Journal of Fluorine Chemistry, *41* (1988) 263–275
Received: February 13, 1988; accepted: June 15, 1988

THE SYNTHESIS AND REARRANGEMENT REACTIONS OF 2,3,4,5,6-PENTAFLUOROBENZYL METHYL SULPHOXIDE AND 1,1-BIS(PENTAFLUOROPHENYL)METHYL METHYL SULPHOXIDE

Gerald M. BROOKE and J.A.K. Jamie FERGUSON

Chemistry Department, Science Laboratories, South Road, Durham DH1 3LE (U.K.)

SUMMARY

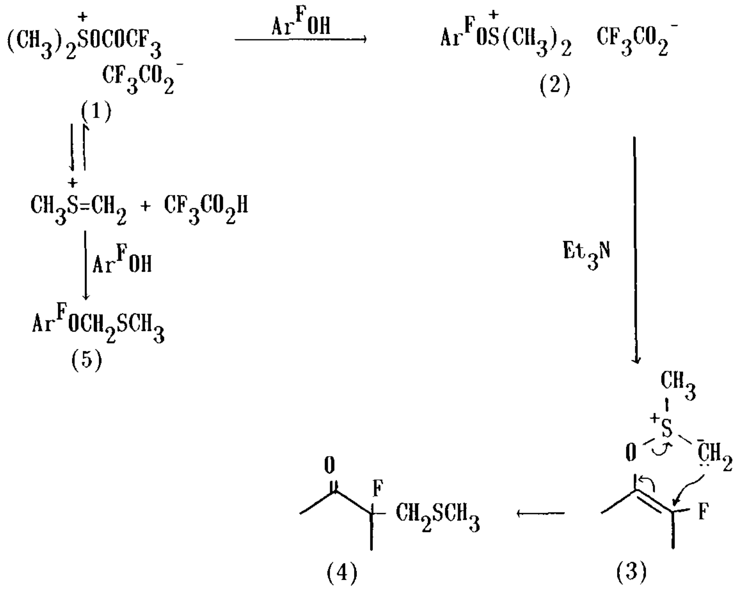
2,3,4,5,6-Pentafluorobenzyl methyl sulphoxide (6) and 1,1-bis(pentafluorophenyl)methyl sulphoxide (9) were synthesised from hexafluorobenzene and sodium methylsulphinylmethide. Flash vapour phase thermolysis of (6) at 410°C gave 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl (11) whereas static vapour phase thermolysis at 140-190°C gave (11), 2,3,4,5,6-pentafluorobenzyl alcohol (12) and 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl disulphide (13). Decafluorobenzophenone (14) and bis(pentafluorophenyl)methanol (15) are thermolysis products of compound (9) at 115-122°C, accompanied by 4-methanoyl-nonafluorobenzophenone (16) formed by the thermolysis of (19), the unisolated material derived from (9) by nucleophilic substitution of one para-fluorine by $CH_3SOCH_2^-$. Central to the formation of (12), (13), (14), (15) and (16) are sulphenate esters formed by '1,2'-rearrangements, while homolysis of the C-SO(CH_3) bond in (6) and dimerisation of the benzyl radical gives (11).

INTRODUCTION

We described in a recent paper [1] the reactions of polyfluoro-arenols and -heteroarenols with the complex (1) formed with dimethylsulphoxide (DMSO)

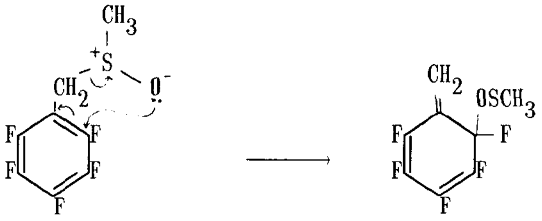
0022-1139/88/$3.50

and trifluoroacetic anhydride, followed by reaction with triethylamine: de-aromatised materials (4) were the main products resulting from the deprotonation of the oxysulphonium salt (2) followed by a 2,3-sigmatropic rearrangement of the resulting ylide (3) but in one case a small amount of an ether (5) was formed by the reaction of the starting material with $Me\overset{+}{S}{=}CH_2$, Scheme 1.



