768. *Perfluoroalkyl Compounds of Nitrogen. Part I. Perfluoroalkyl-nitroso- and -nitro-compounds.*

By (Miss) J. Banus.

Perfluoronitrosomethane and perfluoro-1-nitrosopropane have been prepared in good yield by the action of ultra-violet light on gaseous mixtures of the corresponding iodides with nitric oxide in silica vessels, mercury being present to remove iodine. These compounds are very reactive : they decompose when kept at room temperature or shaken with mercury or with alkali, and are smoothly oxidised to the nitro-compounds, which are stable to alkali. Magnetic and some optical properties of the nitroso-compounds are discussed.

STANDARD methods for the preparation of perfluoroalkylamines of the type $R_F{\cdot}NF_2$, $(R_F)_2NF$, and $(R_F)_3N$,* and of the perfluoroalkyl cyanides $R_F{\cdot}CN$, are now well established, the first three by fluorination of C–N compounds, and the last by fluorination, and by dehydration of the acid amide. The cyanides are useful intermediates for the preparation of compounds containing the groups $R_F{\cdot}CO{\cdot}$ or $R_F{\cdot}C{\cdot}$, but not as yet for compounds R_FX where X is an atom other than carbon. The "amines" have little organic chemistry; † they are almost as inert as the fluorocarbons themselves and the nitrogen is of course non-basic, as in nitrogen trifluoride.

A route has now been found, *via* a homolytic reaction, from the fluorocarbon iodide R_FI to the nitroso-compound $R_F{\cdot}NO$ (see Banus, *Nature*, 1953, **171**, 173). It was observed (Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041) that primary homolytic reactions of fluorocarbon iodides can generally be said to parallel those of their hydrocarbon analogues, and thus, on irradiation of the iodide in presence of nitric oxide and of mercury (to remove iodine), the free perfluoroalkyl radical combines with nitric oxide to form $R_F{\cdot}NO$. These may be converted by oxidation, reduction, or condensation reactions into a variety of nitrogen compounds.

Perfluoroalkyl compounds (other than those of type $R_F{\cdot}C{<}$) with reactive functional groups containing nitrogen have been reported from time to time, but no standard methods have been evolved. No nucleophilic reactions of the perfluoroalkyl iodides have so far been found (Banus, Emeléus, and Haszeldine, *J.*, 1951, 60). Ruff and Giese (*Ber.*, 1936, **69**, 684) reported a 1 : 1 mixture, which they could not separate, of $CF_3{\cdot}NO$ and a so-called $F{\cdot}CO{\cdot}NF_2$, as a by-product of the action of elementary fluorine on silver cyanide, which contained the oxide and nitrate as impurities. Many of the properties described for $CF_3{\cdot}NO$ have not been confirmed in the present work. Ruff and Giese also reported $CF_3{\cdot}N{:}N{\cdot}CF_3$ (*Ber.*, 1936, **69**, 598, 604, 684; see also Ruff and Willenberg, *Ber.*, 1940, **73**, 724), formed by fluorination of silver cyanide or of cyanogen iodide; and $CF_3{\cdot}NH{\cdot}CF_3$ was obtained by Ruff and Willenberg (*loc. cit.*) by fluorination of ICN by phosphorus pentafluoride containing hydrogen fluoride as impurity. The compounds $R_F{\cdot}CF{:}NF$ are

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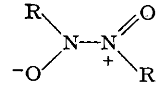
* In these and other formulæ, R_F denotes perfluoroalkyl.

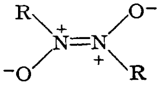
formed in fluorination reactions; they are very reactive, but have not been used synthetically.*

