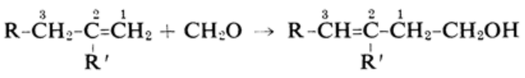
The Thermal Condensation of Formaldehyde with Aliphatic Olefins

By Shoji WATANABE and Kyoichi SUGA

(Received July 18, 1963)

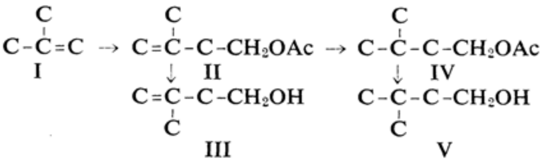
The addition of formaldehyde to olefins is known as the Prins reaction.[1] In a previous paper,[2] the preparation of a limonenylcarbinol, 1, 8(9)-*p*-menthadien-10-yl-carbinol, and its various derivatives was reported. The present paper describes the thermal condensation of paraformaldehyde with aliphatic olefins in the presence of acetic anhydride.

Various workers have shown that the principal products of thermal olefin-formaldehyde condensations are unsaturated primary alcohols in which the double bond is located at a position adjacent to its original site in the starting olefins.[3] In this study all condensations were carried out in acetic anhydride, at temperatures varying from 180 to 210°C, the products obtained being mainly acetates.



$$R-\overset{3}{C}H_2-\underset{R'}{\overset{2}{C}}=\overset{1}{C}H_2 + CH_2O \rightarrow R-\overset{3}{C}H=\underset{R'}{\overset{2}{C}}-\overset{1}{C}H_2-CH_2OH$$

The isoprene process is in two stages. The first stage involves the use of the Prins reaction, in which isobutylene is reacted with formaldehyde under mild conditions to give 4, 4-dimethylmethadioxane as the principal product. The 4, 4-dimethyl-methadioxane is then decomposed to isoprene in the second stage, with a recycle of the by-product formaldehyde. This method is used as the industrial process for making isoprene.[4,5] In the presence of acetic acid and acetic anhydride, the reaction of isobutylene with formaldehyde was studied.[6] The authors also studied the thermal condensation of isobutylene (I) with paraformaldehyde under various reaction conditions in an attempt to prepare an unsaturated primary alcohol, 3-methyl-3-buten-1-ol (III).



From the condensation of isobutylene (I) with paraformaldehyde in the presence of acetic anhydride (at 180°C), 3-methyl-3-butenylacetate (II) was obtained in ca. a 30% yield. The hydrolysis of this II gave 3-methyl-3-buten-1-ol (III). The structure of III was established as (1) by reduction and hydrolysis or by hydrolysis and reduction, giving 3-methyl-butan-1-ol (V). II and III showed strong absorption in their infrared spectra at 890 cm^{-1}, indicating that they possessed the end methylene group.

In this condensation reaction, some etheric compounds, the structure of which was not determined, were obtained in ca. 13% yield.

As catalysts, aluminum chloride, zinc chloride, boron trifluoride etherate, iron carbonyl, titanium tetrachloride and anhydrous stannic chloride were used, and the products were analyzed with gas-liquid chromatography. The results are shown in Table I. From this results, it is established that the condensation gave the acetate of the unsaturated primary alcohol 3-methyl-3-buten-1-ol (III) and etheric compounds.

The condensation of 2-ethyl-1-hexene (VI) with paraformaldehyde at 220°C in the presence of acetic anhydride gave an acetate VII in ca. a 66% yield. By the saponification of this acetate VII, the corresponding alcohol VIII was obtained. Analysis, the hydroxy value and the bromine value indicated that the product was an adduct of one mole of formaldehyde to VI ($C_9H_{18}O$ VIII). The infrared absorption spectrum showed the absorption band characteristic of a primary alcohol type at 1050 cm^{-1}, and those characteristic of a trisubstituted ethylene type at 1660 cm^{-1} and 830 cm^{-1}. The gas liquid chromatogram of VIII showed two peaks, the areas of which were nearly equal. From these facts, it is thought that VIII is a mixture of VIII$_A$ and VIII$_B$. The reduction of VIII gave a saturated primary alcohol (IX), the gas-liquid chromatogram of which showed only one peak. The

---

[1] H. J. Prins, *Proc. Acad. Sci. Amsterdam*, **22**, 51 (1919); *J. Chem. Soc.*, **118**, 42 (1920).

[2] K. Suga and S. Watanabe, This Bulletin, **32**, 1100, 711 (1959).

[3] a) O. Kriebitz, *Ber.*, **32**, 57 (1899); b) A. T. Blomquist, M. Passer, C. S. Schollenberger and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 4972 (1957); c) G. Ohloff, *Arch. Pharm.*, **287**, 258 (1954); d) K. Suga and S. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 749, 1142 (1962).

[4] A. Y. Giraud, *Chem. Eng. Progress*, **57**, (9), 66 (1961).

