[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, LABORATORIES OF THE MOUNT SINAI HOSPITAL]

Synthesis of 1'-Dehydro-β-ionone

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In a recent publication[1] we have indicated the role of 2,2,6-trimethyl-1-ethynylcyclohexanol[2] as a useful intermediate in the synthesis of vitamin A. We have accomplished the dehydration of this carbinol (III) by the use of thionyl chloride and pyridine to 2,2,6-trimethyl-1-ethynylcyclohexene-1 (IV), a compound which takes a central position in a projected total synthesis of vitamin A.[1] The physical properties of this hydrocarbon and the successful synthesis of tetrahydroionone therefrom in high yield confirms its structure. The physical properties of hydrocarbon fractions, previously described[3] as 2,2,6-trimethyl-1-ethynylcyclohexene-1, differ considerably. One of us[4] had previously referred to the dehydration of the carbinol over an alumina catalyst in analogy to the dehydration of the simple 1-ethynylcyclohexanol. Subsequent studies, however, had thrown doubt on the nature of the dehydration product. As will be reported in a subsequent paper,[5] dehydration over alumina is accompanied by methyl migration and by migration of hydrogen from the ring into the side chain, leading to aromatization. Besides the resulting benzenoid hydrocarbon, there is found in small amounts an acetylenic fraction of which an insignificant portion, in turn, may be the desired 2,2,6-trimethyl-1-ethynylcyclohexene-1. The major part of the acetylenic fraction, however, lacks the conjugation of the double bond with the triple bond.

Condensation of acetic anhydride with the Grignard derivative of the true acetylenic hydrocarbon yielded 1'-dehydro-β-ionone (V). This compound shows the typical spectral qualities expected from a conjugated system so closely related to β-ionone; its $\lambda_{\max}$ is 288 mμ with an extinction of $\epsilon_{\max}$ 11,800, and its refractive index is $n^{20}\text{D}$ 1.5205. It was subsequently hydrogenated and yielded a tetrahydroionone (VI) whose semicarbazone was found to be identical with that of an authentic sample of tetrahydroionone to which Prelog[6] assigns the *cis*-configuration.

The Grignard derivative of 2,2,6-trimethyl-1-ethynylcyclohexene-1 was condensed with acetaldehyde; the resulting DL-dehydro-β-ionol (VII) was catalytically hydrogenated to DL-tetrahydroionol (VIII); this, in its turn, was oxidized to a saturated ketone (VI) characterized by three derivatives, which were again identical with those obtained from tetrahydroionone prepared from β-ionone.

The dehydration of 1-ethynylcyclohexanol to ethynylcyclohexene over alumina proceeds with relative ease. The difficulty encountered in the instance of the trimethyl compound is due, not merely to the fact that only one, instead of four hydrogen atoms, is available, but also to steric considerations[7] and to the further complication that a neopentyl alcohol type system is present.[8] It is generally believed that elimination of the elements of water is predicated upon the *trans*-position of hydrogen and hydroxyl with respect to each other. Two diastereomeric racemates are possible for 2,2,6-trimethyl-1-ethynylcyclohexanol-1, only one of which may be expected to dehydrate without rearrangement, namely, that carbinol which carries the ortho hydrogen atom *trans* to the hydroxyl group. The reaction of sodium acetylide with trimethylcyclohexanone (I) may be anticipated to yield a mixture of both forms.[9] From the negative outcome of dehydration experiments, one is led to assume that the *cis*-diastereomer prevails in the reaction mixture. Thus, we set out to replace the hydroxyl group by a group X in a reaction which probably proceeds with racemization at carbon atom 1. This should lead to a product containing a higher percentage of the *trans*-compound. Removal of HX from the resulting mixture should then lead to the proper hydrocarbon. As the carbinol did not react with dry hydrogen chloride, thionyl chloride in excess pyridine was employed. This did not lead to a simple replacement of hydroxyl by chlorine, but the proper hydrocarbon was isolated in 15% yield. The major reaction product (60%) was a chloro compound of the elementary composition $C_{11}H_{17}Cl$. This substance still contained the $-C{\equiv}CH$ grouping as it formed a silver salt, which speaks against the formation of an allene.[10] The chlorine atom is easily removable, rendering unlikely the formulation of this compound as a vinyl chloride derivative.[11] Replacement of chlorine by hy-

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[1] Sobotka and Chanley, THIS JOURNAL, **70**, 3914 (1948).

