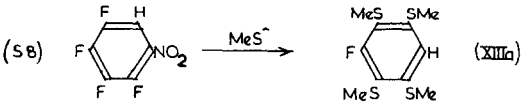
group will not readily activate a meta fluorine and the methyl group is known to be an activating group for electrophilic substitution. The substitution reaction had to be carried out in DMF rather than ethylene glycol/pyridine as solvent. DMF is known to be a better solvent than ethylene glycol/pyridine for nucleophilic substitution reactions of this type [1]. Substitution of the fluorine in 2-fluoro-4-nitroaniline(S14) occurred readily in ethylene glycol/pyridine solvent. The nitro group is



now para to the fluorine and activating it towards nucleophilic substitution and although the amino group is deactivating, the effect is least at the meta position [10]. It was not possible to substitute the fluorine in 4-fluro-2-nitroaniline (S15) even in refluxing ethylene glycol/pyridine. Here the general deactivating effect of the amino group enhances the



difficulty of substituting a fluorine meta to a nitro group. The nitro group can be replaced in nucleophilic substitution but this usually occurs in solvents such as DMF [7]. In only one case was substitution of the nitro group indicated in the reactions described here. The mass spectrum

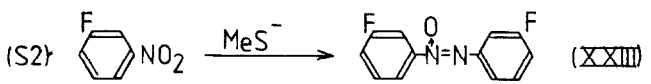


of the crude product XIII indicated peaks at m/e 280 (XIIIa) as well as at m/e 279 (XIII), although XIIIa could not be isolated. Substitution of

pentafluoronitrobenzene (S10) allowed pentakis(methylthio) nitrobenzene XVIII to be prepared, leaving the nitrogroup intact. Previous results had indicated that pentakis(methylthio)nitrobenzene could not be prepared on this type of reaction from pentafluoronitrobenzene [2] .

Similar type of nucleophilic substitution reactions have been observed with the benzenethiolate anions and the dichloronitrobenzenes, although the chlorine atoms rather than the nitrogroups were replaced in solvent DMF [11] .

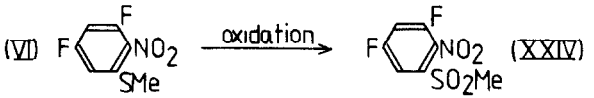
The reaction of m-fluoronitrobenzene (S2) with the methanethiolate anion gave an unexpected product, 3,3'-difluoroazoxybenzene (XXIII), previously prepared by the oxidation of 3,3'-difluoroazobenzene [12] . A similar reaction has been reported with 4-chloronitrobenzene which reacted



with the hydrosulfide anion and methyl sulfate to form mainly 4,4'-dichloroazoxybenzene, although a very small amount or 4-nitrothioanisole was also found [13] . The desired product 3-nitrothioanisole has been prepared from reduction of the corresponding disulfide and subsequent methylation [14] or from 3-thiocyanato nitrobenzene on treatment with methanol [15] . The reduction of the nitro group to the azoxybenzene derivative appears to be a characteristic of the method employed by Hodson and Handley [13] . If the procedure is modified by forming the thiolate anion in situ with the aromatic substrate and excess thiol the formation of azoxybenzenes is negligible [16] .

A number of compounds previously reported in the literature have been prepared in our studies. Some were prepared by analogous methods and some by methylation of the corresponding thiol or its metal salts [17,18] . Nitration of m-$(MeS)_2C_6H_4$ yielded 1,3,4-$C_6H_3(SMe)_2NO_2$ [19] .

The oxidation of the methylthio group is well known and is achieved using hydrogen peroxide in acetic acid [20] . The oxidation of some compounds were studied and the desired sulfones produced



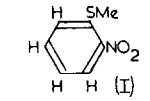
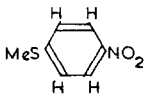
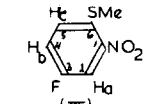
Reduction of the nitro group in 2,4-dimethylthionitrobenzene with tin and hydrochloric or acetic acids gave 2,4-dimethylthioaniline [21] , but more recent practical textbooks suggest that the reduction of a nitrogroup

in the presence of various other groups, such as the methylthio group, will give a large number of products. Attempted reductions of IV and VI with metals (Sn,Fe) and acid did not enable one well defined product to be isolated.

