The Thermal Condensation of Formaldehyde with Cycloolefins

By Shoji WATANABE

(Received April 14, 1964)

In a previous paper,[1] observations of the behavior of representative aliphatic olefins in their thermal condensation with formaldehyde were reported. It seemed desirable to extend this research by examining also the thermal condensation of some cycloolefins with formaldehyde. The present paper will describe the products obtained from β-pinene, camphene, thujopsene, dihydrothujopsene, 3-*p*-menthene, cyclohexene, 1-butyl-2, 6, 6-trimethyl-1-cyclohexene and 1-(2′-buten-1′-yl)-2, 6, 6-trimethyl-1-cyclohexene in their respective condensations with formaldehyde.

In this study all condensations with paraformaldehyde were carried out in acetic anhydride and at temperatures varying from 180 to 220°C, the products obtained being mainly acetates of olefinic, primary alcohols, in which the double bond, except those in the condensation products from camphene,[2] was located at a position adjacent to its original site in the starting olefins. The various condensation products are given in Table I.

β-Pinene (I) and camphene (III), which have an end methylene group, react readily with paraformaldehyde to give predominantly 2-acetoxyethyl-6, 6-dimethyl-bicyclo[3, 1, 1]-hept-2-ene (II) (nopyl acetate) and 8-acetoxymethylcamphene (V) respectively. From camphene, however, 8-hydroxymethylcamphene, isoborneol and isobornyl acetate were also obtained in fairly good yields under the experimental conditions shown in Table I.

The thermal condensations of thujopsene (V),[3] dihydrothujopsene (VIII) and 3-*p*-menthene (XI), which have a trisubstituted double bond, afforded rather complicated results. From the crude condensation product of thujopsene (V), an unsaturated acetate and an ether were separated successfully by means of column chromatography using a silica gel column. The acetate was saponified to give an alcohol, $C_{16}H_{27}OH$, which absorbed 95% of one equivalent amount of hydrogen over an Adams catalyst. The infrared spectrum showed primary hydroxyl absorption bands at 3300 and 1045 cm^{-1}, and a characteristic band of the trisubstituted double bond at 820 cm^{-1}. Therefore, this compound must be 1, 2, 3, 4, 4_a, 5, 6, 8_a-octahydro-6-(hydroxymethyl)-1, 1, 4_a, 7, 8_a-pentamethylnaphthalene (VI). The structural assignment was further supported by the nuclear magnetic resonance spectrum, as will be shown in the "Experimental" section (Fig. 1). On the other hand, the ether, $C_{17}H_{26}O$, F_1, was considered to be a cyclic ether, since the infrared spectrum showed a strong absorption band at 1100 cm^{-1}. The nuclear magnetic resonance spectrum indicated the signal of the allyl proton at 7.8 τ. The signal at 6.3 τ is presumably due to protons on the cyclic ether ($-CH_2-O-CH_2-$), while the signal at 9.3 τ was presumably due to the protons of the cyclopropane ring (Fig. 2). From this spectral evidence and from comparison with a similar case recently reported,[4] it was considered that this cyclic ether was 3, 4, 5, 6, 7, 8, 8_a, 9, 10,-10_a-decahydro-5, 5, 8_a-trimethyl-10, 10_a-methylene-1*H*-2-oxa-anthracene (VII).

Although dihydrothujopsene (VIII) scarcely reacted at all with paraformaldehyde in acetic

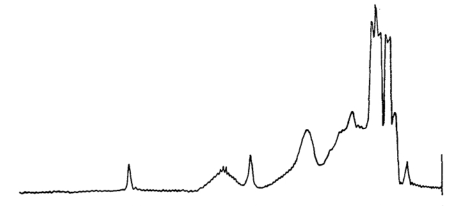


Fig. 1. The nuclear magnetic resonance spectrum of VI.

Fig. 2. The nuclear magnetic resonance spectrum of VII.

