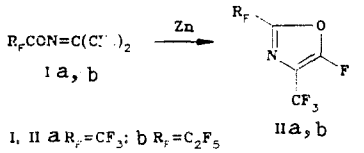
SYNTHESIS OF PERFLUORINATED OXAZOLES

V. M. Koshelev, I. N. Barsukov, N. V. Vasil'ev, and A. F. Gontar'

UDC 547.221

The literature contains no information on the synthesis of perfluorooxazoles. It is known that fluorine-containing aryloxazoles can be obtained by the reaction of hexafluoroacetone aroylimines with $SnCl_2$ or by the reaction of cycloadducts of hexafluoroacetone aroylimines with trialkyl phosphites [1, 2]. This method was found to be unacceptable in the synthesis of perfluorinated oxazoles from hexafluoroacetone perfluoroacylimines.

It was observed that cyclodefluorination of perfluoroacylimines Ia and Ib was accomplished by some metals indioxane and, in addition, 2-(perfluoroalkyl)-4-(trifluoromethyl)-5-fluorooxazoles (IIa and IIb) were formed. Of the metals (magnesium, tin, aluminum, and zinc) that were studied in these reactions, only zinc and tin exerted a defluorinating effect. The best yield of oxazoles was attained in the presence of zinc.



Thus, a mixture of perfluoroacylimine Ia or Ib and zinc in dioxane was heated in a closed vessel for 30-35 h at 100°C. We obtained 2,4-bis(tri-fluoromethyl)-fluorooxazole (IIa) in 27% yield, with bp 63°C and n_D^{20} 1.3065. IR spectrum (gas phase): 1680 cm^{-1}; (thin layer): 1580, 1680, 1740, 1770 cm^{-1}. Fluorine-19 NMR spectrum: −14.1 (doublet, $J_{CF_3,CF}$ = 10 Hz, CF_3), −10.8 (singlet, CF_3), 36.9 ppm (broadened quartet, CF).

2-(Pentafluoroethyl)-4-(trifluoromethyl)-5-fluorooxazole (IIb). The yield was 34%, bp 74°C, and n_D^{20} 1.3125. IR spectrum (thin layer): 1580, 1680, 1740, 1770 cm^{-1}. Fluorine-19 NMR spectrum: −12.3 (doublet, $J_{CF_3,CF}$ = 10.5 Hz, CF_3), 7.4 (broadened singlet, CF), 39.7 (broadened singlet, CF_2), 38.6 ppm (broadened quartet, CF).

The data of the elemental analysis correspond to the calculated values.

LITERATURE CITED

1. R. Ottlinger, K. Burger, H. Goth, and J. Firl, Tetrahedron Lett., No. 50, 5003 (1978).
2. K. Burger and H. Dieter, Chem. Ztg., 110, 89 (1986).

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1699-1700, December, 1989. Original article submitted April 17, 1989.

 0009-3122/89/2512-1418$12.50