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REACTIONS OF SOME FLUOROAROMATICS WITH THE ETHOXIDE ANION

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SUMMARY

The reactions of sodium ethoxide in ethanol with various fluoroaromatics, $C_6F_{6-n}H_n$, $C_6F_{5-n}H_nNO_2$, C_6F_5X (X = CF_3, C_6F_5, $COCH_3$, CH_2Br), C_6Cl_6 and $\underline{m}$-$H_2C_6Cl_4$ have been studied. Partial substitution of the aromatic halogen was observed. The new products have been characterized by elemental analysis, NMR (H-1 and F-19), infrared and mass spectroscopy.

INTRODUCTION

In this paper the reactions of the ethoxide anion with various fluorobenzenes were examined. This is an extension of the study of the reactions of thiolate anions with several fluorobenzenes [1]. A direct comparison of, for instance, the ethanethiolate and ethoxide anions with the same fluorobenzene cannot be made, as the reaction conditions, particularly solvent, were different.

Relatively little has been reported about the reactions of fluoroaromatics with the ethoxide anion, although the methoxide anion has been studied in numerous analogous reactions. In general the ethoxide anion is a better nucleophile than the methoxide anion, and the ethanethiolate anion is a considerably better nucleophile than either for the displacement of fluorine.

RESULTS AND DISCUSSIONS

The reactions of the ethoxide anion in absolute ethanol with various fluoroaromatics have been studied. Schematically the reactions can be

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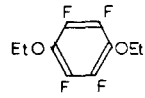
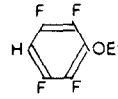
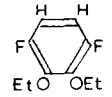
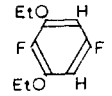
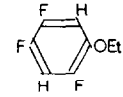
represented as

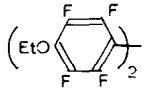
C_6F_6 $\xrightarrow[EtOH]{EtO^-}$  (I)

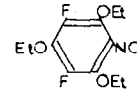
C_6F_5H ⟶  (II)

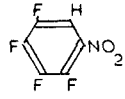
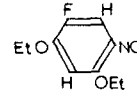
o-$H_2C_6F_4$ ⟶  (III)

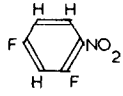
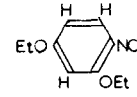
m-$H_2C_6F_4$ ⟶  (IV)

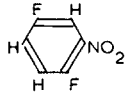
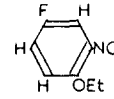
p-$H_2C_6F_4$ ⟶  (V)

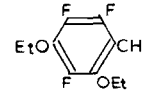
$C_6F_5C_6F_5$ ⟶  (VI)

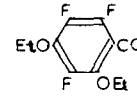
$C_6F_5NO_2$ ⟶  (VII)

 ⟶  (VIII)

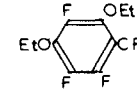
 ⟶  (IX)

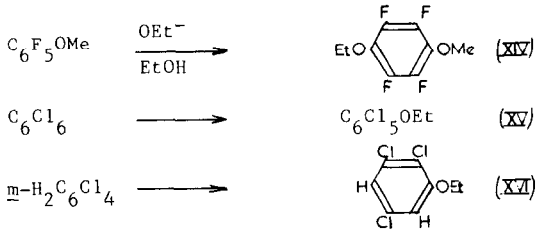
 ⟶  (X)

$C_6F_5CH_2Br$ ⟶  (XI)

C_6F_5COCl ⟶  (XII)

$C_6F_5COCH_3$ ⟶ (II)

$C_6F_5CF_3$ ⟶  (XIII)



All the compounds isolated were the major products and these have been characterized. The products were not, apparently, dependent on the stoichiometry of the reactants.

