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18. **Takuichi Miki and Yujiro Hara** : Studies on Ethylenic Compounds. II.* Synthesis of a New Isomer of Ionone with Allene Group.

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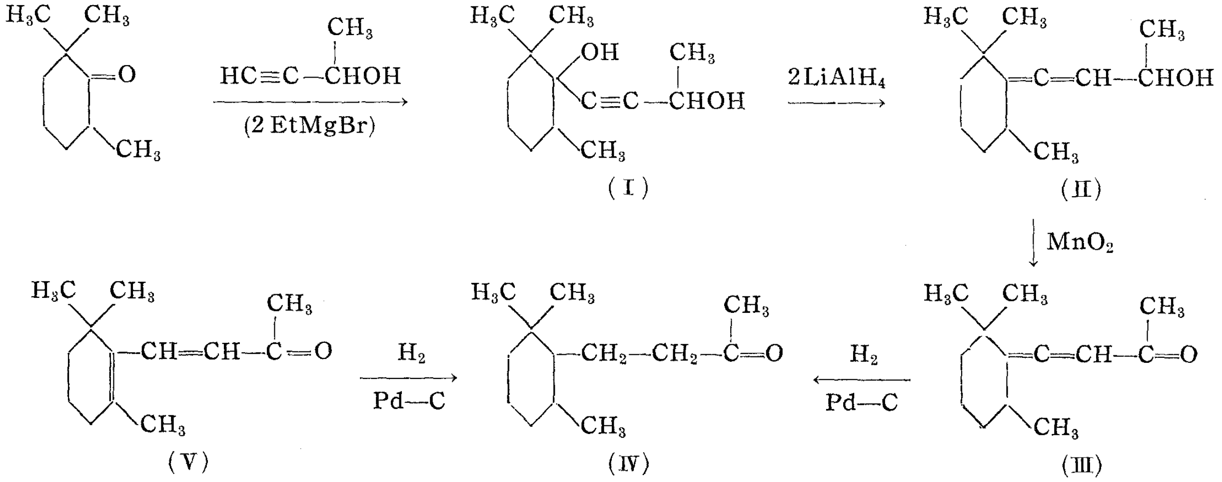
Recently, Bates and Jones1) reported that a reduction accompanied with dehydration occurred on the treatment of diphenylbutynediol with an excess of lithium aluminum hydride. The British workers also observed that α,α'-acetylenediol was converted to α,α'-monoenediol and allenic alcohol by a similar procedure.2) It appeared interesting to apply this new method to the synthesis of some compounds having the ionone structure.



In the preceding paper,3) we reported that 2,6,6-trimethylcyclohexanone was transformed to 1-(1′-hydroxy-2′,6′,6′-trimethylcyclohexyl)but-1-yn-3-ol (I). The acetylenediol (I) was further reduced and dehydrated to an allenic alcohol, 1-(2′,6′,6′-trimethylcyclohexylidene)but-1-en-3-ol (II), by the action of two moles of lithium aluminum hydride in 95% yield. The product was proved to be an allenic alcohol (II) by its infrared spectrum which exhibits a strong band at 1957 cm^{-1} indicating the presence of an allene group (Fig. 1-A). The ultraviolet spectrum also supports the assigned structure since it has an absorption maximum at 230 mμ(ε 2,700). Since Ball, *et al.*4) found that manganese dioxide was an effective reagent for the oxidation of vitamin A to retinene, this has been widely used to oxidize many polyene alcohols and allyl alcohols to their corresponding carbonyl compounds. The application of this reaction to some aromatic alcohols5) and α, β-acetylenic alcohol6) has already been described. Such mild conditions are also expected to convert the allenic alcohol (II) to the corresponding allenone (III), 1-(2′,6′,6′-trimethylcyclohexylidene)but-1-en-3-one, in an excellent yield. The infrared spectrum of this compound exhibits two absorp-

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1) cf. P. Nayler, M. C. Whiting : J. Chem. Soc., **1954**, 4006.

2) E. R. Bates, E. R. H. Jones, M. C. Whiting : *Ibid.*, **1954**, 1854.

