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PARTICIPATION BY THE NEIGHBORING FUNCTIONAL GROUP IN THE EPOXIDATION REACTION

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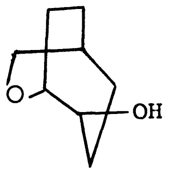
Reactions of m-chloroperbenzoic acid with the medium ring olefins possessing the neighboring hydroxymethyl or carboxyl functional group afforded a simple synthetic route to bicyclic ethers or lactones.

During the course of studying the effects of neighboring epoxy group in solvolysis reactions, various compounds containing epoxide ring have been prepared. Epoxidation of 4-(hydroxymethyl)cyclopentene and cyclopent-3-enol have been reported to give a mixture of the corresponding syn and anti epoxides.[1] However, our attempts to epoxidize 5-(hydroxymethyl)cycloheptene, 4-cycloheptenecarboxylic acid, 5-(hydroxymethyl)cyclooctene and 4-cyclooctenecarboxylic acid afforded unusual products instead of the expected epoxides. We report here the epoxidation reactions of these compounds.

Reactions of 5-(hydroxymethyl)cycloheptene[2] with m-chloroperbenzoic acid in methylene chloride, chloroform, or benzene afforded a very viscous crude oil which yielded a white hygroscopic semi-solid upon purification (yield 32%): ^{1}H-NMR spectrum (CCl_4, τ): 6.04-7.70 (m,4H), 7.0 singlet (1H) superimposed on multiplet between 6.25-7.25 (1H), 7.70-8.85 (m,8H); IR (film, cm^{-1}): 3410 (s), 1045 (s), 1075 (s); MS spectrum: m/e 142. Based on these spectral data, the product was identified as exo-7-oxabicyclo[3.2.2]nonan-2-ol (1).[3]



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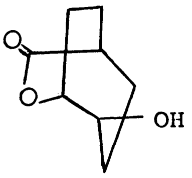

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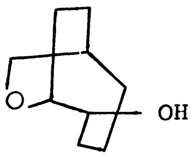

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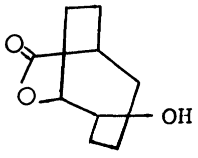

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Similarly, when 4-cycloheptenecarboxylic acid was epoxidized, the corresponding hydroxy bicyclic lactone (2) was isolated as a white crystalline solid (yield 30%): mp 164-165°C; ^{1}H-NMR spectrum ($CDCl_3$, τ): 5.48 (m,1H), 6.02 (m,1H), 6.81 (s,1H), 7.19 (m,1H) and 7.60-8.55 (m,8H); IR (KBr, cm^{-1}): 3430 (s), 1740 (s), 1038, 1060 (m).

The general nature of this reaction could be demonstrated by carrying out the similar reaction on the compounds of higher analogues. Epoxidation of 5-(hydroxymethyl)cyclooctene afforded a semi-solid bicyclic ether (3): ^{1}H-NMR (CCl_4, τ): 5.95-6.60 (m,3H), 6.68 (d, J = 6Hz, 1H), 7.08 (s, 1H), 7.21 (m,1H) and a complex multiplet between 7.50-9.20 (10H); IR (film, cm^{-1}): 3405 (s), 1055 and 1075 (s).

A similar reaction of 4-cyclooctenecarboxylic acid furnished a solid product of hydroxy bicyclic lactone (4): mp 128-129°C; ^{1}H-NMR spectrum ($CDCl_3$, τ): 5.20-5.56 (m,1H), 5.81-6.18 (m,1H), 7.10 (s,1H) superimposed on a multiplet between 6.92-7.22 (1H), 7.62-8.73 (m,10H); IR (KBr, cm^{-1}): 3400 (s), 1810 (s) and 1025, 1050 and 1090 (m).

These reactions demonstrate that the epoxidation reaction of the medium cyclic alkenes which possess properly oriented neighboring hydroxymethyl or carboxyl functional groups could provide a convenient synthetic route to the bicyclic systems containing the ether or lactone moiety. In principle, the observed products which resulted from the participation of the hydroxymethyl or carboxyl group could occur simultaneously at the transition state of epoxidation or subsequently to the epoxide formation.[4)] However, our initial studies on the kinetics of epoxidation of these compounds showed no evidence for the rate acceleration relative to the reaction without the neighboring functional group participation. A slight increase in rate constant upon increasing the dielectric constant of the medium was also observed. Therefore, it is likely that the reaction proceeds via an intermediate epoxide which undergoes rapid ring opening by intramolecular displacement of the neighboring functional group.[4,5)] Since epoxides and δ-lactones are widely spread in plants, occurrence of such a reaction is quite probable to those compounds containing a similar epoxide moiety described here.

Acknowlwdgement

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3) The exo configuration is a consequence of trans opening of the epoxide ring. All the new compounds 1, 2, 3 and 4 gave the correct elemental analysis.

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