Prins Products from 6-Methyl-β-cyclogeraniolene and Synthesis of 6-Methyl-β-cyclolavandulylideneacetone

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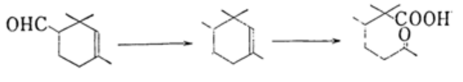
The condensation of 6-methyl-β-cyclogeraniolene (1, 3, 3, 4-tetramethyl-1-cyclohexene) (II) with formaldehyde has recently been determined[1,2] to afford 6-methyl-α-cyclogeraniol acetate and 6-methyl-γ-cyclogeraniol acetate, both of which are known[3,4] to be important intermediates for the synthesis of irones. The method employed in the reaction has seemed somewhat unusual, however, for the Prins reaction as generally acknowledged.

The present work was undertaken with the object of determining the structures of some cyclic compounds which might be produced when hydrocarbon II was subjected to the usual conditions for the Prins reaction. The starting hydrocarbon in this work was obtained by Wolff-Kishner reduction of 2, 2, 4-trimethyl-3-cyclohexenylmethanal (I)[1,2,5,6], and the structure assigned to II was attained from infrared data in which the bands due to the trisubstituted double bond (1679 and 798 cm^{-1}) were shown, from the results of oxidation with ozone and/or potassium permanganate, which gave β-methylgeronic acid (IV)[7], and moreover, from the nuclear magnetic resonance spectrum[8] (Fig. 1), in which a singlet peak (−0.34 p. p. m.) showed the olefinic proton peculiar to only II of the structures under consideration.



I II IV

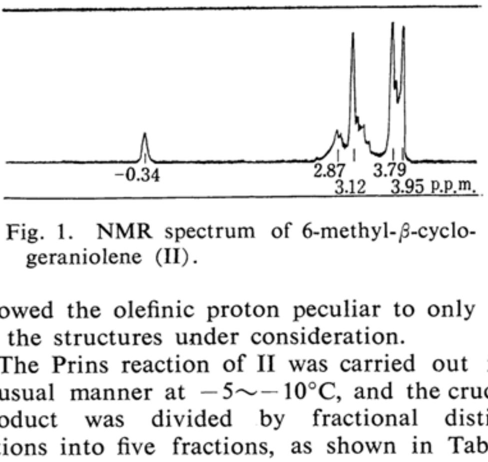


Fig. 1. NMR spectrum of 6-methyl-β-cyclogeraniolene (II).

The Prins reaction of II was carried out in a usual manner at −5∼−10°C, and the crude product was divided by fractional distillations into five fractions, as shown in Table I below. The fraction I was demonstrated by gas chromatography and some other means to consist principally of II. From elementary, gas chromatographic and infrared analyses, the principal components of fractions II and IV were revealed to be an unsaturated cyclic oxide and an acetate of unsaturated primary alcohol respectively, while fraction III was also indicated to be a mixture of approximately equal quantities of these two compounds. In order to separate the constituents from each other, the combined fractions of III and IV were treated with alkali and then with boric acid. The oxide was then readily distilled off in vacuo, while the boric ester of the alcoholic component remained in the viscous residue. Redistillation of fraction II combined with the recovered oxide afforded a homogeneous substance, $C_{12}H_{20}O$, whose infrared spectrum showed the presence of a cyclic ether (1111) and an

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[1] Y. Fujita, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **80**, 452 (1959).

[2] Y. Fujita, Dissertation submitted for the doctorate to the Tokyo Institute of Technology, 1959.

[3] H. Favre and H. Schinz, *Helv. Chim. Acta*, **35**, 1627 (1952).

[4] H. Favre and H. Schinz, ibid., **41**, 1374 (1958).

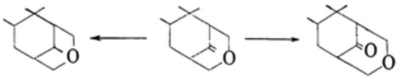
[5] O. N. Jitkow and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 1979 (1941).

[6] U. Steiner and H. Schinz, *Helv. Chim. Acta*, **34**, 1176 (1951).

[7] P. Bächli and H. Schinz, ibid., **34**, 1174 (1951).

