Photolysis of 1,3-Cyclohexadiene.—A commercial sample of diene was redistilled before use (b.p. 80°) and this material was homogenous by g.l.c. Photolyses of diene were carried out as described above. With a Pyrex filter, the ratio of diene to 1,3,5-hexatriene after 10 hr. was 270:8.5. This ratio is similar to that observed in irradiation of III under the same conditions. This mixture was photolyzed further after removal of the filter. After an additional 5 hr., the ratio of diene to triene was 25:162; after 6 hr. 40 min., the ratio was 1.0:8.25. The final photomixture was concentrated under reduced pressure, and the residue was separated by g.l.c. on a Dow 710 column at 69°. The materials of retention times 4.5 and 5.9 min. were collected in a liquid nitrogen trap connected to the gas outlet. The colorless liquids had infrared and ultraviolet spectra in excellent agreement with those reported for *cis-* and *trans*-1,3,5-hextriene.[15]

In runs where diene and triene were removed by distillation, substantial amounts of high-boiling material remained. While we have no evidence that this material results from photolysis and not from "dark" reactions of cyclohexadiene and triene, the presence of this material is consistent with reports of the photochemical formation of dimers and other high-boiling compounds.[16,17]

Analysis for Benzene in the Photomixtures.—Benzene is not cleanly separated from 1,3-cyclohexadiene and 1,3,5-hexatriene by g.l.c. on the columns mentioned above, but is separated on a PDEAS column (phenyldiethanolamine succinate). A 2% solution of benzene in ether was prepared to compare with the photolysis mixture. The latter, alone, gave a single peak at 2.84 min. (mixture of diene and triene), while a mixture of equal amounts of the dilute benzene solution and the concentrated photomixture gave two distinct peaks at 4.5 (benzene) and 2.84 min. Thus, to the limit of the validity of this analysis, benzene is not present in the photomixture from photolysis of ketone III. A similar experiment eliminates benzene from the photomixture formed on photolysis of cyclohexadiene.

Acknowledgment.—The authors are grateful to the Army Research Office (Durham) for support of this research through Grant DA-ARO(D)-31-124-G425 (D. I. S. and F.-T. H. L.) and the Petroleum Research Fund, administrated by the American Chemical Society, for grants in support of this work (A. P. and P. G. G.).

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[16] G. O. Schenck, S.-P. Mannsfield, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **19b**, 19 (1964).

[17] R. J. De Kock, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim.*, **79**, 922 (1960).

The Cyclization of Epoxy Olefins. II. The Attempted Formation of a Bornenol System[1]

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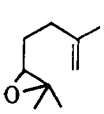
Treatment of 2,3,3-trimethyl-4-vinylcyclopentene, prepared unambiguously from α-campholenaldehyde, with perphthalic acid yields an inseparable mixture of stereoisomeric monoepoxides. Acid-catalyzed rearrangement of the oxide mixture yields only 2,3,3-trimethyl-4-vinylcyclopentanone and 2,2,3-trimethyl-4-vinylcyclopent-3-enol. No bicyclic cyclization product is found. From the relative proportions of the *cis* and *trans* isomers of the cyclopentanone, however, a minimum value for the isomer composition of the starting epoxide may be obtained.

The acid-catalyzed cyclization of epoxy olefin systems as a model for terpenoid biogenesis has been accomplished in a number of cases. Boron fluoride treatment of geraniolene monoepoxide (**1**) resulted in the partial formation of cyclic products,[3] and the use of another Lewis acid, stannic chloride, caused the formation of only the cyclic compounds **2** and **3**.[4] Subsequently, van Tamelen was able to isolate bicyclic products from the reaction of epoxyfarnesyl acetate with boron fluoride and other acid catalysts.[5]



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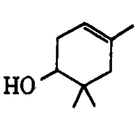

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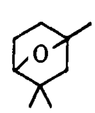
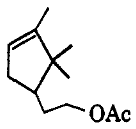