---

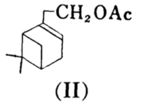
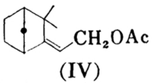
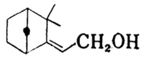
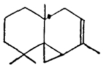
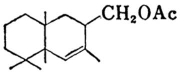
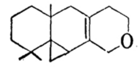
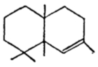
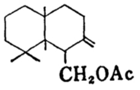
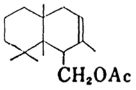
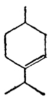
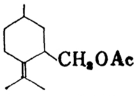
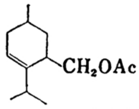
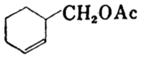
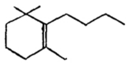
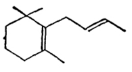
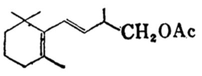
[1] S. Watanabe and K. Suga, This Bulletin, **36**, 1495 (1963).

[2] Y. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 827 (1960).

[3] S. Watanabe and K. Suga, ibid., **84**, 993 (1963).

[4] A. Arai, *Kobayashi Rigaku Kenkyusho Hokoku*, **10**, 29 (1960).

TABLE I. CONDENSATION OF OLEFIN WITH FORMALDEHYDE IN ACETIC ANHYDRIDE

Olefin		Reaction temp. °C	Reaction time hr.	Recovered olefin %	Product (yield, %)
Name	Structure				
β-Pinene (I)		200—205*1	5	31	 (60) (II)
Camphene (III)		180	5	53	 (20) and  (4), (IV) Isobornyl acetate*3 (17) and Isoborneol*3 (10)
Thujopsene (V)		185	3	38	 (10) and  (10) Acetate of VI (VII)
Dihydrothujopsene (VIII)		200—210*2	10	85	 and  (5) Acetate of IX Acetate of X
3-*p*-Menthene (XI)		200	3	57	 and  (22) Acetate of XII$_B$ Acetate of XII$_A$
Cyclohexene (XV)		220	9	50	 (12) (XVI)
2, 6, 6-Trimethyl-1-butyl-1-cyclohexene (XVII)		200—210*2	10	75	A primary alcohol, $C_{14}H_{26}O$ (XVIII) (6)
2, 6, 6-Trimethyl-1-[2′-butyl-1′-yl]-1-cyclohexene (XIX)		220	10	60	 (10) Acetate of XX

*1 Under 100 kg./cm^2 of hydrogen pressure.
*2 Acetic acid and a trace of H_2SO_4 added.
*3 Identified with authentic samples.

anhydride, it did react in a mixture of acetic anhydride, acetic acid and a trace of concentrated sulfuric acid to give an inhomogeneous acetate, which was then saponified to an inseparable mixture of unsaturated isomeric alcohols, $C_{16}H_{27}O$. The infrared bands at 810, 860 and 1040 cm^{-1} indicated the presence of a trisubstituted double bond, a terminal methylene, and a primary hydroxyl group. Thus, the mixture presumably consisted of 1, 2, 3, 4,-4_a, 5, 6, 7, 8, 8_a-decahydro -7 - methylene - 8 -(hydroxymethyl)-1, 1, 4_a, 8_a-tetramethylnaphthalene (IX) and 1, 2, 3, 4, 4_a, 5, 8, 8_a-octahydro-8-(hydroxymethyl)-1, 1, 4_a, 7, 8_a-pentamethylnaphthalene (X). The saponification of the condensation product from 3-*p*-menthene (XI) gave a mixture of unsaturated alcohols. The direct separation of the isomeric components by fractional distillation and gas chromatography was unsuccessful. The infrared absorption spectrum showed an absorption band at 810 cm^{-1}, indicating the presence of a trisubstituted ethylenic bond. Reduction gave 3-hydroxymethyl-*p*-menthane (XIV). Oxidation with potassium permanganate gave acetone, indicating the presence of an isopropylidene group, while oxidation with chromic anhydride gave an α, β-unsaturated aldehyde which was thought to be 3-formyl-3(4)-*p*-menthene (XIII). These results suggested that 3-hydroxymethyl-4(5)-*p*-menthene (XIIA) and 3-hydroxymethyl-4(8)-*p*-menthene (XIIB) were the main components of the mixture.