The products were characterized by chemical analyses and molecular weight determinations by mass spectroscopy. The mass spectra were not analyzed in detail. The various functional groups present were identified by infrared spectroscopy. The actual orientation of the products, assuming that no rearrangement had occurred, was determined by NMR spectroscopy. The proton and fluorine spectra were usually sufficient to indicate an unambiguous structure. Where this was not so, the carbon-13 spectrum was examined and a definite structure could be deduced. Details of the NMR spectra are shown in Table 1. The proton spectra were usually recorded in $CDCl_3$ solution, but in some cases the aromatic proton part of the spectrum was better resolved in C_6D_6 solution.

TABLE 1

Summary of NMR Spectra†

Compound	Chemical shifts/ppm		Coupling constants/Hz
 (I)	H(Me)	2.49S	
	H(ArH)	7.41M	
	H(ArH)	8.23DDD	$J(H-H_p)$0.4, $J(H-H_o)$8.2, $J(H-H_m)$1.5
 (II)	H(Me)	2.55S	
	H(ArH)	8.13M, 7.28M	A_2B_2spectrum
 (III)	H(Me)	2.50S	
	H(ArH$_a$*)	7.51DDD	$J(H-F_o)$8.4, $H(H-H_m)$2.7, $J(H-H_p)$~0.3
	H(ArH$_{b,c}$*)	6.44M	
	F	117.38DT	J(F-H) 8.4, 2xJ(F-H)6.1
	C(C-1)	146.71	1/2 peak width ~ 5Hz
	C(C-2)	134.78D	J(C-C-C-C-F)3.2
	C(C-3)	127.41D	J(C-C-C-F)7.1
	C(C-4)	121.64D	J(C-C-F)22.0
	C(C-5)	159.02D	J(C-F)248.2
	C(C-6)	113.17D	J(C-C-F)26.3
	C(Me)	16.19S	

† Measured in $CDCl_3$ with TMS as internal standard (^1H, ^{13}C) or $FCCl_3$(^{19}F)

* Measured in C_6D_6 solution

(continued overleaf)

TABLE 1 *(cont.)*

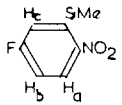
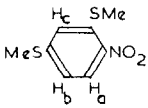
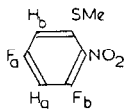
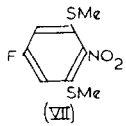
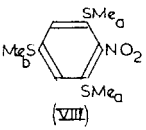
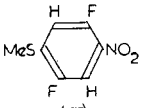
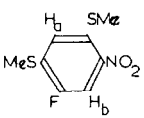
Compound	Chemical shifts/ppm		Coupling constants/Hz
 (IV)	H(Me)	2.48S	
	H(ArH_a*)	7.62DD	J(H-F_m)5.4, J(H-H_o)9.0
	H(ArH_b*)	6.45DD	J(H-F_o)9.8, J(H-H_m)2.5
	H(ArH_c*)	6.13DDD	J(H-F_o)7.1, J(H-H_m)2.6, J(H-H_o)9.1
	F	103.30DDD	J(H-F_o)7.0, 9.8, J(H-F_m)5.4
 (V)	H(Me*)	1.68S	
	H(Me*)	1.82S	
	H(ArH_a*)	7.86D	J(H-H_o)8.7
	H(ArH_b*)	6.39DD	J(H-H_o)8.7, J(H-H_m)1.9
	H(ArH_c*)	6.60D	J(H-H_m)1.9
 (VI)	H(Me)	2.52S	
	H(ArH_a)	5.87DDD	J(H-H_2)2.6, J(H-F_o)8.2, 3(H-F_o)9.8
	H(ArH_b)	6.02DDD	J(H-H_2)2.4, J(H-F_o)9.8, J(H-F_p)1.8
	F(F_a)	102.39DDD	J(F-H_o)9.1, J(F-F_o)11.5
	F(F_b)	115.12DDD	J(F-H_p)1.5, J(F-H_o)9.8, J(F-F_m)11.5
 (VII)	H(Me)	2.46S	
	H(ArH)	6.79D	J(F-H_o)9.0
 (VIII)	H(Me_a)	2.46S	
	H(Me_b)	2.54S	
	H(ArH)	6.88S	
 (IX)	H(Me)	2.53S	
	H(ArH)	7.01DD	J(H-F_m)6.0, J(H-F_o)11.0
	H(ArH)	7.76DD	J(H-F_m)6.2, J(H-F_o)9.0
	F	115.70DDD	J(F-H_o)9.1, J(F-H_m)6.2, J(F-F_p)15.5
	F	121.34DDD	J(F-H_o)11.0, J(F-H_m)6.2, J(F-F_p)15.2
 (X)	H(Me)	2.51S	
	H(Me)	2.56S	
	H(ArH_a)	7.01D	J(H-F_m)7.0
	H(ArH_b)	7.93D	H(H-F_o)9.8
	F	117.30DDD	J(F-H_o)10.2, J(F-H_m)7.0, J(F-Me) 0.8