3

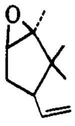
Although the familiar bridged bicyclic system of camphor and related terpenes is probably not derived naturally by an *oxidative* cyclization, it was of interest to explore the possibility of forming this structure from an epoxy olefin. To this end we chose for a starting material the monocyclic diene **4**. This compound has been previously reported[6] as a product from the Hofmann elimination of N,N-dimethyl-α-camphylamine. The yield of **4** was so low, however, that the compound was characterized by a boiling point only. It was necessary, therefore, to prepare the diene unambiguously and in preparative yield. Pyrolysis of the acetate **5** afforded a material of the expected elemental composition in 85% yield which differed in boiling point from the substance previously reported to be **4**. Spectral measurements, however, showed that the expected diene was indeed the product of pyrolysis. In the infrared, bands at 918 and 1005 cm.$^{-1}$ demonstrated the presence of the vinyl grouping, and four vinyl hydrogens in the appropriate pattern were displayed in the n.m.r. spectrum between 4.9 and 5.98 p.p.m. Conversion of the diene to the epoxy olefins **6a** and **b** was effected with monoperphthalic acid. The usual difference in reactivity of mono- and polysubstituted double bonds predicts the formation of principally this epoxidation product.[7] Confirmation was again afforded by spectral evidence.

4



5

6a



6b

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[1] This investigation was supported by the National Institutes of Health, Grant No. GM 11728-01

[2] Taken in part from the Ph.D. Thesis of C. J. C., Wayne State University, Detroit 2, Mich.

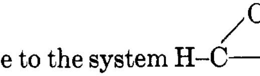
[3] D. J. Goldsmith, *J. Am. Chem. Soc.*, **84**, 3913 (1962).

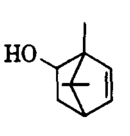
[4] D. J. Goldsmith and T. J. Lajiness, unpublished observation.

[5] E. E. van Tamelen, A. Storni, E. J. Hessler, and M. Schwartz, *J. Am. Chem. Soc.*, **85**, 3295 (1963).

[6] L. Bouveault and G. Blanc, *Compt. rend.*, **136**, 1462 (1903).

[7] D. Swern, *Org. Reactions*, 378 (1953).

The n.m.r. spectrum showed no ring olefinic protons, the presence of the vinyl side chain, and a resonance at 2.99 attributable to the system  $\mathrm{H{-}\overset{O}{\widehat{C{-}C}}{-}}$. Of less certainty, however, was the stereochemistry. Clearly, for purposes of cyclization, the isomer bearing the epoxide oxygen and the vinyl group in a *trans* relationship, **6a**, is the desired one. Only with this isomer might a concerted ring closure to **7** occur, whereas in the *cis* compound, **6b**, the intervention of a carbonium ion, **8**, would be required for the formation of the new carbon–carbon bond. Previous work, however, suggested that the major product from the epoxidation of **4** ought to be the desired *trans* isomer. Henbest has shown,[8] for example, that epoxidation of 4-methylcyclopentene leads to a mixture of epoxides in the ratio of 3:1, *trans* to *cis*. Our material, however, was homogeneous by gas chromatography on a number of columns. In addition, reduction of **6** with lithium aluminum hydride led to an alcohol **9** which also showed a single symmetrical peak under varying chromatographic conditions. On the assumption that the *trans* epoxide was the major if not the sole component of the oxidation product, this material was treated with anhydrous stannic chloride in benzene in an attempt to effect cyclization. Two products isomeric with the starting material were formed from **6**, neither of which corresponded to the desired bornenol **7**. The minor (33%) and more volatile component appeared to be, on the basis of its infrared and n.m.r. spectra, the ketone **10**, and this assignment was verified by the independent synthesis described below. Gas chromatography of the ketone obtained by epoxide rearrangement revealed, however, that it was a mixture of isomers in the ratio of 1.8:1. The rearrangement of epoxides to ketones under the influence of Lewis acids has been shown to be stereospecific.[9] For example, the steroidal epoxide **11** gives only the less stable 5β,6 ketone on treatment with boron fluoride. The ratio of the *trans* to *cis* (**10a**:**10b**) ketones obtained from **6a,b** therefore should indicate at least a minimum value for the isomeric composition of the epoxides. In order to identify the individual ketones they were prepared by an alternative stereoselective route. Hydroboration–oxidation of the olefin **5** led to a mixture of ketones, **12**, which were subject to pyrolytic elimination of the acetate group. Again a mixture of **10a** and **10b** was obtained but in this case the *cis* isomer predominated, in the ratio of 1.5:1. The conclusion that **10b** is the major component of this mixture is based on the known steric sensitivity of hydroboration.[10a] 4-Methylcyclopentene, for example, is converted in 75% yield to *trans*-3-methylcyclopentanol and the oxidation procedure used here has been shown not to effect equilibration of isomeric ketones.[11] In addition, the more stable isomer of the two is the *cis* compound **10b**. Equilibration of the two yielded a mixture containing less than 5% **10a**. The lower energy of the *cis* isomer *vs.* the *trans* is presumably a function of the "envelope" conformation of the five-membered ring. In this arrangement both the methyl and the vinyl groups occupy essentially equatorial positions[12] (**10c**).



