

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

A. V. Voronkov, N. A. Simonov, O. P. Yablonskii,
S. G. Koshel', and V. V. Voronkov

Yaroslavl State Technical University, Moskovskii pr. 88, Yaroslavl, 150023 Russia

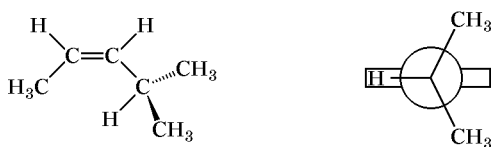
"Yarsintez Research Institute" Public Corporation, Yaroslavl, Russia

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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.

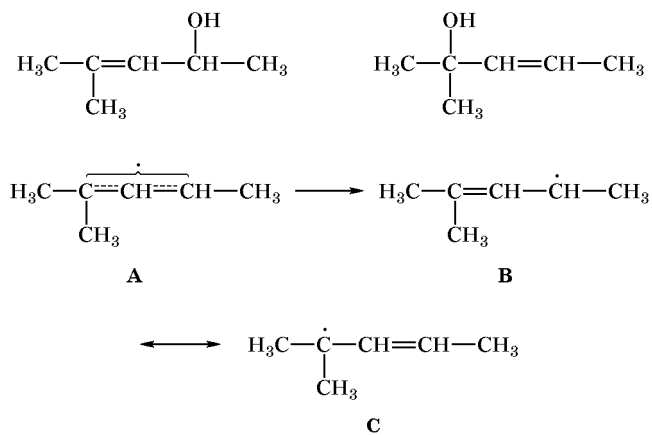


Steric hindrances in substituted *cis*-allyl radical make the formation of the corresponding oxidation products impossible, as follows from the results of our study of products of low-temperature oxidation of 2-methyl-2-pentene. By oxidation of 2-methyl-2-pentene at 70°C we obtained unsaturated hydroperoxides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

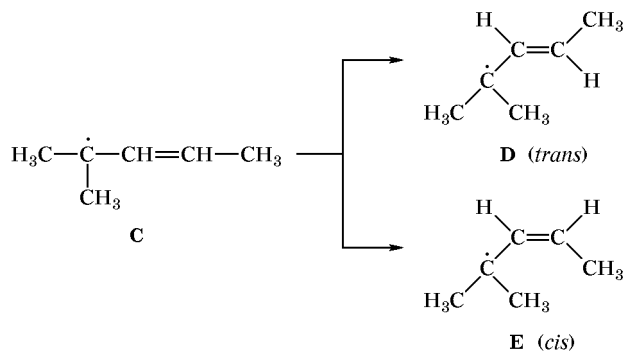
Tertiary radical **C** can exist as two isomers: *cis* and *trans*. However, the *cis* configuration (**E**) is characterized by steric repulsion between alkyl groups, so

that its formation is hindered (Scheme 3). Therefore, only one of the two tertiary alcohols corresponding to

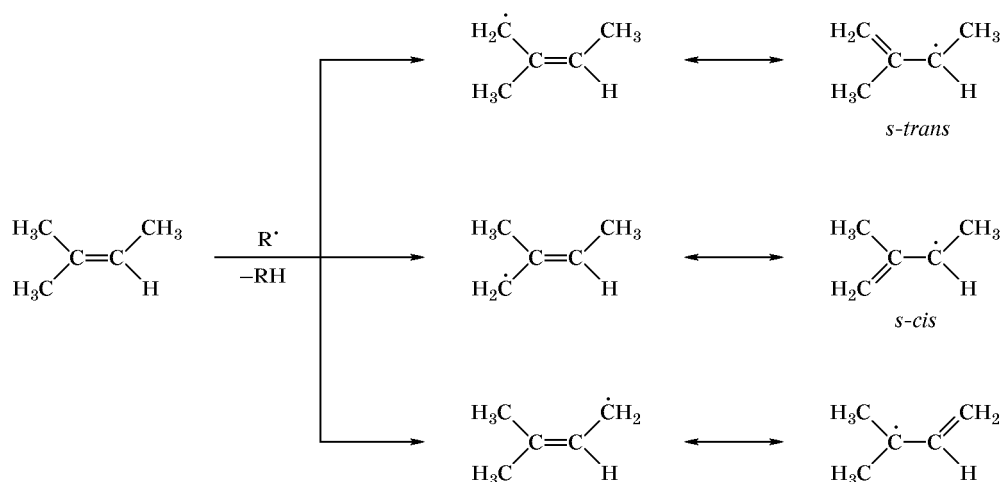
Scheme 2.



Scheme 3.



Scheme 4.

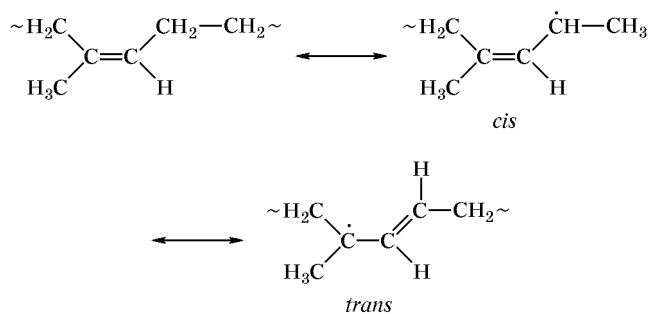


two isomeric allyl type radicals should be formed preferentially, namely *trans*-2-methyl-3-penten-2-ol. This assumption was proved by us experimentally using NMR and IR spectroscopy.

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 ($\delta\text{C-H}$ in *trans*-HC=CH), 1678 ($\nu\text{C=C}$, *trans*). ^1H NMR spectrum, δ , ppm: 1.15, 1.55, 3.93, 5.40.

REFERENCES

1. Voronenkov, V.V. and Musabekov, Yu.S., *Neftekhimiya*, 1968, vol. 8, no. 5, pp. 713–717.
2. Nonhebel, D.C. and Walton, J.C., *Free-Radical Chemistry*, Cambridge: Cambridge Univ., 1974.
3. Kryukov, S.I., Yablonskii, O.P., Voronenkov, V.V., and Simanov, N.A., *Zh. Org. Khim.*, 1971, vol. 7, no. 4, pp. 629–632.
4. Belyaev, V.A., Yablonskii, O.P., Voronenkov, V.V., and Pokrovskaya, Z.N., *Neftekhimiya*, 1973, vol. 13, no. 5, pp. 715–717.