Scheme 1

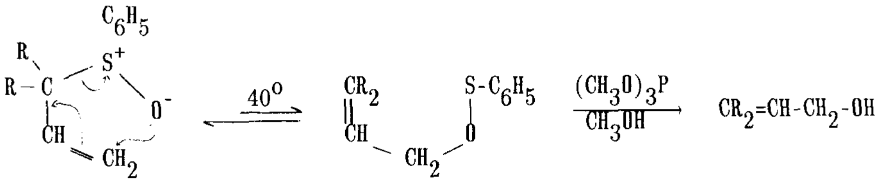
Isomeric with the ylide functionality in (3) is the methylsulphinylmethyl group CH_3SOCH_2, so we argued that 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) was a potential candidate for an analogous 2,3-sigmatropic rearrangement reaction, Scheme 2. Although this sulphoxide-sulphenate



(6)

Scheme 2

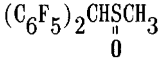
rearrangement has not been demonstrated with aromatic systems providing the unsaturated fragment of the C_3 unit, allylic sulphoxides (7) readily undergo a thermal rearrangement to the thermodynamically less stable sulphenate ester (8) which may be trapped by a thiophile (trimethyl phosphite) to give an allylic alcohol [2], Scheme 3.



(7) (8)

Scheme 3

In this paper we report: the preparation of compound (6) and its thermolysis reactions; the synthesis of 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) and the identification of products from its thermal decomposition.

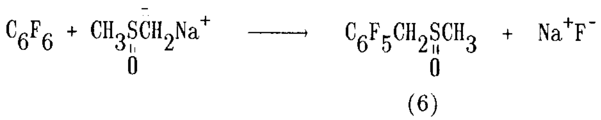


$(C_6F_5)_2CH\underset{\underset{O}{\|}}{S}CH_3$

(9)

RESULTS AND DISCUSSION

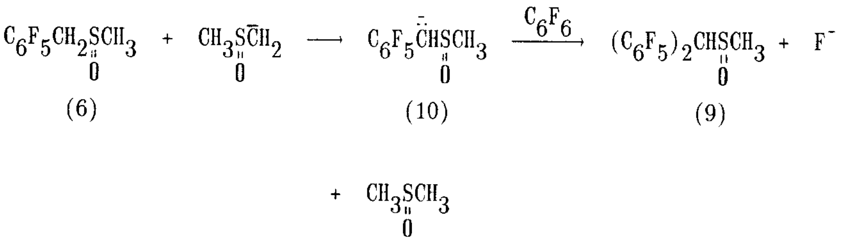
Hexafluorobenzene in tetrahydrofuran at -74°C was treated with sodium methylsulphinylmethide (1 equivalent) in dimethyl sulphoxide [3] and the mixture was quenched with water at this temperature to give 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) (37%), Scheme 4.



$$C_6F_6 + CH_3\underset{\substack{\|\\ O}}{S}\overset{-}{C}H_2Na^+ \longrightarrow \underset{(6)}{C_6F_5CH_2\underset{\substack{\|\\ O}}{S}CH_3} + Na^+F^-$$

Scheme 4

When hexafluorobenzene was reacted with one equivalent of sodium methylsulphinylmethide in DMSO at 15°C, the temperature rapidly rose to 20°C and on work-up the product consisted of unreacted C_6F_6 and 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) (31%), the structure of which was most readily deduced from its ^1H nmr spectrum: there were two singlets in the aliphatic region in the ratio of 1:3. In this reaction, compound (6) formed initially must be deprotonated by the sodium methylsulphinylmethide to give the more stable carbanion (10) which reacted with more hexafluorobenzene at the higher reaction temperature, Scheme 5.