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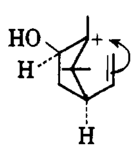

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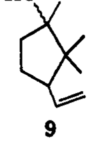

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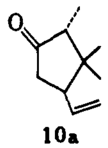
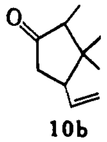
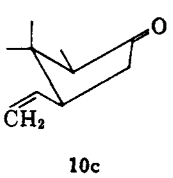


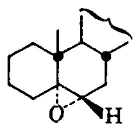
10a



10b



10c



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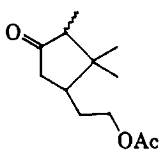
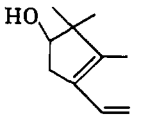


12

These results indicate that the initial epoxide mixture must have contained at least 64% of **6a**. That this is a minimum value is indicated by the structure of the second product obtained from stannic chloride treatment of **6**. This compound, the major product from the rearrangement, contains a hydroxyl group and, from the n.m.r. spectrum, a vinylic methyl and three olefinic hydrogens. This evidence in conjunction with an intense ultraviolet maximum at 243 mμ suggested the rearranged dienol **13**. Confirmation of this structure was provided by the close similarity of the spectrum of the model diene **14**,[13] prepared from β-campholenic acid (**15**). In addition, the higher homolog **16** prepared by Stork[14] displays an ultraviolet maximum at 240 mμ.



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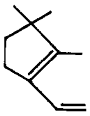

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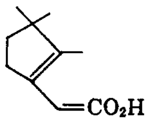

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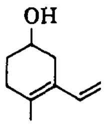

16

Since one of the asymmetric centers of **6** is destroyed in the production of **13**, the structure of this compound gives no direct indication of the isomeric composition of the starting epoxide. It is reasonable to assume, however, that **6a** is converted to **13** faster than the *cis* isomer. Two factors make this conclusion probable. Only the *trans* isomer has the epoxide oxygen, the mi-

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(8) H. B. Henbest, *Proc. Chem. Soc.*, 159 (1963).

(9) H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.*, 4596 (1957).

(10) (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962. A referee has pointed out the possibility that equilibration of the ketone might occur during pyrolysis of the keto acetate. Acid-catalyzed rearrangements, at least of olefinic systems, do not usually occur during pyrolysis [C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960)]. The pyrolysis procedure used here, moreover, is one that allows the preparation of 2-cyclohexenone, a material notably succeptible to pyrolitic transformation, in 91% yield.[10b] These points are, of course, only suggestive of the steric course of the pyrolysis and some epimerization may occur. The ketone ratio observed in the product, however, is not the equilibrium value and the stereochemical assignments should be as shown. We are investigating the problem of epimerization during pyrolysis experimentally. (b) K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

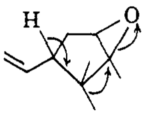
(11) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951, 2952 (1961).

