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10. **Morizo Ishidate and Masahisa Yoshida**: The Cleavage of Camphor Ring. III. The Formation of 1-Methyl-4-acetylcyclohexan-2-one by the Photochemical Decomposition of *trans*-π-Oxocamphor.

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Due to the peculiar tension of the bicyclopentanone ring, the aldehyde group at C_7 in *trans*-π-oxocamphor (1) suffers varied reactions. Apart from the reactivity to oxygen[1] and hydrogen peroxide,[2] the oxocamphor tends to decompose partially into carbon monoxide and santenone (α and β)[3] (III), both in the presence and absence of oxygen, and by alkali hydrolysis into formic acid and santenone.[4] These phenomena, however, are nothing unusual in some aldehyde compounds.

Now it was found that on autoxidation of *trans*-π-oxocamphor in the air, either in a solution or in a solid state, another transformation product besides those substances mentioned is formed. The new product is characterized by the active methylene reaction (nitroprusside or picric acid test). In the absence of oxygen (in carbon dioxide atmosphere), however, the transformation products of *trans*-π-oxocamphor remained negative to the active methylene test.

With the aid of a repeated liquid column chromatography employing alumina, a fraction giving a positive nitroprusside test was collected and purified by distillation. This substance was optically inactive and gave bis(dinitrophenylhydrazone) of m.p. 210~215°(decomp.). The analytical data and the mixed fusion of the bis-(dinitrophenylhydrazone) as well as its absorption spectrum were proved to be identical with those of 1-methyl-4-acetylcyclohexan-2-one (VI).

Quite recently, it has been shown by one[5] of the authors that 1-methyl-4-acetylcyclohexan-2-one (VI) is formed quantitatively from *trans*-7-hydroxy-π-apocamphor (V) under spontaneous rearrangement. Accordingly, it seems without doubt that *trans*-7-hydroxy-π-apocamphor (7-hydroxy-α-santenone) should be produced as an intermediate on the autoxidation of *trans*-π-oxocamphor.

Although 1-methyl-4-acetylcyclohexan-2-one is a minor product from the autoxidation of *trans*-π-oxocamphor, its formation is remarkably accelerated by light, especially that of shorter wave length. The mechanism of this photochemical decomposition might be explained by radical-catalysed reaction as shown.

The activated *trans*-π-oxocamphor decomposes into santenone (II) and carbon monoxide, while the intermediate santenone radical (II′) attaches a molecular oxygen to give a peroxide radical (III′). The latter under interaction with aldehyde (I) forms the peroxide (III), which with another aldehyde gives isoketopinic acid (IV) besides 7-hydroxy-π-apocamphor (V), which is isolated as 1-methyl-4-acetylcyclohexan-2-one (VI).

Experimental

Photochemical Decomposition of *α-trans-π*-Oxocamphor (I)—i) In the absence of oxygen: A solution of 10 g. of (I) in 1 L. of CO_2-saturated water was placed in a 2-L. flask. After replacing the air with CO_2, the flask was closed with a rubber stopper and exposed to sunlight for 10 days. The gas in the flask was introduced to a CO tester[6] which contained ammonium molybdate and