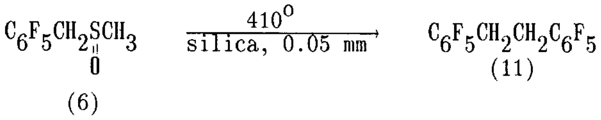


$$\underset{(6)}{C_6F_5CH_2\underset{\substack{\|\\ O}}{S}CH_3} + CH_3\underset{\substack{\|\\ O}}{S}\overset{-}{C}H_2 \longrightarrow \underset{(10)}{C_6F_5\overset{-}{C}H\underset{\substack{\|\\ O}}{S}CH_3} \xrightarrow{C_6F_6} \underset{(9)}{(C_6F_5)_2CH\underset{\substack{\|\\ O}}{S}CH_3} + F^- + CH_3\underset{\substack{\|\\ O}}{S}CH_3$$

Scheme 5

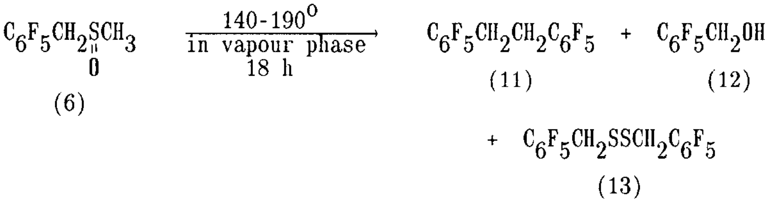
The reaction of α-sulphoxide stabilised carbanions with unsaturated fluorocarbons for the preparation of new carbon-carbon bonds has not been reported previously; it supplements the recently reported use of closely related α-phenylsulphonyl carbanions in synthetic reactions with perfluorinated aromatic compounds [4].

The thermolysis reactions of 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) were investigated under two sets of reaction conditions: flash vapour phase thermolysis and static vapour phase thermolysis. When compound (6) was distilled in vacuo through a quartz tube packed with silica at 410^0 only one product was formed, the known 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl (11) (87%) [5], Scheme 6. Under static vapour phase thermolysis conditions, in which the sulphoxide (6) was heated in vacuo at 140-190^0 for 18 h, a complex mixture containing at least eight components was formed, but only three have been separated and identified: 2,2',3,3',4,4',-5,5',6,6'-decafluorodibenzyl (11) (27%), 2,3,4,5,6-pentafluorobenzyl alcohol (12) (22%) [5,6] and 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl disulphide (13) (7%), Scheme 7. The structure of (13) was readily deduced by



$$\underset{(6)}{C_6F_5CH_2\underset{\underset{O}{\|}}{S}CH_3} \xrightarrow[\text{silica, 0.05 mm}]{410^0} \underset{(11)}{C_6F_5CH_2CH_2C_6F_5}$$