The starting materials divide themselves into three main groups, the simple halogenobenzenes including the fluorobenzenes $C_6F_{6-n}H_n$ chlorobenzenes and decafluorobiphenyl; the nitrofluorobenzenes $C_6F_{5-n}H_nNO_2$, and some pentafluorobenzene derivatives C_6F_5X. The reactions of hexafluorobenzene, with various alkoxides have yielded the pentafluorophenylethers, C_6F_5OR, (R = Me[2,3], Et[4], CH_2CF_3[5], CCl_3[5], $CH_2CF_2CF_2CF_2CF_2H$[5],

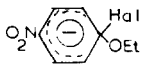
$$C_6F_6 + OR^- \longrightarrow C_6F_5OR + \underline{p}\text{-}(RO)_2C_6F_4$$

and the diether $\underline{p}$-$(RO)_2C_6F_4$ (R = Me[6] CH_2CF_3[5]). Similarly the reactions of hexachlorobenzene yielded C_6Cl_5OR (R = Me[7,8] $CHMe_2$[7], CMe_3[9]) and $C_6Cl_4(OR)_2$ (R = Me[8], $CH_2CF_2CF_2CF_2CF_2H$[5]). However, using the chlorofluorobenzenes, C_6Cl_5F, $C_6F_2Cl_4$, and 1,3,5-$Cl_3C_6F_5$, the fluorine was replaced preferentially [5,8]. The products isolated in this paper $\underline{p}$-$(EtO)_2C_6F_4$, C_6Cl_5OEt from hexafluoro- and hexachloro-benzenes have not been reported previously. TLC of the crude reaction product from hexafluorobenzene and sodium ethoxide showed that $\underline{p}$-$(EtO)_2C_6F_4$ was the only product, and presumably negligible amounts of the other isomers $\underline{o}$-$(EtO)_2C_6F_4$ and $\underline{m}$-$(EtO)_2C_6F_4$ have been formed. This must be contrasted with the reaction of pentafluoroanisole with sodium methoxide in methanol where all three isomers of $(MeO)_2C_6F_4$ were formed, but the <u>para</u> isomer was the major product (52%) (<u>meta</u> isomer 32% and <u>ortho</u> isomer 16%) [10]. Analogous reactions of thiolate anions in ethylene glycol/pyridine as solvent with hexafluorobenzene gave the di- and tetra- substituted products $\underline{p}$-$(RS)_2C_6F_4$ and $\underline{p}$-$F_2C_6(SR)_4$ [1,11,12] and with hexachlorobenzene gave $C_6Cl_4(SMe)_2$ and $C_6Cl_2(SMe)_4$ [11,13]. Decafluorobiphenyl reacted with the methanethiolate anion to give substitution of one or three fluorines on each ring [11] and with the methoxide anion to give $\underline{p},\underline{p}'$-$MeOC_6F_4C_6F_4OMe$ [14], analogous to the ethoxy product isolated.

Pentafluorobenzene reacted with the methoxide anion to give the methyl analog of II [12,15] but the reactions of alkoxides with tetrafluoro- and tetrachloro-benzene have not been reported. The orientation of the substitution observed is ortho and para to the hydrogen.

It has been found that the nitro group is activating and ortho para directing in substitution reactions of halogenated nitrobenzenes with a variety of nucleophiles [16,17]. This observation is confirmed in the reactions reported here. The fluorine meta to the nitro group has not been replaced. Comparison with the reactions of the simple fluorobenzenes shows that the nitro group acts as an activating group and more fluorines are replaced, for example comparison of pentafluorobenzene and pentafluoronitrobenzene.

Kinetic studies on the reactions of sodium ethoxide with the p-halogenonitrobenzenes show the formation of an intermediate Meissenheimer complex [18]



Substitution of the nitro group was not observed, although pentachloronitrobenzene and tetrachloronitrobenzene react with sodium methoxide in methanol to form pentachloroanisole and tetrachloroanisole [19,8].

The reactions of some of the other substrates, C_6F_5X, have been studied with alkoxide or phenolate anions [6,20,21,22] and substitution occurred para to the group X. Multiple substitution of fluorine sometimes occurred with the ethoxide anion but was not usually observed with the methoxide anion.

