

Anal. Calcd. for C_7H_8O : C, 77.75; H, 7.46. Found: C, 77.63; H, 7.58.

Oxidation of *exo*-Bicyclo[3.2.0]hept-6-en-3-ol (8).—Oxidation of *exo*-bicyclo[3.2.0]hept-6-en-3-ol as above gave bicyclo[3.2.0]hept-6-en-3-one (9) identical in infrared absorption with the product obtained in the oxidation of *endo*-bicyclo[3.2.0]hept-6-en-3-ol (7).

Hydrogenation of Bicyclo[3.2.0]hept-6-en-3-one (9).—Bicyclo[3.2.0]hept-6-en-3-one (9, 70 mg.) in 15 ml. of methanol containing Adams catalyst absorbed one equivalent of hydrogen. Careful removal of the solvent gave bicyclo[3.2.0]heptan-3-one (10) identical in infrared absorption to an authentic sample provided by Dr. R. Srinivasan.⁹ The semicarbazone of the product melted at 197–199° dec. pure and mixed with authentic bicyclo[3.2.0]heptan-3-one semicarbazone.⁹

Lithium Aluminum Hydride Reduction of Bicyclo[3.2.0]hept-6-en-3-one (9).—A solution of bicyclo[3.2.0]hept-6-en-3-one (9, 5 mg.) in 1 ml. of anhydrous ether was added to a slurry of lithium aluminum hydride (5 mg.) in 0.5 ml. of ether. The excess hydride was decomposed with moist sodium sulfate. Removal of the ether after drying over magnesium sulfate gave the mixed alcohols 7 and 8. Vapor phase chromatographic analysis showed this to be a 9:1 mixture of 7 and 8. The alcohols were identified by adding pure 7 and pure 8 to separate samples of the mixture and observing the enhancement of the v.p.c. peaks due to each component.

Bicyclo[3.2.0]hept-6-en-2-ol.—A mixture of 2,4-cycloheptadienol and 3,5-cycloheptadienol (1.7 g.) obtained by lithium aluminum hydride reduction of the 2,4-cycloheptadienone-3,5-cycloheptadienone mixture obtained in the Hofmann degradation of tropinone methiodide,¹¹ was dissolved in 100 ml. of anhydrous ether and irradiated in a quartz vessel with a General Electric UA-3 mercury arc lamp for 4 days. The solvent was removed under reduced pressure giving 1.5 g. of crude photoalcohols (7, 8 and 13). This mixture was resolved by vapor phase chromatography on a 6-ft. by 3/8 in. column containing 15% Ucon LB550-X on 80–100 mesh Celite at 148° into three alcohols with retention times 12.8 min. (7), 16.3 min. (13) and 18.1 min. (8). The alcohols 7 and 8 were identified by comparison of infrared absorption and vapor phase chromatographic retention. The remaining alcohol (13) showed nuclear magnetic resonance absorption at 4.08, 6.04, 6.70, 7.00, 7.96 and 8.27 τ .

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.18; H, 9.04.

Irradiation of 5-Methoxy-2,4-cycloheptadienone (19).—A solution of 330 mg. (2.39 mM) of 19 in 75 ml. of anhydrous ether in a quartz vessel fitted with a reflux condenser was irradiated with a General Electric UA-3 mercury arc lamp for 70 minutes at a distance of 15 cm. The ether solution was concentrated under reduced pressure, and the yellow residue was molecularly distilled giving 290 mg. (88%) of 20, as a very pale yellow liquid. The ultraviolet absorption spectrum of 20 showed $\lambda_{max}^{95\% EtOH}$ 332 m μ (1,120) and end absorption.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.50; H, 7.51.

Conversion of 5-Methoxybicyclo[3.2.0]hept-6-en-2-one to 5-Methoxy-2,4-cycloheptadienone.—(A) A 2.26×10^{-4} M solution of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in ethanol after 30 min. at 60° showed an ultraviolet spectrum identical to that of 5-methoxy-2,4-cycloheptadienone (19). The extinction at 328 m μ showed that transformation was quantitative.

