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Stereochemistry of seven-membered heterocycles: XLIII. Steric structure of diastereoisomeric 8,8- dichloro(dibromo)-4-R-3,5-dioxabicyclo[5.1.0]octanes

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Abstract

Dichloro- and dibromocyclopropanation of 2-substituted 1,3-dioxacyclohept-5-enes according to Makosza resulted in formation of the corresponding 4-substituted 8,8-dichloro(dibromo)-3,5-dioxabicyclo-[5.1.0]octanes in good yields. Ultrasonic activation of the process considerably shortened the reaction time. According to the ¹³C NMR spectra, the chair-twist equilibrium is essentially displaced toward the chair conformer for the exo isomers and toward the twist conformer for the endo structures. Similar results were obtained by AM1 semiempirical calculations which indicated that the CCl \cdots O interaction largely determines the conformational equilibrium. The state of the diastereoisomer epimerization equilibrium depends on the size of the substituent at the acetal carbon atom.

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