Addition of Free Radicals to Unsaturated Systems. Part VI.*
Free-radical Addition to the Nitroso-group.

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Trifluoronitrosomethane is rapidly and quantitatively converted into the brownish-red *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine on exposure to ultra-violet light; this is interpreted as involving a free-radical addition to the N–O bond, with the radical $CF_3 \cdot \dot{N} \cdot O \cdot CF_3$ as intermediate. Other possibilities [particularly $(CF_3)_2N \cdot O \cdot NO$] for the product are considered and discarded. Spectroscopic evidence is presented.

TRIFLUORONITROSOMETHANE (Haszeldine, *J.*, 1953, 2075; Haszeldine and Jander, *J.*, 1953, 4172) is a deep blue monomeric gas which condenses to a deep blue liquid. Its Trouton constant (21·9) indicates that the liquid is not associated. As pointed out earlier, the perfluoroalkylnitroso-compounds differ from other nitroso-compounds, since they cannot isomerise in the same way as their unsubstituted analogues ($>CH \cdot NO \longrightarrow >C\colon N \cdot OH$) and they do not dimerise, even at $-150°$, to give dimers of the type (I).

Trifluoronitrosomethane is completely stable in the dark, even after several years, but on exposure to light, and particularly to ultra-violet light, the blue gas (b. p. $-87°$) changes almost quantitatively into a brownish-red gas of much higher boiling point (10°). This product is stable at moderate temperatures, and is unaffected by water or hydrochloric acid, but is decomposed by aqueous sodium hydroxide; it has a normal Trouton constant (21·5). The compound, $C_2O_2N_2F_6$, is not the dimer of the type (I; R = CF_3), since it is deeply coloured; furthermore the blue trifluoronitrosomethane is not liberated when the

compound is heated alone or is dissolved in an organic solvent. All known dimers of nitroso-compounds are colourless (even when R = Ph), and revert, at least in part, to the coloured monomer when heated or dissolved. Possible constitutions are (II)—(IX), and that the compound is *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine (IX) is shown by spectroscopic evidence.

Absorption of $C_2O_2N_2F_6$.
Ultra-violet spectrum.

Vapour	$\lambda_{max.}$ 374 mμ	$\varepsilon_{max.}$ 20	$\lambda_{min.}$ 320 mμ	$\varepsilon_{min.}$ 8·5
Slight inflections	398 mμ, ε 16·6	390 mμ, ε 18·4	378 mμ, ε 19·5	368 mμ, ε 19·5
	356 mμ, ε 18·0	349 mμ, ε 16·0	341 mμ, ε 12·5	

Infra-red spectrum of vapour in 5—10-μ region (C.S. 81 *) 5·47, 5·55 (v.s. doublet), 5·65 (w), 6·14 (w), 6·65 (v.w.), 7·62 (v.s.), 7·85 (v.s.), 7·98 (m), 8·19 (v.s.), 8·83 (w), 9·35 (v.s.), 10·20 (v.s.), 11·75 (v.s.), 12·98 (v.s.), 13·98 (v.s.).

* Spectra thus denoted have been deposited with the Society. Photocopies may be obtained, price 3*s.* 0*d.* each per spectrum, on application, stating the C.S. number, to the General Secretary.

Its ultra-violet spectrum (Table; see also Fig. in preceding paper) shows a maximum at 374 mμ with fine structure from 340 to 400 mμ. The following possible constitutions can thus be discarded on the basis of chemical properties and colour : (II), since hypo-

* Parts I—V, *J.*, 1952, 2504; 1953, 1199, 1592, 3559, 3565.

nitrites and azo-ethers are colourless and unstable (HO·N:N·OH in 0·1N-HCl, inflection 244 mμ, ε 80; in 0·1N-NaOH, $\lambda_{max.}$ 244 mμ, ε 3550, inflection 294 mμ, ε 25; Körtum and Finckh, *Z. physikal. Chem.*, 1940, **48**, *B*, 32. Ph·N:N·OMe is colourless; Bamberger, *Ber.*, 1895, **28**, 225); (III) and (VI), since they would be colourless like an azoxy-compound (MeN:NMe·O⁻ in EtOH : $\lambda_{max.}$ 217 mμ, ε 7250; inflection 274 mμ, ε 45; Langley, Lythgoe, and Rayner, *J.*, 1952, 4191); (IV), since *iso*nitramines are colourless [*e.g.*, *ON*-dimethyl-*iso*nitramine, Me·N:N(OMe)·O⁻; Franchimont and Umbgrove, *Rec. Trav. chim.*, 1896, **15**, 213]; (V), since it would be colourless; and (VIII), since nitramines are colourless (see preceding paper). Both (VII) and (IX) are possible on grounds of colour (see preceding paper). Compounds analogous to (VII) are unknown, and would be expected to be unstable, and to have an ultra-violet spectrum like that of a nitrite, since the amine nitrogen can contribute little to resonance :