(12) E. L. Eliel, "The Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 248.

(13) The *gem*-dimethyl group of **13** is found as a pair of singlets in the n.m.r. The model diene, **14**, having no asymmetric center, displays only a single resonance line for this group.

(14) G. Stork, S. S. Wagle, and P. C. Mukharji, *J. Am. Chem. Soc.*, **75**, 3197 (1953).

grating methyl group, and the departing proton appropriately arranged for concerted reaction (see **17**), and secondly, the rearrangement of this isomer relieves a considerable steric interaction on the periphery of the five-membered ring. This latter factor, illustrated in **18**, is also presumably one reason why rearrangement rather than cyclization occurs with this system. The rate of cyclization is probably mainly retarded because the transition state, unless it closely resembles product, would have a minimum amount of overlap of the orbitals forming the new bond. The geometry here does not allow the olefin system and the developing p-like orbital of the ring carbon to be coplanar until bond formation has progressed to a large degree. We are studying other systems in which the geometry for cyclization is more favorable.



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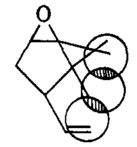

18

Experimental[15]

dl-α-**Campholenic Acid.**—The fusion of sodium *dl*-10-camphorsulfonate with potassium hydroxide according to the method of Bredt, Rochussen, and Heusch[16] provided *dl*-α-campholenic acid in 49% yield, b.p. 80–85° (0.45 mm.), $n^{27.8}\mathrm{D}$ 1.4674 [lit.[17] b.p. 137° (1 mm.), $n^{26}\mathrm{D}$ 1.4682]. Methyl *dl*-α-campholenate, prepared by treatment of the acid with ethereal diazomethane, had b.p. 67–70° (3.0 mm.), $n^{24}\mathrm{D}$ 1.4556 [lit.[17] b.p. 104–109° (17 mm.), $n^{24}\mathrm{D}$ 1.4550]. The ester appeared homogeneous by vapor phase chromatography, employing a silicone gum rubber column on firebrick at 170°.

dl-α-Campholenic acid was also prepared from camphor oxime by the method of Tiemann.[18] The material prepared in this manner contained a significant amount (*ca.* 30%) of the β isomer, estimated by vapor phase chromatographic analysis.

2,3,3-Trimethyl-4-(2-hydroxyethyl)cyclopentene.—A solution of 6.35 g. (0.035 mole) of *dl*-methyl α-campholenate in 50 ml. of anhydrous ether was added to a stirred suspension of 3 g. (0.08 mole) of lithium aluminum hydride in 75 ml. of anhydrous ether over a period of 25 min. The mixture was allowed to stir for an additional 45 min., whereupon excess hydride was destroyed by the addition of a saturated solution of potassium sodium tartrate. The ether was decanted and the colorless precipitate was washed with several portions of fresh ether. The combined ether washings were dried over anhydrous sodium sulfate and concentrated to give 5.7 g. (77%) of a colorless oil. The oil was distilled through a jacketed 0.7 × 35 cm. Podbielniak column and the alcohol was collected over the range 66–67° (0.7 mm.), $n^{26}\mathrm{D}$ 1.4687 [lit.[17] b.p. 64° (0.47 mm.), $n^{28}\mathrm{D}$ 1.4708]. The alcohol was also prepared in 90% yield by lithium aluminum hydride reduction of α-campholenic acid and in 95% yield from the sodium borohydride reduction of α-campholenaldehyde. The latter was prepared in 55% yield from α-pinene oxide (Food Machinery and Chemical Corp.) by the method of Arbuzow,[19] modified by the substitution of zinc chloride for zinc bromide.

