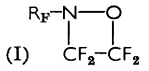
279. *Perfluoroalkyl Derivatives of Nitrogen. Part VIII.* Trifluoronitrosoethylene and its Polymers.*

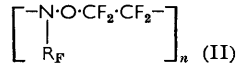
By C. E. Griffin and R. N. Haszeldine.

Trifluoronitrosoethylene results from the photochemical reaction of trifluoroiodoethylene with nitric oxide. It yields a fused-ring dimer and a homopolymer. Reaction with a fluoro-olefin $CF_2{:}CX_2$ (X = F or Cl) gives an oxazetidine or a 1 : 1 copolymer. Its dichloride, $CF_2Cl{\cdot}CFCl{\cdot}NO$, prepared by chlorination of trifluoronitrosoethylene, by reaction of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane with nitric oxide or, in low yield, of chlorotrifluoroethylene with nitrosyl chloride, affords related oxazetidines or copolymers on treatment with fluoro-olefins.

A perfluoroalkylnitroso-compound $R_F{\cdot}NO$ reacts with a fluoro-olefin such as tetrafluoroethylene to give an oxazetidine (I) and a 1 : 1 copolymer (II) with the $-N{\cdot}O{\cdot}C{\cdot}C-$ repeating unit in the main chain.[1] The polymer can be an oil, a wax, or an elastomer depending on the conditions and the nature of the olefin. The oxazetidine predominates in reactions carried out at *ca.* 100° and the polymer predominates at *ca.* 0°.

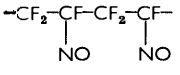


(I)

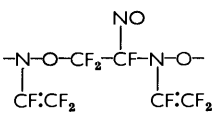


(II)

The effect of conjugation with the nitroso-group is now reported, specifically by synthesis and study of trifluoronitrosoethylene, $CF_2{:}CF{\cdot}N{:}O$. The possibility exists with this compound of homopolymerisation in a variety of ways to give one or more of the units (III—VII):



(III)



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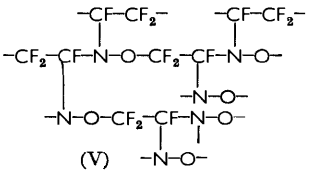

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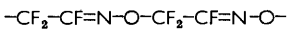
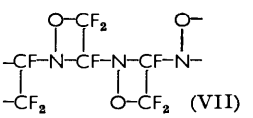


(VI)



(VII)

These arise as follows: (III) Normal vinyl polymerisation through the C=C; the polymer would contain one nitroso-group per ethylene unit and have an intense blue colour.

* Part VII, Barr and Haszeldine, *J.*, 1960, 1151. Preliminary publication, *Proc. Chem. Soc.*, 1959, 369.

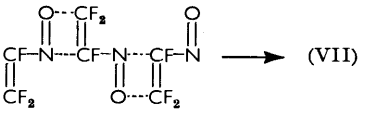
[1] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

(IV) Formation of the $-N{\cdot}O{\cdot}C{\cdot}C-$ chain by reaction of the nitroso-group of one molecule with the $CF_2{:}CF$ group of a second; vinyl groups and nitroso-groups would alternate as side chains down the polymer, which would be intensely blue.

(V) A highly cross-linked polymer formed by interaction of the side-chains of polymer (IV).

(VI) Reaction of trifluoronitrosoethylene as a diene to give a linear polymer containing C=N groups.

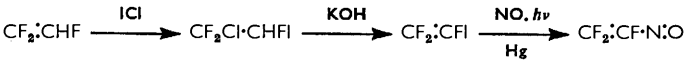
(VII) Polymerisation by oxazetidine formation:



These polymers can be distinguished (*a*) by colour, (*b*) by infrared spectroscopy to show the presence or absence of $-CF{:}CF_2$, $-N{:}O$, $-C{:}N-$ groups, and (*c*) by physical properties to be associated with the presence or absence of cross-linking.

Comparison of trifluoronitrosoethylene with hexafluorobuta-1,3-diene is also of interest, since the latter is very difficult to homopolymerise and shows little conjugation between the double bonds.[2]

Trifluoronitrosoethylene was synthesised by the following route:

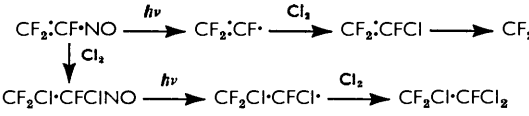


Reaction of iodine monochloride with trifluoroethylene gave predominantly 1-chloro-1,1,2-trifluoro-2-iodoethane,[3] as shown by its conversion by anhydrous potassium hydroxide in paraffin into trifluoroiodoethylene [3] with very little chlorotrifluoroethylene. The compounds $CF_2Cl{\cdot}CHFI$ and $CF_2{:}CFI$ show characteristic ultraviolet absorption associated with the $>CFI$ chromophore.[4]

