423. *Reactions of Fluorocarbon Radicals. Part X.* Polyfluoroalkyl Nitroso- and Nitro-compounds.*

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Nitric oxide combines with the perfluoroalkyl radicals $CF_3\cdot[CF_2]_n\cdot$ produced photochemically from the corresponding perfluoroalkyl iodides, to give the intensely blue, monomeric nitroso-compounds $CF_3\cdot[CF_2]_n\cdot NO$ (n = 1, 2, 3, 4, or 6). The compounds $CClF_2\cdot CF_2\cdot NO$, $CBrF_2\cdot CF_2\cdot NO$, $CBrF_2\cdot NO$, $CClF_2\cdot NO$, and $(C_2F_5)(CF_3)CF\cdot NO$ are similarly obtained. Oxidation of the corresponding nitroso-compounds yields $CF_3\cdot NO_2$, $C_2F_5\cdot NO_2$, $C_3F_7\cdot NO_2$, and $CClF_2\cdot NO_2$. The compounds $CClF_2\cdot CF_2\cdot NO_2$, $CClF_2\cdot CClF\cdot NO_2$, and $CClF_2\cdot CCl_2\cdot NO_2$ are obtained by the reaction of nitrosyl chloride with tetrafluoroethylene, chlorotrifluoroethylene, and 1 : 1-dichlorodifluoroethylene, respectively; nitrosyl bromide and tetrafluoroethylene similarly yield 1-bromotetrafluoro-2-nitroethane. 1-Chlorotetrafluoro-2-nitroethane can also be obtained from tetrafluoroethylene and nitryl chloride. Nitrogen dioxide readily combines with $CClF\colon CF_2$, $CCl_2\colon CF_2$, or C_2F_4 to give the corresponding dinitro-compounds. Attempts to replace the chlorine or bromine in $CClF_2\cdot NO_2$ or $CBrF_2\cdot CF_2\cdot NO_2$ by fluorine lead mainly to carbon–nitrogen bond fission.

THIS paper records the beginning of an investigation initiated some years ago into the preparation and properties of polyfluoro-compounds containing nitrogen, and is concerned with polyhalogeno-nitroso- and -nitro-alkanes.

Ruff and Giese (*Ber.*, 1936, **69**, 598, 684) obtained a low yield of a blue gas when silver cyanide was treated with fluorine, and concluded that it was trifluoronitrosomethane, and that the oxygen it contained arose from the silver nitrate present as impurity. The trifluoronitrosomethane was contaminated with a colourless gas from which it could not be separated, and from a series of qualitative reactions Ruff and Giese concluded that the colourless very stable compound was $F\cdot CO\cdot NF_2$. Trifluoronitrosomethane was believed to isomerise to the trifluoroformamide :

$$CF_3\cdot NO \text{ (blue; b. p. } -84^\circ\text{; f. p. } -196{\cdot}6^\circ) \longrightarrow F\cdot CO\cdot NF_2 \text{ (colourless; b. p. } -82{\cdot}4^\circ\text{; f. p. } -152{\cdot}2^\circ)$$

Pure trifluoronitrosomethane has now been obtained by irradiation of a mixture of trifluoroiodomethane and nitric oxide in the presence of mercury, which removes the iodine atom liberated and combines with any nitrogen dioxide formed :

$$CF_3I \xrightarrow{h\nu\text{ ,Hg}} CF_3\cdot \xrightarrow{\text{NO}} CF_3\cdot NO$$

The nitroso-compound is a gas with a magnificent deep blue colour, and on cooling yields a deep blue liquid and purple solid. Its ultra-violet and infra-red spectra have been recorded and, with a study of the rearrangement postulated by Ruff and Giese, will be reported by Dr. J. Jander.

Extension of the above method to the homologues of trifluoroiodomethane described earlier (*J.*, 1949, 2856; *J.*, 1952, 4259; *Nature*, 1950, **166**, 192) gave the blue compounds $CF_3\cdot[CF_2]_n\cdot NO$ (n = 1, 2, 3, 4, or 6) in low conversion but high yield (cf. *ibid.*, 1951, **168**, 1028). Molecular-weight determinations show that the compounds are not associated, and this agrees with the Trouton constant of 21·2 recorded for trifluoronitrosomethane by Ruff and Giese (*loc. cit.*). The synthetic method is of general application, and the fluoro-iodides $CClF_2\cdot CIF_2$, $CBrF_2\cdot CIF_2$, $CBrIF_2$, and $CClIF_2$ gave the corresponding nitroso-compounds. The first two of these fluoro-iodides were prepared from tetrafluoroethylene by reaction with iodine mono-chloride or -bromide. A secondary perfluoroalkyl-nitroso-compound was also prepared [$(C_2F_5)(CF_3)CF\cdot NO$].