2,3,3-Trimethyl-4(2-acetoxyethyl)cyclopentene (**5**).—The acetate **5**, prepared as described by Shriner, Fuson, and Curtin[20] by the reaction of 40 g. (0.26 mole) of the above alcohol, with 200 ml. of acetic anhydride, containing 20 g. of sodium acetate, was obtained in 89% yield as a colorless oil, b.p. 74–76° (1.9 mm.), $n^{26}\mathrm{D}$ 1.4545 [lit.[17] b.p. 65° (0.46 mm.), $n^{28}\mathrm{D}$ 1.4541].

2,3,3-Trimethyl-4-vinylcyclopentene (**4**).—The acetate **5** was pyrolyzed through a recycling apparatus modified from a design of Johnson, *et al.*[10b] The apparatus consisted of a 0.7 × 30 cm. heated Pyrex tube, packed with 0.125-in. helices and equipped with a 3-mm.-o.d. condensate return tube, and a Claisen head to which was attached a jacketed 0.7 × 35 cm. Podbielniak column. In a typical run, 95 g. (0.48 mole) of acetate was pyrolyzed under the following conditions: pyrolysis column temperature, 455 ± 10°; oil-bath temperature, 205–225°; fractionating column temperature, *ca.* 65°; pressure, *ca.* 145 mm. The diene **4**, collected in a 100-ml. flask immersed in a Dry Ice–acetone bath, was taken up in ether, washed with 10% sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, and concentrated. Distillation through a 0.8 × 50 cm. spinning-band column gave 54 g. (83%) of colorless diene: b.p. 149° (lit.[6] b.p. 157–158°); $n^{22}\mathrm{D}$ 1.4546; $\nu_{\max}^{\text{neat}}$ 1639 (w), 1370 (m, doublet), 1010 (m, doublet), 1001 (s), and 810 cm.$^{-1}$ (m, doublet); n.m.r. singlets at 0.77 and 0.95, multiplet at 1.65, broad multiplet at 2.27, and complex multiplets at 4.90–5.98. The material eluted as a single substance from a Tide column at 146°.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.36; H, 11.88.

2,3,3-Trimethyl-4-vinylcyclopentene 1,2-Oxide (**6a,b**).—To a cold, stirred solution of 13.7 g. (0.11 mole) of diene **4** in chloroform was added dropwise 186 ml. (0.1 mole) of a 0.545 *M* etheral solution of monoperphthalic acid. The mixture was allowed to warm to room temperature and stir for 3 hr. It was then filtered, washed with 10% sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, concentrated, and flash distilled at reduced pressure through a short-path distillation apparatus to yield 13 g. of a colorless sweet-smelling oil. Fractionation afforded 10 g. (60%) of epoxide **6a,b**: b.p. 110–113° (100 mm.); $n^{25.5}\mathrm{D}$ 1.4528; $\nu_{\max}^{\text{neat}}$ 1653 (m), 1460 (m, doublet), 1379 (m, doublet), 926 (s), and 851 cm.$^{-1}$ (s); n.m.r. singlets at 0.70, 0.94, and 1.25, complex multiplet centered at 1.80, finely split multiplet at 2.99, and complex multiplets from 4.74 to 5.92. The epoxide eluted as a single substance from Tide, silicone gum rubber, Carbowax 20M, and γ-methyl-γ-nitropimelonitrile columns.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 79.09; H, 10.48.

