Experimental

***p*-Toluenesulfonylhydrazine.**—*p*-Toluenesulfonylchloride (100 g.) was dissolved in the least possible amount of benzene and a mixture of 60 g. of hydrazine hydrate and 10 ml. of water was added with cooling and stirring. After the initial vigorous reaction had subsided, the mixture was allowed to stand for 3 hours and the crystalline hydrazine filtered. Rapid recrystallization from water yielded the hydrazine, m.p. 109–110°, reported[10] m.p. 112°. Unless the recrystallization is done rapidly a considerable loss of product results.

Preparation of Tosylhydrazones. (a) **2-Butanone Tosylhydrazone.**—The *p*-toluenesulfonylhydrazine, 10 g., was dissolved in 125 ml. of 1 *N* HCl and an equimolar amount of 2-butanone added with stirring. After standing for one hour the reaction mixture was filtered and the product recrystallized from an ethanol–water mixture to give an 85% yield of white crystalline hydrazone, m.p. 123–124°.

(b) **3-Methyl-2-butanone Tosylhydrazone.**—The *p*-toluenesulfonylhydrazine, 8 g., was dissolved in 100 ml. of 1% ethanolic HCl and an equimolar amount of the ketone was added. The solution was heated at reflux for 0.5 hour and, after cooling, an equal volume of water was added and the solution cooled to −10°. The product was collected and recrystallized from ethanol-water, m.p. 121–122°.

(c) **4-Methyl-2-pentanone tosylhydrazone**, which was prepared by method b, melted at 116–117°.

Decomposition of the Hydrazones.—The decompositions in each case were carried out by heating a sample of the hydrazone in ethylene glycol containing an excess of 1 *N* sodium ethyleneglycolate. The decomposition of the hydrazone of 2-butanone is typical. The hydrazone (1.00 g., 0.004 mole) was dissolved in 20 ml. of 1 *N* sodium ethyleneglycolate in ethylene glycol. The mixture was heated to 170° in an oil-bath, at which temperature nitrogen evolution became rapid. The hydrocarbon products were collected in a flask which was cooled in a Dry Ice-bath and the nitrogen was collected in a gas buret. The hydrocarbons occupied a volume of 33.1 ml. at standard temperature and pressure (35% yield) and 93 ml. of nitrogen was collected.

Analysis of Products.—The condensable products were analyzed by gas chromatography. The butenes were separated on a 12.5 foot column of N,N-dibutylformamide on Celite, the pentenes on a similar 4.5 foot column and the hexenes on a 4.5 foot silver nitrate–ethylene glycol column. Identifications were made by comparison with authentic samples or mixtures. Triplicate analyses gave precisely concordant results. The butenes also were analyzed by mass spectrometry and the results were in excellent agreement with those obtained by gas chromatography.

Butenes.—1-Butene was obtained by the pyrolysis of *n*-butyl acetate.[4] *cis*- and *trans*-2-butene were obtained by the pyrolysis of *sec*-butyl acetate.[4] *n*-Butane was obtained from the Matheson Co.

Pentenes.—3-Methyl-1-butene was obtained by the pyrolysis of 3-methyl-1-butyl acetate.[4] 2-Methyl-1-butene and 2-methyl-2-butene were obtained by the pyrolysis of *t*-amyl acetate.[4]

Hexenes.—Pyrolysis of 4-methyl-2-pentyl acetate gave a mixture of three products. Careful fractionation of the mixture through a 30-plate column separated it into a lower boiling fraction which was mainly 4-methyl-1-pentene, and a mixture of *cis*- and *trans*-4-methyl-2-pentene. It was assumed that the *cis* isomer, the higher boiling of the two, which is formed in smaller amount during the pyrolysis and which would be expected to form a stronger complex with silver nitrate, would be eluted later during the chromatography.

Decomposition of the Hydrazone in the Pressure of Thiophenoxide.—The tosylhydrazone of 2-butanone, 1.00 g., was placed in 20 ml. of 1 *N* sodium ethyleneglycolate solution which was 0.5 *N* in thiophenoxide ion. A slow stream of nitrogen was passed through the solution and the mixture was heated at 170°. The volatile products were collected, and their volume measured under standard conditions. The yield was 33.4%. Gas phase chromatography of these products showed that the same ratio of products had been formed.

