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Regio- and Stereo-selectivities in the Epoxidations of Limonene, *endo*-Dicyclopentadiene, and *exo*-Dicyclopentadiene

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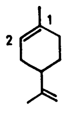
The regio- and stereo-selectivities were observed in the radical and peracid epoxidations of limonene, *endo*-, and *exo*-dicyclopentadienes. The observations were considered in view of the proposed mechanisms for these reactions.

It has been believed that the epoxidation by molecular oxygen of olefin induced by a radical initiator proceeds through a peroxy-radical attack to open the double bond,[1] while the epoxidation by peracid proceeds through an electrophilic attack of the peracid oxygen to make a three-membered cyclic transition state.[2] In our experiments connected with studies of the unsensitized photooxidations of limonene and dicyclopentadienes,[3] we observed substantial regio- and stereo-selectivities in the radical and peracid epoxidations. These observations were then considered in the light of the proposed mechanisms.

Results

Limonene (**1**), *endo*-dicyclopentadiene (**2**), and *exo*-dicyclopentadiene (**3**) were oxidized with molecular oxygen at 40—60 °C (Ox I) and with peracid (Ox II). The epoxides **4**—**10** were isolated in pure states by preparative gas chromatography, and the product identification was carried out spectroscopically (see Experimental Section). The ratios of the regioisomers in each case were calculated; they are shown in Table 1.



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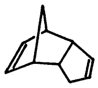

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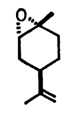

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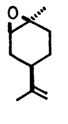

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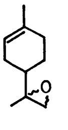

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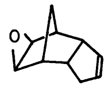

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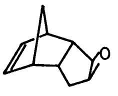

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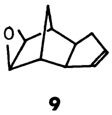

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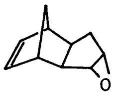

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Table 1. Product ratios in the epoxidations of 1-3

	(4+5)/6	7/8	9/10
Ox I	4.8	7.0	7.4
Ox II	14.0	1.3	3.7

Discussion

It was found that the 1,2-epoxidation of **1** by the radical-initiated oxidation proceeds in quite a stereoselective manner, affording mainly the *trans*-isomer **4**.* This result should be contrasted with that of the peracid epoxidation, where a 1 : 1 mixture of *trans*- and *cis*-isomers (**4** and **5**) has been obtained.[6] This observation can now be interpreted in terms of the general pattern of radical attack on 4-substituted cyclohexene.[7]

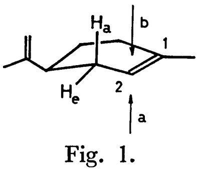

Fig. 1.

Presumably, the initial attack of the peroxy radical occurs at C-2 rather than at C-1 in view of Markownikov's principle (Fig. 1). The a-attack (*trans* to isopropenyl) at C-2 would be preferable to the alternative b-attack, since the b-attack creates a larger energy by its interference with the neighboring quasi-axial hydrogen (H_a), thus leading to the more unfavorable twisted-boat transition state. This type of attack can reasonably be said to lead to the preferential formation of **4** over **5**, as has actually been observed.

As is revealed by Table 1, the relative reactivity of each double bond in **1**—**3** was characteristic of the oxidation method. With **1**, the regioselectivity was observed in Ox II, while with **2** and **3**, the selectivity was observed to a larger extent in Ox I. These observations can be explained by the following consideration. The epoxidation with peracid has been interpreted as proceeding by an electrophilic attack of peracid oxygen on the double bond, thus producing a three-membered cyclic transition state.[2] It has generally been accepted that, in the reactions proceeding through a four-, five-, or six-membered cyclic transition state, the reactivity of a strained double bond is greatly enhanced as compared with that of a strain-free double bond, because a great deal of strain-energy release is expected in the transition state, while in the reaction proceeding through a three-membered cyclic transition state, scarcely any strain-energy release is expected in the transition state, and the strain present in the double bond can not play a very important role

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* A previous experiment dealing with this problem has not led to any definite result.[4] A non-stereospecific radical epoxidation has, however, been reported with α-terpineol.[5]

in the reactivity.[8] Evidently, each double bond in **1** is characterized mostly by its electron density rather than by its strain energy, while the situation is reversed with **2** and **3**, since the double bond in the norbornene moiety is confined under strained circumstances. In the Ox II of **1**, where the reactivity of the double bond is determined mostly by the electron density, three-substituted olefin would be epoxidized preferentially over the two-substituted olefin, and a high selectivity should result. The selectivity would be reduced with Ox I, since there is little difference in strain energy between the two double bonds in **1**. The minor preference for the formation of **4** and **5** over **6** is probably a reflection of the electrophilic nature of the radical reaction.[9]

Contrary to the results with **1**, we observed a substantial regio selectivity in Ox I with **2** and **3**. Evidently the radical epoxidation *via* double-bond opening proceeds much faster with a double bond of strained norbornene. In Ox II, however, there was little selectivity between the two double bonds. A slight preference in the reactivity of norbornene double bond, particularly with **3**, induces us to picturize the transition state as involving a *loose* three-membered cyclic ring, thus affording an additional, although small, energy of strain release. The extreme low **7**/**8** ratio with **2** may be considered as a consequence of π-interaction through the space between the two double bonds in **2**, which interaction is evidently lacking in **3**.[10]

Experimental

Only experiments which do not overlap with those reported in our previous paper[3] are described here.

Starting Material. **3**: Prepared according to the method reported by Bartlett.[11]

Peracid Oxidation. Olefin (0.5 g) and perbenzoic acid (0.5 g) were dissolved in chloroform (6 ml) and stirred for 12 hr at 0 °C.

Product Identification. **5**: IR; Identical with the reported.[6] NMR; δ 1.25 (3H, s), 1.67 (3H, s), 2.85 (1H, d), and 4.65 (2H, s). **9**: IR; 1620 and 850 cm^{-1}. NMR; δ: 1.75 (2H, ABq, *endo*-methylene with an anisotropic effect by the epoxy ring), 2.96 (2H, s), and 5.43 (2H, m). **10**: IR; 1572 and 840 cm^{-1}. NMR; δ 1.40 (2H, b.s, *endo*-methylene), 3.10 (1H, d), 3.43 (1H, t), and 6.06 (2H, b.s).

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