Few alkyl nitroso-compounds are monomeric under normal conditions, and four main types may now be distinguished: (*a*) Those which contain the $>CH\cdot NO$ group form

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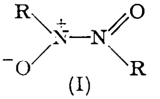
* Part IX, *J.*, 1953, 1548.

colourless dimers or isomerise to the oxime >C:N·OH (*e.g.*, MeNO; Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516). (*b*) Those which contain hydrogen and halogen on the α-carbon atom isomerise only slowly, but form colourless dimers :

$$\text{CHRX·NO} \longrightarrow \text{CRX:N·OH or (CHRX·NO)}_2;\ \text{X} = \text{Cl, Br.}$$

(*c*) Those which contain the nitroso-group attached to a tertiary carbon atom cannot isomerise, but yield colourless dimers [*e.g.*, $(Me_3C·NO)_2$]. The colourless dimers of (*b*) and (*c*) often partly dissociate to the blue monomer when heated or melted, or dissolved in an organic solvent, and their structures can be represented by resonance forms of type (I) (Fenimore, *ibid.*, 1950, **72**, 3226; Darwin and Hodgkin, *Nature*, 1950, **166**, 827). (*d*) The polyfluoro-nitroso-compounds, which do not form dimers under normal conditions. This is attributed to the powerful inductive effect of the polyfluoroalkyl group which reduces the availability for bond formation of the lone pair of electrons of the nitrogen atom in the nitroso-compounds and so prevents dimer formation of type (I). The absence of basic character in the fluoro-amines [*e.g.*, $N(CF_3)_3$, $FN(CF_3)_2$] is another example of this effect (Haszeldine, *J.*, 1951, 102; *Research*, 1951, **4**, 338). The compounds $CMe_2X·NO$ (X = Cl or Br) exist mainly in the blue monomeric form (Piloty, *Ber.*, 1898, **31**, 452).


(I)

Perfluoronitroalkanes were required for studies on perfluoroalkylamines, but application of the usual synthetic methods (*e.g.*, reaction with silver nitrite) to the corresponding iodo-compounds failed (Banus, Emeléus, and Haszeldine, *J.*, 1951, 60). Four alternative methods have been devised : (*a*) Oxidation of the nitroso-compounds. (*b*), (*c*), and (*d*) Reaction of nitrosyl chloride, nitryl chloride, or nitrogen dioxide with fluoro-olefins.

Treatment of the appropriate nitroso-compound with dimanganese heptoxide, lead dioxide, or chromic oxide gave the compounds $CF_3·NO_2$ (fluoropicrin), $C_2F_5·NO_2$, $C_3F_7·NO_2$, and $CClF_2·NO_2$. Their boiling points are compared with those of related compounds in Table 1. It is noteworthy that dichloro- and trichloro-nitromethane have similar boiling points which are only slightly higher than that of the unsubstituted compound, despite the marked increase in molecular weight (cf. $CH_3·CO_2H$, b. p. 118°; $CCl_3·CO_2H$, b. p. 197°). Comparison of $EtNO_2$, $CF_3·CH_2·NO_2$, and $C_2F_5·NO_2$ shows that replacement of hydrogen by fluorine on the α-carbon atom causes a very large decrease in boiling point, and this can be related to the inductive effect of the group attached to the readily polarised NO_2 group (cf. the nitriles : $CH_3·CN$, b. p. 82°; $CF_3·CN$, b. p. −64°).

TABLE 1. *Boiling points.*

MeNO$_2$ 101°				EtNO$_2$ 115°		PrNO$_2$ 132°	
$CCl_3·NO_2$	112°	$CH_2Cl·NO_2$	123°	$CF_3·CH_2·NO_2$ ...	96° [2]	$CF_3·(CH_2)_2·NO_2$	135° [1, 2]
$CClF_2·NO_2$ ...	25	$CHCl_2·NO_2$	107	$C_2F_5·NO_2$	0	$C_3F_7·NO_2$	25
$CF_3·NO_2$	−20	$CCl_3·NO_2$	112				

[1] Schechter and Conrad, *J. Amer. Chem. Soc.*, 1950, **72**, 3371. [2] McBee, Hass, and Robinson, *ibid.*, p. 3579.

Ruff and Giese (*loc. cit.*) reported that their blue compound failed to react with chromic oxide, and Hückel (*Nach. Ges. Wiss. Göttingen*, 1946, 36; *Chem. Abs.*, 1949, **43**, 6793) in a preliminary note reported that lead dioxide oxidised the nitroso-compound, but did not describe the properties of the product.

