Journal Fluorine Chemistry, 20 (1982) 759–764
Received: December 21, 1981

CONDENSATION OF 1,2-DIBROMOTETRAFLUOROETHANE WITH VARIOUS POTASSIUM THIOPHENOXIDES AND PHENOXIDES

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SUMMARY

$BrCF_2CF_2Br$ reacts easily with various potassium thiophenoxides and phenoxides to give respectively 2-bromo tetrafluoroethyl thioethers and ethers. The lipophilicity of $C_6H_5SCF_2CF_2Br$ and $C_6H_5OCF_2CF_2Br$ is measured and compared with that of the well known $C_6H_5SCF_2CF_2H$ and $C_6H_5OCF_2CF_2H$.

INTRODUCTION

Recently we showed that CF_2Br_2 and CF_2BrCl react with potassium thiophenoxides and phenoxides to give aromatic compounds substituted by SCF_2Br and OCF_2Br [1,2]. Hansch constants Π of these groups are high ; they are similar to that of SCF_3 and OCF_3 [1].

It seemed interesting to study the lipophilicity of longer perfluoroalkyl groups and so we prepared thiophenates and phenates of the type $ArSCF_2CF_2Br$ and $ArOCF_2CF_2Br$. These compounds are obtained by condensation of potassium thiophenoxides and phenoxides with $BrCF_2CF_2Br$ which is a non toxic fire extinguishing agent [3].

$$\underset{\underline{1}}{ArXK} + \underset{\underline{2}}{BrCF_2CF_2Br} \longrightarrow \underset{\underline{3}}{ArXCF_2CF_2Br} + \underset{\underline{4}}{ArXCF_2CF_2H}$$

X=O,S

The proportions of <u>3</u> and <u>4</u> are dependent on X and the nature of the substituents on the aromatic nucleus. To simplify we describe the cases of the most significant substituents from electronic point of view. The synthesis of <u>4</u> has been previously described by D.C. ENGLAND and coll. [4].

0022-1139/82/0000-0000/$02.75

RESULTS AND DISCUSSION

Condensation of $BrCF_2CF_2Br$ with thiophenoxides

Different solvents were tried for the condensation of $BrCF_2CF_2Br$ with thiophenoxides ArS^- ; a great deal of disulfide ArSSAr was formed. However, this by-product is considerably reduced under phase transfer conditions (C_6H_6, KOH 50 %, TEBA) previously used with CF_2Br_2 and CF_2BrCl [1,2].

Results are summarized in the Table I.

TABLE I

Condensation of $BrCF_2CF_2Br$ with different potassium thiophenoxides under phase transfer conditions

Thiophénol	$ArSCF_2CF_2Br$ %	$ArSCF_2CF_2H$ %	Yield
$4CH_3C_6H_4SH$	50	50	50
C_6H_5SH	40	60	35
$4ClC_6H_4SH$	25	75	30
$4NO_2C_6H_4SH$	15	85	5

The total yield and the proportion of the bromo-derivative decrease from $4CH_3C_6H_4SK$ to $4NO_2C_6H_4SK$ as the nucleophilicity of these thiophenoxides decreases.

Condensation of $BrCF_2CF_2Br$ with phenoxides

For the condensation of $BrCF_2CF_2Br$ with phenoxides dry dimethylformamide gives the higher yields of the desired products <u>3</u>. However, the reaction is not generally spontaneous(*) ; as in the case of CF_2Br_2 and CF_2BrCl [1,2] the addition of a small amount of mercaptan is necessary to perform the condensation. All mercaptans initiate the reaction ; we have used propylmercaptan which leads to volatile by-products, easy to eliminate.

(*) Potassium 2-allylphenoxide, prepared by action of KOH/18 crown 6 in DMF is an exception and reacts spontaneously with CF_2Br_2 (see next paper - p. 765).

TABLE II

Condensation of $BrCF_2CF_2Br$ with different potassium phenoxides in DMF

Phénol	$ArOCF_2CF_2Br$%	$ArOCF_2CF_2H$%	Yield
$4CH_3C_6H_4OH$	95	5	40
C_6H_5OH	93	7	28
$4ClC_6H_4OH$	83	17	24
$4NO_2C_6H_4OH$	38	62	15

As for thiophenoxides, the reactivity of phenoxides decrease with their nucleophilicity from $4CH_3C_6H_4OK$ to $4NO_2C_6H_4OK$.

An ionic chain mechanism can be postulated by analogy with the one proposed before with CF_2Br_2 and CF_2BrCl [1,2].

initiation (N.B.): $RS^- + BrCF_2CF_2Br \longrightarrow RSBr + {}^-CF_2CF_2Br$

propagation : ${}^-CF_2CF_2Br \longrightarrow CF_2{=}CF_2 + Br^-$

$\underset{(X=O,S)}{ArX^-} + CF_2{=}CF_2 \longrightarrow ArXCF_2CF_2^-$

$ArXCF_2CF_2^- + BrCF_2CF_2Br \longrightarrow \underset{\underline{3}}{ArXCF_2CF_2Br} + {}^-CF_2CF_2Br$

termination : $ArXCF_2CF_2^- + \text{"H"}_{\textbf{solvent}} \longrightarrow \underset{\underline{4}}{ArXCF_2CF_2H}$

The initiation by RS^- observed in the case of phenoxides is in favor of this chain mechanism. As we proposed before with CF_2Br_2 and CF_2BrCl [1,2] ArO^- is probably too 'hard' to attack $BrCF_2CF_2Br$ in the first step of the reaction but can react with tetrafluoroethylene in the propagation step [4]. In this scheme $BrCF_2CF_2Br$ is both a brominating agent and a tetrafluoroethylene precursor.

