Fluorocarbon Derivatives of Nitrogen. Part 6.[1] Reactions of Some Perfluorinated Nitroso-compounds with Hydrogen Sulphite Ion: Conversion of Fluorocarbon Olefins into Perfluoro-ketone Oximes

By **Ronald E. Banks** * and **Neil Dickinson,** Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The sequence of events $R_F^1R_F^2CFNO + HSO_3^-$ aq. $\longrightarrow R_F^1R_F^2CFN(OH)SO_3^- \longrightarrow R_F^1R_F^2CFNHOH \longrightarrow R_F^1R_F^2C=NOH$ is proposed to account for the production of N-trifluoromethylhydroxylamine, perfluoropropanohydroximoyl fluoride, perfluoroacetone oxime, and perfluorocyclobutanone oxime when the nitroso-compounds CF_3NO, $n-C_3F_7NO$, $(CF_3)_2CFNO$, and $\overline{CF_2CF_2CF_2CFNO}$, respectively, are treated with aqueous potassium hydrogen sulphite; understandably, perfluoro-1-nitrosopropane reacts with the same reagent in the presence of lead(IV) oxide to give the purple water-soluble oxyl $n-C_3F_7N(O\cdot)SO_3^-K^+$. Since perfluoro-2-nitrosopropane and perfluoronitrosocyclobutane are easily obtained *via* the route $R_F^1CF=CFR_F \longrightarrow$ (with $KF-CF_3CO_2Ag$) $R_F^1CFAgCF_2R_F \longrightarrow$ (with NOCl) $R_F^1CF(NO)CF_2R_F$ $(R_F^1 = CF_3,\ R_F = F;\ R_F^1R_F = CF_2CF_2)(R_FCF_2 = R_F^2)$, the reductive defluorination with aqueous hydrogen sulphite anion completes a fluorocarbon olefin $\longrightarrow$ fluorocarbon ketone oxime conversion.

DURING pioneering work [2] on the preparation of aqueous (purple) solutions containing sodium or potassium N-trifluoromethylsulphamate N-oxyl (1) *via* the route $CF_3NO + M^+HSO_3^-$ aq. $\longrightarrow [CF_3N(OH)SO_3^-\ M^+$ (2)] $\longrightarrow$ (with PbO_2 or $KMnO_4$) $CF_3N(O\cdot)SO_3^-\ M^+$ (1; M = Na or K), Freear [3] found that use of excessively long reaction periods prior to the addition of an oxidising agent caused complete conversion of the nitroso-compound into inorganic products $[CO_2,\ F^-,\ SiF_6^{2-}$ (Pyrex vessels were employed), and $(NH_3OH)_2^+\ SO_4^{2-}]$; this led him to develop a one-pot procedure for the synthesis of the oxyl (1). These observations, coupled with knowledge of the sequences $ArNO_2 + HSO_3^- \longrightarrow ArNO \longrightarrow ArN(OH)SO_3^- \longrightarrow ArNHOH \longrightarrow etc.$ (the Piria reaction [4]) and $CCl_3NO + SO_2$ in EtOH aq. $\longrightarrow CCl_2=NOH$ (ref. 5) $\longrightarrow$ (with H_2O) NH_2OH, HCl, CO_2,[6] led to the supposition [3] that N-hydroxy-N-trifluoromethylsulphamate ion readily undergoes hydrolysis to provide N-trifluoromethylhydroxylamine (3), an obvious source of difluoroformaldehyde oxime and hence hydroxylamine.

Current research into the chemistry of N-trifluoromethylsulphamate N-oxyl (1) [7] engendered an opportunity to check Freear's observations; the positive outcome motivated us to carry out experiments on higher homologues of trifluoronitrosomethane, the results of which are embodied in Scheme 1.