(B) A solution of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in 0.1 N sulfuric acid after 1 min. at room temperature showed the same ultraviolet absorption maxima as 5-methoxy-2,4-cycloheptadienone (19) in 0.1 N sulfuric acid. Both solutions slowly developed the 235 m μ absorption characteristic of 2-cyclohepten-1,5-dione (the acid hydrolysis product of 19).⁴

5-Methoxybicyclo[3.2.0]heptan-2-one (21).—A solution of 0.1016 g. of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in 25 ml. of methanol absorbed 0.98 equivalent of hydrogen using Adams catalyst. The catalyst was removed by filtration, and the methanol was removed under reduced pressure. Molecular distillation of the residue gave a colorless, sweet-smelling liquid. The infrared absorption spectrum of 21 was identical to that of authentic tetrahydrophoto- γ -tropolone methyl ether.¹³

Irradiation of 2-Methyl-3,5-cycloheptadienone.—A solution of 2-methyl-3,5-cycloheptadienone (0.73 g.) in 100 ml. of ether in a quartz vessel equipped with an internal cooling coil and an outlet for gas collection was irradiated with a General Electric UA-3 mercury arc lamp for 6.5 hr. Carbon monoxide (95% of theory) was collected and identified by infrared comparison. The ethereal solution was concentrated by careful distillation, and the product was separated by preparative scale vapor phase chromatography. The product thus obtained showed λ_{max}^{EtOH} 252 (26,800), 261 (36,400), 271 m μ (28,900) and infrared maxima at 3.23, 3.32, 3.43, 3.51, 5.56, 6.11, 6.16, 6.91, 6.98, 7.29, 10.42, 10.67 and 11.19 μ .

A portion of the product absorbed 3.07 equivalents of hydrogen over palladium-on-carbon in pentane. The product was identified as *n*-heptane by comparison of vapor phase chromatographic retention and infrared absorption with an authentic sample.

Irradiation of 3,5-Cycloheptadienone.—A solution of 3,5-cycloheptadienone (2.73 g.) in 50 ml. of anhydrous ether was irradiated (General Electric UA-3 mercury arc lamp) in a quartz vessel fitted with an internal cooling coil and a gas collection apparatus. After 27 hours no more gas was evolved, and the irradiation was stopped. The gas which had been collected was identified as carbon monoxide by comparison of infrared spectra. The ether and low boiling product were separated from starting material by distillation. The product was separated from the ether by preparative vapor phase chromatography on a 6-ft. by 3/8 in. column containing 15% Ucon LB 550-X on 80–100 mesh Celite at 71°. The product showed ultraviolet absorption at 246, 256 and 266 m μ and infrared maxima at 3.22, 3.31, 4.30, 5.52, 6.15, 6.90, 7.00, 9.95, 10.15, 10.67 and 11.10 μ in good agreement with the values reported for a mixture of *cis*- and *trans*-1,3,5-hexatrienes.¹⁸

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

The Structure of Two Minor Products of the Pyrolysis of Thujone

BY W. VON E. DOERING, M. R. WILLCOTT, III, AND M. JONES, JR.

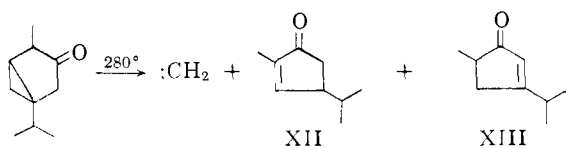
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The hypothesis of Eastman¹ that the extrusion of methylene is needed to explain the formation of two C_9 -ketones in the pyrolysis of thujone is no longer required, since the ketones are in fact C_{10} and have the structures 2,5-dimethyl-5-isopropylcyclopent-2-enone (I) and 2,4-dimethyl-4-isopropylcyclopent-2-enone (II).

Having for some years been interested in various aspects of carbenes, including their preparation and addition to olefins, we noted with more than casual

(1) R. H. Eastman and A. V. Winn, *J. Am. Chem. Soc.*, **82**, 5908 (1960).

concern the recently published assertion that thujone decomposes thermally to give, along with carvotanacetone, two C_9 -ketones by the *loss of methylene*.¹ We contemplated confirming the intermediacy of methylene by trapping experiments, but



deemed it prudent first to complete the less arduous task of authenticating the structures of the C_9 -ketones.

