Letters to the Editor

Reactions of α,β-dibromo-β-(fluoroalkyl)ketones with ethylenediamine

*O. G. Khomutov and K. I. Pashkevich**

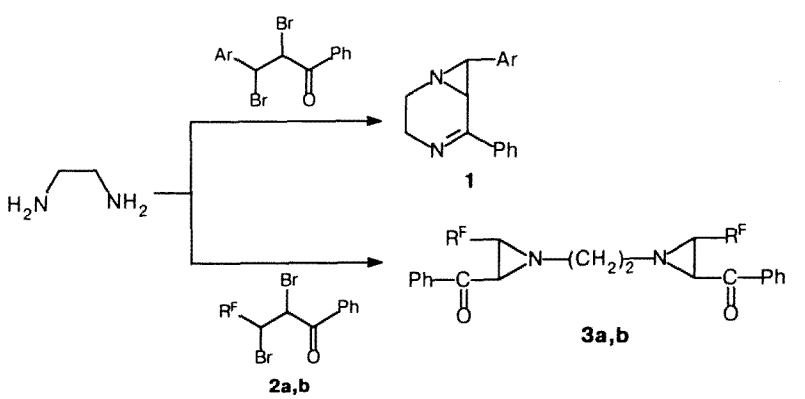
Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 20 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation. Fax: 007 (343 2) 44 0026

It is known that α,β-dibromoketones react with ethylenediamine (EDA) to give 1,4-diazabicyclo[4.1.0]hept-4-enes (**1**) (Scheme 1).[1] We established that α,β-dibromo-(β-fluoroalkyl)ketones (**2**) (obtained from the corresponding α,β-enones[2] and used without purification) react under the same conditions with equimolar amount of EDA in the presence of Et_3N to give ethylenediaziridines (**3a,b**).

This is apparently due to the fact that the substituent R^F enhances the aziridine ring formation. Thus, in the case of non-fluorinated α,β-dibromoketones, the completion of the reaction requires boiling and prolonged storage, whereas ketones **2** react with EDA almost instantaneously. Both aziridine rings in compounds **3** have *trans*-configuration ($J_{\alpha\text{-H},\beta\text{-H}}$ = 2.50—2.58 Hz).

***N,N'*-Ethylenedi[2-benzoyl-3-(1,1,2,2-tetrafluoroethyl)aziridine] (3a).** Br_2 (0.69 g, 4.31 mmol) was added dropwise to a solution of 1-phenyl-4,4,5,5-tetrafluoropent-2-enone-1 (1 g, 4.31 mmol) in 15 mL of hexane. The reaction mixture was allowed to stand for 2 h and concentrated, and the residue was dissolved in 30 mL of MeOH. Then Et_3N (0.87 g, 8.62 mmol) and EDA (0.26 g, 4.31 mmol) were added, and the mixture was left for 24 h, poured into 100 mL of H_2O, and extracted with $CHCl_3$. The extract was dried with $MgSO_4$ and concentrated, and the residue was chromatographed on a column with silica gel (the eluent was $CHCl_3$). Compound **3a** (0.77 g, 67%) was obtained as a light yellow oil. IR

Scheme 1



R^F = $H(CF_2)_2$ (**a**), C_6F_{13} (**b**); Ar = 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, Ph

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(thin film), ν/cm^{-1}: 1672 (C=O). ^1H NMR ($CDCl_3$), δ: 2.48—3.50 (m, 4 H, 2 CH_2); 3.30 (br.t, 2 H, 2 β-H, $^3J_{H,F}$ = 9.8 Hz); 3.96 (d, 2 H, 2 α-H, $J_{\alpha\text{-}H,\beta\text{-}H}$ = 2.50 Hz); 6.12 (tt, 2 H, 2 HCF_2, $^2J_{H,F}$ = 52.2 Hz, $^3J_{H,F}$ = 5.1 Hz); 7.30—8.01 (m, 10 H, 2 Ph).