1,2,2-Trimethyl-3-vinylcyclopentanol (**9**).—To a large excess of lithium aluminum hydride in 25 ml. of anhydrous ether was added with stirring 1.15 g. (0.0076 mole) of epoxide **3** in 5 ml. of anhydrous ether. The mixture was allowed to stir at room temperature for 16 hr. The excess hydride was decomposed with a saturated aqueous solution of potassium sodium tartrate and the resulting mixture was continuously extracted with ether for 12 hr. The ether was washed with water, dried over anhydrous sodium sulfate, and concentrated to leave 900 mg. of a yellow oil. Short-path distillation afforded the alcohol **9** as a colorless oil: b.p. 84–85° (13 mm.); $n^{25}\mathrm{D}$ 1.4768; $\nu_{\max}^{\text{neat}}$ 3413 (s), 1639 (m), 1005 (m), 917 (s), and 875 cm.$^{-1}$ (m); n.m.r. methyl singlets at 0.65, 0.86, and 1.14, complex multiplet centered at *ca.* 1.75, broad multiplet at 2.60, and complex multiplets from 5.17 to 6.33. The alcohol appeared as a single substance on silicone gum rubber, Tide, Carbowax 20M, 30% polyglycol, and γ-methyl-γ-nitropimelonitrile vapor phase chromatographic columns.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.71; H, 11.58.

2,3,3-Trimethyl-4-(2-acetoxyethyl)cyclopentanone.—The procedure employed was essentially that of Brown.[11] To a mixture of 5.0 g. (0.025 mole) of acetate **5**, 0.78 g. (0.0205 mole) of sodium borohydride, and *ca.* 10 mg. of zinc chloride in 28 ml. of dry ether, was added 1.04 ml. (*ca.* 0.0085 mole) of boron fluoride etherate in 5 ml. of dry ether over a 5–10-min. period. The reaction mixture was allowed to stir for 2 hr. at room temperature. The excess sodium borohydride was destroyed by the addition of 4 ml.

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(15) Melting points and boiling points are uncorrected. Microanalyses are by Midwest Microlab, Inc., Indianapolis, Ind. Infrared spectra were obtained with a Perkin-Elmer 137-B spectrophotometer and ultraviolet spectra with a Cary Model 14 spectrophotometer. Gas chromatography measurements were made with an F and M Model 720 instrument or in 7-ft. glass columns. N.m.r. spectra were obtained on a Varian DP-60 spectrometer and chemical shift values are given in parts per million relative to tetramethylsilane (internal standard).

(16) Reported in a footnote in J. Bredt, J. Houben, and P. Levy, *Chem. Ber.*, **35**, 1286 (1902).

(17) R. Sauers, *J. Am. Chem. Soc.*, **81**, 925 (1959).

(18) F. Tiemann, *Chem. Ber.*, **29**, 3006 (1896).

(19) B. Arbuzow, *ibid.*, **B68**, 1430 (1935).

(20) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 212.

of water. To this mixture was added with cooling 32 ml. of an aqueous solution of chromic acid (11.0 g. of sodium dichromate dihydrate and 8.25 ml. of concentrated acid, diluted to 45 ml. with water); the mixture was stirred overnight. The aqueous layer was separated and extracted with ether (10 ml.) three times; the ether layers were combined, washed thoroughly with water, dried over sodium sulfate, and concentrated to yield 5.47 g. of a slightly yellow oil. Distillation provided 1.9 g. of a colorless oil, b.p. 80–85° (1.2 mm.), which, on vapor phase chromatographic analysis, was shown to be *ca.* 90% of one component. Preparative vapor phase chromatography provided an analytically pure sample of the keto acetate: $n^{25}\mathrm{D}$ 1.4588; $\nu_{\max}^{\text{neat}}$ 1742, 1736, 1250, and 1047 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.79; H, 9.41.

