Reactions of Fluorocarbon Radicals. Part XIV.[*] *Hexafluoroazoxymethane.*[†]

By J. Jander and R. N. Haszeldine.

[Reprint Order No. 4753.]

Reaction of trifluoronitrosomethane with active carbon or with aqueous sodium hydroxide yields hexafluoroazoxymethane and trifluoronitromethane. Ruff and Giese's claim to have prepared trifluoroformamide from trifluoronitrosomethane is disputed. Ultra-violet and infra-red spectroscopic properties of hexafluoroazoxymethane are presented and discussed. The characteristic wave-lengths in the infra-red for compounds containing nitrogen and oxygen can be used diagnostically for fluorine compounds with only slight change.

Ruff and Giese (*Ber.*, 1936, **69**, 598, 684) obtained impure trifluoronitrosomethane from silver cyanide and fluorine and concluded that the impurity was the colourless, very stable trifluoroformamide, into which the nitroso-compound could be isomerised almost quantitatively by treatment with a variety of reagents including sodium hydroxide and active carbon :

$$CF_3{\cdot}NO \text{ (b. p. } -84°) \longrightarrow F{\cdot}CO{\cdot}NF_2 \text{ (b. p. } -82{\cdot}4°)$$

This reaction would be novel in the chemistry of fluorine compounds since (*a*) it involves the quantitative transfer of fluorine from carbon to nitrogen, and (*b*) the product, which is essentially a derivative of carbonyl fluoride, *i.e.*, an acyl fluoride, is reported to be stable to

---

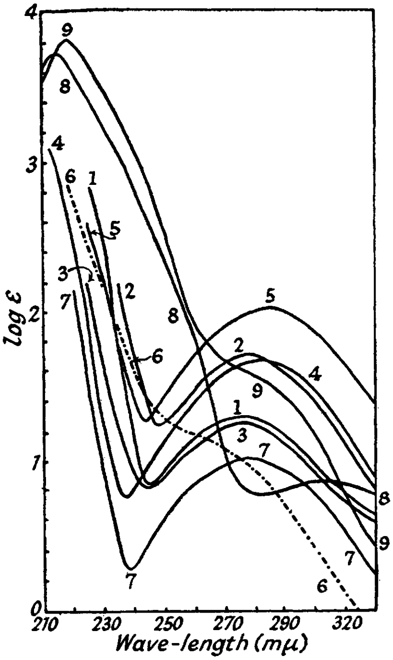
[*] Part XIII, preceding paper.

[†] Presented at the meeting of the American Chemical Society in Chicago, Sept. 1953.

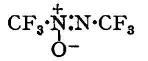
heat, acids, water, and alkali. Re-investigation of the reactions of trifluoronitrosomethane gives results which contradict those of Ruff and Giese.

Pure trifluoronitrosomethane, prepared by the reaction of trifluoroiodomethane with nitric oxide (Haszeldine, *J.*, 1953, 2075; Jander and Haszeldine, *loc. cit.*), is slowly decolorised when heated with active charcoal, and yields a colourless compound $C_2ON_2F_6$ of molecular weight 182 (cf. $F{\cdot}CO{\cdot}NF_2$: *M*, 99) and b. p. 7°, trifluoronitromethane (Haszeldine, *loc. cit.*), and (by decomposition in silica apparatus) carbon dioxide and silicon tetrafluoride. The colourless compound, which shows a normal Trouton constant, could be (I), (II), or (III), and (III) can be eliminated on grounds of colour, since nitrosamines are yellow (Haszeldine and Jander, *J.*, 1954, 691). Distinction between (I) and (II) is made in favour of (I) on spectroscopic grounds.

Hexafluoroazoxymethane (I) shows a weak long-wave-length and a very powerful short-wave-length maximum ($\lambda_{max.}$ 303, ε 17·4; $\lambda_{max.}$ 211, ε 8000; $\lambda_{min.}$ 280, ε 6·0) and thus shows a marked resemblance to azoxymethane (Figure, curve 9) and other azoxyalkanes; these show a weak but marked inflection in the 270—290 mμ region (see Langley, Lythgoe, and Rayner, *J.*, 1952, 4191) instead of the 303 mμ maximum in the fluorine compound.