[8] The NMR spectra herein recorded were measured with a Varian High Resolution spectrometer, medel V-4300C. All spectra were taken at 56.4 Mc. of a 10% solution of the samples in carbon tetrachloride with an external reference standard of water. All chemical shifts were determined by the side band method. The authors wish to thank Drs. Ichiro Yamaguchi and Naohiro Hayakawa of the Japan Atomic Energy Research Institute for their courtesy in obtaining the spectra.

exocyclic methylene group (3062, 1665, 1414 and 887 cm⁻¹). On catalytic hydrogenation this oxide gave a saturated oxide, $C_{12}H_{22}O$, and on ozonolysis it afforded formaldehyde and a keto-ether, $C_{11}H_{18}O_2$, which was characterized by the presence of bands in the infrared region at 1722 and 1095 cm⁻¹. Thus, the structures of 6, 6, 7-trimethyl-9-methylene-3-oxabicyclo [3, 3, 1] nonane (VII), 6, 6, 7, 9-tetramethyl-3-oxabicyclo [3, 3, 1] nonane (VIII) and 6,6,7-trimethyl-9-oxo-3-oxabicyclo [3,3,1] nonane (IX) were assigned respectively for the unsaturated cyclic oxide, the saturated oxide and the keto-ether.


VIII VII IX

The alcohol regenerated from the borate above was found to be an unsaturated primary alcohol, $C_{11}H_{20}O$, and its allophanate, m. p. 167.5°C, was proved to be identical with that of the compound which had been assigned by Fujita[2,9] to 6-methyl-α-cyclogeraniol. Moreover, the alcohol resembled in many respects 6-methyl-α-cyclogeraniol, synthesized by Favre and Schinz[3], to which it had once erroneously been assigned by the present authors[10]. Indeed, the infrared spectrum of the alcohol showed the presence of hydroxyl (3325 and 1041 cm⁻¹) and trisubstituted double bond (1660 and 822 cm⁻¹); however, the nuclear magnetic resonance spectrum failed to conform to the postulated structure. Since the spectrum[8] (Fig. 2) showed for the olefinic proton the singlet peak (−0.52 p. p. m.), which indicates the absence of hydrogen on the carbon atoms adjacent to the olefinic carbon bearing hydrogen, the structure of 6-methyl-α-cyclolavandulol (V) was now furnished to the alcohol. Consequently, it seemed reasonable to consider that the attack of the Prins reagent is extremely difficult on the double bond of II and also that under the reaction conditions II is readily isomerized into 6-methyl-α-cyclogeraniolene (III), which is immediately affected by the reagent to yield V. Examination with the molecular model really showed that the axial approach of the reagent to the double bond in II suffers a large steric hindrance from the gem. dimethyl group and also suggested that III presumably takes the conformation represented as IIIa when it participates in the reaction.

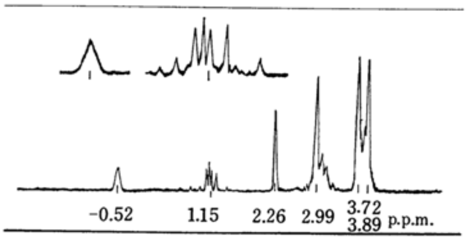
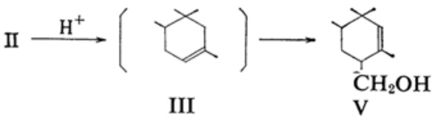
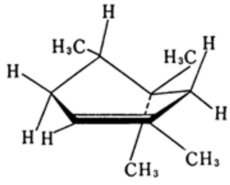


Fig. 2 NMR spectrum of 6-methyl-α-cyclo lavandulol (V).


III V

Va, the acetate


IIIa

Fraction V (Table I) was presumed from the infrared data to contain some acetic esters. An attempted pyrolysis at 350∼370°C afforded a small amount of low-boiling liquid which on hydrolysis gave the oxide VII and the alcohol V, whereas most of the high-boiling acetate was recovered unchanged. The latter compound was hydrolyzed to give rise to a glycol which gave a bis-*p*-nitrobenzoate and which was assigned to 3, 3, 4-trimethyl-1-(β-hydroxyethyl)-6-hydroxymethyl-1-cyclohexene (X) by infrared data, in which bands due to a primary hydroxyl (3330 and 1034 cm⁻¹) and to a trisubstituted double bond (1679 and 807 cm⁻¹) were indicated. Thus it was concluded that the fraction V consisted of X-diacetate (Xa) and appreciable amounts of 6,6,7,9-tetramethyl-9-acetoxy-3-oxabicyclo [3,3,1] nonane (XI) and 1, 3, 3, 4-tetramethyl-6-hydroxymethyl-1-cyclohexanol diacetate (XIIa). Although the formation of prim-tert. glycol has been described in many papers[11-16], this is probably the first example in which primary glycol has been isolated.

