Reactions of Fluorocarbon Radicals. Part XIII. Alternative Syntheses, Properties, and Spectra of Trifluoro-nitroso- and -nitro-methane.†*

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New syntheses for trifluoronitrosomethane, and optimum conditions for the reaction of trifluoroiodomethane with nitric oxide, are described. The nitroso-compound is readily oxidised by oxygen or hydrogen peroxide to give trifluoronitromethane in high yield; improved physical properties are reported. Ultra-violet and infra-red spectra of trifluoronitrosomethane, trifluoronitromethane, and related unsubstituted *C*-nitroso- and *C*-nitro-compounds are discussed, with particular reference to the effect of substitution on the region of characteristic absorption. Comparisons with *O*- and *N*-nitroso- and *O*- and *N*-nitro-compounds show them to be easily distinguished spectroscopically from the *C*-nitroso- and *C*-nitro-compounds.

THE synthesis of a series of polyfluoroalkyl nitroso-compounds was first described in Part X (Haszeldine, *J.*, 1953, 2075; see also *Nature*, 1951, **168**, 1028, and Banus, *ibid.*, 1953, **171**, 4343); alternative and better syntheses are now described for trifluoronitrosomethane and trifluoronitromethane.

Optimum conditions have been derived for the photochemical reaction of trifluoroiodomethane with an excess of nitric oxide in the presence of mercury:

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

With a pressure of *ca.* ten atmospheres the yield is high but the conversion is low (20%). The conversion is considerably improved (90%) if the reaction is carried out at atmospheric pressure or below, and for the preparation of small quantities this is the better method. Mercury plays an important rôle by removing iodine and reacting with dinitrogen tetroxide produced as by-product—this tetroxide causes appreciable breakdown and purification becomes difficult. In one experiment where the mercury was not shaken, trifluoronitromethane but not trifluoronitrosomethane was detected amongst the products, *i.e.*:

$$CF_3\cdot + NO_2 \longrightarrow CF_3\cdot NO_2;\ \text{or}\ CF_3\cdot NO \xrightarrow{NO_2} CF_3\cdot NO_2 + \text{decomp.}$$

Trifluoronitrosomethane decomposes at moderate temperatures to give (in glass) silicon tetrafluoride, carbon dioxide, and a small amount of trifluoronitromethane, and the thermal reaction of trifluoroiodomethane with nitric oxide is thus not a suitable preparative method.

Tristrifluoromethylarsine, readily prepared from trifluoroiodomethane and arsenic

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* Part XII, Haszeldine, *J.*, 1953, 3761.

† Presented in part at the Amer. Chem. Soc. Meeting, Chicago, Sept. 1953.

(Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552), yields trifluoronitrosomethane when treated with nitrosyl chloride :

$$As(CF_3)_3 \xrightarrow{NOCl} CF_3{\cdot}NO + AsCl_3$$

The yield is low, since side-reactions, notably the formation of chlorotrifluoromethane, predominate. The photochemical reaction of tristrifluoromethylarsine with nitric oxide also gives low yields of the nitroso-compound.

Trifluoroacetyl iodide, which is a ready source of trifluoromethyl radicals (W. C. Francis, unpublished results), when irradiated in the presence of nitric oxide and mercury, yields trifluoronitrosomethane :

$$CF_3{\cdot}COI \xrightarrow{h\nu,\ Hg} CF_3{\cdot}\dot{C}O \xrightarrow{NO} CF_3{\cdot}NO + CO$$

but the simplest route for the preparation of the *pure* nitroso-compound is still from trifluoroiodomethane; larger quantities of less pure nitroso-compound are best prepared from silver trifluoroacetate (Haszeldine and Jander, *J.*, 1953, 4172).

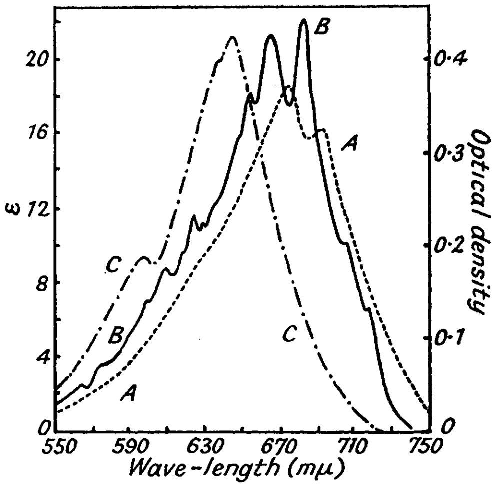


FIG. 1.