[2] Sobotka, Progress Reports 1942–1944, Final Report 1944 to OSRD, distributed by Office of Production Board, Nos. 77, 214–215 (1947).

[3] *Cf.* Milas, MacDonald and Black, THIS JOURNAL, **70**, 1829 (1948).

[4] See ref. 2, Progress Reports of October 28, 1943 and February 25, 1944.

[5] Chanley and Sobotka, THIS JOURNAL, **71**, 4140 (1949).

[6] Prelog and Frick, *Helv. Chim. Acta*, **31**, 417 (1948).

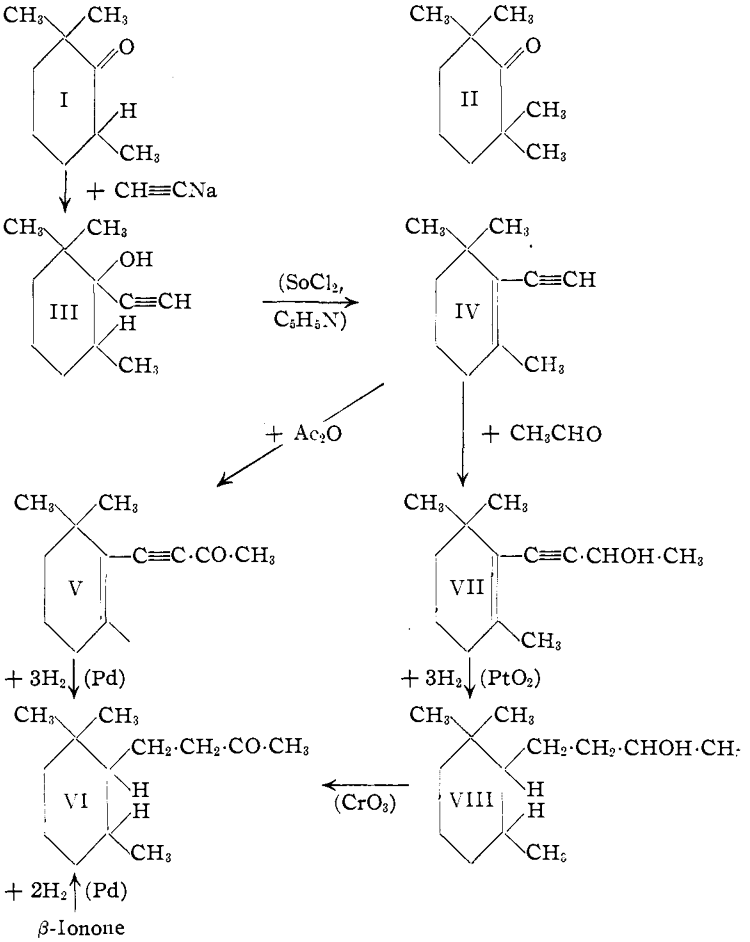
[7] Bartlett and Pockel, THIS JOURNAL, **59**, 820 (1937); Bartlett and Bavley, *ibid.*, **60**, 2416 (1938); Price, *ibid.*, **61**, 1847 (1939); Price and Karabinos, *ibid.*, **62**, 1159 (1940).

[8] Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 179, esp. 188, 192–194 (1946); see also Dostrovsky and Hughes, *ibid.*, 157, 161, 164, 166, 169 (1946).

[9] Wang and Hu, *J. Chin. Chem. Soc.*, **10**, 1 (1943); *cf.* ref. 5. Careful fractional distillation of the carbinol did not afford any separation; the carbinol boiled over a range of 1° and the various portions collected did not differ from one another in their refractive index.

