Oxetanes. XI. The Cyclization of 3-Hydroxymethylcarvomenthol[1,2]

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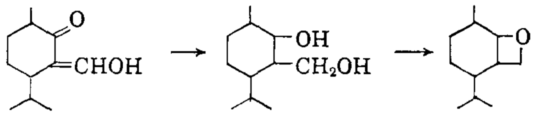
The remarkable formation of the bicyclic oxetane, 2-methyl-5-isopropyl-7-oxabicyclo[4.2.0]octane, by hydrogenation of 3-hydroxymethylenecarbomenthone, reported by Rupe and Schäfer,[3] could not be repeated; instead, a good yield of 3-hydroxymethylcarvomenthol was obtained. Attempted acid-catalyzed cyclization of this diol gave 3-methyl-α-terpinene. The bicyclic oxetane was prepared by the reaction of 3-tosyloxymethylcarvomenthol with potassium *t*-butoxide in *t*-butyl alcohol, and was characterized by infrared and NMR spectra and by formation of a diacetate stereoisomeric with that from the diol.

An unusually facile closure of the oxetane (trimethylene oxide) ring was reported by Rupe and collaborators, a number of years ago.[3,4] Ordinarily, closure of the oxetane ring is considerably more difficult than that of three, five and six-membered cyclic ethers,[5] but these workers reported two cases of apparently spontaneous cyclization of 1,3-diols.

In the first of these,[3] hydrogenation of 3-hydroxymethylcarvomenthone (I), over a nickel catalyst was said to give directly the bicyclic oxetane, 2-methyl-5-isopropyl-7-oxabicyclo[4.2.0]octane (III), accompanied by 3-hydroxymethylcarvomenthone and 3-methylenecarvomenthone, but no 3-hydroxymethylcarvomenthol (II). It was believed that the latter had actually formed but had undergone a very easy dehydration to the oxethane, under the influence of the catalyst or on distillation. Since there does not appear to be any structural feature that would facilitate ring closure in this case, such as has been observed in the case of 2β-chloromethyl-3β-tropanol,[6] such an occurrence would be of great interest. Indeed, one might expect the fused ring structure actually to increase the difficulty of oxetane formation, due to increased strain.



I II III

Application of the same procedure to 2-hydroxymethylenecyclohexanone gave only the diol, 2-hydroxymethylcyclohexanol, but use of a "silica gel" catalyst resulted in a 20% yield of a compound designated as 7-oxabicyclo[4.2.0]octane.[3] This was also reported formed, in 6% yield, by warming the diol with dilute sulfuric acid, a reaction which Rosowsky and Tarbell[7] have recently reported that they are unable to repeat.

Unfortunately, the oxetane structures for these products cannot be regarded as proven. They were supported only by elemental analyses and observation of ferrocyanic acid adducts.[8] In addition, the product considered to be III was sufficiently unreactive towards sodium metal, so that it could be distilled from it, and it was obtained after a separation of ketonic material by semicarbazone formation.

The recent, well substantiated synthesis of 7-oxabicyclo[4.2.0]octane by independent groups[7,9,10] with boiling point several degrees lower than that reported by Rupe and Klemm[4] further weakens the case for the latter's structure. Unfortunately, they did not report other physical properties which could be compared. It seems possible that their compound may have been the isomeric 2-methylcyclohexanone, which has a boiling point similar to that reported by Rupe and Klemm, and which has been obtained by palladium-catalyzed hydrogenation of 2-hydroxymethylenecyclohexanone.[11,12] Indeed Rupe and his collaborators had obtained α-methyl ketones from hydrogenation of certain other α-hydroxymethylene ketones[13] and in the two cases where oxetanes were reported, α-methyl ketones were not. Also, 1,3-diols may be converted to carbonyl compounds on treatment with acid.[14]

Rupe's first case, the catalytic hydrogenation of 3-hydroxymethylenecarvomenthone to the bicyclic oxetane (III),[3] has been reinvestigated in the pres-

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[1] Preceding paper in the series: S. Searles, E. F. Lutz, and M. Tamres, *J. Am. Chem. Soc.*, **82**, 2932 (1960).

[2] Abstracted from the Ph.D. thesis of H. E. M., Kansas State University, 1961. This work was supported in part by National Science Foundation Grant G3502.