The yield of trifluoronitrosoethylene from the photochemical reaction of nitric oxide with trifluoroiodoethylene was low, despite a fairly detailed examination of reaction variables. The extensive breakdown is caused by the susceptibility of the $C{:}C$ in trifluoroiodo- or nitroso-ethylene to attack by NO, NO_2 radicals, etc., as well as by the other decomposition reactions associated with the reactive fluoroalkylnitroso-compounds.[5] Reaction at higher pressures gave hexafluoro-4,4-di-iodobut-1-ene as by-product by free-radical dimerisation of trifluoroiodoethylene.[3]

Trifluoronitrosoethylene is a vivid deep blue gas (b. p. $-23{\cdot}7°$) that shows no indication of association in the liquid or vapour phase. Its ultraviolet spectrum shows the broad band in the 665—685 mμ region characteristic of the $>CF{\cdot}NO$ group.[5] Its infrared spectrum shows the typical $CF_2{:}CF$ absorption at 5·55 μ (cf. $CF_3{\cdot}[CF_2]_n{\cdot}CF{:}CF_2$ 5·56 μ), together with the $N{:}O$ stretching vibration at 6·25 μ (cf. $CF_3{\cdot}[CF_2]_n{\cdot}NO$ 6·23 μ). These values suggest that there is little or no conjugation of the $C{:}C$ and $N{:}O$ unsaturation electrons.

Trifluoronitrosoethylene reacts smoothly with chlorine in the dark to give 1,2-dichlorotrifluoro-1-nitrosoethane. Photochemical chlorination leads to the formation of chlorotrifluoroethylene and 1,1,2-trichlorotrifluoroethane by formation of the trifluorovinyl radical:



[2] Haszeldine, *J.*, 1952, 4423.
[3] Park, Seffl, and Lacher, *J. Amer. Chem. Soc.*, 1956, **78**, 59.
[4] Haszeldine, *J.*, 1953, 1764.
[5] Jander and Haszeldine, *J.*, 1954, 912, 919; Haszeldine and Mattinson, *J.*, 1957, 1741.

The nitroso-group in 1,2-dichlorotrifluoro-1-nitrosoethane, as in other fluoroalkylnitroso-compounds, is readily displaced by chlorine photochemically.

Attempts to convert trifluoronitrosoethylene into trifluoronitroethylene by heating it with oxygen, under the conditions found suitable for conversion of trifluoronitrosomethane into trifluoronitromethane,[5] were unsuccessful and only breakdown resulted.

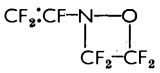
Aqueous-alkaline hydrolysis of trifluoronitrosoethylene was very fast and gave oxalic acid essentially quantitatively, probably by a reaction sequence similar to that suggested for hydrolysis of heptafluoronitrosopropane.[1]

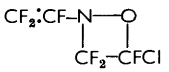
Somewhat unexpectedly, trifluoronitrosoethylene does not homopolymerise on exposure to ultraviolet radiation at low pressure; the major reaction was one of breakdown although some hexafluorobuta-1,3-diene was formed:

$$CF_2{:}CF{\cdot}NO \xrightarrow{h\nu} CF_2{:}CF{\cdot} \longrightarrow CF_2{:}CF{\cdot}CF{:}CF_2$$

The thermal stability of the nitroso-compound at low pressures was also greater than expected; the formation of hexafluorobutadiene and breakdown products was only slow at 125°.

Tetrafluoroethylene and chlorotrifluoroethylene do not yield cyclobutane derivatives on reaction with trifluoronitrosoethylene at 85—90°, but react preferentially with the nitroso-group to give the oxazetidines (VIII) and (IX). At lower temperatures, and particularly at 0°, elastomeric 1 : 1 copolymers (X) and (XI) are formed, as when trifluoronitrosomethane reacts with these fluoro-olefins. The assignment of the structure (IX) to the oxazetidine and of (XI) to the copolymer, with the oxygen atom attached to the CFCl group or the CF_2 group respectively, is based on the proved structures of the oxazetidine and 1 : 1 copolymer from trifluoronitrosomethane and chlorotrifluoroethylene.[6]


(VIII)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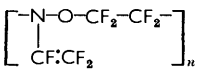
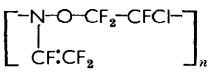
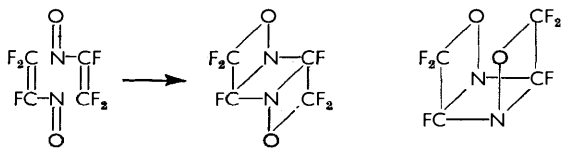

(X)


(XI)

The fact that the nitroso-group in trifluoronitrosoethylene readily led to compounds (IX)—(XI) suggested further attempts to achieve homopolymerisation. Use of chlorotrifluoromethane as an inert gas to increase the reaction pressure to approx. 40 atm., a temperature of 80°, and photochemical initiation brought about smooth conversion of trifluoronitrosoethylene into the fused-ring compound (XII) and the homopolymer (VII). The formation of perfluoro-4,8-dioxa-1,5-diazabicyclo[2,2,$0^{2,5}$]octane (XII) involves oxazetidine ring formation by combination of the nitroso-group of one molecule with the trifluorovinyl group of the second; *cis*- and *trans*-isomers are theoretically possible:


trans (XII) *cis*

As might be expected, there was no indication of isomerisation of trifluoronitrosoethylene by internal formation of the four-membered ring:

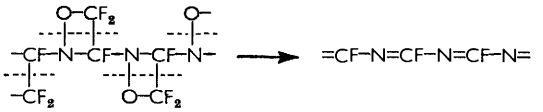
Absence of $-N{:}O$, $-NO_2$, $-N{:}N-$, $-N{:}\overset{+}{N}(\bar{O})-$, $-O{\cdot}NO$, $-O{\cdot}NO_2$, $>N{\cdot}O{\cdot}NO$, $>N{\cdot}NO$,

[6] Barr, Haszeldine, and Willis, *Proc. Chem. Soc.*, 1959, 230; *J.*, in the press.

$>N{\cdot}NO_2$, $>C{:}N-$, $>C{:}C<$, $>C{:}O$ on ultraviolet- and infrared-spectroscopic examination supports the proposed structure (XII).

Similar examination of the translucent elastomeric homopolymer supports the ring structure of (VII). Structures such as (III) and (IV) can be eliminated since the homopolymer is not blue; (V) is eliminated since the homopolymer is an elastomer, not a highly cross-linked insoluble resin; (VI) is eliminated since the characteristic strong CF=N absorption in the 5—6 μ region is absent.

When heated at 400° the homopolymer changes from an elastomer into a pale yellow solid without carbonisation or appearance of organic fragments of low molecular weight by chain degradation. Carbonyl fluoride is evolved, and the residual solid exhibits absorption of the $CF{:}N{\cdot}CF$ group. The following reaction thus apparently takes place, at least in part:



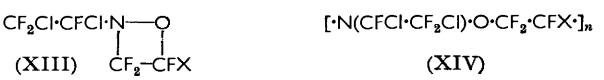
The homopolymer of trifluoronitrosoethylene thus contains a $-C{\cdot}N{\cdot}C{\cdot}N{\cdot}C{\cdot}N-$ chain, and represents a new class of polymer.

An alternative route to trifluoronitrosoethylene was sought by the synthesis of 1,2-dichlorotrifluoro-1-nitrosoethane from the corresponding iodide:

$$CF_2{:}CFCl \xrightarrow{ICl} CF_2Cl{\cdot}CFClI \xrightarrow{NO.h\nu} CF_2Cl{\cdot}CFCl{\cdot}NO \longrightarrow CF_2{:}CF{\cdot}NO$$

The yield of the nitroso-compound from the iodide was not good, since deiodochlorination tended to occur in presence of mercury and was followed by oxidative breakdown of the chlorotrifluoroethylene or reaction of the olefin with the nitroso-compound. The compound $CF_2Cl{\cdot}CFCl{\cdot}NO$ was identical with that obtained earlier by reaction of trifluoronitrosoethylene with chlorine. Reaction of 1,2-dichlorotrifluoro-2-iodoethane with nitric oxide in the absence of mercury led to the accumulation of dinitrogen tetroxide which caused extensive breakdown to carbonyl fluoride, etc. Liquid-phase reactions in presence of mercury led to coupling,[7] to give $(CF_2Cl{\cdot}CFCl)_2$ and to mercurial formation, $CF_2Cl{\cdot}CFCl{\cdot}HgI$.

The nitroso-compound $CF_2Cl{\cdot}CFCl{\cdot}NO$ reacts with oxygen at 100° to form the corresponding nitro-compound, identical with the product obtained by reaction of chlorotrifluoroethylene with nitrosyl chloride or with nitryl chloride.[8] Tetrafluoroethylene converts the nitroso-compound into the oxazetidine (XIII; X = F) or the 1 : 1 copolymer (XIV;



(XIII) (XIV)

X = F), depending on the reaction temperature. Similar products (XIII; X = Cl) and (XIV; X = Cl) are formed by reaction with chlorotrifluoroethylene.

The reaction of nitrosyl chloride with chlorotrifluoroethylene [8] was also re-investigated, since the $NOCl{-}C_2F_4$ reaction has been shown to yield the oxazetidine $CF_2Cl{\cdot}CF_2{\cdot}\overline{N{\cdot}O{\cdot}CF_2{\cdot}CF_2}$ or the 1 : 1 copolymer $[{\cdot}N(CF_2{\cdot}CF_2Cl){\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}]_n$ under suitable conditions,[9] as well as the nitro-compound $CF_2Cl{\cdot}CF_2{\cdot}NO_2$. Use of an excess of chlorotrifluoroethylene gave low yields of the nitroso-compound $CF_2Cl{\cdot}CFCl{\cdot}NO$ and mainly the dichloronitrotrifluoroethane. Reaction carried out in the vapour phase at —15° produced the copolymer (XIV; X = Cl). Use of an excess of nitrosyl chloride gave only the compounds $CF_2Cl{\cdot}CFCl{\cdot}NO_2$ and $CF_2Cl{\cdot}CFCl_2$.