Control Experiments.—Pure olefins, or olefin mixtures differing in composition from those produced in the reaction, were slowly introduced below the surface of the reaction mixture at 170°. In no case did any detectable isomerization take place.

AMES, IOWA

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(10) K. Freudenberg and F. Blummel, *Ann.*, **440**, 51 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis of 1-Acetyl-4-Isopropenyl-1-Cyclopentene

BY JOSEPH WOLINSKY AND WALTER BARKER

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The synthesis of 1-acetyl-4-isopropenyl-1-cyclopentene (IV) from limonene monoxide is described. This substance proved to be identical with a ketone isolated from Spanish *Eucalyptus globulus*, thus necessitating a minor revision of the previously accepted structure for the naturally occurring ketone.

The related terpene lactones isolated from various Iridomyrmex species of ants[1] and from oil of catnip[2] have been the subject of considerable interest in recent years. While the preparation of iridomyrmecin, from ants, has been recently reported,[3] nepetalactone, from catnip, has not yet been synthesized. It was our original intention to undertake the preparation of these compounds, but, as it developed, our plan was not fulfilled; for reasons which will become apparent from the sequel, we instead synthesized 1-acetyl-4-isopropenyl-1-cyclopentene, a substance which proved to be identical with an unusual terpene ketone found in Spanish *Eucalyptus globulus*.[4]

Our approach, outlined in Chart I, began with the acid-catalyzed hydrolysis of limonene monoxide. Cleavage of the resulting diol I with sodium metaperiodate led to the keto-aldehyde II as indicated by the infrared spectrum of the resulting oil which displayed a maximum at 3.7 μ associated with an aldehydic hydrogen atom, in addition to a very strong carbonyl band at 5.8 μ and terminal methylene absorption at 6.08 and 11.25 μ. The presence of a medium band at 3.0 μ probably stemmed from the starting diol I since treatment of the crude cleavage product with Brady reagent[5] afforded a single derivative corre-

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(1) R. Fusco, R. Trave and A. Vercellone, *Chim. e Industr.*, **37**, 251 (1955); G. W. K. Cavill, D. L. Ford and H. D. Locksley, *Austr. J. Chem.*, **9**, 288 (1956); *Chemistry & Industry*, 465 (1956); G. W. K. Cavill and H. D. Locksley, *Austr. J. Chem.*, **10**, 352 (1957).

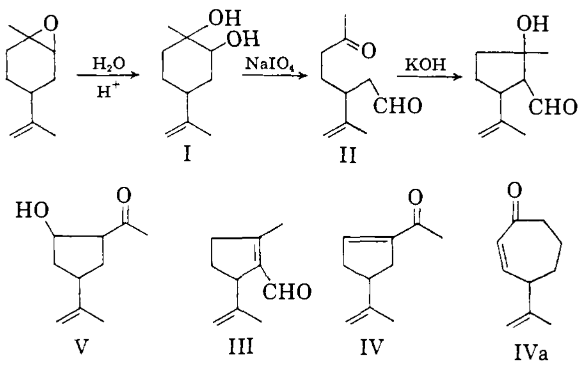
(2) S. M. McElvain and E. J. Eisenbraun, THIS JOURNAL, **77**, 1599 (1955); J. Meinwald, *ibid.*, **76**, 4571 (1954); R. B. Bates, E. J. Eisenbraun and S. M. McElvain, *ibid.*, **80**, 3420 (1958).

(3) F. Korte, J. Falbe and A. Zschocke, *Tetrahedron*, **6**, 201 (1959); F. J. Clark, G. I. Fray, R. H. Jaeger and R. Robinson, *ibid.*, **6**, 217 (1959).

(4) H. Schmidt, *Ber.*, **80**, 528 (1947); **80**, 533 (1947).

(5) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

CHART I

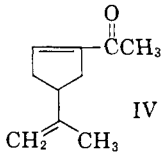


sponding to the bis-2,4-dinitrophenylhydrazone of II.