Cyclohexene (XV) reacted with paraformaldehyde to give (2-cyclohexenyl)methyl acetate (XVI) as the main product.

From the condensation product of 2, 6, 6-trimethyl-1-butyl-1-cyclohexene (XVII), which has a tetrasubstituted olefinic bond, an unsaturated alcohol, $C_{14}H_{26}O$, F_1 (XVIII) was obtained in a very poor yield. The infrared absorption spectrum indicated, however, that it was a primary alcohol, the structure of which has not yet been determined.

From the condensation of 2, 6, 6-trimethyl-1-[2′-buten-1′-yl]-1-cyclohexene (XIX) and paraformaldehyde, an unsaturated alcohol, $C_{14}H_{24}O$, F_2 (XX) was obtained in a poor yield. Its ultraviolet absorption spectrum (λ_{max} 242 mμ) indicated that it contained a dienic group. The infrared absorption spectrum showed the characteristic absorption bands of a trans-olefinic bond and a primary hydroxyl group. Therefore, 2-methyl-4-[2′, 6′, 6′-trimethyl-1′-cyclohexen-1′-yl]-3-buten-1-ol (XX) is a reasonable assignment for the alcohol.

The foregoing observations indicate that the thermal condensation of formaldehyde with cycloolefins in the presence of acetic anhydride occurs most readily with end methylene-type olefins, $CH_2=CR_1R_2$, and that trisubstituted olefins ($R_1CH=CR_2R_3$) and disubstituted olefins ($R_1CH=CHR_2$) are less reactive. Tetrasubstituted olefins of the $R_1R_2C=CR_3R_4$ type are least reactive.

Experimental

Materials. — β-Pinene, camphene, thujopsene, 3-*p*-menthene and cyclohexene were obtained from the Takasago Perfumary Co., Ltd.

*Dihydrothujopsene (VIII)*5) was prepared by the hydrogenation of thujopsene over palladised charcoal; b. p. 129—130°C/13 mmHg; d_D^{20} 0.9252; n_D^{20} 1.5039. The gas chromatogram showed one peak.

The preparation of *1-(2′-butenyl)-2, 2, 6-trimethyl-1-cyclohexene (XIX)*6) was carried out as follows. A mixture of 450 g. of β-ionone, 280 cc. of absolute ethanol, and 250 g. of hydrazine hydrate was refluxed for 4 hr. To this mixture, 800 g. of diethylene glycol, 180 g. of potassium hydroxide and 70 cc. of benzene were added, and the new mixture was refluxed for 2 hr. Fractional distillation gave 200 g. of crude 1-(2′-butenyl)-2, 6, 6-trimethyl-1-cyclohexene (XIX) (b. p. 75—135°C/45—50 mmHg), which was then fractionally redistilled to give 100 g. of an oil, b. p. 81.5°C/5 mmHg; d_D^{20} 0.8469; n_D^{21} 1.4836 (reported6) b. p. 91—93°C/11 mmg; d_4^{18} 0.8580; n_D^{18} 1.4795); molecular refraction: 60.18 (calcd. for $C_{13}H_{22}$, F_2, 59.10). IR (liq. film): ν_{max} 970 cm^{-1} (trans-olefinic bond). The gas chromatogram showed one peak.

1-Butyl-2, 6, 6-trimethyl-1-cyclohexene (XVII) was obtained by the hydrogenation of 1-(2′-butenyl)-2, 6, 6-trimethyl-1-cyclohexene (XIX) at 20 kg./cm^2 hydrogen pressure and room temperature, using a Pd-C catalyst. Distillation gave an oil (b. p. 73—78°C/3 mmHg; d_4^{20} 0.8460; n_D^{20} 1.4700). Bromine value: 100 (calcd. for $C_{13}H_{24}$, F_1, 89). NMR: 8.4 τ ($=\overset{|}{C}-CH_3$), 9.05 τ (*gem*-dimethyl group), 9.1 τ ($-CH_3$).