Pentafluoroacetophenone must be cleaved by the ethoxide anion, forming pentafluorobenzene, which is subsequently substituted

$$C_6F_5COCH_3 + OEt^- \longrightarrow C_6F_5H + CH_3CO_2Et$$

An analogous reaction of decafluorobenzophenone with potassium cyanide in ethanol, forming pentafluorobenzene and ethyl pentafluorobenzoate has been observed [23]

$$(C_6F_5)_2CO + EtO^- \longrightarrow (C_6F_5)_2C(O^-)(OEt) \xrightarrow{H^+} C_6F_5H + C_6F_5CO_2Et$$

Similarly benzophenone reacted with potassium t-butoxide forming benzene and butyl benzoate, although reduction to Ph_2CHOH occurred with potassium ethoxide [24].

The reaction of pentafluorobenzoyl chloride gave the substituted acid. the acid chloride, presumably, either forms the ester in the basic alcoholic solution, which is hydrolysed at the quenching stage or the sodium salt is formed in the basic alcoholic solution. The reaction of methoxide anion with pentafluorobenzoic acid gave para substitution only [21,25]

Pentafluorobenzyl bromide reacted as expected to give the benzyl ether, with substitution of the aromatic ring ortho and para to the methylene group.

$$C_6F_5CH_2Br + 3EtO^- \longrightarrow (EtO)_2C_6F_3CH_2OEt + 2F^- + Br^-$$

The reaction of octafluorotoluene with sodium ethoxide showed the formation of 1-ethoxy-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene, when a 1:1 or 2.5:1 stoichiometry of EtO^-:ArF was employed [20,26]. Disubstitution was found in the reactions reported here with a reactant stoichiometry EtO^-:ArF of 8:1.

TABLE 1

Reaction stoichiometry and products

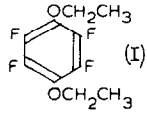
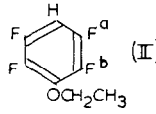
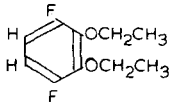
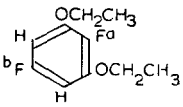
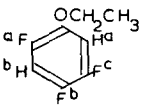
Product	Reactant Ratio RO^-:Substrate (method)†	Time	Yield (%)	Purification*
I	5:1(A)	1h	15	1:EtOH
I	10:1(B)	1h	10	1:EtOH
II	4:1(A)	1h	3	2
II	10:1(B)	1h	2	2
III	6:1(A)	7d	22	3
IV	6:1(A)	7d	53	1:MeOH
V	6:1(A)	7d	6	3
VI	8:1(A)	1h	58	1:EtOH
VII	6:1(A)	1h	48	4
VII	6:1(B)	1h	15	4
VIII	2:1(A)	1h	78	1:EtOH
VIII	2:1(B)	1h	60	1:EtOH
IX	2:1(A)	1h	82	1:EtOH/Pet Ether
IX	2:1(B)	1h	77	1:EtOH/Pet Ether
X	1:1(A)	1h	39	1:EtOH
X	2:1(B)	1h	11	1:EtOH
XI	8:1(A)	1d	38	3
XII	10:1(A)	10h	15	1:Pet Ether
XIII	8:1(A)	1h	27	2
XIV	10:1(A)	1h	25	3
XV	10:1(A)	1d	26	1:EtOH
XVI	6:1(A)	7d	10	1:EtOH

*1 = Recrystallization, 2 = Distillation, 3 = Vacuum distillation, 4 = Column chromatography

† Method A: solvent 100% EtOH
Method B: solvent 95% EtOH

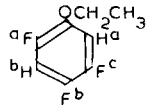
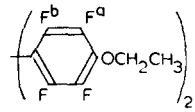
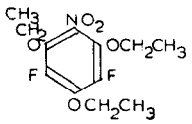
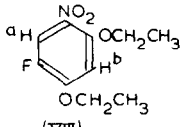
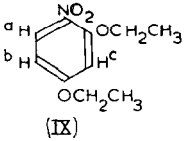
TABLE 2