Hückel (*Nachr. Akad. Wiss. Göttingen,* Math.-Physik. Klasse, 1946, No. 1, 55) stated that $CF_3\cdot NO_2$ was obtained in small yield by the action of ClF_3 on $CF_2Br\cdot NO_2$, and by the oxidation of $CF_3\cdot NO$ with lead dioxide or manganese heptoxide, and that $CF_3\cdot NCO$ was obtained by a Curtius degradation, but did not give details in either case. Many other workers have reported failures with Hofmann, Curtius, and Lossen degradations of perfluoro-acid derivatives. A perfluoroalkyl-nitro-compound was made by Coffman *et al.* (*J. Org. Chem.*, 1949, **14**, 747) in 7% yield by addition of N_2O_4 to C_2F_4 under pressure. They give physical properties of the compound but no chemical properties or proof of structure (cf. Hass and Whitaker, U.S.P. 2,447,504/1948; no yield given). Many unsuccessful attempts have been made to fluorinate chloropicrin. Haszeldine (*Nature*, 1951, **169**, 1028), while the present work was in progress, reported the conversion of perfluoroalkyl iodides into nitroso- and nitro-compounds, but without details of preparation or properties. Later, Dacey (*Discuss. Faraday Soc.*, 1953, **14**, 87, 133) obtained $CF_3\cdot NO$, without characterising it, by photolysis of CF_3I in presence of nitric oxide, and reported a personal communication that Dale had made it from silver trifluoroacetate and nitrosyl chloride. The author had used Dale's method but obtained poor yields.

These nitroso-compounds, in contrast to their hydrocarbon analogues, do not dimerise; if one assumes that all compounds $(R\cdot NO)_2$ have the constitution (I) (two forms) with some contribution from (II), as has been established for the aromatic nitroso-compound dimers

(I)





(II)

(Darwin and Hodgkin, *Nature*, 1950, **166**, 827; Fenimore, *J. Amer. Chem. Soc.*, 1950, **72**, 3226; Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1937, pp. 213 *et seq.*), one would expect $R_F\cdot NO$ to be stabilised by the strong inductive pull of the R_F group (cf. also Pauling's adjacent-charge rule, "The Nature of the Chemical Bond," Cornell Univ. Press, 1940, pp. 199 *et seq.*). Further, one would not expect $R_F\cdot NO$ to rearrange spontaneously to form an aldoxime analogue, with the electronegative fluorine replacing hydrogen. Coe and Doumani (*J. Amer. Chem. Soc.*, 1948, **70**, 1516) describe $(CH_3\cdot NO)_2$, formed in the photochemical decomposition of *tert.*-butyl nitrite, the evanescent blue colour that appears on warming it, and its spontaneous conversion into $(CH_2{:}N\cdot OH)_3$. Hammick *et al.* (*J.*, 1935, 30, 1679; 1937, 489), working with aliphatic nitroso-compounds stabilised by electronegative α-substituents, studied their photo-decomposition and photo-oxidation; where α-hydrogen atoms were present, the primary process appeared to be the elimination of NOH. The thermal decomposition was not investigated. In contrast with the earlier work (Ruff and Giese, *loc. cit.*), the perfluoroalkyl-nitroso-compounds have now been found to decompose spontaneously at room temperature, faster in the gas phase, and the disproportionation and other products will be described in a later communication. Ruff's isomerisation to "$F\cdot CO\cdot NF_2$" has not been confirmed. The perfluoroalkyl-nitroso-compounds are deep blue gases with a tinge of green, the liquids are inky blue, and the solids almost purple. The colour of nitroso-compounds has aroused much speculation, but is not yet understood. Lewis ("The Valence and Structure of Atoms and Molecules," 1923, 28) suggested that they might be paramagnetic, as oxygen is, and Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 3225) suggested a triplet structure. More recently, Lewis and Kasha (*ibid.*, 1945, **67**, 994) assumed that the characteristic band in the visible was due to a singlet–triplet transition, a similar suggestion having been made for nitrosyl chloride by Jahn (*J. Chem. Phys.*, 1938, **6**, 335). However, Wilson (*J. Amer. Chem. Soc.*, 1934, **56**, 747) found nitrosyl chloride, nitrosobenzene, and *p*-nitrosodimethylaniline to be diamagnetic, and this was confirmed for gaseous nitrosyl chloride by Beeson and Coryell (*J. Chem.*

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* [Added, Oct. 12th, 1953.] Azomethines, $R_F\cdot N{:}CF\cdot R_F$, including $CF_3\cdot N{:}CF_2$, have now been made by pyrolysis of tertiary perfluoro-amines, and addition of hydrogen fluoride has yielded $R_F\cdot NH\cdot R_F$ (personal communication from The Minnesota Mining and Manufacturing Co.)

