[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Relationship between Structure and Odor in the Case of Certain Derivatives of 2,2,4-Trimethyl-Δ^3-cyclohexene Aldehyde[1]

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As the violet-scented synthetics have always been objects of great interest to the practical perfumer, researches have been conducted from time to time to learn more about the relation between structure and odor in this group, and the investigation reported in the following pages is a further contribution to the elucidation of this problem.

The best known and most extensively used synthetic violet perfumes, the ionones, are compounds of the formula, RCH=CHCOMe, in which R is a trimethylcyclohexenyl radical.

Merling and Welde,[3] who were among the first to investigate the connection between the violet odor of these compounds and their chemical constitution, came to the conclusion that to possess a violet aroma the —CH=CHAc side chain must be adjacent to a methyl group of the cyclogeraniolene nucleus.

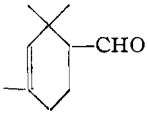
More recently, Naves[4] has stated that there are two different groups of ionone perfumes: (a) those possessing a true violet odor, and which carry methyl groups in both ortho positions to the —CH=CHAc side chain; and (b) those of a rose odor, which have only one *o*-methyl group, as in the —CH=CHAc derivatives of 2,4- and 2,5-dimethyl-Δ^3-cyclohexene.

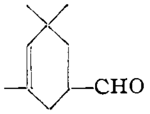
The new ionone isomer described beyond, however, having a *gem*-dimethyl group *ortho* and a methyl group *para* to the side chain, also exhales a definite violet odor.

Based upon the evidence so far accumulated in the literature, and upon our own experience, it appears that in the ionone group, the violet odor is dependent upon the presence of a cyclohexene nucleus, carrying at least three methyl groups on the ring, two of which must be adjacent to the side chain, either as one *gem*-dimethyl group, or as a single methyl on each side of the chain. The position of the double bond in the nucleus affects the quality but not the type of odor. The introduction of a second double bond into the nucleus, however, destroys the violet odor, for the —CH=CHAc derivative of 2,2,4-trimethyl-$\Delta^{4,6}$-hexadiene, smells like dry leaves.

The 2,2,4-trimethyl-Δ^3-cyclohexene aldehyde (I) was chosen for study for the following reasons: (a) it is an isomer of the important cyclocitrals; (b) it has the 1,3,4 tri-substitution configuration, so often encountered in natural, as well as synthetic, perfume products, and so favorable to the development of violet-scented ionones; and (c), although it has been reported in the patent literature,[5] its structure has not been proved, nor have its derivatives been described.

The aldehyde (I) is prepared from 1,1,3-trimethylbutadiene-1,3 and acrolein by heating under pressure. Such a condensation might result in either (A) or (B), or a mixture of the two.

(A) 

 (B)

The patents[5] adopt (A) as the probable formula, because in the similar condensation with crotonaldehyde the *gem*-dimethyl takes the position adjacent to the aldehyde group.[6] We have confirmed the correctness of this formula (A) by oxidizing the aldehyde to the corresponding acid and dehydrogenating the latter to 2,4-dimethylbenzoic acid.

Acetals of cyclocitral type generally have pleasant ethereal odors.[7,8] The ease of their formation appears to depend somewhat upon the location of the nuclear double bond. When the latter is in the Δ^3-position, they react readily with absolute ethanol containing 1% hydrogen chloride yielding the acetal, as in the case of the acetal (II) described beyond; whereas, when the double bond is in the Δ^2-position, the production of the diethylacetal is best achieved by the use of ethyl orthoformate in methanol solution catalyzed by hydrochloric acid. No diethylacetal of β-cyclocit-

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(2) Present address: Verley Chemical Co., Chicago, Illinois.

(3) Merling and Welde, *Ann.*, **366**, 123 (1909).

(4) Naves, *Parfums de France*, **12**, 255 (1934).

(5) Soc. Anon. M. Naef & Cie, (a) Brit. Patent 309,911 (1928); (b) French Patent 672,025 (1929); (c) Swiss Patent, *Chem. Zentr.*, **102**, I, 2938 (1931).

(6) Diels and Alder, *Ann.*, **470**, 62 (1929).

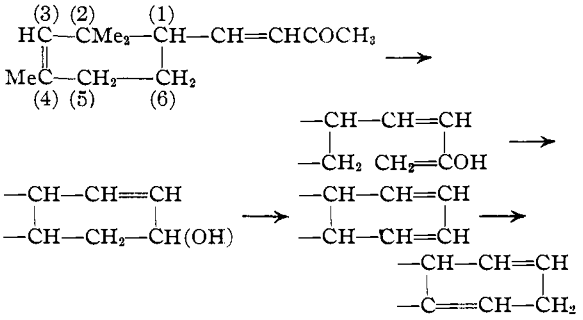
(7) Kuhn and Wendt, *Ber.*, **69B**, 1555 (1936).