Condensation Procedure. — A mixture of 1 mol. of an olefin, 1 mol. of paraformaldehyde, and 0.5 mol. of acetic anhydride was heated at 180—220°C in a stainless autoclave for several hours. After it had been cooled, the reaction mixture was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulfate, and then treated in ordor to separate the components. For the respective condensations, the main conditions are given in Table I.

The Condensation of β-Pinene (I) with Formaldehyde. — From a mixture of 45 g. of I, 17 g. of acetic anhydride and 10 g. of paraformaldehyde, 14 g. of I and 41 g. of an oily product boiling at 98—168°C/10 mmHg were obtained. This product was proved by means of gas liquid chromatography to consist of 90% of 2-acetoxyethyl-6, 6-dimethyl-bicyclo[3, 1, 1]-hept-2-ene (II), and 8% of a high boiling fraction. Fractional distillation gave pure II (b. p. 98—100°C/10 mmHg). The saponification of II gave 6, 6-dimethyl-bicyclo[3, 1, 1]-hept-2-enyl ethanol (nopol), since the gas chromatogram and the infrared spectrum were identical with those of an authentic sample, b. p. 98—102°C/8 mmHg; d_4^{11} 0.9716; n_D^{13} 1.4945; bromine value, 99.51 (calcd. for $C_{11}H_{18}O$, F_1, 90.12); hydroxyl group, 8.62% (calcd. for monohydric alcohol, 10.2%).

The Condensation of Camphene (III) with Formaldehyde. — From a mixture of 340 g. (2.46 mol.) of III, 66.5 g. (2.2 mol.) of paraformaldehyde and 107 g. of acetic anhydride, 180 g. of III and 150 g. of a crude product (b. p. 100—130°C/7 mmHg) were obtained. This product consisted of 34% isobornyl acetate, 21% isoborneol, 40% 8-acetoxymethylcamphene (IV) and 5% 8-hydroxymethylcamphene, according to the gas liquid chromatographic analysis. The mixture (65 g.) was distilled to give the following fractions: (a) 20 g., b. p. 97—98°C/4 mmHg, (b) 25 g., b. p. 114—114.5°C/4 mmHg. The saponification of fraction b (24 g.) gave 18 g. of 8-hydroxymethylcamphene, b. p. 110—115°C/5 mmHg; d_4^{25} 0.9810; n_D^{25} 1.5016; molecular refraction, 50.20 (calcd. for $C_{11}H_{18}O$, F_1, 49.66); phthalic acid monoester, m. p. 127°C (reported2) m. p. 127—127.5°C); 3, 5-dinitrobenzoate, m. p. 89°C. The saponification of the fraction a gave isoborneol (m. p. 130°C).

The Condensation of Thujopsene (V) with Formaldehyde. — From a mixture of 50 g. of thujopsene (V), 9 g. of paraformaldehyde and 13 g. of acetic anhydride, 19 g. of an unsaturated hydrocarbon and 12 g. of a crude product (b. p. 120—140°C/5 mmHg; d_4^{18} 1.0196; n_D^{22} 1.5193) were obtained. The saponification of the crude product (50 g.) gave an oil (37 g.), b. p. 135—140°C/5 mmHg; d_4^{22} 1.0097; n_D^{22} 1.5216; hydroxyl group, 4.45% (calcd. for monohydric alcohol, 7.23%). The liquid chromatography of 10 g. of the oil with silica gel (70 g.) gave 4 g. of a viscous oil (A) from the

---

5) S. Forsen and N. T. Norin, *Acta Chem. Scand.*, **15**, 592 (1961).

6) R. Fischer, G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **34**, 1577 (1951).

elute with benzene and 4 g. of a viscous oil (B) from the elute with methanol.

