# $\Delta^{9(10)}$-Octal-1-one and its Molecular Compound[1)]

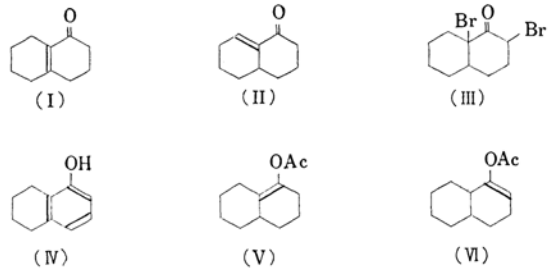
By Akira SUZUKI* and Takeshi MATSUMOTO

(Received August 16, 1962)

In the course of a study on the synthesis of a certain diterpenoid[2)] the authors stood in need of the synthesis of $\Delta^{2(3)}$-octal-1-one from decal-1-one. It is well known that the bromination of 6-ketocholestanyl acetate[3)] at low temperature gives a 5-bromo-derivative, which is converted into an isomeric 7-bromoketone on heating in acetic acid containing hydrogen bromide. Although there have been few papers[4)] reporting the bromination of decal-1-one at the time this work was initiated, the authors attempted to synthesize $\Delta^{2(3)}$-octal-1-one through bromination of *trans*-decal-1-one, followed by conversion of thus obtained 9-bromo-derivative into 2-bromo-isomer, and then by dehydrobromination.

The reaction of *trans*-decal-1-one with an equivalent of bromine in chloroform at low temperature led to a mixture of bromoketones, from which a dibromodecalone, melting at 94～95°C and being designated as " dibromide ", was isolated. The yield of dibromoketone depended upon the rate of addition of bromine. The NMR spectrum (40 Mc.) of a mixture of bromoketones contained resonance lines centered at 5.41$\tau$[5)] attributable to the hydrogen atom at the $C_2$ position of 2-bromodecal-1-ones. It was, however, found that the quantity of 2-bromo-derivatives was several per cent by the estimation of the relative peak area. At the time such results were ascertained, Zimmerman and Mais[6)] reported that the monobromination product of *trans*-decal-1-one in acetic acid containing hydrogen bromide at low temperature consists of ca. 80% of 9-bromodecalones (cis and trans) and ca. 20% of 2-bromo-isomers.

The crude bromination product, which appeared to be chiefly composed of 9-bromodecalones, was treated with hydrogen bromide in acetic acid solution, but the isomerization shown in 6-ketocholestanyl acetate[3)] could not be effected. The first attempt to synthesize $\Delta^{2(3)}$-octal-1-one from *trans*-decal-1-one was thus unsuccessful. However, the dehydrobromination product of bromodecalones described above is expected to be either $\Delta^{8(9)}$-octal-1-one (II) or $\Delta^{9(10)}$-octal-1-one (I). The literature describes[7-23)] a variety of reactions leading to an octal-1-one, to which usually the structure I is assigned.




Although the chemical properties of this substance were in accord with structure I, the observation[13)] that the compound exhibited an ultraviolet absorption maximum at 243 m$\mu$ led Campbell and Harris to assign structure II to this octalone. The present authors therefore undertook the elucidation of the structure of the unsaturated ketone, which is also a

* Present address: Chemical Process Engineering Department, Faculty of Engineering, Hokkaido University, Sapporo.