Eastman and Winn¹ isolated these two ketones in small amount by gas chromatography along with the major product, carvotanacetone. Assignment of structure was based on four types of information. The retention times relative to thujone (11 min.) of fraction A (XII of E and W) and fraction B (XIII of E and W) were 11 and 14 minutes, respectively, and were considered consistent with C_9 -ketones but not C_{10} . The elementary analyses were more consistent in carbon content with C_9 -ketones (although the hydrogen content pointed to C_{10}) [Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found for fraction A: C, 77.88, 77.55; H, 10.48, 10.45. Found for fraction B: C, 78.13, 77.93; H, 10.66, 10.56]. The infrared [film: 5.90 μ for fraction A; 5.88 and 6.09 μ for fraction B] and ultraviolet [λ_{max} 229 $m\mu$ (ϵ 7200) for fraction A and 230 $m\mu$ (ϵ 7100) for fraction B] absorption spectra taken together pointed to a monosubstituted cyclopentenone.^{2,3}

In repeating the pyrolysis of thujone, we obtained two compounds, I and II, having the same relative retention times as reported for fractions A and B and having infrared absorption in carbon tetrachloride at 1700 cm^{-1} (5.88 μ) and 1707 cm^{-1} (5.86 μ), respectively. The ultraviolet absorption spectra showed maxima (I, 228 $m\mu$; II, 230 $m\mu$) at essentially the same wave lengths reported for fractions A and B although the extinction coefficients, calculated assuming molecular weights of either 138 or 152, were higher [I, ϵ_{152} 9,700 (ϵ_{138} 8,830); II, ϵ_{152} 11,200 (ϵ_{138} 10,200)]. Initially, elementary analyses were not reproducible, but became satisfactorily so when special precautions were exercised [Found for I: C, 78.61; H, 10.70. Found for II: C, 78.85, 78.86; H, 10.75, 10.85]. Within the limitation of the small number of physical properties with which comparison can be made, there is little reason to doubt the identity of our compounds I and II with the compounds XII (fraction A) and XIII (fraction B) of Eastman and Winn.

Molecular weights were determined by mass spectrometry. Both substances I and II gave their highest mass peak at 152 m/e , showed almost nothing at 138, and had their most intense peaks at 110 [I: 152 (2.5), 138 (0.5), 137 (4.5), 110 (100), 109 (44); II: 152 (22), 138 (1.3), 137 (1.3), 110 (100), 109 (76)].⁴ The dihydro derivatives of I and II (to be mentioned later) show parent peaks at 154 m/e and essentially no peaks at 139 or 140 m/e . Accordingly, the substances are not C_9 -ketones, but C_{10} . The idea that methylene is extruded from

(2) A. E. Gillam and T. F. West, *J. Chem. Soc.*, 811 (1941); 486 (1942).

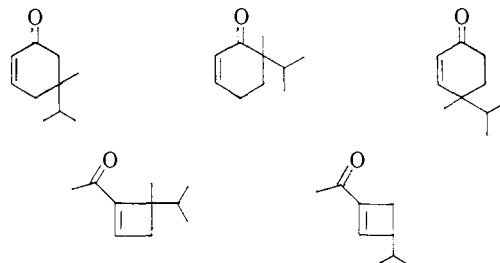
(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., J. Wiley and Sons, Inc., New York, N. Y., 1958, pp. 148-149.

(4) We wish to thank Dr. R. A. Brown, Esso Research and Engineering Co., for determining these molecular weights.

thujone during pyrolysis deserves no further consideration.

As an unrelated problem, there remains the question of the correct structures of I and II, now that the formulations of Eastman and Winn have become untenable. Oxidation of I and II by ozonolysis and subsequent treatment with hydrogen peroxide in acetic acid affords α -methyl- α -isopropylsuccinic acid.^{5,6} The identity of this acid is confirmed by comparison with an authentic sample synthesized from methyl isopropyl ketone and ethyl cyanoacetate by a procedure adapted from one described by Vogel.⁷ Six of the ten carbon atoms are thus completely described. The presence of three of the remaining four carbon atoms in an α,β -unsaturated ketone grouping seems assured from the infrared spectrum, the ultraviolet spectrum, the absence of aldehyde absorption in the range from -1 to $+1$ τ of the n.m.r. spectrum and the formation of dihydroketones on catalytic hydrogenation. These structural conditions can be satisfied by formulation as a cyclohexenone, a cyclopentenone or an acetylcyclobutene grouping.

The cyclohexenone formulations are incompatible with several observations: the ozonolysis to a succinic acid; the presence of a single vinyl hydrogen



[I, 2.93 τ ; II, 3.02 τ] and a methyl group at a double bond or carbonyl group⁸ [a singlet of relative area 3 at 8.28 τ in I and 8.29 τ in II]; the observed maxima in the ultraviolet at 228 $m\mu$ (I) and 230 $m\mu$ (II) [expected 225 $m\mu$ ⁹]; the infrared absorption of 1700 cm^{-1} (I) and 1707 cm^{-1} (II) [expected for cyclohexenones: 1674-1684 cm^{-1} (ref. 3, pp. 147-148)]; and the presence of bands at 1735 and 1742 cm^{-1} in the infrared spectra of dihydro-I and II, respectively [expected 1706-1720 cm^{-1} (ref. 3, p. 147)].