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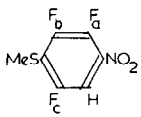
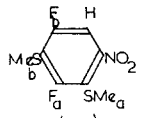
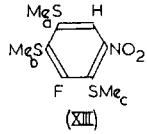
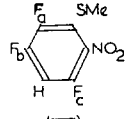
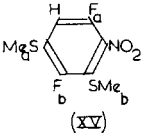
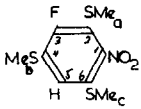
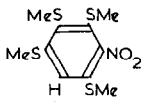
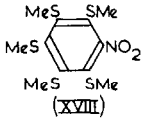
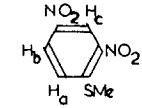
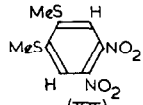
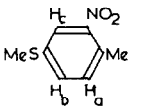
TABLE 1 *(cont.)*

Compound		Chemical shifts/ppm	Coupling constants/Hz
 (XI)	H(MeS)	2.65T	$J(Me-F_o)$1.55
	H(ArH)	7.63M	$H(H-F_o)$9.0, $J(H-F_m)$5.8, $J(H-F_p)$2.4
	$F(F_a)$	146.1M	$J(F-F_o)$21.1, $J(F-F_p)$13.3, $J(F-H_m)$5.7
	$F(F_b)$	125.9DD	$J(F-F_o)$21.2, $J(F-F_m)$1.0
	$F(F_c)$	109.9T	$J(F-F_p)$11.3, J(F-Me)1.3
 (XII)	$H(Me_a)$	2.53D	$J(Me-F_o)$2.00
	$H(Me_b)$	2.61T	$J(Me-F_o)$1.30
	H(ArH)	7.43DD	$J(H-F_o)$8.6, $J(H-F_p)$2.0
	$F(F_a)$	93.0M	$J(F-F_m)$8.2, $J(F-H_p)$2.0
	$F(F_b)$	104.0M	$J(F-F_m)$8.1, $J(F-H_o)$8.1, J(F-Me)1.1
 (XIII)	$H(Me_a)$	2.45S	
	$H(Me_b)$	2.44D	$J(Me-F_o)$ 1.4 1.7
	$H(Me_c)$	2.44D	$J(Me-F_o)$ 1.1 0.8
	H(ArH)	7.30D	$J(H-F_p)$1.8
	F	94.86M	1/2 peak width 5Hz
 (XIV)	H(Me)	2.56D	J(Me-F)1.3
	H(ArH)	7.10TD	$J(H-F_o)$9.0, $J(H-F_m)$6.2
	$F(F_a)$	132.5M	$J(F-F_o)$22.0, $J(F-F_p)$13.2, $J(F-H_m)$6.4, J(F-Me)1.1
	$F(F_b)$	127.1M	$J(F-F_o)$22.6, $J(F-F_m)$4.8, $J(H-F_o)$9.1
	$F(F_c)$	123.8M	$J(F-F_p)$13.2, $J(F-F_m)$4.7, $J(H-F_o)$8.5
 (XV)	$H(Me_a)$	2.50S	
	$H(Me_b)$	2.48D	$J(Me-F_o)$1.3
	H(ArH)	6.96DD	$J(H-F_o)$9.5, $J(H-F_m)$5.9
	$F(F_a)$	126.8DD	$J(F-H_o)$9.5, $J(F-F_p)$14.0
	$F(F_b)$	114.9DDQ	$J(F-H_m)$6.2, $J(F-F_p)$14.5, J(F-Me) 1.0