2,3,3-Trimethyl-4-vinylcyclopentanone (10a,b).—The keto acetate from above (1.9 g. of 90% purity) was pyrolyzed through the previously described recycling apparatus under the following conditions: pyrolysis column temperature, 500 ± 10°; oil-bath temperature, 70°; pressure, *ca.* 30 mm. The crude distillate was taken up in ether, washed with 10% sodium bicarbonate solution and water, dried, and concentrated to leave 1.2 g. of a pale yellow oil. The oil was fractionated through a jacketed 0.7 × 35 cm. Podbielniak column to give the ketone **10a,b** as a colorless oil: b.p. 85–90° (30 mm.); $n^{25}\mathrm{D}$ 1.4617; $\nu_{\max}^{\text{neat}}$ 1739, 1639, and 922 cm.$^{-1}$. The material eluted as a single substance from a Tide column at 145°. The ketone was assumed to be a mixture of C-2 epimers. On an 8-ft. 10% Carbowax 20M column at 143° the epimers were shown to be present in the ratio of 1:5.1 with the minor isomer eluting first.

Anal. Calcd. for $C_{10}H_{15}O$: C, 78.89; H, 10.60. Found: C, 78.60; H, 10.83.

β-Campholenic Acid (15).—β-Campholenonitrile was prepared by the method of Buchman and Sargent[21] in 55% yield from camphor oxime. The material had b.p. 88–90° (7.6 mm.) and $n^{25}\mathrm{D}$ 1.4675 (lit.[18] b.p. 220–230°, $n^{20}\mathrm{D}$ 1.4705). The distillate nitrile, 24 g. (0.16 mole), was refluxed for 36 hr. in a mixture of 10.2 g. of potassium hydroxide, 25 ml. of water, and 40 ml. of ethanol. The ethanol was removed by distillation, and the mixture was refluxed for an additional 2 hr. After cooling, the aqueous solution was washed with pentane, acidified with concentrated hydrochloric acid, and extracted several times with ether. The combined ether extracts were washed with water, dried, and concentrated to yield 26.0 g. (96%) of a slightly yellow oil which crystallized on trituration with cold pentane. Recrystallization from pentane afforded 22.5 g. (80%) of β-campholenic acid (**15**) as a colorless powder, m.p. 50–51.5° (lit.[18] m.p. 52°), $\nu_{\max}^{\mathrm{CHCl_3}}$ broad absorption from 2950 to 3500 and a sharp peak at 1710 cm.$^{-1}$. The n.m.r. spectrum of methyl β-campholenate, prepared by treatment of the acid with ethereal diazomethane, was void of any vinyl proton absorption.

1-(2-Hydroxyethyl)-2,3,3-trimethylcyclopentene.—The title compound, prepared in 90% yield by reduction of β-campholenic acid with excess lithium aluminum hydride in refluxing ether, was obtained as a colorless oil: b.p. 85–87° (5 mm.); $n^{25}\mathrm{D}$ 1.4707; $\nu_{\max}^{\text{neat}}$ 3300, 2900, 1650 (w), 1460, and 1100 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.71; H, 11.70.

The 3,5-dinitrobenzoate crystallized from light petroleum ether as pale yellow plates, m.p. 75–77°.

Anal. Calcd. for $C_{17}H_{20}N_2O_6$: C, 58.61; H, 5.79. Found: C, 58.77; H, 5.81.

1-(2-Acetoxyethyl)-2,3,3-trimethylcyclopentene.—The title compound was prepared in 82% yield by the procedure[20] described for the acetate **5**. The material was obtained as a colorless oil: b.p. 81–83° (3.0 mm.); $n^{24.8}\mathrm{D}$ 1.4518; $\nu_{\max}^{\text{neat}}$ 2940, 1740, and 1225 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.40; H, 10.15.

1-Vinyl-2,3,3-trimethylcyclopentene (14).—The pyrolysis of 5.95 g. (0.03 mole) of 1-(2-acetoxyethyl)-2,3,3-trimethylcyclopentene was carried out employing the previously described recycling apparatus under the following conditions: pyrolysis column temperature, 450–475°; oil-bath temperature, 160°; fractionating column temperature, 85°; pressure, 122 mm. The crude distillate, after washing with 10% sodium bicarbonate, weighed 4.6 g. Distillation at atmospheric pressure was accompanied by some decomposition and there was obtained 2.02 g. of material, b.p. 90–100°. The analytical sample was obtained by preparative vapor phase chromatography from a Tide column at 115°. The retention time was 12.5 min. The diene was obtained as a colorless oil: $n^{23}\mathrm{D}$ 1.4837; $\nu_{\max}^{\text{neat}}$ 2910, 1795 (weak, overtone), 990, and 900 cm.$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 243 mμ (ε 21,700); n.m.r. singlet at 0.99, multiplet at 1.66, broad triplet at 2.37, triplet at 4.88, quartet at 5.11, and broad multiplet centered at 6.65.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.00; H, 11.62.