Reactions between Perfluoronitrosoalkanes and Aqueous Potassium Hydrogen Sulphite.—Trifluoronitrosomethane reacts rapidly and exothermically with aqueous potassium hydrogen sulphite at ambient temperature; the N-hydroxy-N-trifluoromethylsulphamate anion (2) formed initially disappears fairly quickly (*ca.* 2 h), as indicated by failure to cause a purple colouration $[CF_3N(O\cdot)SO_3^-]$ on addition of lead(IV) oxide to the solution. To determine if the sulphamate (2) undergoes hydrolysis to N-trifluoromethylhydroxylamine (3), a CF_3NO–$KHSO_3$ (aq.) –Et_2O mixture (1 : 1 molar ratio of nitroso-compound to hydrogen sulphite) was shaken for 2 h at

20 °C. Distillation of the ether layer gave an ether complex † of the hydroxylamine with approximate composition CF_3NHOH,Et_2O (48% yield); this material
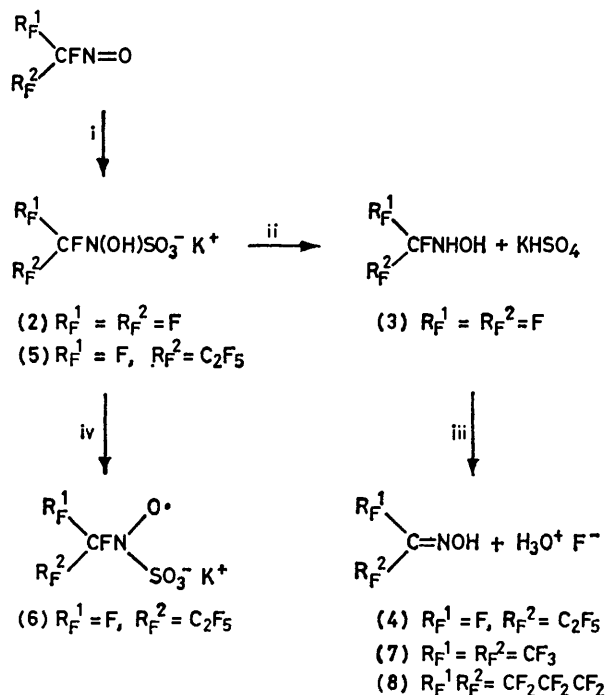

SCHEME 1 *Reagents*: i, $KHSO_3$ aq., 20 °C (plus Et_2O when $R_F^1 = R_F^2 = F$ and $R_F^1 = F$, $R_F^2 = C_2F_5$); ii, hydrolysis *in situ*; iii, H_2O; iv, PbO_2

slowly etched glass, and trifluoronitrosomethane was evolved when it was treated with acidified (H_2SO_4) sodium dichromate. No attempt was made to study the mechanism of complete degradation of N-trifluoromethylhydroxylamine to inorganic entities (see above),

† Adoption of this stratagem for achieving the isolation of N-trifluoromethylhydroxylamine was prompted by Russian work on the reduction $CF_3NO + HI \longrightarrow CF_3NHOH$.[8a]

which occurs when aqueous solutions of its precursor (2) are stored in Pyrex for 2—3 days at room temperature.

Repetition of the experiment with perfluoro-1-nitrosopropane in place of its lower homologue yielded (63%) an ether complex of perfluoropropanohydroximoyl fluoride (4),* with composition $C_2F_5CF=NOH$,-$0.92Et_2O$. Dehydrofluorination of the perfluoro-n-propyl analogue of (3) is an obvious source of (4),[8] but it is not inconceivable that the overall defluorosulphonation of N-hydroxy-N-perfluoro-n-propylsulphamate anion (5) proceeds via a more direct mechanism (see Scheme 2).