The redistillation of A gave 3, 4, 5, 6, 7, 8, 8_a, 9, 10,-10_a-decahydro-5, 5, 8_a-trimethyl-10, 10_a-methylene-2*H*-2-oxa-anthracene (VII), b. p. 136°C/5 mmHg; bromine value, 139.2 (calcd. for $C_{17}H_{26}O$, F_1, 115.6). IR (liq. film): ν_{max} 1100 cm^{-1} (a cyclic ether). NMR:[7] 7.8 τ (allyl proton), 8.85, 8.87, 9.37 τ (three methyl groups), 6.3 τ ($-CH_2-O-CH_2-$), 9.3 τ (cyclopropane ring).

Found: C, 81.37; H, 10.28. Calcd. for $C_{17}H_{26}O$ (VII): C, 82.34; H, 11.36%.

Similarly, 1, 2, 3, 4, 4_a, 5, 6, 8_a-octahydro-6-(hydroxymethyl)-1, 1, 4_a, 7, 8_a-pentamethylnaphthalene (VI) was obtained from B, b. p. 139°C/5 mmHg; d_4^{15} 0.9907; n_D^{15} 1.5194; bromine value, 68.3 (calcd. for $C_{16}H_{26}O$, F_1, 74.6); hydroxyl group, 6.00% (calcd. for $C_{16}H_{25}(OH)$, 7.23%). IR: ν_{max} 3300, 1045 cm^{-1} (primary alcohol), ν_{max} 820 cm^{-1} (trisubstituted double bond). NMR: 4.93 τ (singlet, $-\overset{|}{\underset{|}{C}}-CH=\underset{|}{C}-$), 6.4 τ ($-\overset{|}{C}H-CH_2OH$).

Found: C, 81.18; H, 11.10. Calcd. for $C_{16}H_{28}O$ (VI): C, 81.29; H, 11.97%.

The Condensation of Dihydrothujopsene (VIII) with Formaldehyde. — From 124 g. of VIII, 21.6 g. of paraformaldehyde, 30.6 g. of acetic anhydride, 18 g. of acetic acid and one drop of concentrated sulfuric acid, 7 g. of a pale yellow oil (135—150°C/3 mmHg; n_D^{20} 1.5040; d_4^{20} 0.9920) was obtained. The saponification of this product gave an alcoholic compound. Liquid chromatography with silica gel gave a crude alcohol from the elute with methanol. The molecular distillation of this alcohol with a pot still gave 3 g. of 1, 2, 3, 4, 4_a, 5, 6, 7, 8, 8_a-decahydro-7-methylene-8-(hydroxymethyl)-1, 1, 4_a, 8_a-tetramethylnaphthalene (IX) and 1, 2, 3, 4, 4_a, 5, 8, 8_a-octahydro-8-(hydroxymethyl)-1, 1, 4_a, 7, 8_a-pentamethylnaphthalene (X). Bath temperature, 70°C/10^{-3} mmHg; d_4^{20} 0.9918; n_D^{20} 1.5193. IR: ν_{max} 810 cm^{-1} (a trisubstituted olefinic bond), ν_{max} 860 cm^{-1} (an end methylene group) and ν_{max} 1040 cm^{-1} (a primary hydroxy group). NMR: 5.3 τ ($-\overset{|}{C}=CH_2$), 4.6 τ ($CH_2-CH=\overset{|}{C}-$), 6.4 τ ($-\overset{|}{C}H-CH_2OH$).

Found: C, 79.72; H, 11.39. Calcd. for $C_{16}H_{28}O$: C, 81.29; H, 11.97%.

