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LETTERS TO THE EDITOR

OPTICALLY ACTIVE α-CHLOROOXIRANS OBTAINED BY DARZEN'S REACTION AND THEIR ABSOLUTE CONFIGURATION

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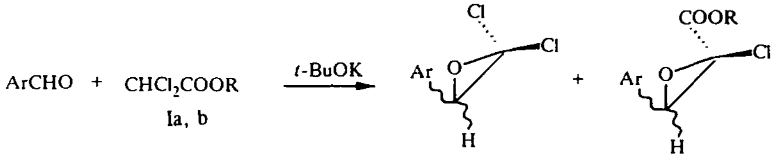
α-Chlorooxirans obtained by Darzen's reaction from dichloroacetates and aldehydes [1] are attractive synthetic equivalents for some types of synthons [2]. In contrast to the simpler glycidates obtained by Darzen's reaction with monochloroacetates [3], the question of the stereochemistry of these highly reactive polyfunctional oxirans has not been raised, even though since they have two chiral centers on the ring, they should be formed as a mixture of two diastereomeric racemates. Nevertheless, no attempt has been made to obtain optically active α-chlorooxirans.

To determine the three-dimensional structure of these heterocycles, we used (−)- and (+)-menthyl esters of dichloroacetic acid Ia and Ib in Darzen's condensation. Introduction of chirally discriminating menthyl residues into α-chlorooxirans converts the two racemates into four diastereomers which can be separated. Thus, mixtures formed in reactions of dichloroacetates (Ia and Ib) with *p*-nitrobenzaldehyde (according to high-efficiency high-pressure chromatography data on a chiral stationary phase) contain at least four compounds. According to PMR spectra (500 MHz), these four compounds are α-chlorooxirans differing in the chemical shift of the proton in the β position of the three-membered ring (4.58 and 4.54 ppm), which corresponds to differences in the *Z* and *E* isomers.



Ia, b

IIa, b, IVa, b

IIIa, b, Va, b

Ar = 4-$O_2NC_6H_4$

I–V a R = (−)-menthyl, b R = (+)-menthyl

II *Z*, 2*S*,3*S*; IV *E*, 2*S*, 3R
III *Z*, 2R, 3R; V *E*, 2R, 3*S*

Of the four diastereomeric chlorooxirans IIa-Va and IIb-Vb formed from each of the enantiomeric menthyldichloroacetates (Ia, b), in both cases we could isolate in pure form the predominant isomers with chemical shift 4.58 ppm in the PMR spectra. The absolute configuration of these compounds, comprising an enantiomeric pair, was determined by x-ray diffraction as IIa and IIIb (*Z* isomers). According to chromatography data, the diastereomeric purity of the isolated compounds is practically 100%, while the diastereoselectivity of Darzen's reaction is 25-30% in favor of the *Z* isomers. We could not isolate other *Z* isomers IIb, IIIa, and all the *E* isomers IVa, b, Va, b appearing in the chromatograms and PMR spectra in pure form by recrystallization because of their tendency toward rapid spontaneous isomerization to the corresponding menthyl esters of phenylchloropyrotartaric acid ArCHClCOCOOR.

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Z-2-Chloro-2-carbomenthoxy-3-(4-nitrophenyl)oxirans (IIa and IIIb). Powdered potassium *tert*-butoxide (7.48 mmoles) was added to a solution of 7.48 mmoles (−)- or (+)-menthyldichloroacetates Ia or Ib and 7.48 mmoles *p*-nitrobenzaldehyde in 25 ml tetrahydrofuran, maintaining the temperature at −78°C. After stirring for 3 h at this temperature, the reaction mixture was warmed up to room temperature (5 h), after which stirring was continued for 12 h more. The solvent was removed under vacuum; 30 ml CH_2Cl_2, and a saturated aqueous solution of sodium chloride was added to the residue, then it was neutralized with hydrochloric acid. The organic layer was removed, the aqueous layer was extracted (3 × 30 ml) with CH_2Cl_2, washed with a saturated aqueous solution of sodium chloride, and dried with magnesium sulfate. Then the solvent was evaporated. Yield of the mixture of four diastereomers was 97%. The mixtures were recrystallized on standing. Their recrystallization from hexane yields the *Z* isomers IIa and IIIb. T_{mp} 126-128.5°C; for isomer IIa $[\alpha]_D^{21.2}$ is −112.1°C (c 1.61, $CHCl_3$); isomer IIIb has the same magnitude with opposite sign. The elemental analysis and PMR spectroscopy data correspond to the structures confirmed by the x-ray diffraction.

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