A, $CMe_3{\cdot}NO$ in light petroleum. Optical density scale.
B, $CF_3{\cdot}NO$ vapour. ε scale.
C, $CHMeCl{\cdot}NO$ in light petroleum. Optical density scale.

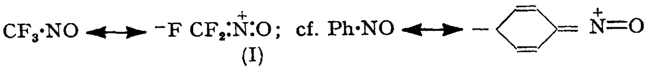
Trifluoronitrosomethane is a blue gas, which is stable in clean glass apparatus, in presence of mercury and in absence of light, and is conveniently purified by utilising its remarkably low melting point (see Experimental part). It condenses to a deep blue liquid at −86·6° (cf. Ruff and Giese's value of −84°; see Haszeldine, *J.*, 1953, 2075), and has a normal Trouton constant of 21·9 which indicates that the compound is not associated; the molecular weight of the gas is normal. There is no evidence for the formation of a dimer of the type $CF_3{\cdot}N(O^-){\cdot}{}^+N(\colon O){\cdot}CF_3$ (see Part X), and this is supported by spectroscopic examination of trifluoronitrosomethane.

Spectra of Nitroso-compounds.—The ultra-violet spectra of nitroso-compounds are of great theoretical interest. The nitroso-group is electronically similar to oxygen and the monomeric nitroso-compounds are diamagnetic, which suggests that the lowest triplet state is higher than the singlet state. The ultra-violet spectra of trifluoronitrosomethane and related compounds are shown in Table 1. It is very probable that by use of modern photoelectric spectrophotometers the single broad band reported in the earlier literature for nitroso-compounds would be resolved into two or more bands. Monomeric *C*-nitroso-compounds are characterised by a weak absorption band in the region 650—700 mμ. Table 1(*a*) shows that when R in a nitroso-compound R·NO contains only alkyl groups on the α-carbon atom, the absorption is in the region 670—690 mμ, but that when chloro-, phenyl, or nitro-groups are present on the α-carbon atom there is a progressive shift in wave-length to *ca.* 650 mμ. This can be correlated with increase in inductive effect of R with consequent decrease in importance of structures $R{\cdot}{}^+N{-}O^-$ relative to $R{\cdot}N{=}O$ in the excited state. One might expect that this effect would be at a maximum when R is perfluoroalkyl, but the low-intensity absorption maximum for trifluoronitrosomethane (683 mμ) is considerably shifted relatively to α-chloro-nitroso-compounds, and is more like that for 2-methyl-2-nitroso-propane (Fig. 1) or nitrosobenzene. This indicates that structures such as (I), made possible by the tendency for fluorine to participate in hyperconjugation (see *J.*, 1952, 3490; 1953, 922), play an important part.