The scarcity of suitable model compounds makes prediction of the ultraviolet and carbonyl infrared spectra of the acetylcyclobutene structures uncertain. The infrared absorption bands at 1735 and 1742 cm^{-1} of the dihydro derivatives seem significantly higher than one would expect of acetylcyclobutane derivatives [aliphatic carbonyl falls between 1705-1725 cm^{-1} (ref. 3, p. 132); alkyl cyclopropyl ketones fall between 1686-1704 cm^{-1} (ref. 3, p. 138); while Criegee and Louis report¹⁰

(5) J. Porath, *Arkiv Kemi*, 1, 385 (1949).

(6) R. H. Eastman and A. Oken, *J. Am. Chem. Soc.*, 75, 1029 (1953).

(7) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green, Ltd., London, 1954, p. 459.

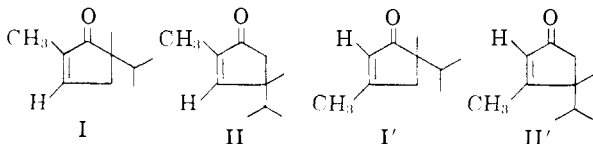
(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

(9) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Arnold, Ltd., London, 1954, pp. 94, 95.

(10) R. Criegee and G. Louis, *Ber.*, 90, 417 (1957).

absorption at 1709 cm.^{-1} for the carbonyl groups in 2,3-diacetyl-2,3,5,6-tetramethylbicyclo[2.2.0]hex-5-ene and 1690 cm.^{-1} (shoulder 1710 cm.^{-1}) for *cis,trans,cis*-1,2,3,4-tetraacetyl cyclobutane.¹¹ One will return to the bearing of the results of deuterium exchange on the plausibility of the cyclobutene structures.

Two pairs of structures are derived from the α,β -unsaturated cyclopentenone system: an α -methyl- β -hydrogen pair, I and II, and a β -methyl- α -hydrogen pair, I' and II'. Strong spectroscopic



support for the former pair, I and II, may be derived from the chemical shift of the vinyl hydrogen in the n.m.r. spectrum. This hydrogen atom appears at $2.93\ \tau$ in I and $3.02\ \tau$ in II. In a considerable number of compounds, hydrogen in the α -position of α,β -unsaturated carbonyl compounds appears in the range, 3.80 – $4.46\ \tau$ [these include crotonaldehyde ($3.95\ \tau$) and mesityl oxide ($4.03\ \tau$),¹² several 3-keto- Δ^4 steroids (4.34 – $4.46\ \tau$),¹³ β,β -dimethylacrolein ($4.15\ \tau$),⁸ 4-hydroxy and 4-methoxypiperitone (4.23 and $4.40\ \tau$),¹⁴ isophorone ($4.18\ \tau$),¹⁵ 1-methoxy-4-keto-bicyclo[3.2.0]hepta-2,6-diene ($4.34\ \tau$)¹⁶ and several other related derivatives (3.80 – $4.34\ \tau$),¹⁷ and 3-methylcyclopentenone ($4.30\ \tau$)¹⁸] while hydrogen in the β -position appears in the range 2.36 – $3.39\ \tau$ [crotonaldehyde ($3.15\ \tau$),¹² a Δ^{16} -21-keto steroid ($3.39\ \tau$),¹³ 1-methoxy-4-ketobicyclo[3.2.0]hepta-2,6-diene ($2.78\ \tau$)¹⁶ and related compounds (2.36 – $2.75\ \tau$),¹⁷ and carvotanacetone ($3.30\ \tau$)]. There is a less striking but still significant difference in the position of the α - and β -methyl group [α -methyl: carvotanacetone ($8.28\ \tau$); β -methyl: crotonaldehyde ($7.98\ \tau$),¹² pent-3-ene-2-one ($7.95\ \tau$),¹² 1-methoxy-2-keto-4-methylbicyclo[3.2.0]hepta-3,6-diene ($7.88\ \tau$),¹⁷ 4-hydroxy and 4-methoxypiperitone (8.07 and $8.08\ \tau$)¹⁴ and 3-methylcyclopentenone ($7.93\ \tau$)¹⁸]. In I and II the vinyl hydrogen is at 2.93 and $3.02\ \tau$ consistent with its being a β -hydrogen, while the vinyl methyl groups in both I and II are at $8.28\ \tau$ consistent with an assignment to the α -position. Structures I' and II' therefore appear quite improbable.