Summary of NMR data*

Compound		Chemical shifts (p.p.m.)	Coupling constants (Hz)
 (I)	CH_3	1.33 T	J(H-H) 7.0
	CH_2	4.25 QT	J(H-H) 7.0, $J(CH_2-F_o)$0.5
	F	156.9 S	
 (II)	CH_3	1.39 T	J(H-H) 7.0
	CH_2	4.32 QT	J(H-H) 7.0, $J(CH_2-F_o)$0.8
	ArH	7.18 TT	$J(H-F_o)$10.6, $J(H-F_m)$7.2
	F^b	138.4 DT	$J(F-H_o)$10.6, $J(F-F_o)$21.0
	F^a	155.4 DTT	$J(F-CH_2)$0.9, $J(F-H_m)$8.1, $J(F-F_o)$20.6
 (III)	CH_3	1.39 T	J(H-H) 7.0
	CH_2	4.14 Q	J(H-H) 7.0
	ArH	6.39 M	
	F	132.5 M	
	CH_3(C-13)	15.59 S	
	CH_2(C-13)	70.13 T	$J(CH_2-O-C-C-F)$1.3
	Ar(H)(C-13)	109.97 DD	J(C-C-F)16.1, J(C-C-C-F)14.(
	Ar(O)(C-13)	141.53 DD	J(C-C-F)9.6, J(C-C-C-F)8.6
	Ar(F)(C-13)	152.89DD	J(C-F)243.3, J(C-C-C-F)3.6
 (IV)	CH_3	1.44 T	J(H-H)7.1
	CH_2	4.03 Q	J(H-H)7.1
	ArH	6.27 DD	$J(H-F)$10.2, $J(H-F_m)$6.0
	F^b	114.7 DT	J(F-H)9.9, $J(F-F_p)$10.4
	F^a	164.2 DT	$J(F-H_m)$5.7, $J(F-F_p)$10.8
 (V)	CH_3	1.47 T	J(H-H)7.0
	CH_2	4.03 Q	J(H-H)7.1
	H^a	6.76 DT	$J(H-F_o)$11.6, $J(H-F_m)$7.8
	H^b	6.94 DT	$J(H-F_o)$10.5, $J(H-F_m)$7.4

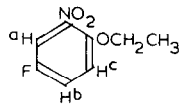
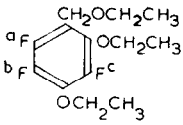
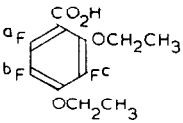
(Continued)

TABLE 2 (Cont.)

Compound		Chemical shifts(p.p.m.)	Coupling constants (Hz)
 (V)	F^a	134.4 DDD	$J(F-H_o)$10.6, $J(F-H_m)$7.5, $J(F-F_p)$12.7
	F^b	143.7 DDD	$J(F-H_o)$10.8, $J(F-H_m)$7.7, $(F-F_o)$21.6
	F^c	140.0 DDD	$J(F-H_o)$11.3, $J(F-H_m)$17.5, $J(F-F_o)$,21.6, $J(F-F_p)$12.2
 (VI)	CH_3	1.46 T	J(H-H) 7.0
	CH_2	4.38 QT	J(H-H) 7.0, $J(CH_2-F_o)$0.6
	F^a	138.2 DD	$J(F-F_o)$18.8, $J(F-F_p)$5.6
	F^b	154.9 DD	$J(F-F_o)$20.2, $J(F-F_p)$5.1
 (VII)	CH_3	1.35 T(2)	J(H-H) 7.0
		1.42 T(1)	J(H-H) 7.0
	CH_2	4.24 QD(2)	J(H-H) 7.0, $J(CH_2-F_o)$0.8
		4.33 QT(1)	J(H-H) 7.0, $J(CH_2-F_o)$0.8
	F	148.4 S	
 (VIII)	CH_3	1.40 T	J(H-H) 7.0
		1.43 T	J(H-H) 7.0
	CH_2	4.26 Q	J(H-H) 7.0
		4.30 Q	J(H-H) 7.0
	ArH^a	7.79 D	$J(H-F_o)$11.0
	ArH^b	7.00 D	$J(H-F_m)$ 7.2
	F	140.2 DD	$J(F-H_o)$10.6, $J(F-H_m)$6.8
 (IX)	CH_3	1.39 T	J(H-H) 7.0
		1.41 T	J(H-H) 7.0
	CH_2	4.17 Q	J(H-H) 6.8
		4.24 Q	J(H-H) 6.9
	ArH^a	7.89 DD	$J(H-H_o)$ 9.0, $J(H-H_p)$0.5
	ArH^b	6.60 DD	$J(H-H_o)$ 9.0, $J(H-H_m)$2.4
	ArH^c	6.72 DD	$J(H-H_m)$ 2.3, $J(H-H_p)$0.5