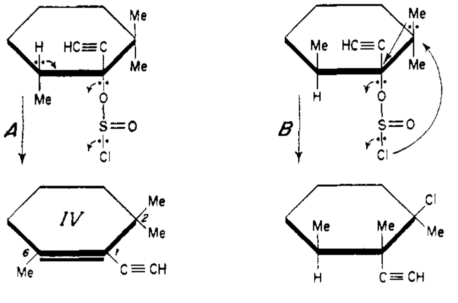
[10] A. W. Johnson, "Chemistry of Acetylenic Compounds," Arnold and Co., London, 1946, pp. 62, 71.

[11] Hurd and Jones, THIS JOURNAL, **56**, 1924 (1934), have shown that the action of thionyl chloride–pyridine on 1-ethynylcyclohex-



droxyl did not regenerate the original carbinol, but gave rise to a new carbinol, presumably with an altered carbon skeleton. The chloro compound, when treated with reagents used for dehydrohalogenation, did not yield the desired hydrocarbon.

The chloro compound can be derived from the *cis*-carbinol under the following assumption: Since no simple elimination reaction is possible in this stereomer of the hypothetical –OSOCl intermediate (B), the latter may react in two other ways, namely, by formation of the corresponding chloro compound, with loss of sulfur dioxide, or by rearrangement and subsequent addition of the chloride ion to another part of the molecule. The latter presumably occurs according to a reaction exemplified by scheme B. Contraction of the ring is not excluded nor migration of the methyl group on carbon atom 6, rather than that on carbon atom 2. The *trans*-form reacts according to scheme A which involves the loss of a proton from carbon atom 6 and the simultaneous loss of sulfur dioxide and chloride ion, leading to the formation of the "ene–yne" system. An alternative explanation, equally compatible with the results, is that scission of the C–O bond in the intermediate addition product results in the generation of a carbonium ion, which assumes a planar configuration, implying racemization at carbon atom 1. From this carbonium ion both reactions may proceed in proportion to their respective reaction rates, and lead to the products isolated. This mechanism appears to be less likely.[12] We consider it most probable that the modest yield of the correct hydrocarbon in the thionyl chloride–pyridine reaction originated from the *trans*-form present in the carbinol. Work is in progress to establish the structure of the chloro compound.



Experimental

The ultraviolet absorption spectra were obtained with a Beckman spectrophotometer Model DU using 95% ethanol as solvent except as otherwise noted. We are indebted for the microanalyses to the late Dr. Gertrude Oppenheimer and her associates, Microchemical Laboratory, California Institute of Technology, Pasadena, California.

o-Methylcyclohexanone was prepared for us by Givaudan-Delawanna, Inc., Delawanna, N. J., through the courtesy of Drs. Luthy and Fiori by the catalytic hydrogenation of purest *o*-cresol and subsequent oxidation of the resulting 2-methylcyclohexanol with dichromate.

Preparation of 2,2,6-Trimethyl-1-cyclohexanone (I) and 2,2,6,6-Tetramethyl-1-cyclohexanone (II).[12a]—The introduction of one methyl group into *o*-methylcyclohexanone has been described by one of us.[13] The crude dimethylcyclohexanone fraction of b. p. 169–173° was further methylated in two to three mole batches by the use of sodamide and methyl iodide under the same conditions as in the preparation of the dimethyl compound. The reaction was brought to conclusion by refluxing the mixture for seven hours. After decomposition of the reaction mixture with 10% sulfuric acid, the organic layer was

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anol produced some 1-ethynylcyclohexene, but for the most part 1-(α-chlorovinyl)-cyclohexene-1. Such a conjugated diene system, carrying a chlorine atom, would show λ_{max} around 230–235 mμ; *cf.* Bowden, Brauder and Jones, *J. Chem. Soc.*, 948 (1946). Our product showed no absorption in the ultraviolet.

(12) *Cf.* Bartlett and Brown, THIS JOURNAL, **62**, 2927 (1940).

(12a) We are greatly indebted to Givaudan-Delawanna, Inc., whose Mr. Kaiser prepared for us considerable quantities of trimethylcyclohexanone and the corresponding ethynylcarbinol by the methods here described.