Final assignment of structures to compounds I and II is made on the basis of a difference in behavior on attempted base-catalyzed exchange of deuterium. The ketone II easily exchanges two hydrogen atoms in deuterium oxide and deuterio-

(11) R. Criegee, G. Schröder, G. Maier and H. Fischer, *Ber.*, **93**, 1553 (1960).

(12) G. V. D. Tiers, "Characteristic N.M.R. Shielding Values for Hydrogen in Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

(13) J. N. Shoolery and M. F. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

(14) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3972 (1961).

(15) H. Conroy in "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 287 and ff.

(16) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

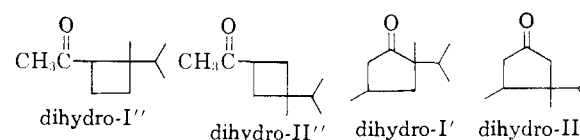
(17) W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, *ibid.*, **83**, 1768 (1961).

(18) G. Karustis, Yale University, private communication.

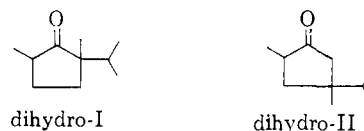
methanol and has then lost the absorption at 7.80 – $7.96\ \tau$ in the n.m.r. without any other observable change. Under the same conditions ketone I does not undergo appreciable exchange, consistent with the generally much slower exchange of γ -hydrogen. Compound I is accordingly assigned structure I and compound II, structure II. Consistent with this assignment is the fact that the much more strongly hindered carbonyl group in I fails to react with 2,4-dinitrophenylhydrazine whereas II easily forms a crystalline derivative.

These structural conclusions are strengthened appreciably by considering the degree to which the dihydro derivatives of I and II undergo base-catalyzed exchange of deuterium. The experiments were carried out by boiling the saturated ketones (each of which is an unresolved mixture of two epimers) in deuteriomethanol and sodium deuterioxide in deuterium oxide, recovering the exchanged ketones by simple distillation to avoid reversal of exchange, checking later on the purity by g.l.p.c., and analyzing for the distribution of deuterated species by mass spectrometry.¹⁹

The weak points in the arguments presented before concerned the possibility that the compounds might have cyclobutene structures, the dihydro derivatives of which would be dihydro-I'' and dihydro-II'', or structures in which the methyl group were β to the ketone function (dihydro-I' and dihydro-II', respectively). It is clear that com-



plete exchange of α -hydrogen in these four molecules would lead to the incorporation of four deuterium atoms each in dihydro-II'' and dihydro-II' and two and four deuterium atoms in dihydro-I' and dihydro-II', respectively. By contrast, di-



hydro-I and dihydro-II would exchange one and three atoms of deuterium, respectively. The results are unequivocally in accord with the latter structures: before exchange dihydro-I shows a parent mass of 154 with a peak of 15.5% of that intensity at 155, corresponding to the theoretical value of about 10% as the contribution from ¹³C isotope.²⁰ After exchange the major peak is at 155 (156 is 15.3% of this peak under the same operating conditions as before). Accordingly, one hydrogen atom has been exchanged. Before exchange dihydro-II likewise shows a parent mass at 154 (155 is 15.4% of this peak, again at incomplete resolution), while, after exchange, which was essentially

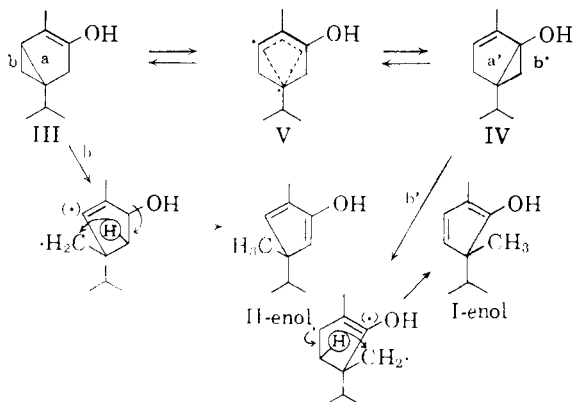
(19) We acknowledge with warmest thanks the collaboration of Drs. J. E. Callen and W. L. Courchene, Procter and Gamble Co., Miami Valley Laboratories, Cincinnati 39, Ohio, in evaluating the extent of deuterium exchange.

