SYNTHESIS OF 1-BENZYL-2-TRIFLUOROMETHYLAZIRIDINE BY THE GABRIEL REACTION

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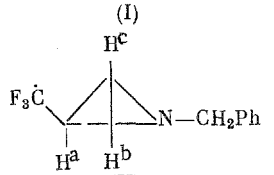
UDC 542.91:547.71'161

Fluorinated aziridines are usually obtained by the addition of diazomethane at a C=N bond [1, 2] or nucleophilic elimination of fluorolefins [3]. The synthesis of nonfluorinated aziridines is often carried out using the Gabriel reaction through cyclization of β-haloalkylamines. In the present work, we have shown that benzylamine adds smoothly to 1,1,1-trifluoro-2-bromopropene to form β-bromoalkylamine (I). This is the first report of the Gabriel cyclization of (I) for the synthesis of fluoroaziridine (II).

$$CF_3CBr=CH_2 \xrightarrow{PhCH_2NH_2} CF_3CHBrCH_2NHCH_2Ph \xrightarrow[DMF]{Et_3N}$$

(I)



(II)

A sample of (I) was obtained from equimolar amounts of the reagents at 20°C over 10 days in 50% yield, bp 120°C (10 mm), n_D^{20} 1.4930. PMR spectrum (60 MHz in CCl_4 from HMDS, δ, ppm, J, Hz): 1.53 br s (NH), 2.90, 3.02 (CH_2, ABX spectrum, $^2J_{AB}$ = 7, $^3J_{AX}$ = 3.6, $^3J_{BX}$ = 0), 3.65 s (CH_2Ph), 4.15 m (CH), 7.15 m (Ph). ^{19}F NMR spectrum (60 MHz, from CF_3CO_2H, δ, ppm, J, Hz): −7.3 d (CF_3, ^3J = 7.5).

A sample of (II) was obtained from (I) by the action of Et_3N in DMF at 153°C over 3 h in 90% yield, bp 100°C (10 mm), n_D^{20} 1.4662. PMR spectrum (400 MHz in C_6D_6, δ, ppm, J, Hz): 0.69 d.d (H^b, $^3J_{ab}$ = 6.6, $^4JCF_3,H^b$ = 0.7), 1.39 d.d.q (H^a, $^3J_{ac}$ = 3.2, $^3JCF_3,H^a$ = 5.1), 1.60 d (H^c, $^2J_{bc}$ = 0), 2.69, 2.92 (CH_2Ph, AB spectrum, $^2JCH_2$ = 13.4), 7.04 m (Ph). ^{19}F NMR spectrum (60 MHz from CF_3CO_2H, δ, ppm, J, Hz): −7.6 d (CF_3, J = 5.1).

The structures of these compounds were also supported by mass spectral and elemental analysis data. The authors thank I. I. Chervin for taking and interpreting the PMR spectrum of (II).

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0568-5230/86/3503-0675$12.50