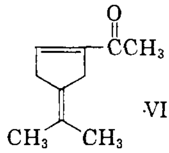
It was anticipated that cyclization of the keto-aldehyde II would lead to either the unsaturated aldehyde III or the unsaturated ketone IV.[6,7] When an ethereal solution of crude II was shaken for 30 minutes with dilute potassium hydroxide,[8] there was isolated in fair yield, a colorless liquid showing b.p. 66–68° (1.5 mm.). Examination of the infrared spectrum of this substance indicated the presence of a conjugated carbonyl group, λ_{max} 6.02 and 6.18 μ, and a terminal methylene group, 11.25 μ. The absence of a band at 3.7 μ associated with an aldehydic hydrogen atom suggested the cyclization product was the unsaturated ketone IV. This assignment was confirmed by comparing the ultraviolet absorption spectrum of the cyclization product, λ_{max} 239 mμ, ϵ, 11,200, with the spectra of similarly constituted compounds.[9] Whereas 1-acetyl-1-cyclopentene shows maximal absorption at 239 mμ,[10,11] 2-cycloheptenone and compounds related to the unsaturated aldehyde III absorb at 227[12] and 248–258 mμ,[7,13] respectively.

In addition, a second liquid, appreciably higher boiling than ketone IV, was obtained on treating the keto-aldehyde with dilute alkali. This substance exhibited absorption in the infrared at 2.75, 2.85, 5.80, 6.05 and 11.25 μ, characteristic of hydroxyl, saturated carbonyl and terminal methylene groups, respectively. On stirring an ethereal solution of this substance with alkali, the unsaturated ketone IV was produced; thus, the higher boiling liquid is, clearly, the β-hydroxy ketone V.

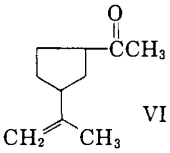
A ketone, $C_{10}H_{14}O$, has been isolated from Spanish *Eucalyptus globulus* by Schmidt.[4] This ketone yielded 1-acetyl-3-isopropyl-cyclopentane on hydrogenation over nickel, while chemical reduction using sodium and moist ether, followed by oxidation of the resulting alcohol, afforded an unsaturated ketone, pinolone, which has generally been considered to be a mixture of VI and VII. On this basis it was concluded that the natural ketone was either 1-acetyl-4-isopropylidene-1-cyclopentene (VIII) or 1-acetyl-4-isopropenyl-1-cyclopentene (IV) and of these VIII was chosen because of the optical inactivity of the ketone.[14]



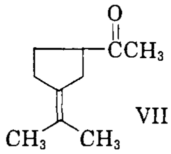
IV



VIII



VI



VII

In order to clarify the structure of the natural ketone it became desirable to compare it with our synthetic ketone IV and this was done with a sample provided by Dr. Harry Schmidt.[16] This sample, though yellow following ten or more years of storage, was shown to be homogeneous by the appearance of a single sharp band on vapor phase chromatography. The sample distilled over a very narrow range affording a colorless liquid and leaving little, if any, residue. Although our synthetic ketone was optically active and the natural ketone inactive, a careful comparison of their infrared spectra, in chloroform solution, established their identity. Furthermore, the infrared spectra (potassium bromide pellets) of their semicarbazone derivatives were indistinguishable.

Additional evidence for the isopropenyl side chain in the natural ketone was provided by ozonolysis which afforded formaldehyde, isolated as its 2,4-dinitrophenylhydrazone. Chromatography of this derivative demonstrated the absence of detectable amounts of acetone 2,4-dinitrophenylhydrazone.

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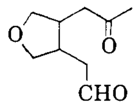
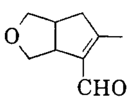
(6) While the seven-membered ring ketone IVa might also be derived from II it was never seriously considered in view of the precedent for condensations giving five-membered rings.

(7) Relative to this intramolecular aldol condensation, N. L. Wendler and H. L. Slates, THIS JOURNAL, **80**, 3937 (1958), have observed that cyclization of the following 1,6-keto-aldehyde afforded an unsaturated aldehyde rather than the corresponding unsaturated ketone.





(8) J. B. Brown, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3624 (1950).