(20) The value is higher than expected because separation between the 154 and 155 peak was not complete under the operating conditions.

complete, the parent mass is 157 (158 is 15.3% of this mass) corresponding to the exchange of three hydrogen atoms.

It is relevant to the problem of cracking patterns of ketones that the most intense peak in dihydro-I is at m/e 112 corresponding to loss of propylene (mol. wt. 42) and consistently the most intense peak in monodeuteriodihydro-I is at 113, corresponding again to loss of propylene. Rearrangement of a hydrogen atom to the C₇-ketone accompanies loss of the three-carbon fragment. Dihydro-II, on the other hand, in the main loses the isopropyl radical (mol. wt. 43) giving a strong peak at 111 (and a somewhat weaker peak at 110 corresponding to loss of propane). In trideuteriodihydro-II, the strongest peak, in this range, is at 114 corresponding to loss of C₃H₇. However, the next strongest peak is not at 113 corresponding to loss of C₃H₈ but at 112 corresponding to loss of C₃H₇D. To a readily discernible extent the hydrogen atom needed to produce propane in the fragmentation originates at the α -position.

The mechanism of the formation of I and II can only be surmised at this time. The hypothesis of Eastman and Winn that the enol tautomer of thujone (III) is the precursor of carvotanacetone also serves to accommodate the formation of II. From this enol homolysis of either bond a or b gives an allyl radical and may be followed by transfer of an α -hydrogen atom in the first instance and β in the second leading to carvotanacetone and the enol of II, respectively. Analogy for the shift of α -



hydrogen is to be found in the thermal isomerization of cyclopropane to propylene²¹ while analogy for the shift of a γ -hydrogen exists in the photolytic transformation of cyclohexanone to pentene-1.²²

As explanation of the more remarkable formation of I, one may hypothesize the rearrangement of thujone enol III to the allyl alcohol IV. This change resembles the isomerization of vinylcyclopropane to cyclopentene.²³ Homolysis of the appropriate bond (b') of the three-membered ring in IV followed by a migration of a β -hydrogen atom

would lead, quite analogously, to the enol of I. Although an arrangement V formulated by Eastman and Winn (XVI \rightarrow XVII) as an intermediate in the formation of carvotanacetone may quite reasonably be involved in the rearrangement of III to IV either as an intermediate or transition state, it is impossible to decide at the present time whether this same arrangement is the direct precursor of I- and II-enols. In any event the sequence by which thujone is transformed to I is of sufficient interest to warrant closer scrutiny.

Experimental²⁴

Thujone.—Two samples were used in the repetitions of the work of Eastman and Winn. One had been obtained as the by-product of isolating fenchone from oil of *Thuja occidentalis* by distillation through a 12-ft., helix-packed column of about 100 theoretical plates. This sample (T₁) had b.p. 94–94.5° at 28 mm., n_D^{20} 1.4490, and could be shown by g.l.p.c. to contain about 1% of fenchone. We obtained a purer sample (T₂) by converting T₁ to its semicarbazone, recrystallizing to constant m.p. 184–186° and $[\alpha]_D^{20} + 42.0^\circ$ (reported²⁵ m.p. 186–188°, $[\alpha]_D^{20} + 42.0^\circ$), and regenerating by hydrolysis with 1 N aqueous sulfuric acid. This sample (T₂) was no longer contaminated by fenchone and had $[\alpha]_D^{20} - 9.13^\circ$.

Thermal Isomerization of Thujone.—Following the procedure of Eastman and Winn,¹ thujone (0.5 ml., T₂) was sealed under nitrogen in an ampoule and heated in boiling diphenyl ether at 265°. At suitable intervals, samples were removed and analyzed by g.l.p.c. For this analysis, a 5-ft. column of Carbowax 20M on firebrick was used at 5–20 lb. helium and 150–180°. The most volatile product formed was isolated by g.l.p.c. and identified by its infrared absorption spectrum as *p*-cymene (authentic sample from Matheson, Coleman and Bell). The retention times of the other products are given relative to that of *p*-cymene as 1: thujone and I (compound XII, fraction A of E. and W.), 2.06; II (compound XIII, fraction B of E. and W.), 2.87; an unknown substance of b.p. 215°, 3.20; and carvotanacetone, 5.08.