Chlorodifluoronitromethane gave mainly chlorotrifluoromethane when heated with antimony trifluorodichloride, *i.e.*, fission of the carbon–nitrogen bond occurred in preference to replacement of chlorine by fluorine :

$$CClF_2·NO_2 \xrightarrow{SbF_3Cl_2} CClF_3 + NO_2F$$

Pyrolysis of trifluoronitromethane in a platinum tube did not produce carbon tetrafluoride, hexafluoroethane, tetrafluoroethylene, or perfluoro*cyclo*butane, but gave a mixture which was probably nitrosyl fluoride, carbon dioxide, and carbonyl fluoride, *i.e.*, $CF_3·NO_2 \longrightarrow NOF + COF_2$. Pyrolysis in a silica apparatus gave only silicon tetrafluoride, carbon dioxide, and oxides of nitrogen. Perfluoronitropropane gave similar products when pyrolysed in platinum, but also yielded small amounts of hexafluoropropene and pentafluoropropionyl fluoride :

$$C_3F_7{\cdot}NO_2 \longrightarrow NOF + C_2F_5{\cdot}COF, \text{ or } C_3F_7{\cdot}NO_2 \longrightarrow C_3F_7{\cdot} \xrightarrow{NO_2} C_2F_5{\cdot}COF$$

$$C_3F_7{\cdot}NO_2 \longrightarrow C_3F_6 + NO_2F$$

The main product of the reaction of nitrosyl chloride with a fluoro-ethylene is the nitro-compound, *i.e.*, the addition reaction is followed by oxidation :

$$CF_2{:}CXY \xrightarrow{NOCl} CClF_2{\cdot}CXY{\cdot}NO \longrightarrow CClF_2{\cdot}CXY{\cdot}NO_2$$

The compounds $CClF_2{\cdot}CF_2{\cdot}NO_2$, $CClF_2{\cdot}CClF{\cdot}NO_2$, and $CClF_2{\cdot}CCl_2{\cdot}NO_2$ were prepared in good yield, and the reaction is not limited to fluoro-olefins, since trichloroethylene gave 1 : 1 : 1 : 2-tetrachloro-2-nitroethane. It is assumed that nitrosyl chloride reacts as NO^+Cl^- and not by a free-radical mechanism, and that the direction of addition to the fluoro-olefin is the same as in other reactions involving ionic intermediates (*e.g.*, iodine monochloride, Haszeldine, *J.*, 1952, 4423; alcohols and amines, Miller, Fager, and Griswold, *J. Amer. Chem. Soc.*, 1948, **70**, 431), where the negative substituent becomes attached to the CF_2 group of the olefin. Evidence for the constitution of the nitro-compound from trichloroethylene is the formation of trichloroacetic acid on treatment with concentrated sulphuric acid. The reaction of nitrosyl bromide with tetrafluoroethylene similarly yielded 1-bromotetrafluoro-2-nitroethane.

Infra-red spectroscopic studies reported in another series show that the NO_2 group in aliphatic compounds is characterised by its asymmetric and symmetric stretching vibrations (*ca.* 6·45 and 7·24—7·35 μ), and that when a powerful electron-attracting group [*e.g.*, CBr_3, CCl_3, $C(NO_2)_3$] is attached directly to the NO_2 group these bands shift to shorter and longer wave-length respectively (6·18—6·28 μ; 7·65—7·85 μ). The infra-red spectrum of 1-chlorotetrafluoro-2-nitroethane shows strong absorption at 6·18 and 7·85 μ which supports its formulation as a nitro-compound, as distinct from the isomeric nitrite. Its ultra-violet spectrum shows a maximum which is characteristic for nitro-compounds containing halogen on the α-carbon atom (see Table 2).

TABLE 2. *Ultra-violet spectra in light petroleum.*

	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
$Pr^n{\cdot}NO_2$	280	23	247	10
$CHEtCl{\cdot}NO_2$	283·5	28	249	13·5
$CMe_2Cl{\cdot}NO_2$	283·5	28	248·5	8
$CClF_2{\cdot}CF_2{\cdot}NO_2$ (vapour)	282·5	48	236·5	5·8
$CCl_3{\cdot}NO_2$	278·5	52	247·5	16

Attempts were made to replace the bromine in 1-bromotetrafluoro-2-nitroethane by fluorine, and so provide a general route to the synthesis of perfluoronitroalkanes from the olefins :

$$CF_2{:}CX_2 \longrightarrow CBrF_2{\cdot}CX_2{\cdot}NO_2 \longrightarrow CF_3{\cdot}CX_2{\cdot}NO_2$$

where X = F, perfluoroalkyl, perfluoro*cyclo*alkyl, etc. Reaction with bromine trifluoride gave only a low yield of perfluoronitroethane, however, and the main product was bromopentafluoroethane. Antimony trifluorodichloride also caused carbon–nitrogen bond fission to yield bromopentafluoroethane, and perfluoronitroethane was not isolated. The formation of chlorotrifluoromethane from the attempted replacement of chlorine by fluorine in $CClF_2{\cdot}NO_2$ has been described above.