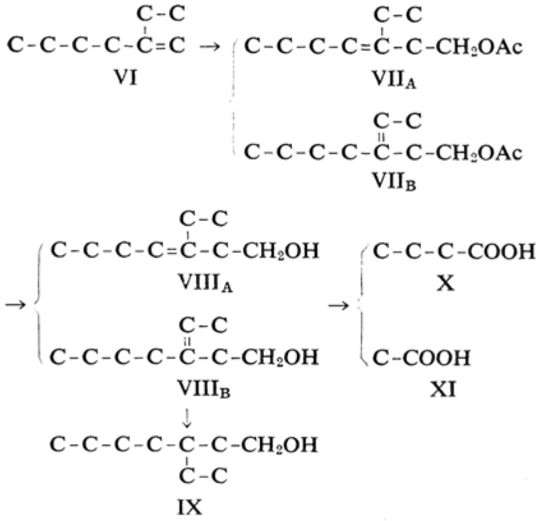
[5] K. Fukui, Y. Ōe, H. Kitano, *J. Chem. Soc. Japan., Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 1667 (1959).

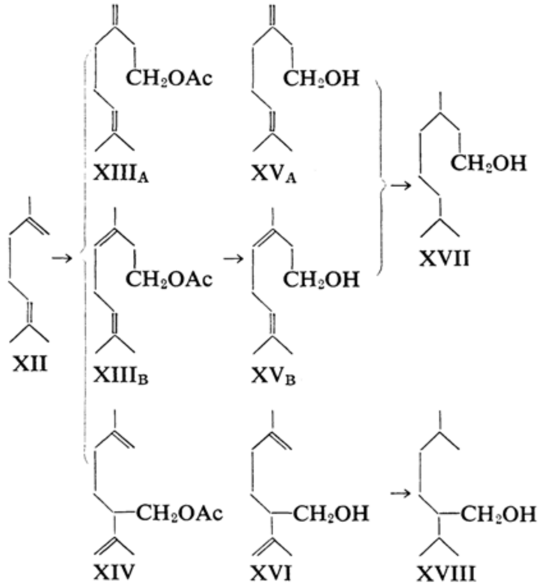
[6] A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 78 (1955).

TABLE I

Additive component	Main products (yield, %) Lower boiling point fraction	 $C{=}\overset{C}{\overset{|}{C}}{-}C{-}CH_2OAc$	 Higher boiling point fraction
Acetic anhydride		25	10
Acetic anhydride*		30	10
$SnCl_4$			8
$SnCl_4$, Acetic anhydride			21
$AlCl_3$	3		
BF_3, Acetic anhydride			21
$Fe(CO)_4$, Acetic anhydride		35	10
$Fe(CO)_4$	30		15
$TiCl_4$, Acetic anhydride		15	5
$TiCl_4$	10		

* The initial pressure with H_2 was 100 kg./cm².

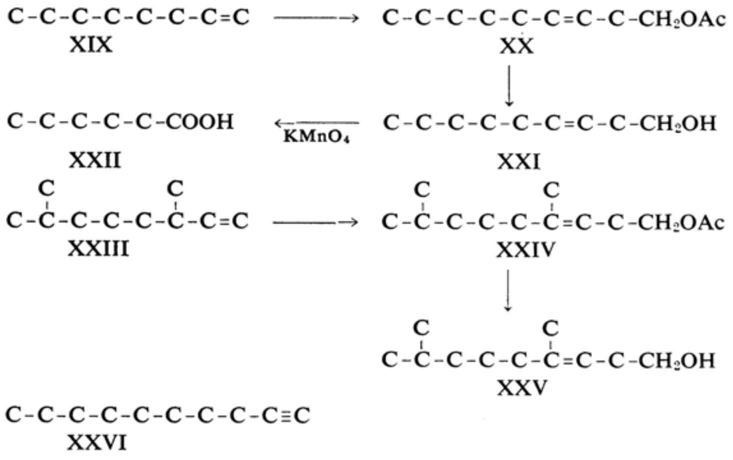




oxidation of VIII with potassium permanganate gave lactic acid (X) and acetic acid (XI). From the above results, it has been concluded that the alcohol VIII was an equivalent mixture of 3-ethyl-3-heptenol ($VIII_A$) and 3-ethylidene-heptanol ($VIII_B$).

The condensation of formaldehyde with 2, 6-dimethyl-1, 5-heptadiene (XII) under conditions similar to those used for 2-ethyl-1-hexene gave a mixture of three unsaturated alcohols, XV_A, XV_B and XVI, in ca. a 40% yield. This product, which showed a narrow boiling point range, gave no solid derivatives, and its direct separation into the three isomeric components with fractional distillation was unsuccessful. The reduction of the mixture of the alcohols, XIII and XIV, gave a product composed of 65% tetrahydrogeraniol (XVII) and 35% tetrahydrolavanduol (XVIII). This composition was established by comparing the gas-liquid chromatogram of the reduction product with those of known mixtures of pure XVII and XVIII. The mixture of XVII and XVIII was separated by means of column chromatography, using activated alumina gel. XVII and XVIII were identical in infrared spectra with authentic XVII and XVIII. Similarly, the mixture of XV and XVI was separated by means of liquid chromatography, using activated alumina gel.