Reaction of Epoxide 3 with Stannic Chloride.—The epoxide **6a,b**, 10.0 g. (0.065 mole) in 250 ml. of dry benzene, was stirred at room temperature with 0.25 ml. (0.00214 mole) of stannic chloride for 10 hr. The reaction mixture was poured over ice and filtered with suction through Celite. The benzene layer was separated, washed with water, dried, and concentrated to leave 10.0 g. of a yellow oil. Vapor phase chromatographic analysis of the crude oil on a Tide column at 145° indicated, in the order of increasing retention time, the following components: epoxide, 9% at 4.9 min.; a ketone, 29% at 8.5 min.; an unknown material, 4% at 9.6 min.; and an alcohol, 58% at 16.6 min. (the above yields are percentages of the volatile products). The pure components were separated by a rapid preliminary fractional distillation; the fractions with b.p. 40–45° (0.8–2 mm.) consisted mainly of the ketone, while the fractions with b.p. 42–50° (0.08 mm.) were mainly the alcohol. Pure samples were obtained by preparative vapor phase chromatography on a Tide column. The pure ketone had $n^{25}\mathrm{D}$ 1.4618; $\nu_{\max}^{\text{neat}}$ 2940, 1739, and 920 cm.$^{-1}$. The ketone was homogeneous on vapor phase chromatography on a Tide column (identical in retention time with the synthetic material described above). It was, however, separated on a Carbowax 20M column into two components, present in the ratio of 1.8:1, with the major component eluting first. The two components were also identical with those obtained by the pyrolysis of the keto acetate described above.

Anal. Calcd. for $C_{10}H_{15}O$: C, 78.89; H, 10.60. Found: C, 78.65; H, 10.92.

The pure alcohol, 2,3,3-trimethyl-4-vinylcyclopentanol (**13**), had $n^{25}\mathrm{D}$ 1.5107; $\nu_{\max}^{\text{neat}}$ 3300, 2910, 1800 (weak, overtone), 1650, 1600, 1065, 995, and 900 cm.$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 243 mμ (ε 21,230); n.m.r. pair of singlets at 1.06, multiplet at 1.69, singlet at 2.04, broad absorption centered at 2.65, triplet at 3.94, quartet at 4.93, multiplet at 5.13, and a broad multiplet centered at 6.64.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.87; H, 10.48.

Equilibration of the Ketone Mixture.—The ketone **10a,b** prepared by rearrangement of the epoxide **6a,b** was reanalyzed after standing 5 months. The original *cis* to *trans* ratio of 1:1.8 had changed to 1:1. To a solution of 20 mg. of this mixture in 5 ml. of absolute methanol was added 5 mg. of sodium methoxide; the flask was stoppered and allowed to stand at room temperature for 10 days. The mixture was diluted with water, and 1 drop of 10% acetic acid was added. The bulk of the methanol was removed (water aspirator) and the mixture was extracted with ether. The ether extracts were washed with 10% aqueous sodium bicarbonate solution and water, dried over sodium sulfate, and concentrated to leave about 10 mg. of a pale yellow oil. The crude oil was analyzed directly by vapor phase chromatography on Carbowax 20M. The ketone mixture contained only a small amount (*ca.* 3–5%) of the *trans* isomer.

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[21] E. R. Buchman and H. Sargent, *J. Org. Chem.*, **7**, 140 (1942).