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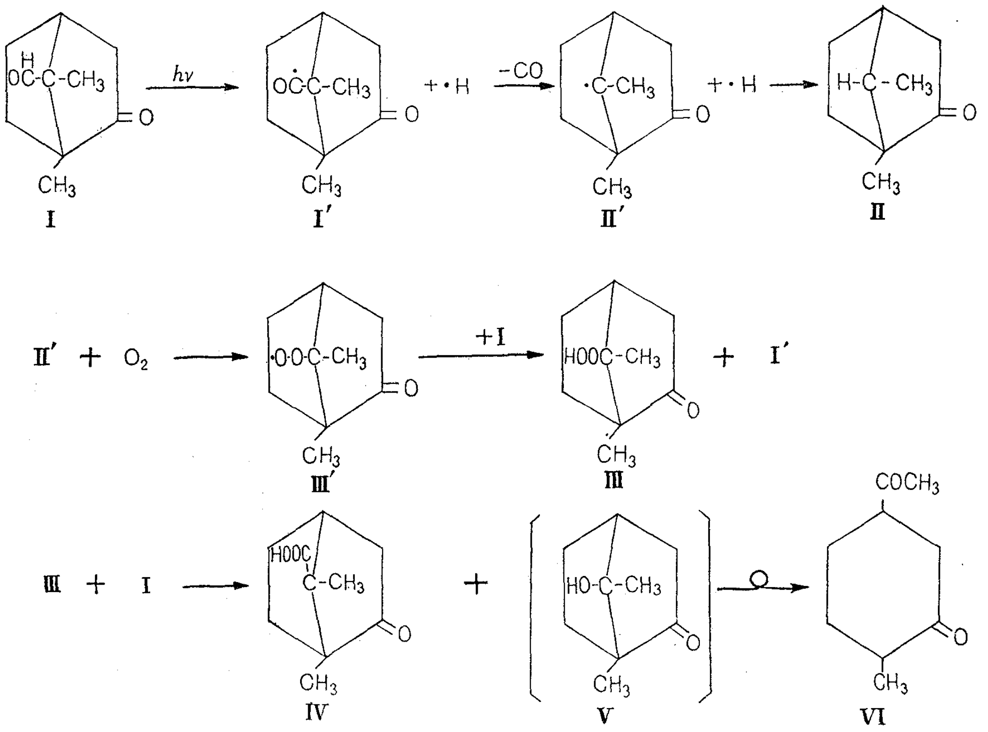

palladium sulfate on silica gel. The amount of CO produced was estimated as ca. 76 mg., which corresponds to the decomposition of ca. 4.5% of (I).

The mother liquor which gave a negative nitroprusside test was extracted with ether. The ether layer was washed consecutively with $NaHSO_3$ and Na_2CO_3 solution to remove (I) and formic acid. The ether residue was distilled with steam. From the first portion of the distillate α-santenone was isolated as its semicarbazone (m.p. 235°).

ii) In the presence of oxygen : Separation of 1-methyl-4-acetylcyclohexan-2-one (VI) : A solution of 10 g. of (I) in 1 L. of water was placed in a 2-L. flask, stoppered, and allowed to stand in sunlight for 10 days. The amount of CO produced was estimated as ca. 456 mg. by the same method as above, which corresponds to the decomposition of 27% of (I). The mother liquor gave a strong positive reaction with nitroprusside and picric acid reagents.

By the colorimetric measurement of the methyl ketone employing picrinic acid, the amount of the methyl ketone (VI) in the solution was estimated as 250 mg., i.e. ca. 2.5% of the theoretical.

The solution was then extracted with ether. The ether solution, after being washed with Na_2CO_3 solution, was evaporated. The residue weighed 3.5 g. which was then dissolved in petroleum ether and passed through Al_2O_3(100 g.) column (40 mm. diameter). The column was eluted with benzine-benzene (1:1), benzene, and benzene-EtOH (4:1).

The eluates which gave positive nitroprusside reaction were collected and evaporated (yield: 0.5 g.). For further purification the substance was again subjected to alumina chromatography using benzine-$CHCl_3$ and benzine-benzene to collect the methyl ketone fraction. The fraction was then distilled in vacuum to obtain a fraction of b.p$_{18}$ 130~135°. The substance was optically inactive (5% EtOH solution). U.V. : $\lambda_{max}^{H_2O}$ 245 mμ (315), 275 mμ (145), which are identical with those of the synthetic preparation of (VI).

Bis(2,4-dinitrophenylhydrazone) of (VI) : Obtained as yellow prisms of m.p. 210~215° (decomp.). The mixed fusion with the authentic sample gave no depression. *Anal.* Calcd. for $C_{21}H_{22}O_8N_8$: C, 49.01; H, 4.31; N, 21.79. Found : C, 49.52; H, 3.97; N, 21.68.

Summary

By photochemical reaction in the presence of oxygen *trans*-π-oxocamphor decomposes to 1-methyl-4-acetylcyclohexan-2-one, besides carbon monoxide and santenone. The occurrence of the first indicates the formation of 7-hydroxy-α-santenone as an intermediate. In the absence of oxygen, however, 1-methyl-4-acetylclohexan-2-one, accordingly 7-hydroxysantenone, was not formed.

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