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Steric Factors in Liquid-Phase Oxidation of Olefins with *iso* Structure

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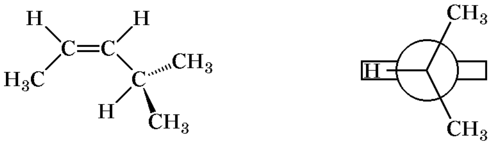
Abstract—Products of liquid-phase oxidation of 2-methyl-2-butene and 2-methyl-2-pentene were studied by NMR and IR spectroscopy. Steric hindrances in liquid-phase oxidation of olefins with *iso* structure were shown to arise from branching of the alkyl group at the α-carbon atom.

NMR and IR study of products of liquid-phase oxidation (hydroperoxides) of a mixture of *cis*- and *trans*-4-methyl-2-pentenes at 70°C showed that only the *trans* isomer is oxidized. The *cis* isomer remains almost unchanged [1]. The reason is steric repulsion of the alkyl groups in *cis*-4-methyl-2-pentene, which disrupts σ,π-conjugation between the tertiary α-C−H bond and the double bond. As a result, formation of stable (planar) allyl type radical is hindered [2]. This conclusion is supported by spatial models of the hydrocarbon and the radical (Scheme 1).

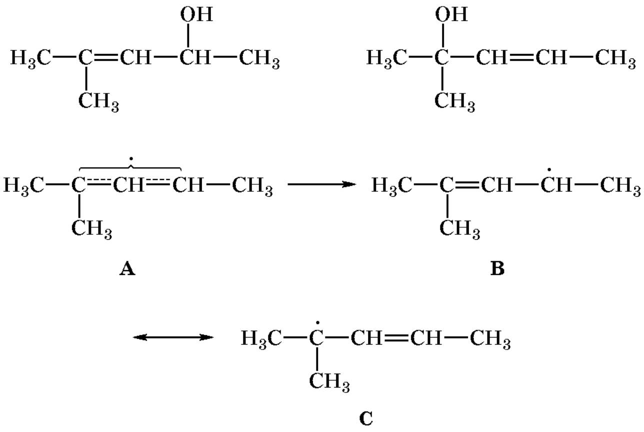
Scheme 1.



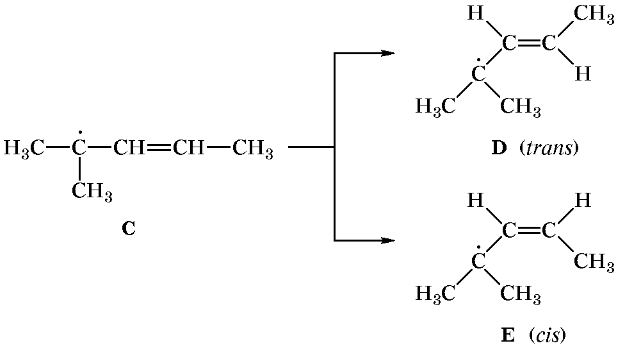
Steric hindrances in substituted *cis*-allyl radical make the formation of the corresponding oxidation products impossible, as follows from the results of our study of products of low-temperature oxidation of 2-methyl-2-pentene. By oxidation of 2-methyl-2-pentene at 70°C we obtained unsaturated hydroperoxides and unsaturated alcohols [3] which correspond to two canonical structures **B** and **C** of intermediate allyl type radical **A** (Scheme 2).

Tertiary radical **C** can exist as two isomers: *cis* and *trans*. However, the *cis* configuration (**E**) is characterized by steric repulsion between alkyl groups, so that its formation is hindered (Scheme 3). Therefore, only one of the two tertiary alcohols corresponding to

Scheme 2.



Scheme 3.



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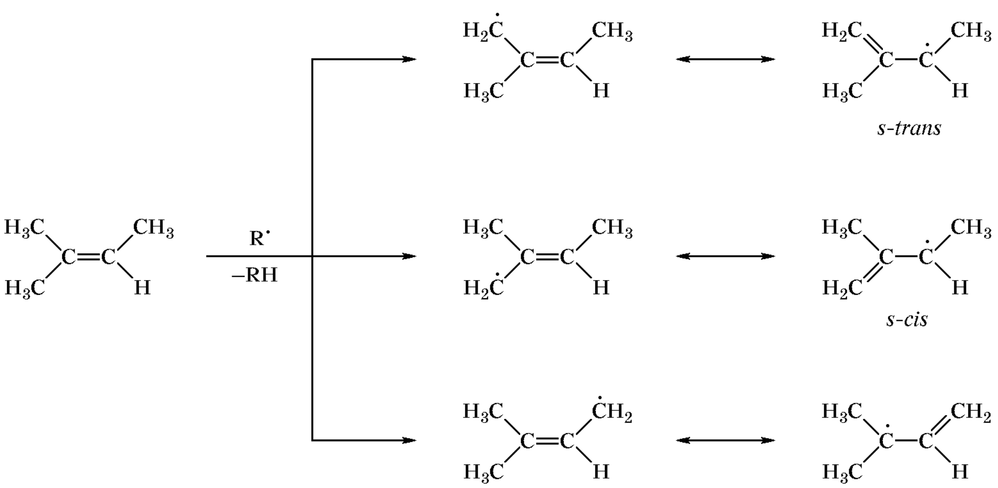
Scheme 4.