The mechanism of the Prins reaction has been frequently discussed, and it is generally

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[9] The authors are indebted to Dr. Yutaka Fujita of the Tokyo Institute of Technology for furnishing a sample of the allophanate, m. p. 166∼167°C.

[10] Presented by A. Arai and I. Ichikizaki at the 4th Symposium on Perfumery, Terpene and Essential Oil Chemistry, Sapporo, July, 1960 (Abstract, p. 20).

[11] A. Brenner, U. Steiner and H. Schinz, *Helv. Chim. Acta*, **35**, 1336 (1952).

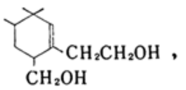
[12] A. T. Blomquist and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 6025 (1957).

[13] E. E. Smissman and R. A. Mode, ibid., **79**, 3447 (1957).

[14] Y. Matsubara and Y. Watanabe, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 651 (1959).

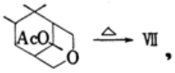
[15] J. Colonge and J. Crabalona, *Bull. soc. chim.*, **1959**, 1505.

[16] E. E. Smissman and D. T. Witiak, *J. Org. Chem.*, **25**, 471 (1960).

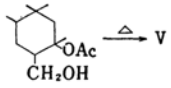


X

Xa, the diacetate



XI

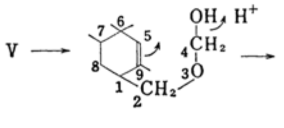


XII

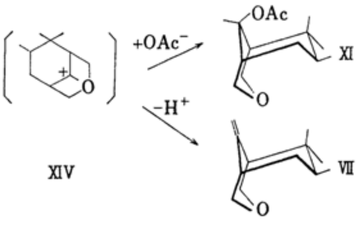
XIIa, the diacetate

accepted[12,13,16] that the first step involves the protonation of a neutral formaldehyde molecule and that the resultant hydroxymethylcarbonium ion carries out an axial attack on a cycloolefinic carbon.

The formation of VII and XI offers valuable evidence for the initial axial attachment of the protonated formaldehyde molecule to the double bond in III. These two compounds were plausibly assumed to be produced from an intermediate XIV, which might be provided via the dehydrative cyclization of the hypothetical compound XIII, formed presumably from the interaction between V and another formaldehyde molecule. According to stereochemical considerations, both VII and XI can apparently take up only the 1,5-diaxial conformation and likely have strainless double-chair forms. If the substituent, $-CH_2OCH_2OH$, in XIII takes the equatrial orientation, the effective approach of C-(4) to C-(5) for cyclization would be obviously impossible; therefore, the hydroxymethylene group in V must have the axial orientation. This was rationally explained independently on the basis of the nuclear magnetic resonance spectrum (Fig. 2), in which the multiplet centering at 1.15 p.p.m. is clearly ascribed to two non-equivalent protons of hydroxymethylene, which is further split by the adjacent ring hydrogen. The non-equivalence of the hydroxymethylene protons is probably due to the restriction of free rotation. Therefore, all the results mentioned above were compatible with the conclusion which involves the initial axial attachment of the hydroxymethylcarbonium ion[12,13,16] to the double bond of cyclic olefins.

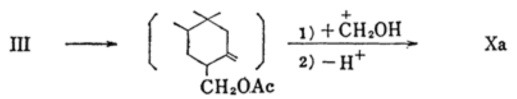


XIII



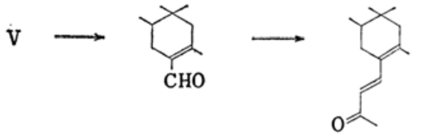
XIV

Additionally, the formation of the primary glycol diacetate Xa might be explained by the attack of another hydroxymethylcarbonium ion on the double bond in the temporarily-formed 6-methylcyclolavandulol acetate (VIa) and the successive elimination of hydrogen.