(9) In a single instance a product was isolated which contained *ca.* 10–15% of what appeared to be the unsaturated aldehyde III. This was indicated by a weak band at 3.7 μ in the infrared, by a slight shift of the ultraviolet maximum to 240–241 mμ, with a significant broadening of the absorption band and a corresponding lowering of intensity, and by vapor phase chromatography where a definite shoulder was observed on the band arising from ketone IV.

(10) I. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1940).

(11) W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 2297 (1955).

(12) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954).

(13) T. R. Ames, J. L. Beton, A. Bowers, T. G. Halsall and E. R. H. Jones, *ibid.*, 1905 (1954).

(14) An alternate conclusion favoring IV might have been reached considering the relative stability of the natural ketone. Thus, a compound like VIII might be expected to isomerize readily to an acetyl cyclopentadiene derivative, especially under the conditions of isolation which involved the preparation and regeneration of a bisulfite adduct and a semicarbazone derivative. A statement[15] regarding the "isomerization of the exocyclic double bond into the ring during hydrolysis of the semicarbazone derivative" can be accommodated by either IV or VIII.

(15) J. Simonsen and D. H. R. Barton, "The Terpenes," University Press, Cambridge, 1952, Vol. III, 2nd edition, p. 531.

(16) The authors wish to express their appreciation to Dr. Harry Schmidt for generous samples of the natural ketone and its semicarbazone derivative.

Finally, the nuclear magnetic resonance spectrum of the natural ketone, obtained at 56.4 mc. in a magnetic field of approximately 13,300 gauss,[17] was in complete accord with structure IV. The spectrum of IV displayed peaks at 8, 120, 223–240, 256 and 287 c.p.s. whose area varied in a ratio of approximately 1:2:5:3:3, respectively. The resonance at 8 c.p.s can be assigned to the vinylic hydrogen atom at C_2, while that at 120 c.p.s. is definitely associated with the two hydrogen atoms of a terminal methylene group. The single hydrogen at C_4 is not completely resolved from the absorption of the four hydrogen atoms at C_3 and C_5 found at *ca.* 236 c.p.s. The two non-equivalent methyl groups satisfactorily account for the peaks at 256 and 287 c.p.s.[18]

Acknowledgment.—The authors are most grateful to Mr. W. E. Baitinger for determining the nuclear magnetic resonance spectrum and to Mrs. M. Dilling for recording the infrared spectra.

Experimental[21]

8-*p*-Menthene-1,2-diol.—A mixture of 181.8 g. (1.19 moles) of limonene monoxide and one liter of 1% sulfuric acid was shaken occasionally for an hour and, after chilling thoroughly, the precipitate was removed. The crude solid was dissolved in boiling water and a small amount of yellow oil removed. Cooling afforded 50 g. of white solid which, after drying over phosphorus pentaoxide, showed m.p. 73–74°, $[\alpha]_D$ 28.75° (*c* 0.0334, chloroform); reported[18] m.p. 72.5–73.5°.

Periodate Cleavage of Diol I.—To a cold solution of 36.0 g. (0.21 mole) of diol I in 30 ml. of tetrahydrofuran was added a solution of 50.2 g. (0.23 mole) of sodium metaperiodate in 350 ml. of water. This mixture, which slowly deposited a white solid, presumably sodium iodate, was set aside for 3 days. The tetrahydrofuran was removed under diminished pressure and the resulting mixture extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and the ether removed. The resulting oil gave a positive iodoform test. This keto-aldehyde II was not purified further; it was used directly in subsequent steps.

The 2,4-dinitrophenylhydrazone derivative from the crude oil showed m.p. 146–147° after several recrystallizations from ethanol. Examination of the mother liquors gave no evidence for the presence of a second derivative.

Anal. Calcd. for $C_{22}H_{27}N_8O_8$: C, 50.00; H, 4.58; N, 21.20. Found: C, 50.00; H, 4.32; N, 21.15.