1, $CH_3{\cdot}NO_2$ *in light petroleum.*
2, $CCl_3{\cdot}NO_2$ *in light petroleum.*
3, $CCl_3{\cdot}NO_2$ *vapour.*
4, $CClF_2{\cdot}CF_2{\cdot}NO_2$ *vapour.*
5, $CClF_2{\cdot}CF_2{\cdot}NO_2$ *in light petroleum.*
6, $EtO{\cdot}NO_2$ *in light petroleum.*
7, $CF_3{\cdot}NO_2$ *vapour.*
8, $CF_3{\cdot}N{:}^{+}\underset{O^-}{N}{\cdot}CF_3$ *vapour.*
9, $CH_3{\cdot}N{:}^{+}\underset{O^-}{N}{\cdot}CH_3$ *vapour.*



$CF_3{\cdot}\underset{O^-}{\overset{+}{N}}{:}N{\cdot}CF_3$ (I) $CF_3{\cdot}O{\cdot}N{:}N{\cdot}CF_3$ (II) $(CF_3)_2N{\cdot}NO$ (III)

Comparison with other compounds containing nitrogen and oxygen is made in the Figure. Definite distinction cannot be made between (I) and (II) on the basis of ultra-violet spectroscopy however, since detailed studies on azo-ethers have not been reported, although it is known that the compound $Ph{\cdot}N{:}N{\cdot}OMe$ is colourless (Bamberger, *Ber.*, 1895, **28**, 225) and that hyponitrous acid has $\lambda_{max.}$ 244 mμ, ε 3550, inflection 294 mμ, ε 25, in 0·1N-sodium hydroxide, and has inflection 244 mμ, ε 80, in 0·1N-hydrochloric acid (Kortüm and Finckh, *Z. physikal. Chem.*, 1940, *B*, **48**, 32).

The infra-red spectrum of the compound $C_2ON_2F_6$ clearly shows it to be (I) and not (II); an azoxy-group, electronically similar to a *C*-nitro-group, shows asymmetric and symmetric stretching vibrations, and these characteristic bands are at 6·37 and 7·80, 7·94 μ for hexafluoroazoxymethane, *i.e.*, shifted to shorter and longer wave-length respectively relative to the corresponding bands in azoxymethane (Table; Langley *et al.*, *loc. cit.*; cf. $CF_3\cdot NO_2$ and $Me\cdot NO_2$ in the Table). The nitrogen–oxygen vibration in the infra-red varies in a characteristic manner depending on whether the oxygen is in a nitroso-, nitro-, or azoxy-group, and whether the nitrogen atom is attached to carbon, nitrogen, oxygen, or halogen. The characteristic wave-lengths are shown in the Table, and it is evident that the wave-lengths established for compounds unsubstituted by fluorine can be used diagnostically, with only slight change, for the corresponding fluorine compounds.

Both trifluoronitromethane and hexafluoroazoxymethane are formed when trifluoronitrosomethane is heated with carbon :

$$3CF_3\cdot NO \longrightarrow CF_3\cdot{}^{+}N(O^{-}){:}N\cdot CF_3 + CF_3\cdot NO_2$$

although breakdown of trifluoromethyl groups is an important side-reaction. The azoxy-compound boils some 90° below azoxymethane (cf. $Me\cdot NO_2$, b. p. 101°, $CF_3\cdot NO_2$, b. p. −31°), again revealing the marked influence of fluorine-substitution on boiling point. Although stable to water, aqueous base or acid, and at moderate temperatures, hexafluoroazoxymethane does not show the stability attributed by Ruff to the products from trifluoronitrosomethane, and it seems very probable that " trifluoroformamide " was actually hexafluoroethane or fully fluorinated methylamine ($CF_3\cdot NF_2$) produced during the fluorination; these colourless compounds boil close to trifluoronitrosomethane, and are thermally and chemically extremely stable.