VIa

Finally, the synthesis of 6-methyl-β-cyclolavandulylideneacetone (XVI) from alcohol V was carried out. Modified Oppenauer oxidation of V with *p*-benzyloxybenzaldehyde as a hydrogen acceptor[17] afforded a high yield of 6-methyl-β-cyclolavandulal (XV), characterized as the semicarbazone whose ultraviolet spectrum revealed the presence of an α,β-unsaturated carbonyl group, while the expected α-isomer was not yielded. Condensation of XV with acetone in the presence of sodium hydride afforded 6-methyl-β-cyclolavandulylideneacetone (XVI)[18], with a strong violet odor, which was authorized by the infrared spectrum and by the light-absorption properties of its solid derivatives.



XV XVI

Experimental[19]

6-Methyl-β-cyclogeraniolene (II). — The Wolff-Kishner reduction of 2,2,4-trimethyl-3-cyclohexenylmethanal (I) was carried out essentially by the method of Fujita[1,2]. Distillation of the reduction product over sodium gave a colorless liquid, b.p. 56~57°C/18 mmHg, whose gas chromatogram, obtained at 196°C with a hydrogen flow of 17.2 ml./min., showed a small peak (about 2% of the total) at a retention time of 3.3 min. and a larger peak (98%) at 3.8 min. The small peak ascribed to an unknown substance disappeared after the sample had been purified by two redistillations with a 40 cm. Vigreux column. The hydrocarbon II had b.p. 60.5~61°C/24 mmHg and $n_D^{18.5}$ 1.4557 (lit.[1] b.p. 59.5~60.5°C/23 mmHg, n_D^{26} 1.4530). IR (film):

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[17] A. Arai and I. Ichikizaki, This Bulletin, 35, 504 (1962).

[18] R. Vonderwahl and H. Schinz, *Helv. Chim. Acta*, 35, 2005 (1952).

[19] All melting points were taken on a Kofler-block, and the temperatures are uncorrected. The infrared spectra were determined with a Nippon Bunkō model IR-S spectrophotometer with sodium chloride optics and the ultraviolet spectra, with a Hitachi model EPU-2A spectrophotometer. The gas chromatograms were obtained using a copper column (250 cm.×0.6 cm. ϕ) packed with a Celite DM-13A which was coated with a Carbowax-6000.

1679, 834, 798 (>C=CH-), 1389, 1379, 1362 (CH_3), 854 cm^{-1} (1,3,3,4-tetrasubstituted cyclohexene ring). The NMR spectrum is shown in Fig. 1.

Found: C, 86.76; H, 13.32. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12%.

Oxidation of II.—*a) With Ozone.*—Ozonized oxygen (concentration: 17 g./m^3) was passed through a solution of II (1.2 g.) in carbon tetrachloride (15 ml.) with a flow of 0.5 l./min. over a period of 2.5 hr. The temperature was maintained at $-5\sim-10$°C by cooling. Acetic acid (5 ml.) and 30% hydrogen peroxide (1.5 ml.) were added, and the resultant solution was left for 12 hr. at room temperature. After the bulk of the solvent had been removed in vacuo, the residue was made alkaline with 10% aqueous alkali and washed with petroleum ether to remove the neutral substances. The aqueous layer was then made acid with 5% hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over sodium sulfate and evaporated to leave a viscous oil (0.5 g.), which was distilled to give β-methylgeronic acid (IV) (0.35 g.), b. p. 130$\sim$135°C/0.8 mmHg, n_D^{21} 1.4564. IR (film): 3060 (broad), $\sim$2680, 1715, 1700, 1472, 1415, 1383, 1369, 1286, 1248, 1167, 1142, 939 cm^{-1} (broad).

The semicarbazone crystallized from methanol in prisms, m. p. 142$\sim$143°C (lit.[7] m. p. 141$\sim$142°C).

Found: C, 54.38; H, 8.90. Calcd. for $C_{11}H_{21}O_3 \cdot N_3$: C, 54.30; H, 8.70%.

The 2,4-dinitrophenylhydrazone crystallized from ether-petroleum ether in the form of yellow crystals, m. p. 130$\sim$130.5°C (lit.[7] m. p. 130.5$\sim$131.5°C).

Found: C, 53.04; H, 6.34. Calcd. for $C_{16}H_{22}O_6 \cdot N_4$: C, 52.45; H, 6.05%.