(13) J. D. Chanley, THIS JOURNAL, **70**, 244 (1948).

dried and carefully fractionated in a packed column of 15 theoretical plates. Two main fractions boiling from 171–176° and from 176–183°, respectively, were collected. In order to achieve further purification, we resorted to fractional crystallization of the semicarbazones.

Semicarbazones of Fraction b. p. 171–176°.—To 100 g. of this fraction dissolved in 1000 ml. of 95% ethyl alcohol, 84 g. of semicarbazide hydrochloride and 126 g. of sodium acetate trihydrate, dissolved in 1000 ml. of water, were added with stirring over a period of twenty minutes. After standing an additional ten minutes, the crude semicarbazone of 2,2-dimethylcyclohexanone separated; yield, 37 g.; m. p. 190–193°. The filtrate was then allowed to stand for three hours in the ice-box, where a mixture of di- and trimethylcyclohexanone crystallized. The filtrate from the second crop was then refluxed for a few hours and eventually 850 ml. of ethanol was distilled off. The resulting mixture was left in the ice-box overnight. The next day the crude semicarbazone of trimethylcyclohexanone was collected.

Semicarbazone of Fraction b. p. 176–183°.—This fraction contained an inconsequential amount of the dimethyl compound, but was contaminated with the tetramethyl compound, which does not form a semicarbazone. It was, therefore, worked up differently. One hundred grams of the crude ketones was dissolved in 1000 ml. of 95% ethanol and the same quantities of semicarbazide hydrochloride and sodium acetate in water were added as above. After refluxing for ninety minutes, the mixture was allowed to stand in the ice-box overnight. The crude semicarbazone was collected the next day. Its yield was 50% of the theoretical for this fraction. The combined impure semicarbazones (from fractions of b. p. 171–176° and 176–183°) were twice recrystallized from absolute ethanol; m. p. 207–209°; reported 220°.[14] The yield of the semicarbazone, calculated on the methylcyclohexanone, from which we had started, was 25–30%.

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.88; H, 9.70; N, 21.31. Found: C, 60.93; H, 9.95; N, 21.72.

Two hundred and fifty-six grams of the combined purified semicarbazone were mixed with 220 g. of phthalic anhydride and steam distilled until one liter of distillate was collected. The oily layer was separated, dried over sodium sulfate and distilled through a packed column of 15 theoretical plates; yield, 165 g. (91%) of pure trimethylcyclohexanone; b. p. 178.7–179° at 767 mm.; $n^{20}D$ 1.4480, $n^{25}D$ 1.4460, d^{25}_4 0.8983, *MR*, calcd. 41.59. Found: *M R* 41.62; reported,[3] 177–178.5° (758 mm.), $n^{25}D$ 1.4465.

Anal. Calcd. for $C_9H_{16}O$: C, 77.08; H, 11.50. Found: C, 76.97; H, 11.79.

The oxime prepared from this ketone melted at 103°; reported,[15] 104–105°.

The 2,4-dinitrophenylhydrazone melted at 141°.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: N, 17.5. Found: N, 17.8.

Tetramethylcyclohexanone (II), which does not form a semicarbazone had remained behind in the mother liquor and because of its high volatility was also found in the ethanol distillates. The ketone was purified by distillation. It boiled at 183.5–184° (772 mm.), m. p. 15°; $n^{20}D$ 1.4473; reported,[15] b. p. 182–184° (753 mm.), $n^{15.6}D$ 1.4484.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.44; H, 11.74.

2,2,6-Trimethyl-1-ethynylcyclohexanol-1 (III) was prepared in half-mole batches from the pure ketone with sodium acetylide in liquid ammonia following the procedure of Campbell.[16] The compound was obtained in 71% yield; b. p. 121–121.5° (49–50 mm.), 93° (13–14 mm.), $n^{20}D$ 1.4791, $n^{25}D$ 1.4770; reported,[8] b. p. 88–90° (20 mm.) $n^{25}D$ 1.4740. The compound formed an insoluble silver salt with alcoholic silver nitrate.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.58; H, 10.84.