[3] H. Rupe and K. Schäfer, *Helv. Chim. Acta*, **11**, 471 (1928).

[4] H. Rupe and O. Klemm, *ibid.*, **21**, 1538 (1939).

[5] *E.g.*, G. Forsberg, *Acta Chem. Scand.*, **8**, 135 (1954); E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960).

[6] (a) Ö. Kovács, G. Fodor, and I. Weisz, *Helv. Chim. Acta*, **37**, 892 (1954). (b) Ö. Kovàcs, I. Weisz, P. Zoller, and G. Fodor, *ibid.*, **39**, 99 (1956).

[7] A. Rosowsky and D. S. Tarbell, *J. Org. Chem.*, **26**, 2255 (1961).

[8] A nonspecific test, given by most oxygenated and nitrogenous organic compounds, as well as some olefins, according to F. Holzl and J. Krakora, *Monatsh.*, **64**, 97 (1934), P. DuPrat, *Bull. inst. pin.*, **17**, 36 (1933) [*Chem. Abstr.*, **27**, 2675 (1933)], K. Stephen and T. Hammerich, *J. prakt. Chem.*, **129**, 285 (1931) and others.

[9] H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, 3575 (1960).

[10] V. J. Traynelis and J. G. Dadura, *J. Org. Chem.*, **26**, 1813 (1961), who reported vapor phase chromatographic retention time rather than boiling point.

[11] W. Herz and W. Bloch, *Z. physik. Chem.*, **110**, 24 (1924).

[12] A. Koetz and E. Schaeffer, *J. prakt. Chem.*, **88**, 604 (1913).

[13] H. Rupe and H. Müller, *Helv. Chim. Acta*, **4**, 853 (1921).

[14] A. Fisher and B. Winter, *Monatsh.*, **21**, 301 (1900); T. Hackhofer, *ibid.*, **22**, 97 (1901).

ent work. Since the nature of Rupe's catalyst was not specified in either this paper or others, we have employed Raney nickel in the present work. The effects of varying temperature, pressure, and time were found to be minor.

The main product from the hydrogenation was 3-hydroxymethylcarvomenthol, the diol expected but not isolated previously.[3] Obtained in 55–60% yields, it was characterized by its elemental analysis, infrared spectrum, formation of a diacetate and mono-*p*-toluenesulfonate, and subsequent reactions described below.

Examination of the by-products gave no evidence for the presence of the bicyclic oxetane (III) in any fraction, nor was there any fraction boiling as low as had been reported for III. The principal by-products were carvomenthone and carvomenthol, which co-distilled as a low-boiling fraction and amounted to 15–27% yield. Their presence can be explained as due to retrograde aldol condensation of 3-hydroxymethylcarvomenthone, a likely intermediate in the hydrogenation to the diol (Chart I). This cleavage, which was probably catalyzed by traces of alkali in the Raney nickel, would give formaldehyde and carvomenthone, which partly hydrogenated to carvomenthol.

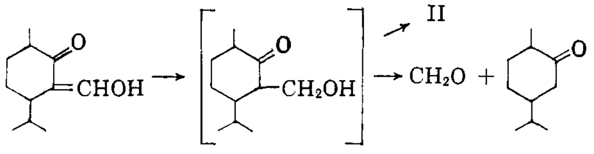

Chart I. Reactions with Raney Nickel Catalyst

Contrary to Rupe and Schäfer's supposition,[3] 3-hydroxymethylcarvomenthol was found to be unaffected by heat during distillation, or by heating with fresh catalyst, or by treating with dilute sulfuric acid, followed by neutralization before distillation. Distillation of the acidulous mixture without neutralization did, however, result in observable splitting out of water. The product was 3-methyl-α-terpinene (IV), isolated in 67% yield and identified by comparison of physical constants with those previously reported, as well as its infrared and NMR spectra. There was no evidence for the formation of any oxetane in this reaction.