Scheme 6

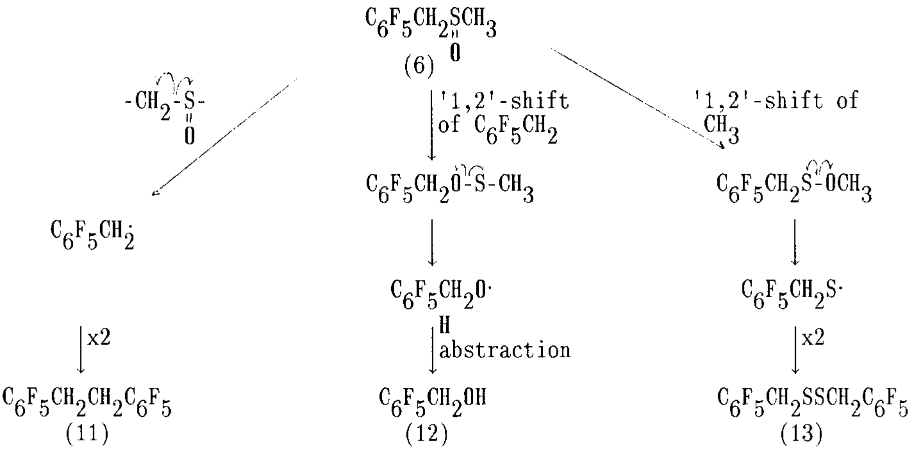


$$\underset{(6)}{C_6F_5CH_2\underset{\underset{O}{\|}}{S}CH_3} \xrightarrow[\text{in vapour phase, 18 h}]{140\text{-}190^0} \underset{(11)}{C_6F_5CH_2CH_2C_6F_5} + \underset{(12)}{C_6F_5CH_2OH} + \underset{(13)}{C_6F_5CH_2SSCH_2C_6F_5}$$

Scheme 7

mass spectroscopy; and by ^1H and ^{19}F nmr spectroscopy which showed only one type of proton and three types of fluorine respectively.

The formation of (11) from (6) in Scheme 6 and of all the products in Scheme 7 can be rationalised as follows. Homolytic cleavage of the $C\text{-}SO(CH_3)$ bond in (6) and dimerisation of the 2,3,4,5,6-pentafluorobenzyl radical gives (11), while a '1,2'-rearrangement of the 2,3,4,5,6-pentafluorobenzyl group or of the methyl group onto oxygen followed by homolytic cleavage of the O-S bonds (sulphenate esters) gives the alcohol (12) (after a hydrogen atom abstraction) and the disulphide (13) (after a dimerisation reaction) respectively, Scheme 8. The intermediacy of sulphenate esters formed by

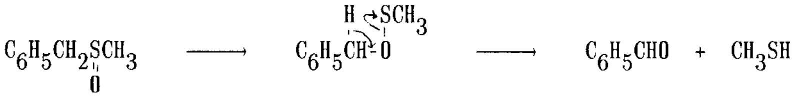


Scheme 8

'1,2'-rearrangements have been proposed previously in the thermolysis reactions of sulphoxides [7].

A thermolysis reaction of 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) was observed accidentally during the work-up following its presumed formation in a large scale reaction of hexafluorobenzene and sodium methylsulphinyl methide at -13°C to -20°C. The crude reaction product was heated in vacuo at 115-122°C over 6 h and the volatile material was separated into four components: 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) (12%); decafluorobenzophenone (14) (1.5%) [6]; bis(pentafluorophenyl)methanol (15) (1.5%) [6]; and 4-methanoyl-nonafluorobenzophenone (16) (0.5%). The structure of (16) was deduced principally from its mass spectrum [correct mass of the parent ion, M^+, 372, and base peak at 195 (C_6F_5CO)]; from its ^1H nmr spectrum (one singlet, δ_H at 10.35 due to -CHO), and from its ^{19}F nmr spectrum (nine fluorine atoms, present as five signals, one signal being due to one fluorine, each of the other four being due to two fluorines; the presence of a para disubstituted tetrafluorobenzene ring only can accommodate these data).

It has been proposed that the formation of aldehydes in the thermolysis reactions of sulphoxides proceed via an initial '1,2'-rearrangement to a sulphenate ester followed by a β-elimination reaction [8]. Of particular interest is the transformation of compound (17) into benzaldehyde (87%), Scheme 9. No pentafluorobenzaldehyde was isolated in the thermolysis

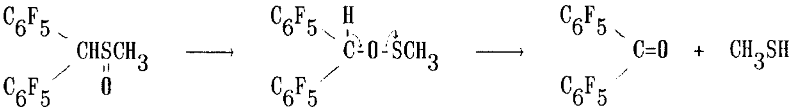


$$C_6H_5CH_2\underset{\underset{O}{\|}}{S}CH_3 \longrightarrow C_6H_5\overset{H\ \curvearrowright SCH_3}{CH\!-\!O} \longrightarrow C_6H_5CHO + CH_3SH$$

(17)

Scheme 9

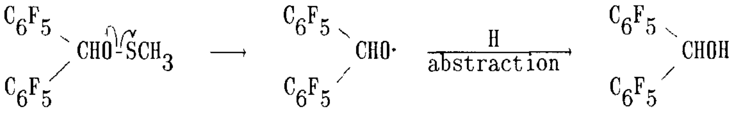
reactions of (6), but the presence of decafluorobenzophenone (14) [presumably from 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9)] in the reaction described above can be rationalised on the basis of this mechanism, which invokes the formation of the intermediate sulphenate ester (18), Scheme 10.