The infrared absorption spectrum of XV indicates the presence of a primary alcohol group (absorption peak at 1050 cm^{-1}), an end methylene group (at 890 cm^{-1}) and a trisubstituted ethylene group (at 825 cm^{-1}). These results suggest a mixture of 3-methylene-7-methyl-6-octen-1-ol (XV_A) and 3, 7-dimethyl-3, 6-octadien-1-ol (XV_B) for the XV. Similarly, the infrared absorption spectrum of XVI indicates the presence of a primary alcohol group (absorption peak at 1050 cm^{-1}) and an end methylene group (890 cm^{-1}). These results



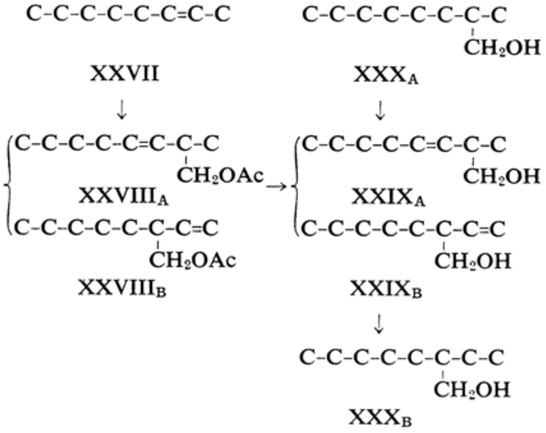
suggest the structure of 2-isopropenyl-5-methyl-5-hexenol for the XVI. As has been mentioned above, the procedure for synthesizing C_{10}-terpene alcohols from C_9-unsaturated olefins and formaldehyde with thermal condensation is a new method. The preparation of various terpene alcohols using this method is now in progress at our laboratory.

From the condensation of octene-1 (XIX), 3-nonen-1-ol acetate (XX) was obtained in ca. a 30% yields. The hydrolysis of this product gave 3-nonen-1-ol (XXI). The oxidation of this alcohol with potassium permanganate gave the known hexanoic acid, indicating that the structure was 3-nonen-1-ol. The infrared absorption spectrum of XXI indicates the presence of a trans configuration (at 965 cm^{-1}).

Similarly, from the condensation of 3,7-dimethyl-1-octene (XXIII), 4,8-dimethyl-3-nonen-1-ol (XXV) was obtained in ca. a 30% yield through the acetate XXIV. Analysis, quantitative acetylation, the bromine value and the infrared absorption spectrum (825 cm^{-1}, 1050 cm^{-1}) indicated that the structure was 4,8-dimethyl-3-nonen-1-ol (XXV).

The condensation of paraformaldehyde with decyn-1 (XXVI) under conditions similar to those above mentioned did not give any alcoholic compounds.

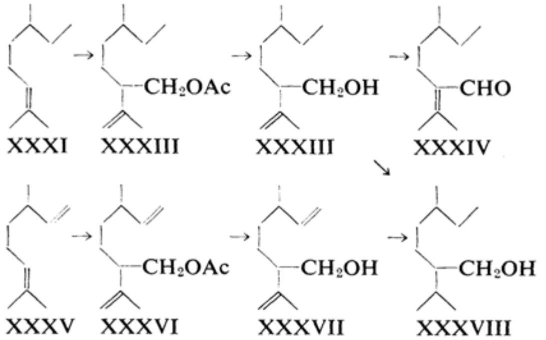
From the condensation of octene-2 (XXVII), an unsaturated acetate (XXVIII) was obtained in ca. an 11% yield. The saponification of XXVIII gave an unsaturated primary alcohol XXIX. The gas liquid chromatography of XXIX showed that it consisted of two components, and the saturated alcohol XXX consisted of two components, too. This product, which showed a narrow boiling point range, gave no solid derivatives, however, and its direct separation into the two isomeric components by means of fractional distillation and liquid chromatography was unsuccessful. The



infrared absorption spectrum indicates the presence of a primary alcohol group (absorption peak at 1040 cm^{-1}), an end vinyl group (absorption peaks at 910 cm^{-1} and 990 cm^{-1}) and a trans configuration of –CH=CH– (absorption peak at 967 cm^{-1}) The product III prepared by the catalytic hydrogenation of XXIX had no double bonds as an end vinyl group and a trans configuration visible in the infrared absorption spectrum. These results suggest the mixture of 2-methyl-3-octen-1-ol ($XXIX_A$) and 3-oxymethyl-1-octene ($XXIX_B$) for the original unsaturated alcohol.

Under conditions similar to those used for XXVII, the condensations of oleic acid, methyl oleate, oleylalcohol and oleylacetate, which has a disubstituted double bond (–CH=CH–), yielded no good results.