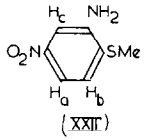
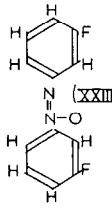
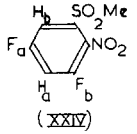
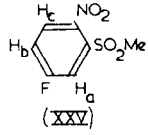
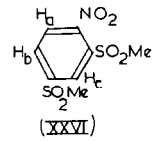
(continued overleaf)

TABLE 1 *(cont.)*

Compound	Chemical shifts/ppm		Coupling constants/Hz
 (XVI)	H(Me_a)	2.46D	J(Me-F_o)0.7
	H(Me)	2.48S	
	H(Me)	2.52S	
	H(ArH)	7.24D	J(H-F)7.0
	F	103.43DQ	J(F-H_m)7.0, J(F-Me) 0.8
	C(Me_a)	18.70D	J(C-S-C-C-F)6.1
	C(Me_b)	15.00D	J(C-S-C-C-F)2.8
	C(Me_c)	18.72S	
	C(C-1)	151.73	1/2 peak width 6Hz
	C(C-2)	118.48D	J(C-C-F)24.2
	C(C-3)	158.19D	J(C-F)247.3
	C(C-4)	131.09D	J(C-C-F)20.0
	C(C-5)	128.45D	J(C-C-C-F)3.6
	C(C-6)	126.63D	J(C-C-C-C-F)4.9
 (XVII)	H(Me)	2.43S 3	Intensity Ratio
	H(Me)	2.47S 6	
	H(Me)	2.52S 3	
	H(ArH)	7.05S 1	
 (XVIII)	H(Me)	2.47S 2	Intensity Ratio
	H(Me)	2.56S 1	
	H(Me)	2.59S 2	
 (XIX)	H(Me)	2.61S	
	H(ArH_a)	7.53D	J(H-H_o)8.8
	H(ArH_b)	8.40DD	J(H-H_o)8.8, J(H-H_m)2.4
	H(ArH_c)	9.11D	J(H-H_m)2.4
 (XX)	H(Me)	1.46S*, 2.72 (DMSO,D_6)	
	H(ArH)	8.755*, 8.95 (DMSO,D_6)	
 (XXI)	H(Me)	1.79S	
	H(Me)	2.14S	
	H(ArH_a)	6.48D	J(H-H_o)8.4
	H(ArH_b)	6.83DD	J(H-H_o)8.2, J(H-H_m)2.0
	H(ArH_c)	7.54D	J(H-H_m)2.0

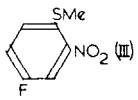
(continued on facing page)

TABLE 1 *(cont.)*

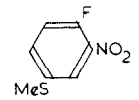
Compound	Chemical shifts/ppm		Coupling constants/Hz
 (XXII)	H(Me*)	1.74S	
	H(NH_2*)	3.40S	
	H(ArH_a*)	7.03D	J(H-H_o)8.6
	H(ArH_b*)	6.66D	J(H-H_m)2.4
	H(ArH_c*)	7.36DD	J(H-H_o)8.6, J(H-H_m)2.4
 (XXIII)	H(ArH)	7.99M	
	H(ArH)	6.77M	
	F	94.71DDD	J(F-H_o)10.7, J(F-H_o)8.1, J(F-H_m)6.3
	F	93.74M	J(F-H_o)10.1, J(F-H_o)8.1, J(F-H_m)5.7, J(F-H_o) 0.3
 (XXIV)	H(Me*)	2.41S	
	H(ArH_a*)	5.80DD	J(H-H)2.8, J(H-F_o)9.2, J(H-F_o)7.6
	H(ArH_b*)	7.00DDD	J(H-H)2.7, J(H-F_o)7.4, J(H-F_p)2.7
	F(F_a)	87.24DT	J(F-F_m)10.47, J(F-H_o)7.3
	F(F_b)	103.54DDD	J(F-F_m)10.49, J(F-H_o)8.8, J(F-H_p)1.7
 (XXV)	H(Me*)	1.62S	
	H(ArH_a*)	7.42DD	J(H-H_m)2.8, J(H-F_o)7.8
	H(ArH_b*)	6.13DDD	J(H-H_m)2.8, J(H-H_o)8.8, J(H-F_o)7.0
	H(ArH_c*)	6.73DD	J(H-H_o)8.8, J(H-F_m)4.5
	F	101.29DDD	J(F-H_o)7.8, J(F-H_o)6.9, J(F-H_m)4.4
 (XXVI)	H(Me‡)	3.34S	
	H(Me‡)	3.53S	
	H(ArH_a)	8.28DD	J(H-H_o)8.0, J(H-H_p)0.6
	H(ArH_b)	8.55DD	J(H-H_o)8.1, J(H-H_m)1.9
	H(ArH_c)	8.62DD	J(H-H_m)2.0, J(H-H_p)0.7

