[Contribution from Noyes Chemical Laboratory, University of Illinois]

An Isomer of Citronellal

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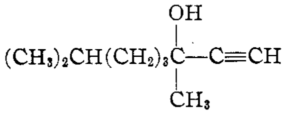
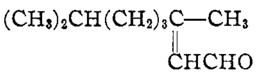
The course suggested by Price and Dickman[3] for the disappearance of citral and citronellal in acid solutions involved primary cyclization of the carbonyl group with the ϵ,ζ-double bond. It thus seemed likely that a dihydrocitral isomeric with citronellal, but with the double bond conjugated to the carbonyl group rather than more remotely located, might be considerably more stable in dilute acid solution.

Rupe and Giesler[4] have reported the preparation of a product, assigned the structure of the dihydrocitral (II) we desired, by the rearrangement of the carbinol I, formed from condensation of methyl isohexyl ketone with acetylene.



$(CH_3)_2CH(CH_2)_3C(OH)(CH_3)-C\equiv CH$

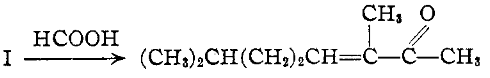
I



$(CH_3)_2CH(CH_2)_3C(CH_3)=CHCHO$

II

A number of analogous products prepared by Rupe by this "rearrangement" have been shown to be α,β-unsaturated ketones, rather than aldehydes.[5] The material we obtained from this "rearrangement" did not behave like an aldehyde and on further investigation, it too proved to be an α,β-unsaturated ketone, 3,7-dimethyl-3-octen-2-one (III).



$\mathrm{I} \xrightarrow{HCOOH} (CH_3)_2CH(CH_2)_2CH=C(CH_3)-C(=O)-CH_3$

III

As reported by Rupe,[4] III gave two semicarbazones, evidently *cis–trans* isomers at the double bond. We found a melting point for the low-melting semicarbazone (139°) some 17° above that reported by Rupe.[4]

The presence of the double bond in III was indicated by bromine and permanganate test and hydrogenation to a saturated ketone, the acetyl group by positive iodoform reaction, the position of the double bond by oxidation to isocaproic acid and the α,β-unsaturated carbonyl grouping by ultraviolet absorption spectra. It is of passing interest to note that the location of the absorption maxima (232 mμ.) was half-way between the positions suggested by Woodward[6] for mono-(225 ± 5 mμ.) and disubstituted (239 ± 5 mμ.) double bonds conjugated to a carbonyl group. As a check, the ultraviolet absorption of mesityl oxide, also an α,β-disubstituted, α,β-unsaturated methyl ketone, was measured. In this case, the observed maximum, 237 mμ., is in good agreement with Woodward's rule.

The most likely course for the conversion of the carbinol I to the ketone III would appear to be initial dehydration to a vinylacetylene homolog. Vinylacetylenes are readily hydrated to α,β-unsaturated ketones, vinylacetylene itself to methyl vinyl ketone.

Experimental[7]

***i*-Hexyl methyl ketone** was prepared by the acetoacetic ester synthesis in 39–47% yields[8]; b. p. 170–171°, n^{20}D 1.4146 (lit.,[8] b. p. 165°, n^{20}D 1.4144).

Methyl-*i*-hexylethynylcarbinol.—The ketone above was condensed with acetylene essentially according to the directions of Gould and Thompson for β-ionone.[9] Approximately 200 cc. of dried ether was cooled in a Dry Ice–alcohol-bath and saturated with acetylene. Portions of sodium (totaling 19.5 g., 0.5 gram-atom) in 250 cc. of anhydrous *t*-amyl alcohol and *i*-hexyl methyl ketone (totaling 64 g., 0.5 mole) in 75 cc. of ether were added simultaneously during two hours. The mixture was stirred and acetylene passed in throughout the time of addition. The Dry Ice-bath was then replaced with an ice-bath and stirring continued for two more hours.