The 3,5-dinitrobenzoate prepared in pyridine and recrystallized from 95% ethanol melted at 141°. The yield of this derivative was very small.

Anal. Calcd. for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.78. Found: C, 60.01; H, 5.98; N, 8.31.

2,2,6,6-Tetramethyl-1-ethynylcyclohexanol was prepared by the same method as above, b. p. 129.5° (50 mm.), m. p. 36–37°, $n^{30}D$ 1.4775.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.03; H, 11.41.

Preparation of 2,2,6-Trimethyl-1-ethynylcyclohexene-1 (IV) and the Chloro Compound $C_{11}H_{17}Cl$.—To 100 g. of the pure trimethylcarbinol, dissolved in 150 ml. of dry pyridine, was added 71.2 g. of thionyl chloride, purified according to Fieser,[17] dissolved in 150 ml. of dry pyridine, with stirring in the cold (ice-bath) over a period of two hours. The mixture was allowed to react for one further hour and then poured into 2000 ml. of ice water and thoroughly extracted ten times with 200-ml. portions of petroleum ether (b. p. 40–60°). The combined extracts, after washing with sodium carbonate solution, water, saturated sodium chloride solution and drying over anhydrous potassium carbonate, in the presence of traces of hydroquinone, were distilled *in vacuo* through a packed column of ten to twelve theoretical plates. Two main fractions were collected; the hydrocarbon fraction boiled at 69–70° (13 mm.), $n^{20}D$ 1.4915, $n^{25}D$ 1.4892, $\epsilon_{max.}$ 13,000, at $\lambda_{max.}$ 227 mμ. The yield was 13.5 g. or 15%. On standing, the compound polymerized even at ice-box temperature, unless stabilized by hydroquinone. The compound gave a precipitate (silver salt) with alcoholic silver nitrate.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.73; H, 11.22.

The second fraction, the chloro compound, boiled at 96° (14 mm.), $n^{20}D$ 1.5030 and amounted to 60 g. (54%).

Anal. Calcd. for $C_{11}H_{17}Cl$: C, 71.53; H, 9.28; Cl, 19.20. Found: C, 72.44; H, 9.73; Cl, 19.00.

By boiling with the stoichiometric amount of silver nitrate in 75% ethanol, four-fifths of the chlorine was removed from this compound and an additional amount of silver nitrate produced the formation of a silver acetylide which was then decomposed by ammonium thiocyanate. In this manner we obtained in one experiment a carbinol of the same elementary composition as the original carbinol, but differing in its physical properties: b. p. 83° (13 mm.), $n^{20}D$ 1.4754.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 80.03; H, 10.94.

1′-Dehydro-β-ionone (V).—To a solution of 0.067 mole of ethylmagnesium bromide in 25 ml. of dry ether was added 10 g. (0.067 mole) of 2,2,6-trimethyl-1-ethynylcyclohexene-1 in 25 ml. of ether over a period of one hour. The mixture was stirred and refluxed for an additional two hours and allowed to stand overnight under nitrogen. The Grignard compound, thus formed, was added with stirring during two hours to a solution of 13.8 g. of acetic anhydride in 40 ml. of dry ether at −70°. The mixture, after reacting another two hours, was decomposed with saturated ammonium chloride solution. The organic layer was then distilled *in vacuo*. The product 6.5 g. (50% yield) was collected boiling at 119–120° (10 mm.), $n^{20}D$ 1.5205, $\lambda_{max.}$ 288 mμ, $\epsilon_{max.}$ 11,800.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.32; H, 9.55.

The semicarbazone prepared in the usual manner and recrystallized from ethanol (platelets) melted at 129.2°; $\lambda_{max.}$ 292 mμ, $\epsilon_{max.}$ 20,800.

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[14] Masson, *Compt. rend.*, **154**, 518 (1912).

[15] Cornubert, *Bull. soc. chim.*, **41**, 894 (1927).

[16] K. Campbell, B. Campbell and Eby, THIS JOURNAL, **60**, 2282 (1938).

[17] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 381.

Anal. Calcd. for $C_{14}H_{21}N_3O$: N, 16.99. Found: N, 16.70, 17.01.

