

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

***N,N'*-Ethylene(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. $\text{C}_{32}\text{H}_{18}\text{F}_{26}\text{N}_2\text{O}_2$. Calculated (%): C, 40.18; H, 1.90; F, 51.64; N, 2.93. IR (Vaseline

oil), ν/cm^{-1} : 1660 (C=O). $^1\text{H NMR}$ (CDCl_3), δ : 2.71–3.26 (m, 6 H, 2 CH_2 , 2 $\beta\text{-H}$); 3.79 (d, 2 H, 2 $\alpha\text{-H}$, $^3J_{\alpha\text{-H},\beta\text{-H}} = 2.58$ Hz); 7.39–8.09 (m, 10 H, 2 Ph).

References

1. H. W. Heine and R. P. Henzel, *J. Org. Chem.*, 1969, **34**, 171.
2. R. R. Latypov, V. D. Belogai, and K. I. Pashkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 123 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 108 (Engl. Transl.)].

Received April 1, 1996

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

V. V. Rozhkov,^a I. I. Chervin,^b A. V. Prosyaniuk,^a and R. G. Kostyanovsky^{b*}

^aUkrainian State University of Chemistry and Technology,
6 prosp. Gagarina, 320005 Dnepropetrovsk, Ukraine.
Fax: 007 (056 2) 47 7478

^bN. 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

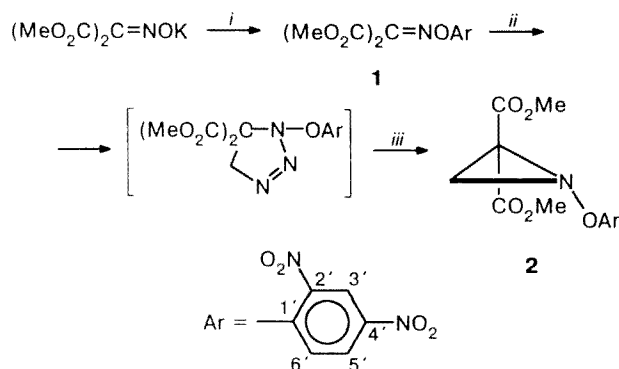
1-Alkoxyaziridine-2,2-dicarboxylates¹ proved to be ideal objects for developing a general procedure for complete resolution into antipodes^{2–6} that can be used for various classes of compounds with an asymmetrical nitrogen atom.⁷

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. $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_9$. 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). $^1\text{H NMR}$ (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.

1 H, 5'-H, $^3J = 9.2$ Hz, $^4J = 2.4$ Hz); 8.92 (d, 1 H, 3'-H, $^4J = 2.4$ Hz). ^{13}C NMR (DMSO- d_6), δ : 53.86 (q, MeO, $^1J = 149.7$ Hz); 54.26 (q, MeO, $^1J = 149.7$ Hz); 117.6 (d, 6'-C, $^1J = 174.1$ Hz); 122.0 (dd, 5'-C, $^1J = 174.4$ Hz, $^3J = 4.4$ Hz); 130.3 (dd, 3'-C, $^1J = 172.9$ Hz, $^3J = 4.4$ Hz); 149.34 (s, C=N); 154.0 (m, 1'-C); 142.6 (m, 2'-C); 136.5 (m, 4'-C); 158.2 (q, CO, $^3J = 4.4$ Hz); 158.9 (q, CO, $^3J = 4.4$ Hz).

Aziridine (2). The yield was 21%, m.p. 110–112 °C (from PrⁱOH). Found (%): C, 42.26; H, 3.25; N, 12.33. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_9$. Calculated (%): C, 42.23; H, 3.25; N, 12.31. IR (KBr pellets), ν/cm^{-1} : 3100 (CH_2 cycle); 1600, 1536 (C_6H_3 , NO_2). ^1H NMR (CDCl_3), δ : 2.95 (d, 1 H, CH_2 cycle, $^2J = -4.0$ Hz); 3.46 (d, 1 H, CH_2 cycle, $^2J = -4.0$ Hz); 3.81 (s, 3 H, MeO); 3.88 (s, 3 H, MeO); 8.13 (d, 1 H, 6'-H, $^3J = 9.2$ Hz); 8.48 (dd, 1 H, 5'-H, $^3J = 9.2$ Hz, $^4J = 2.1$ Hz); 8.88 (d, 1 H, 3'-H, $^4J = 2.1$ Hz). ^{13}C NMR (DMSO- d_6), δ : 41.64 (dd, 3-C, $^1J = 175.8$ Hz, $^1J = 183.1$ Hz); 50.67 (s, 2-C); 53.54 (q, MeO, $^1J = 148.2$ Hz); 53.60 (q, MeO, $^1J = 148.2$ Hz); 116.7 (d, 6'-C, $^1J = 174.4$ Hz); 121.6 (dd, 5'-C, $^1J = 174.4$ Hz, $^3J = 4.4$ Hz); 130.2 (dd, 3'-C, $^1J = 172.9$ Hz, $^3J = 5.8$ Hz); 135.9 (t, 4'-C, $^2J = ^3J = 5.8$ Hz); 141.0 (m, 2'-C); 155.8 (m, 1'-C); 162.1 (m, CO, $^3J = 4.4$ Hz); 164.7 (m, CO, $^3J = 4.4$ Hz).

Aziridine **2** (100 mg) was crystallized from *S*-(-)-2-methylbutan-1-ol (1 mL). After washing with Et_2O and drying *in vacuo*, aziridine (+)-**2** was obtained in a yield of 23 mg, m.p. 119–120 °C, $[\alpha]_{\text{D}}^{15} +1.2^\circ$ (*c* 2.8, Me_2CO). After evaporation of the mother liquor *in vacuo*, washing with Et_2O , and drying, aziridine (-)-**2** was obtained in a yield of 65 mg, m.p. 114–115 °C, $[\alpha]_{\text{D}}^{15} -0.97^\circ$ (*c* 7.6, Me_2CO). Previously,⁴ an analogous enantiomeric enrichment was observed for 1-alkoxyaziridines upon crystallization from an optically active solvent.

This work was supported by the International Association for the Promotion of Cooperation with Scientists from the Newly Independent States of the Former Soviet Union (INTAS, Grant 94-2839).

References

1. R. G. Kostyanovsky, A. V. Prosyaniuk, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 482 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
2. R. G. Kostyanovsky, V. F. Rudchenko, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1685; 2621 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
3. R. G. Kostyanovsky and V. F. Rudchenko, *Dokl. Akad. Nauk SSSR*, 1976, **231**, 878 [*Dokl. Chem.*, 1976, **231** (Engl. Transl.)].
4. R. G. Kostyanovsky, V. F. Rudchenko, and G. V. Shustov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1687 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
5. V. F. Rudchenko, O. A. D'yachenko, A. B. Zolotoi, L. O. Atovmyan, and R. G. Kostyanovsky, *Dokl. Akad. Nauk SSSR*, 1979, **246**, 1150 [*Dokl. Chem.*, 1979, **246** (Engl. Transl.)].
6. V. F. Rudchenko, O. A. D'yachenko, A. B. Zolotoi, L. O. Atovmyan, I. I. Chervin, and R. G. Kostyanovsky, *Tetrahedron*, 1982, **38**, 961.
7. F. A. Davis and R. H. Jenkins, in *Asymmetric Synthesis*, Eds. J. D. Morisson and J. W. Scott, Acad. Press, New York, 1984, **4**, 313.

Received June 18, 1996