$$(CF_3)_2N \cdot O \cdot N {=} O \longleftrightarrow (CF_3)_2N {-} \overset{+}{O} {=} N {-} O^-$$

cf.
$$(CF_3O)(CF_3)N \cdot N {=} O \longleftrightarrow (CF_3O)(CF_3)\overset{+}{N} {=} N {-} O^-$$
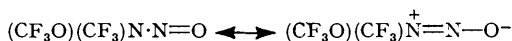
Unlike nitrites and nitrosamines, $C_2O_2N_2F_6$ does not show a high-intensity band in the near ultra-violet, although the end-absorption is strong (ε 540 at 220 mμ, 900 at 210 mμ). Its absorption maximum lies very close to that of the β-methyl ester of Traube's compound or to that of a nitrosamine (see preceding paper), and it is noteworthy that *ON*-dimethyl-*N*-nitrosohydroxylamine is described as a stable yellow oil (Boese, Jones, and Major, *J. Amer. Chem. Soc.*, 1931, **53**, 3530). This suggests that (IX) is much more probable than (VII).

The infra-red spectrum of the compound $C_2O_2N_2F_6$ is also in favour of (IX). It is known that there is only a slight shift (<0·5 μ) in the characteristic vibrations of nitro-, nitroso-, and azoxy-compounds, when fluorine is substituted on the α-carbon atom or atoms (Haszeldine, *J.*, 1953, 2525; Haszeldine and Jander, in the press). The spectrum of $C_2O_2N_2F_6$ (Table) shows the carbon–fluorine vibration at 8·19 and possibly 7·85 μ; there are no strong bands between 5·7 and 7·5 μ, the region shown to be characteristic of the nitrite group. The strong bands at 7·62 (N=O) and 9·35 μ (N—O) fall, however, into the region shown in the preceding paper to be characteristic of nitrosamines, *i.e.*, are in accord with constitution (IX). If the compound had constitution (VII) then the doublet at 5·47, 5·55 μ, and the 10·20, 11·75, or 12·98 μ bands would have to be assigned to the —O·NO system, and the shifts from the usual nitrite vibrations would be abnormally large; on the basis of (IX), the 5·5-μ doublet is assigned to a combination frequency, and the fact that it is at a similar wave-length to the N:O vibration in nitrosyl chloride (Table 2, preceding paper) is probably fortuitous.

The spectroscopic evidence is thus in favour of (IX), but full confirmation of the above argument must await a detailed chemical investigation in a field where there are at present no established reference compounds.

If it is assumed that on irradiation trifluoronitrosomethane decomposes into a trifluoromethyl radical and nitric oxide, then the following mechanism for the formation of *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine can be suggested :

$$CF_3 \cdot NO \xrightarrow{h\nu} CF_3 \cdot + NO$$

$$CF_3 \cdot + CF_3 \cdot N {=} O \longrightarrow CF_3 \cdot \overset{\cdot}{N} \cdot O \cdot CF_3$$

$$CF_3 \cdot \overset{\cdot}{N} \cdot O \cdot CF_3 + NO \longrightarrow CF_3 \cdot N(NO) \cdot O \cdot CF_3$$

or
$$CF_3 \cdot \overset{\cdot}{N} \cdot O \cdot CF_3 + CF_3 \cdot NO \longrightarrow CF_3 \cdot N(NO) \cdot O \cdot CF_3 + CF_3 \cdot \longrightarrow etc.$$
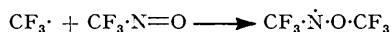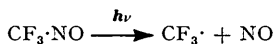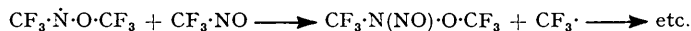
The addition of a trifluoromethyl radical to a carbon–carbon double bond is well established (see, *e.g.*, Parts I—V), but free-radical addition to a nitrogen–oxygen double bond has not been noted earlier. The CF_3 radical initiates the reaction by attack on the more negative atom, to give the relatively more stable radical [cf. (VII) which could be formed by a similar mechanism involving attack on the nitrogen atom to give $(CF_3)_2N \cdot O$ as inter-

mediate]. The chain reaction similar to that proposed for the reaction of trifluoroiodo-methane with olefins (Part I) explains why compounds of the type $(CF_3)_2N\cdot O\cdot CF_3$ or $CF_3\cdot N(NO)\cdot O\cdot NO$ are not formed. Free-radical attack on the oxygen atom of a C:O group in a quinone has been established recently (Waters *et al.*, *J.*, 1950, 1764; 1952, 4666). Support for the above radical mechanism is given by the isolation of hexafluoroethane as by-product.