***N,N'*-Ethylenedi(2-benzoyl-3-perfluorohexylaziridine) (3b)** was obtained analogously from 1-benzoyl-2-perfluorohexylethylene (10 g, 22 mmol), Br_2 (3.52 g, 22 mmol), Et_3N (5.06 g, 50 mmol), and EDA (1.5 g, 22 mmol). After recrystallization from hexane, the yield of compound **3b** was 7.79 g (74%), colorless crystals, m.p. 102.5—103.0 °C. Found (%): C, 39.79; H, 2.00; F, 51.53; N, 3.01. $C_{32}H_{18}F_{26}N_2O_2$. Calculated (%): C, 40.18; H, 1.90; F, 51.64; N, 2.93. IR (Vaseline oil), ν/cm^{-1}: 1660 (C=O). ^1H NMR ($CDCl_3$), δ: 2.71—3.26 (m, 6 H, 2 CH_2, 2 β-H); 3.79 (d, 2 H, 2 α-H, $^3J_{\alpha\text{-}H,\beta\text{-}H}$ = 2.58 Hz); 7.39—8.09 (m, 10 H, 2 Ph).

References

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Synthesis and optical activation of dimethyl 1-(2,4-dinitrophenyloxy)aziridine-2,2-dicarboxylate

*V. V. Rozhkov,[a] I. I. Chervin,[b] A. V. Prosyanik,[a] and R. G. Kostyanovsky[b]**

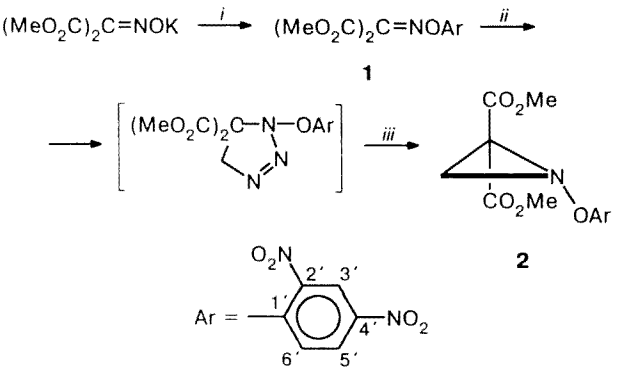
[a]Ukrainian State University of Chemistry and Technology, 6 prosp. Gagarina, 320005 Dnepropetrovsk, Ukraine. Fax: 007 (056 2) 47 7478
[b]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: 007 (095) 938 2156. E-mail: kost@chph.rc.ac.ru

1-Alkoxyaziridine-2,2-dicarboxylates[1] proved to be ideal objects for developing a general procedure for complete resolution into antipodes[2—6] that can be used for various classes of compounds with an asymmetrical nitrogen atom.[7]

In this work, the first representative of 1-aryloxyaziridines, namely, dimethyl 1-(2,4-dinitrophenoxy)aziridine-2,2-dicarboxylate **2**, was synthesized by the reaction of diazomethane with dimethyl mesoxalate *O*-(2,4-dinitrophenyl)oxime (**1**) (Scheme 1). We succeeded in obtaining both enantiomerically enriched forms of **2** by crystallization from an optically active solvent. Unlike 1-alkoxyaziridines, an increase in the inversion barrier should be expected for compound **2** because the electronegativity of the sp^2 carbon atom is higher than that of the sp^3 carbon atom. Moreover, aziridine **2** is a promising synthon for preparing 1-hydroxyaziridine-2,2-dicarboxylates.

***O*-Aryloxime (1).** The yield was 42%, m.p. 108—110 °C (from Pr^iOH). Found (%): C, 40.39; H, 2.74; N, 12.86. $C_{11}H_9N_3O_9$. Calculated (%): C, 40.37; H, 2.77; N, 12.84. IR (KBr pellets), ν/cm^{-1}: 1740 (CO); 1600, 1542 (C=N, C_6H_3, NO_2). ^1H NMR ($CDCl_3$), δ: 4.02 (s, 3 H, MeO); 4.07 (s, 3 H, MeO); 8.03 (d, 1 H, 6′-H, ^3J = 9.2 Hz); 8.5 (dd,

Scheme 1



Reagents and conditions: *i.* Chloro-2,4-dinitrobenzene in MeCN in the presence of a catalytic amount of 18-crown-6, boiling for 6 h; *ii.* An ethereal solution of CH_2N_2 in CH_2Cl_2, −6 °C, 7 days; *iii.* A catalytic amount of CF_3COOH, −6 °C, 5 h.

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