REPLACEMENT OF THE NITROSO GROUP IN PERFLUORONITROSOALKANES

(UDC 542.91 + 547.231 + 546.16)

B. L. Dyatkin, A. A. Gevorkyan, and I. L. Knunyants

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10,
pp. 1873-1875, October, 1965
Original article submitted December 21, 1964

In the investigation of the reactivity of perfluoronitrosoalkanes, we noted a lability of the nitroso group in tert-perfluoronitrosobutane $(CF_3)_3C{-}N = O$, where the C−N bond easily undergoes oxidation [1] and hydrogenolysis [2]. This mobility also is manifested in the easy exchange reaction of $(CF_3)_3C{-}N = O$ with halogens. Exchange occurs when a mixture of the reagents is heated to 60-70° for several hours. It is interesting to note that the nitroso compound in the absence of halogens is comparatively stable under these conditions; evidently cleavage of the C−N bond results from the attack of a radical-like halogen particle

$$X_2 \rightleftarrows 2X\cdot$$

$$(CF_3)_3C - N = O \xrightarrow{X\cdot} (CF_3)_3C - X + \dot{N}O$$

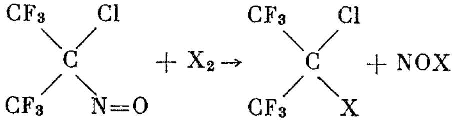
$$\dot{N}O \xrightarrow{X\cdot} NOX$$

The action of Cl_2 and Br_2 leads to $(CF_3)_3CCl$ and $(CF_3)_3CBr$ in yields close to 60%; at the same time NOCl and NOBr are formed. Under the action of I_2, on the other hand, NO is formed and oxidizes the nitrosoalkane. Hence, together with $(CF_3)_3CI$ (33% yield), after hydrolysis, $(CF_3)_3COH$ is obtained (46% yield):

$$\begin{array}{l}(CF_3)_3C{-}N{=}O \xrightarrow{I\cdot} (CF_3)_3C{-}I + NO \\ \big|\xrightarrow{NO} [(CF_3)_3C{-}O{-}N{=}O] \xrightarrow{H_2O} (CF_3)_3C{-}OH\end{array}$$

The synthesis of tert-perfluorobutyl halides from the readily available $(CF_3)_3C{-}N = O$ is of interest for synthesis.

Analogously to tert-perfluoronitrosobutane, 2-chloro-2-nitrosoperfluoropropane also reacts with halogens:



The exchange, as is shown in the case of the action of Br_2, is accompanied by oxidation at the C−N bond, with the formation, after hydrolysis, of perfluoroacetone hydrate, in about 10% yield.

The ease of exchange depends to a great degree upon the nature of the radical bonded to the nitroso group. The stability of the tertiary radical $(CF_3)_3C\cdot$ is due to the fact that its unpaired electron is concentrated among the nine fluorine atoms. The radical $(CF_3)_2CCl\cdot$ is a secondary radical; however, the presence of chlorine at the radical center brings its properties close to those of the tertiary radical [3]. When the nitroso group is bonded to a less stable perfluorocarbon radical, another picture is observed. Thus, 1-chlorotrifluoro-2-nitro-1-nitrosoethane $O_2NCF_2CFCl{-}N = O$, when heated with Cl_2, forms $O_2NCF_2CFCl_2$, in 85% yield; however, the action of Br_2 and I_2, just like heating the nitroso compound in the absence of halogens, leads to the same dichloride in 50% yield. Evidently the radical $O_2NCF_2CFCl\cdot$ is capable of stabilizing Cl, but not Br or I, and in this case preferentially undergoes disproportionation, with the formation chiefly of the dichloride. 1-Chlorotrifluoro-1,2-dinitroethane of course in small amounts has been isolated as one of the other disproportionation products. Such a disproportionation of $CF_3CFCl{-}N = O$, $ClCF_2CFCl{-}N = O$ and $CF_3CCl_2{-}N = O$ during heating has recently been described [4].