TABLE 1. *Ultra-violet spectra of nitroso-compounds.*

	Solvent	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\varepsilon_{min.}$
(*a*) C-*Nitroso-compounds.*									
$CF_3\cdot NO$	Vapour [1]	718	6·7	715	6·5	624	12·0	614	8·5
		705	10·5	704	10·0	608	9·0	602	6·5
		683	23·0	676	17·0	600	7·0	580	3·5
		665	21·5	658	17·5	578	4·0	568	2·3
		654	18·5	632	11·0	566	2·5	310—510	<0
		628	11·5	626	11·0	266	20	241	15
$Me_3C\cdot NO$	Light	692	—	685	—	287	—	266	—
	petroleum [1]	674	—	458—498	—				
	Ether [1]	675	—	440—460	—	296	—	265	—
		Inflection: 686—692 mμ.							
$CMe_2Cl\cdot CMe_2\cdot NO$	Benzene [2]	690	17·9	—	—	—	—	—	—
$CMe_2Br\cdot CMe_2\cdot NO$	Benzene [2]	690	17·8	—	—	—	—	—	—
$CHMe_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot NO$	Benzene [3]	685	—	—	—	—	—	—	—
$Me\cdot CO\cdot CH_2\cdot CMe_2\cdot NO$	Benzene [4]	670	—	—	—	—	—	—	—
$CMe_3\cdot CMeCl\cdot NO$	Benzene [2]	670	17·1	—	—	—	—	—	—
$O_2N\cdot CMe_2\cdot NO$	Benzene [2]	655	21·3	—	—	—	—	—	—
$\overline{CH_2\cdot(CH_2)_4\cdot C}Cl\cdot NO$	Benzene [2]	655	17·9	—	—	—	—	—	—
$Ph\cdot CMeCl\cdot NO$	Benzene [2]	650	17·0	—	—	—	—	—	—
$CHMeCl\cdot NO$	Light	648	11·4	604	4·9	319	250	252	26·5
	petroleum [1]	597	5·0	460—468	<0	—	—	—	—
	Inflections: 638 mμ, ε, 10·5; 557 mμ, ε, 1·5								
(*b*) N-*Nitroso-compounds*									
$(CF_3O)(CF_3)N\cdot NO$	Vapour [5]	374	20	320	8·5	—	—	—	—
		Slight inflections: 340—400 mμ							
$Me_2N\cdot NO$	Light	374	105	369	90	351	98	301	3
	petroleum [5]	361	125	354	94	232	5900	—	—
c) O-*Nitroso-compounds*									
$BuO\cdot NO$	Light	384·5	33	381·5	31	333	56	326·5	27
	petroleum	370	70	364	49	323	37	318	23
		356	87	349	46	314	27	310·5	24
		344	77	337·5	36	222	1700	—	—
(*d*) *Nitrosyl chloride*									
(Main peaks only)	Vapour	$\lambda_{max.}$, 610, 598·5, 590, 584, 568·5, 562, 547·5, 540·5, 537, 524, 517, 478, 473, 335							

[1] Present work. [2] Hammick and Lister, *J.*, 1937, 489. [3] Anderson, Crumple, and Hammick, *J.*, 1935, 1680. [4] Anderson and Hammick, *J.*, 1935, 30. [5] Jander and Haszeldine, *J.*, 1954, 691, 696.



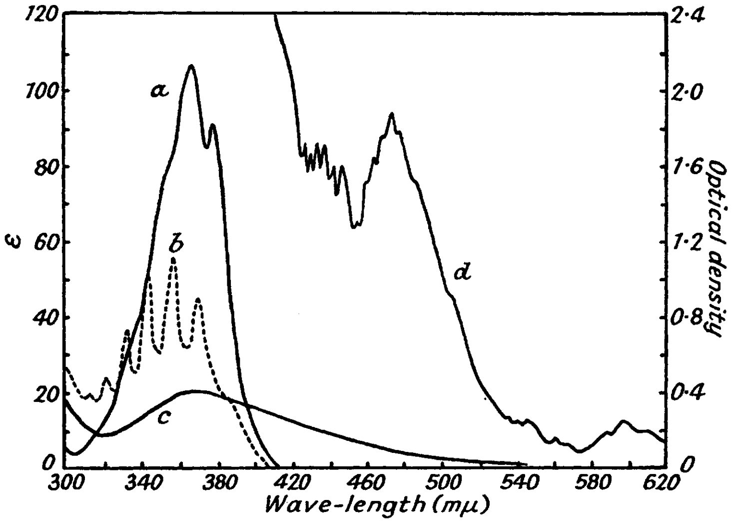
(I)

Lewis and Kasha attribute the long wave-length absorption of other *C*-nitroso-compounds to a singlet–triplet transition (*J. Amer. Chem. Soc.*, 1945, **67**, 994), and suggest that, as in oxygen, powerful resonance in the nitroso triplet state involving dipolar forms holds the two atoms closely together and prevents the odd electrons from wandering into R, *i.e.*, R in R·NO is relatively unimportant in determining colour, as is actually found. More recently Orgel (*J.*, 1953, 1276) has suggested that the transition involved is a singlet–singlet σ–π.

The spectrum of trifluoronitrosomethane shows appreciable fine structure in its long wave-length band, which could undoubtedly be resolved further by operating at lower temperatures. The band at lower wave-length (266 mμ) shows no fine structure, and between the two bands the absorption is extremely weak, so that the position of the minimum could not be determined accurately. The nitroso-compound will clearly be diamagnetic.