1) Read in part before the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.
2) T. Matsumoto and A. Suzuki, This Bulletin, **34**, 274 (1961).
3) I. M. Heilbron, E. R. H. Jones and F. S. Spring, *J. Chem. Soc.*, **1937**, 801.
4) F. Galinovsky, *Ber.*, **76**, 230 (1943).
5) H. Conroy and R. A. Raphael's " Advances in Organic Chemistry, Methods and Results ", Vol. II, Interscience Publishers, Inc., New York (1960), pp. 287—291.
6) H. E. Zimmerman and A. Mais, *J. Am. Chem. Soc.*, **81**, 3644 (1959).
7) W. Hückel, R. Danneel, A. Schwartz and A. Gercke, *Ann.*, **474**, 121 (1929).
8) W. Hückel and M. Blohm, ibid., **502**, 114 (1933).
9) W. Hückel and H. Naab, ibid., **502**, 136 (1933).
10) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, **1935**, 1637.
11) J. W. Cook and C. A. Lawrence, ibid., **1937**, 817.
12) C. D. Nenitzescu and V. Przemetzky, *Ber.*, **74**, 676 (1941).
13) W. P. Campbell and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941).
14) G. C. Harris, ibid., **64**, 720 (1942).
15) A. J. Birch, *J. Chem. Soc.*, **1944**, 430.
16) A. J. Birch, A. R. Murray and H. Smith, ibid., **1951**, 1945.
17) M. I. Bowman, C. C. Ketterer and A. U. Chamberlain, *J. Org. Chem.*, **18**, 905 (1953).
18) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **75**, 3717 (1953).
19) A. L. Wilds and N. A. Nelson, ibid., **75**, 5360 (1953).
20) K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953).
21) R. K. Hill and R. T. Conley, *Chem. & Ind.*, **1956**, 1314.
22) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).
23) M. F. Ansell and J. W. Ducker, *J. Chem. Soc.*, **1960**, 5219.

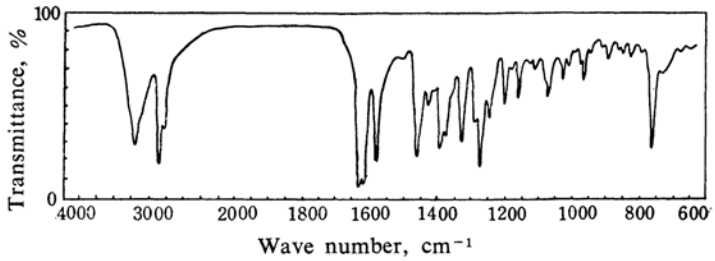



Fig. 1. Infrared spectrum of "solid octalone" (KBr Tablet).

possible intermediate for the synthesis of certain diterpenes. The crude 9-bromodecalones, previously described, could be converted into an octalone, b. p. 133~136°C/14 mmHg, by thermal dehydrobromination at 145°C; the octalone was tentatively named "liquid octalone". The identity of this product with that described in the literature was established by conversion to the 2, 4-dinitrophenylhydrazone, oxime, and semicarbazone. At the same time, there could be obtained a crystalline compound which had m. p. 58~59°C and was designated as "solid octalone". The latter compound afforded the same 2, 4-dinitrophenylhydrazone, oxime and semicarbazone as the those from "liquid octalone". The authors supposed at this stage that though the chemical and physical properties of "liquid octalone" are similar to the octalone which was previously reported[7-23], the "solid octalone" is a purer sample. Contrary to expectation, the elemental composition of the latter compound corresponded to $(C_{10}H_{13}O)_n$ rather than to that of the expected octalone, $C_{10}H_{14}O$ (see Experimental). Moreover, the infrared spectrum of the "solid octalone" (Fig. 1.) exhibited absorption bands at 3200, 1637, 1623, 1587 and 760 $cm^{-1}$. These bands suggest presence of a hydroxyl group and aromatic ring.

That the octal-1-one afforded the corresponding 2, 4-dinitrophenylhydrazone in a quantitative yield, was described by Campbell and Harris[13]. The "solid octalone", however, could only afford the same derivative in about a 50% yield.

From the above results, the authors next supposed that the "solid octalone" was a molecular compound of the octalone I or II, and a phenolic substance, perhaps, 5, 6, 7, 8-tetrahydronaphth-1-ol, because the presence of 2, 9-dibromodeca-1-one in the reaction mixture of the bromination of *trans*-decalone was indicated, as will be shown later. The obtained experimental data seem to support this assumption, which can be summarized as follows:

(1) The elemental composition completely agrees with that of the molecular complex $C_{20}H_{26}O_2 (=C_{10}H_{14}O+C_{10}H_{12}O)$.