The third method for the preparation of polyfluoronitroalkanes involves the reaction of nitryl chloride with the fluoro-olefin : tetrafluoroethylene gave 1-chlorotetrafluoro-2-nitroethane identical with the material from nitrosyl chloride :

$$C_2F_4 \xrightarrow{NO_2Cl} CClF_2{\cdot}CF_2{\cdot}NO_2$$

The reaction of nitrogen dioxide with polyhalogeno-olefins (Biltz, *Ber.*, 1902, **35**, 1528; Argo, James, and Donnelly, *J. Phys. Chem.*, 1919, **23**, 578; Coffman *et al.*, *J. Org. Chem.*, 1949, **14**, 747) has now been extended to chlorotrifluoroethylene, 1 : 1-dichlorodifluoroethylene, and tetrafluoroethylene, and found to yield the corresponding dinitro-compounds :

$$CF_2{:}CX_2 \xrightarrow{NO_2} NO_2{\cdot}CF_2{\cdot}CX_2{\cdot}NO_2$$

The above reactions thus give compounds of the general type RX being studied in this series of papers, where R is a polyfluoro-group and X is a potentially reactive group (see *J.*, 1951, 588). The influence of the strongly electronegative R on the properties of X (NO or NO_2) is being investigated.

EXPERIMENTAL

The nitrogen compounds described below may be lachrymators and have been manipulated in a vacuum-system wherever possible.

Preparation of Fluoro-iodides.—The perfluoroalkyl iodides were prepared by the reaction of iodine with the silver salt of the appropriate acid (*J.*, 1952, 4259), or by the interaction of trifluoroiodomethane or pentafluoroiodoethane and tetrafluoroethylene (*Nature*, 1950, **166**, 192). Nonafluoro-2-iodobutane was obtained by the photochemical reaction of trifluoroiodomethane with hexafluoropropene (Haszeldine and Steele, Amer. Chem. Soc. Meeting, Atlantic City, 1952).

Chlorodifluoroiodomethane and bromodifluoroiodomethane were prepared as earlier (*J.*, 1952, 4259).

Tetrafluoroethylene (2·0 g.), sealed in a 50-ml. Pyrex tube with a 10% excess of iodine monochloride and slowly heated to 50°, gave, after washing with 10% aqueous sodium hydroxide to remove traces of iodine, drying (P_2O_5), and distillation, 1-*chlorotetrafluoro*-2-*iodoethane* (94%), a colourless liquid, b. p. 56·5°, $n_D^{18\cdot5}$ 1·393 (Found : C, 8·9%; *M*, 261. C_2ClF_4I requires C, 9·1%; *M*, 262·5).

Interaction of tetrafluoroethylene (2·0 g.) and iodine monobromide (10% excess), at a maximum temperature of 80°, similarly yielded 1-*bromotetrafluoro*-2-*iodoethane* (90%), b. p. 80·5—81·0°, n_D^{16} 1·433 (Found : C, 8·0%; *M*, 307. C_2BrF_4I requires C, 7·8%; *M*, 307).

Ultra-violet spectra : $CClF_2{\cdot}ClF_2$ (vapour) $\lambda_{max.}$ 269 mμ (ε 245), $\lambda_{min.}$ 220 (ε 24); (light petroleum solution) $\lambda_{max.}$ 272 (ε 295), $\lambda_{min.}$ 215 (ε 17). $CBrF_2{\cdot}ClF_2$ (vapour) $\lambda_{max.}$ 269·5 (ε 343), $\lambda_{min.}$ 237·5 (ε 125); (light petroleum solution) $\lambda_{max.}$273 (ε 385), $\lambda_{min.}$ 236 (ε 140).

Nitric oxide, nitrogen dioxide, nitrosyl chloride, and nitrosyl bromide were purified by distillation through a packed column, or by fractional condensation in a vacuum-system, and were transferred to the reaction vessel *in vacuo*.