(8) Arbusov, Zinowjewa and Fink, *J. Gen. Chem.*, *U. S. S. R.*, **7**, 2278 (1937).

ral has been found in the literature. Apparently the closer the nuclear double bond is to the aldehyde group, the more difficult it becomes to form the acetal.

In line with the eucalyptus-like odor of the carbinol (IV), is the similar odor of the isomeric β-cyclogeraniol, while the α-cyclogeraniol is a viscous liquid without noteworthy aroma. It is of interest that while none of these cyclic isomers possesses the rose aroma of the acyclic geraniol, the odor of the acetate of α-cyclogeraniol is not unlike that of geranyl acetate, and the isomeric acetate of (IV) has also a powerful fragrant geranium-like scent.

When the ionone isomer (IX), prepared from this aldehyde (I) by condensation with acetone, was heated with phosphorus pentoxide, there resulted a $C_{13}H_{18}$ hydrocarbon, which refused to form an addition compound with maleic anhydride, and gave 1,3-dimethylnaphthalene when dehydrogenated by fusion with sulfur. It is suggested, therefore, that the reaction probably took the following course:



A proton from the nuclear carbon atom (6) attaches itself to the side chain carbon atom carrying the OH group. Cyclization ensues with the intermediate formation of a bicyclic secondary alcohol, which loses water and suffers a molecular rearrangement by a shift in the position of a double bond. As Whitmore[9] explains such phenomena, "If the proton removed is not the same as the one added, the result will then be a change in the original position of the double bond."

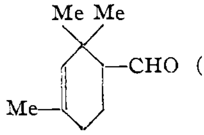
By treatment of the new ionone (IX) with allylmagnesium bromide, the expected tertiary alcohol was formed, and from it a new hexatriene (XII). In this connection it will be recalled that Karrer, *et al.*,[10] found that while α-ionone formed the tertiary alcohol with allylmagnesium bromide, β-ionone apparently underwent an addition of allyl bromide at a —C=C— linkage. The yield of tertiary alcohol obtained with the new ionone (IX) was 20% greater than that secured under identical conditions with α-ionone. This suggests the influence of the location of the nuclear double bond in such reactions, for in β-ionone it is in conjugation with the double bonds of the side chain, while in (IX) it is still farther away from conjugation than in α-ionone.

In the dehydration of the tertiary alcohol (XI) to the hexatriene (XII), we were guided by the experience of Karrer and his co-workers[10] who found, in an analogous case, that when phenyl isocyanate was used as the dehydrating agent, the yield of triene was only 27%. By employing thionyl chloride in pyridine solution, at low temperature, however, a procedure which Chuang, Tien and Ma[11] found so satisfactory for the preparation of ethyl 2-methyl-Δ^1-cyclohexenylacetate, the new carbinol (XI) gave a 55% yield of the triene (XII).

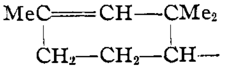
In the application of the Reformatzky reaction, using ethyl bromacetate, to α- and β-cyclocitrals, von Braun and Kurtz[12] reported that the α-isomer gave the expected β-hydroxy ester, while the β-isomer formed mainly the unsaturated β-cyclocitrylideneacetic ester. In the case of the new cyclocitral isomer (I), the product was similar to that formed with α-cyclocitral, namely, the hydroxy ester (VII).

FLOW SHEET

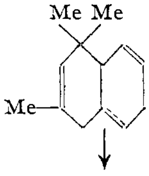
The aldehyde



(I) was the initial material from which the following derivatives were synthesized, in which R represents the nucleus



$RCH(OEt)_2$ (II)
$RCOOH$ (III) ⟶ 1,3-dimethylbenzoic acid
$RCH_2(OH)$ (IV) ⟶ acetate
$RCH(OH)Me$ (or Et) (V) ⟶ $RCOMe$ (or Et) (VI)
$RCH(OH)CH_2COOH$ (VII) $(RCH(OH)CH_2)_2CO$ (VIII)
$RCH{=}CHCOMe$ (IX) ⟶
$RCH{=}CHC(Me)(OH)CH_2CH{=}CH_2$ (XI)
↓



(X) $RCH{=}CHC(Me){=}CHCH{=}CH_2$ (XII)

1,3-Dimethylnaphthalene

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[9] Whitmore, THIS JOURNAL, **54**, 3277, footnote 13 (1932).
[10] Karrer, *et al.*, *Helv. Chim. Acta*, **15**, 878 (1932).
[11] Chuang, Tien and Ma, *Ber.*, **69B**, 1502 (1936).
[12] Von Braun and Kurtz, *ibid.*, **70**, 1009 (1937).