‡ Measured in acetone (D_6) solution

The product from the monosubstitution of S4 could have two possible structures III, or XXVII.

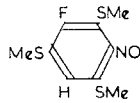


(III)



(XXVII)

The aromatic proton spectrum, both in $CDCl_3$ and C_6D_6 solution was not resolved sufficiently well to allow the separation of the signals of the three different hydrogens and determination of the coupling constants. Although there was only one signal in the fluorine spectrum the coupling constants could not be assigned unabiguously. Therefore the C-13 spectrum was examined. The carbon attached to the nitro group gives a broad peak and the other coupling constants are similar to the literature values [22] and clearly indicate structure III rather than XXVII . In the case of XVI , the structure is also confirmed in the C-13 spectrum where additionally



(XVI)

the methyl carbon is split into a doublet by coupling with the fluorine, J(C-S-C-C-F) [23].

The structures of all the other products were deduced from their proton and fluorine spectra, and correlation of the observed coupling constants with the literature values [9]. The splitting of the methyl protons by ortho fluorines depends on the other group ortho to the fluorine or methyl thio group, and is of considerable assistance in assigning possible structures [2].

The reactions described in this paper are all straighforward one-step reactions that usually allow the products to be isolated in reasonable yields. Hence they could be of considerable synthetic value.

EXPERIMENTAL

All the reagents were available commercially. Microanalyses were performed by Canadian Micro analytical Services, Vancouver or Mikroanalytisches Laboratorium Beller, Gottingen, West Germany. The analytical data and physical properties of the new compounds are shown in Table 2. All the products were varying degrees of yellow.

Mass spectra (70ev) were recorded on a Du Port/C.E.C. Model 21-491 mass spectrometer using direct introduction techniques. NMR spectra were recorded on a Varian HA 100(H-1 or F-19), XL 100 (C-13) or Bruker

TABLE 2

Chemical analyses and physical properties

Compound	m.p./°C b.p./°C/Torr	Calculated(%) C	H	N	Found(%) C	H	N
I*	60.7-61.5	49.7	4.14	8.28	49.5	4.15	8.02
II*	68-70	49.7	4.14	8.28	49.9	4.17	8.21
III	116.5-117.5	45.0	3.21	7.48	45.4	3.36	7.42
IV	97.5-98.5	45.0	3.21	7.48	45.4	3.30	7.23
V*	108.5-110.0	44.7	4.18	6.51	44.9	4.11	6.66
VI	91.5-92.5	40.9	2.44	6.83	41.3	2.47	6.93
VII	159-62	41.2	3.46	6.00	40.8	3.28	5.85
VIII*	143-5	41.4	4.25	5.36	41.5	3.87	5.34
IX	91-92	40.9	2.44	6.83	41.5	2.64	6.65
X	135.5-137	41.2	3.46	6.01	41.1	3.46	6.05
XI	109-111/1.5	37.7	1.81	6.28	37.0	2.26	6.36
XII	59-62	38.2	2.81	5.57	38.3	2.78	5.57
XIII	74.5-76	38.7	3.61	5.02	39.5	3.67	4.95
XIV	65/30	37.7	1.81	6.28	38.2	2.02	6.33
XV	92-6/0.10	38.2	2.81	5.57	38.1	2.85	5.61
XVI	89-91	38.7	3.62	5.01	39.0	3.62	5.08
XVII	103-104.5	39.1	4.27	4.56	39.2	4.06	4.83
XVIII	90-91.5	37.4	4.28	3.96	37.8	4.02	3.77
XIX	124-5	39.3	2.80	13.1	39.8	2.85	13.4
XX	226-7	36.9	3.10	10.76	36.9	2.98	10.70
XXI	285/760	52.4	4.95	7.64	53.4	5.29	7.63
XXII	102.5-104	45.6	4.39	15.21	45.7	4.11	15.09
XXIII*	44.5-47.5	61.5	3.44	11.96	61.3	3.18	11.70
XXIV	144-5	35.5	2.12	5.90	35.5	1.81	5.76
XXV	94-97.5	38.4	2.76	6.39	38.5	2.19	6.54
XXVI	228-32	34.4	3.25	5.02	34.3	2.92	4.78