In this experiment, no formaldehyde was detected in the reaction mixture.

b) With Potassium Permanganate.—A solution of II (1.38 g.) in petroleum ether (b. p. 38$\sim$45°C, 30 ml.) was added to an aqueous solution (150 ml.) of potassium permanganate (3.16 g., 3 "O"), and the mixture was stirred vigorously at 5$\sim$10°C for 4 hr. Methanol was added, and the resultant mixture was warmed at 60°C for 10 min. to decompose the excess of permanganate and then filtered. The precipitate was repeatedly washed with hot water. The filtrate and washings were combined and concentrated to ca. 30 ml. in vacuo, acidified with 10% hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, evaporated and distilled to give an oil (0.3 g.). Its semicarbazone gave no mixed melting point depression with that of IV obtained by the method of a).

Prins Reaction with II.—A solution of II (35 g.) in acetic acid (23 ml.) diluted with ether (8.5 ml.) was added drop by drop over a period of 1 hr. into a mixture of paraformaldehyde (10.3 g.), acetic acid (46 ml.), ether (12.5 ml.) and concentrated sulfuric acid (8.5 ml.), and vigorous stirring was then continued for 7 hr. The temperature was maintained at $-5\sim-10$°C by cooling. The reaction mixture was allowed to stand overnight at 0°C, then poured into an ice-cooled 15% aqueous sodium carbonate solution (280 ml.) and extracted with ether. The ether extract was washed with water, dried over magnesium sulfate and evaporated to leave a red-brown oily residue (33.5 g.) which, on repeated fractionations through a 25 cm. Vigreux column, yielded the five representative fractions cited in Table I.

Distillation of fraction I over sodium gave a homogeneous substance (4.3 g.) with a b. p. 51.5°C/14.5 mmHg and $n_D^{18.5}$ 1.4557, which was identified as being the starting hydrocarbon II. Gas chromatogram, infrared and NMR spectra comparisons and ozonolysis showed that II is not subject to isomerization during the reaction.

6-Methyl-*α*-cyclolavandulol (V).—Combined fractions of III (4.4 g.) and IV (2.9 g.) (Table I) were hydrolyzed by treating them with potassium hydroxide (5.5 g.) in methanol (40 ml.) and water (20 ml.) at room temperature for 44 hr. After removal of the solvent in vacuo, the resulting mixture was neutrallized with 10% hydrochloric acid and extracted with petroleum ether. The petroleum ether extract was washed with water, dried over sodium sulfate and evaporated. The residual oil was heated with boric acid (0.5 g.) at a bath temperature of 160°C and at 500 mmHg for 30 min.; meanwhile, the water formed was distilled off. This work-up was repeated with another boric acid (1.0 g.) to make the esterification of the alcohol complete. The reaction mixture was then distilled gradually until the bath temperature reached 170°C at 0.75 mmHg to give a colorless liquid (2.0 g.), n_D^{25} 1.4833, which was shown by infrared and gas chromatographic analyses to consist mainly of the unsaturated cyclic oxide, and to leave the boric ester as an orange syrup, which was taken up in hot benzene (40 ml.) and hydrolyzed by shaking it with a hot 0.5% aqueous sodium carbonate solution. The

TABLE I. FRACTIONATION OF THE REACTION MIXTURE

Fraction No.	B. p. °C/mmHg	n_D^T	Fraction wt., g.	Composition C, H %	Infrared maxima cm^{-1}
I	51$\sim$51.5/14.5	1.4557^{18}	4.6		
II	70$\sim$76/4.0	1.4857^{18}	11.5	79.53 11.32	3060m, 1775m, 1661 s, 1418w, 1110 s, 887 s, 761m
III	72$\sim$75/1.5	1.4782^{20}	4.4	76.11 10.90	3062w, 1739 s, 1662m, 1240 s 1110 s, 1035m, 888m 866m
IV	62$\sim$65/0.75	1.4742^{20}	3.0	75.60 11.03	1740 s, 1237 s, 1040 s, 864m, 820w
V	100$\sim$116/0.75	1.4953^{20}	6.2	69.42 9.92	1738 s, 1679w, 1234 s, 1109 s, 1029m, 864m, 805w

benzene layer was dried over sodium sulfate, evaporated and distilled to afford 6-methyl-α-cyclolavandulol (V) (3.5 g.) as a colorless oil, b. p. 117∼118°C/15 mmHg, n_D^{23} 1.4825. IR (film): 3325, 1041, (OH), 1660, 822 (>C=CH–), 1390, 1379, 1364 (CH_3), 857 cm^{-1} (1, 3, 3, 4, 6-pentasubstituted cyclohexene ring). The NMR spectrum is shown in Fig. 2.