$C_2F_5CF_2NHO^- + H_3O^+ \rightleftharpoons C_2F_5CF_2NHOH + H_2O$
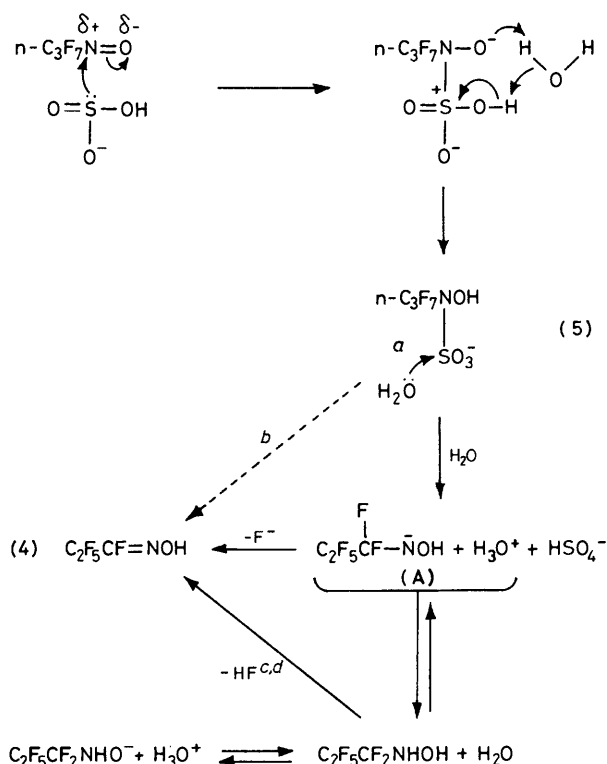
SCHEME 2 [a] Naturally, this step will be accelerated should protonation of the nitrogen occur as the acidity of the solution increases. [b] This β-elimination may proceed in ' concerted ' fashion rather than via the nitranion (A). [c] Several mechanisms can be envisaged here, including participation of the nitranion (A). [d] Ready dehydrofluorination of N-per- and -poly-fluoroalkylhydroxylamines to yield hydroxamic acid fluorides or ketone oximes has been noted previously during work on reduction of fluorinated nitroso- and nitro-compounds with HI and H_2-Pd, respectively.[8,12b]
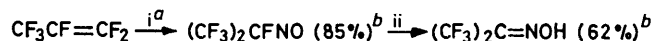
Further experimentation will be needed to resolve whether one or both mechanisms occur (for any perfluoronitrosoalkane), and to determine the influence of solvents other than ether (phase-transfer effect). That attack of aqueous potassium hydrogen sulphite on perfluoro-1-nitrosopropane does produce the corresponding N-hydroxysulphamate (5) can be proved by carrying out the reaction in the presence of lead(IV) oxide: a purple colour develops (less rapidly and reaching a lower

* This is analogous to the isolation of the trifluoromethyl analogue of (4) as the ether complex $CF_3CF=NOH$, $0.7Et_2O$ following reduction of $CF_3CF_2NO_2$ or $CF_3CFClNO$ with H_2-Pd or HBr.[8b]
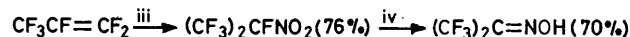
maximum intensity than in an identical experiment with CF_3NO) owing to production of the water-soluble oxyl $n-C_3F_7N(O\cdot)SO_3^-$ K^+ (6); this can be trapped with chlorotrifluoroethylene to yield a 2 : 1 adduct isolable in the form of its bis(tetraphenylarsonium) analogue Ph_4As^+ $n-C_3F_7N(SO_3^-)O\cdot CF_2\cdot CFCl\cdot ON(SO_3^-)C_3F_7-n^+AsPh_4$ —a technique used previously with potassium N-trifluoromethylsulphamate N-oxyl.[7]