*Known compounds
I mp 58-60 [17]
II mp 66-67 [13]
V mp 114 [19]
VIII mp 148-50 [24]
XIX mp 125 [17]
XXIII mp 51 [12]

HFX-90 (F-19). In the H and C-13 spectra $CDCl_3$ solutions were used with TMS as internal standard while the F-19 spectra were recorded in $CCl_4/CFCl_3$ solution using $CFCl_3$ as internal standard or $CDCl_3$ solution with C_6F_6 as internal standard. Infrared spectra were recorded as a Perkin Elmer model 457 spectrophotometer as their films, as mulls with Nujol or hexachlorobutadiene, or as KBr discs.

The nucleophilic substitution reactions were performed as described previously for the ethylene glycol/pyridine solvent mixture [2] except

that the reactions were studied at ice bath temperatures, rather than refluxing solvent. The reaction of S13 was studied in refluxing DMF [1]. Each reaction was studied using 10 mMoles of fluoroaromatic. Details of the reactant stoichiometry, methods of purification of products and yields are shown in Table 3. No substitution product was obtained in the reaction of S15.

The oxidation reactions were studied on a 10 mMole scale using 80 mL of 30% H_2O_2/acetic acid (volume ratio 1:3). Oxidation of VI gave 60% yield of XXIV which was purified by sublimation and oxidation of 10 mMoles of the crude product of the reaction of S5 yielded the oxidized products of IV and V, XXV (35% yield), and XXVI (yield about 5%) respectively.

TABLE 3

Reaction stoichiometry and products

Starting Compound	Product	Reactant ratio Me S:substrate	Yield %	Purification†
S1	I	1:1	70	1:benzene
S3	II	1:1	80	1:hexane
S4	III	1:1	70	1:MeOH
		2:1	90	
S5	IV	1:1	95	1:hexane
S5	V	2:1	40	1:hexane
S6	VI	1:1	70	1:hexane
S6	VII	2:1	17	5
S6	VIII	4:1	37	1:EtOH
S7	IX	1:1	50	1:hexane
S7	X	4:1	60	1:EtOH
		2:1	65	
S8	XI	1:1	34	2,3,4
S8	XII	2:1	20	5
S8	XIII	4:1	20	1:hexane
S9	XIV	1:1	25	2
S9	XV	2:1	79	2,4
S9	XVI	4:1	6	5,1:EtOH
S9	XVII	4:1	15	1:hexane
S10	XVIII	6:1	28	1:EtOH,5
S11	XIX	1:1	43	1:hexane
S12	XX	2:1	64	5
S13	XXI ‡	1:1	25	2,3
S14	XXII	3:1	5	*
S2	XXIII	3:1	12	2,1:EtOH

† 1 = Recrystallization, 2 = Distillation, 3 = Column chromatography, 4 = Gas chromotography, 5 = sublimation

* Precipated with HCl

‡ Reaction studied in refluxing DMF

Reductions of 10 mMoles of benzene solutions of IV and VI were attempted using 20 mMoles Sn in 40 ml conc. HCl and Fe/HCl as reducing agents. It was not possible to isolate and characterize any product from these reactions.

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