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ADDITION REACTIONS BETWEEN O-NITROSOBIS(TRIFLUOROMETHYL)HYDROXYLAMINE AND FLUORINATED OLEFINS

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SUMMARY

O-Nitrosobis(trifluoromethyl)hydroxylamine gives addition products at room temperature with 1,1-difluoro-2,2-dichloroethylene and 1,1-difluoro-2-fluoro-2-bromoethylene. No reactions occurred with a few other chlorinated and fluorinated olefins even at elevated temperatures.

INTRODUCTION

Hitherto, the chemistry involving the reactions of O-nitrosobis-(trifluoromethyl)hydroxylamine is limited to a few papers since its discovery by Haszeldine and Jander in 1954 [1]. It undergoes hydrolysis to afford the corresponding bis(trifluoromethyl)hydroxylamine [2]. Later in 1974, Vorob'ev, Filator and Englin found that O-nitrosobis(trifluoromethyl)hydroxylamine reacts with PCl_5 and S_2F_{10} to afford $(CF_3)_2NOPCl_5$ and $(CF_3)_2NOSF_5$ respectively [3]. A recent report highlights the ease of cleavage of the $(CF_3)_2NO$-NO bond in its reactions with $(CF_3)_3M$ (M = P, As and Sb) to give oxidation and substitution products [4]. This paper describes further cleavage reactions of $(CF_3)_2NONO$ extended to a couple of halogenated olefins.

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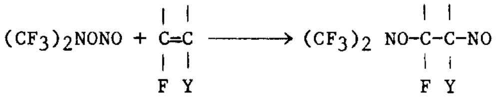
RESULTS AND DISCUSSION

O-Nitrosobis(trifluoromethyl)hydroxylamine reacts slowly at room temperature with 1,1-dichloro-2,2-difluoroethylene to yield a 1:1 addition compound (I) in 86% yield, based on the amount of the olefin used. Compound (I) is a deep blue, heavy liquid, characteristic of nitroso compounds.

The reaction between O-nitrosobis(trifluoromethyl)hydroxylamine and bromotrifluoromethylene in a 1:1 ratio at room temperature follows more or less the same course. On fractionation of the reaction mixture, a deep blue heavy liquid (II) was isolated at -55°C (passed the -45°C trap). The yield was 33.5% based on the amount of bromotrifluoroethylene used. Elemental analyses showed that compounds (I) and (II) are 1:1 addition compounds.

O-Nitrosobis(trifluoromethyl)hydroxylamine gave no reactions with perfluorocyclohexene, octofluoro-2-butane, 1,1-difluoroethylene, tetrachloroethylene and trichloroethylene even when the mixtures were heated to 80°C for 3 days. Under these reaction conditions, only about 90% of reactants could be recovered. There were already signs of some decomposition of the hydroxylamine. There was, however, no evidence of addition products.

The above reactions between O-nitrosobis(trifluoromethyl)-hydroxylamine and the halogenated olefins can probably be represented by the equation:



$$(CF_3)_2NONO + \underset{F}{\overset{F}{C}}{=}\underset{Y}{\overset{X}{C}} \longrightarrow (CF_3)_2\ NO\text{-}\underset{F}{\overset{F}{C}}\text{-}\underset{Y}{\overset{X}{C}}\text{-}NO$$

I : X = Y = Cl

II: X = Br, Y = F

This is because of the nucleophilic character of the bis(trifluoromethyl)nitroxy group which attacks the carbon containing the more electronegative fluorine atoms.

The structures of the derivatives are confirmed by their infrared spectra. They show characteristic absorption due to the nitroso and bis(trifluoromethyl)nitroxy groups. A tentative assignment of the infrared bands is summarised in Table 1.

The above results suggest the need for further research to rationalise the way O-nitrosobis(trifluoromethyl)hydroxylamine reacts with substituted olefins. The findings also open up new possibilities involving its reactions with other unsaturated organic compounds.

EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 337 Grating Infrared Spectrophotometer which covers the range 4000-400 cm^{-1}. O-Nitrosobis(trifluoromethyl)hydroxylamine was prepared according to Emeleus and co-workers [4]. The substituted olefins used in the reactions were obtained from The Matheson Co, N.J., USA.

Reaction of 1,1-dichloro-2,2-difluoroethylene with O-nitrosobis(trifluoromethyl)hydroxylamine

1,1-Dichloro-2,2-difluoroethylene (0.3900 g, 2.93 mmoles) and O-nitrosobis(trifluoromethyl)hydroxylamine (0.5924 g, 2.99 mmoles) *in vacuo* were condensed together into a Pyrex glass ampoule of 100 ml capacity. The sealed ampoule was allowed to stand at room temperature for 14 hours. A deep blue liquid remained in the ampoule. The mixture was fractionated immediately to give two main fractions:

i a deep blue liquid, (I) (0.5320 g, 1.61 mmoles), trapped at the -60°C trap (passed the -35°C trap). The yield was 55%, based on the amount of 1,1-dichloro-2,2-difluoroethylene used. (Analyses gave: mol. wt. 331; C, 15.49%, Cl, 22.36%, F 45.53%; $C_4Cl_2F_8N_2O_2$ requires mol. wt.; 331; C, 14.50%, Cl, 21.45%, F, 45.92%.) The infrared spectrum showed the following absorptions: 1800, 1790(vw) (doublet), 1620(m), 1325(vs), 1275(vs), 1235(vs), 1218(s), 1180(w), 1142(m), 1045(m), 980(m), 890(w), 855(m), 835(w) and 715(m) cm^{-1}.

ii a yellow liquid (0.4181 g) trapped at the -126°C trap. It was shown by the infrared spectrum to be a mixture of the reactants, namely, O-nitrosobis(trifluoromethyl)hydroxylamine and 1,1-dichloro-2,2-difluoroethylene. The second fraction was allowed to stand in a sealed ampoule for one more day. It yielded another deep blue liquid (0.2868 g, 0.87 mmole), which was trapped at -60°C (passed the -35°C trap). The infrared spectrum and molecular weight determination showed that it was the same substance as the deep blue liquid (I) obtained previously. The total yield of liquid (I) was 86%, based on the amount of 1,1-dichloro-2,2-difluoroethylene used. A mixture of unreacted O-nitrosobis(trifluoromethyl)hydroxylamine and 1,1-dichloro-2,2-difluoroethylene (0.1140 g) was recovered at the -196°C trap. A trace amount of chlorine was also detected in this mixture. When the mixture was passed into silver nitrate solution, a white precipitate of silver chloride was formed.

TABLE 1

The vibrational spectra* of addition products of $(CF_3)_2NONO$ and olefins

$(CF_3)_2NO.C_2Cl_2F_2.NO$	$(CF_3)_2NO.C_2BrF_3.NO$	Tentative Assignment
1800 1790 doublet, vw		
1620 m	1610 1595 doublet, m	N=O stretching of C-N=O group
1325 vs	1325 vs	C-F stretching
	1305 sh	
1275 vs	1275 sh	
	1238 vs	
1235 vs	1238 vs	
1218 s	1220 s	
1180 w	1182 m	
1142 m	1145 m	
	1100 m	
1045 m	1042 m	N-O stretching of $(CF_3)_2NO$ group
980 m	970 m	C-N-C stretching
890 w	910 w	
855 m		
835 w	832 m	
	785 w	
	740 730 715 m(triplet)	CF_3 deformation
715 m		

* observed frequencies in cm^{-1}

Vapour pressure measurements of the deep blue liquid (I) over the temperature range of 30°C to 58°C can be represented by the following equation:

$$\log_{10}P(\text{mm}) = 12.69 - \frac{3333}{T}$$

Physical constants derived by the vapour pressure measurements give:

Latent heat of vaporization: 15.3 Kcal/mole

Extrapolated boiling point : 67°C

TABLE 2

Vapour pressures of $(CF_3)_2NOC_2Cl_2F_2NO$

P(mm)	$\log_{10}P$(mm)	T(°C)	T(K)	$(^1/T)\times10^{-3}(K^{-1})$
47.0	1.672	30.0	303	3.300
75.5	1.878	35.0	308	3.247
95.0	1.978	39.0	312	3.205
127.0	2.104	42.0	315	3.175
191.0	2.281	45.0	318	3.145
238.0	2.377	47.0	320	3.125
270.0	2.431	49.0	322	3.106
314.0	2.497	51.0	324	3.086
422.0	2.625	53.0	326	3.067
442.0	2.645	55.0	328	3.049
554.0	2.744	57.0	330	3.030

Reaction of bromotrifluoroethylene with O-nitrosobis(trifluoromethyl)hydroxylamine

Bromotrifluoroethylene (0.5859 g, 3.64 mmoles) and O-nitrosobis(trifluoromethyl)hydroxylamine (0.7103 g, 3.59 mmoles) were condensed *in vacuo* into a pyrex glass ampoule of 80 ml capacity. After standing for twenty hours at room temperature, a dark-green liquid and a pale yellowish-orange gas remained in the ampoule.

After fractionation, there was a drop of heavy colourless nonvolatile liquid left in the glass ampoule. The volatile products on fractionation gave:

i a colourless liquid trapped at the -20°C trap (passed the -10°C trap). The yield was 0.2172 g. (Elemental analysis gave C, 15.73%, Br, 14.2%, F, 33.8.) The infrared spectrum showed absorptions at 1780, 1760 (m, doublet), 1610(m), 1340sh, 1320(vs), 1295sh, 1275(vs), 1220(s), 1180(m), 1155(m), 1135sh, 1080(m), 1040(w), 970(s), 920(w), 905(w), 820(w), 790(sh) and 715(s) cm^{-1}.

ii a deep-blue liquid (II) (0.4393 g, 1.22 mmoles) trapped at the -55°C trap (passed the -45°C trap). The yield was 33.5%, based on the amount of bromotrifluoroethylene used. Analysis gave C, 12.94%, F, 46.63%, Br, 23.61%, N, 7.18%; $C_4F_9BrN_2O_2$ requires C, 13.37%, F, 47.63%, Br, 22.28%, N, 7.80%. The infrared spectrum showed absorptions at 1610, 1595(m, doublet), 1325(vs), 1305(sh), 1275(vs), 1238(vs), 1220(s), 1182(m), 1145(m), 1100(m), 1042(m), 970(m), 910(w), 832(m), 785(w) and 740, 730, 715(m, triplet) cm^{-1}.

iii a mixture of the reactants, namely, bromotrifluoroethylene and O-nitrosobis(trifluoromethyl)hydroxylamine (0.4891 g) was recovered at the -196°C trap.

Vapour pressure measurements of the deep blue liquid (II) over the temperature range of 3°C to 34.5°C can be represented by the equation:

$$\log_{10}P(\text{mm}) = 7.772 - \frac{1782}{T}$$

which gives:

Latent heat of vaporization: 8.15 Kcal/mole

Extrapolated boiling point : 91°C

Trouton's constant : 22.4

TABLE 3

Vapour pressures of $(CF_3)_2NO.C_2BrF_3.NO$

P(mm)	$\log_{10}$Pmm)	T(°C)	T(K)	$(^1/T)\times10^{-3}(K^{-1})$
21.5	1.332	3.0	276.0	3.623
27.5	1.439	8.0	281.0	3.559
34.0	1.531	12.0	285.0	3.509
38.0	1.580	15.0	288.0	3.472
46.0	1.663	18.5	291.5	3.431
51.5	1.712	21.0	294.0	3.401
58.0	1.763	23.0	296.0	3.378
67.0	1.826	26.5	299.5	3.339
76.0	1.881	29.5	302.5	3.306
95.0	1.978	34.5	307.5	3.252

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