Experimental

The Diels-Alder reactions were performed in sealed glass tubes heated electrically. Fractionations were conducted in an all-glass apparatus, containing a 25-cm. Vigreux column. The thermometers used were calibrated against a set of total immersion thermometers certified by the U. S. Bureau of Standards. All melting and boiling points have been corrected for stem exposure. Melting points were determined in a Thiele tube. Densities were taken with a 0.5-cc. pycnometer. Refractive indices were measured at 25° with an Abbe refractometer.

We are indebted to Mr. Saul Gottlieb, of these laboratories, for the analyses recorded.

1,1,3-Trimethylbutadiene-1,3.—A modification of Fellenberg's procedure[13] was employed. The Grignard reagent was prepared from 40 g. of methyl iodide, 60 cc. of anhydrous ether, and 7 g. of magnesium turnings. When nearly all of the magnesium had dissolved, the mixture was cooled to 0°, and a solution of 28 g. of mesityl oxide in dry ether added dropwise, maintaining the temperature below 5°. After refluxing the mixture for thirty minutes, it was left overnight, and then poured slowly into an ice-cold aqueous solution of 32 g. of ammonium chloride. The ether layer was separated, washed with water, dried over anhydrous magnesium sulfate, the ether driven off, and the residue distilled with a crystal of iodine. The hydrocarbon was separated from the water in the receiver, dried over anhydrous magnesium sulfate, and distilled over sodium; yield of the trimethylbutadiene, 16 g. (or 58% based on the mesityl oxide); b. p. 94–96° at 771 mm. Fellenberg reported the b. p. as 92–93° at 750 mm. He used sodium to dehydrate his tertiary alcohol. We have found that the use of iodine instead increases the yield of diene by 20%.

Maleic anhydride addition compound, prepared as described by Diels and Alder[14]; white needles, from petroleum ether, m. p. 49–50° (literature,[14] 49°).

2,2,4-Trimethyl-Δ^3-cyclohexene Aldehyde (2,2,4-Trimethyl-Δ^3-tetrahydrobenzaldehyde) (I).—A mixture of 11 g. of the trimethylbutadiene and 7 g. of acrolein was heated in a sealed tube for thirty-eight hours at 145–150°. The contents of several such tubes were united, the excess of acrolein distilled off, and the residue fractionated under diminished pressure. All distillations were conducted in an atmosphere of carbon dioxide. The yields were 75–85%, and the b. p. 52–54° at 3 mm. Re-distilled for the determination of physical constants: b. p. 80° at 12 mm.; n^{25}_{D} 1.4680; d^{13}_4 0.933. The figures given for this aldehyde in the Naef patents[5] are b. p. 78–79° at 12 mm.; 55–57° at 4 mm.; d^{13}_4 0.933.

Upon completion of this distillation, it was found advisable to clean the flask immediately with ethylene dichloride, or the gummy residue hardened to a rubbery mass practically insoluble in all solvents tried.

Semicarbazone.—Fine white needles, m. p. 200–201°. The Naef patents[5] record the m. p. as 197–198°.

2,4-Dinitrophenylhydrazone.—Small yellow needles from acetone, m. p. 164–165°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: N, 16.8. Found: N, 16.6.

Acetal (II).—The procedure followed for the preparation of this derivative was similar to that employed by Adkins, Semb and Bolander[15] in the preparation of fural acetal.

A mixture of 10 g. of the aldehyde (I), 40 cc. of absolute ethanol, and 0.25 cc. of concentrated hydrochloric acid (sp. gr., 1.21), was allowed to stand for two days and then poured into 300 cc. of water containing 1 g. of sodium carbonate. An oil separated, which was dried over anhydrous magnesium sulfate, and fractionated under reduced pressure. A colorless oil was collected, b. p. 126–128° at 22 mm., of pleasant pine-sap odor; yield, 4 g., or 30%; n^{25}_{D} 1.4590; d^{25}_4 0.9202; M_{D} calcd., 67.41; M_{D} obsd., 67.15.

Anal. Calcd. for $C_{14}H_{26}O_2$: C, 74.3; H, 11.6. Found: C, 74.5; H, 11.5.