(N.B.) a) R = Ar when the nucleophile is a thiophenoxide

b) $R = CH_3CH_2CH_2$ for phenoxides

In a same manner, KNUNYANTS [5] showed that addition of 1,2-dibromotetrafluoroethane to 2-hydroxyethyl mercaptan produced the corresponding disulfide $HOCH_2CH_2SSCH_2CH_2OH$ and tetrafluoroethylene.

The formation of hydrogenated by-products is also in favor of the mechanism Under phase transfer conditions (ArSK reactions) as we explained in a preceding paper [2], the reaction probably takes place in the organic phase and the "H" protonating $ArSCF_2CF_2^-$ is brought in small quantity by the solvation water of the ions pair ArS^- $C_6H_5CH_2\overset{+}{N}(Et)_3$ removed from aqueous phase to organic phase.

Measurement of Hansch constants Π_R [6] shows that the bromoderivatives 3 have a higher lipophilicity than that of the well-known compounds 4 [4].

R	$S(CF_2)_2Br$	$O(CF_2)_2Br$	$S(CF_2)_2H$	$O(CF_2)_2H$
π_R	1,10	0,86	0,81	0,69

These new compounds may be interesting from a biological point of view.

EXPERIMENTAL

^1H n.m.r. spectra were recorded on a Perkin-Elmer R24A at 60 MHz. ^{19}F n.m.r. spectra were recorded on a Jeol C60 HL. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^1H data and relative to external $CFCl_3$ for ^{19}F data (solvent : $CDCl_3$). All mass spectra (obtained on a AEI MS 30 spectrometer at 70 ev) and elemental analysis are in good agreement with the proposed structures.

1 - Potassium phenoxides are obtained by reacting in methanol potassium hydroxide with phenols. All salts and DMF must be very dry to reduce the formation of by-product 4.

2 - Potassium thiophenoxides are obtained in situ in the phase transfer conditions (C_6H_6, KOH 50 %, TEBA).

3 - Condensation of $BrCF_2CF_2Br$ with thiophenoxides : 200 ml of C_6H_6, triethylbenzylammonium chloride (TEBA) (500 mg) and 200 ml of 50 % KOH are mixed under vigorous stirring. Thiophenol (0.1 mole) is then added simultaneously with $BrCF_2CF_2Br$ (0.15 mole) at room temperature. When the thiophenol is solid (for example $4NO_2C_6H_4SH$), it is dissolved in 10-20 ml of C_6H_6 and the

TABLE III

Characteristics of the compounds.

Products	b.p. °C/mmHg or m.p	^{1}H n.m.r.	^{19}F n.m.r.
$4CH_3C_6H_4SCF_2CF_2Br$ nc	114/40	s(3H)=2.1 s(4H)=7.2	t(2F)CF_2Br=58.4 t(2F)SCF_2=80.1 J_{FF}=10 Hz
$C_6H_5SCF_2CF_2Br$ nc	99/40	m=7.4	t(2F)CF_2Br=59.2 t(2F)SCF_2=81.7 J_{FF}=8.5 Hz
$4ClC_6H_4SCF_2CF_2Br$ nc	117/30	m=7.6	t(2F)CF_2Br=58.4 t(2F)SCF_2=80 J_{FF}=8.5 Hz
$4NO_2C_6H_4SCF_2CF_2Br$ nc	m.p =75°C	m=7.8	t(2F)CF_2Br=59.2 t(2F)SCF_2=80 J_{FF}=8.5 Hz
$4CH_3C_6H_4OCF_2CF_2Br$ nc	86/30	s(3H)=2.4 s(4H)=7	t(2F)CF_2Br=66.7 t(2F)OCF_2=83 J_{FF}=7.6 Hz
$C_6H_5OCF_2CF_2Br$ nc	76/40	s=7.2	t(2F)CF_2Br=67.5 t(2F)OCF_2=83.4 J_{FF}=5.6 Hz
$4ClC_6H_4OCF_2CF_2Br$ nc	80/30	m=7.2	t(2F)CF_2Br=65 t(2F)OCF_2=81.7 J_{FF}=5.6 Hz
$4NO_2C_6H_4OCF_2CF_2Br$ nc	m.p =65°C	m=7.4	t(2F)CF_2Br=69.2 t(2F)OCF_2=84.2 J_{FF}=5.6 Hz

same procedure as above is used. After warming at 30°C for three hours, 200 ml of water are added. The organic phase is separated and washed with water. C_6H_6 is evaporated and the mixture is purified by steam distillation, then dried on Na_2CO_3. Pure liquid products are obtained by distillation using a spinning band column. When the mixture is a solid (for example with $4NO_2C_6H_4SH$) pure products are obtained by thin layer chromatography [SiO_2-pentane].

4 - Condensation of $BrCF_2CF_2Br$ with phenoxides: Potassium phenoxide (0.05 mole) and a small amounts of propylmercaptan (0.005 mole) are dissolved in 250 ml of dry DMF under an argon atmosphere. Then $BrCF_2CF_2Br$ (0.075 mole) is added dropwise at room temperature. After warming to 40°C for four hours, 300 ml of 17 % HCl are added. The aqueous phase is extracted with ether. Ether is evaporated and the residue is purified as with thiophenoxides.

The characteristics of the compounds are summarized in the Table III.

ACKNOWLEDGEMENT

The authors are grateful to the Rhône-Poulenc Society for support of this work.

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