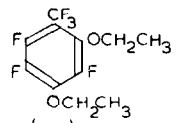
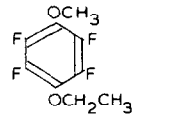
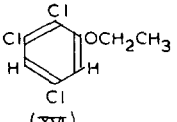
(Continued overleaf)

TABLE 2 (Cont.)

Compound		Chemical shifts(p.p.m.)	Coupling constants (Hz)
 (X)	CH_3	1.39 T	J(H-H) 7.0
	CH_2	4.24 Q	J(H-H) 6.9
	ArH^a	7.86 DDD	$J(H-F_o)$ 7.6, $J(H-H_m)$2.8, $J(H-H_p)$ 0.5
	ArH^b	7.57 DDD	$J(H-F_o)$ 6.9, $J(H-H_m)$2.7, $J(H-H_o)$ 8.9
	ArH^c	7.01 DDD	$J(H-F_m)$ 4.6, $J(H-H_o)$9.0, $J(H-H_p)$ 0.6
	F	119.2 DT	$J(F-H_o)$ 7.0, $J(F-H_m)$4.5
 (XI)	CH_3	1.18 T	J(H-H) 7.0
		1.35 T	J(H-H) 7.0
		1.36 T	J(H-H) 7.0
	CH_2	3.51 Q	J(H-H) 7.0
		3.91 Q	J(H-H) 7.0
		4.37 Q	J(H-H) 7.0
		4.47 D	$J(CH_2-F_o)$2.2
	F^a	143.4 DDT	$J(F-CH_2)$1.9, $J(F-F_o)$22.1, $J(F-F_p)$10.4
	F^b	156.5 D	$J(F-F_o)$21.6
	F^c	148.3 D	$J(F-F_p)$ 9.7
 (XII)	CH_3	1.40	J(H-H) 7.0
		1.42	J(H-H) 7.0
		1.44	J(H-H) 7.0
	CH_2	4.19 Q	J(H-H) 7.0
		4.13 Q	J(H-H) 7.0
		4.25 QT	J(H-H) 7.0, $J(CH_2-F_o)$0.8
	OH	10.30 S	
	F^a	138.5 DD	$J(F-F_o)$20.7, $J(F-F_p)$11.3
	F^b	155.1 D	$J(F-F_o)$20.7
	F^c	147.3 D	$J(F-F_p)$11.3

(Continued)

TABLE 2 (Cont.)

Compound	Chemical shifts(p.p.m.)		Coupling constants (Hz)
 (XIII)	CH_3	1.28 T	J(H-H) 7.0
	CH_2	3.90 Q	J(H-H) 7.0
	CF_3	54.7 S	Half peak width 6HZ
	ArF	146.2 S	Half peak width 6.4HZ
 (XIV)	CH_3	1.39 T	J(H-H) 7.1
	CH_2	4.18 Q	J(H-H) 7.0
	OCH_3	4.02 T	$J(H_3C-F_o)$ 1.0
	F	157.2 M	
$C_6Cl_5OCH_2CH_3$ (XV)	CH_3	1.93 T	J(H-H) 7.0
	CH_2	4.09 Q	J(H-H) 7.0
 (XVI)	CH_3	1.48 T	J(H-H) 7.0
	CH_2	4.02 Q	J(H-H) 7.0
	ArH	6.74 D	$J(H-H_m)2.4$
	ArH	7.02 D	$J(H-H_m)2.4$