2,2,4-Trimethyl-Δ^3-cyclohexenoic Acid (III).—When the aldehyde (I) was oxidized with silver oxide, according to the directions of Kuhn, Badstübner and Grundmann[16] for the preparation of citrylideneacetic acid, long white needles were obtained (from dilute AcOH), m. p. 86–87°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5. Found: C, 71.4; H, 9.7.

This compound has been reported in the Naef patents,[5] as synthesized from 1,1,3-trimethylbutadiene and acrylic acid, and with a b. p. of 135–140° at 12 mm.

The dehydrogenation of the acid (III) was effected in much the same manner as that described by Lehmann and Paasche[17] in their proof of the structure of 4-methyl-Δ^3-cyclohexenoic acid.

A mixture of 0.6 g. of the acid (III) with 0.6 g. of crystalline selenium, in a small round-bottom flask with a long air condenser, was heated for thirty-six hours at 270–290°. The cold pulverized melt was extracted with a 10% aqueous sodium hydroxide solution, the filtered extract washed with ether and acidified with sulfuric acid. The acid solution was extracted with ether, the extract dried over anhydrous magnesium sulfate, and the solvent removed. The 2,4-dimethylbenzoic acid which remained formed small white plates, m. p. 125–126° (literature, m. p. 126°).

2,2,4-Trimethyl-Δ^3-cyclohexenylcarbinol (IV).—The reduction of the aldehyde (I) to the alcohol (IV) was effected by the familiar Ponndorf[18] method, which Kuhn and his co-workers[19] found satisfactory for the preparation of the α- and β-cyclogeraniols.

The apparatus consisted of a 100-cc. flask, equipped with a 35-cm. Vigreux column, the upper end of which was connected with a downward water-cooled condenser, to permit the escape of acetone as formed. All operations were conducted in an atmosphere of carbon dioxide.

In the preparation of the aluminum isopropoxide by the Young, Hartung and Crossley[20] procedure, it was found advisable to wash the aluminum first with water, then with alcohol, and finally with ether, and dry it thoroughly in a desiccator before use. The commercial C. P. isopropyl alcohol (b. p. 82–83°) was dehydrated by refluxing with

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[13] Fellenberg, *Ber.*, **37**, 3578 (1904).

[14] Diels and Alder, *Ann.*, **470**, 102 (1929).

[15] Adkins, Semb and Bolander, THIS JOURNAL, **53**, 1853 (1931).

[16] Kuhn, Badstübner and Grundmann, *Ber.*, **69B**, 98 (1936).

[17] Lehmann and Paasche, *ibid.*, **68B**, 1068 (1935).

[18] Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926).

[19] (a) Kuhn and Hoffer *Ber.*, **67**, 358 (1934); (b) Kuhn and Wendt, *ibid.*, **69B**, 1555 (1936).

[20] Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

magnesium and iodine, as recommended by Lund and Bjerrum.[21]

To 8 g. of the aluminum isopropoxide, there was added 10 g. of the aldehyde (I) and 30 cc. of absolute isopropanol. The solution was distilled slowly for two to three hours at a bath temperature of 110–120°. The acetone began to come over at 60°, the major portion of the distillate was collected at 75°, and about 10 cc. of isopropanol at 81.5°. The residual mixture was distilled with steam. The distillate formed two layers. The oily layer was separated, and the aqueous one extracted with ether. The ether extract was added to the oil and the mixture dried over anhydrous magnesium sulfate and distilled, the pressure being reduced after removal of the ether. A colorless viscous liquid was obtained, of pleasant eucalyptus oil odor; yield, 7 g., or approximately 70%. It did not solidify on standing for several days in a refrigerator. Its physical constants were: b. p. 113–113.5° at 13 mm.; n^{25}_D 1.4795; d^{25}_4 0.9293; M_D calcd. 47.16, M_D obsd. 47.10.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.7. Found: C, 77.7; H, 11.9.

Experiments were carried out also for the preparation of this alcohol (IV) from 1,1,3-trimethylbutadiene-1,3 and allyl alcohol, by the procedure of Alder and Windemuth,[22] but were unsuccessful. Equimolecular proportions of the diene and allyl alcohol were heated together in sealed tubes under various conditions of time and temperature. When the mixture was heated for thirty six hours at 200°, there was obtained a light oil, of agreeable camphoraceous odor, b. p. 89–97° at 10 mm., but which did not react with sodium, or give analytical figures agreeing with those calculated for the alcohol.

3,5-Dinitrobenzoate.—Rosets of thin white needles, m. p. 63–64°.