Treatment of perfluoro-2-nitrosopropane with aqueous potassium hydrogen sulphite at room temperature in the presence of lead(IV) oxide did not lead to a purple colouration indicative of the formation of the oxyl $(CF_3)_2CFN(O\cdot)SO_3^-$ K^+; however, work-up of the aqueous product provided perfluoroacetone oxime (7). In the absence of the metal oxide, which, we assume, failed to compete effectively with water for the addition product $(CF_3)_2CFN(OH)SO_3^-$, thereby allowing preferential formation of the hydroxylamine $(CF_3)_2CFN$-HOH, the oxime (7) was produced in at least 62% yield. This conversion is analogous to the reductive dehalogenation of trichloronitrosomethane ($\longrightarrow CCl_2=NOH$)[5] and of 1-chloro-2-nitrosocyclohexane ($\longrightarrow$ cyclohexanone oxime)[9] with aqueous hydrogen sulphite anion,

Route A

$$CF_3CF=CF_2 \xrightarrow{i\,a} (CF_3)_2CFNO \ (85\%)^b \xrightarrow{ii} (CF_3)_2C=NOH \ (62\%)^b$$

Route B[12]

$$CF_3CF=CF_2 \xrightarrow{iii} (CF_3)_2CFNO_2(76\%) \xrightarrow{iv} (CF_3)_2C=NOH(70\%)$$

SCHEME 3 Reagents: i, KF + CF_3CO_2Ag in MeCN at 20 °C, followed by NOCl; ii, $KHSO_3$ aq., 20 °C; iii, AHF–100% HNO_3, 60 °C; iv, Pd–H_2 (40 atm.), methanol, 20 °C. [a] This method, which involves formation of $(CF_3)_2CFAg$ and its conversion into the nitroso-compound in situ, stems from other work on the synthetic applications of perfluoroalkylsilver compounds.[13] [b] Yields were not optimized.

and we have adapted it to synthesize perfluorocyclobutanone oxime (8) (54% yield) starting from perfluoronitrosocyclobutane. Both secondary perfluorinated nitrosoalkanes used in this work were procured by indirect addition of the elements of nitrosyl fluoride across a C=C bond in a common[10] fluoro-olefin (perfluoropropene and perfluorocyclobutene), as exemplified in Scheme 3 (Route A); this constitutes an attractive alternative to methods requiring nitrosyl fluoride itself,[11] and completes the evidence on which we propose the following general sequence for synthesis of perfluorinated ketone oximes: $R_F^1CF=CFR_F \longrightarrow [R_F^1CFAgCF_2-R_F] \longrightarrow R_F^1CF(NO)CF_2R_F \longrightarrow R_F^1C(:NOH)CF_2R_F$ (R_F^1 = perfluoroalkyl, R_F = F; R_F^1 = R_F = perfluoroalkyl; $R_F^1R_F$ = α,ω-perfluoropolymethylene) (note: $R_FCF_2 = R_F^2$ of Scheme 1). Conversion in the laboratory of commercial perfluoropropene into perfluoroacetone oxime in this manner is a more appealing proposition than the long-standing Russian method,[12] which requires the manipulation of anhydrous hydrogen fluoride (Scheme 3, Route B); the last stage in each Route is presumed (see Scheme 1 and ref. 12b) to involve

the same intermediate, *viz.* N-perfluoroisopropylhydroxylamine.

EXPERIMENTAL

Spectroscopic Analyses.—N.m.r. and mass spectra were obtained with a Perkin–Elmer R32 instrument [^{1}H at 90 and ^{19}F at 84.6 MHz, using external Me_4Si and CF_3CO_2H references, respectively (shifts to low field designated positive in both cases)], and a Kratos MS45 spectrometer (electron beam energy 70 eV), respectively. E.s.r. spectra were obtained using a Varian E9 instrument, *g* values being determined by comparison with data for diphenylpicrylhydrazyl (DPPH).

Starting Materials.—Trifluoronitrosomethane and perfluoro-1-nitrosopropane were prepared *via* pyrolysis of the corresponding alkanoyl nitrites.[14] Perfluoro-2-nitrosopropane and perfluoronitrosocyclobutane were synthesised *via* treatment of perfluoropropene and perfluorocyclobutene, respectively, with anhydrous potassium fluoride plus silver trifluoroacetate in acetonitrile, followed by nitrosyl chloride.[15] Aqueous solutions of potassium hydrogen sulphite were prepared by dissolving reagent-grade potassium disulphite in distilled water (concentrations of $KHSO_3$ were checked iodometrically).