[7] Haszeldine, *J.*, 1955, 4291.
[8] Haszeldine, *J.*, 1953, 2075.
[9] Barr and Haszeldine, *J.*, 1960, 1151.

All attempts to dechlorinate the compound $CF_2Cl{\cdot}CFCl{\cdot}NO$ to trifluoronitrosoethylene by standard methods were unsuccessful. Reagents were sought that would effect dechlorination without attack on the nitroso-group, but even tributyl phosphite, which dechlorinates 1,1,2-trichlorotrifluoroethane successfully:

$$CF_2Cl{\cdot}CFCl_2 + (BuO)_3P \longrightarrow CF_2{:}CFCl + BuCl + (BuO)_2P(O)Cl$$

failed to yield trifluoronitrosoethylene. The only route currently available for the last compound is thus the photochemical generation of trifluorovinyl radicals and their combination with nitric oxide.

Experimental

Volatile reactants and products were purified and manipulated in a conventional vacuum-system, with repeated trap-to-trap fractional distillation and condensation. Air, moisture, etc., were thus excluded and handling losses were negligible. The identity of products was confirmed by molecular-weight determination (Regnault's method), analysis, physical properties, infrared spectra (Perkin–Elmer spectrophotometer model 21 with sodium chloride optics), ultraviolet spectra (Unicam instrument), and vapour-phase chromatography. Intermediate fractions and mixtures were analysed by a combination of these techniques, or by removal of one or more of the components by chemical reaction. Reactions were normally carried out in sealed Pyrex, Dreadnought, or silica tubes, filled and emptied by use of the vacuum-system so that transfer losses were negligible.

Trifluoroethylene.—Chlorotrifluoroethylene (57·1 g., 0·49 mole), anhydrous hydrogen bromide (41·0 g., 0·50 mole), and activated charcoal (7·7 g.; heated to 100° *in vacuo*, then cooled *in vacuo*) were heated in a 300 ml. stainless-steel autoclave at 175° for 20 hr. Distillation gave 2-bromo-1-chloro-1,2,2-trifluoroethane (76%), b. p. 53·7°/760 mm. Haszeldine and Steele [10] report b. p. 52·5°.

2-Bromo-1-chloro-1,2,2-trifluoroethane (147·5 g., 0·75 mole), added dropwise during 4 hr. to zinc dust (128·5 g.) in refluxing ethanol (300 ml.), gave unchanged starting material (0·053 mole, 7%) and trifluoroethylene (43·7 g., 0·533 mole, 77%) of spectroscopic purity.

Trifluoroiodoethylene.—Park, Seffl, and Lacher's procedure [3] was followed for the reaction of iodine monochloride with trifluoroethylene. 1-Chloro-1,1,2-trifluoro-2-iodoethane was obtained in 52% yield (Found: C, 9·5; H, 0·8%; *M*, 244. Calc. for C_2HClF_3I: C, 9·8; H, 0·4%; *M*, 244), b. p. 82·9° (isoteniscope), $\lambda_{max.}$ (in light petroleum) 264 (ε 305), $\lambda_{min.}$ 221 (ε 70), $\lambda_{max.}$ (in ethanol) 258 mμ (ε 284), $\lambda_{min.}$ 220 mμ (ε 130).

Reaction of 1-chloro-1,2,2-trifluoro-2-iodoethane with powdered potassium hydroxide ("AnalaR" pellets crushed inside a dry-box and stored *in vacuo* before use) suspended in liquid paraffin gave trifluoroiodoethylene in 41% yield (Found: C, 11·8%; *M*, 208. Calc. for C_2F_3I: C, 11·6%; *M*, 208), b. p. 34·2°: (isoteniscope), $\lambda_{max.}$ (vapour) 259 mμ (ε 96), $\lambda_{min.}$ 233 mμ (ε 40), $\lambda_{max.}$ (in light petroleum) 260 mμ (ε 160), $\lambda_{min.}$ 236 mμ (ε 85).

Trifluoronitrosoethylene.—In a typical experiment, trifluoroiodoethylene (5·45 g., 21·4 mmole), nitric oxide (1·61 g., 53·5 mmole), and mercury (100 ml.) in a 2-l. silica flask were irradiated for 48—76 hr. with a 250 w Hanovia ultraviolet lamp. The flask was shielded so that the surface of the mercury was not directly illuminated. The course of the reaction could be followed by the development of a faint blue colour. The excess of nitric oxide was removed by admission of oxygen to the flask and agitation of the mercury to remove final traces of dinitrogen tetroxide, and the volatile products were slowly pumped off (1 hr.) through two traps in series cooled by liquid nitrogen. Distillation gave unchanged trifluoroiodoethylene (1%), *trifluoronitrosoethylene* (0·219 g., 1·99 mmole; 9%) (Found: C, 21·8; N, 12·3%; *M*, 111. C_2ONF_3 requires C, 21·6; N, 12·6%; *M*, 111), and a mixture of carbon dioxide, carbonyl fluoride, and silicon tetrafluoride (21·0 mmole).