Phys., 1938, **6**, 656) and for nitrosobenzene by Farquharson (*Trans. Faraday Soc.*, 1936, **32**, 219) and other workers. McClure (*J. Chem. Phys.*, 1949, **17**, 905) has criticised Lewis and Kasha's assignment on various grounds, so it can only be assumed that the nitroso-compounds are in a singlet state. The perfluoroalkylnitroso-compounds are diamagnetic in the liquid state, and the molecular susceptibilities measured by the Gouy method were found to be equal to the sum of the atomic susceptibilities. The spectrum in the visible and in the ultra-violet region closely resembles that of 3-bromo-2 : 4-dimethyl-3-nitropentane (" di*iso*propylbromonitrosomethane ") (Lewis and Kasha, *loc. cit.*), and those of Hammick's α-substituted compounds, observed in the visible region. Mr. J. Dunderdale (of this laboratory) is examining the infra-red spectra of the new compounds described here, and Dr. D. J. Millen the micro-wave spectra of perfluoro-nitro- and -nitroso-methane.

Various methods of preparation of the nitroso-compounds have been tried, but the most efficient has been irradiation of a gaseous mixture of the iodide and nitric oxide, at just under atmospheric pressure, in a silica bulb in the presence of a globule of mercury. Shaking with mercury in a sealed tube decreases the yield; in fact, a pure nitroso-compound is decomposed completely if shaken with mercury for 1 day. The nature of the light source considerably affected the yield; the most suitable was a mercury lamp consisting of an argon-filled fused-silica spiral with Swedish-iron electrodes, operated at 4000 v and 200—240 mA. This ran cold, and gave almost pure 2537 Å radiation of high intensity. Little or no diperfluoroalkylmercury or perfluoroalkylmercury halide was found in the products, but carbon dioxide, silicon tetrafluoride (these from decomposition of the perfluoroalkyl radical on the silica), fluorocarbon, and traces of $CF_3{\cdot}NO$ and $C_2F_5{\cdot}NO$ (in the preparation of $C_3F_7{\cdot}NO$) were all present, together with nitro-compounds, and nitrogen compounds of higher molecular weight. The overall yield was sometimes as high as 80%. Preparations in which the reagents were sealed under pressure in a silica Carius tube, but not shaken, were also less successful, and yields fell to *ca.* 20%.

The nitroso-compounds were also prepared by the action of nitrosyl chloride on the silver perfluorocarboxylate: $R_F{\cdot}CO_2Ag + NOCl \longrightarrow R_F{\cdot}NO + AgCl + CO_2$, but the yields were less than 15% and separation of the nitroso-compound from the other decomposition products was very tedious. SiF_4, $R_F{\cdot}R_F$, $R_F{\cdot}NO_2$, and traces of R_FCl, were found.

The gases were purified by quick washing with concentrated aqueous potassium hydroxide, for, although this slowly decomposes the nitroso-compounds, separation of the crude mixture by distillation was very difficult. The gases were then twice distilled in a Fenske-packed still with reflux temperature —78·5° wherever possible, middle cuts being taken, and stored frozen in liquid oxygen to obviate decomposition. Preliminary values for the physical constants were measured on samples of which the molecular weights, determined by the gas-density method, were within 1% of 99 and 199, the theoretical values for $CF_3{\cdot}NO$ and $C_3F_7{\cdot}NO$. Some decomposition was evident even during the time taken by such measurements, which were therefore done as quickly as possible, and in some cases the gas was re-purified between measurements. Mercury was excluded; gas pressures were measured with a diaphragm gauge, and temperatures with a copper–constantan thermocouple calibrated against a platinum-resistance thermometer.

The nitroso-compounds are readily oxidised to the nitro-compounds, *e.g.*, by 30% hydrogen peroxide at 100—130° in a sealed tube. These were distilled in the Fenske-packed still with reflux temperature —78·5°, and found to be stable compounds, colourless in the gas or liquid state and white solids at low temperature. There is no reaction with alkali.

