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Abstract

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Stereochemistry of σ,π-Conjugation

Autoxidation of Rigid Allylic Systems

In our previous works on the spatial conditions of σ,π-conjugation (^{1}), it was shown that in rigid bicyclic structures the C—H and C—Hg bond at the bridgehead of a bicyclic structure, situated in the α-position to a carbonyl, is not activated by the carbonyl. The mercury of α-chloromercurycamphenilone and mercury-bis-α-camphenilone is not replaced by hydrogen under the action of acids and is not exchanged for radioactive mercury with Hg^{203} and $Hg^{203}Cl_2$, as occurs in α-mercurated ketones with mercury not located at the bridgehead. The α-hydrogen atom of camphenilone is not nitrated, not sulfonated, and not brominated. Usually, σ,π-conjugation of the system A—C—C=O is excluded when the axis of the σ-bond and the π-plane are perpendicular. Activation of the C—H bond is also observed in allylic systems H—C—C=C. Along with heterolytic substitution (metalation), they are especially characterized—unlike H—C—C=O systems—by homolytic substitution of hydrogen (homolytic σ,π-conjugation (^{1a})). Thus, allylic hydrogen is brominated by bromosuccinimide and is oxidized by hydroperoxide by atmospheric oxygen—reactions proceeding by a chain mechanism. Such is the oxidation of tetralin to the hydroperoxide (^{2}), cyclohexene (^{3}), isopropylbenzene (^{4}), Δ^3-*p*-menthene (^{5}), and other terpenes, cyclenes, and alkylbenzenes.

The present work aims to determine whether there exist the same conditions for excluding H—C—C=C conjugation as those we have demonstrated for H—C —C=O conjugation.

We investigated the susceptibility to oxidation by oxygen of such terpene hydrocarbons in which (owing to the presence of a methylene bridge) the C—H bond in the α-position to the double bond is spatially fixed relative to the latter, namely: bornylene (I), camphene (II), and δ-fenchene (III).

[[chemical structural formulas of bornylene (I), camphene (II), and δ-fenchene (III)]]

In the indicated sense, these hydrocarbons are compounds with a rigid structure. In the oxidation reaction we introduced two samples of bornylene and camphene, chemical structures labeled (IV) and (V)

Figure 1: chemical structures labeled (IV) and (V)

obtained by different routes, in order to exclude the possibility of error due to impurities.

It turned out that these three hydrocarbons, in experiments involving many hours of oxidation by oxygen at 40, 60, and 80° in the presence of such active initiators as cobalt and manganese stearates, do not absorb oxygen. After oxidation, the hydrocarbons were recovered from the solution unchanged.

Under these conditions, nonrigid allylic systems are readily oxidized by molecular oxygen in the presence or even in the absence of initiators.

For comparison, we carried out, under analogous conditions, the autoxidation of hydrocarbons with similar but nonrigid* structures, namely Δ^2-*n*-menthene (IV) and γ-fenchene (V)

Δ^2-*n*-menthene exhibited the ability, usual for an allylic group, to be oxidized by oxygen. Thus, even at 40° the oxidation of Δ^2-*n*-menthene in the presence of cobalt stearate proceeded at the rate normal for such hydrocarbons. After the unchanged Δ^2-*n*-menthene had been distilled off, the hydroperoxide obtained as a result of oxidation was distilled in vacuo and its constants were determined. In the case of γ-fenchene, oxidation is possible at the methyl group, for which a lower oxidation rate is characteristic; however, this hydrocarbon also proved capable of oxidation under sufficiently mild conditions. At 60° it oxidized slowly, whereas at 80° the oxidation of γ-fenchene proceeded at a normal rate.

Thus, the experiments described here show that in homolytic σ,π-conjugation the influence of the same spatial factors is manifested as in heterolytic conjugation.

Indeed, in bornylene, fenchene, and camphene the spatial relationships of the CH bond under study and the double bond are the same as in camphenylone. In these hydrocarbons the axis of the σ bond of the allylic hydrogen is rigidly fixed, as a result of the presence of a methyl bridge, in a position close to perpendicular with respect to the axis of the π bond.

It should be expected that also in other hydrocarbons with an allylic system, a hydrogen atom in a rigid CH unit with a C—H bond fixed perpendicular to the axis of the π bond (as, for example, the α-hydrogen at the base of the bridge in the molecule of α-pinene) will not exhibit lability. Therefore, the currently accepted scheme for the conversion of α-pinene into sobrerol (6) is doubtful and must be verified.

Experimental Part

The **preparation** of bornylene was carried out by two methods: 1) from borneol by Chugaev' s xanthogenate method (7), m.p. 101—102°; 2) from bornyl chloride by Meerwein' s method (8), with additional purification from an admixture of camphene, m.p. 104—105°. Literature data: m.p. 103—104° (7) and 103—104°, 107° (8).

Camphene was prepared: 1) by dehydration of isoborneol (9), m.p. 46—48°, b.p. 158—160°; 2) by dehydration of borneol (10), m.p. 47—49°. Literature data: m.p. 47—53° (10), m.p. 45—46°, b.p. 158—159° (11).