3) T. Miki, Y. Hara : This Bulletin, **4**, 85(1956).

4) S. Ball, *et al.* : Biochem. J. (London), **42**, 519(1948).

5) S. Sugasawa, K. Mizukami : This Bulletin, **2**, 341(1954).

6) L. Weisler, J. M. Dieterle : U. S. Pat. 2,672,481(1954)(C. A., **49**, 3260(1955)).

tions at 1938 and 1678 cm^{-1}, characteristic of the allenic chromophore and conjugated carbonyl group, respectively, but it has no absorption indicating the hydroxyl group which was observed in the infrared spectrum of the allenic alcohol (II)(Fig. 1 B). The ultraviolet spectrum possesses an absorption maximum at 230 mμ(ε 16,000) showing the presence of a carbonyl group conjugated with allene group. The allenone (III) is a new isomer of ionone, but its two double bonds are located outside the ring. The compound has not the odor of other isomers of ionone but of camphor.

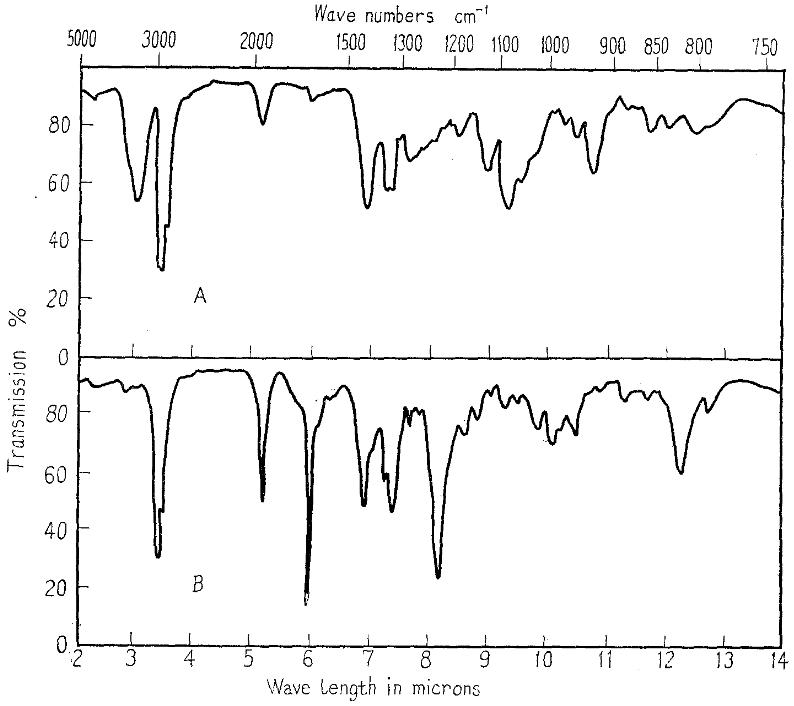

Fig. 1. Infrared spectra

A. 1-(2′,6′,6′-Trimethylcyclohexylidene)but-1-en-3-ol (II)

B. 1-(2′,6′,6′-Trimethylcyclohexylidene)but-1-en-3-one (III)

Although the 2,4-dinitrophenylhydrazone of *cis*-tetrahydroionone,[7] which was prepared from β-ionone (V) by catalytic hydrogenation, melted at 120°, that of the tetrahydroionone (IV), obtained from the allenone (III) by the same reduction, showed m.p. 92° even after several recrystallizations. However, a mixture of both compounds showed a medium melting point. Also their paper partition chromatography proved that they have the same Rf value. From the facts mentioned above, the latter material seems to be a mixture of *cis*- and *trans*-tetrahydroionones.

The authors wish to thank Dr. S. Kuwada and Dr. T. Matsukawa for their helpful and stimulating interest in this work. The authors are also indebted to Mr. T. Toga for his aid in preparing intermediates and in paper partition chromatography, to Mr. M. Kan and his associates for performing the microanalyses, and to Mr. H. Kamio and Mr. T. Shima for the determination of absorption spectra.