Attempts were made to prepare the nitro-compounds by a more direct route, by heating the silver perfluoroalkanecarboxylate with dinitrogen tetroxide, and by irradiating the iodide in the presence of dinitrogen tetroxide and of mercury. These gave small yields of the nitro-compounds, mixed with large quantities of other decomposition products which were difficult to separate. Attempts to effect nucleophilic reactions of the perfluoroalkyl iodides, *e.g.*, with silver nitrite, are still being made.

The behaviour of these nitrogen-containing functional groups under the conditions of extreme inductive effect found in R_FN compounds (and in the absence of potential protons) is of considerable interest. There is, for example, the possibility of testing the theory of resonance of double-bonded forms, as proposed by Pauling for the chlorofluoromethanes ("The Nature of the Chemical Bond," Cornell Univ. Press, 1942, 235), by reference to the bond lengths in $CF_3{\cdot}NO$, $CF_3{\cdot}NO_2$, etc.; and also the possibility of nitrosonium- and nitronium-ion mechanisms arising in the reactions of $R_F{\cdot}NO$ and $R_F{\cdot}NO_2$.

EXPERIMENTAL

Volatile compounds were handled in a vacuum system, and molecular weights determined by the gas-density method (the accuracy is usually limited only by deviations from ideal-gas behaviour). Carius tubes were filled and sealed *in vacuo*. Distillation, unless qualified, implies the use of a small Fenske-packed still, operated at reduced pressure, with −78·5° reflux; the take-off is regulated by means of a vacuum-tap, and the pressure above the column gives an indication of variations in the distillate. Low temperatures were obtained by the use of slush baths (melting solids), and were measured with a copper–constantan thermocouple previously calibrated against a platinum-resistance thermometer. Pressures were measured with a mercury manometer, or for compounds that are affected by mercury, a glass-diaphragm gauge. Fluorine was determined by the calcium fluoride method, after sodium fusion.

Perfluoroalkyl Iodides.—These were made by the silver-salt method, washed with alkali, and distilled.

Nitric Oxide.—Reduction of nitrite by ferrous ion (*Inorg. Synth.*, 1946, **2**, 126) was adapted for use with a vacuum system.

*Perfluoronitrosomethane and Perfluoro-*1*-nitrosopropane.*—In a typical preparation 370 mm. of R_FI and 380 mm. of NO were let in at room temperature to the fused silica bulb of 220-c.c. capacity, with a vacuum tap and joint attached, and containing 5 c.c. of mercury. The tap was closed, and the bulb irradiated (almost touching the mercury resonance lamp previously described) for 2—3 hours. The development of blue colour was a useful guide to the progress of the reaction. The volatile mixture was then taken back into the vacuum-system, and stored at liquid-oxygen temperatures, the nitric oxide having been pumped off. The silica bulb then contained mercury and mercuric iodides, with a little oxide and nitrate, etc., but almost no $R_F{\cdot}HgI$ or $Hg(R_F)_2$ (recognised by their characteristic smell). However, the mercury was disturbed to leave a fresh surface, and the bulb re-filled with gaseous reactants and irradiated, this process being repeated four or five times before it was necessary to wash the bulb out, so long as the sides that were being irradiated were clear of the solid products, which collected at the bottom. After about 20 such irradiations the bulked product mixture was passed through 10% aqueous sodium hydroxide in a sintered-disc Drechsel bubbler to remove iodine, CO_2, COF_2, SiF_4, NO_2, and N_2O_3, then freed from water by passage through traps at −78·5°, and then, in the case of *perfluoro-*1*-nitrosopropane*, distilled (Found: F, 66·1%; *M*, 199. C_3ONF_7 requires F, 66·8%; *M*, 199). Fractions were collected, and those whose molecular weight was within 1% of 199 were combined and stored at −183°.

The saturation vapour pressure for this compound is given by $\log P$ (mm.) = 9·035 − 1593/T, according to which the b. p. (extrapolated) is −14·5°, the latent heat of evaporation at the boiling point (L_e) 7270 cal., and the Trouton coefficient 28, suggesting that the liquid is strongly associated. The m. p. was determined in a Stock apparatus as −151°.