Reactions of Aqueous Potassium Hydrogen Sulphite.—(a) *With trifluoronitrosomethane.* The nitroso-compound (3.22 g, 32.5 mmol) was condensed, *in vacuo,* into a Pyrex Rotaflo reaction tube (300 cm^3) containing diethyl ether (17 cm^3), water (15 cm^3), and potassium hydrogen sulphite (33 mmol) at −196 °C. The sealed tube was allowed to warm to room temperature then shaken vigorously; immediately a rapid, slightly exothermic reaction occurred, causing almost complete disappearance of the deep blue colour characteristic of trifluoronitrosomethane. After the tube had been shaken mechanically for 2 h, the ether layer [plus extracts obtained by shaking the aqueous phase with fresh ether (10 cm^3)] was dried (MgSO$_4$; 30 min) then distilled in a semi-micro Vigreux unit to give an ether complex of N-trifluoromethylhydroxylamine (2.52 g, 15.6 mmol, 48%) (Found: C, 31.3; H, 6.6; F, 34.5. Calc. for CH$_2$F$_3$NO,-0.82C$_4$H$_{10}$O: C, 31.8; H, 6.3; F, 35.25%), b.p. 77—79 °C at 741 mmHg, λ$_{max.}$ (film) 3.08vbr μm (O–H and N–H str.); *m/z* 101 (CF$_3$NHOH$^{+\cdot}$, 17%), 81 (CF$_2$=NOH$^{+\cdot}$, 70%), 74 (C$_4$H$_{10}$O$^{+\cdot}$, 80%), 69 (CF$_3^+$, 73%), and 59 (C$_2$H$_5$O=CH$_2^+$, 100%); δ$_F$ (*ca.* 50% soln. in Et$_2$O) +6.6 p.p.m.; δ$_H$ (neat liq.) +0.87 (C*H*$_3$CH$_2$O, t), +3.22 (CH$_3$C*H*$_2$O, q), and +6.5 p.p.m. (N*H* and O*H*, vbr, s) (rel. int. 21 : 14 : 10), which etched glass and so was stored in polythene prior to analysis.

(b) *With perfluoro-1-nitrosopropane.* The first experiment above involving trifluoronitrosomethane was repeated using perfluoro-1-nitrosopropane (7.04 g, 35.4 mmol) as the substrate, together with potassium disulphite (3.9 g ≡ 35.1 mmol KHSO$_3$), diethyl ether (15 cm^3), and water (15 cm^3), to give an *ether complex* of *perfluoropropanohydroximoyl fluoride* (5.47 g, 22.0 mmol, 63%) (Found: C, 32.1; H, 4.1; F, 45.6; N, 5.8. C$_3$HF$_6$NO,0.92C$_4$H$_{10}$O requires C, 32.2; H, 4.1; F, 45.8; N, 5.6%), b.p. 90—93 °C, λ$_{max.}$ (film) 3.10vbr (O–H str.) and 5.89 μm (C=N str.); δ$_F$ (neat liq.) −6.9 (CF$_3$, dt, J_{CF_3,CF_2} 2 Hz), −11.0 (CF, tq, J_{CF,CF_3} 16.4, J_{CF,CF_2} 4.5 Hz), and −43.0 p.p.m. (CF$_2$, dq) (rel. int. 3 : 1 : 2); δ$_H$ (same sample) +0.87 (C*H*$_3$CH$_2$O, t), +3.20 (CH$_3$C*H*$_2$O, q), and +10.25 p.p.m. (OH, vbr, s); *m/z* 181 (CF$_3$CF$_2$CF=NOH$^{+\cdot}$, 35%), 162 (CF$_3$CF$_2$CNO$^{+\cdot}$, 22%), 119 (C$_2$F$_5^+$, 45%), 112 (C$_2$HF$_3$NO$^+$, 79%), 100

(C$_2$F$_4^+$, 14%), 92 (C$_2$F$_2$NO$^+$, 46%), 74 (C$_4$H$_{10}$O$^{+\cdot}$, 66%), 69 (CF$_3^+$, 100%), and 59 (C$_2$H$_5$O=CH$_2^+$, 92%). The reaction tube was visibly etched.