In a larger experiment, 60 g. of thujone (T₁) was heated 15 days under nitrogen in a sealed tube at 270 \pm 5°. On being opened, this sample was at atmospheric pressure and did not evolve gas. The product was distilled in a 100-plate spinning-band column at 755 mm. The forerun, b.p. up to 186°, was mainly *p*-cymene; fenchone appeared at 191–193°, followed by I, b.p. 196–196.4°, II, b.p. 211–211.5°, and the unknown material, b.p. 215–216°. The residue was mainly carvotanacetone. Purified by g.l.p.c., this material had $\lambda_{\text{max}}^{\text{OH}}$ 235 m μ (ϵ 10,100) [reported⁹ (p. 102), $\lambda_{\text{max}}^{\text{OH}}$ 233 (ϵ 9150)]; absorption in the infrared at 1665 cm.⁻¹ [reported¹ 1670 cm.⁻¹]; an n.m.r. spectrum consisting of a doublet at 9.1–9.0 τ (relative area 6), a singlet at 8.3 τ (3), a multiplet at 7.9 τ (2), a multiplet at 3.3 τ (1) and a further multiplet at 9.1–9.0 τ (2) under the doublet; and gave a semicarbazone, m.p. 177–178° [reported²⁶ m.p. 177–178°].

It may be mentioned that carvotanacetone is recovered unchanged after being heated 108 hr. at 205°.

2,5-Dimethyl-5-isopropylcyclopent-2-enone (I).—For further examination compound I was purified by g.l.p.c. and shown to be free of thujone (from which it is otherwise inseparable on the Carbowax column) by examination of the infrared spectrum (bands at 1730, 3054, 3020 cm.⁻¹ characteristic of thujone, and not of I, were completely absent)²⁷ and by attempted semicarbazone formation.

The n.m.r. spectrum showed these absorptions: a doublet ($J = 6$ c.p.s.) at 9.42 and 9.34 τ (relative area 3); a second

(24) Microanalyses are by Schwarzkopf Microanalytical Laboratories, Woodside 77, Long Island, N. Y. Ultraviolet spectra were measured on the Cary recording spectrophotometer model 11, infrared spectra were obtained on the Perkin-Elmer infrared spectrophotometer model 221, and the n.m.r. spectra on the Varian V-4300 N.M.R. spectrometer operated at 60 mc. M.p.'s are corrected.

(25) A. G. Short and J. Reed, *J. Chem. Soc.*, 2016 (1938).

(26) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p. 241.

(27) Compound I, which fails itself to form a semicarbazone (see below), is also obtained from the T₂ sample of thujone and consequently is not an impurity in the starting material.

(21) B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(22) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 1546, 2601 (1959).

(23) Mentioned in a recent review by E. Vogel, *Angew. Chem.*, **72**, 4 (1960), published in detail by C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4897 (1960), and encountered in several examples, of which the transformation of 1,2-dicyclopropylethylene to 3-cyclopropylcyclopentene [W. von E. Doering and W. R. Roth, unpublished] is one.

doublet ($J = 6$ c.p.s.) at 9.20 and 9.09 τ (3), a multiplet at 9.4–9.0 τ (1), a singlet at 9.00 τ (3), four lines (two doublets) ($J < 3$ c.p.s.) at 8.3 τ (3), a multiplet at 8.0–7.7 τ (2) and a doublet ($J = 3$ c.p.s.) at 2.93 τ (1).

Deuterium exchange was attempted both at room temperature and at 90° by treating 12 mg. of I in 200 mg. of deuteriomethanol with 10 mg. of sodium methoxide for 12 hr. In neither case was any change observed in the n.m.r., particularly in the multiplet at 8.0–7.7 τ .

It was not possible to prepare either a 2,4-dinitrophenylhydrazone or a semicarbazone under the usual conditions.

2,4-Dimethyl-4-isopropylcyclopent-2-enone (II).—This substance could easily be purified by chromatography and had this n.m.r. spectrum: a pair of doublets ($J = 6$ c.p.s.) at 9.15, 9.10, 9.05 and 9.00 τ (relative area 6); a multiplet at 9.2–9.0 τ (1); two singlets at 8.85 τ (3) and 8.28 τ (3); a doublet ($J = 9$ c.p.s.) at 7.96 and 7.81 τ (2) and a singlet at 3.02 τ (1).

A 2,4-dinitrophenylhydrazone, m.p. 120–121° from ethanol, could be obtained easily by the usual procedure.

When 12 mg. of II was treated in 200 μ l. of deuteriomethanol with 10 mg. of sodium methoxide at room temperature for 20 hr., recovered material no longer showed the doublet at 7.9 τ in the n.m.r., although the rest of the spectrum was unchanged.