The Condensation of 3-*p*-Menthene (XI) with Formaldehyde. — From a mixture of 180 g. of XI, 60 g. of paraformaldehyde and 75 g. of acetic anhydride, 102 g. of XI and 60 g. of a crude acetate (b. p. 90—110°C/5 mmHg) were obtained. The saponification of the product gave 25 g. of a mixture of 3-hydroxymethyl-*p*-menthene; b. p. 100—104°C/5 mmHg; n_D^{30} 1.4815; d_4^{30} 0.9160; molecular refraction, 52.21 (calcd. for $C_{11}H_{20}O$, F_1, 51.85); hydroxyl group, 10.81% (calcd. for monohydric alcohol, 10.11%); bromine value, 107 (calcd. for $C_{11}H_{20}O$, F_1, 95); IR (liquid film): ν_{max} 1050 cm^{-1} (a primary alcohol), 810 cm^{-1} (a trisubstituted double bond).

3,5-Dinitrobenzoate was recrystallized from methanol; m. p. 79—80°C.

Found: N, 7.88. Calcd. for $C_{18}H_{22}O_6N_2$: N, 7.73%.

3-Hydroxymethyl-*p*-menthane (XIV).—3-Hydroxymethyl-*p*-menthene (XII) was hydrogenated over a nickel catalyst in a methanol solution at 150°C under 50 kg./cm^2 of initial hydrogen pressure to give 3-hydroxymethyl-*p*-menthane (XIV); b. p. 91—94°C/5 mmHg; n_D^{20} 1.4738. The gas chromatogram showed one peak.

3-Formyl-3-*p*-menthene (XIII).—To a mixture of 8 g. of XII and 50 cc. of glacial acetic acid, a mixture of 8 g. of chromic anhydride and 50 cc. of glacial acetic acid was added over an hour's period with vigorous agitation at 25°C; the mixture was then stirred for 2 hr., after which it was treated as usual. By fractional distillation, 3 g. of XIII (b. p. 70—80°C/5 mmHg) was obtained.

This gave a positive reaction with Schiff's reagent and reduced an ammoniacal silver nitrate solution.

2,4-Dinitrophenylhydrazone was recrystallized from a mixture of pyridine and methanol in the form of red needles; m. p. 141—142°C; UV: λ_{max} 380 mμ, ε 24000.

Found: N, 16.14. Calcd. for $C_{17}H_{22}O_4N_4$: N, 16.18%.

The Oxidation of XII with Potassium Permanganate. — A mixture of 7 g. of potassium permanganate and 50 cc. of water was added to 4 g. of XII and 20 cc. of water with vigorous agitation over a 30 min. period, the mixture was then left at room temperature for two days. After the unreacted potassium permanganate had been decomposed with hydrogen peroxide, the solution was filtered and extracted with ether. The ethereal solution (A) was washed with water and dried over anhydrous sodium sulfate. The aqueous solution and the washings were then combined (B). The solution A was distilled to give a small amount of a carbonyl compound, the structure of which was not determined. From the solution B, a carbonyl compound was separated as crude 2, 4-dinitrophenylhydrazone. Liquid chromatography with a silica gel column gave yellow needles (m. p. 121°C), which was identical with that of an authentic sample of acetone 2, 4-dinitrophenylhydrazone.

The Condensation of Cyclohexene (XV) with Formaldehyde.—From a mixture of 82.1 g. (1 mol.) of cyclohexene (XV), 30 g. (1 mol.) of paraformaldehyde and 51 g. (0.5 mol.) of acetic anhydride, 40 g. of a crude product was obtained. Distillation gave 10 g. of 1-hydroxymethyl-2-cyclohexene and 5 g. of a high-boiling fraction. 1-Hydroxymethyl-2-cyclohexene has the following properties: b. p. 74°C/11 mmHg; d_4^6 0.9816; d_4^{25} 0.9697; n_D^{15} 1.4914; n_D^{25} 1.4825; molecular refraction, 33.2 (calcd. for $C_7H_{12}O$, F_1, 33.2); bromine value, 127.5 (calcd. for $C_7H_{12}O$, F_1, 142). α-Naphthylurethan, m. p. 87°C (reported 87°C[8]).

Found: C, 76.66; H, 6.82. Calcd. for $C_{18}H_{19}O_2N$: C, 76.48; H, 6.81%.