Polyhalogenoalkyl Nitroso-compounds.—The following general procedure was adopted for the preparation of the nitroso-compounds: The fluoro-, fluorochloro-, or fluorobromo-iodide (0·01—0·02 mole, depending on its volatility) was sealed in a 100-ml. silica tube with mercury (20—30 ml.) and nitric oxide (0·02—0·04 mole). The tube was shaken vigorously in a horizontal position in a vibro-shaker, and irradiated by a Hanovia S 250 lamp at 5—10 cm. distance; intimate mixing of the liquid and vapour with mercury was essential for good yields. After irradiation for 6—7 hr., a blue colour could be seen in the vapour or liquid phase. Irradiation was continued for 3—7 days, and the contents of the tube were fractionated *in vacuo* to remove the excess of nitric oxide. Final purification was achieved as follows. Compounds of b. p. >40°: distillation through a semimicro-column in an atmosphere of nitrogen and under reduced pressure to prevent possible isomerisation by excessive heating. Compounds of b. p. <40° : fractionation in a vacuum-system followed by treatment with ice-cold dilute aqueous alkali for 2—3 min. and refractionation. Special treatment was necessary for trifluoronitrosomethane which cannot be freed from excess of nitric oxide by distillation in a vacuum-system : air or oxygen was admitted into a bulb containing the crude nitroso-compound, and the nitrogen dioxide so formed was separated by further fractionation. Final purification was effected by shaking the nitroso-compound with ice-cold 2% sodium hydroxide solution in a sealed tube for 3—5 min. to remove traces of oxides of nitrogen, carbon dixoide, and carbonyl fluoride, followed by repeated fractionation *in vacuo*.

The deep blue *compounds* so prepared are given in Table 3, and apart from trifluoronitrosomethane (Ruff and Giese, *loc. cit.*) are new. The yield is based on the iodo-compound used, and the yield based on the iodo-compound taken is shown in parentheses. For carbon analysis, the compounds were pyrolysed in a stream of oxygen over silver vanadate at 700°; nitrogen analysis was effected in the usual way. Molecular weights were determined by Regnault's method, and the b. p. of a middle cut of a particular fraction was measured in an isoteniscope.

Addition of Nitrosyl Chloride to Halogeno-olefins.—(a) *Tetrafluoroethylene.* Nitrosyl chloride (13·2 g., 0·2 mole) was sealed *in vacuo* in a 200-ml. Pyrex tube with tetrafluoroethylene (5·0 g., 0·05 mole) and slowly heated to 50°. On cooling, it was noted that the volume of the liquid phase had increased. The tube was cooled in liquid nitrogen, then opened, and more tetrafluoroethylene was added (4·0 g., 0·04 mole); after reheating and cooling, the contents of the reaction vessel were fractionated *in vacuo* to remove unchanged nitrosyl chloride and then distilled to give 1-*chlorotetrafluoro*-2-*nitroethane* (63%), b. p. 36—37°, n_D^{22} 1·3145 (Found: C, 12·9; N, 7·7%; *M*, 181. $C_2O_2NClF_4$ requires C, 13·2; N, 7·7%; *M*, 181·5), as a colourless liquid. Treatment of the fraction containing residual nitrosyl chloride with aqueous sodium hydroxide left 1 : 2-dichlorotetrafluoroethane (8%), b. p. 4° (Found: *M*, 170. Calc. for $C_2Cl_2F_4$: *M*, 171).

TABLE 3. *Nitroso-compounds.*

Compound	B. p.	Yield (%)	Found C, %	Found N, %	Found *M*	Required C, %	Required N, %	Required *M*
$CF_3\cdot NO$	−84° [1]	75 (10)	—	14·0	99	—	14·2	99
$C_2F_5\cdot NO$	−42	80 (10)	16·4	9·0	150	16·1	9·4	149
$C_3F_7\cdot NO$	−12	83 (16)	18·4	6·9	199	18·1	7·0	199
$C_4F_9\cdot NO$	16—17°/730 mm.	81 (8)	19·5	5·5	249	19·3	5·6	249
$C_5F_{11}\cdot NO$	19—20°/230 mm. (50°/760 mm., micro)	71 (12)	20·0	—	298	20·1	4·7	299
$C_7F_{15}\cdot NO$	39—40°/63 mm. (95°/760 mm., micro)	75 (14)	21·1	3·4	400	21·0	3·5	399
$(C_2F_5)(CF_3)CF\cdot NO$	23—25°	86 (23)	19·0	5·8	249	19·3	5·6	249
$CClF_2\cdot CF_2\cdot NO$ ...	−2	68 (11)	14·4	8·3	165	14·5	8·5	165·5
$CBrF_2\cdot CF_2\cdot NO$ ...	18	52 (10)	—	6·6	210	11·4	6·7	210
$CBrF_2\cdot NO$	*ca.* −12 [2]	50 (10)	7·8	8·8	160	7·5	8·7	160
$CClF_2\cdot NO$	*ca.* −35 [2]	50 (10)	10·6	12·4	114	10·4	12·1	115·5

[1] B. p. given by Ruff and Giese, *loc. cit.* [2] B. p. approximate, since the compound was difficult to purify with the amount available; experiments on one-quarter of the usual scale.