The nitroso-group absorption in 2-methyl-2-nitrosopropane is sensitive to solvent changes; in ethyl ether, for example, the long wave-length maximum is unresolved and the position of the short wave-length maximum is shifted by 9 mμ relatively to its position in light petroleum. A marked solvent effect of 15 mμ with loss of fine structure was noted recently for nitrosamines (Haszeldine and Jander, *J.*, 1953, 691). The nitroso-group absorption in these *N*-nitroso-compounds is considerably displaced to shorter wave-length relatively to the corresponding absorption for *C*-nitroso-compounds [Table 1(*b*)]; the weak long wave-length band again shows the characteristic fine structure of the nitroso-group even when fluorine is present in the molecule [*e.g.*, *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine, Table 1(*b*)], and it is very probable that the same fundamental transition as for *C*-nitroso-compounds is involved. The shift to shorter wave-length for the *N*-nitroso-compounds might be attributed to partial electron transfer in the ground state from the lone pair on nitrogen to the antibonding π orbital.

FIG. 2.



(*a*) Diethylnitrosamine in light petroleum.
(*b*) Amyl nitrite in light petroleum.
(*c*) *N*-Nitroso-*ON*-bistrifluoromethylhydroxylamine vapour.
(*d*) Nitrosyl chloride vapour. Optical density scale.

The nitroso-group in *O*-nitroso-compounds, *e.g.*, nitrites, is much less sensitive to solvent changes (Haszeldine and Jander, *loc. cit.*), and shows absorption similar to that for *N*-nitroso-compounds but with marked resolution of the band [Table 1(*c*)]. The strong absorption at shorter wave-length (220—230 mμ) observed in nitrites and nitrosamines is absent from the spectra of *C*-nitroso-compounds. Finally, when the nitroso-group is attached to an auxochrome such as chlorine ($Cl-N=O \longleftrightarrow {}^{+}Cl=N-O^{-}$), there is multiple weak absorption in the visible region [Table 1(*d*); see also Goodeve and Katz, *Proc. Roy. Soc.*, 1939, **172**, *A*, 432]. The two main bands at 475 and 595 mμ may be attributed to singlet–singlet or singlet–triplet transitions in the nitroso-group. The nitroso-group absorption is compared in Fig. 2.

The infra-red spectrum of trifluoronitrosomethane is shown in Table 2; the carbon–fluorine absorption produces the broad bands near 8·0 μ, and the stretching vibration of the nitroso-group is clearly at 6·25 μ. The infra-red spectra of other monomeric *C*-nitroso-compounds have not been reported, and measurements have therefore been made on 2-methyl-2-nitrosopropane and nitrosobenzene. Both these compounds exist as colourless dimers of the type $R{\cdot}N(O-){\cdot}{}^+N(:O)R$ in the solid state, but are converted into the blue or green monomers in solution. The spectrum of dimeric 2-methyl-2-nitrosopropane shows strong C–H absorption at 6·8 μ, but only weak bands elsewhere in the 6·0—7·0 μ region; there is a very strong band at 7·34 μ. The monomer is formed in tetrachloroethylene solution and the 7·34 μ band is considerably reduced in intensity; this band is therefore assigned to the N:O vibration in the dimer. The strong C–H band is at 6·8 μ in the spectrum of the solution, and a new strong band appears at 6·46 μ; this band is clearly the N:O stretching vibration in the monomer. The N–O vibration in the dimer can be assigned to the strong band at 7·88 μ or possibly 8·50 μ. An alternative assignment of the above bands (but less likely in view of the intensity changes) is that the N:O vibration in the dimer is at 6·8 μ with the carbon–hydrogen absorption of the *tert.*-butyl group at 7·35 μ.

Nitrosobenzene dimer shows C–H absorption at 6·93 μ and a strong band at 7·19 μ attributed to the N:O vibration; the last band cannot be the C–H absorption, since nitrobenzene does not have a band here. Medium bands appear at 6·63 and 6·72 μ, and one of these is the ring absorption. In tetrachloroethylene solution the 6·63 μ band (now at 6·61 μ) becomes very strong relative to the C–H band now at 6·9 μ, and the 7·2 μ band disappears; the N:O stretching vibration in the monomer is thus at 6·61 μ.