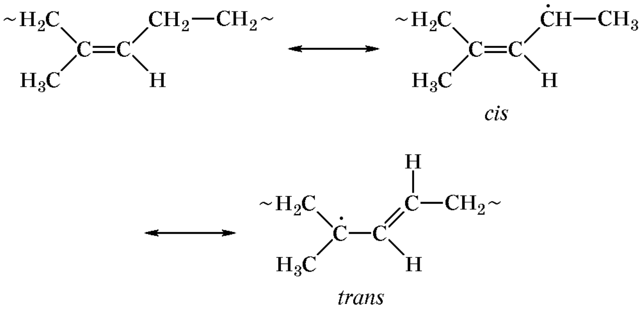


two isomeric allyl type radicals should be formed preferentially, namely *trans*-2-methyl-3-penten-2-ol. This assumption was proved by us experimentally using NMR and IR spectroscopy.

No steric effect was observed in the oxidation of olefins with *iso* structure which lack branching at the α-carbon atom. The major products of oxidation of 2-methyl-2-butene at 60°C were the corresponding secondary and tertiary hydroperoxides at a ratio of 2 : 1 (Scheme 4). Presumably, abstraction of hydrogen from the three methyl groups in 2-methyl-2-butene occurs with similar probabilities. Other conditions being equal, the ratio of hydroperoxides depends on the contributions of canonical structures to intermediate allyl type radical. Scheme 4 shows that the statistical probability for oxidation of secondary radical is twice as large as that for tertiary radical.

The structures of 2-methyl-2-pentene and 2-methyl-2-butene resemble the structure of elementary unit in natural rubber. When studying the mechanism of oxidation of natural rubber, the formation of tertiary allyl type radical was presumed (Scheme 5) [4].

Scheme 5.



However, the fact that the tertiary allyl type radical has *trans* configuration which is free of steric repulsion was not taken into account. Thus, steric factors in the oxidation of olefins with *iso* structure become determining when the hydrocarbon chain is branched at the α-carbon atom.

EXPERIMENTAL

The IR spectra were recorded on a UR-10 instrument. The ^1H NMR spectra were obtained on a Tesla BS-467C spectrometer in CCl_4. The chemical shifts were measured relative to hexamethyldisiloxane as internal reference. The reaction mixture was analyzed by gas–liquid chromatography on a Chrom-5 instrument equipped with a flame-ionization detector; carrier gas nitrogen.

2-Methyl-2-butene was oxidized with an oxygen–nitrogen mixture at 60°C (20 atm) in a glass reactor. The reaction time was 8 h (until the oxidate contained 0.8 to 1.0 wt % of hydroperoxides). Unreacted 2-methyl-2-butene was distilled off under reduced pressure at a temperature not exceeding 15°C. The resulting product contained more than 50 wt % of hydroperoxide. Its amount was determined by iodometric titration. ^1H NMR spectrum, δ, ppm: 1.15, 1.60, 4.30, 4.85, 5.10, 5.90, 9.60.

2-Methyl-2-pentene was oxidized with atmospheric oxygen at 60°C until the oxidate contained 10–15 wt % of hydroperoxide.

Products of oxidation of 2-methyl-2-pentene were reduced with sodium sulfite. Subsequent rectification gave two alcohols: 2-methyl-3-penten-2-ol and 2-methyl-2-penten-4-ol.

Methyl-3-penten-2-ol. bp 121.5–122°C, d_4^{20} 0.8343, n_D^{20} 1.4290. IR spectrum, ν, cm^{-1}: 970 (δ C–H in *trans*-HC=CH), 1678 (ν C=C, *trans*). ^{1}H NMR spectrum, δ, ppm: 1.15, 1.55, 3.93, 5.40.

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