(9) (18) (14)

Scheme 10

The formation of bis(pentafluorophenyl)methanol (15), however, can be accounted for by the competing homolysis of the $O\text{-}SCH_3$ bond in (18) and hydrogen abstraction, Scheme 11. It is conceivable that oxidation of the alcohol (15)

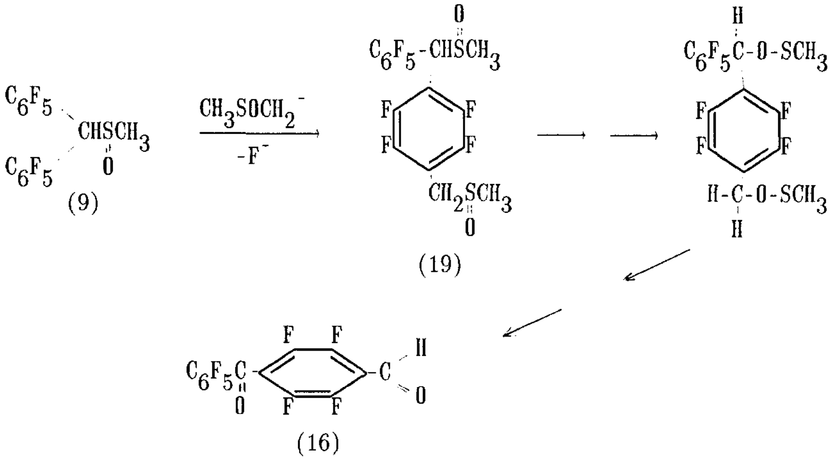


(18) (15)

Scheme 11

in the prevailing 'dialkyl sulphoxide' environment in the reaction mixture could provide an alternative route to the ketone (14).

The formation of the small amount of 4-methanoyl-nonafluorobenzophenone (16) in the large scale reaction of hexafluorobenzene with sodium methylsulphinylmethide can be explained on the basis of the intermediacy of compound (19) formed by nucleophilic substitution of one para fluorine in 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) by $CH_3SOCH_2^-$, followed by two '1,2'-rearrangements and two β-elimination reactions, Scheme 12.



Scheme 12

In conclusion, the thermolysis reactions of 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) reported in this paper have established that while there is no evidence for a 2,3-sigmatropic rearrangement reaction, '1,2' rearrangements of the sulphoxide to sulphenate esters play a significant role in accounting for the reaction products. The same '1,2'-rearrangement is central to the thermolysis reaction of 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) and in accounting for the formation of (16).

EXPERIMENTAL

^1H (60 MHz) and ^{19}F nmr (56.4 MHz) spectra were obtained with a Varian EM360L spectrometer or ^1H (250 MHz) and ^{19}F (235 MHz) spectra with a Bruker AC250. Chemial shifts are downfield from internal TMS (δ_H), or upfield from internal $CFCl_3$ (δ_F). Mass spectroscopy data were obtained with a VG 7070E instrument. Molecular ions M^+ are quoted for electron ionisation.