Experimental

1-(2′,6′,6′-Trimethycyclohexylidene)but-1-en-3-ol (II)—A solution of 21.2 g. (0.1 mole) of the acetylenediol (I) in 150 cc. of dehyd. ether was added at 0° to a suspension of 7.2 g. (0.2 mole) of commercial $LiAlH_4$ in 200 cc. of dehyd. ether. After refluxing with stirring for 8 hrs., the mixture was cooled and the excess of $LiAlH_4$ was decomposed with water. The ethereal solution was worked up with a saturated tartaric acid solution and water and dried over anhyd. Na_2SO_4. After evaporation of the solvent the residue was distilled *in vacuo* and 18.5 g. of the fraction of

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7) V. Prelog, H. Frick : Helv. Chim. Acta, **31**, 417(1948).

b.p$_{18}$ 125$\sim$135° was collected. Yield, 95.4%. On redistillation 15.3 g. of the product, b.p$_{18}$ 130$\sim$131°, n_D^{19} 1.4954, was obtained. λ_{max}^{EtOH} 230 mμ(ε 2,700). *Anal.* Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found : C, 80.06; H, 11.53.

1-(2′,6′,6′-Trimethylcyclohexylidene)but-1-en-3-one (III)—To a solution of 3 g. of the allenic alcohol (II) in 100 cc. of petr. ether (b.p. 60$\sim$90°) was added 17 g. of activated MnO_2. After shaking for 24 hrs. at room temperature, the mixture was filtered and the solid was thoroughly washed with ether. The filtrate and the washings were combined and evaporated under a reduced pressure. The residual oil gave 2.6 g. of (III), b.p$_{18}$ 135°, n_D^{19} 1.5043, upon vacuum distillation. λ_{max}^{EtOH} 230 mμ(ε 16,000). *Anal.* Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found : C, 81.01; H, 10.62.

2,4-Dinitropheylhydrazone : Red needles, m.p. 178°, after recrystallization from petr. ether (b.p. 60$\sim$80°). *Anal.* Calcd. for $C_{19}H_{26}O_4N_4$: C, 61.27; H, 6.48; N, 15.05. Found : C, 61.20; H, 6.55; N, 14.98.

Hydrogenation of the Allenone (III) **to Tetrahydroionone** (IV)—A solution of 1.2 g. of the allenone (III) in 50 cc. EtOAc was hydrogenated at atmospheric pressure employing 500 mg. of 4% Pd-C as a catalyst and 300 cc. of H_2 was consumed at 22°. The residual oil, obtained after filtration of the reaction mixture and evaporation of the solvent, was then distilled *in vacuo*. The product, 1.2 g., b.p$_{20}$ 136°, was collected. The 2,4-dinitropheylhydrazone was recrystallized from a mixture of petr. ether (b.p. 60$\sim$90°) and EtOH as yellow plates, m.p. 92°, which melted at 105$\sim$110°, on admixture with the corresponding derivative, m.p. 120°, of *cis*-tetrahydroionone.7) *Anal.* Calcd. for $C_{19}H_{28}O_4N_4$: C, 60.62; H, 7.50; N, 14.88. Found : C, 60.93; H, 7.46; N, 14.98.

Paper Chromatography of 2,4-Dinitrophenylhydrazones of Tetrahydroionones (IV)—The compounds were chromatographed with a mixture (10 : 1) of petr. ether (b.p. 40$\sim$80°) and benzene on strips of Toyo Roshi No. 131, dried at room temperature after wetting with 20% MeOH solution of phenyl cellosolve, by the one-dimensional ascending method.

2,4-Dinitrophenylhydrazone	Rf
Tetrahydroionone (IV) obtained from the allenone (III)	0.55
cis-Tetrahydroionone	0.55

Summary

By treatment with an excess of lithium aluminum hydride, 1-(1′-hydroxy-2′,6′,6′-trimethylcyclohexyl)but-1-yn-3-ol (I) was converted to 1-(2′,6′,6′-trimethylcyclohexylidene)but-1-en-3-ol (II), which was further oxidized to the corresponding allenone (III), a new isomer of ionone, by the action of activated manganese dioxide.

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