Ruff and Giese reported that with 8% aqueous sodium hydroxide trifluoronitrosomethane was converted almost quantitatively (42·1 ml. of gas ⟶ 40·6 ml.) into the alkali-stable trifluoroformamide. With pure trifluoronitrosomethane completely different results are now reported. The blue colour rapidly fades when the nitroso-compound is shaken with aqueous base, and there is immediate formation of fluoride with decrease in the amount of gaseous material. The reaction has been followed by infra-red spectroscopic examination : trifluoronitromethane and hexafluoroazoxymethane are the only gaseous products, and there is no product which corresponds to trifluoroformamide; prolonged alkali-treatment completely destroys the gaseous material. Trifluoronitromethane is known to be unstable to aqueous alkali; the azoxy-compound is stable unless shaken with the base. A reaction similar to that observed by Bamberger for nitrosobenzene (*Ber.*, 1900, **33**, 1939) thus occurs, at least in part:

$$3CF_3\cdot NO \longrightarrow CF_3\cdot NO_2 + CF_3\cdot{}^{+}N(O^{-}){:}N\cdot CF_3;\ \text{cf. } 3Ph\cdot NO \longrightarrow Ph\cdot NO_2 + Ph\cdot{}^{+}N(O^{-}){:}NPh$$

Characteristic vibrations of compounds containing nitrogen and oxygen.

(a) *Nitroso-compounds.*

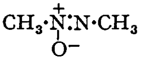
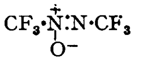
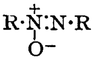
C–NO monomers		N–NO		O–NO		X–NO	
$Me_3C\cdot NO$	6·46 μ	$R_2N\cdot NO$	7·10—7·40 ($N{:}O$) 9·15—9·55 ($N–O$)	$RO\cdot NO$	5·76 6·07 6·23 } triplet * ($N{:}O$) 12·5 ($N\cdot O$)	NOCl	5·50 5·60 } doublet
$Ph\cdot NO$	6·61	$(CF_3O)(CF_3)N\cdot NO$	7·62 ($N{:}O$) 9·35 ($N–O$)			NOBr	5·55
$CF_3\cdot NO$	6·25					NOF	5·42

* Rotational isomerism.

(b) *Nitro-compounds.*

	C–NO_2			N–NO_2		O–NO_2
$Me\cdot NO_2$	6·38 (as.)	7·25 (sym.)	$R_2N\cdot NO_2$	6·1–6·5 (as.) 7·2–8·0 (sym.)	$RO\cdot NO_2$	6·12 (as.) 7·80 (sym.)
$CBr_3\cdot NO_2$	6·28 (as.)	7·66 (sym.)				
$CCl_3\cdot NO_2$	6·21 (as.)	7·65 (sym.)				
$CClF_2\cdot CF_2\cdot NO_2$	6·18 (as.)	7·85 (sym.)	R = alky			
$CF_3\cdot NO_2$	6·13 6·17 } doublet (as.)	7·64 7·78 7·87 } triplet (sym.)				

(c) *Azoxy-compounds.*

 $CH_3\cdot\underset{O^-}{\overset{+}{N}}{:}N\cdot CH_3$	6·55 (as.)	7·45 (sym.)	 $CF_3\cdot\underset{O^-}{\overset{+}{N}}{:}N\cdot CF_3$	6·37 (as.) 7·80 7·94 } doublet (sym.)
 $R\cdot\underset{O^-}{\overset{+}{N}}{:}N\cdot R$	6·6–6·7 (as.)	7·6–7·8 (sym.)		

A possible reaction scheme is formation in solution of an ion such as $CF_3\cdot{}^+NH(O^-)\cdot OH$ which, by reduction of the nitroso-compound, yields the hydroxylamine, $CF_3\cdot NH\cdot OH$, and trifluoronitromethane. The decomposition of the hydroxylamine into fluoride and carbonate would be consistent with the known properties of compounds containing the $-CF_2\cdot NH-$ groups; the competitive reaction with trifluoronitrosomethane would yield hexafluoroazoxymethane.

It must thus be concluded that trifluoronitrosomethane can be converted into hexafluoroazoxymethane and trifluoronitromethane, but not into trifluoroformamide; this compound has yet to be prepared.

EXPERIMENTAL

Trifluoronitrosomethane was prepared from trifluoroiodomethane and nitric oxide by the method described earlier (*J.*, 1953, 2075, preceding paper); its purity was tested by infra-red spectroscopic examination.