The conditions used were varied widely in attempts to improve the yield of trifluoronitrosoethylene. Experiments were carried out in the absence of mercury to determine whether polymeric material was formed, but only breakdown products and complex mixtures resulted. In a reaction to test the effect of higher pressure, trifluoroiodoethylene (9·2 mmole) and nitric

[10] Haszeldine and Steele, *J.*, 1957, 2800.

oxide (18·4 mmole) were sealed in a 125 ml. Pyrex tube and irradiated for 92 hr. with the liquid phase protected from direct radiation. Distillation gave dinitrogen tetroxide (removed by reaction with mercury), trifluoroiodoethylene (1·7 mmole), and a mixture of carbonyl fluoride, carbon dioxide, and silicon tetrafluoride (9·3 mmole). An oil remaining in the reaction tube was removed by ether-extraction and distilled, to give hexafluoro-4,4-di-iodobut-1-ene (0·389 g., 0·94 mmole, 21%), b. p. 161—162°/758 mm. (micro-b. p.), v. p. 624 mm./146°, n_D^{20} 1·4796. Park *et al.*[3] report b. p. 146°/622 mm., n_D^{20} 1·4794.

Reactions carried out in shaken sealed silica or Pyrex tubes containing trifluoroiodoethylene, nitric oxide, and mercury exposed to ultraviolet light of various intensities gave only 1—5% of trifluoronitrosoethylene.

Properties of Trifluoronitrosoethylene.—The compound is a blue gas which condenses to an intensely blue liquid. Its vapour pressure, determined over the narrow range −23° to −26°, is represented by the equation $\log_{10} p$ (mm.) = 8·2515 − 1340/T, whence the calc. b. p. is −23·7°, the latent heat of vaporisation is 5410 cal./mole, and Trouton's constant is 21·7. Ultraviolet absorption spectrum of the vapour in the region 300—700 mμ: max. 679·5 (ε 5·15), 666 (ε 5·47), 663 mμ (ε 5·38); min. 677, (ε 5·06); 664 (ε 5·34); minor maxima appear at 619 and 611 mμ.

Reactions of Trifluoronitrosoethylene.—(a) *With chlorine.* Chlorine (1·2 mmole) and trifluoronitrosoethylene (1·0 mmole), sealed in a 20 ml. Pyrex tube and kept in the dark for 21 days gave, after removal of unused chlorine with mercury, trifluoronitrosoethylene (4%) and 1,2-*dichlorotrifluoro*-1-*nitrosoethane* (93%) (Found: C, 13·3; N, 7·5%; *M*, 182. $C_2ONCl_2F_3$ requires C, 13·2; N, 7·7%; *M*, 182). The product is a blue liquid with vapour pressure, measured over the narrow range 34—37°, represented by the equation $\log_{10} p$ (mm.) = 7·4865 − 1425/T, whence the calc. b. p. is 36·2°, the latent heat of vaporisation is 6930 cal./mole, and Trouton's constant is 22·4. It has $\lambda_{max.}$ (vapour) 681 mμ (ε 9·3); (in light petroleum) 680 mμ (ε 15·5).

Exposure of trifluoronitrosoethylene (2·0 mmole) and chlorine (2·0 mmole) to ultraviolet light for 3 hr. gave unchanged nitroso-compound (51%), chlorotrifluoroethylene (21%), and 1,1,2-trichlorotrifluoroethane (15% based on CF_2:CF·NO), but no 1,2-dichlorotrifluoro-1-nitrosoethane.

(b) *Oxidation.* An attempt to prepare trifluoronitroethylene from trifluoronitrosoethylene (0·4 mmole) and oxygen (initial pressure 700 mm.) in a 25 ml. Pyrex tube at 74° for 10 hr. gave only dinitrogen tetroxide, carbon dioxide, carbonyl fluoride, and silicon tetrafluoride by complete destruction of the nitroso-compound.

(c) *Hydrolysis.* Trifluoronitrosoethylene (0·6 mmole) was shaken with 1% aqueous sodium hydroxide (5 ml.) in a sealed tube until all blue colour was destroyed (3 min.). The boiled solution was combined with the combined aqueous washings, and passed through a Dowex 50 column (H^+ form; 8 ml. volume of resin); the column was then washed with 5 ml. of water. The combined eluant was evaporated to dryness at room temperature *in vacuo* and dried over phosphoric anhydride to give oxalic acid (71·7 mg., 95%), m. p. and mixed m. p. 101—101·5° (Found: C, 19·3; H, 4·7. Calc. for $C_2H_2O_4,2H_2O$: C, 19·1; H, 4·8%). Blank experiments with standard sodium oxalate solutions showed that 95—96% of the theoretical amount of oxalic acid was recovered by the above procedure. Aqueous alkaline hydrolysis of trifluoronitrosoethylene thus yields oxalic acid in 99% yield. Ammonium and fluoride ions were detected by qualitative tests.

Saturated aqueous barium hydroxide solution hydrolyses trifluoronitrosoethylene at a much slower rate.