(2) In the infrared spectrum, the bands at 1587 and 760 $cm^{-1}$ correspond to aromatic ring, 1637 $cm^{-1}$ to the conjugated carbonyl group, 1623 $cm^{-1}$ to a conjugated double bond, and 3200 $cm^{-1}$ to the bonded hydroxyl group.

(3) The "solid octalone" affords the same 2, 4-dinitrophenylhydrazone, oxime and semicarbazone obtained from the "liquid octalone" which is regarded as the octalone I or II.

(4) The yield of the 2, 4-dinitrophenylhydrazone is about 50%.

(5) Furthermore, through the aid of NMR spectroscopy, the "solid octalone" was suggested to be a molecular compound consisting of hydronaphthol V and octalone I rather than II. The absorption spectrum[24] (Fig. 2) is roughly divided into two parts, at a low and high applied magnetic field. The former, part A, is characteristic of proton resonance for aromatic, vinyl, and phenolic hydroxyl hydrogens[25], and the latter, part B, for other alicyclic hydrogens[25]. The intensity ratio between parts A and B, $I_A/I_B$ which is given by the area ratio, is 5.3. The calculation value is 5.5 for the molecular compound made up of IV and I, while it is 4.2 for that composed of IV and II.

In hope confirming the structure, the authors next attempted the separation of components. After chromatography on alumina, there could

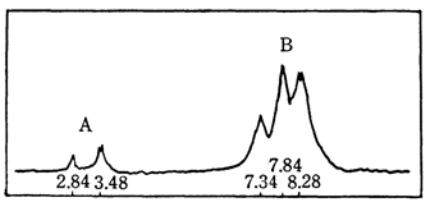



Fig. 2. The NMR spectrum of "solid octalone" in $CCl_4$.

24) The NMR spectra were taken on a Varian 40 Mc. instrument at Tohoku University through the courtesy of Prof. Genjiro Hazato, Drs. Tsuneo Ikenoue and Kensuke Takahashi, to whom the authors are pleased to express their sincere thanks.

25) H. S. Gutowsky, D. S. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), pp. 50—71; see also Ref. 5.

be quantitatively isolated from the "solid octalone", a crystalline compound, m. p. 70~71°C and a liquid fraction. The former compound was characterized, as expected, as 5, 6, 7, 8-tetrahydronaphth-1-ol (V) and the latter compound as the "liquid octalone" by comparison with authentic sample. Conversely, the "solid octalone" could be obtained by mixing the two components in the proportion of one to one in mole.

Next, the authors discuss the structure of the "liquid octalone". The ultraviolet spectrum shows a maximum at 245 m$\mu$ ($\varepsilon$ 12000) (lit., House and Thompson[29], 245.5 m$\mu$ ($\varepsilon$ 12400); Campbell and Harris[13], 243 m$\mu$ ($\varepsilon$ 11000)) characteristic of an $\alpha,\beta$-unsaturated ketone. The basis on which Campbell and Harris[13] considered the structure to be octalone II, is that the maximum at 243 m$\mu$ falls within the range (234 to 244 m$\mu$) which was shown by Woodward[26] to be characteristic of $\alpha,\beta$-unsaturated ketones having one hydrogen on the doubly bound carbon atoms, and the only octal-1-one which meets this requirement is the $\Delta^{8(9)}$-derivative II. However, according to Woodward's calculation rule[26,27] for ultraviolet spectrum, the most probable maximum for $\Delta^{9(10)}$-octalone I ought to be situated at about 247 m$\mu$[28]. Further evidence, therefore, is needed before a definite decision between the 8, 9 and 9, 10 positions of the double bond can be made. In the present work, the question was solved by the aid of NMR spectroscopic method. The NMR spectrum (40 Mc.) of the "liquid octalone" exhibited no absorption below 7 $\tau$. It has been therefore confirmed that the structure of the "liquid octalone" is $\Delta^{9(10)}$-octal-1-one (I). Recently, the same result had been reported by House and Thompson[29]. Consequently the "solid octalone" is the molecular compound of I and 5, 6, 7, 8-tetrahydronaphth-1-ol (IV).