Found: C, 78.50; H, 11.93. Calcd. for $C_{11}H_{20}$·O: C, 78.51; H, 11.98%.

The allophanate crystallized from methanol in colorless crystals, m. p. 167.5°C, which gave no mixed melting point depression with that (m. p. 166∼167°C) of the so-called 6-methyl-α-cyclogeraniol furnished by Fujita[2,9].

Found: C, 61.44; H, 8.83. Calcd. for $C_{13}H_{22}O_3$·N_2: C, 61.39; H, 8.72%.

6, 6, 7-Trimethyl-9-methylene-3-oxabicyclo[3, 3, 1]-nonane (VII).—Fraction II (11.2 g.) (Table I), combined with the above-recovered fraction (2.0 g.) containing oxide, was fractionated over sodium through a 25 cm. Vigreux column to give a fore-run (2.0 g.) with a menthol-like odor, b. p. 96∼99.5°C/16.5 mmHg and $n_D^{25.5}$ 1.4828∼1.4832, and a colorless oil (8.9 g.), b, p. 100∼100.5°C/16.5 mmHg, $n_D^{25.5}$ 1.4852, both of which easily consumed bromine in a carbon tetrachloride solution. Redistillation of the latter afforded 6, 6, 7-trimethyl-9-methylene-3-oxabicyclo[3,3,1]nonane (VII) (8.5 g.) with a strong menthol-like odor, b. p. 72∼72.5°C/3.7 mmHg, $n_D^{25.5}$ 1.4853, whose gas chromatogram obtained at 211°C with a hydrogen flow of 28.8 ml./min. showed a single peak at a retention time of 9.3 min.

IR (film): 3062, 1665, 1414, 887 (>C=CH_2), 1775 (over-tone of δ CH (887)), 1111 (ether, C–O–C), 1393, 1380, 1374 (CH_3), 1235, 1198 ($H_3C\text{–}\overset{|}{\underset{|}{C}}\text{–}CH_3$), 1009, 760 cm^{-1} (unassigned).

Found: C, 79.60; H, 11.33. Calcd. for $C_{12}H_{20}$·O: C, 79.94; H, 11.18%.

From gas chromatography, the fore-run (Found: C, 80.29; H, 11.36%) was shown to consist largely of VII contaminated with ca. 7% of another unknown substance, which appeared as a broad peak at a retention time of 7.6 min. under the same conditions as above; this substance could not be isolated.

6, 6, 7, 9-Tetramethyl-3-oxabicyclo[3, 3, 1]nonane (VIII).—The unsaturated cyclic oxide VII (2.25 g.) in ethyl acetate (20 ml.) was hydrogenated at one atmosphere in the presence of a palladium-calcium carbonate catalyst (5% Pd, 1.0 g.) until one molar equivalent (315 ml. at 21.6°C) of hydrogen had been absorbed. Removal of the catalyst and solvent, followed by distillation of the residue, afforded 6, 6, 7, 9 - tetramethyl - 3 - oxabicyclo[3, 3, 1]nonane (VIII) (1.9 g., 83%) as a colorless liquid with a menthol-like odor, b. p. 110°C/16 mmHg and n_D^{21} 1.4835, which did not decolorize a solution of bromine in carbon tetrachloride. IR (film): 1398, 1386, 1376, 1366 (–CH_3), 1236, 1194 ($H_3C\text{–}\overset{|}{\underset{|}{C}}\text{–}CH_3$), 1176, 1134 ($H\overset{|}{\underset{|}{C}}\text{–}CH_3$), 1088 cm^{-1} (ether, C–O–C).

Found: C, 79.06; H, 12.16. Calcd. for $C_{12}H_{22}$·O: C, 79.06; H, 12.16%.