(c) *With perfluoro-2-nitrosopropane.* The nitroso-compound (5.42 g, 27.2 mmol) was condensed, *in vacuo,* into a cold (−196 °C) thick-walled Pyrex tube containing potassium disulphite (1.66 g ≡ 15.0 mmol of KHSO$_3$) in water (10 cm^3); the tube was sealed (PTFE Rotaflo valve), allowed to warm to room temperature, and shaken overnight in a steel guard. After removal of unchanged perfluoro-2-nitrosopropane (13.6 mmol, 50%) from the now badly etched reaction vessel, the two-phase liquid product was transferred to a separating funnel; the lower pale-blue hydrate phase (2.64 g) was collected and added dropwise to a stirred 4 : 1 mixture of concentrated sulphuric acid and oleum contained in an ice-cooled round-bottomed flask (50 cm^3) which was evacuated continuously (oil pump) *via* a trap cooled to −196 °C. After 30 min, the flask was warmed slowly to *ca.* 50 °C until no more material appeared to be collecting in the cold trap; distillation of the condensate in a one-piece semi-micro Vigreux unit gave perfluoroacetone oxime [1.53 g, 8.45 mmol, 62% based on (CF$_3$)$_2$CFNO consumed] (Found: C, 20.0; H, 0.4; F, 62.5; N, 8.0. Calc. for C$_3$HF$_6$NO: C, 19.9; H, 0.55; F. 63.0; N, 7.7%), b.p. 72—74 °C (lit.,[12] 69—71 °C), λ$_{max.}$ (film) 2.9vbr (O–H str.) and 6.01 μm (C=N str.); δ$_F$ (neat liq.) +8.9 and +11.3 p.p.m. [two quartets ($^4J_{FF}$ 6 Hz) of equal intensity]; δ$_H$ +9.36 p.p.m. (br, s); *m/z* 181 (*M*$^{+\cdot}$, 29%), 161 (*M*$^{+\cdot}$ − HF, 76%), 112 (*M*$^{+\cdot}$ − CF$_3\cdot$, 66%), and 69 (CF$_3^+$, 100%). Treatment of the oxime with benzoyl chloride in the presence of pyridine, as described in the literature,[16] gave its *O*-benzoyl derivative (Found: C, 42.0; H, 1.8; F, 39.5; N, 4.9. Calc. for C$_{10}$H$_5$F$_6$NO$_2$: C, 42.1; H, 1.8; F, 40.0; N, 4.9%), m.p. 33—34 °C (lit.,[16] 34—35 °C), λ$_{max.}$ (liq. film) 5.58s (C=O str.) and 6.08m μm (C=N str.); δ$_F$ (*ca.* 50% soln. in CCl$_4$) +11.4 and +13.6 p.p.m. [two quartets ($^4J_{FF}$ 6 Hz) of equal intensity]; δ$_H$ (same soln.) +7.38—7.70 (complex, *m*-, *p*-H) and +7.98—8.16 p.p.m. (complex, *o*-H) (rel. int. 3 : 2).