TABLE 2. *Infra-red spectra.*

$CF_3{\cdot}NO$ vapour (C.S. 82) *	3·16 (w), 3·60 (w), 4·18 (w), 5·10, 5·17 (w doublet), 5·45 (w), 6·25 (vs), 7·83 (vs), 8·0 (vs), 8·47 (s), 9·73 (m), 10·25 (m), 10·5 (w), 12·35 (m), 13·53, 13·68, 13·86 (s triplet).
$CF_3{\cdot}NO_2$ vapour (C.S. 83)	3·39 (w), 3·70 (w), 4·10 (w), 5·66 (w), 6·13, 6·17 (vs doublet), 7·31 (m), 7·64, 7·78, 7·87 (vs triplet), 8·59, 8·64, 8·69, 8·73 (vs quadruplet), 10·0 (w), 11·50, 11·62, 11·72 (s triplet), 13·20, 13·33, 13·44 (vs triplet).

m = medium, s = strong, vs = very strong, w = weak.

* Spectra thus marked have been deposited with the Chemical Society. Photocopies, price 3*s*. 0*d*. per copy per spectrum, post free, may be obtained from the General Secretary on application quoting the C.S. no.

The shift of the N:O absorption from 6·5—6·6 to 6·25 μ when fluorine is present in the molecule parallels the shift in the band for nitro-compounds (see below) and carbonyl compounds (Haszeldine, *Nature*, 1951, **168**, 1028).

Ruff and Giese (*Ber.*, 1936, **69**, 598, 684) reported that trifluoronitrosomethane could not be oxidised (*e.g.*, that there is no reaction with 60% nitric acid after 3 hours, with chromic anhydride in acetic acid, with Caro's acid, with acid permanganate, or with hydrogen peroxide), but in an earlier paper (Haszeldine, *J.*, 1953, 2075) it was shown that vigorous oxidising agents yielded trifluoronitromethane. Yields were low and there was appreciable decomposition. In the same paper the preparation of 1-chloro-2-nitrotetrafluoroethane by reaction of nitrosyl chloride with tetrafluoroethylene under mild conditions was reported, and it follows that oxidation of the nitroso-group (formed initially) to the nitro-group must have occurred readily. In accord with this deduction, it has now been found that trifluoronitromethane can be prepared in high yield (80%) by reaction of the nitroso-compound with oxygen at 100° or with hydrogen peroxide at 50°. The nitro-compound can now be readily purified, and the boiling point originally reported (Haszeldine, *loc. cit.*) is corrected to −31·1°; the nitro-compound has a normal Trouton constant.

Spectra of Trifluoronitromethane.—The ultra-violet absorption spectrum of trifluoronitromethane ($\lambda_{max.}$ 279, ε 11·0; $\lambda_{min.}$ 239, ε 2·0) resembles that of other alkyl and halogeno-alkyl nitro-compounds (cf. *J.*, 1953, 2525), but the intensity of absorption is lower than that for trichloronitromethane. *N*-Nitro-compounds show much more powerful absorption than *C*-nitro-compounds, but at a lower wave-length (*e.g.*, $Me_2N{\cdot}NO_2$ in dioxan, $\lambda_{max.}$ 240 mμ, ε 6300). Nitrates, as representative *O*-nitro-compounds, show a low-intensity inflection at *ca.* 260 mμ and thus have general resemblance to *C*-nitro-compounds, but differ considerably from *N*-nitro-compounds. The reverse is true for *O*-, *C*-, and *N*-nitroso-compounds (see above). The importance of resonance of the type $X{-}N{=}O \longleftrightarrow {}^+X{=}N{-}O^-$ (X = N, O, or Cl) on the absorption spectra of compounds containing nitrogen and oxygen has been emphasised earlier (Haszeldine and Jander, *J.*, 1953, 691), and is again shown by the marked difference in spectra of trifluoro-nitroso- and -nitro-methane.