6, 6, 7-Trimethyl-9-oxo-3-oxabicyclo[3, 3, 1]nonane (IX).—The unsaturated cyclic oxide VII (0.5024 g.) in carbon tetrachloride (15 ml.) was ozonized at −10°C for 3 hr., after which time the resultant solution did not consume bromine in a carbon tetrachloride solution. At the end of the apparatus a trap containing water (20 ml.) was equipped to absorb the formaldehyde carried away by the gas stream during the reaction. The reaction mixture was heated under reflux with water (30 ml.) for 2 hr. in a flask fitted with a reflux condenser, the top of which had previously been connected with the water trap. The water in the trap was warmed with a solution of dimedone (0.9 g.) in ethanol (40 ml.) at 60°C for 10 min. to yield the formaldehyde-dimedone condensation product (0.1733 g., 21.2%). The carbon tetrachloride solution was dried over calcium chloride, evaporated in vacuo and distilled to give 6, 6, 7-trimethyl-9-oxo-3-oxabicyclo[3, 3, 1]nonane (IX) (0.25 g., 50%) as a colorless liquid, b. p. 84∼84.5°C/1.5 mmHg, n_D^{25} 1.4850. IR (film): 1722 (C=O), 1094 (ether, C–O–C), 1398, 1370 (CH_3), 1220, 1185 ($H_3C\text{–}\overset{|}{\underset{|}{C}}\text{–}CH_3$), 861 cm^{-1} (unassigned).

Found: C, 72.06; H, 10.08. Calcd. for $C_{11}H_{18}$·O_2: C, 72.49; H, 9.96%.

The semicarbazone crystallized from methanol-ethyl acetate in the form of prisms, m. p. 224∼225°C.

Found: C, 60.00; H, 8.99. Calcd. for $C_{12}H_{21}O_2$·N_3: C, 60.22; H, 8.85%.

The 2, 4-dinitrophenylhydrazone crystallized from methanol-ethyl acetate in the form of yellow needles, m. p. 248∼249.5°C.

Found: C, 56.51; H, 6.34. Calcd. for $C_{17}H_{22}O_5$·N_4: C, 56.34; H, 6.12%.

Pyrolysis Followed by Alkaline Hydrolysis of the Mixed Acetates (Fraction V in Table I).—Fraction V (6.0 g.) was heated at 350∼370°C and 500 mmHg under nitrogen for 4 hr. The pale yellow pyrolyzate (4.9 g.) was taken up in ether and washed with 2% aqueous sodium hydrogencarbonate and with water to remove the acetic acid formed and then dried over sodium sulfate. Removal of the solvent followed by fractionation of the residue gave two fractions, b. p. 74∼75°C/2.8 mmHg, $n_D^{21.5}$ 1.4911 (0.5 g.) (Found: C, 80.39; H, 11.32%) and b. p. 100∼105°C/0.7 mmHg, $n_D^{21.5}$ 1.4964 (3.9 g.). The low-boiling fraction was hydrolyzed by treating it with potassium hydroxide (0.5 g.) in ethanol (10 ml.) at room temperature for 40 hr. The reaction mixture was neutralized with 10% hydrochloric acid and extracted 5 times with ether. The combined ether extracts were washed with water, dried and evaporated. Distillation of the residue gave a colorless liquid (0.3 g.), b. p. 65∼72°C/1.5 mmHg, $n_D^{22.5}$ 1.4858 (Found: C, 79.16; H, 11.57%), which was not yet homogeneous and which showed in the infrared region bands at 3080, 1660, 1413, 891 and 1110 cm^{-1}, attributable to oxide VII, and medium bands at 3350 (broad) and 1041 cm^{-1}, attributable to alcohol V. A small amount of the allophanate of V was obtained, in fact. The high-boiling fraction was hydrolyzed in a similar manner before being used with potassium hydroxide

(1.8 g.) in methanol (20 ml.) to afford 3,3,4-trimethyl-1-(β-hydroxyethyl)-6-hydroxymethyl-1-cyclohexene (X) (1.6 g.) as a viscous liquid, b. p. 123~125°C/0.7 mmHg, n_D^{29} 1.4979. IR (film): 3330, 1034 (OH), 1679, 842, 807 (>C=CH–), 1392, 1378, 1368 (CH_3), 866 cm^{-1} (1,3,3,4,6-pentasubstituted cyclohexene ring).

Found: C, 73.21; H, 11.20. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%.