Since perfluoronitrosomethane was too volatile to be refluxed in the available still, it was purified as far as possible by passage through traps at −162° (*iso*pentane slush-bath), and by devices which utilise the observation that the compound is liquid at liquid-oxygen temperatures, while its impurities presumably are not; *e.g.*, C_2F_6 melts at −100°. Thus the mixture was slowly condensed into a vertical glass tube about 6 mm. in internal diameter and left to run down through a constriction (the whole being kept at −183°) although it does tend to wet the ring of colourless crystals to some extent. The solid material was then pumped off upwards and collected for examination, and the process repeated. The *perfluoronitrosomethane* presumably still contained dissolved impurities, and the molecular weights of purified samples were usually high, *e.g.*, by 1·5—2%, and the fluorine content slightly high, which is abnormal in estimations by the calcium fluoride method (Found: F, 57·9%; *M*, 99. $CONF_3$ requires F, 57·6%; *M*, 99). The vapour-pressure equation is therefore presented tentatively, and will be checked and improved as better methods of distillation are devised: $\log P$ (mm.) = 8·006 − 925·8/T, giving b. p. (extrapolated) −92·6°, L_e 4218 cal., and the Trouton coefficient 23·4. Ruff and Giese (*loc. cit.*) obtained −84° as the b. p. of their inseparable mixture, and −82·4° as the b. p. of the "$F{\cdot}CO{\cdot}NF_2$" component. The Trouton coefficient may be considered to be high, as low-boiling gases usually have low Trouton coefficients. The low m. p.s of $CF_3{\cdot}NO$ (below $-183°$) and of $C_3F_7{\cdot}NO$ suggest that these molecules are not very polar, but on the other hand nitric oxide has a high Trouton coefficient, 26·1.

Magnetic Measurements.—The diamagnetic susceptibilities of the liquid nitroso-compounds were measured in sealed tubes at room temperature by Gouy's method, and found to agree, within experimental error (some 4—5%), with the sum of the atomic susceptibilities, $-44{\cdot}4$ and $-102{\cdot}4$ c.g.s.u. for $CF_3{\cdot}NO$ and for $C_3F_7{\cdot}NO$, respectively. Conductivity water was used as standard.

Ultra-violet Spectrum.—The spectrum of $C_3F_7{\cdot}NO$ in the visible and the ultra-violet region was measured at room temperature, with a transmission-reading Cary recording spectrophotometer. The vapour was contained in a 4-cm. silica cell, filled to pressures between 5 and 75 cm. of mercury. The blue colour of the gas is due to a very weak absorption band, for which $\varepsilon_{\text{max.}} = 19{\cdot}0$ at 6840 Å, of oscillator strength (*f*-value) 0·00020 in the red. This band is markedly asymmetrical but, apart from six irregularly spaced and very poorly resolved vibrational bands, is almost structureless. The following are representative of the spectral slit-widths used in this region: 45 Å at 7000 Å, 17 Å at 6500 Å, 7 Å at 6000 Å. A region of more intense absorption begins at 2400 Å. Between these two chief band systems there was invariably very weak banded absorption ($\varepsilon < 0{\cdot}2$), the intensity of which varied from sample to sample, and which is therefore confidently ascribed to small and variable quantities of impurity. It is clear from the spectrum that photodecomposition is not in question here at least insofar as free radicals might be concerned (cf. Hammick's nitroso-compounds, which contained α-hydrogen; *loc. cit.*).

