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THE INTERACTION OF PERFLUORONITROSOALKANES WITH CARBANIONS

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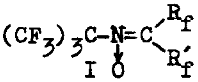
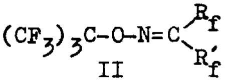
In 1970 we found perfluoro-tert.-butyl anion $(CF_3)_3C^-$, generated from perfluoroisobutene (PFIB) and KF in dimethyl formamide medium to react easily with perfluoronitrosoalkanes[1]. According to general views on the polarization of the nitroso group and considering the nucleophilic attack being directed on the positively charged nitrogen atom, the perfluoronitrone structure (I) was ascribed to products of this reaction. However further investigation showed that in fact they have the alternative structure (II).



$(CF_3)_3C-\underset{\downarrow\atop O}{N}=C\begin{matrix}R_f\\R_f'\end{matrix}$

I



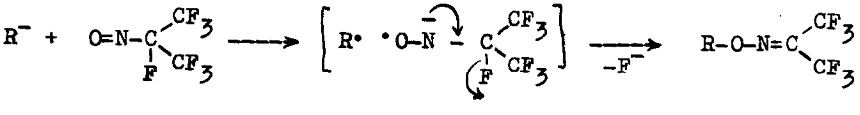
$(CF_3)_3C-O-N=C\begin{matrix}R_f\\R_f'\end{matrix}$

II

The product obtained from PFIB, 2-nitrosoperfluoropropane and KF when reduced by means of $NaBH_4$ gives perfluoro-tert.-butanol $(CF_3)_3D-OH$ and 2-amino-2-H-perfluoropropane $(CF_3)_2CH-NH_2$, which corresponds to structure (II) and cannot be explained by structure (I).

The reaction of 2-nitrosoperfluoropropane with PhMgBr proceeds analogously, giving hexafluoroacetone oxime phenyl ether $Ph-O-N=C(CF_3)_2$, reduction of which by $NaBH_4$ leads to phenol and $(CF_3)_2CH-NH_2$.

Thus in both cases attack of carbanion on the oxygen atom of the nitroso group takes place, this direction of the attack being opposite to the expected one. The possible explanation is based on the assumption that the first stage of this reaction is one-electron transfer from carbanion to nitroso group, with the subsequent elimination of fluoride ion from the position-α to the nitrogen atom and recombination of the resultant radicals



R = $(CF_3)_3C$: yield 36.5%; b.p. 77-78°; IR-spectrum: 1660 cm^{-1} (C=N); NMR F^{19} spectrum: δ_1= -6.1 (singlet), and two quadruplets, δ_2= -8.6, δ_3= -11.5 p.p.m. (here and below CF_3COOH as external standard), J = 6.3 Hz.

R = C_6H_5: yield 42.3%; b.p. 32-34° at 6 mm; IR-spectrum: 1640 cm^{-1} (C=N); NMR F^{19} spectrum: δ_1= -10.55, δ_2= -12.85 p.p.m. (quadruplets), J = 5.6 Hz. Both structures were supported by mass-spectra. Analytical data are satisfactory.

The reduction of $NaBH_4$ was carried out in DMF medium; $(CF_3)_3C$-OH and $(CF_3)_2CH$-NH_2 were identified with authentic samples[2,3] by GLC and NMR methods.

The interaction of nitroso compounds with zinc alkyls and with Grignard compounds is known to include carbanion attack on the nitrogen atom, while the reaction of PhLi with Ph-N=O leads to Ph_2NH and PhOH, which we interpret as a result of an anomalous attack of Ph^- on the oxygen atom followed by splitting of Ph_2N-O-Li by the action of the second molecule of PhLi[4]. The reason for the inverse orientation is not discussed; apparently, it could be interpreted as a consequence of the one-electron transfer, since the ability of Ph-N=O to accept one electron is known[5]. The same property is characteristic also of perfluoronitrosoalkanes[6]. The lack of success of our attempts to prove the supposed mechanism of interaction of $(CF_3)_3C^-$ or Ph^- with $(CF_3)_2CF$-N=O by ESR and CIDNP methods may be explained by the rapidity of the "cage" reaction.

References

1. B.L. Dyatkin, S.R. Sterlin, L.G. Zhuravkova and I.L. Knunyants, USSR Pat. No311905 (1970); Bull,izobr. 1971, No. 25.
2. E.P. Mochalina, B.L. Dyatkin, Izv.AN SSSR, Chem.Div., 1965, 926.
3. I.L. Knunyants, B.L. Dyatkin, ibid., 1964, 923.
4. P. Buck, G. Köbrich, Tetrahedron Letters, 1967, 1563.
5. C.J.W. Gutch, W.A. Waters, Proc.Chem.Soc., 1964, 230.
6. V.A. Ginsburg, A.N. Medvedev, M.F. Lebedeva, S.S. Dubov, A.Ya. Yakubonich, Zhur. Ob. Khim., 35, 1418 (1965).