(b) *Chlorotrifluoroethylene.* The procedure of (a) was applied to chlorotrifluoroethylene (0·10 mole) and nitrosyl chloride (0·23 mole), with a final reaction temperature of 100°. The material of b. p. $<30°$ was removed by vacuum-fractionation, and the residual material was washed with water, dried (P_2O_5), and distilled, to give 1 : 2-*dichlorotrifluoro*-2-*nitroethane* (67%), b. p. 75—76° (Found: C, 12·1; N, 7·3%; *M*, 198. $C_2O_2NCl_2F_3$ requires C, 12·1; N, 7·1%; *M*, 198), and 1 : 1 : 2-trichlorotrifluoroethane (16%), b. p. 46—48° (Found: *M*, 187. Calc. for $C_2Cl_3F_3$: *M*, 187·5).

(c) 1 : 1-*Dichlorodifluoroethylene.* This compound (0·06 mole) and nitrosyl chloride (0·15 mole), treated as in (b) above, gave 1 : 1 : 2-*trichlorodifluoro*-1-*nitroethane* (57%), b. p. 72—73°/151 mm., 117—118°/760 mm. (micro) (Found: N, 6·6; Cl, 49·5; F, 17·5%; *M*, 212. $C_2O_2NCl_3F_2$ requires N, 6·5; Cl, 49·7; F, 17·7%; *M*, 214·5), and 1 : 1-difluorotetrachloroethane (18%), b. p. 91—92°.

The still-residues from experiments (a), (b), and (c) above probably contain organic nitrates.

(d) *Trichloroethylene.* Trichloroethylene (5·0 g.) was heated with an excess of nitrosyl chloride (6·5 g.) at 100° for 2 hr., to give, after distillation in an atmosphere of nitrogen after washing with water and drying (P_2O_5), unchanged trichloroethylene (0·5 g.), pentachloroethane (1·1 g.), b. p. 158—160°, and 1 : 1 : 1 : 2-*tetrachloro*-2-*nitroethane* (62%), b. p. 95—96°/40 mm. (Found: N, 6·6; Cl, 66·4. $C_2HO_2NCl_4$ requires N, 6·6; Cl, 66·7%). A 2-g. sample of the last product was added dropwise to ice-cold concentrated sulphuric acid (10 ml.), the mixture was heated under reflux for 1 hr., and the product was removed *in vacuo*. Redistillation gave trichloroacetic acid (52%).

Interaction of Nitrosyl Bromide and Tetrafluoroethylene.—Nitrosyl bromide (3·3 g.; prepared from nitric oxide and bromine) was sealed with tetrafluoroethylene (2·0 g.) and kept at 0° for 1 week, then heated to 55° during 4 hr. The product was distilled rapidly in a vacuum-system to remove nitrosyl bromide, etc., and the crude residual product was washed once with ice-water, dried (P_2O_5), and distilled, to give 1-*bromotetrafluoro*-2-*nitroethane* (37%), b. p. 56—58° (Found: N, 6·0; Br, 35·6%; *M*, 222, 224. $C_2O_2NBrF_4$ requires N, 6·2; Br, 35·4%; *M*, 226), 1 : 2-dibromotetrafluoroethane (*ca.* 10%), b. p. 44—46°, and unidentified products.

Reaction of Nitryl Chloride with Tetrafluoroethylene.—Nitryl chloride was prepared from 100% nitric acid and anhydrous chlorosulphonic acid (Dachlauer, G.P. 509,405/1929), and was purified by distillation through a short low-temperature column. It had b. p. −16°. Schumacher and Sprenger (*Z. anorg. Chem.*, 1929, **182**, 139) report b. p. −15°.

Tetrafluoroethylene (2·0 g.) was sealed with nitryl chloride (20% excess) and the mixture was allowed to warm slowly to room temperature. After 2 hr. the tube was heated to 60°, then cooled, and the contents were fractionated in a vacuum-system, to give 1-chlorotetrafluoro-2-nitroethane (57%), b. p. 36—38°, identical with the material obtained from nitrosyl chloride and tetrafluoroethylene.