In order to be able to recognize better any 2-methyl-5-isopropyl-7-oxabicyclo [4.2.0]octane formed in this work, it was prepared by an independent method. The 3-hydroxymethylcarvomenthol, obtained from the hydrogenation, was converted to its mono-*p*-toluenesulfonate ester (V), and this was treated with potassium *t*-butoxide in *t*-butyl alcohol by a procedure similar to that used by Clayton and Henbest[15] in another oxetane synthesis. This gave the desired bicyclic oxetane (III) in 30% yield, along with a 42% yield of 3-methyl-α-terpinene. The former had a boiling point about 10° lower than reported by Rupe and Schäfer for their compound,[3] and the optical rotation was considerably lower, although in the same direction.

The structure of the oxetane was established as the expected 2-methyl-5-isopropyl-7-oxabicyclo-[4.2.0]octane by its infrared and NMR spectra, as well as the elemental analysis. In the infrared, it showed strong absorption bands at 10.0 and 10.35 μ, characteristic of the cyclohexane and oxetane rings.[16,17] The NMR spectrum showed a series of seven bands at 5.12–6.23 τ, which are in the region for α-protons in an oxetane ring.[18] This spectral data resembles closely that reported very recently for 7-oxabicyclo[4.2.0]octane.[8,9]

Furthermore, treatment of the bicyclic oxetane with acetic anhydride in the presence of pyridine hydrochloride gave an excellent yield of a diacetate (VI) which was identical in all respects, including infrared spectrum but excluding optical rotation, to the diacetate (VII) prepared directly from 3-hydroxymethylcarvomenthol. The two diacetates should indeed be stereoisomers, since this method of opening the oxetane ring has been shown in a similar case[6b] to proceed with inversion of the more substituted α-carbon atom.

It seemed of interest to attempt the synthesis of the oxetane (III) from the diol (II) by the relatively simple, new method of preparing oxetanes from 1,3-diols *via* the carbonate esters of the latter.[19,20] The reaction of 3-hydroxymethylcarvomenthol, with ethyl carbonate in the presence of a catalytic amount of sodium ethoxide, however, did not give the expected carbonate ester or the oxetane (III). The products were an unsaturated carbonate ester and an allylic alcohol, each in 35–40% yield.

The allylic alcohol was shown to be 3-methylene-carvomenthol (IX) by analysis and by identity of infrared spectra and other physical properties with a sample prepared independently by the lithium aluminum hydride reduction of 3-hydroxymethylene-carvomenthone,[21] and is probably derived from the cyclic carbonate ester (VIII) by a process of β-elimination (Chart II). Carbonate esters possessing β-hydrogen atoms are very prone to undergo such β-elimination.[20] The unsaturated carbonate ester gave analytical figures for $C_{14}H_{24}O_3$ and an infrared spectrum characteristic of a trisubstituted

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(15) R. B. Clayton and H. B. Henbest, *J. Chem. Soc.*, 1982 (1937).

(16) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

(17) The oxetane band is normally at 10.2 μ [G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953)], but ring distortion is known to cause bathochromic shifts to longer wave lengths (ref. 1). 7-Oxabicyclo[4.2.0]octane is reported to have this band at 10.4 μ (ref. 7 and 9).

(18) The α-protons of oxetane appear at 5.4τ (equivalent of -0.06δ, reported by H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954), and Rosowsky and Tarbell (ref. 9) report quartets centering at 5.1, 5.4, and 6.1 τ for 7-oxabicyclo-[4.2.0]octane.

(19) D. B. Pattison, *J. Am. Chem. Soc.*, **79**, 3455 (1957).

(20) S. Searles, D. G. Hummel, S. Nukina, and P. E. Throckmorton, *ibid.*, **82**, 2928 (1960).

(21) This reaction is analogous to the reduction of 2-hydroxymethylenecyclohexanone reported by A. J. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