The reaction mixture was immediately hydrolyzed by pouring on cracked ice acidified with dilute sulfuric acid. The ether layer was washed three times with water and dried over magnesium sulfate. The ether was removed and the carbinol distilled from a modified Claisen flask to yield 31 g. (41%) of product, b. p. 65–67° (6 mm.) (lit.[4] 75–82° (10 mm.)), n^{20}D 1.4400. This material gave a positive bromine and potassium permanganate test. It also formed a yellow precipitate with ammoniacal silver nitrate showing the presence of an acetylenic hydrogen.

If in the above method the reaction mixture was not cooled sufficiently or if the reaction mixture was allowed to stand for too long a time before being worked up, a dark orange solution was obtained instead of the pale yellow solution. Upon working up this reaction in the same manner as described before, a large amount of high boiling liquid was obtained. The greater portion of this liquid distilled at 130–132° (5 mm.), n^{20}D 1.4814. The liquid was colored a bright yellow. It gave tests for unsaturation but negative tests with all other classification reagents.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.74; H, 12.26. Found: C, 86.8; H, 12.09.

This analysis indicated that the liquid was largely hydrocarbon with a small amount of impurity. The formation of a hydrocarbon could be accounted for by formation of a glycol, 2,6,9,13-tetramethyl-7-tetradecyne-6,9-diol, which would be easily dehydrated to a dienyne during distillation.

Other methods were tried in attempting to prepare methylisohexylethynylcarbinol but were not found to give as satisfactory results. The use of sodamide in ether[4] and of sodium acetylide in liquid ammonia[10] were both employed. In the first case large amounts of high boiling

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[3] Price and Dickman, *Ind. Eng. Chem.*, in press.

[4] Rupe and Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).

[5] See, *e. g.*, Hurd and Jones, This Journal, **56**, 1924 (1934); Hurd and Christ, *ibid.*, **59**, 118 (1937).

[6] Woodward, This Journal, **63**, 1123 (1941); **64**, 76 (1942).

[7] Analyses by Miss Theta Spoor.

[8] Gilman and Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 241, 248, and 361.

[9] Gould and Thompson, This Journal, **57**, 340 (1935).

[10] Campbell, Campbell and Eby, This Journal, **60**, 2882 (1938).

liquid were obtained while in the latter case considerable amounts of starting material were isolated.

3,7-Dimethyl-3-octen-2-one.—The 3,7-dimethyl-3-octen-2-one was formed by the rearrangement of methylisohexylethynylcarbinol with formic acid. The procedure used was the same, with certain modifications, as that described by Rupe.[4] Both 86 and 70% formic acid were used. Better results were obtained with the latter concentration of acid.

Thirty-one grams of methyl-*i*-hexylethynylcarbinol and 45 g. of water were boiled in 226 g. of 86% formic acid to yield 15 g. (48.4%) of 3,7-dimethyl-3-octen-2-one boiling at 75-78° (6 mm.); $n^{20}D$ 1.4527, d^{20}_4 0.8503, *MR* (calcd.), 47.9, *MR* (found), 48.8. The exaltation of 0.9 unit is in good agreement for that observed for compounds containing similar conjugated systems. The oil was colorless and had a lemon-like taste and odor.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.85; H, 12.02.

The rearrangement product gave a positive permanganate and bromine test for unsaturation, negative Tollens and fuchsin-aldehyde test and a positive iodoform test.

The **semicarbazones** were prepared in aqueous alcohol. Semicarbazone (A) crystallized out of solution and was filtered. Water was then added to the filtrate, which was cooled in a beaker of ice, and semicarbazone (B) crystallized out.

Semicarbazone (B) was crystallized repeatedly before all of the first semicarbazone was removed. Semicarbazone (A) was obtained reasonably pure after one recrystallization. Semicarbazone (A) was formed in approximately ten times the amount of semicarbazone (B).

Semicarbazone A, m. p. 170° (lit.,[4] 170°). *Anal.* Calcd. for $C_{11}H_{21}N_3O$: C, 62.56; H, 9.95; N, 19.89. Found: C, 62.94; H, 10.07; N, 19.91. Semicarbazone B, m. p. 139° (lit.,[4] 122°). Found: C, 62.62; H, 10.09; N, 20.11.