Factors affecting the Yields of Nitroso-compounds.—The overall yield of reasonably pure material from the method described was about 75% for $C_3F_7{\cdot}NO$ and somewhat less for $CF_3{\cdot}NO$, relative to the iodide taken; little or no iodide was recovered. With care, these yields could be improved, and they were of course reduced when the compound was extensively purified for physical measurements; *e.g.*, when the products of the irradiations of 18 propyl iodide and nitric oxide mixtures were bulked, washed, and distilled, 1350 c.c.* (*i.e.*, 5·53 g., 82%) of perfluoronitrosopropane of molecular weight 199 ± 2 were obtained. With other sources of ultra-violet light, the proportion of $R_F{\cdot}NO$ to decomposition products was drastically reduced, perhaps because the increase of temperature, with a lamp running hot, accelerated decomposition reactions. The preparation was also less efficient when carried out in a sealed tube under pressure; *e.g.*, 1028 c.c. of perfluoropropyl iodide were sealed, with 1040 c.c. of nitric oxide and 5 c.c. of mercury in a silica Carius tube of approximately 95 c.c. capacity, and this was then placed inside the spiral mercury resonance lamp for 5 hr. A very large amount of mercuric nitrate was formed, together with oxide, etc., and very little nitroso-compound, presumably owing to bad mixing; similar sealed-tube preparations of perfluoronitrosomethane were slightly more successful, perhaps because of the greater volatility of methyl than of propyl iodide. When the tube was shaken (outside the spiral), the yield increased somewhat, but not above 20%, measured on the iodide taken; 205 c.c. of $C_3F_7{\cdot}NO$ were recovered. In general, the greater the proportion of decomposition products, which are complex, the greater is the loss of nitroso-compound in the separation process, and this widens the gap between the yields from good and from bad preparations.

Decomposition Reactions of the Nitroso-compounds.—14·5 C.c. of perfluoronitrosopropane were sealed in a glass tube together with 5 c.c. of mercury, and the tube was shaken at room temperature until the blue colour disappeared completely. This took 24 hr. for $C_3F_7{\cdot}NO$, and about 20 hr. for $CF_3{\cdot}NO$ in a similar experiment. This reaction was accelerated when the temperature was raised, as in the vicinity of an ultra-violet lamp. The products of this reaction and of the decomposition of the nitroso-compounds at room temperature alone or with animal charcoal will be discussed in a later communication, and also their relation to other perfluoroalkyl-nitrogen compounds separated during the preparation of the nitroso-compounds.

Preparation from the Silver Salt.—In view of the success of the silver salt preparation of the perfluoroalkyl iodides a similar reaction was attempted: $R_F{\cdot}CO_2Ag + NOCl \longrightarrow R_F{\cdot}NO + CO_2 + AgCl$. It was hoped, also, to shorten by one step the route from the commercially available acid to the nitroso-compound. Nitrosyl chloride was made by the action of sodium chloride on nitrosyl hydrogen sulphate, made by the interaction of sulphur dioxide and nitric acid (*Inorg. Synth.*, 1946, **2**, 251). To 4 g. of $C_3F_7{\cdot}CO_2Ag$ (0·0125 mole) and 10 c.c. of heptacosafluorotributylamine (an inert solvent) were added 1·2 c.c. (0·025 mole) of liquid NOCl, and the tube was then heated for 10 days, the temperature being increased daily as no blue

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* Here, and for similar measurements recorded later, volumes are corrected to N.T.P.

coloration could be seen. The final temperature was 210°, and still no blue colour was visible, either at room temperature or at $-182°$, although such colour might have been masked by NOCl. The volatile materials were taken off and washed with alkali, much CO_2, SiF_4, etc., being present. The washings deposited silicic acid on acidification. After tedious fractionation, 9·8 c.c. of $C_3F_7{\cdot}NO$, representing a yield of 13·5% measured on the silver salt taken, were obtained. Perfluoro-nitropropane and -hexane were identified in the products by molecular-weight determination, tensimetry, and quantitative analysis. The less volatile residue smelt strongly of fluorocarbon acid, and the silver was present as chloride. No nitrate was detected.