Moreover, the dibromodecalone, m. p. 94~95°C, which was previously named "dibromide", is probably 2, 9-dibromodecal-1-one (III) for the reason that the bromide, on heating with collidine, gives 5, 6, 7, 8-tetrahydronaphth-1-ol (IV). The "dibromide" appears to correspond to a dibromodecalone reported by Galinovsky[4] and by Zimmerman and Mais[6]. The infrared spectrum of III showed an absorption at 1726 $cm^{-1}$ characteristic of carbonyl vibration, whereas that of parent decal-1-one at 1705 $cm^{-1}$. Considering Corey's observation[30] for $\alpha,\alpha'$-dibromocyclohexanone derivative, this wave number between the two ketones indicates that one bromine atom is axial and the other is equatorial in the dibromodecalone III. Further evidence, however, is necessary for determination of the complete stereochemistry.

In order to introduce a functional group only at the 2 position of decal-1-one, the authors next undertook to prepare the enol acetate VI. The reaction of *cis*-decal-1-one with acetic anhydride in the presence of *p*-toluenesulfonic acid was reported by Zimmerman and Mais[6] to yield an enol acetate. However, that the enol acetate prepared from *trans*-decal-1-one by tehir method has no absorption below 7$\tau$ in the NMR spectrum, has been ascertained in the course of the present work[31]. The product therefore may be regarded as practically pure $\Delta^{1(9)}$-enol acetate V.

## Experimental[32]

By the procedure of Johnson[33], *trans*-decal-1-one was prepared. The infrared spectrum of the decalone differed markedly from that of the cis compound[6]. For example, at 950 $cm^{-1}$, where the former showed a minimum, the latter exhibited a maximum. Conversely, at 907 $cm^{-1}$, *cis*-decalone had a minimum while trans-isomer showed a maximum. It was found through the infrared analysis that the decalone prepared in the above manner is an almost pure trans compound.

**Bromination of *trans*-Decal-1-one.**—A solution of 30.0 g. (0.2 mol.) of *trans*-decalone in 100 ml. of chloroform was kept at −20 to −10°C while a solution of 32.0 g. (0.2 mol.) of bromine in 100 ml. of chloroform was added dropwise with stirring over a period of 3 hr. The resulting solution was further stirred for 2 hr. under cooling and then washed successively with water, aqueous sodium bicarbonate, and saturated aqueous sodium chloride. After the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure at room temperature, 45.0 g. of crude 9-bromodecalone was obtained.

In the case of rapid addition of bromine to chloroform, the "dibromide" III was obtained. For example, 10.4 g. (0.065 mol.) of bromine in 30 ml. of chloroform was added to the decalone, 10.0 g. (0.065 mol.) in 30 ml. of chloroform for 20 min. After the reaction mixture was treated by the procedure described above, removal of the solvent in vacuo left an oily residue from which

26) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941).
27) R. B. Woodward, ibid., **64**, 76 (1942).
28) According to Fieser's modified calculation rule, this value is 249 m$\mu$. L. F. Fieser and M. Fieser, "Steroids", Reinhold Publishing Co., New York (1959), p. 19.
29) H. O. House and H. W. Thompson, *J. Org. Chem.*, **26**, 3729 (1961).
30) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 3297 (1953).
31) Independently, House and Thompson also obtained the same conclusion. See Ref. 29.
32) All melting and boiling points are uncorrected. Unless otherwise specified, infrared spectra were taken on a Koken model DS-301 infrared spectrophotometer with sodium chloride optics. Ultraviolet spectra were measured in 95% ethanol solution by means of a Beckman model DK-2 spectrophotometer. The authors are indebted to Mr. K. Narita for microanalysis.
33) W. S. Johnson, *J. Am. Chem. Soc.*, **65**, 1322 (1943).

on cooling 1.0 g. of crystalline material, m. p. 88～93°C, was obtained. The sample for analysis was prepared by recrystallization from petroleum ether (b. p. 30～60°C) ; it had m. p. 94～95°C, IR(KBr) 1726 $cm^{-1}$ (ketone group).