Anal. Calcd. for $C_{17}H_{20}N_2O_6$: C, 58.6; H, 5.7. Found: C, 58.5; H, 5.9.

Acetate.—To a 50-cc. flask equipped with condenser and mercury-sealed stirrer, and containing 4 g. of the alcohol (IV) and 20 cc. of pyridine, there was added gradually through the condenser 4 g. of acetyl chloride, and the vigorous action which ensued was controlled by immersing the flask in ice water from time to time. A copious precipitate of pyridine hydrochloride separated. After standing at room temperature for six to eight hours, the reaction mixture was poured into cold dilute sulfuric acid, the oil separated, the aqueous layer extracted with ether, the ether extract added to the oil, and the mixture washed first with dilute hydrochloric acid, then with a 10% aqueous sodium carbonate solution, and finally with water. After drying over anhydrous magnesium sulfate, the ether was removed, and the residual oil distilled under diminished pressure. A colorless heavy liquid, of very pleasant geranium-like odor, was obtained, b. p. 115–116° at 13 mm.; yield 3.5 g., or 66%: n^{25}_D 1.4645; d^{25}_4 0.9576; M_D calcd., 56.68; obsd., 56.54.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.6; H, 10.5.

β-(2,2,4-Trimethyl-Δ³-cyclohexenyl)-ethanol (V).—A Grignard reagent prepared from 6.4 g. of methyl iodide, 1.6 g. of magnesium turnings, and 35 cc. of anhydrous ether, was refluxed for thirty minutes, then cooled to 0° and 10 g. of the aldehyde (I) added at such a rate that the temperature did not rise above 5°. After refluxing for an hour, the mixture was cooled, hydrolyzed by an ice-cold solution of 14 g. of ammonium chloride, the ether layer removed, washed with water, dried over anhydrous magnesium sulfate and distilled. A colorless liquid, of fresh mint odor, was obtained, b. p. 105–107° at 15 mm.; yield, 8 g., or 75%: n^{25}_D 1.4769; d^{25}_4 0.9217; M_D calcd., 51.76; obsd., 51.49.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.6; H, 11.9. Found: C, 78.5; H, 12.1.

The above procedure is based upon that used by Arbuzov, Zinowjewa and Fink[8] for the synthesis of ethyl-2,5-dimethyl-Δ³-cyclohexenylcarbinol.

Phenylurethan.—Prepared from the alcohol and phenyl isocyanate, at room temperature, collected with petroleum ether and crystallized from dilute ethanol, it formed fine white needles, m. p. 105–105.5°.

Anal. Calcd. for $C_{18}H_{25}O_2N$: C, 75.2; H, 8.7. Found: C, 74.9; H, 8.9.

γ-(2,2,4-Trimethyl-Δ³-cyclohexenyl)-propanol (V).—Prepared as described for the corresponding ethanol derivative, the yield from 12 g. of the aldehyde (I), 8.5 g. of ethyl bromide, and 2 g. of magnesium, was 10 g., or 70%, of a colorless oil, of a sweet grass odor, b. p. 118–119° at 15 mm.: n^{25}_D 1.4812; d^{25}_4 0.9249; M_D calcd., 56.36; obsd., 56.02.

Anal. Calcd. for $C_{12}H_{22}O$: C, 75.0; H, 9.0. Found: C, 74.9; H, 9.0.

Phenylurethan.—Thin, white needles, from dilute ethanol, m. p. 109–110°.

Anal. Calcd. for $C_{19}H_{27}O_2N$: C, 79.0; H, 12.2. Found: C, 78.8; H, 12.1.

Methyl 2,2,4-Trimethyl-Δ³-cyclohexenyl Ketone (VI).—To 5 g. of the corresponding alcohol (V), at room temperature, there was added a solution of 5 g. of crystallized sodium dichromate in 40 cc. of water and 5.5 g. of concentrated sulfuric acid, and the mixture was stirred vigorously for thirty minutes, during which period its temperature rose to 58°. After standing overnight, the upper layer was separated and the lower one extracted with ether. The ether extract was added to the separated upper layer and the mixture washed successively with water, dilute sodium carbonate solution, and water, and dried over magnesium sulfate. The ether was removed and the residue distilled under diminished pressure. The yield of colorless oil, of an agreeable fresh minty aroma, b. p. 99–100° at 13 mm., was 3.8 g., or 76%: n^{25}_D 1.4677; d^{25}_4 0.9166; M_D calcd., 50.42; obsd., 50.31.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.5; H, 10.8. Found: C, 79.5; H, 10.9.