Oxidation of Nitroso- to Nitro-compounds.—(a) *Trifluoronitrosomethane.* Dimanganese heptoxide (*ca.* 1 g.; prepared by dropwise addition of potassium permanganate solution to cold concentrated sulphuric acid, followed by dropwise addition of ice-water, then removal of the brown heptoxide layer) was sealed in a Carius tube with trifluoronitrosomethane (0·3 g.) and slowly allowed to warm to 0°. After 24 hr. in the dark the tube was heated to 25° for 2 hr., then cooled, and the volatile contents were transferred to a vacuum-system. Repeated fractionation gave *trifluoronitromethane* (49%), b. p. −20° (isoteniscope) (Found: C, 10·6; N, 12·4%; *M*, 115. CO_2NF_3 requires C, 10·4; N, 12·2%; *M*, 115). Care must be taken, since several reaction tubes exploded during this reaction.

Use of a solution of dimanganese heptoxide (*ca.* 1·5 g.) in glacial acetic acid (3 ml.) gave a 26% yield of trifluoronitromethane from trifluoronitrosomethane (0·4 g.).

Chromic oxide (1·6 g.), heated to 70° for 10 hr. with trifluoronitrosomethane (0·2 g.), gave trifluoronitromethane (b. p. −21°) in 38% yield. With glacial acetic acid (4 ml.) as solvent, a similar reaction gave a 27% yield of the nitro-compound.

Trifluoronitrosomethane (0·42 g.), sealed with lead dioxide (5·5 g.) and heated to 100° for 48 hr., gave a 37% yield of trifluoronitromethane (b. p. −18°). Yields were not consistent: successive experiments at 20°, 45°, 70°, and 100° gave 32, 15, 8, and 29% yields.

Carbon dioxide, silicon tetrafluoride, and carbonyl fluoride were by-products from the oxidation of trifluoronitrosomethane and, after an initial fractionation in the vacuum-system to remove carbon dioxide, the residual material was shaken twice with ice-water and once, rapidly, with ice-cold 2% aqueous sodium hydroxide. Final purification was effected in the vacuum-system.

(b) *Pentafluoronitroethane and heptafluoronitropropane.* Pentafluoronitrosoethane (0·3 g.), treated with dimanganese heptoxide as in (a) above, gave *pentafluoronitroethane* (33%), b. p. −1° to 0° (isoteniscope) (Found: C, 14·4; N, 8·3%; *M*, 165. $C_2O_2NF_5$ requires C, 14·5; N, 8·5%; *M*, 165). Lead dioxide similarly gave a 30% yield of the nitro-compound (b. p. 0—1°).

Dimanganese heptoxide and heptafluoronitrosopropane (0·5 g.) similarly gave *heptafluoronitropropane* (41%), b. p. 25° (isoteniscope) (Found: C, 16·8; N, 6·6%; *M*, 214. $C_3O_2NF_7$ requires C, 16·7; N, 6·5%; *M*, 215). Lead dioxide gave a 22% yield of the nitro-compound, b. p. 26° (isoteniscope).

(c) *Chlorodifluoronitromethane.* The oxidation of chlorodifluoronitrosomethane (0·2 g.) was difficult to effect without extensive decomposition. Dimanganese heptoxide [(a) above] gave a 15% yield at 20°, and lead dioxide a 10% yield at 75°. The combined crude product was redistilled, to give *chlorodifluoronitromethane*, b. p. 24—25° (isoteniscope) (Found: C, 8·9; N, 10·5; Cl, 26·7%; *M*, 131. CO_2NClF_2 requires C, 9·1; N, 10·6; Cl, 27·0%; *M*, 131·5).

Interaction of Chlorodifluoronitromethane and Antimony Trifluorodichloride.—Antimony trifluoride (5·0 g.) and chlorine (1·5 g.) were heated to 100° for 1 hr. in a small steel autoclave. After cooling, chlorodifluoronitromethane (0·2 g.) was condensed in, and the autoclave was heated to 100° during 6 hr. The volatile reaction products were shaken with cold 2% aqueous sodium hydroxide for 3 min., transferred to a vacuum-system, and fractionated, to give unchanged chlorodifluoronitromethane (*ca.* 10%), chlorotrifluoromethane (53%), and dichlorodifluoromethane (8%). The last two compounds were identified by their infra-red spectra. Trifluoronitromethane could not be detected as a product.

Reaction of 1-*Bromotetrafluoro-2-nitroethane with Antimony Trifluorodichloride and with Bromine Trifluoride.*—The nitro-compound (0·3 g.) and antimony trifluorodichloride (5·0 g.) heated to 160° for 4 hr. in a small autoclave gave bromopentafluoroethane (41%), b. p. −21°, 1-bromotetrafluoro-2-nitroethane (27%), and a mixture of unidentified products with b. p. $< -30°$, probably containing nitryl and nitrosyl fluorides, carbon dioxide, carbonyl fluoride, etc. Pentafluoronitroethane was not detected.