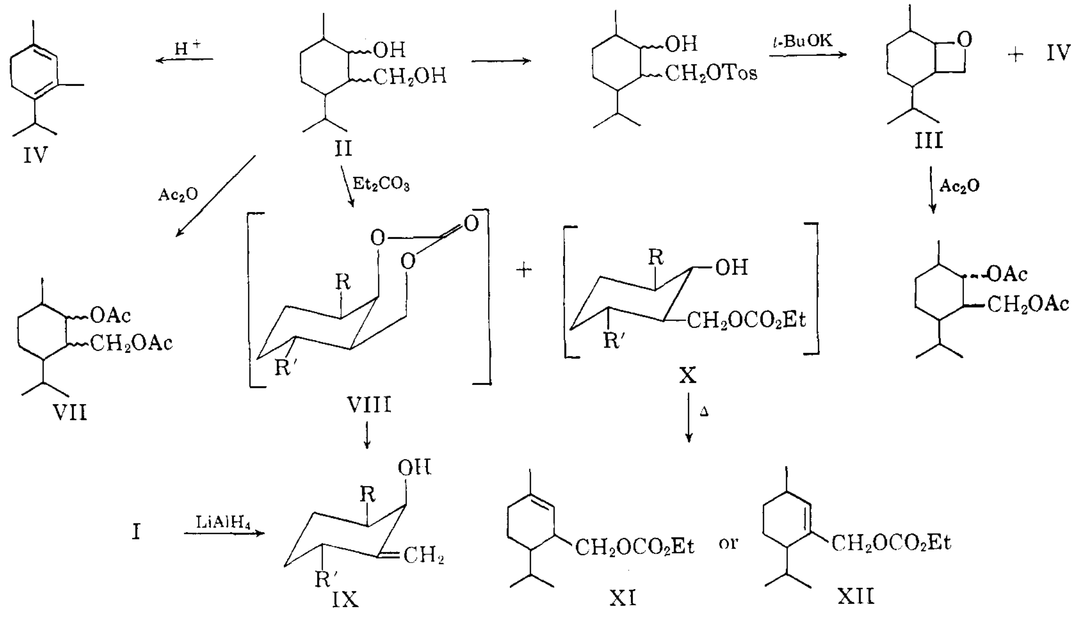

Chart II. Interrelationships of Compounds Studied.

ethylene. It would appear, therefore, to be ethyl 3-(*p*-menth-1(or 2)-enyl)-methylcarbonate (X or XI), which would be expected to form during the distillation of a mixed carbonate ester (X) to ethanol and the *trans* form of the diol.

These observations suggest that our 3-hydroxymethylcarvomenthol was a mixture of stereoisomers having the hydroxyl and hydroxymethyl groups *cis* or *trans* to each other.[22] It is probably to be expected that such isomerization might be introduced during the hydrogenation of 3-hydroxymethylenecarvomenthone, because of the tautomeric equilibria in the 1,3-dicarbonyl system.

Experimental

***l*-Carvomenthone** was prepared by the hydrogenation of *d*-carvone in methanolic solution over palladium–calcium carbonate catalyst (method of Vavon[22]) and also in ethanolic solution over W-2 Raney nickel catalyst (method of Badoche[22]), in each case under an initial hydrogen pressure of 50 p.s.i. Following isolation by distillation, the product had b.p. 90° (19 mm.), n^{21}_{D} 1.4552). The yield was 91% when nickel was used and 51%, accompanied by a 20% yield of carvacrol, when palladium was used.

3-Hydroxymethylenecarvomenthone.—A solution of 40 ml. of ethyl formate in 50 ml. of dry benzene was added dropwise to a stirred suspension of 17.3 g. of sodium methoxide in 200 ml. of benzene. Thirty-three grams of carvomenthone was then added during 30 min. with stirring and cooling of the mixture with an ice bath. The latter was removed after the addition, and the mixture was allowed to stand with stirring, overnight. It was hydrolyzed by the addition of cold 10% sulfuric acid, and the aqueous layer separated and extracted with ether three times. The combined organic extracts were extracted with cold 4% potassium hydroxide solution, which was then acidified with 10% sulfuric acid (with cooling), followed by ether extraction. The dried, filtered ether solution was distilled to give 20 g. (68%) of a clear liquid, b.p. 124° (20 mm.) reported[3] 118° (12 mm.), n^{20}_{D} 1.4969.