2,4-Dinitrophenylhydrazone.—Bright yellow needles, from ethanol, m. p. 146–147°.

Anal. Calcd. for $C_{17}H_{22}O_4N_4$: C, 59.0; H, 6.4. Found: C, 59.1; H, 6.4.

Ethyl 2,2,4-Trimethyl-Δ³-cyclohexenyl Ketone (VI).—By oxidation of the corresponding alcohol (V), as described above, using 8 g. of the alcohol (V), 10 g. of crystallized

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[21] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[22] Windemuth, *ibid.*, **71B**, 1939 (1938).

sodium dichromate, 11 g. of concentrated sulfuric acid, and 80 cc. of water, the exothermic reaction raised the temperature of the mixture to 61°. The product was a colorless oil, b. p. 118–118.5° at 18 mm., of a pleasant minty and fruity odor; yield, 5.5 g., or 70%: $n^{25}{}_D$ 1.4752; $d^{25}{}_4$ 0.9235: M_D calcd., 55.03; obsd., 54.89.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 79.4; H, 11.4.

2,4-Dinitrophenylhydrazone.—Small yellow needles, from ethanol, m. p. 138–139°.

Anal. Calcd. for $C_{18}H_{24}O_4N_4$: C, 60.0; H, 6.7. Found: C, 59.9; H, 6.7.

β-Hydroxy-β-(2,2,4-trimethyl-Δ^3-cyclohexenyl)-propionic Acid (VII).—In a 500-cc. 3-necked flask, carrying a separatory funnel and two condensers (with protecting calcium chloride tubes), there were placed 20 g. of the aldehyde (I), 25 cc. of dry benzene, and 9 g. of sheet zinc which had been sandpapered clean and cut into small pieces. A few cc. of a benzene solution of ethyl bromoacetate (22 g. of the ester in 10 cc. of benzene) was run into the mixture from the separatory funnel and the flask heated with a free flame to initiate the reaction. After the addition of all of the ester, the mixture was refluxed for two hours, cooled, and shaken up with ice-cold 20% sulfuric acid. The supernatant layer was removed and washed successively with 1% sulfuric acid, 5% aqueous sodium bicarbonate solution, and water, dried over magnesium sulfate, and distilled. After removal of the benzene, a pale yellow oil of agreeable odor was collected, b. p. 120–121.5° at 2 mm.; yield of this **ethyl ester** was 14 g., or 70%, based on the aldehyde (I) used: $n^{25}{}_D$ 1.4777; $d^{25}{}_4$ 0.9989; M_D calcd., 67.38; obsd., 67.79.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 70.0; H, 10.1. Found: C, 70.3; H, 10.1.

This ester was saponified by potassium hydroxide in methanol solution and purified by distillation under diminished pressure, collecting the fraction b. p. 150–153° at 1.5 mm.; yield, 1.8 g., of a thick sirup, which crystallized after standing in a desiccator for ten days. Recrystallized from petroleum ether, it formed fine white needles, m. p. 133–134°.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.9; H, 9.5. Found: C, 68.1; H, 9.7.

Di-[β-(2,2,4-trimethyl-Δ^3-cyclohexenyl)(β-Hydroxy)ethyl] Ketone (VIII).—The barium salt of the above acid (VII) was dried to constant weight at 120° and subjected to direct combustion, which evidently resulted in its conversion first into the ketone as the following analytical figures indicate.

Anal. Calcd. for $C_{23}H_{28}O_3$: C, 49.3; H, 6.8. Found: C, 49.4; H, 6.9.

The residual ash consisted of barium carbonate.

Methyl β-2,2,4-Trimethyl-Δ^3-cyclohexenylvinyl Ketone (IX).—To a mixture of 12 g. of the aldehyde (I) with 36 g. of acetone, there was added a cold solution of sodium ethylate (from 0.5 g. of sodium and 10 cc. of absolute ethanol) during fifteen minutes. The temperature of the mixture rose to 47° and the color of the solution changed to red. After two hours, the reaction was terminated by the addition of 2 g. of tartaric acid in 10 cc. of water. More water was added and the oil which separated was distilled with steam. The distillate was extracted with ether, the ethereal extract dried over magnesium sulfate, the ether removed, and the residue distilled in an atmosphere of carbon dioxide. A pale yellow oil was thus obtained, b. p. 124–126° at 8 mm., with a spicy cedarwood odor which, when diluted, possessed a definite violet fragrance, not unlike that of the isomeric ionones; yield, 10 g., or 66%. A micro-boiling point determination, by the Siwolobov method, gave a b. p. for the ketone of 254–256° at atmospheric pressure.