(d) *Irradiation under low pressure.* The nitroso-compound (2·1 mmole), irradiated in a 20 ml. Pyrex tube for 78 hr., gave unchanged trifluoronitrosoethylene (3%), carbon dioxide, silicon tetrafluoride, nitrous oxide, and hexafluorobutadiene (0·06 mmole), identified by means of its infrared spectrum.

(e) *Thermal stability.* Trifluoronitrosoethylene (1·6 mmole), heated in a 10 ml. Pyrex tube at 100° for 150 hr., was substantially unchanged (87% recovered); carbonyl fluoride and silicon tetrafluoride were produced.

In a second experiment the nitroso-compound (1·6 mmole) was heated at 100° (48 hr.), 110° (24 hr.), and 125° (48 hr.), after which the blue colour was almost totally destroyed. Fractionation gave unchanged trifluoronitrosoethylene (0·17 mmole, 11%), silicon tetrafluoride, carbonyl fluoride, and carbon dioxide, together with a low yield of hexafluorobutadiene.

(f) *With tetrafluoroethylene.* Trifluoronitrosoethylene (7·2 mmole) and tetrafluoroethylene

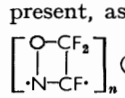
(7·2 mmole) heated in a 20 ml. Pyrex tube at 85° for 10 hr. gave *perfluoro*-(2-*vinyl*-1,2-*oxazetidine*) (69%) (Found: C, 22·7; N, 6·5%; *M*, 211. C_4ONF_7 requires C, 22·8; N, 6·6%; *M*, 211), b. p. 41—43° (micro).

In a second experiment, trifluoronitrosoethylene (7·4 mmole) and tetrafluoroethylene (7·4 mmole) reacted during 48 hr. at 0° in a 50 ml. Pyrex tube with disappearance of the blue colour, to give the 1 : 1 *copolymer* $[\cdot N(CF{:}CF_2)\cdot O\cdot CF_2\cdot CF_2\cdot]_n$ (71%) [Found: C, 22·9; N, 6·4%. $(C_4ONF_7)_n$ requires C, 22·8; N, 6·6%]. The polymer was a thick colourless gel, which when triturated with ether gave a tough translucent elastomer, insoluble in the common organic solvents.

(g) *With chlorotrifluoroethylene.* When trifluoronitrosoethylene (4·0 mmole) and chlorotrifluoroethylene (4·0 mmole) were heated at 90° for 7 hr. the product was 4-*chloro*-3,3,4-*trifluoro*-2-(*trifluorovinyl*)-1,2-*oxazetidine* (57%) (Found: C, 21·0; N, 6·2%; *M*, 226. C_4ONClF_6 requires C, 21·1; N, 6·2%; *M*, 227·5) b. p. 73—75°. No polymeric material was apparent, and all the nitroso-compound had disappeared.

In a parallel experiment carried out at 0° for 2 days the oxazetidine was not formed and the 1 : 1 *copolymer* $[\cdot N(CF{:}CF_2)\cdot O\cdot CF_2\cdot CFCl\cdot]_n$ of the nitroso-compound and chlorotrifluoroethylene was isolated (53% yield) [Found: C, 21·1; N, 6·3%. $(C_4ONClF_6)_n$ requires C, 21·1; N, 6·2%] as an elastomer with good " snap."

(h) *Dimerisation and homopolymerisation.* Trifluoronitrosoethylene (20·1 mmole) was sealed in thick-walled, narrow-bore silica tube of 5 ml. capacity, together with chlorotrifluoromethane to give a maximum pressure at room temperature of 40 atm. Precautions were taken in manipulating the tube which could cause serious damage on explosion. As soon as the tube reached room temperature, it was exposed first to infrared radiation to raise its temperature to approx. 80°, then to ultraviolet radiation for 30 min. The tube was re-frozen in liquid nitrogen, then opened, and the colourless gaseous products were distilled to give *perfluoro*-4,8-*dioxa*-1,5-*diazabicyclo*[2,2,$0^{2,5}$]*octane* (56%) (Found: C, 21·4; N, 12·4%; *M*, 222. $C_4O_2N_2F_6$ requires C, 21·6; N, 12·6%; *M*, 222), b. p. 45°, as a colourless liquid, and a mixture of carbonyl fluoride, silicon tetrachloride and carbon dioxide. There was no evidence for the formation of hexafluorobutadiene or its dimers, etc. The weak general absorption in the ultraviolet spectrum in the 200—250 mμ region in particular suggests that only the N–O single bond is present, as in the compound $(CF_3)_2N\cdot O\cdot CF_3$.


(A)

The residual material in the reaction tube was a colourless, translucent elastomeric gum, the homopolymer of trifluoronitrosoethylene, *poly*(*perfluoro*-1,2-*oxazetidin*-2,3-*ylidene*) (A) (28%) [Found: C, 21·7; N, 12·8. $(C_2ONF_3)_n$ requires C, 21·6; N, 12·6%]. It was soluble in perfluoromethylcyclohexane but not in the common organic solvents. Examination of the ultraviolet spectrum of a saturated solution in perfluoromethylcyclohexane, and of the infrared spectrum of a film on rock salt, failed to reveal absorption associated with multiple C–O, C–C, C–N, N–N, N–O, etc., bonds.

