Novel Stereochemical Feature of Epoxidation with Hydrogen Peroxide–Tris(acetylacetonato)iron(III) System

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Summary *trans*-Epoxide is obtained as the major product in the reaction of hydrogen peroxide–tris(acetylacetonato) iron(III) system with both *cis* and *trans*-olefins such as stilbene, octadecenol, and the methyl ester of unsaturated higher fatty acids.

STEREOSELECTIVE β-epoxidation of cholesterol and its analogues with hydrogen peroxide, catalysed by tris(acetylacetonato)iron(III) (H_2O_2–Fe^{3+}), has been reported previously.[1] This stereoselectivity differs from the α-epoxidation with peracids[2] or alkyl peroxides catalysed by metal complexes,[3] and led us to investigate further epoxidation with H_2O_2–Fe^{3+} which is unique in that it mainly gives *trans*-epoxides from both *cis*- and *trans*-olefins. All reported epoxidations of known steric course give *cis*-epoxides from *cis*-olefins and *trans*-epoxides from *trans*-olefins,[4] with only one exception where such stereospecificity is not found in a photosensitized epoxidation.[5] Recently, it was reported that the enzymatic epoxidation in *P. oleovorans* proceeds primarily with inversion of the original *trans*-olefin geometry.[6] We report here epoxidation by H_2O_2–Fe^{3+} which appears to be a model system for biological epoxidations.

In a typical reaction, a solution of $Fe(acac)_3$ (acac = acetylacetonato) (2·7 mmol) and the olefin (0·26 mmol) in 50 ml acetonitrile was thermostatted at 40 °C. A solution of hydrogen peroxide (30%) (49 mmol) was added dropwise with continuous stirring. The mixture was stirred for 40 min, and Na_2SO_3 was then added. The mixture was extracted with ether, and the organic layer was washed with aqueous NaCl, dried (Na_2SO_4) and evaporated to give a residue, g.l.c. of which showed that the major products were epoxides. Analysis of these epoxides revealed the striking stereochemical feature of this reaction (Table).

TABLE. Epoxidation of olefins.

olefin	Conversion/%	Using H_2O_2–$Fe(acac)_3$[a] Epoxide Yield/%	*trans*:*cis*	Using MCPBA in CH_2Cl_2[b] Epoxide Yield/%	*trans*:*cis*
cis-Stilbene	62	68	96: 4	96	0:100
trans-Stilbene	100	78	96: 4	90	100: 0
Methyl oleate	59	78	83:17	90	0:100
Methyl elaidate	63	72	86:14	85	100: 0
cis-9-Octadecen-1-ol ..	67	72	80:20	89	0:100
trans-9-Octadecen-1-ol ..	59	51	89:11	92	100: 0

[a] acac = Acetylacetonato. [b] MCPBA = *meta*-Chloroperbenzoic acid.

While alkyl hydroperoxides catalysed by transition metals[7] or peracids[8] are known to epoxidize olefins with retention of geometry, H_2O_2–Fe^{3+} epoxidizes both *cis*- and *trans*-stilbenes to *trans*- as well as *cis*-oxides in the ratio of **96**:**4**. As shown in the Table, this novel stereochemistry of epoxidation by H_2O_2–Fe^{3+} was also observed for other *cis*- and *trans*-alkenes such as methyl oleate, methyl elaidate, and *cis*- and *trans*-9-octadecen-1-ol. Under our experimental conditions, the possibility of isomerization of *cis*-olefin or *cis*-epoxide to the corresponding *trans*-isomer was ruled out after examination of the olefin recovered after epoxidation and that of the epoxide recovered after similar treatment. These facts indicate that epoxidation by H_2O_2–Fe^{3+} takes place *via* equilibration of the original olefin geometry, in contrast to the complete retention of geometry in epoxidation by peracids. We therefore conclude that the reaction proceeds *via* an intermediate which is derived from the olefin and which can rotate around the C–C bond, thus attaining conformational equilibrium.

It is also possible that FeO^{3+}, which is believed to participate in chemical and biological oxidations with hydrogen peroxide catalysed by ferric complexes,[9] takes part in our epoxidation. If FeO^{3+} ion shows substantial radical character, as suggested by Hamilton,[10] epoxidation should proceed *via* the biradical intermediate which is an adduct of the olefin with the FeO^{3+} ion and has a sufficiently long lifetime to attain equilibrium in conformation.

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