Ozonolysis of I and II to α -Methyl- α -isopropylsuccinic Acid.—A solution of 152 mg. of I in methyl acetate was ozonized at -70° . The ozonide was treated at room temperature with a 1:1 mixture of acetic acid and 30% hydrogen peroxide. Concentration of the reaction mixture *in vacuo* afforded crystalline material (149 mg., 86%) from which colorless crystals of m.p. 139.5–142° [reported⁵ m.p. 148–149° for *dl*; m.p. 126–127° for *d*-acid] were obtained by two recrystallizations from acetonitrile.

Similarly, 100 mg. of II gave 65 mg. (57%) of the same acid, m.p. 137–141°.

Following a procedure of Vogel,⁷ an authentic sample of α -methyl- α -isopropylsuccinic acid, m.p. 144.5–146°, was prepared. This material had an infrared spectrum (potassium bromide pellet) identical with that of the two samples above.

The anhydride, prepared by evaporative distillation of a mixture of the acid and phosphorus pentoxide at 100° and 10 mm., was an uncrystallizable oil.

Exchange of Deuterium in Dihydro-I and II.—On catalytic hydrogenation of 152 mg. of I in tetrahydrofuran over Adams platinum oxide, 82% of one equivalent of hydrogen was absorbed. Attempted purification by g.l.p.c. gave mainly one substance having its strongest absorption in the infrared at 1730 cm^{-1} . The n.m.r. spectrum showed about seven lines in the 9.3–8.8 τ region (13) and a complicated multiplet between 8.8–7.7 τ (5).

Deuterium exchange was effected by treating 30 mg. of dihydro-I in 1.5 ml. of 1 *N* sodium deuterioxide in deuterium oxide and 1.8 ml. of deuteriomethanol for 9 days at room temperature under nitrogen. The ketone was recovered by diluting with 3 ml. of deuterium oxide, extracting with three 3-ml. portions of dry pentane, blowing off the pentane in a stream of nitrogen and distilling molecularly at 1 μ and room temperature. Although purification by g.l.p.c. was avoided for fear of removing some of the deuterium, analysis showed only a single peak.

The same sequence of experiments was carried out with II. The absorption of 0.92 equivalent of hydrogen gave dihydro-II (absorption at 1742 cm^{-1} and an n.m.r. spectrum with several lines in the region of 9.1–8.85 τ (13), a multiplet in the region 8.85–8.05 τ (2) and two lines between 8.05 and 7.90 τ (3). Deuteration was effected in a manner similar to that outlined above.

The mass spectrometric analysis¹⁰ was carried out with a Bendix time-of-flight mass spectrometer model 12–101 fitted with a heated inlet system of the type developed at the Dow Chemical Co. This system permits observation of the spectrum over a considerable period of time at an essentially constant pressure. The spectra were recorded simultaneously at two levels of sensitivity by a model 906-C Visicorder

TABLE I
RELATIVE INTENSITIES OF PEAKS IN THE MASS SPECTROMETRIC CRACKING PATTERNS

Mass of peak				
	1	2	3	4
158				9
157				59
156		3		
155	4	24	7	
154	28	14	48	
115				10
114		7		62
113	10	65		25
112	88	46	10	33
111	10	6	70	7
110			34	
101				7
100				10
99				4
98	4	11	2	7
97	20	14	11	8
96	29	33	2	
95			10	
87				12
86				100
85	8	13		41
84	68	72	22	8
83	17	14	100	13
82	4	4	33	
81	8	10		
72				7
71	5	6		41
70	17	21	18	46
69	100	100	77	16
68	4	5	10	
67	9	7	14	
58				12
57	4	6	2	32
56	11	16	10	23
55	36	27	74	19
54	7	5	3	6
53	11	9	13	

oscillograph. Mass calibration depended on the presence of peaks from the singly and doubly charged isotopes of mercury.

The results of examining dihydro-I, monodeuteriodihydro-I, dihydro-II and trideuteriodihydro-II are shown in Table I. The intensities have been adjusted relative to the most intense peak as 100. That dihydro-I has only one exchangeable hydrogen appears from examining the spectrum in the region of the parent mass and in the 112–113 region resulting from loss of C_3H_6 .

That dihydro-II has three exchangeable hydrogen atoms appears clearly in the regions of the parent mass, the parent minus C_3H_7 and C_3H_8 and the 83–86 region where C_3H_{11} seems to be the main fragment lost.

Although it seems inappropriate to discuss here the detailed features in the cracking pattern of the two ketones and their deuterated relatives, the data in Table I do allow one to speculate on the course of fragmentation.