Further purification of the compound, for the determination of physical constants, was carried out as follows. A mixture of 8 g. of the ketone, 8 cc. of water, and 16 cc. of 35% sodium bisulfite solution was extracted with ether, and the aqueous solution then decomposed by the addition of a 10% sodium hydroxide solution. The liberated ketone was collected promptly in ether, the ether solution washed with a 10% tartaric acid solution, then with water, dried over magnesium sulfate, and distilled in an atmosphere of carbon dioxide: b. p. 135° at 12 mm.; $n^{25}{}_D$ 1.4943; $d^{25}{}_4$ 0.9568; M_D calcd., 58.23; obsd., 58.43.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.2; H, 10.5. Found: C, 80.9; H, 10.8.

The above methods of preparation and purification are based upon the work of Tiemann[23] with the ionones.

Semicarbazone.—White plates, from dilute ethanol, m. p. 183–184°.

Anal. Calcd. for $C_{14}H_{23}ON_3$: C, 67.4; H, 9.3. Found: C, 67.6; H, 9.3.

2,4 - Dinitrophenylhydrazone.—As orange microscopic needles, from petroleum ether, m. p. 143–144°.

Anal. Calcd. for $C_{19}H_{24}O_4N_4$: N, 15.0. Found: N, 14.8.

1,1,3-Trimethyl-1,4,6,9-tetrahydronaphthalene (X).—The cyclodehydration of the above ketone (IX) was accomplished with phosphorus pentoxide, using a modification of the method employed by Bardhan and Sengupta[24] for the preparation of octahydrophenanthrene.

A mixture of 7 g. of the ketone with 14 g. of phosphorus pentoxide was refluxed for ten minutes under reduced pressure and at a bath temperature of 90°, the reaction proceeding quite violently. Without interrupting the vacuum, the condenser was then turned downward, the bath temperature raised to 170°, and the distillate collected at 128–138° at 12 mm. The yield of this crude hydrocarbon was 3 g., or 47%. Purified by two rectifications over sodium, this ionene isomer possessed the following physical constants: b. p. 132–134° at 12 mm.; $n^{25}{}_D$ 1.5215; $d^{25}{}_4$ 0.9399; M_D calcd., 56.55; obsd., 56.42.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.4; H, 10.6. Found: C, 89.5; H, 10.6.

The use of iodine, in place of phosphorus pentoxide, for the cyclodehydration of the ketone, proved unsatisfactory.

Repeated attempts to form a maleic anhydride addition compound, including the heating of the mixed compounds in toluene solution for ten hours in sealed tubes at 100°, all failed, and this convinced us that the olefin bonds in the hydrocarbon could not be in conjugation, and that the structure therefore was probably that of a 1,4,6,9-tetrahydronaphthalene derivative.

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[23] Tiemann, (a) *Ber.*, **31**, 808 (1898); (b) **33**, 3722 (1900).

[24] Bardhan and Sengupta, *J. Chem. Soc.*, 2522 (1932).

1,3-Dimethylnaphthalene.—Following the procedure of Price, Davidson and Bogert,[25] in the dehydrogenation of 1,1,2-trimethyltetralin, a mixture of 3 g. of the hydrocarbon (X) with 1.2 g. of sulfur was heated with a small flame until the vigorous evolution of hydrogen sulfide had subsided somewhat. It was then refluxed gently for two and one-half hours, and finally distilled under reduced pressure. There was obtained 1 g. of a yellow oil, b. p. 126–142° at 10 mm. Barnett and Sanders[26] have reported the b. p. of pure 1,3-dimethylnaphthalene as 107° at 1 mm.

Attempted dehydrogenation of the tetrahydro compound by the use of isoamyl disulfide[27] proved unsuccessful, and the original disulfide was recovered unchanged.

Picrate.—Bright orange needles, from methanol, m. p. 116–117° (literature,[26] 118°).

Anal. Calcd. for $C_{18}H_{15}O_7N_3$: C, 56.1; H, 3.9. Found: C, 55.8; H, 4.0.

Styphnate.—Fine yellow needles, from dilute ethanol, m. p. 132–133°.

Anal. Calcd. for $C_{18}H_{15}O_8N_3$: C, 53.8; H, 3.8. Found: C, 54.0; H, 3.8.

When either the picrate or styphnate was treated with dilute ammonium hydroxide or a 10% sodium carbonate solution, the dimethylnaphthalene separated as a yellow oil, of faint, but agreeable odor.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.9.