Further studies on free-radical addition reactions with nitroso-compounds will be described in a later paper.

EXPERIMENTAL

Trifluoronitrosomethane, prepared from trifluoroiodomethane or from silver trifluoroacetate by the methods described earlier (Haszeldine, *J.*, 1953, 2075; Haszeldine and Jander, *J.*, 1953, 4172), was purified by distillation *in vacuo*.

Photochemical Reaction of Trifluoronitrosomethane.—Trifluoronitrosomethane (0·1 g.), sealed in a 0·5-ml. Pyrex tube and left in the dark for 4—5 years, was recovered unchanged.

The nitroso-compound (0·95 g.) was kept in a previously evacuated 3-l. soda-glass bulb sealed to an 80-ml. trap. The bulb was painted black, but the trap was left exposed to diffuse daylight for 2 weeks. The condensed nitroso-compound was then green. Fractionation *in vacuo* gave N-*nitroso*-ON-*bistrifluoromethylhydroxylamine* (0·19 g., 20% conversion, 95% yield), a reddish-brown liquid, b. p. 10° (Found : C, 12·0; N, 14·2%; *M*, 198. $C_2O_2N_2F_6$ requires C, 12·1; N, 14·1%; *M*, 198), and unchanged trifluoronitrosomethane.

In another experiment trifluoronitrosomethane (0·20 g.) was kept in a previously-evacuated 3-l. bulb and exposed to full daylight (and sunlight) for 36 hr. The condensed green liquid was fractionated to give N-nitroso-*ON*-bistrifluoromethylhydroxylamine (0·15 g., 75% conversion). The unchanged starting material was returned to the bulb and left until the colour of trifluoro-nitrosomethane had disappeared (*ca.* 7 weeks). Distillation and spectroscopic analysis revealed N-nitroso-*ON*-bistrifluoromethylhydroxylamine (0·194 g., 97% total), hexafluoroethane (4 mg., 2%), silicon tetrafluoride (1 mg.), trifluoronitromethane (*ca.* 1 mg.), and trifluoronitrosomethane (*ca.* 1 mg.).

An almost quantitative yield of N-nitroso-*ON*-bistrifluoromethylhydroxylamine was obtained by exposure of trifluoronitrosomethane (0·05 g.) in a 5-ml. Pyrex tube to ultra-violet light. There was *ca.* 10% reaction after 1 hr. and complete reaction after 40 hr.

Properties of N-*Nitroso-*ON-*bistrifluoromethylhydroxylamine.*—The vapour pressure, measured between $-1°$ and $+10°$, is given by $\log_{10} P$ (mm.) $= 7\cdot576 - 1329\cdot1/T$, where T is the temperature (K). The b. p. is calculated as 9·9°, the latent heat of vaporisation as 6080 cal./mole, and Trouton's constant as 21·5.

Reactions of N-*Nitroso-*ON-*bistrifluoromethylhydroxylamine.*—(a) *On being heated.* The compound (0·050 g.), heated at 100° for 1 hr. in a 5-ml. silica tube, became slightly paler. After 3 days a small amount of a non-condensable gas had been formed, and distillation of the residual material gave a fraction (0·045 g.) shown by infra-red examination to contain unchanged starting material and an unidentified compound characterised by strong bands at 6·0 and 6·65 μ; the mixture (*M*, 183) could not be separated by distillation *in vacuo*. Trifluoronitrosomethane was not a reaction product. Prolonged heating (4 weeks) caused attack on the silica tube.

(b) *With aqueous reagents.* There was no reaction when N-nitroso-*ON*-bistrifluoromethyl-hydroxylamine was kept with water or 20% hydrochloric acid at room temperature, or at 50° for 6 hr.

Decomposition was complete after 24 hr. in a sealed tube with 10% sodium hydroxide at room temperature. A trace of hexafluoroethane was detected in the otherwise unidentified small amount of gaseous product, and qualitative tests on the aqueous solution for fluoride and nitrite were positive.

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