Reaction of Hexafluorobenzene with Sodium Methylsulphinylmethide

(a) Sodium methylsulphinylmethide in DMSO (25 ml, 1.73 M, 43.2 mmol) was added to hexafluorobenzene (8.136 g, 43.7 mmol) in dry tetrahydrofuran (THF) (100 ml) at -74°C. The mixture was maintained at this temperature for 90 min, water was added at this low temperature and the solution warmed to room temperature. The solution was extracted with ether, the extracts dried ($MgSO_4$) and the solvent evaporated. The crude residue was shown by ^{19}F nmr spectroscopy to contain one main product and unreacted C_6F_6, which was removed by evaporation in vacuo at 0.05 mmHg to give 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (6) (3.928 g, 37%) nc mp 96-97°C (from diethyl ether) (Found: C, 39.65; H, 2.15; M^+, 244, $C_8H_5F_5OS$ requires C, 39.35; H, 2.06%; M, 244); $\delta_F(CDCl_3)$ 140.5 (dm, 2-F, 6-F), 153.4 (t, 4-F) and 161.9 ppm (tm, 3-F, 5-F); $\delta_H(CDCl_3)$ 2.6 (s, CH_3) and 4.1 (s, CH_2).

(b) Sodium methylsulphinylmethide in dimethyl sulphoxide (DMSO) (5.5 ml, 2.8 M; 15.4 mmol) was added dropwise to a stirred solution of hexafluorobenzene (2.877 g, 15.5 mmol) in DMSO (20 ml) at 15°C whereupon the temperature rose rapidly to 20°C. After 50 min. at room temperature the mixture was worked up as in (a) to give the crude product, again shown to contain unreacted C_6F_6 by ^{19}F nmr. Evaporation of the mixture as in (a) gave 1,1-bis(pentafluorophenyl)methyl methyl sulphoxide (9) (0.982 g, 31%) nc mp 116-116.5°C (from methanol) (Found: C, 41.30; H, 0.6; M^+, 347. $C_{14}H_4F_{10}OS$ requires C, 40.99; H, 0.98%; $M-CH_3SO$, 347); $\delta_F(CDCl_3)$ 137.1, 138.7 (two m, unassigned 2-F, 6-F, 2'-F, 6'-F), 151.3, 152.0 (two tm, 4-F, 4'-F) and 160.2, 161.4 ppm (two m, unassigned 3-F, 5-F, 3'-F, 5'-F); $\delta_H(CDCl_3)$ 2.68 (s, CH_3) and 5.42 (s, CH).

(c) Hexafluorobenzene (80.1 g, 0.431 mol) was added over 35 min to a suspension of sodium methylsulphinylmethide [from NaH (11.9 g, 0.496 mol) and DMSO (95 ml) and then diluted with dry THF (200 ml)] initially at -20°, the temperature rising to -13°C. After a further 15 min., the mixture was poured onto dilute H_2SO_4 (4 M) pre-cooled to -5°C and worked up as in (a). The crude oily product (74.6 g) was distilled in vacuo at 0.05 mmHg with an external temperature of 115-122°C over 6 h to give a sticky green solid (38.6 g) which was dissolved in diethyl ether and allowed to crystallise at -18°C. Compound (6) (12.61 g, 12%) was separated by filtration, the filtrate evaporated and the residue was partially resolved into three enriched fractions by chromatography on silica using $CHCl_3$ as eluant: fraction 1 (4.53 g) was further separated by chromatography on silica using CCl_4 as eluant to give decafluorobenzophenone (14) (1.20 g, 1.5%) identical with an authentic sample; fraction 2 (6.17 g) was further separated on a silica column using CCl_4 as eluant to give <u>4-methanoyl-nonafluorobenzophenone (16)</u> (0.46 g, 0.5%) <u>nc</u> mp 128-129°C [from light petroleum (bp 60-80°)] (Found: C, 44.9; H, 0%; M^+, 372. $C_{14}HF_9O_2$ requires C, 45.18; H, 0.27%; M, 372); $\delta_F(CDCl_3)$ 141.0 (m), 141.6 (m), 143.6 (m), 144.5(m) and 159.5 ppm (m) in the ratio 2:2:2:1:2 respectively; $\delta_H(CDCl_3)$ 10.35 (CHO); and fraction 3 (6.13 g) was washed with water to remove DMSO and recrystallised from light petroleum (bp 40-60°C) to give bis(pentafluorophenyl)methanol (15) (1.26 g, 1.5%) mp 76-78°C (lit [6] mp 79-80°), identical with the material obtained from the treatment of decafluorobenzophenone with BH_3-THF.