Bromine trifluoride (4 ml.) in a small autoclave was cooled in liquid nitrogen whilst 1-bromotetrafluoro-2-nitroethane (0·8 g.) was distilled in. The autoclave was sealed and immersed in ice where it was left for 6 hr. It was then vigorously shaken at 20° for 2 hr., and at 50°

for 1 hr. The volatile products were removed, washed with water, and distilled in a vacuum-system, to give pentafluoronitroethane (15%) (see above), bromopentafluoroethane (47%), unchanged bromotetrafluoronitroethane (8%), and unidentified volatile compounds.

Pyrolysis of Trifluoronitromethane and Heptafluoronitropropane.—Trifluoronitromethane (0·5 g.) was allowed to evaporate from a trap and pass through a platinum tube heated to 500° ± 10° over a 9″ length, and the products were collected in a silica trap cooled in liquid nitrogen. Infra-red spectroscopic examination showed that carbon tetrafluoride was not formed. There was no indication of the formation of a polymer of tetrafluoroethylene type, and the products (b. p <40°) contained a solid (probably carbon dioxide and carbonyl fluoride) which sublimed if the pressure was <700 mm., and a liquid. Approximately half the mixture was sealed with 10% sodium hydroxide solution for 12 hr. Sodium fluoride was precipitated, and no residual gas was detected, *i.e.*, hexafluoroethane, tetrafluoroethylene, perfluoro*cyclo*butane, etc., were not present. The residual product from the experiment was transferred to a vacuum-system; fractionation showed that most of the mixture had b. p. $< -30°$, but small amounts of nitrogen dioxide were separated. Attack on the glass was apparent and yielded silicon tetrafluoride and dinitrogen trioxide, thus revealing the presence of nitrosyl fluoride ($SiO_2 + 4NOF \longrightarrow SiF_4 + 2NO + 2NO_2$).

A similar reaction in a silica tube at 450° gave only a mixture of carbonyl fluoride, carbon dioxide, and oxides of nitrogen; fluorocarbon products were not detected.

Heptafluoronitropropane (0·4 g.), pyrolysed in a platinum tube at 500°, gave a similar mixture of products containing nitrosyl fluoride, carbonyl fluoride, and carbon dioxide. Treatment of a portion of the volatile products with an excess of 5% aqueous sodium hydroxide left hexafluoropropene (*ca.* 8%; identified by its infra-red spectrum). The sodium hydroxide solution was filtered, acidified with concentrated sulphuric acid, and extracted with ether. The ethereal extracts were treated with silver carbonate, and filtered, and the ether was removed, leaving silver pentafluoropropionate (19%) (Haszeldine, *J.*, 1952, 4259), identified by its infra-red spectrum.

Addition of Nitrogen Dioxide to Double Bonds.—Chlorotrifluoroethylene (2·9 g.) was sealed with thoroughly dried nitrogen dioxide (4·6 g.) in a small steel autoclave, and slowly heated to 65° (6 hr.). The products were pumped from the autoclave into a trap cooled by liquid nitrogen, rapidly washed once with water, dried (P_2O_5), and distilled, to give 1-*chlorotrifluoro*-1 : 2-*dinitroethane* (51%), b. p. 98·5—100° (Found : C, 11·4; N, 13·6%; *M*, 205, 206. $C_2O_4N_2ClF_3$ requires C, 11·5; N, 13·4%; *M*, 208·5), and unchanged olefin (22%).

1 : 1-Dichlorodifluoroethylene (2·5 g.), similarly treated with nitrogen dioxide (4·0 g.), gave 1 : 1-*dichlorodifluoro*-1 : 2-*dinitroethane* (47%), b. p. 81—82°/103 mm. [micro-b. p. *ca.* 142°/760 mm. (partial decomp.)] (Found : C, 10·6; Cl, 31·0; N, 12·4. $C_2O_4N_2Cl_2F_2$ requires C, 10·7; Cl, 31·6; N, 12·5%).

Tetrafluoroethylene (5·0 g.) and nitrogen dioxide (10·0 g.), sealed and heated to 60° during 8 hr., gave 1 : 1 : 2 : 2-tetrafluorodinitroethane (53%), b. p. 58·5—59° (Found : *M*, 190. Calc. for $C_2O_4N_2F_4$: *M*, 192). Coffman *et al.* (*loc. cit.*) report b. p. 58—59°.

The author gratefully acknowledges generous gifts of fluorine compounds from Imperial Chemical Industries Limited, during 1947—48, and later from E. I. Dupont de Nemours Inc., and General Chemical Division, Allied Chemical and Dye Corporation.

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