Methyl Allyl β-2,2,4-Trimethyl-Δ³-cyclohexenylvinylcarbinol (XI).—To 1.2 g. of magnesium turnings, activated with a crystal of iodine, and 100 cc. of dry ether, there were added dropwise 8.2 g. of allyl bromide and 8 g. of the ketone (IX) in 25 cc. of dry ether. When the initial reaction had abated, the mixture was refluxed for one and one-half hours, allowed to stand at room temperature for two to three hours, decomposed with crushed ice containing 9 g. of ammonium chloride, and extracted with ether. The ether extract was washed with water, dried over magnesium sulfate, the ether removed, and the residue distilled under reduced pressure. There was thus obtained a heavy colorless oil, of rhubarb odor, b. p. 104–105° at 2 mm.; yield, 7 g., or 65%. This oil was quite unstable and lost water even when distilled at 9 mm. pressure: $n^{25}D$ 1.4920; d^{25}_4 0.9239; M_D calcd., 73.98; obsd., 73.56.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.9; H, 11.2. Found: C, 81.7; H, 11.0.

δ-Methyl-2,2,4-trimethyl-Δ³-cyclohexenyl-α,γ,ε-hexatriene (XII).—To a cooled mixture of 12 g. of the alcohol (XI), 5 g. of anhydrous pyridine, and 25 cc. of dry ether, in a flask protected against ingress of moisture and placed in an ice–salt-bath, there was added dropwise 7.4 g. of thionyl chloride. After this addition, the stirring of the mixture was continued for an hour, maintaining the temperature of the bath below −5° and the mixture then decomposed with ice water. The supernatant layer was separated, the aqueous solution extracted with ether and the ether extract added to the former upper layer. The combined ether solution was washed with 5% hydrochloric acid, and with 5% sodium carbonate solution, the ether removed and the residue distilled at 2 mm. pressure over sodium, giving the following fractions: (a) b. p. 87–88° (6 g.), (b) b. p. 97–98° (2 g.).

These two fractions were united and digested with sodium at 125° until hydrogen was no longer evolved (an hour or more). The filtered oil, rectified over sodium, yielded 6 g., or 54%, of a pale yellow liquid, of pleasant lemon-verbena odor, b. p. 103–104° at 3 mm., quite sensitive to light, and polymerizing on standing.

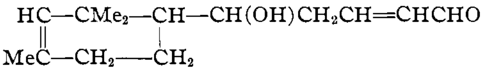
Anal. Calcd. for $C_{16}H_{24}$: C, 88.8; H, 11.2. Found: C, 88.7; H, 11.4.

In chloroform solution, it gave a turbid violet color with antimony trichloride.

Condensation of 2,2,4-Trimethyl-Δ³-cyclohexene Aldehyde with Acetaldehyde.—When this condensation was attempted, in the presence of piperidine acetate[16] as catalyst, to form the corresponding cinnamaldehyde, the product was a reddish oil, of pungent odor, b. p. 84–94° at 6 mm. Analysis of the fraction b. p. 90–94° at 6 mm., gave the following figures.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.7; H, 9.9. Found: C, 75.5; H, 10.3.

Such a formula would correspond to the structure



$$\begin{array}{l}\mathrm{HC{-}CMe_2{-}CH{-}CH(OH)CH_2CH{=}CHCHO}\\ \quad\| \qquad\qquad\quad |\\ \mathrm{MeC{-}CH_2{-}CH_2}\end{array}$$

Efforts to obtain the semicarbazone from this product gave instead the semicarbazone of the original cyclic aldehyde (I), apparently due to a dealdol reaction. Heilbron and Jones[28] had a similar experience in their futile attempts to condense β-cyclocitral with acetaldehyde, using the same catalyst. Their main product was an aldol which they were unable to dehydrate. On the other hand, under similar conditions, Kuhn, *et al.*,[16] have found that citral condenses with acetaldehyde readily to form citrylideneacetaldehyde.

Summary

1. From 2,2,4-trimethyl-Δ³-cyclohexene aldehyde, an isomer of the cyclocitrals, there have been synthesized a number of compounds of interest to the perfumer, among them new isomers of cyclogeraniol, cyclogeranic acid, ionone and ionene.

2. The influence of constitution upon odor, as well as upon chemical reactions, as revealed in the investigation of these new compounds, is discussed.

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[25] Price, Davidson and Bogert, *J. Org. Chem.*, **2**, 542 (1938).

[26] Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

[27] Ritter and Sharpe, THIS JOURNAL, **59**, 2351 (1937).

[28] Heilbron and Jones, *J. Soc. Chem. Ind.*, **55**, 813 (1936).