(d) *With perfluoronitrosocyclobutane.* Experiment (c), involving perfluoro-2-nitrosopropane, was repeated using perfluoronitrosocyclobutane {35.8 mmol [*ca.* 17 mmol (48%) was recovered] contaminated with perfluorocyclobutene used in its synthesis}, potassium disulphite (2.0 g ≡ 18 mmol of KHSO$_3$) and water (12 cm^3) to give *perfluorocyclobutanone oxime* (1.95 g, 10.1 mmol, 54% based on C$_4$F$_7$NO consumed) (Found: C, 24.9; H, 0.8; F, 59.0; N, 7.3. C$_4$HF$_6$NO requires C, 24.9; H, 0.5; F, 59.1; N, 7.25%), b.p. 92—93 °C, λ$_{max.}$ (liq. film) 2.72, 2.79, and 3.0vbr (O–H str.), and 5.93 μm (C=N str.); δ$_F$ (neat liq.) −41.8, −43.9, and −55.4 p.p.m. (CF$_2$C*F*$_2$CF$_2$) (three singlets of equal intensities); δ$_H$ (same sample) +9.18 p.p.m. (br, s); *m/z* 193 (*M*$^{+\cdot}$, 8%), 176 (*M*$^{+\cdot}$ − OH$\cdot$, 33%), 131 (C$_3$F$_5^+$, 25%), 100 (C$_2$F$_4^+$, 68%), 93 (CF$_2$CNOH$^+$, 34%), 76 (CF$_2$-CN$^+$, 100%), 69 (CF$_3^+$, 98%), and 50 (CF$_2^+$, 21%). The reaction vessel became noticeably etched.

Preparation of Potassium N-*Perfluoro-n-propylsulphamate* N-*Oxyl* (with J. FREEAR).—Perfluoro-1-nitrosopropane (3.72 g, 18.7 mmol) was condensed, *in vacuo,* into a cold (−196 °C) Pyrex tube (125 cm^3) fitted with a Rotaflo needle valve and containing water (6 cm^3), potassium hydrogen sulphite (7.50 mmol; from 0.83 g of potassium disulphite), and lead(IV) oxide (*ca.* 1.5 g). The tube was sealed and allowed to warm to room temperature, then shaken for 80 min. After removal of unchanged perfluoro-1-nitrosopropane

(13.0 mmol, 70%), the contents of the tube were washed out with the minimum quantity of water (*ca.* 5 cm³) and the washings were filtered at the pump to give a purple solution containing (by e.s.r. spectroscopy) N-perfluoro-n-propylsulphamate N-oxyl ion [g 2.0062 $\pm$ 0.0001, a_N 1.225, $a_{\alpha F}$ 1.225, $a_{\beta F}$ 0.167 mT in H_2O (*ca.* 10^{-4}M) buffered with KOAc to pH *ca.* 8 ($a_{\gamma F}$ not determinable)]. The solution was buffered with potassium acetate (*ca.* 0.5 g) then shaken under anaerobic conditions with chlorotrifluoroethylene (0.77 g, 6.6 mmol) in an evacuated Rotaflo reaction tube (125 cm³) at room temperature overnight (the purple colour characteristic of the oxyl had disappeared after 2.5 h). After removal of unchanged chlorotrifluoroethylene (6.1 mmol, shown by i.r. spectroscopy to be contaminated with perfluoro-1-nitropropane), the liquid product was filtered to remove traces of a white solid, then treated with a solution of tetraphenylarsonium chloride (0.5 g) in water (10 cm³). The precipitate which formed was dried over phosphorus pentaoxide, *in vacuo*, and found to possess an elemental composition consistent with *bis(tetraphenylarsonium)* 1,2-*bis*(N-*perfluoro-n-propyl*-N-*sulphonatoamino-oxy*)-1-*chloro*-1,2,2-*trifluoroethane* (0.69 g, 0.48 mmol, 8% based on n-C_3F_7NO) (Found: C, 46.5; H, 2.6; F, 22.4; N, 1.8. $C_{56}H_{40}As_2F_{17}ClN_2O_8S_2$ requires C, 46.6; H, 2.8; F, 22.4; N, 1.9%).