δ- and γ-fenchenes were obtained by dehydration of fenchyl alcohol, followed by repeated fractionation of the dehydration product (12). δ-Fenchene: b.p. 139—141°, n_D^{20} 1.4510, d_4^{20} 0.8465. Literature data: b.p. 140—141°, n_D^{20} 1.4502, d_4^{20} 0.8397 (12); b.p. 139—140°, n_D^{20} 1.4486, d_4^{20} 0.8433 (13); b.p. 138.5—141°, n_D^{20} 1.4505, d_4^{20} 0.8376 (14).

γ-Fenchene: b.p. 146—147°, n_D^{20} 1.4589, d_4^{20} 0.8553. Literature data: b.p. 145—147°, n_D^{17} 1.46072, d_4^{20} 0.8547 (12).

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* In the sense of relative fixation in space of the corresponding σ and π bonds.

Preparation of Δ^2-n-menthene was carried out by reduction of α-terpinene (15), b.p. 52-53.5°/10 mm; 154.5-157.5°/746 mm, n_D^{20} 1.4650. Literature data (15), b.p. 55-56°/12 mm, n_D^{20} 1.4610.

To purify the hydrocarbons from traces of impurities affecting the rate of oxidation, all the hydrocarbons studied were distilled repeatedly over metallic sodium before oxidation.

Oxidation was carried out in an apparatus consisting of a thermostat equipped with a mechanical stirrer, to which a "duck" reaction vessel is attached. The thermostat is also equipped with a heater, which is connected to the mains through a relay, a contact thermometer, and control thermometers. From a gasometer oxygen enters an eudiometric tube through a Drechsel bottle with a 50% solution of caustic potash. From the eudiometer the oxygen enters the reaction vessel, passing through a system of two columns and a Tishchenko bottle. One of the columns is filled with soda lime and calcium chloride, the other with calcium chloride only. The Tishchenko bottle is filled with phosphorus pentoxide. All parts of the system are connected by rubber tubes. Before the experiment was begun, the system was tested for tightness. Oxidation was conducted with oxygen at atmospheric pressure. A weighed portion of hydrocarbon in solvent and a weighed portion of initiator (manganese or cobalt stearate), amounting to 0.2 wt.% of the substance being oxidized, were placed in the "duck." To displace air from the system, a stream of oxygen was passed for 15 min, then the "duck" was closed and placed in the thermostat. When the reaction—

Table 11

Hydrocarbon	Sample, g	Solvent	Oxidation time, h	Temperature, °C	Volume of absorbed O_2, ml	Note
Bornylene from borneol	1.0	Benzene 20 ml	6	40	1.8	a
Bornylene from borneol	12.0	Benzene 18 ml	6	60	1.06	b, c
Bornylene from borneol	1.0	Naphthalene 10 g	6	82	3.9	b
Bornylene from bornyl chloride	3.5	Benzene 5 ml	6	60	3.7	b, c
Camphene from isoborneol	10.0	Benzene 20 ml	6	40	2.5	a
Camphene from isoborneol	10.0	The same	6	50	2.3	a, d
Camphene from isoborneol	10.0	» »	6	60	2.7	a, d
Camphene from isoborneol	10.0	Without solvent	9	60	4.0	a, d
Camphene from isoborneol	10.0	» »	6	80	4.3	a, d
Camphene from borneol	1.0	Benzene 2 ml	6	40	2.0	a, d
δ-Fenchene	1.0	Without solvent	8	60	2.7	a

Hydrocarbon	Sample, g	Solvent	Oxidation time, h	Temperature, °C	Volume of absorbed O_2, ml	Note
δ-Fenchene	1.0	» »	6	80	3.5	a
Δ^2-n-Menthene	15.8	» »	18.5	40	907	a, b, d
γ-Fenchene	2.5	» »	13	60	35.0	a, c, e
γ-Fenchene	2.5	» »	21	80	165.4	a, c, e

Notes. 1. In blank experiments with 20 ml of benzene and 0.002 g of cobalt (or manganese) stearate at 60° for 6 h, the decrease in oxygen volume reached 3.7 ml.
2. a —with addition of 0.2% by weight of manganese stearate.
b —with addition of 0.2% cobalt stearate.
c —the bornylene recovered from the experiment had m.p. 93–95°.
d —the camphene recovered from the experiments had m.p. 47–48°.
e —from the oxidized solution, by vacuum fractionation, 9.4 g of unoxidized menthene was recovered. On further vacuum fractionation, fractions were collected: fraction I: b.p. 50–52°/0.31 mm, n_D^{20} 1.4805; fraction II: b.p. 72°/0.31 mm. A viscous, non-distilling residue remained in the flask. Fraction II is the hydroperoxide of Δ^2-n-menthene with the following constants: b.p. 72°/0.31 mm, d_4^{20} 1.0072, n_D^{20} 1.4960, MR_D 49.30. Calculated for $C_{10}H_{18}O_2$: MR_D 49.45; molecular weight: found 165, calculated 170.
f —the oxidation product was subjected to vacuum fractionation. After distillation of unoxidized γ-fenchene, a fraction was collected in the amount of 0.4 g, b.p. 50°/0.1 mm, n_D^{20} 1.4765. The product liberates iodine from an acidified solution of potassium iodide.

the vessel had reached the thermostat temperature, the oxygen level in the eudiometer was recorded, after which the amount of oxygen absorbed was recorded at equal time intervals; the values given in Table 1 have been reduced to normal conditions.

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