From the condensation of 2,6-dimethyl-2-octene (XXXI), an acetate (XXXII) was obtained. The saponification of this acetate gave an unsaturated primary alcohol XXXIII. Analysis ($C_{11}H_{22}O$), the hydroxyl value and the bromine value indicated that the product was an adduct of one mole of formaldehyde



XXXI XXXIII XXXIII XXXIV

XXXV XXXVI XXXVII XXXVIII

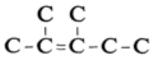
to XXXI. The infrared absorption spectrum showed the absorption bands characteristic of a primary group (absorption peak at 1040 cm^{-1}) and of an end methylene group (strong band at 855 cm^{-1}). Formula XXXIII was established on the basis of a comparison with the infrared spectrum of the product XXXVIII prepared by the catalytic hydrogenation of the end methylene group of the carbinol XXXIII. The hydrogenated carbinol XXXVIII showed remarkable doublet absorption peaks at 1380 cm^{-1} arising from an isopropyl radical. From the above results, it was concluded that the structure of the alcohol XXXIII is 3-methyl-2-(3′-methyl-1′-pentyl)-3-buten-1-ol. By the action of chromic anhydride in glatial acetic acid, an α,β-unsaturated aldehyde, 3-methyl-2-(3′-methyl-1′-pentyl)-2-buten-1-al (XXXIV), was obtained. It gives positive reactions with Schiff's reagent and with Tollen's reagent. The major absorption peaks at 243 mμ in the ultraviolet absorption spectrum suggested the presence of a conjugated enal grouping.

When the proportions of XXXI, paraformaldehyde and acetic anhydride were changed, the yields of XXXII were examined by means of gas-liquid chromatography (Table II). The use of 0.5 mol. of acetic anhydride and 1.25 mol. of paraformaldehyde per mole of XXXI gave the best results.

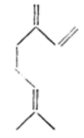
Similarly, from the condensation of 2, 6-dimethyl-2, 7-octadiene (XXXV), 2, 6-dimethyl-3-oxymethyl-1,7-octadiene (XXXVII) was obtained. The infrared absorption spectrum showed the absorption bands characteristic of a primary alcohol at 1040 cm^{-1}, of an end methylene group at 890 cm^{-1}, and of an end vinyl group at 910 and 990 cm^{-1}. The product prepared by the catalytic hydrogenation of XXXVII was identical in infrared absorption spectrum, gas-liquid chromatogram and other physical constants with the XXXVIII which had been prepared from the known XXXIII. These results suggest the structure of 2, 6-dimethyl-3-oxymethyl-1, 7-octadiene (XXXVII) for the original alcohol.

From the condensation of 2, 3-dimethyl-2-pentene (XXXIX), which has a tetrasubstituted double bond, an unsaturated alcohol was obtained in a poor yield, but the structure was not determined.

Finally, from the condensation of myrcene (XXXX), which has a conjugated diene, no alcoholic compound was obtained, only an unsaturated hydrocarbon as the main product


$$\mathrm{C-\overset{C}{\overset{|}{C}}=\overset{C}{\overset{|}{C}}-C-C}$$

XXXIX



XXXX

TABLE II. REACTION OF 2,6-DIMETHYL-2-OCTENE (XXXI) WITH PARAFORMALDEHYDE

Experimental No.	XXXI mol.	Paraformaldehyde mol.	Acetic-anhydride mol.	Recovered XXXI %	XXXII %	High boiling point fraction %	Residue %
1	1.0	1.0	1.0	90	0	0	10
2	1.0	1.25	1.0	87	3	0	10
3	1.0	1.5	1.0	90	0	0	10
4	1.0	1.25	0.25	48	22	0	30
5	1.0	1.25	0.5	2	51	17	30
6	1.0	1.25	0.75	52	21	2	25
7	1.0	1.25	1.0	77	3	0	20
8	1.0	1.0	0.26	39	28	8	25
9	1.0	1.0	0.49	15	48	7	30
10	1.0	1.0	0.55	38	32	5	25
11	1.0	1.0	0.65	82	8	8	10
12	1.0	1.0	1.0	100	0	0	10
13							

Reaction temperature 220°C, reaction time 5 hr.
Gas chromatography; Column; Reoplex 400 (20%) on celite 545, 2.25 m.
Carrier gas; He 47.5 ml./min. Column Temp.; 170°C
Apparatus; Shimadzu GC-1A Type

in ca. a 35% yield. The molecular weight (280), the boiling point (140～150°C/3 mmHg), and the bromine value indicated that the product was a dimer of XXXX. The infrared absorption spectrum did not show the existence of an oxygenated compound.

The foregoing observations indicate that the thermal condensation of paraformaldehyde with aliphatic olefins in the presence of acetic anhydride occurs most readily with end methylene-type olefins, $CH_2=CR_1R_2$, and that trisubstituted olefins ($R_1CH=CR_2R_3$), disubstituted olefins and vinyl olefins ($CH_2=CHR_1$ and $R_1CH=CHR_2$) and tetrasubstituted olefins ($R_1R_2C=CR_3R_4$) are less reactive in these orders.