*Solvents - $CDCl_3$ or d_6-acetone

Standards - TMS internal, H-1 and C-13

- CF_3CO_2H external, F-19, corrected to $CFCl_3$ internal

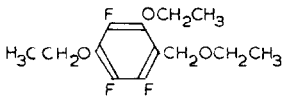
Abbreviations - S - singlet; D - doublet; T - triplet;

Q - quartet; M - multiplet

Two slightly different experimental methods were employed. Sodium ethoxide in absolute ethanol was prepared by adding sodium to absolute ethanol or sodium hydroxide was dissolved in 95% ethanol. Table 1 shows that the yields from the 95% ethanol are not as good as the absolute ethanol In the latter solvent the concentration of the ethoxide anion is probably minimal.

Comparison of the ethoxide anion as a nucleophile with the ethanethiolate anion ion in analogous reactions [1] is difficult due to the somewhat differing reaction conditions, such as solvent. However the thiolate is a better nucleophile in these reactions than the alkoxide as has been reported previously, although in heterocyclic systems this is not the case [27].

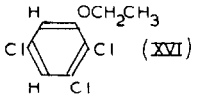
The new products isolated have been characterized by elemental analysis The molecular weights have been confirmed by mass spectroscopy. Infrared spectroscopy has shown the presence of the various functional groups. The NMR spectra of the products have been examined and are tabulated in Table 2. The isomeric configuration can usually be deduced from the aromatic hydrogen-aromatic hydrogen, aromatic hydrogen-fluorine and fluorine-fluorine coupling constants, as observed in the aromatic proton region of the proton spectrum and the fluorine spectrum. This was facilitated by comparison with the spectra of analogous thio compounds [1]. As an example the structure can readily be assigned to XI.



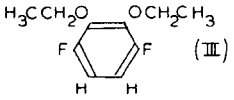
(XI)

The methylene group attached to the aromatic ring is split into a doublet, J 2.2 Hz, due to coupling to one ortho aromatic fluorine. A similar coupling of the methyl group is observed in pentafluorotoluene giving a triplet, J 2.3 Hz [28]. The methylene protons of the ethoxy group may also be coupled to ortho aromatic fluorines, J 1.0 Hz, as similar couplings are found in methoxy derivatives, such as $C_6F_5OCH_3$ or p-$(MeO)_2C_6F_4$ [29], but these were too weak to be resolved. In the fluorine spectrum three distinct fluorine signals were detected corresponding to three fluorines with the orientations as shown. The fluorine ortho to the aromatic methylene group was split into a triplet by coupling to the methylene protons. Similar reasoning can be applied to the other spectra.

The structure of compound XVI can be assigned unambiguously. The aromatic proton spectrum shows two distinct peaks, which can only be present in the structure shown.



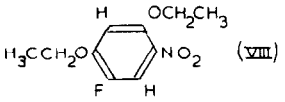
(XVI)

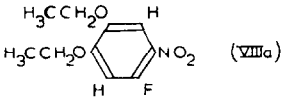


(III)

The structure of III has been confirmed unambiguously from the C-13 NMR spectrum. The aromatic carbon bonded to fluorine is a quartet with coupling constants corresponding to this structure, J(C-F) 243.3Hz and J(C-C-C-C-F) 3.6Hz [30]. The high resolution proton spectrum is exactly the same as the second order spectrum, $[AMX_3]_2$ system, observed in the methylthio analog of III [31]. Further confirmation is observed in the

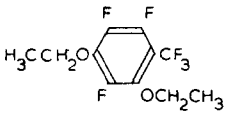
C-13 spectrum of the methylene group, which is coupled to the ortho fluorine, J(C-O-C-C-F) 1.3Hz: a similar coupling of the methyl group in pentafluoroanisole, $C_6F_5OCH_3$, has been reported [32]. Compound VIII cannot be assigned unambiguously as either VIII or VIIIa on the basis of the


(VIII)


(VIIIa)

proton or fluorine spectra, but comparison with other results indicates preferential substitution ortho and para to the nitro group and favours VIII rather than VIIIa.