1-Hydroxymethyl-2-cyclohexene (2 g.) was hydrogenated at 20 kg./cm^2 pressure in a stainless autoclave with Adam's catalyst. The usual workup

---

[7] L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), p. 85.

[8] A. T. Blomquist, J. Verdol, C. L. Adami, J. Wolinsky and D. D. Phillips, *J. Am. Chem. Soc.*, 79, 4978 (1957).

gave 1.0 g. of cyclohexylmethanol; b. p. 176—177°C; n_D^{25} 1.4617 6).

The high boiling fraction was found by gas liquid chromatography to be composed of various components, the structures of which were not determined.

The Condensation of 1-Butyl-2, 6, 6-trimethyl-1-cyclohexene (XVII) with Formaldehyde.—From a mixture of 25 g. of XVII, 7.2 g. of paraformaldehyde, 10.2 g. of acetic anhydride, 6 g. of glacial acetic acid and a trace of sulfuric acid, 3 g. of a crude product were obtained. The saponification of this product gave 1.5 g. of a crude alcohol (b. p. 100—115°C/3 mmHg). The chromatographic purification with activated silica gel gave 1 g. of an alcohol (n_D^{20} 1.4898) from the elution of methanol. The gas chromatogram showed one peak. IR: ν_{max} 1050 cm^{-1} (a primary alcohol).

Found: C, 78.91; H, 12.08. Calcd. for $C_{14}H_{26}O$: C, 79.52; H, 12.87%.

The Condensation of 1-[2'-Butenyl]-2, 6, 6-trimethyl-1-cyclohexene (XIX) with Formaldehyde.—From a mixture of 100 g. of XIX, 16.6 g. of paraformaldehyde and 24 g. of acetic anhydride, the following main fraction (10 g.) was obtained; b. p. 115—130°C/3 mmHg; UV: $\lambda_{max}^{C_2H_5OH}$ 240 mμ, ε 2162; IR: 1760 cm^{-1} (acetate), 1240 cm^{-1} (acetate), 970 cm^{-1} (trans olefinic bond). The saponification of this product gave 5 g. of 2-methyl-4-[2',6',6'-trimethyl-1'-cyclohexene-1'-yl]-3-butene-1-ol (XX), b. p. 110—120°C/3 mmHg; d_4^{15} 0.9164; n_D^{15} 1.5012; molecular refraction, 66.89 (calcd. for $C_{14}H_{24}O$, 66.24); UV: $\lambda_{max}^{C_2H_5OH}$ 242 mμ, ε 3213; IR: 1045 cm^{-1} (a primary alcohol), 970 cm^{-1} (trans-olefinic bond). The gas chromatogram showed one peak.

Found: C, 81.43; H, 11.62. Calcd. for $C_{14}H_{24}O$: C, 80.69; H, 11.63%.

Absorption Spectra. — The infrared absorption spectra were measured by using a Koken IRS spectrophotometer, while the ultraviolet absorption spectra were measured with a "Shimadzu" photometric spectrophotometer type QB-50.

Gas Liquid Chromatography. — The gas liquid chromatography was measured under the following conditions:

I, III, XI and XV: Column, LAC-2R-446 (20%) on Celite 545, 2 m.; temperature, 120°C; carrier gas, He 45 ml./min.

V, VIII, XVII, XIX, II, IV, XII and XVI: Temperature, 180°C; other conditions, the same as above.

VI, VII, IX, X, XVIII and XX: Column; silicone DC 200 (20%) on Celite 545, 2 m.; temperature, 230°C; carrier gas, He 45 ml./min.

The author is indebted to the Takasago Perfumary Co., Ltd., for providing materials; to Professor Sho Ito of Tohoku University for the magnetic resonance spectroscopy, and to Professor Kyoichi Suga of Chiba University for his cordial guidance throughout this work.

Department of Applied Chemistry
Faculty of Engineering
Chiba University
Yayoicho, Chiba