3-Hydroxymethylcarvomenthol (II).—To a solution of 49 g. of 3-hydroxymethylenecarvomenthone in 100 ml. of absolute ethanol was added 20 g. of W-2 Raney nickel catalyst, and the mixture placed in a low pressure shaking bottle under an initial hydrogen pressure of 50 p.s.i. The absorption of hydrogen was about 75% of theoretical after 72 hr. After removal of the catalyst by filtration, the solution was distilled to give 11 g. (26%) of a mixture of about equal parts of carvomenthone and carvomenthol, b.p. 74–76° (0.7 mm.) and 27.5 g. (58%) of 3-hydroxymethylcarvomenthol, b.p. 135–140° (0.7 mm.), n^{20}_{D} 1.4820. The infrared spectrum of the latter contained bands at 2.80, 9.38, and 9.84 μ, characteristic of the two carbinol groups and was entirely lacking in bands in the 6-μ region.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.98; H, 11.71.

Extension of the time of hydrogenation to 168 hr. increased the yield of the diol to 61% and that of the carvomenthone–carvomenthol mixture to 25%, while after 48 hr. the yields were 54% and 14%, respectively. Under 900 p.s.i. for 12 hr., at 75°, the reaction gave 60% of the diol and 26% of carvomenthone–carvomenthol, while under 1500 p.s.i. at 180°, the yields were 56% and 11%.

The composition of the carvomenthone–carvomenthol mixture was deduced by comparison of its infrared spectrum with those of authentic materials and a mixture of them. Ten grams of the mixture was reduced in refluxing ether solution with 2 g. of lithium aluminum hydride, followed by hydrolysis with 20% sodium carbonate solution and drying over magnesium sulfate. Distillation afforded 8 g. (80%) of carvomenthol having b.p. 103–104° (17 mm.), n^{20}_{D} 1.4630 (reported[23] b.p. 220°, n^{22}_{D} 1.4636) and infrared

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[22] The conformational structures in Chart II are written in accordance with the finding of G. Vavon, *Compt. rend.*, **153**, 68 (1911) and M. Badoche, *Bull, soc. chim. France*, 193 (1951), that *l*-carvomenthone is obtained by hydrogenation of *d*-carvone, and the observation of A. K. Bose, *Experimentia*, **8**, 458 (1952), that the methyl and isopropyl groups in carvomenthone and carvomenthol are *trans* and *equatorial.*

[23] O. Wallach, *Ann.*, **277**, 130 (1893).

[24] I. L. Kondakov and E. Lutschinin, *J. prakt. Chem.*, **60**, 271 (1899); G. Vavon, *Compt. rend.*, **153**, 70 (1911).

spectrum identical to that of authentic material. Treatment of 4.5 g. of this reduction product with 10 ml. of acetic anhydride, heated under reflux for 4 hr., gave upon distillation 3.5 g. (58%) of carvomenthyl acetate, b.p. 61–62° (1 mm.), $n^{20}\mathrm{D}$ 1.4469 (reported[24] b.p. 230–231° and 105–107° (11 mm.), $n^{20}\mathrm{D}$ 1.4477), saponification equivalent, 196 (theory, 198).

Oxidation of 4.0 g. of the above carvomenthone–carvomenthol mixture was carried out by shaking 1 hr. with a solution of 5 g. of potassium dichromate and 4 g. of sulfuric acid in 50 ml. of water. Extraction with ether, washing of the extracts with sodium bicarbonate solution and then water, drying and distillation gave 3.1 g. (78% of *l*-carvomenthone, b.p. 199–202°, $n^{20}\mathrm{D}$ 1.4543 (reported[25] b.p. 218–219[25], $n^{30}\mathrm{D}$ 1.4531[25]). The oxime had m.p. 99–100°, $[\alpha]^{20}\mathrm{D}$ −24.7°. (reported[26] m.p. 100–101°, $[\alpha]\mathrm{D}$ −42.3°).

3-Methyl-α-terpinene (IV).—A solution of 3.7 g. of 3-hydroxymethylcarvomenthol in 20 ml. of ether was mixed with 20% sulfuric acid for 15 min., and the ether layer was then separated, dried over sodium sulfate, and distilled under water vacuum pressure. As water droplets condensed with the product, the distillate was dried and redistilled, giving 3.0 g. of a clear oil, b.p. 98–100° (23 mm.) and 187–188° (740 mm.) $n^{20}\mathrm{D}$ 1.4800 (when freshly prepared, 1.4685 after standing 3 days), $[\alpha]^{20}\mathrm{D}$ 0.0° (reported[27] b.p. 184–186° (735 mm.), $n^{25}\mathrm{D}$ 1.4845 $[\alpha]^{25}\mathrm{D}$ 0.04°). The mass spectrum showed a parent peak at 150 mass, which is the molecular weight of 3-methylterpenine. The NMR spectrum showed peaks at 4.61 τ (cyclic olefin, maximum of one vinyl hydrogen), 8.24 τ (vinyl methyl), 8.34 τ (allylic methyl), and 8.81, 9.01, and 9.08 τ (all C-methyl). The infrared spectrum contained bands at 5.91 and 6.10 μ characteristic of a conjugated diene; there was also a medium-weak band at 5.78 μ suggestive of contamination by 3-methylcarvomenthone.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.11; H, 12.86.