Perfluoroalkyl-nitro-compounds.—The nitroso-compounds are smoothly oxidised to the nitro-compounds. This conversion was first effected by the action of manganese heptoxide in acetic acid, but 30% hydrogen peroxide was later found more convenient. In the first experiment 61·8 c.c. of perfluoronitrosopropane were sealed, together with 15 c.c. of 30% hydrogen peroxide, in a Carius tube of about 110-c.c. capacity, and the tube heated for 1-hr. periods successively at 65°, 78°, 90°, and 100°; at 100° the blue colour disappeared. The volatile material was removed, and oxygen pumped off from it, and on distillation carbon dioxide was found to be present in the first fraction. The gas was therefore washed with aqueous 20% potassium hydroxide and redistilled. The bulk of the material, several successive fractions, had a molecular weight of 219, and this was therefore accepted for *perfluoro-*1-*nitropropane* as the compound is not very volatile, and as the different fractions were found to be tensimetrically equivalent and the analysis correct (Found: F, 61·2. $C_3O_2NF_7$ requires F, 61·8%; *M*, 215). Top and tail fractions of lower molecular weight were rejected; 42·1 c.c. (yield 68%) were isolated. This compound had vapour pressures agreeing with $\log P$ (mm.) $= 8{\cdot}072 - 1539/T$, from which the b. p. (extrapolated) is 23·2°, L_e 7023 cal., and the Trouton coefficient 23·7. The residual peroxide contained fluoride ion, probably produced by decomposition of the nitroso-compound. The aqueous alkali washings contained no fluoride ion.

A similar reaction mixture for the preparation of *perfluoronitromethane* was heated successively for 1-hr. periods at 100°, 110°, 120°, and 130° before the blue colour finally disappeared at 140°. After being washed with aqueous alkali the volatile material was distilled through the $-78{\cdot}5°$ column but did not reflux; however, all fractions had a molecular weight of 115 (Found: F, 49·5. CO_2NF_3 requires F, 49·6%; *M*, 115). From the vapour-pressure equation, $\log P$ (mm.) $= 8{\cdot}202 - 1275/T$, the b. p. (extrapolated) is $-33{\cdot}6°$, L_e 5820 cal., and the Trouton coefficient 24·3.

The nitro-compounds are, of course, colourless, and are recovered quantitatively from aqueous alkali.

Interaction of Perfluoropropyl Iodide and Dinitrogen Tetroxide.—The pure tetroxide used was a gift from Dr. A. E. Comyns. 1400 C.c. of the iodide were sealed, together with 2240 c.c. of tetroxide, in a silica Carius tube, which was then irradiated overnight by Osram high-pressure mercury-vapour lamps (type MB/V, 125 w, with the glass envelope removed) as sources of ultra-violet light. Much iodine developed and some white solid was visible. After a further 24 hr. the mixture was frozen in liquid oxygen, whereupon some deep blue coloration was visible. After the product had been washed with alkali the blue colour could no longer be seen (on freezing), and so it was probably due to dinitrogen trioxide rather than to nitroso-compound. The alkali contained much fluoride ion and silica. The product was distilled, and in the first instance 6 fractions of different " molecular weight " were collected. The material of molecular weight 217, formed in about 10% yield based on the iodide, was identified tensimetrically and by qualitative analysis as perfluoronitropropane; the isomeric nitrite would be expected to be much more volatile, and presumably unstable to ultra-violet light. Low-boiling fluorocarbons were not found to any extent, although $CF_3{\cdot}CF{:}CF_2$ and C_6F_{14} were isolated, and characterised tensimetrically and by qualitative analysis. Other products await characterisation by infra-red absorption.

Interaction of Silver Perfluorobutyrate and Dinitrogen Tetroxide.—To 4 g. of the silver salt (0·0125 mole) and 10 c.c. of perfluorotributylamine was added 1 g. (0·011 mole) of tetroxide; the mixture was sealed in a Carius tube of 195 c.c. capacity and heated at 200° overnight. The product was at least as complex as in the previous experiment; a small yield (*ca.* 12%) of nitro-compound, was isolated, and the other compounds await characterisation.

Perfluoropropyl Iodide and Silver Nitrate.—The dry nitrite (0·73 g.), dibutyl ether (10 c.c., distilled from sodium), and the iodide (1 g.) were sealed in a 20-c.c. glass tube, which was then shaken in the dark at room temperature for 120 hr. This method is successful with alkyl nitro-compounds (Kornblum *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 307; 1948, **70**, 746). The more volatile portion was then examined for perfluoronitropropane and for the corresponding nitrite, and the solid residue for silver iodide, with negative results; in fact, the iodide was reasonably quantitatively recovered.

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