1-HYDROXY-2,2-BIS(TRIFLUOROMETHYL)AZIRIDINE

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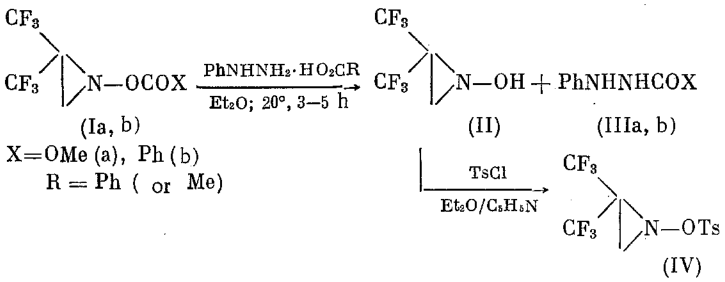
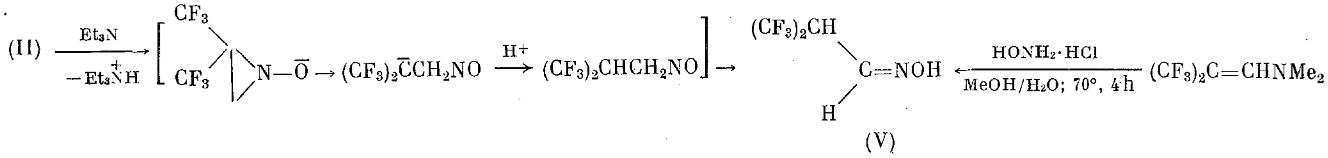
1-Hydroxy-2,2-bis(trifluoromethyl)aziridine (II)* has been obtained by us for the first time. The structure has been demonstrated by spectral methods and also by the identification of the O-tosyl derivative (IV) [2]. The damped inversion of N was observed in the PMR spectrum of (II). Under the action of base, (II) is isomerized into oxime (V), which can be obtained by alternative synthesis.†





Compound (II) decomposed on storage seemingly as a result of oxidative breakdown. Compound $(CF_3)_2C{=}CH_2$ was identified in the mixture by PMR (cf. [3]).

Compounds (Ia, b) were obtained according to [2]. Compound (II) was obtained in 30-50% yield, bp 48-50°C (44 mm). ^{1}H NMR spectrum (360 HMz in C_6D_6 from TMS; δ, ppm; J, Hz): 1.647 (H_A, $^2J_{AB}$ = 4.21 $^4J_{B-CF_3H_A}$ = 2.71); 2.04 (H_B, $^4J_{A-CF_3H_B}$ = 0.77), 4.65 (HO). ^{19}F NMR spectrum (84.6 MHz in CCl_4 from external CF_3COOH; δ, ppm; J, Hz): −9.0 (A − CF_3), −17.4 (B − CF_3), $^4J_{FF}$ = 7.5. Mass spectrum at 70 eV, m/e (rel. int. %): M^+ 195 (10), 178 (100). Compounds (IIIa, b) were obtained in quantitative yield and were identified as described in [4]. Compound (IV) was identified as described in [2]. Compound (V) was obtained rapidly by the quantitative conversion of (II) under the action of Et_3N in CCl_4 at 20°C into the cis isomer of (V) (assignment according to [5]), ^{1}H NMR spectrum (60 MHz in CCl_4 from HMDS; δ, ppm; J, Hz): 4.77 ($HC(CF_3)_2$ $^3J_{HF}$ = $^3J_{HH}$ = 7.5); 6.78 (HCN); 9.25 (HO). ^{19}F NMR spectrum: −13.1 ppm. A mixture of syn and anti (V) was slowly formed from (II) under the action of C_5H_5N in CCl_4 in a syn-anti ratio ∿6:4. Anti-(V) ^{1}H NMR spectrum: 3.72 ($HC(CF_3)_2$, $^3J_{HF}$ = 7.8; $^3J_{HH}$ = 8.2); 7.32 (HCN); 8.6 (HO); ^{19}F NMR: −12.8 ppm. Alternative synthesis from $(CF_3)_2C{=}CNMe_2$ [6] gave a mixture of syn and anti (V) in a ratio ∿4:6, yield was 78%, bp 48-50°C (55 mm), n_D^{20} 1.3275, mass spectrum at 30 eV, m/e (rel. int., %): M^+ 195 (78), 175 (100).

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*Only one compound of such a type is known, viz., 1-hydroxy-2,2-bis(methanesulfonyl)aziridine, the structure of which has not been strictly demonstrated [1].

†Procedure proposed by Yu. V. Zeifman.

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PREPARATION OF AZULENE FROM COBALTOCENE

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Cobalticinium salts form azulene in 10% yield on boiling with NaOH or $NaNH_2$ [1]. When carrying out the heterocyclization of acetylene and acetonitrile in the presence of cobaltocene (150°C, initial acetylene pressure 10 atm) azulene was isolated by us from the reaction mixture in 12% yield calculated on cobaltocene in addition to the main product 2-methylpyridine.

With the aim of clarifying the source of azulene formation experiments were carried out by heating cobaltocene in a series of carefully purified organic solvents and the formation of azulene from cobaltocene was detected for the first time. Experiments were carried out in a rotary autoclave into which a solution of cobaltocene (C 1.5%) was loaded in an atmosphere of Ar containing $<10^{-3}\%$ O_2 and <0.005 g/m^3 H_2O. The argon pressure was made up to 10 atm and the autoclave heated for 4 h. Azulene was isolated from the discharged mixture by column chromatography on silica gel L 40/100 (Chemapol) with n-hexane as eluent. The obtained azulene was identified by UV, IR, and mass spectroscopy. The results of experiments are given in Table 1.

TABLE 1

Solvent	T., °C	Yield of azulene on cobaltocene introduced
Acetonitrile	150	15
Acetonitrile + 2-methylpyridine	150	12
Toluene	150	16
"	200	21

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