Found: C, 38.96; H, 4.66. Calcd. for $C_{10}H_{14}OBr_2$: C, 38.73; H, 4.64%.

**Thermal Dehydrobromination of 9-Bromodecal-1-one.**—The crude 9-bromodecalone, 45.0 g., was heated at 145°C under slightly reduced pressure (ca. 85 mmHg) for 2 hr. and then cooled. Distillation of the residue gave 13.5 g. of "liquid octalone" and 2.0 g. of "solid octalone".

**"Liquid Octalone", Namely $\Delta^{9(10)}$-Octal-1-one (I).**—This ketone has the following physical properties; b. p. 133～136°C/14 mmHg (lit., ca. 140°C/9 mmHg[10], 127～128°C/10 mmHg[18], 134～136°C/13 mmHg[16], 85～92°C/3 mmHg[17], 60～70°C/0.3 mmHg[23]), $n_D^{25}$ 1.5234 (lit., $n_D^{15}$ 1.4996[10], $n_D$ 1.4931[23], $n_D^{25}$ 1.5267[29]). The material had infrared absorption bands at 1660 (conjugated C=O) and 1632 $cm^{-1}$ (cojugated C=C). The NMR spectrum in carbon tetrachloride solution has a series of partially resolved bands in the region 7.5 to 8.6 $\tau$ with no absorption attributable to a vinyl hydrogen atom.

Found: C, 80.24; H. 9.45. Calcd. for $C_{10}H_{14}O$: C, 79.95; H 9.39%.

Reaction of a sample of the ketone with 2, 4-dinitrophenyl hydrazine yielded, after several recrystallizations from *n*-butyl alcohol dark red needles, m. p. 263°C decomp. (lit., m. p. 262°C[16], 266.5～267.5°C[17], 268°C[19], 264～266°C[20], 264.5～265.5°C[22], 271～272°C[23], 266～266.5°C[29]).

Found: C, 58.10; H, 5.31. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49%.

The melting point of the semicarbazone which was recrystallized from ethanol as colorless plates, was 240°C decomp. (lit., m. p. 242～243°C[11], 241～242°C[13,17], 246～247°C[23]).

Found: C, 63.64; H, 8.00. Calcd. for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27%.

The oxime of I, recrystallized from methanol, was colorless needles, melted at 147.5～128°C (lit., 144～145°C[10], 146～147°C[13], 148～149°C[23]).

Found: C, 72.37; H, 9.15. Calcd. for $C_{10}H_{15}ON$: C, 72.69; H, 9.15%.

**"Solid Octalone", viz. Molecular Compound of 5, 6, 7, 8-Tetrahydronaphth-1-ol (IV) and $\Delta^{9(10)}$-Octal-1-one (I).**—The complex, distilled at 145～147°C/14 mmHg, crystallized after standing at room temperature. Recrystallization from petroleum ether (b. p. 30～60°C) gave a pure sample as colorless needles, m. p. 58～59°C.

Found: C, 80.61, 80.72, 80.40, 80.57; H, 8.78, 8.88, 8.94, 9.01. Calcd. for $C_{20}H_{26}O$(=$C_{10}H_{12}O$+$C_{10}H_{14}O$): C, 80.49; H, 8.78%.

Ultraviolet absorption bands (Fig. 3) were found at 246 m$\mu$ ($\varepsilon$ 7160), and infrared absorption bands (Fig. 1) at 3200 (phenolic OH), 1637 (conjugated C=O), 1623 (conjugated C=C), and 1587 $cm^{-1}$ (aromatic ring). The NMR spectrum was reproduced in Fig. 2.

**Separation of Each Component from the Molecular Compound by Chromatography.**—Two hundred milligrams of the molecular compound was chromatographed on alumina (10 g.) packed and washed with ether. Forty fractions were collected as in the following table.