Hexafluoroazoxymethane.—In a typical experiment trifluoronitrosomethane (0·300 g.) was sealed in a 50-ml. silica tube with decolorising charcoal (1·5 g.) which had been activated *in vacuo* at 150° for 1 hr. Only a pale blue colour was apparent at room temperature and this disappeared after the tube had been heated at 100° for 48 hr. The products (0·24 g.), removed by pumping for 1 hr. with the tube heated at 100°, were distilled in a vacuum, to give trifluoronitromethane (0·025 g., 7%), identified by its infra-red spectrum, carbon dioxide, silicon tetrafluoride, etc. (0·085 g.), and *hexafluoroazoxymethane* (0·130 g., 47%), b. p. 6·9° (Found: C, 13·5; N, 15·8; F, 61·7%; *M*, 182. $C_2ON_2F_6$ requires C, 13·2; N, 15·4; F, 62·6%; *M*, 182).

The following vapour pressures were recorded for hexafluoroazoxymethane:

p (mm.)	609·1	663·1	699·5	716·0	742·5	750·5	763·0	771·5
Temp. (°c)	1·6	3·6	4·9	5·4	6·4	6·6	7·0	7·3

whence the vapour pressure equation is $\log_{10} p$ (mm.) $= 7{\cdot}886 - 1407{\cdot}0/T$ (T = temp., °K), the b. p. is calculated as 6·9°, the latent heat of vaporisation is 6410 cals./mole, and Trouton's constant is 22·9.

Hexafluoroazoxymethane is stable to water, 10% hydrochloric acid, or 10% aqueous sodium hydroxide at 20° during 20 days.

Reaction of Trifluoronitrosomethane with Aqueous Sodium Hydroxide.—The nitroso-compound (0·050 g.), shaken with 10% aqueous sodium hydroxide (15 ml.) for 12 hr. in a sealed 50-ml. Pyrex tube, was completely destroyed. The product (0·030 g.) (Found: *M*, 129. Calc. for CO_2NF_3: *M*, 115. Calc. for $C_2ON_2F_6$: *M*, 182) was shown by infra-red spectroscopic examination to be trifluoronitromethane (80%), and hexafluoroazoxymethane (20%).

In a second experiment trifluoronitrosomethane (0·030 g.) was sealed in a 25-ml. Pyrex tube with 7·5% aqueous sodium hydroxide (4·5 ml.) and shaken for 25 min. The infra-red spectrum of the residual volatile material (0·016 g.) revealed trifluoronitrosomethane, trifluoronitromethane, and hexafluoroazoxymethane in an approximate ratio 1 : 6 : 3. The mixture was resealed in the same reaction vessel and was shaken for a further 20 min. Spectroscopic examination of the product (0·003 g.) showed trifluoronitrosomethane, trifluoronitromethane, and hexafluoroazoxymethane in an approximate ratio 1 : 70 : 35. The product, resealed and shaken for 85 min., gave only trifluoronitromethane and hexafluoroazoxymethane (0·001 g.) in a ratio of 2 : 1. Qualitative tests on the aqueous solution for fluoride and nitrite (or nitrate) were positive.

Spectra.—A Unicam Spectrophotometer and Perkin-Elmer Model 21 Double Beam Spectrophotometer were used. The infra-red spectra of hexafluoroazoxymethane and ethyl nitrate are recorded in the annexed Table.

Infra-red spectra.

$CF_3\cdot N{:}{}^+N(O^-)\cdot CF_3$ (C.S. 84*) Main bands	6·37 (vs), 6·65 (w), 7·07 (w), 7·36 (m), 7·57 (s), 7·80 (vs), 7·94 (vs), 8·23 (s), 8·50 (vs), 8·64 (vs), 9·00 (s), 9·83 (w), 10·67 (vs), 12·90, 12·96, 13·02 (vs triplet), 15·1 (vs).
$EtO\cdot NO_2$ (C.S. 85*) Main bands	3·35, 3·45 (s doublet), 6·12 (vs), 6·90 (m), 7·30 (m), 7·80 (vs), 9·87 (vs), 11·0 (vs), 11·6 (vs), 13·14 (m), 14·23 (m).

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

* See footnote, Part XIII, p. 916.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, October 27th,* 1953.]