The infra-red spectrum of trifluoronitromethane (Table 2) shows the asymmetric stretching vibration as a doublet at 6·13, 6·17 μ; tetranitromethane similarly shows a doublet for this band (6·08, 6·19 μ). The symmetric stretching vibration appears as a triplet at 7·64, 7·78, 7·87 μ, and the carbon–fluorine stretching vibration bands are centred on 8·7 μ. The spectrum of trifluoronitromethane supports the assignments made for 1-chloro-2-nitrotetrafluoroethane (*J.*, 1953, 2525), and again shows that the asymmetric and the symmetric band of the nitro-group move to shorter and longer wave-length respectively as the inductive effect of R in $R{\cdot}NO_2$ increases. The C–N vibration in trifluoronitromethane is assigned to the 11·6 μ triplet, and in trifluoronitrosomethane to the 12·35 μ band (cf. $CBr_3{\cdot}NO_2$ 11·9 μ, $CCl_3{\cdot}NO_2$ 11·9 μ, $CClF_2{\cdot}CF_2{\cdot}NO_2$ 11·0 μ); both compounds show the very characteristic well-resolved triplet assigned to the CF_3 deformation (13·20, 13·33, 13·44 μ; 13·53, 13·68, 13·86 μ respectively).

EXPERIMENTAL

Trifluoroiodomethane (*J.*, 1951, 584) was purified and stored *in vacuo.* Nitric oxide, prepared from potassium nitrite, potassium iodide, and sulphuric acid, was passed over calcium chloride, phosphoric anhydride, and soda-lime, and purified by distillation *in vacuo* (Found: *M*, 30·5. Calc. for NO: *M*, 30). Tristrifluoromethylarsine was prepared as described earlier (*J.*, 1952, 2552). Reactions were carried out in sealed silica or Pyrex tubes with the careful exclusion of air or moisture. A Hanovia lamp was used, without the filter, as the source of ultra-violet light.

Reaction of Trifluoroiodomethane with Nitric Oxide.—(a) *Thermal.* Trifluoroiodomethane (1·3 g.), nitric oxide (0·4 g.), and mercury (5 ml.) were sealed in a 50-ml. Pyrex tube and heated in the dark at 100—140° (4 days), then 160° (12 hr.). A yellow solid was deposited on the walls of the vessel, and a blue gas could be seen. A small amount of non-condensable gas was removed, and the volatile products were fractionated to give unchanged trifluoroiodomethane (*ca.* 50%) and a blue gas contaminated with carbon dioxide. The last compound was removed by its preferential absorption by 5% aqueous sodium hydroxide when shaken together for 2—3 min. Further distillation gave trifluoronitrosomethane (3%; 6% based on trifluoroiodomethane used), identified by its infra-red spectrum.

Trifluoroiodomethane (13·9 g.), nitric oxide (4 g.), and mercury (10 ml.), heated to 160° for 6 days in a 100-ml. steel autoclave which was rocked, gave unchanged trifluoroiodomethane, nitric oxide, carbon dioxide, and probably carbonyl fluoride as the only reaction products. After 4 days at 180°, then 2 days at 200°, a similar reaction mixture gave only decomposition products.

In a control experiment trifluoronitrosomethane (0·030 g.) was sealed in a 30-ml. Pyrex tube and heated at 100° (12 hr.), then 145° (24 hr.), without change. After 12 hr. at 160° there was a slight fading of colour, and after 84 hr. at 170° the colour had completely disappeared. The gaseous products were silicon tetrafluoride (mainly), trifluoronitromethane (trace), carbon dioxide, and carbonyl fluoride. A small quantity of a white, water-soluble, crystalline inorganic solid was also formed.

(b) *Photochemical, at greater than atmospheric pressure.* In a typical experiment, trifluoroiodomethane (5·5 g., 0·028 mole), nitric oxide (1·7 g., 0·057 mole), and mercury (15 ml.) were sealed in a 250-ml. silica tube which was fitted with an open-frame heater so that it could be heated and exposed to light. The horizontal tube was shaken vigorously in a vibro-shaker so that the mercury was intimately mixed with the vapour and liquid; this is essential for efficient reaction. The tube was heated to 110° and exposed to ultra-violet light for 7 days. Use of higher temperatures, or longer periods of irradiation, failed to increase the yield substantially. The products from six reaction tubes were combined and distilled *in vacuo* to remove unchanged trifluoroiodomethane (60—80%). The more volatile fraction was mixed with an equal volume of oxygen and kept in the dark for 1 hr. to convert nitric oxide into dinitrogen tetroxide, which was removed by distillation. The almost pure nitroso-compound was finally purified by being shaken with 5% aqueous sodium hydroxide for 10 min. to remove traces of carbon dioxide, etc., and was then redistilled.