Oxidation.—Two grams of ketone was placed in a two-necked flask equipped with a mechanical stirrer and cooled in an ice-bath. Sixty cubic centimeters of 5% sodium carbonate was added and the stirrer started. Four per cent. potassium permanganate was added dropwise, the addition of permanganate being continued until an excess persisted. The mixture was tested for excess permanganate by placing a drop of the mixture on a piece of filter paper. A black center of manganese dioxide was formed, a yellowish ring around this and an outer ring which is colorless in the absence of and pink in the presence of excess permanganate.[8] About 100 cc. of permanganate was added. The excess was destroyed with 1 cc. of alcohol. The manganese dioxide was removed by filtration and the filtrate was made acidic with phosphoric acid. This was then extracted with ether and the ether distilled. A brownish oil with an unpleasant acid-like odor remained.

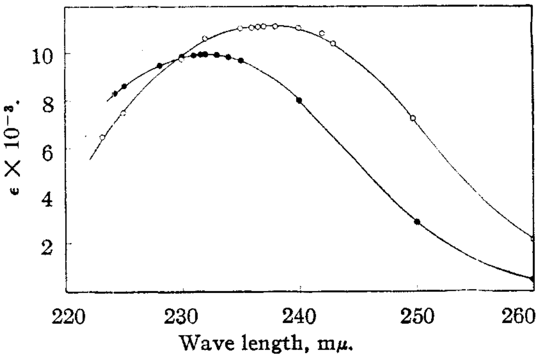

Fig. 1.—Ultraviolet absorption spectra: O, mesityl oxide; ●, 3,7-dimethyl-3-octen-2-one.

The oil was treated with 2 cc. of thionyl chloride and heated under a reflux condenser for thirty minutes. The mixture was cooled and a solution of 1 g. of *p*-toluidine in 30 cc. of benzene added. The mixture was warmed on a steam-bath for two minutes, the benzene solution was then decanted and washed successively with 2 cc. of water, 5 cc. of 5% hydrochloric acid, 5 cc. of 5% sodium hydroxide and 2 cc. of water. The benzene was evaporated and the toluidide recrystallized from alcohol and water. The toluidide melted at 60-61° which agrees with the literature value for *i*-caproic acid.[4]

Hydrogenation.—Three grams (0.02 mole) of ketone was dissolved in 150 cc. of absolute alcohol to which 0.1 g. of platinum oxide catalyst was added. The reaction bottle was placed on an Adams machine. A pressure drop of 4.7 lb. was observed in twenty minutes, corresponding to absorption of 0.02 mole of hydrogen.

The platinum was filtered off and the alcohol evaporated from the ketone. The ketone was distilled at reduced pressure, b. p. 70° (9 mm.), $n^{20}D$ 1.4252.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.90; H, 12.89. Found: C, 76.93; H, 12.86.

The oil was colorless and had a much sweeter, more fragrant odor than the α,β-unsaturated compound. It gave a semicarbazone difficult to purify.

Ultraviolet Absorption.[11]—Several absorption spectra were taken of 3,7-dimethyl-3-octen-2-one. The following represents a typical experiment. One cc. of a solution of 0.01377 g. of ketone in 50 cc. of 95% alcohol was further diluted with 50 cc. of alcohol. A maximum absorption (ϵ = 10,000) was observed at a wave length of 232 mμ. (Fig. 1).

An absorption spectrum was also taken of mesityl oxide with a maximum absorption (ϵ = 11,000) being observed at a wave length of 237 mμ. (lit.,[12] ϵ = 12,500 at 237 mμ.).

Summary

i-Hexylmethylethynylcarbinol, on heating in formic acid, has been shown to rearrange to 3,7-dimethyl-3-octen-2-one, rather than 3,7-dimethyl-3-octenal, as previously reported.

NOTRE DAME, INDIANA RECEIVED FEBRUARY 25, 1947

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[11] The ultraviolet absorption spectra were determined by Mr. I. Feldman.

[12] Scheibe, Rossler and Backenkohler, *Ber.*, **58**, 586 (1925).