From the mother liquors a small amount of a second semicarbazone, fine needles, presumably another form of the former was obtained; m. p. 129–130° (recrystallized from ethanol–water mixture). It showed a marked melting point depression in admixture with the aforementioned semicarbazone. Its ultraviolet absorption spectrum showed $\lambda_{\max.}$ 292 mμ, $\epsilon_{\max.}$ 16,700.

Anal. Calcd. for $C_{14}H_{21}N_3O$: N, 16.99. Found: N, 17.47.

The 2,4-dinitrophenylhydrazone melted after recrystallization from ethanol at 145–145.2°. It showed in alcohol $\lambda_{\max.}$ 372 mμ, $\epsilon_{\max.}$ 28,600; in chloroform $\lambda_{\max.}$ 380 mμ $\epsilon_{\max.}$ 28,800.

Anal. Calcd. for $C_{19}H_{22}N_4O_4$: N, 15.13. Found: N, 15.77.

The ultraviolet absorption spectrum, not previously reported, of the 2,4-dinitrophenylhydrazone of 1-(1'-cyclohexenyl)-butyn-1-one-3[1] showed $\lambda_{\max.}$ 372 mμ, $\epsilon_{\max.}$ 27,800 in alcohol and $\lambda_{\max.}$ 376 mμ, $\epsilon_{\max.}$ 28,100 in chloroform.

Tetrahydroionone Semicarbazone.—1'-Dehydro-β-ionone (0.77 g.) was hydrogenated in 50 ml. of ethanol at atmospheric pressure employing 100 mg. of palladium-on-calcium carbonate (5%) as catalyst. Ninety per cent. of the volume of hydrogen required by one double and one triple bond was consumed. The residual oil, after filtration and evaporation of the solvent, was converted into the semicarbazone derivative. Three recrystallizations from 95% ethanol afforded the pure semicarbazone of tetrahydroionone of melting point 179–180°. This derivative showed no depression on admixture with an authentic specimen, m. p. 182°, which had been prepared by the hydrogenation of β-ionone employing the same catalyst as mentioned above; reported m. p. 183–184°,[6] reported m. p. 179–180°.[18]

It had been mentioned that the dehydration of 2,2,6-trimethyl-1-ethynylcyclohexanol over alumina yielded among other products an acetylenic hydrocarbon fraction. The Grignard compound of this acetylene was condensed with acetic anhydride in the same manner as described above. In a run starting with 7.0 g. of hydrocarbon, b. p. 64–66° (14–15 mm.), $n^{20}\text{D}$ 1.4771, $\lambda_{\max.}$ 227 mμ, $\epsilon_{\max.}$ 4000, we obtained 0.8 g. of an impure ketonic fraction, b. p. 123–127° (20 mm.), which after further purification by evaporative distillation showed $n^{22}\text{D}$ 1.5055. Its spectrum exhibited two absorption maxima at $\lambda_{\max.}$ 224 mμ and $\lambda_{\max.}$ 287 mμ with the respective $\epsilon_{\max.}$ of 9000 and 5000. The semicarbazone prepared from this fraction and recrystallized from ethanol melted at 112–114°; $\lambda_{\max.}$ 265 mμ, $\epsilon_{\max.}$ 14,000. We ascribe this semicarbazone to that compound of the ketonic mixture which is responsible for $\lambda_{\max.}$ 224 mμ.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 79.12; H, 9.57. Calcd. for $C_{14}H_{21}N_3O$: N, 16.99. Found: N, 16.00.

DL-1'-Dehydro-β-ionol (VI).—The Grignard derivative from 14.8 g. (0.10 mole) of 2,2,6-trimethyl-1-ethynylcyclohexene-1 was prepared as above and 4.4 g. of freshly distilled acetaldehyde in 40 ml. of dry ether was added thereto during one hour at −15°. The mixture was allowed to react for another three hours with stirring at 0° and for a further hour at room temperature. After decomposition with saturated ammonium chloride solution, the organic layer was distilled and 12 g. of product (58% yield) was isolated; b. p. 103–104° (2.4 mm.), 108° (3 mm.); $n^{25}\text{D}$ 1.5070, d^{25}_{4} 0.9355; *MR* calcd. 59.11, found 61.27, exaltation 2.16; $\lambda_{\max.}$ 232 mμ, $\epsilon_{\max.}$ 13,000.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.49. Found: C, 81.53; H, 10.59.