Experimental

Materials.—The properties of the materials used are summarized in Table III.

The Condensation with Paraformaldehyde (General Method).—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 an stainless autoclave for several hours. The reaction mixture was extracted with ether. The ethereal solution was then washed with water and drid over anhydrous sodium sulfate. Fractional distillation gave a crude acetate. By saponification with the alcoholic potassium hydroxide of the acetate, the corresponding alcohol was obtained.

The Condensation of Isobutylene (I) with Formaldehyde.—From a mixture of 19 g. of isobutylene (I), 11 g. of paraformaldehyde, and 15 g. of acetic anhydride (reaction temperature, 200～210°C; reaction time, 4 hr.), 15 g. of a crude product was obtained. The crude product (150 g.) fractionally distilled to give the following fractions: (a) 24 g. of the forerun (b. p. 70～140°C); (b) 60 g. of II (b. p. 144°C; d_4^{30} 0.8910; n_D^{29} 1.4150; molecular refraction, 36.00 (calcd. for $C_7H_{12}O_2$, F_1, 35.713); bromine value, 115.01 ($C_7H_{12}O_2$, F_1, 124.7); (c) 33 g. of higher condensation products (b. p. 144～160°C); (d) 30 g. of residue.

The infrared spectrum of the II compound showed strong absorption at 890 cm^{-1} (an end methylene group) and at 1740 cm^{-1} and 1240 cm^{-1} (acetate).

The quantitative hydrogenation of II in methanol using a Raney nickel catalyst required 98% of one molar equivalent of hydrogen. The product was identical with an authentic isoamyl acetate (IV) in infrared absorption spectrum, gas chromatogram and other physical constants.

The saponification of II in the usual way gave 3-methyl-3-butene-1-ol (III); b. p. 132°C, n_D^{20} 1.4340; d_4^{20} 0.8533. The infrared spectrum of III showed strong absorption at 890 cm^{-1} (an end methylene group) and at 1050 cm^{-1} (a primary alcohol group). The quantitative hydrogenation of II in ethyl alcohol using a palladium-carbon catalyst required one molar equivalent of hydrogen. The product was identical with an authentic isoamyl alcohol (V) in infrared absorption spectrum, gas chromatograph and other physical constants.

The Condensation of 2-Ethyl-1-hexene (VI) with Formaldehyde. — From a mixture of 112 g. of VI, 36 g. of paraformaldehyde and 51 g. of acetic anhydride (reaction temperature, 220°C; reaction time, 6 hr.), 122 g. of the crude VII was obtained. The saponification of VII gave a mixture of $VIII_A$ and $VIII_B$. B. p. 81°C/6 mmHg; d_4^{15} 0.8345; n_D^{22} 1.4541; molecular refraction, 45.84 (Calcd. for $C_9H_{17}OH$, F_1, 44.95); hydroxy group, 11.97% (Calcd. for monohydric alcohol, 11.96%); bromine value, 128.4 (Calcd. for $C_9H_{17}OH$, 112.4); infrared absorption spectrum, 1045 cm^{-1}, 1660 cm^{-1} and 830 cm^{-1}.

Found: C, 76.01; H, 12.32. Calcd. for $C_9H_{18}O$: C, 76.02; H, 12.76%.

2-Ethyl-heptanol (IX).—Upon the hydrogenation of VIII in methanol at 130°C under high pressure (40 kg./cm^2) using a Raney nickel catalyst, one molecular equivalent of hydrogen was absorbed. The reduced product IX was carefully distilled. B. p. 79～80°C/6 mmHg.

The Oxidation of VIII with Potassium Permanganate.—A mixture of 29 g. of potassium permanganate, 35 g. of concentrated sulfuric acid and 300 cc. of water was added to a mixture of 10 g. of VIII and 30 cc. of acetone over an hour's time. After the mixture had been left alone overnight,

TABLE III

Olefins	Boiling point °C/mmHg	d_4^t	n_D^t	Note
Isobutylene (I)				From Mitsubishi Oil Co., Ltd.
2-Ethyl-1-hexene (VI)	66～70/120	d_4^{13} 0.7314	n_D^{22} 1.4149	
2,6-Dimethyl-1,5-heptadiene (XII)	69～70/ 80	d_4^{13} 0.7593	n_D^{18} 1.4461	
Octene-1 (XIX)	70.5/140	d_4^{15} 0.7213	n_D^{25} 1.4071	
3,7-Dimethyl-1-octene (XXIII)	58/ 19	d_4^{29} 0.7476	n_D^{31} 1.4190	
Decyne-1 (XXVI)	98～102/ 40			
Octene-2 (XXVII)	121～123	d_4^{24} 0.7178	n_D^{24} 1.4123	
2,6-Dimethyl-2-octene (XXXI)	82～84/ 57		n_D^{20} 1.4300	
Dihydromyrcene (XXXV)	60/ 18	d_4^{17} 0.7540	n_D^{18} 1.4448	
2,3-Dimethyl-2-pentene (XXXIX)	88	d_4^{20} 0.7383	n_D^{25} 1.4094	
Myrcene (XXX)				From Takasago Perfumery Co., Ltd.