A sample of the homopolymer (0·15 g.) in a sealed silica tube was heated at 400° during 2 hr. At 310° the polymer had become pale yellow and at 400° some shrinkage could be detected, although there was little further change in colour. Examination of the volatile products revealed carbonyl fluoride (66%), and small amounts of silicon tetrafluoride and carbon dioxide. The residue was a pale yellow solid without elastomeric character, but was still soluble in perfluoromethylcyclohexane; the solution showed absorption at 5·65 μ to be associated with the $CF{:}N\cdot CF$ group.

1,2-*Dichlorotrifluoro*-1-*nitrosoethane.*—1,2-Dichloro-1,1,2-trifluoro-2-iodoethane was prepared by reaction of purified iodine monochloride with chlorotrifluoroethylene under good temperature control.[1]

In a typical experiment, 1,2-dichloro-1,1,2-trifluoro-2-iodoethane (10·28 g., 36·9 mmole) and nitric oxide (3·30 g., 110 mmole) were heated to 60° in a 20-l. flask of the type described earlier,[1] and irradiated for 20 hr. The iodo-compound was completely vaporised at this temperature. The brown gaseous products were condensed and shaken with mercury to remove dinitrogen tetroxide, then distilled to give unchanged halide (0·66 g., 2·4 mmole), b. p. 100—101°, 1,2-dichlorotrifluoro-1-nitroethane (0·59 mmole, 2%), b. p. 75—76°, and 1,2-dichlorotrifluoro-1-nitrosoethane (4·57 mmole, 13% based on starting iodo-compound) (Found: C, 13·0; N, 7·9%; *M*, 182. Calc. for $C_2ONCl_2F_3$: C, 13·2; N, 7·7%; *M*, 182).

Complete separation of the compounds $CF_2Cl\cdot CFCl\cdot NO$ and $CF_2Cl\cdot CFCl\cdot NO_2$ by distillation *in vacuo* is difficult, but not column fractionation at atmospheric pressure. The ultraviolet

and infrared spectra of the nitroso-compound were identical with those of the compound obtained by reaction of chlorine with trifluoronitrosoethylene.

The conditions were varied in attempts to improve the yield of the nitroso-compound. In the absence of mercury yields of 10—15% were obtained after irradiation for 20 hr.; extension of the irradiation time to 36 hr. reduced the yield to about 5%. Use of a high-intensity ultraviolet source reduced the yield to 5%. Silicon tetrafluoride, carbonyl fluoride, and carbonyl chlorofluoride were the main decomposition products.

Reaction in presence of mercury at 95° for 40 hr. gave 10—15% yields of the nitroso-compound, together with the mercurial $CF_2Cl{\cdot}CFCl{\cdot}HgI$ and, by removal of iodine chloride from the iodo-compound, chlorotrifluoroethylene. If the reaction mixture was kept, further reaction occurred between 1,2-dichlorotrifluoro-1-nitrosoethane and chlorotrifluoroethylene to give either the oxazetidine or the 1 : 1 copolymer depending upon the temperature. Reactions of the iodo-compound and nitric oxide in presence of mercury at lower temperatures, 40—60°, gave 2—5% yields of 1,2-dichlorotrifluoro-1-nitrosoethane, since the starting iodo-compound was mainly in the liquid phase where reaction with mercury tends to yield the mercurial $CF_2Cl{\cdot}CFCl{\cdot}HgI$ or the coupled product $(CF_2Cl{\cdot}CFCl)_2$.

Reactions of 1,2-*Dichlorotrifluoro*-1-*nitrosoethane.*—(a) *Oxidation.* The nitroso-compound (0·28 g., 1·6 mmole) and oxygen (initial pressure 650 mm.) were heated in a 50 ml. Pyrex tube at 100° for 18 hr. Dinitrogen tetroxide was then removed by shaking the product with mercury, and the volatile products were distilled to give unchanged 1,2-dichlorotrifluoro-1-nitrosoethane (*ca.* 2%), a mixture of carbonyl fluoride and carbonyl chlorofluoride (0·56 mmole), and 1,2-dichlorotrifluoro-1-nitroethane (0·58 mmole, 36%) (Found: C, 12·4; N, 6·9%; *M*, 198. Calc. for $C_2O_2NCl_2F_3$: C, 12·1; N, 7·1%; *M*, 198), b. p. 75—76°. The ultraviolet spectrum of the vapour showed maximum absorption at 280 mμ (ε 58) and a minimum at 238 mμ (ε 3·4). Both ultraviolet and infrared spectra were identical with those of the nitro-compound prepared by reaction of nitrosyl chloride with chlorotrifluoroethylene.[8]