An alternative and often more convenient method of purification was as follows: After removal of the excess of nitric oxide as above, the crude nitroso-compound was passed slowly down a vertical glass tube (7 mm., internal diameter) which was cooled on the outside over a 6—8 cm. length by liquid nitrogen in a Dewar vessel. The vertical glass tube passed through the base of the Dewar vessel and was connected by a vacuum-tap to a receiver (50 ml. capacity) which was independently cooled in liquid nitrogen. Under these conditions trifluoronitrosomethane condensed to a blue viscous liquid which flowed down the glass tube, through the tap, and was collected in the receiver; the impurities (carbon dioxide, silicon tetrafluoride, carbonyl fluoride, and traces of trifluoroiodomethane) are solids at −196°, and collected in the tube. The tap was closed, and the purified trifluoronitrosomethane was transferred to a vacuum-system; the process was usually repeated twice to give spectroscopically pure material, containing at most 0·2% of trifluoroiodomethane.

Both methods of purification gave trifluoronitrosomethane in 20% yield based on trifluoroiodomethane taken (*ca.* 80% on trifluoroiodomethane used). The purity was checked by the molecular weight (Found: *M*, 99. Calc. for $CONF_3$: *M*, 99), by spectroscopic examination, or by vapour-pressure measurements. The vapour pressure of trifluoronitrosomethane, measured over the temperature range −99° to −132°, is represented by the equation $\log_{10} p$ (mm.) $= 7{\cdot}674 - 895{\cdot}86/T$, where T is the temperature (K). The b. p. is calculated as −86·6°, the latent heat of vaporisation as 4095 cals./mole, and Trouton's constant as 21·9. Ruff and Giese (*loc. cit.*) reported b. p. −84° for an impure sample (vapour pressure 272 mm. at −99·8°. Calc. from above equation: 347 mm.).

(c) *Photochemical, at less than atmospheric pressure.* A 200-ml. silica tube containing mercury (2 ml.) was filled with a 1 : 1·2 molar ratio of trifluoroiodomethane and nitric oxide to a pressure of 700 mm., and was shaken vigorously whilst exposed to ultra-violet light. Instantaneous reaction with formation of mercuric iodide was apparent, and after 8 hr. the reaction products were treated as above and distilled, to give trifluoronitrosomethane (89%), identified spectroscopically, and unchanged trifluoroiodomethane (6%) and nitric oxide; only small amounts of carbon dioxide and breakdown products were noted.

In similar experiments with total initial pressures of 510, 363, and 109 mm., the yields of trifluoronitrosomethane were 79, 83, and 84%, respectively, with a reaction time of 6 hr. The only disadvantage of this method of preparation is the small amount of trifluoroiodomethane which can be used per experiment in equipment of normal size.

(d) *Formation of trifluoronitromethane.* Trifluoroiodomethane (6·5 g.), nitric oxide (2·0 g.), and mercury (15 ml.) were sealed in a 275-ml. silica tube, heated to 100°, shaken, and irradiated for 4 days. The formation of the nitroso-compound was apparent from the blue colour. The shaking was stopped and the ultra-violet lamp was moved near to the tube. After 2 days the blue colour had disappeared and fractionation gave a non-condensible gas, carbon dioxide, unchanged trifluoroiodomethane, an unidentified product, and trifluoronitromethane (*ca.* 25%), identified by its infra-red spectrum.

Reaction of Tristrifluoromethylarsine with Nitrosyl Chloride and with Nitric Oxide.—Tristrifluoromethylarsine (1·0 g.) and nitrosyl chloride (0·65 g.) were heated in a 50-ml. Pyrex tube at 100° for 2 hr. The products were distilled *in vacuo* through a trap cooled to −140° and the more volatile fraction was shaken with 2% aqueous sodium hydroxide solution (3 min.), then redistilled to give a mixture (0·16 g.) of trifluoronitrosomethane and chlorotrifluoromethane, identified by their infra-red spectra. The yield of the nitroso-compound was *ca.* 2%.