TABLE IV

Fraction No.	Boiling point °C/mmHg	Yield g.	Gas-liquid chromatograph		
			XV_A(B)*	XV_B(C)*	XVI(A)**
1	79/7～94/5	2			
2	94/5～87/2	4	25	17	58
3	87/2	4	31	26	43
4	87/2	4	37	22	31
5	87/2～87.5/2	4.2	42	42	16
6	87.5/2～90/2	5	41	57	2
7	90/2～135/2	5			
The crude alcohol			39	26	35

* Geraniol type ** Lavanduol type

the precipitated part was filtered off. After the reaction-mixture had been alkalined with sodium carbonate, it was evaporated. The concentrated solution was then acidified with sulfuric acid and extracted with ether. After the ether had been evaporated, the residue was an analyzed by gas liquid chromatography; lactic acid (X) and acetic acid (XI) were recognized by comparing then with authentic samples.

The Condensation of 2,6-Dimethyl-1,5-heptadien (XII) with Formaldehyde. — From a mixture of 41 g. of XII, 10 g. of paraformaldehyde and 17 g. of acetic anhydride (reaction temperature, 220°C; reaction time, 4 hr.), 25 g. of crude acetate (b. p. 89～90°C/2 mmHg) was gained. The saponification of this product gave 20 g. of a mixture of XXV and XXVI. This was distilled to give the fractions in Table IV.

The Hydrogenation of XV and XVI.—Upon the hydrogenation of 4 g. of Fr. 2 (Table IV) in methanol at 120°C using a Raney nickel catalyst, two molecular equivalents of hydrogen were absorbed. The reduced product was shown to be a mixture of tetrahydrogeraniol (XVII) (40%) and tetrahydrolavanduol (XVIII) (60%) by gas-liquid chromatography.

The Separation of Mixture of XVI and XVII.—The chromatography of 2 g. of the above-mentioned saturated alcohol (XVII, XVIII) with an activated alumina using benzene (150 cc.) and acetone (150 cc.) gave 100 mg. of tetrahydrogeraniol (purity, 90%) and 100 mg. of tetrahydrolavanduol (XVIII) (purity, 90%) from the elution of acetone. XVII and XVIII were identified by a comparison of the infrared absorption spectra and the gas-liquid chromatography results with those of authentic samples.

Found: C, 75.57; H, 13.53. Calcd. for $C_{10}H_{22}O$ (XVII): C, 75.88; H, 14.01%.

Found: C, 75.62; H, 13.92. Calcd. for $C_{10}H_{22}O$ (XVIII): C, 75.88; H, 14.01%.

Separation of a Mixture of XV and XVI.—The chromatography of 2 g. of the mixture of XV and XVI with an activated alumina using benzene (150 cc.) and acetone (150 cc.) gave 200 mg. of a mixture of XV_A and XV_B (purity, 80%) and 70 mg. of XVI (purity, 80%) from the elution of acetone.

Condensation of Octene-1 (XIX) with Formaldehyde.—From a mixture of 45 g. of XIX, 20.5 g. of acetic anhydride and 14.5 g. of paraformaldehyde (reaction temperature, 220°C; reaction time, 5.5 hr.), 22 g. of a crude acetate (XX) (b. p. 110～120°C/20 mmHg) was gained. The saponification of the product gave 14 g. of XXI. B. p. 114～116°C/25 mmHg; d_4^{12} 0.8630; n_D^{12} 1.4550; molecular refraction, 44.90 (Calcd. for $C_9H_{18}O$, F_1, 44.82); hydroxy group, 11.50% (Calcd. for monohydric alcohol, 11.95%); bromine value, 103.2 (Calcd. for $C_9H_{18}O$, F_1, 112.3); the gas chromatogram shows one peak.

α-Naphthylurethan. — This was prepared as usual and was recrystallized from petroleum benzine. M. p. 75.5°C.

Found: N, 4.42. Calcd. for $C_{20}H_{25}NO_2$: N, 4.498%.

Oxidation of XXV with Potassium Permanganate.—A mixture of 25 g. of potassium permanganate, 21 g. of sulfuric acid and 300 cc. of water was added to 10 g. of XXV over an hour's time while the mixture was agitated. After the mixture had then been left alone overnight, the precipitated material was filtered off. The filtrate was alkalined with potassium hydroxide and then evaporated. After the concentrated solution had been acidified with sulfuric acid, it was extracted with ether. The ether solution was distilled to give 2 g. of caproic acid (XXII), which was identical with the IR and GC of the authentic sample of XXII.

p-Bromphenatylester.—This was prepared as usual and was recrystallized from methanol. It has a m. p. of 72°C, which does not depress the m. p. of an authentic XXII *p*-bromphenatylester with an m. p. of 72°C.

