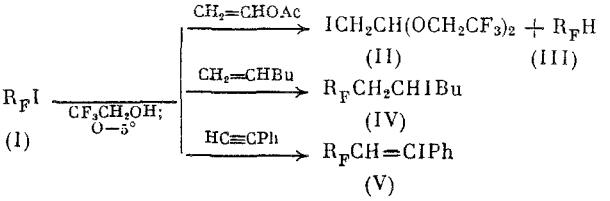
FIRST EXAMPLE OF THE ELECTROPHILIC ADDITION OF PERFLUOROALKYL IODIDES TO UNSATURATED COMPOUNDS

I. N. Rozhkov, S. M. Igumnov, and S. I. Pletnev

UDC 542.955:547.224:547.313:547.538.241

It has been assumed that perfluoroalkyl iodides add to carbon-carbon multiple bonds by a radical-chain mechanism initiated by homolysis of the C–I bond at high temperatures [1]. However, the significant polarization of the C–I bond in tertiary perfluoroalkyl iodides (in $(CF_3)_3CI$, $Q_I = 0.232$, $Q_C = -0.322$ [2]) opens the possibility for its heterolytic cleavage and, thus, the addition of R_FI to multiple bonds under extremely mild conditions.

Indeed, the attack of positive iodide of perfluoro-tert-hexyl iodide (I) on the π-system of alkenes and alkynes is observed in polar solvents with the subsequent reaction of the intermediate cation with the solvent or with the formation perfluorocarbanion formed upon heterolysis



$R_F = C_3F_7C(CF_3)_2$.

The rate of the reaction of (I) with hexene was found to depend on the solvent polarity and increases upon going from ethyl acetate to CF_3CH_2OH and, then, to CF_3CO_2H.

A mixture of 10 mmoles (I) and 10 mmoles unsaturated compound in 15 ml solvent was maintained for 70 h at 0-5°C. The solvent was washed out with water and the organic residue was dried over $MgSO_4$. Vacuum distillation gave the products.

1,1-Bis-(2,2,2-trifluoroethoxy)-2-iodoethane (II) was obtained in 66.4% yield, bp 82-83°C (2 mm). Found: C, 20.51; H, 2.10; F, 31.98%. Calculated for $C_6H_7F_6IO_2$: C, 20.45; H, 1.99; F, 32.39%. PMR spectrum in CCl_4 (δ, ppm): 3.14 d (CH_2I), 3.84 q (CH_2O), 4.85 t (CH). ^{19}F NMR spectrum in CCl_4: −3.9 t (CF_3).

The reaction of (I) with vinyl acetate gave monohydroperfluoroalkane (III) in 71.1% yield identified by gas-liquid chromatography and ^{19}F NMR spectroscopy. 4,4-Bis(trifluoromethyl-1,1,1,2,2,3,3-heptafluoro-6-iododecane (IV) was obtained in 74.9% yield, bp 90-91°C (8 mm) [88°C (7 mm) [2]]. 3,3-Bis(trifluoromethyl)-4,4,5,5,6,6,6-heptafluoro-1-iodo-1-phenyl-1-hexene (V) was obtained in 81.3% yield, bp 103-105°C (8 mm) (102°C (7 mm) [2]).

LITERATURE CITED

1. L. N. Kiseleva, V. I. Dostovalova, F. K. Velichko, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2132 (1988).
2. S. I. Pletnev, S. M. Igumnov, I. N. Rozhkov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2057 (1989).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 226-227, January, 1990. Original article submitted September 14, 1989.

0568-5230/90/3901-0209$12.50