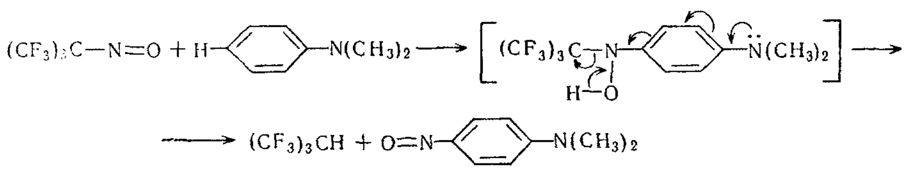
Compound	Yield %	B. p. (m. p.), °C	n_D^{20}	d_4^{20}	Found, %		Calculated, %	
					F	halogen	F	halogen
$(CF_3)_3CCl$	57	25--27			57,38	13,33	57,19	13,93
$(CF_3)_3CBr$	58	(58--59)*			57,03	26,84	57,19	26,76
$(CF_3)_3CI$	33	(56--58)			50,27		49,42	
$(CF_3)_2CCl_2$†	58							
$(CF_3)_2CClBr$	50	51--52	1,3270	1,8460	42,63		42,90	
$O_2NCF_2CFCl_2$‡	85	76	1,3700	1,6340	28,71	35,90	28,78	35,86

*Literature data [8]: m. p. 55.5-57.5°.

†Identified by gas-liquid chromatography.

‡Literature data [9]: b. p. 70.5-71.5° (730 mm); n_D^{25} 1.3669; d_4^{25} 1.6199.

The processes considered are undoubtedly of a radical character; however, in principle, replacement of the nitroso group according to an ionic mechanism is also possible. Thus, we observed a nitrosylating action of $(CF_3)_3C-N=O$ with respect to dimethylaniline, with the formation of $(CF_3)_3CH$ and p-nitrosodimethylaniline, which occurs under very mild conditions—in ether at room temperature. The mechanism of this transformation may be represented by the scheme:



Under the action of $(CF_3)_3C-N=O$ on aniline, there is also a formation of $(CF_3)_3CH$ and the products of nitrosylation of aniline, while, when $(CF_3)_3C-N=O$ and ethanol are heated in a sealed ampoule at 100°, $(CF_3)_3CH$ and the oxidation products of ethanol are formed, probably as a result of the decomposition of ethyl nitrite.

EXPERIMENTAL SECTION

For the production of $(CF_3)_3C-N=O$ and $O_2NCF_2CFCl-N=O$, see [5] and [6], respectively.

2-Chloro-2- nitrosoperfluoropropane. In a round-bottomed flask with small reflux condenser, connected to a trap, cooled to −78°, we placed 4.8 g of perfluoroacetone oxime [7] and 10 ml of ether, cooled to −78°, and introduced 2 ml of liquid chlorine, and then dropwise a solution of 5 ml of dry pyridine in 5 ml of ether. After this, the temperature of the mixture was gradually brought up to room temperature. The nitroso compound formed (together with the ether) was distilled off under vacuum into the trap, and then redistilled twice from conc. sulfuric acid. Yield of 2-chloro-2-nitrosoperfluoropropane 5.6 g (98.2%). Blue liquid with b. p. 22°. Found: F 52.32, 52.83%. C_3F_6ClNO. Calculated: F 52.90%.

Interaction of Nitroso Compounds with Halogens. A mixture of the nitroso compounds with a small excess of the halogen was heated on a water bath to 60-70° for several hours in a sealed glass ampoule. The reaction product was washed free of halogen and the nitrosyl halide with water or a solution of alkali and purified by distillation or sublimation. The results obtained are summarized in the table.

CONCLUSIONS

1. In the interaction of tert-perfluoronitrosobutane and 2-chloro-2-nitrosoperfluoropropane with halogens, there is a replacement of the nitroso group by halogen.

2. tert-Perfluoronitrosobutane nitrosylates amines and alcohols, with the formation of monohydroperfluoroisobutane.

LITERATURE CITED

1. I. L. Knunyants and B. I. Dyatkin, Izv. AN SSSR, Otd. Khim. N., 923 (1964).
2. I. L. Knunyants, B. L. Dyatkin, and E. P. Mochalina, Izv. AN SSSR, Ser. Khim., 1091 (1965).
3. R. N. Haszeldine, J. Chem. Soc., 3565 (1953).
4. D. E. O'Connor and P. Tarrant, J. Organ Chem., 29, 1793 (1964).
5. I. L. Knunyants, É. G. Bykhovskaya, V. N. Frosin, and Ya. M. Kisel', Dokl. AN SSSR, 132, 123 (1960).
6. V. A. Ginsburg, N. F. Privezentseva, N. P. Rodionova, S. S. Dubov, S. P. Makarov, and A. Ya. Yakubovich, Zh. Obshch. Khimii, 30, 2406 (1960).
7. I. L. Knunyants, V. L. Dyatkin, L. S. German, I. N. Rozhkov, and V. A. Komarov, Zh. VKhO im. Mendeleeva, 8, 709 (1963).
8. P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, J. Organ. Chem., 28, 184(1963).
9. J. D. Park, A. P. Stefani, G. H. Crawford, and J. R. Lacher, J. Organ Chem., 26, 3316 (1961).