The Condensation of 3,6-Dimethyl-1-octene (XXIII) with Formaldehyde.—From a mixture of 31 g. of XXIII, 6,7 g. of paraformaldehyde and 11 g. of acetic anhydride (reaction temperature, 220°C; reaction time, 10 hr.), 7 g. of a crude acetate XXIV was obtained. The saponification of XXIV gave 4 g. of XXV. B. p. 120～124°C/20 mmHg; d_4^{29} 0.8363; n_D^{30} 1.4462; molecular refraction, 54.21 (Calcd. for $C_{11}H_{22}O$, F_1, 54.26); bromine value, 75.2 (Calcd. for $C_{11}H_{22}O$, F_1, 93.9); hydroxy group, 9.91% (Calcd. for monohydric alcohol, 9.98%).

Found: C, 76.88; H, 12.85. Calcd. for $C_{11}H_{22}O$ (XXV): C, 77.58; H, 13.02%.

The Condensation of Decyn-1 (XXVI) with Formaldehyde.—From a mixture of 30 g. of XXVI, 6.7 g. of paraformaldehyde and 13.5 g. of acetic anhydride (reaction temperature, 220°C; reaction time, 10 hr.), no acetate was obtained.

The Condensation of Octene-2 (XXVII) with Formaldehyde.—From a mixture of 40 g. of XXVII, 12.5 g. of paraformaldehyde and 18.17 g. of acetic anhydride (reaction temperature, 200~210°C; reaction time, 11 hr.), 7 g. of a crude acetate (XXVIII) (b. p. 80~88°C/9 mmHg) were obtained. The saponification of 20 g. of XXVIII in the usual way gave 14 g. of XXIX (b. p. 92~95°C/7 mmHg; $n_D^{29.5}$ 1.4430; $d_4^{29.5}$ 1.1864; bromine value, 103 (Calcd. for $C_{19}H_{18}O$, F_1, 112); hydroxy group, 13.5% (Calcd. for monohydric alcohol 11.98%); the gas chromatogram shows one peak). The infrared spectrum of the compound XXIX showed a strong absorption at 1040 cm^{-1} (a primary alcohol group) and at 967 cm^{-1}, 910 cm^{-1} and 990 cm^{-1} (a terminal vinyl group and a disubstituted trans-type double bond).

Found: C, 76.01; H, 12.71. Calcd. for $C_9H_{18}O$ (XXIX): C, 76.02; H, 12.75%.

The hydrogenation of XXIX in a methanol solution using a Pd-C catalyst absored one molar equivalent of hydrogen. This infrared absorption spectrum showed no absorption peaks of any double bonds.

Condensation of 2, 6-Dimethyl-2-octene (XXXI) with Formaldehyde. — From a mixture of 32 g. of XXXI, 16 g. of acetic anhydride and 6 g. of paraformaldehyde (reaction temperature 220°C; reaction time, 5 hr.), 10 g. of a crude acetate XXXII were obtained (b. p. 90~97°C/7 mmHg). This (137 g.) was distilled to give the following fractions: (a) 59 g. of XXXII (b. p. 81~81.5°C/3 mmHg; n_D^{10} 1.4504; d_4^{10} 0.8913; molecular refraction, 64.06 (Calcd. for $C_{13}H_{24}O_2$, 63.42); saponification value, 240 (Calcd. for $C_{13}H_{24}O_2$, 264); bromine value, 65.3 (Calcd. for $C_{13}H_{24}O_2$: F_2, 75.3); the gas chromatogram shows one peak); (b) 12 g. of higher condensation products (b. p. 120~130°C/2 mmHg.; d_4^{21} 0.9313; n_D^{21} 1.4745; bromine value, 85.8; hydroxyl group, 13.5%).

The saponification of XXXII (20 g.) gave an alcoholic compound, XXXIII (12 g.). B. p. 92~93°C/5 mmHg; n_D^{10} 1.4615; d_4^{10} 0.8598; molecular refraction, 54.43 (Calcd. for $C_{11}H_{22}O$: F_1, 54.06%); hydroxyl group, 9.15% (Calcd. for $C_{11}H_{22}O$, 9.99%); bromine value, 80.5 (Calcd. for $C_{11}H_{22}O$, 93.9); the gas chromatogram shows one peak.

Found: C, 76.60; H, 13.11. Calcd. for $C_{11}H_{22}O$ (XXXIII): C, 77.46; H, 13.00%.

2, 6-Dimethyl-3-oxymethyl-octane (XXXVII). — The quantitative hydrogenation of XXXIII in methanol using a Raney nickel catalyst in an autoclave (initial H_2 pressure, 35 kg./cm^2) required 99% of one molar equivalent of hydrogen. From 3 g. of XXXIII there were obtained 2 g. of XXXVII (b. p. 89~91°C/5 mmHg; n_D^{8} 1.4520; the gas chromatogram shows one peak).