DL-Tetrahydroionol (*cis*) **(VIII).**—One and four-tenths of a gram of dehydro-β-ionol was hydrogenated in the presence of platinum oxide at atmospheric pressure in 50 ml. of purified glacial acetic acid as solvent. The theoretical amount of hydrogen was absorbed. The reaction product, after evaporative distillation at 50° (2–3 mm.), amounted to 1.2 g., $n^{20}\text{D}$ 1.4700; reported $n^{20}\text{D}$ 1.4717,[19a] $n^{20}\text{D}$ 1.4770.[19b]

One gram of the above tetrahydroionol was oxidized in 10 ml. of glacial acetic acid by 0.55 g. of chromium trioxide at 80° during one hour. The reaction mixture, diluted with water, was extracted with petroleum ether (b. p. 30–60°). After washing with sodium carbonate solution and drying over sodium sulfate, the product was evaporatively distilled at 38° (3 mm.); yield, 0.74 g., $n^{22}\text{D}$ 1.4655. Reported $n^{22}\text{D}$ 1.4660 (*cis*)[6]; $n^{22}\text{D}$ 1.4634 (*trans*). The semicarbazone prepared from the above ketone and recrystallized from ethanol melted at 179–180° and again showed no melting point depression on admixture with authentic tetrahydroionone semicarbazone.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from methanol, m. p. 118.5–120°, and showed no depression of melting point on admixture with an authentic sample, m. p. 119–120.5°, which had been prepared from the hydrogenation product of β-ionone; reported m. p. 120–120.5°.[19b]

The 4-phenylsemicarbazone was prepared. The melting point rose gradually from 104° for the crude reaction product to 114–115° (clear melt at 118°) on recrystallizations from methanol. Prelog[6] reports m. p. 109–110° for the 4-phenylsemicarbazone of the hydrogenation product of ionone, while he finds 133° for the analogous derivative derived from dihydrocyclocitral to which he ascribes *trans*-substitution on the ring. To our surprise, both the tetrahydroionone obtained by our synthesis and that obtained by the hydrogenation of β-ionone, gives rise to two 4-phenylsemicarbazones melting at 109–110° and 114–115° (clear melt at 118°). These two forms may be obtained alternatively from methanol solution, depending on conditions, not completely understood, as their recrystallization may not always be influenced by seeding with one form. We consider the two forms allomorphs of Prelog's *cis*-form, since we were able to derive each from the other one. No melting point depressions were observed in mixture of the lower or the higher-melting derivatives, prepared from the synthetic and authentic tetrahydroionone. Moreover, mixtures of the lower-melting form and higher-melting form from either source (synthetic and authentic) melted over the intermediate range, showing no depression.

Acknowledgment.—We wish to thank Miss Bernice Hamerman and Mrs. Edith Rosen Kaplan for their able and painstaking assistance.

Summary

1. The preparation of 2,2,6-trimethylcyclohexanone and 2,2,6,6-tetramethylcyclohexanone and of the ethynyl carbinols, derived from them, is described.

2. The dehydration of 2,2,6-trimethyl-1-ethynylcyclohexanol by means of thionyl chloride and pyridine leads to 2,2,6-trimethyl-1-ethynylcyclohexene-1.

3. The acetylenic analogs of β-ionone (1'-dehydro-β-ionone) and of β-ionol were prepared and their structure was confirmed by conversion into the perhydro compounds.

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[18] Ruzicka, Seidel and Pfeiffer, *Helv. Chim. Acta*, **31**, 827 (1948).

[19] (a) Kandel, *Ann. chim.*, **11**, 73 (1939); (b) Naves and Bachman, *Helv. Chim. Acta*, **26**, 2151 (1943).