1-Acetyl-4-isopropenyl-1-cyclopentene (IV).—An ethereal solution of crude II, from 36 g. of diol I, was shaken for 30 minutes with a 10% solution of potassium hydroxide. The ether layer was removed and the dark brown aqueous layer washed several times with ether. The combined ether solutions were dried over anhydrous magnesium sulfate and the ether removed *in vacuo*. Distillation afforded the following fractions: a, *ca.* 7.0 g., b.p. 87–89° (5.0 mm.); b, *ca.* 8.0 g., b.p. 116–125° (5.0 mm.); residue, *ca.* 10 g. of dark viscous oil.

Distillation of fraction a gave a center cut which showed b.p. 67–68° (1.5 mm.), $n^{17}D$ 1.4985, $[\alpha]_D$ 25.1° (*c* 0.023, chloroform).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.12; H, 9.29.

The semicarbazone derivative of IV melted at 195–196° after several recrystallizations from methanol, $[\alpha]_D$ 43.5° (*c* 0.0236, chloroform), λ_{max} 264 mμ, ϵ 25,900.

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.58; H, 8.44; N, 20.30.

The 2,4-dinitrophenylhydrazone crystallized from ethanol as red plates, m.p. 178–180°.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.95. Found: C, 58.45; H, 5.63; N, 17.17.

The β-hydroxy-ketone V, b.p. 107–110° (1.5 mm.), $n^{20}D$ 1.4912, was obtained by distillation of fraction b. The 2,4-dinitrophenylhydrazone prepared from this liquid showed m.p. 181–183°, undepressed when mixed with a sample of the 2,4-dinitrophenylhydrazone of ketone IV.

Stirring an ethereal solution of V with 10% potassium hydroxide afforded a liquid, b.p. 68–70° (1.5 mm.), whose infrared spectrum, in chloroform solution, was identical with that of ketone IV.

Ketone from Spanish Eucalyptus globulus.—The sample obtained from Dr. Schmidt[16] was distilled affording a colorless liquid, b.p. 66–67° (1.55 mm.), λ_{max} 239 mμ, ϵ 11,400.

The semicarbazone derivative, yellow after years of storage, was recrystallized several times from methanol prior to comparing its infrared spectrum with that of a synthetic sample.

Ozonolysis of IV.—A solution of 303 mg. of the natural ketone IV in 10 ml. of acetic anhydride, cooled in a Dry Ice–trichloroethylene-bath, was ozonized fror 30 minutes. The resulting solution was poured into a stirred slurry of 2 g. of zinc and 150 ml. of water. Distillation into a solution of 2,4-dinitrophenylhydrazine reagent afforded 159 mg. of a yellow solid, m.p. 162–165°. Chromatography, using silica gel and eluting with 4% ether–petroleum ether, afforded 20 mg. of an oily red solid which could not be induced to crystallize and 125 mg. of a yellow solid, long needles from ethanol, m.p. 164–166°, undepressed when mixed with an authentic sample of formaldehyde 2,4-dinitrophenylhydrazone.

LAFAYETTE, IND.

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(17) The spectrometer employed for this measurement was a Varian Associates V-4300-B high resolution n.m.r. spectrometer with associated 12″ electromagnet system equipped with a super stabilizer.

(18) It has been suggested, without evidence, that the naturally occurring ketone may not actually exist as such in nature.[15] While the ketone IV might be formed by a pinacolic change from a precursor such as $\Delta^{8(9)}$-*p*-menthen-1-ol-2-one,[15] a more attractive precursor might be dipentene or the diol I.[19] Cleavage of I to the keto-aldehyde II and cyclization would give IV. Alternatively, IV may stem from an intermediate such as homoterpenyl ketone.[20]

(19) H. Schmidt, *Ber.*, **82**, 11 (1952), has demonstrated that the diol I is produced on autoxidation of limonene.

(20) Y. R. Naves, *Bull. soc. chim. France*, 1372 (1958); M. Harispe, A. Boime, P. Ham and R. Charonnat, *ibid.*, 478 (1958).

(21) All boiling points and melting points are uncorrected. Infrared spectra were determined using a Perkin–Elmer double beam spectrometer, model 21. Ultraviolet spectra were measured with a Cary recording spectrophotometer, model 10-11M. The microanalyses were performed by Dr. C. S. Yeh and associates.