3-Methyl-2-(3′-methyl-1′-pentyl)-2-buten-1-al (XXXIV).—To a mixture of 6 g. of XXXIII, 10 g. of acetone and 10 g. of glacial acetic acid, a mixture of 12 g. of chromic anhydride, 30 g. of acetic acid, 5 g. of water and 2 g. of concentrated sulfuric acid was added over a 30 minute period at 0°C while the mixture was being vigorously agitated. After the mixture had then been stirred for 4.5 hr., it was poured into a large amount of water and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 2 g. of XXXIV were obtained (b. p. 68~72°C/1~2 mmHg; λ_{max} 243 mμ, ε 1310). This substance gave a positive reaction with Schiff's reagent and reduced an ammoniacal silver nitrate solution.

2, 4-Dinitrophenylhydrazone.—This was prepared as usual and was recrystallized from a mixture of pyridine and methanol. M. p. 209°C: λ_{max} 390 mμ ε 4080.

Found: N, 17.69. Calcd. for $C_{17}H_{24}O_4N_4$: N, 16.56%.

The Condensation of 3, 7-Dimethyl-1, 6-octadiene (XXXV) with Formaldehyde.—From a mixture of 79 g. of XXXV, 17 g. of paraformaldehyde and 28.5 g. of acetic anhydride (reaction temperature, 200°C; reaction time, 4 hr.), 25 g. of crude XXXVI (b. p. 100~130°C/4 mmHg) were obtained. The saponification of this product (92 g.) gave 71 g. of a crude alcohol. This was distilled to give the following fractions: (a) 28 g. of XXXVII (b. p. 81.5°C/3 mmHg; n_D^{26} 1.4645; d_4^{26} 0.8590; molecular refraction, 54.36 (Calcd. for $C_{11}H_{20}O$: F_2, 53.59); hydroxyl group, 9.06% (Calcd. for monohydric alcohol, 10.1%); bromine value, 201 (Calcd. for $C_{11}H_{20}O$: F_2, 189.9); the gas chromatography shows one peak).

Found: C, 77.49; H, 12.19. Calcd. for $C_{11}H_{20}O$ (XXXVII): C, 78.49; H, 11.98%.

(b) 5 g. of higher condensation products (b. p. 100~110°C/3 mmHg).

Hydrogenation of 2, 6-Dimethyl-3-oxymethyl-1, 7-octadiene (XXXVII).—The quantitative hydrogenation of XXXVII in isopropylalcohol using Raney nickel in an autoclave (initial H_2 pressure, 38 kg./cm^2) required 98% of two molar equivalents. B. p. 93°C/3 mmHg; n_D^{8} 1.4523. The infrared spectrum and the gas-liquid chromatogram of this product agreed with XXXVIII, which had been similarly prepared from XXXIII.

The Condensation of 2, 3-Dimethyl-2-pentene (XXXIX) with Formaldehyde.—From a mixture of 26 g. of XXXIX, 9 g. of paraformaldehyde and 13 g. of acetic anhydride (reaction temperature, 220°C; reaction time, 8 hr.), 3 g. of a crude acetate (b. p. 120~125°C/3 mmHg) were obtained. The saponification of this product gave 0.5 g. of an alcoholic compound, the structure of which was not determined.

Condensation of Myrcene (XXXX) with Formaldehyde.—From a mixture of 45 g. of XXXX, 10 g. of paraformaldehyde and 17 g. of acetic anhydride (reaction temperature, 210~220°C; reaction time, 5 hr.), the following main fraction was obtained: (a) 13.7 g. of an unsaturated hydrocarbon (b. p. 140~150°C/3 mmHg: d_4^{25} 0.8793; n_D^{25} 1.5001; bromine value, 205; molecular weight, 280).

Absorption Spectra. — The infrared absorption spectra were measured by using a Koken IRS spectrophotometer, while the ultraviolet absorption spectrum were measured with a "Shimadzu" photometric spectrophotometer Type QB-50 using isopropyl alcohol as the solvent.

Gas-Liquid Chromatography. — Gas-liquid chromatography was measured under the following conditions: II, III, IV, V, VI, XII, XIX, XXI, XXIII, XXVI, XXVII, XXXI, XXXV, XXXIX and XXXX: column; LAC-2R-446 (20%) on Celite 545, 2 m.; temperature, 120°C; carrier gas He 45 ml./min.

VII, VIII, IX, XIII, XIV, XV, XVI, XVII, XVIII, XX, XXI, XXIV, XXV, XXVIII, XXIX, XXX, XXXII, XXXIII, XXXIV, XXXVI, XXXVII and XXXVIII: Temperature, 180°C; the other conditions were the same as above.

X, XI and XXII: column; Silicone D C 200 on Celite 545, 2 m.; temperature, 150°C; carrier gas, He 45 ml./min.

The authors are indebted to the Takasago Perfumery Co., Ltd., for providing materials.

Department of Applied Chemistry
Faculty of Technology
Chiba University
Matsudo-shi, Chiba