The experiment described above was repeated, but the aqueous tetraphenylarsonium chloride was added to the solution containing potassium N-perfluoro-n-propyl-sulphamate N-oxyl without first trapping the oxyl with chlorotrifluoroethylene, causing a mauve solid to precipitate. This product was purified by precipitation from acetone (*ca.* 3 cm³) with water (*ca.* 15 cm³), dried *in vacuo* over phosphorus pentaoxide, and subjected to elemental analysis as quickly as possible since its colour began to fade; the results obtained were unsatisfactory for the expected tetraphenylarsonium N-perfluoro-n-propylsulphamate N-oxyl [Found: C, 50.0; H, 2.8; N, 1.5% (2 days after isolation); and C, 54.7; H, 3.3; N, 0.0% (after 5 days). Calc. for $C_{27}H_{20}AsF_7NO_4S$: C, 48.9; H, 3.0; N, 2.1%].

REFERENCES

[1] Part 5, R. E. Banks and D. R. Choudhury, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1443.
[2] R. E. Banks, D. J. Edge, J. Freear, and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. 1*, 1974, 721.
[3] J. Freear, personal communication.
[4] E. E. Gilbert, 'Sulfonation and Related Reactions,' Interscience, New York, 1965, p. 417; Z. Vrba and Z. J. Allan, *Collect. Czech. Chem. Commun.*, 1968, 33, 431.
[5] W. Prandtl and W. Dollfus, *Ber.*, 1932, 65B, 754.
[6] M. Sartori, 'The War Gases,' Churchill, London, 1939, p. 78.
[7] R. E. Banks and N. Dickinson, submitted to *J. Fluorine Chem.*, 1981, 18, 299.
[8] (*a*) A. Ya. Yakubovich, V. A. Ginsburg, S. P. Makarov, V. A. Shpanskii, N. F. Privezentseva, L. L. Martynova, B. V. Kir'yan, and A. L. Lemke, *Dokl. Akad. Nauk SSSR*, 1961, 140, 1352; (*b*) B. L. Dyatkin, A. A. Gevokyan, and I. L. Knunyants, *J. Gen. Chem. USSR*, 1966, 36, 1340.
[9] E. Müller, D. Fries, and E. Metzger, *Chem. Ber.*, 1955, 88, 1891.
[10] R. E. Banks, 'Fluorocarbons and Their Derivatives,' 2nd edn., Macdonald, London, 1970.
[11] B. L. Dyatkin, E. P. Mochalina, R. A. Bekker, S. R. Sterlin, and I. L. Knunyants, *Tetrahedron*, 1967, 24, 4291; S. Andreades, *J. Org. Chem.*, 1962, 27, 4163.
[12] (*a*) I. L. Knunyants, B. L. Dyatkin, L. S. German, I. N. Rozhkov, and V. A. Komarov, *Zh. Vses. Khim. Obshch. im. D.I. Mendeleeva*, 1963,*8*, 709 (*Chem. Abstr.*, 1964, 60, 9132 g); (*b*) I. L. Knunyants, L. S. German, I. N. Rozhkov, and B. L. Dyatkin, *Bull. Acad. Sci. USSR*, 1966, 226.
[13] B. L. Dyatkin, B. I. Martynov, L. G. Martynova, N. G. Kizim, S. R. Sterlin, Z. A. Stumbrevichute, and L. A. Fedorov, *J. Organomet. Chem.*, 1973, 57, 423.
[14] R. E. Banks, K. C. Eapen, R. N. Haszeldine, A. V. Holt, T. Myerscough, and S. Smith, *J. Chem. Soc., Perkin Trans. 1* 1974, 2532; R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc. C*, 1966, 1350.
[15] R. E. Banks, N. Dickinson, and A. P. Morrissey, in preparation.
[16] Yu. V. Zeifman, E. G. Abduganiev, E. M. Rokhlin, and I. L. Knunyants, *Bull. Acad. Sci. USSR*, 1972, 2667.