(b) *With tetrafluoroethylene.* The steady reaction during 18·5 hr. of the nitroso-compound (0·87 g., 5·0 mmole) with tetrafluoroethylene (0·75 g., 7·5 mmole) at 80° in a 200 ml. Pyrex tube was followed by the disappearance of the characteristic blue nitroso-colour. Fractionation gave unchanged tetrafluoroethylene (2·7 mmole), 2-(1,2-*dichlorotrifluoroethyl*)-3,3,4,4-*tetrafluoro*-1,2-*oxazetidine* (0·7 mmole, 15%) (Found: C, 16·7; N, 4·9%; *M*, 282. $C_4ONCl_2F_7$ requires C, 17·0, N, 5·0%; *M*, 282), b. p. 84·6° (isoteniscope), and the 1 : 1 *copolymer* $[{\cdot}N(CFCl{\cdot}CF_2Cl){\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}]_n$ (0·83 g., 60%) [Found: C, 16·8; N, 5·1. $(C_4ONCl_2F_7)_n$ requires C, 17·0; N, 5·0%] as a colourless thick oil. The polymer was insoluble in the common organic solvents.

When the same reactant ratio was used in an experiment at 100° for 20 hr., the yield of the oxazetidine rose to 48% and no polymer was formed.

(c) *With chlorotrifluoroethylene.* 1,2-Dichlorotrifluoro-1-nitrosoethane (8·3 mmole) and chlorotrifluoroethylene (13·3 mmole), heated at 100° in a 100 ml. Pyrex tube for 5·5 hr., gave unchanged nitroso-compound (0·78 mmole), chlorotrifluoroethylene (8·9 mmole), 1,2-dichlorotrifluoro-1-nitroethane (0·4 mmole, 5%), and the colourless viscous 1 : 1 *copolymer* $[{\cdot}N(CFCl{\cdot}CF_2Cl){\cdot}O{\cdot}CF_2{\cdot}CFCl{\cdot}]_n$ (0·65 g., 26%) [Found: C, 16·3; N, 5·0. $(C_4ONCl_3F_6)_n$ requires C, 16·1; N, 4·7%]. Ultraviolet and infrared spectroscopic examination showed the absence of nitrogen–oxygen double bonds.

In a second experiment, 1,2-dichlorotrifluoro-1-nitrosoethane (7·9 mmole) and chlorotrifluoroethylene (7·9 mmole) were sealed in a tube which was placed in a furnace preheated to 120°. After 2 hr., distillation gave 4-*chloro*-2-(1,2-*dichlorotrifluoroethyl*)-3,3,4-*trifluoro*-1,2-*oxazetidine* (17%) (Found: C, 15·9; N, 4·8%; *M*, 300. $C_4ONCl_3F_6$ requires C, 16·1; N, 4·7%; *M*, 298·5) b. p. 116—117° (micro), polymer (11%), and breakdown products.

Reaction of Nitrosyl Chloride with Chlorotrifluoroethylene.—This reaction was investigated under a variety of conditions. Low yields (2—5%) of 1,2-dichlorotrifluoro-1-nitrosoethane resulted from reactions involving an excess of chlorotrifluoroethylene at 100° for 72 hr., or at 20° for 6 weeks; the compounds $CF_2Cl{\cdot}CFCl_2$ and $CF_2Cl{\cdot}CFCl{\cdot}NO_2$ noted earlier were each formed in 20—40% yield. Only low yields of polymer were obtained.

When chlorotrifluoroethylene (10·2 mmole) and nitrosyl chloride (4·9 mmole) were kept at −15° for 5 days in a 350 ml. Pyrex tube (only vapour phase present initially), the colourless viscous ether-soluble copolymer $[{\cdot}N(CFCl{\cdot}CF_2Cl){\cdot}O{\cdot}CF_2{\cdot}CFCl{\cdot}]_n$ (0·184 g.) [Found: C, 16·4; N, 5·1. Calc. for $(C_4ONCl_3F_6)$: C, 16·1; N, 4·7%] was formed, on the walls of the tube. Use

of equimolar amounts of nitrosyl chloride and chlorotrifluoroethylene failed to increase the yield of 1,2-dichlorotrifluoro-1-nitrosoethane of its copolymer.

Use of an excess of nitrosyl chloride (2 : 1) at 100° with a reaction time of 1—5 days gave 1,2-dichlorotrifluoro-1-nitroethane (50—70%) and 1,1,2-trichlorotrifluoroethane (11—17%); yields reported earlier [4] for similar conditions were 67% and 16% respectively.

Reaction of 1,1,2-Trichlorotrifluoroethane with Tributyl Phosphite.—Tributyl phosphite (5·5 g., 22 mmole) and 1,1,2-trichlorotrifluoroethane (2·0 g., 10·8 mmole) formed a pale yellow solution in a 125 ml. Pyrex tube at 20°: they were kept at 85° for 48 hr. The relatively volatile products, when fractionated, gave unchanged 1,1,2-trichlorotrifluoroethane (8·8 mmole, 82%) and chlorotrifluoroethylene (0·76 mmole, 38% yield based on reactant consumed) (Found: *M*, 117. Calc. for C_2ClF_3: *M*, 116·5) identified by means of its infrared spectrum. Butyl chloride was identified in the products of b. p. >50°.

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