The structure of XIII would be expected to be


XIII

Substitution of octafluorotoluene with sodium ethoxide in ethanol (reaction ratio $C_7F_8:OC_2H_5^-$, 1.0:1.0 [20] or 1.0:2.5[26]) gave only monosubstitution para to the trifluoromethyl group and further substitution would be expected to give XIII. The fluorine NMR spectra, both of the trifluoromethyl group and the aromatic fluorines, were poorly resolved and do not confirm this structure unambiguously.

The mass spectra have not been examined in detail, but all confirm the molecular weights, and a characteristic feature is the loss of one or more 28 m.u. (C_2H_4) from the molecular ion. These fragmentations are, in some

$$C_{10}H_{10}F_4O_2^{+\cdot} \xrightarrow{*} C_8H_6F_4O_2^{+\cdot} + C_2H_4$$
(I)

$$C_8H_6F_4O_2^{+\cdot} \xrightarrow{*} C_6H_2F_4O_2^{+\cdot} + C_2H_4$$

cases, confirmed by the observations of meta stable peaks.

EXPERIMENTAL

All reagents were available commercially. Microanalyses were performed by Canadian Microanalytical Services, Vancouver. The analytical data and physical properties of the new compounds are shown in Table 3.

TABLE 3

Physical properties and chemical analyses

Compound	mp/°C bp/°C/Torr	Calculated			Found (%)		
		C	H	N	C	H	N
I	49.0-49.4	50.0	4.82	---	50.4	4.24	---
II	48.5/760	49.5	3.09	---	49.4	3.29	---
III	76/0.05	59.4	5.96	---	59.4	6.41	---
IV	71.0-71.8	59.4	5.96	---	58.9	6.00	---
V	29/0.05	54.6	3.97	---	54.7	4.04	---
VI	70.0-70.6	49.7	2.61	---	49.6	2.17	---
VII	d	49.5	5.15	4.81	49.2	5.61	5.31
VIII	105.5-106.5	52.4	5.24	6.11	52.0	5.39	6.05
IX	83.5-84.2	56.9	6.16	6.64	56.8	5.73	6.62
X	34.0-34.5	51.9	4.32	7.57	51.8	4.28	7.49
XI	80/2	56.0	6.11	---	55.7	6.00	---
XII	75-76	50.0	4.21	---	50.0	4.23	---
XIII	52/0.05	45.8	3.51	---	46.0	3.29	---
XIV	30/0.2	48.2	3.57	---	48.8	3.97	---
XV	82-83	32.6	1.71	---	32.9	1.22	---
XVI	52.0-52.5	42.6	3.13	---	42.7	2.96	---

d= liquid decomposing upon distillation

Mass spectra (70eV) were recorded on a DuPont/CEC Model 21-491 mass spectrometer using direct introduction techniques. NMR spectra were recorded on a Varian HA-100 (H-1), Varian EM 360L (H-1 and F-19) or Varian CFT-20 (C-13). The infrared spectra were recorded on a Perkin Elmer 683 Infrared Spectrometer as thin films or KBr discs.

The nucleophilic solution was obtained by dissolving sodium in 100% ethanol (method A) or sodium hydroxide in 95% ethanol (method B). A standard aliquot of the fluoroaromatic (30 to 100 mmoles) was added to the requisite amount of nucleophile in ethanol and refluxed. The reaction was quenched by pouring onto ice/HCl. Solid products were filtered off and liquids extracted with ether. Purification was by standard techniques. Table 1 shows details of all reactions. Only the major products were isolated.

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