In a second experiment tristrifluoromethylarsine (3·3 g.) and nitrosyl chloride (2·2 g.) were heated from 0° to 200° at atmospheric pressure in a flask connected *via* a reflux condenser at −78° to a trap cooled in liquid nitrogen, so that trifluoronitrosomethane could escape from the reaction mixture as soon as formed. Only small amounts of the nitroso-compound were detected.

An experiment in which tristrifluoromethylarsine and nitrosyl chloride were mixed with mercury in a silica tube and exposed to ultra-violet light failed to yield more than traces of trifluoronitrosomethane.

Tristrifluoromethylarsine (2·0 g.), nitric oxide (0·9 g.), and mercury (10 ml.) were sealed in a 180-ml. silica tube which was vigorously shaken and exposed to ultra-violet light for 5 days. After a preliminary purification of the products in a vacuum-system, the mixture of nitric oxide and nitroso-compound was treated as described above, to give trifluoronitrosomethane (0·085 g., 4%) (Found: *M*, 96), identified by its infra-red spectrum.

Trifluoronitrosomethane from Trifluoroacetyl Iodide.—The iodo-compound (4·5 g.), nitric oxide (1·3 g.), and mercury (10 ml.), sealed in a 180-ml. silica tube, heated (100°), shaken, and irradiated for 4 days, gave mercuric iodide, carbon monoxide, carbon dioxide, an unidentified mercurial, and trifluoronitrosomethane (4%).

Trifluoronitromethane.—In a typical experiment trifluoronitrosomethane (0·100 g.) was sealed with oxygen (700 mm. pressure) in a 40-ml. Pyrex tube and heated at 100° until the blue colour disappeared (*ca.* 10 days). The contents of the tube were pumped slowly through a series of traps cooled in liquid oxygen, and the condensed material was distilled *in vacuo*, to give unchanged trifluoronitrosomethane (0·010 g.), small amounts of decomposition products, and trifluoronitromethane (0·090 g., 78%), b. p. −31·1° (Found: C, 10·5; N, 11·9%; *M*, 115. Calc. for CO_2NF_3: C, 10·4; N, 12·2%; *M*, 115). The infra-red spectrum, b. p., and molecular weight were unchanged after treatment of the nitro-compound with ice-cold 2% aqueous sodium hydroxide for 2 min.

The following vapour pressures have been recorded :

p (mm.)	649·3	673·2	703·2	718·2	735·2	742·2	749·2	758·2	767·2	782·2
Temp. (° c)	−34·4	−33·6	−32·7	−32·3	−31·9	−31·6	−31·5	−31·1	−30·9	−30·5

whence the vapour pressure equation for this limited range is $\log_{10} p$ (mm.) $= 7{\cdot}541 - 1128{\cdot}3/T$, where T = temperature (K). The b. p. is calculated as −31·1°, the latent heat of vaporisation as 5160 cals./mole, and Trouton's constant as 21·3. Haszeldine (*J.*, 1953, 2075) reported b. p. −21° for a sample prepared by vigorous oxidation of trifluoronitrosomethane. The yield of the nitro-compound by the earlier procedure was low and the difference in b. p. (recorded in an isoteniscope) is caused by impurity in the earlier specimen.

An alternative simple method of oxidation of trifluoronitrosomethane involves hydrogen peroxide. The nitroso-compound (0·9 g.) and a 50% excess of 30% hydrogen peroxide were heated in a sealed tube for 4 days. The blue colour had then disappeared, and distillation *in vacuo* gave trifluoronitromethane (76%), identified spectroscopically, and a small amount of carbon dioxide; the aqueous solution gave a positive test for fluoride ion.

Spectra.—A Unicam Spectrophotometer and a Perkin-Elmer 21 Double Beam Spectrophotometer were used. The latter had rock-salt optics. The molar extinction coefficient for vapours is given by $\varepsilon = 760D \times 22{\cdot}4 \times 290/273pl$, where D = optical density, p = gas pressure (mm.), and l = cell length (cm.).

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