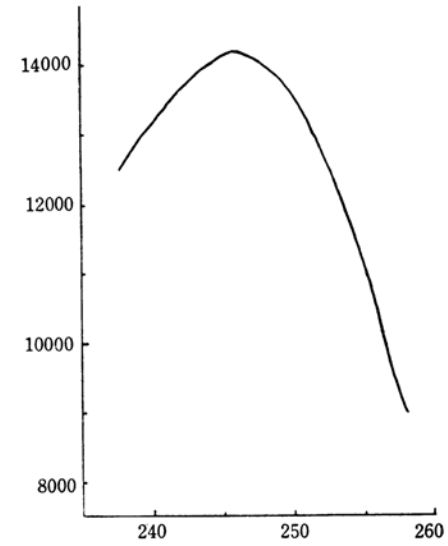


Fig. 3

| Fraction No. | Eluant | Residue |
|---|---|---|
| 1—10 | Ether; 50 ml. | Colorless oil, 95 mg. |
| 11—40 | Ether; 150 ml. | Colorless crystal, 102 mg. m. p. 65～68°C |

The colorless liquid, $n_D^{25.7}$ 1.5270, was identified by comparison of infrared spectra with $\Delta^{9(10)}$-octal-1-one (I). The colorless crystal afforded a pure sample by recrystallization from petroleum ether (b. p. 30～60°C), m. p. 70～71°C.

Found: C, 80.93; H, 8.02. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

The latter compound was characterized as 5, 6, 7, 8-tetrahydronaphth-1-ol (V) on the basis of mixed melting point determination with the authentic sample prepared by Papa's procedure[34].

Conversely, the molecular compound was yielded by mixing an equivalent amount of the former component with the latter. The identity of these two complex compounds was proved by melting and mixed melting point determinations.

**Dehydrobromination of 2, 9-Dibromodecal-1-one (III) with Collidine.**—A mixture of 100 mg. of the dibromodecalone (III) and 5 ml. of collidine was heated at 150°C for 20 min. under a nitrogen atmosphere. The resulting mixture was diluted with 6 N hydrochloric acid and then extracted with ether. The ether extracts were washed successively with 2 N hydrochloric acid, 5% aqueous sodium bicarbonate and water, and dried over anhydrous sodium sulfate. The solution was concentrated in vacuo to leave a pale brown oil, which on trituration with petroleum ether completely crystallized. Upon recrystallization from petroleum ether, it

34) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.* 7, 587 (1942).

formed colorless needles, m. p. 70~71°C. This compound was confirmed to be 5, 6, 7, 8-tetrahydronaphth-1-ol (IV) by the observation of mixed melting point with an authentic sample.

**Preparation of the Enol acetate (V).**—A mixture of 6.0 g. of *trans*-decal-1-one, 1.3 g. of *p*-toluenesulfonic acid and 150 ml. of acetic anhydride was heated under reflux in such a way that the acetic acid formed was allowed to distil from the reaction mixture. After 7 hr. 1.24 g. of anhydrous potassium acetate was added and the excess of acetic anhydride was almost completely evaporated under reduced pressure. The residue was cooled, diluted with benzene and washed successively with water, 5% aqueous sodium bicarbonate and water. The organic layer was concentrated and distilled to give 6.1 g. of enol acetate as a colorless liquid, b. p. 60~65°C/0.7 mmHg (lit., b. p. 63~66°C/0.75 mmHg[6], 68~79°C/0.6 mmHg[29]).

Found: C, 74.42; H, 9.30. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

IR (film) 1751 (C=O stretching) and 1217 $cm^{-1}$ (C−O stretching).

According to the report by House and Thompson [29], the enol acetate fraction prepared by a similar method was a mixture of $\Delta^{1(9)}$-enol acetate (V) (90%), *trans*-$\Delta^{1(2)}$-enol acetate (VI) (5%), and a component believed to be the *cis*-$\Delta^{1(2)}$-enol acetate. The product in the present experiment, however, has no absorption below 7$\tau$ in the NMR spectrum and may be regarded as practically pure $\Delta^{1(9)}$-enol acetate (V).

*Department of Chemistry*
*Faculty of Science*
*Hokkaido University*
*Sapporo*