SYNTHESIS OF 1-PHENYL-2,2-DIFLUORO-3,3-BIS(TRIFLUOROMETHYL)AZIRIDINE

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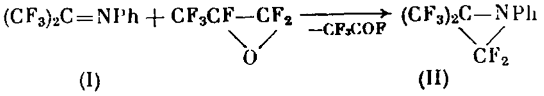
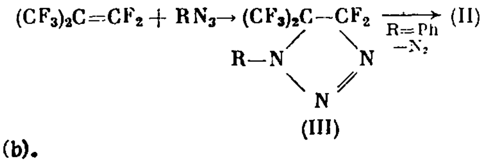
One of the common methods for the synthesis of haloaziridines is the cycloaddition of halocarbenes to azomethines [1]. However, it has not yet been possible to extend this method for fluoroaliphatic compounds. Thus, attempts to obtain the reaction of pentafluoroazopropene with various sources of :CF_2 have not been successful [2]. In turn, the reaction of the benzoylimine of hexafluoroacetone with :CF_2 generated by the thermolysis of hexafluoropropylene oxide (HFPO) leads mainly to the 1,4-cycloadduct, and the corresponding aziridine is formed in insignificant yield [3].

We have studied the reaction of HFPO with hexafluoroacetone anil (I) and found that this reaction at 180-190°C leads to about 50% yield of the cycloadduct of anil (I) with :CF_2, namely, 1-phenyl-2,2-difluoro-3,3-bis(trifluoromethyl)aziridine (II). We were unable to



obtain aziridine (II) or its dichloroanalog by the reaction of anil (I) with such dihalocarbene sources as $Ph_3P(Br)CF_2Br$ + KF [4], $(CF_3)_2Hg$ + NaI [5], or CCl_3SiF_3 [6]. On the other hand, we have found that aziridine (II) is formed in the reaction of octafluoroisobutylene (OFIB) with phenyl azide, apparently as a result of the elimination of N_2 from intermediate triazoline (IIIa). However, the reaction of OFIB with benzyl azide leads to stable triazoline (IIIb), which is not converted to the corresponding aziridine under the reaction conditions [7]



R = Ph (a); $PhCH_2$ (b).

In contrast to OFIB oxide and thiooxide, which readily react with nucleophiles including the F^- anion [8, 9], their nitrogen analog — aziridine (II) — is inert relative to fluoride ions. Thus, it is not altered in the presence of CsF in solvents such as acetonitrile and diglyme at 20-80°C.

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Perkin—Elmer R-32 spectrometer at 84.6 MHz, and the chemical shifts are given in ppm relative to CF_3CO_2H as the external standard. The gas—liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph on a column packed with Krytox on Chromosorb W.

1-Phenyl-2,2-difluoro-3,3-bis(trifluoromethyl)aziridine (II). a) A mixture of 13.9 g anil (I) [10] and 12 g OHFPO was heated in a 100-ml steel autoclave for 16 h at 180-190°C. The gaseous products were removed, and distillation of the residue gave 12 g of a fraction with bp 50-65°C (10 mm) containing 60% (II) and 40% (I) as indicated by gas—liquid chromatographic analysis. In order to remove (I), the mixture was distilled over conc. H_2SO_4. A yield of 7.7 g (45%) (II) was obtained with bp 78-80°C (60 mm), n_D^{20} 1.3910. Found: C 40.77; H 1.79; F 52.25%. Calculated for $C_{10}H_5F_8N$: C 41.20; H 1.79; F 52.23%. ^{19}F NMR spectrum: −12.7 t (CF_3), 40.4 h (CF_2), J = 9 Hz.

b) A mixture of 8 g phenyl azide, 15 ml Freon-113, and 14 g OFIB was heated in a 50-ml steel autoclave for 18 h at 170°C. Distillation gave 5.9 g of a fraction with bp 35-80°C

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(10 mm) containing 60% (II) as indicated by gas–liquid chromatography; this sample was shown by NMR spectroscopy to be identical to that described above.

1-Benzyl-4,4-difluoro-5,5-bis(trifluoromethyl)-1,2,3-triazoline (IIIb). A mixture of 11.4 g benzyl azide, 35 ml Freon-113, and 20 g OFIB was heated in a 100-ml steel autoclave for 16 h at 190°C. Distillation gave 24.5 g (87%) triazoline (IIIb), bp 69-71°C (3 mm), n_D^{20} 1.4230. Found: C 39.24; H 1.56; F 45.83%. Calculated for $C_{11}H_7F_8N_3$: C 39.64; H 2.10; F 45.64%. ^{19}F NMR spectrum: –9.6 g (CF_3), 14.0 h (CF_2), J = 10.5 Hz.

CONCLUSIONS

1-Phenyl-2,2-difluoro-3,3-bis(trifluoromethyl)aziridine was obtained by the cycloaddition of difluorocarbene to hexafluoroacetone anil or by the reaction of octafluoroisobutylene with phenyl azide.

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