REACTION OF PEROXYDISULFURYL DIFLUORIDE WITH 2-HYDROPERFLUOROISOBUTANE

A. V. Fokin, A. I. Rapkin,
V. I. Matveenko, V. Yu. Zakharov,
and Yu. N. Studnev

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A large number of examples have been reported for the radical abstraction of hydrogen atoms from fluorinated and nonfluorinated hydrocarbons by peroxydisulfuryl difluoride, $(OSO_2F)_2$, with the formation of HSO_3F and the corresponding esters of fluorosulfuric acid [1]. This reaction begins at from 10 to 20°C. On the other hand, it has not been possible to obtain a reaction between $(OSO_2F)_2$ with CH acids [2]. In the present work, we found that one of the strongest Ch acids, $(CF_3)_3CH$, does not react with $(OSO_2F)_2$ in a closed volume even at 120-130°C. The addition of HSO_3F to the reaction mixture did not lead to this reaction. However, the reaction begins in the presence of SbF_5 or a mixture of SbF_5 and HSO_3F at from 50 to 60°C

$$(OSO_2F)_2 + (CF_3)_3CH \xrightarrow{HSO_3F/SbF_5 \text{ or } SbF_5} (CF_3)_3COSO_2F + HSO_3F$$

Apparently some polarization of the O—O bond occurs in this reaction as well as in the reaction with fluorochlorohydrocarbons [3] in highly acidic media (HSO_3F/SbF_5 or SbF_5) and $(OSO_2F)_2$ as an electrophilic reagent.

A mixture of 7.8 g (0.039 mole) $(OSO_2F)_2$, 9.4 g (0.043 mole) $(CF_3)_3CH$, and 1 g (0.0046 mole) SbF_5 was heated in a sealed glass ampule for 2 h at 60-90°C. Fractionation of the reaction mass gave 11.2 g (89.6%) tert-perfluorobutyl fluorosulfate bp 69-70°C, d_4^{26} 1.761, n_D^{26} 1.28. Found: C 15.31; F 60.14; S 9.83%. Calculated for $C_4F_{10}O_3S$: C 15.09; F 59.75; S 10.06%. ^{19}F NMR spectrum (ppm, relative to CF_3CO_2H): −11.8 s ($3CF_3$), −125.4 s (SF).

LITERATURE CITED

1. A. V. Fokin, Yu. N. Studnev, L. D. Kuznetsova, and I. N. Krotovich, Usp. Khim., 51, 1258 (1982).
2. A. F. Eleev and G. A. Sokol'skii, Zh. Org. Khim., 18, 975 (1982).
3. A. V. Fokin, Yu. N. Studnev, A. I. Rapkin, and V. I. Matveenko, Izv. Akad. Nauk SSSR, Ser. Khim., 715 (1985).

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