The bis-*p*-nitrobenzoate crystallized from ethanol-ethyl acetate in the form of needles, m. p. 131~132°C.

Found: C, 62.41; H, 5.52; N, 5.54. Calcd. for $C_{26}H_{28}O_8N_2$: C, 62.89; H, 5.68; N, 5.64%.

6-Methyl-β-cyclolavandulal (XV).—A mixture of alcohol V (2.0 g.) and aluminum isopropoxide (1.0 g.) was heated at a bath temperature of 70~80°C and at 13 mmHg for 1.5 hr. to form V-aluminate, and then *p*-benzyloxybenzaldehyde (3.78 g., 150%) was added in one portion. The resultant mixture was preheated at a bath temperature of 80°C under ordinary pressure for 2 min. to give the melt, which was subsequently distilled by raising the temperature from 110 to 180°C under nitrogen to afford a product, b. p. 60~101°C/4 mmHg. Redistillation of the product through a 7 cm. Vigreux column afforded 6-methyl-β-cyclolavandulal (XV) (1.35 g., 68.5%), b. p. 93~96°C/13 mmHg, $n_D^{27.5}$ 1.4790.

Found: C, 79.51; H, 10.88. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92%.

The semicarbazone crystallized from methanol-ethyl acetate in the form of prisms, m. p. 224~225°C (partly decomp.). λ_{max}^{EtOH} 272 mμ (ε, 30300).

Found: C, 64.62; H, 9.69; N, 18.88. Calcd. for $C_{12}H_{21}ON_3$: C, 64.54; H, 9.48; N, 18.82%.

The 2,4-dinitrophenylhydrazone chromatographed on alumina in benzene and crystallized from ethanol-ethyl acetate in the form of red needles, m. p. 207~208°C.

Found: C, 59.04: H, 6.38; N, 16.01. Calcd. for $C_{17}H_{22}O_4N_4$: C, 58.94; H, 6.40; N, 16.18%.

6-Methyl-β-cyclolavandulylideneacetone (XVI).—A solution of XV (1.1 g.) in acetone (10 ml.) was added drop by drop to an acetone solution containing sodium hydride (40 mg.) at room temperature, and the resultant solution was stirred for 6 hr. and then allowed to stand overnight under nitrogen at this temperature. After the solvent had been removed, the residue was taken up in ether, washed with 2 N hydrochloric acid and with water, dried over sodium sulfate and evaporated. Distillation under nitrogen gave a fore-run (0.4 g.), 62~90°C/0.85 mmHg, which consisted largely of unchanged XV and of an oil (0.75 g.), 90~110°C/0.7 mmHg, $n_D^{25.5}$ 1.4940~1.5118. Redistillation of the latter gave the ketone XVI (0.55 g.) as a pale yellow oil with a strong violet odor, b. p. 105~110°C/0.7 mmHg, $n_D^{25.5}$ 1.5118. IR (film): 1675 (C=O, conju.), 1624, 1594 (C=C, conju.), 1382, 1369 (gem. dimethyl), 1268 ($COCH_3$), 970 cm^{-1} (–CH=CH–, *trans*).

Found: C, 81.42; H, 10.94. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75%.

The 4-phenylsemicarbazone crystallized from methanol-ethyl acetate in the form of fine needles, m. p. 198~199°C, which rapidly turned yellow on exposure to light or air. λ_{max}^{EtOH} 234 mμ (log ε, 4.04), 301 (4.58). (lit.[18]) m. p. 196~197°C, λ_{max}^{EtOH} 234 mμ (log ε, 4.70). 307 (4.12)).

Found: C, 74.31; H, 8.66. Calcd. for $C_{21}H_{29}ON_3$: C, 74.30; H, 8.61%.

The 2,4-dinitrophenylhydrazone crystallized from methanol-ethyl acetate in the form of dark-red, silk-like needles, m. p. 209°C. $\lambda_{max}^{CHCl_3}$ 391 mμ (log ε, 4.55). (lit.[18]) m. p. 197.5°C, $\lambda_{max}^{CHCl_3}$ 397 mμ (log ε, 4.50)).

Found: C, 62.24; H, 6.76; N, 14.22. Calcd. for $C_{20}H_{26}O_4N_4$: C, 62.16; H, 6.78; N, 14.50%.

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