<u>Thermolyses of 2,3,4,5,6-Pentafluorobenzyl methyl sulphoxide (6)</u>

(a) <u>Flash Vapour Phase Reaction</u>

The sulphoxide (6) (0.508 g) was distilled through a quartz tube [60 cm x 1.5 cm diameter] packed with silica fibre 20 cm x 1.5 cm diameter, at 410°C, into a trap cooled with liquid air connected to a high vacuum (0.05 mmHg).

The product was 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl (11) (0.328 g, 87%) mp 104-104.5^{o}C [from light petroleum (bp 40-60^{o}C)] (lit [5] mp 107-108^{o}C) (Found: C, 46.35; H, 0.80; M$^+$, 362. $C_{14}H_4F_{10}$ requires C, 46.43; H. 1.11%; M, 362); δ_F(CDCl$_3$) 145.3, 157.0 and 163.2 ppm in the ratio 2:1:2; δ_H(CDCl$_3$) 3.0 (s, CH$_2$).

(b) Static Vapour Phase Reaction

The sulphoxide (6) (1.438 g) was sealed in vacuo in a 10 l. flask and placed in an oven initially at 190^{o}C and then after 7 h, the temperature was reduced to 140^{o}. After a total heating period of 18 h, the contents of the flask were washed out with ether and the solvent evaporated. Thin layer chromatography of the residue on silica using light petroleum (bp 40-60^{o}) showed the presence of at least eight components. Volatile material (0.61 g) was removed from the mixture in vacuo at room temperature/0.05 mmHg and separated by the chromatography on silica (15 x 5 cm diameter) using light petroleum (bp 40-60^{o}C) followed by CH$_2$Cl$_2$ as eluants to give two components: (1) 2,3,4,5,6-pentafluorobenzyl alcohol (12) (0.261 g, 22%) identified by comparison with an authentic sample; and (ii) the decafluorodibenzyl compound (11) (0.150 g, 14%).

The residue from the evaporation of the volatile materials was separated by chromatography on silica using light petroleum (bp 40-60^{o}C) as eluant to give two components: (1) further 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl (11) (0.138 g, 13%); and (ii) 2,2',3,3',4,4',5,5',6,6'-decafluorodibenzyl disulphide (13) (0.094 g, 7%) nc mp 145.5-146^{o}C [from light petroleum (bp 40-60^{o}C)] (Found: C, 39.71; H, 1.10; M$^+$ 426. $C_{14}H_4F_{10}S_2$ requires C, 39.44; H, 0.09%; M, 426); δ_F(CDCl$_3$) 142.9, 154.6 and 162.0 ppm in the ratio 2:1:2 respectively; δ_H(CDCl$_3$) 3.92 (s, CH).

ACKNOWLEDGEMENT

We thank the S.E.R.C. for a research studentship to (J.A.K.J.F.).

REFERENCES

1 G.M. Brooke and J.A.K.J. Ferguson, J. Chem. Soc., Perkin Trans. 1, (1987) 2091.

2 D.A. Evans and G.C. Andrew, Acc. Chem. Res., 7 (1974) 147; R.W. Hoffmann, S. Goldmann, N. Maak, R. Gerlack, F. Frickel and G. Steinback, Chem. Ber., 113 (1980) 819.

3 E.J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84 (1962) 866; 87 (1965) 1345.

4 R.D. Chambers and M. Todd, J. Fluorine Chem., 27 (1985) 237.

5 J.M. Birchall and R.N. Haszeldine, J. Chem. Soc., (1961) 3719.

6 A.K. Barbour, M.W. Buxton, P.L. Coe, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1961) 808.

7 F.A. Davis, T.W. Panunto, S.B. Awad and R.L. Billmers, J. Org. Chem., 49 (1984) 1228.

8 W. Carruthers, I.D. Entwistle, R.A.W. Johnstone and B.J. Millard, Chem. and Ind., (1966) 342.