3-Tosyloxymethylcarvomenthol.—A solution of 30 g. of 3-hydroxymethylcarvomenthol and 32 g. of *p*-toluenesulfonyl chloride in 110 g. of pyridine was allowed to stand at room temperature for 36 hr. It was then quenched with iced hydrochloric acid (110 g. of 36% hydrochloric acid in 600 g. of ice water) and extracted with five 50-ml. portions of ether. The ether solution was washed with 5% sodium bicarbonate, and with water, dried over magnesium sulfate and evaporated, to give a clear sirup which was crystallized from petroleum ether. The yield amounted to 47.5 g. (91%) of white crystals, m.p. 116–116.5°.

Anal. Calcd. for $C_{18}H_{28}SO_4$: S, 9.41. Found: S, 9.47.

Pyrolysis of 46 g. of 3-tosyloxymethylcarvomenthol was carried out by heating the compound in a small distillation apparatus under 20 mm. pressure. The distillate of oily liquid containing water droplets was taken up in ether, dried over magnesium sulfate, and redistilled to give 5.0 g. (25%) of 3-methyl-α-terpinene, b.p. 80° (16 mm.), $n^{20}\mathrm{D}$ 1.4800. The infrared spectrum was identical to that of the previous sample.

2-Methyl-5-isopropyl-7-oxabicyclo[4.2.0]octane (III).—To 47.5 g. of 3-tosyloxymethylcarvomenthol was added a solution of potassium *t*-butoxide in *t*-butyl alcohol. An exothermic reaction occurred, causing a temperature rise to 50°, and an immediate precipitate of potassium *p*-toluenesulfonate separated. An additional 250 ml. of *t*-butyl alcohol was added, and the mixture was allowed to stand overnight. The aqueous extracts from extraction with five 50-ml. portions of water, were washed with ether, and the combined *t*-butyl alcohol and ether solutions were dried over magnesium sulfate and distilled to give 7.0 g. of the bicyclic oxetane as a clear, colorless liquid of menthol-like odor, b.p. 96–99° (14 mm.), and 78° (2.5 mm.), $n^{20}\mathrm{D}$ 1.4620, $[\alpha]^{30}\mathrm{D}$ +8.1°. The NMR spectrum contained a series of weak, sharp bands 5.12, 5.42, 5.66, 5.78, 5.89, 6.02, and 6.23 τ, all in the region for oxetane α-C*H* and C*H*₂, as well as 8.82 τ (CH_3—C—C—O), and 9.02, 9.09, and 9.17 τ (CH_3—C). The infrared spectrum contained bands at 10.00 and 10.35 μ characteristic of the cyclohexane and oxetane rings.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.08; H, 11.83.

Continued heating *in vacuo* of the crude reaction product, after removal of the oxetane fraction, resulted in decomposition of the residue and distillation of an oily liquid containing water droplets. This distillate was taken up in ether, dried over magnesium sulfate, and redistilled to yield 4.5 g. (41%) of colorless liquid, b.p. 88–89° (20 mm.), $n^{20}\mathrm{D}$ 1.4688. The infrared spectrum was identical to that of 3-methyl-α-terpinene. It is believed to have arisen from pyrolysis of unchanged 3-tosyloxymenthol.

2-Acetoxy-3-acetoxymethyl-*p*-menthane. A. From II.—A solution of 10 g. of 3-hydroxymethylcarvomenthol in 50 ml. of pyridine was treated with 11 g. of acetyl chloride and allowed to stand overnight. The mixture was poured into ice water, extracted with ether, and the ether solution was washed with 2% hydrochloric acid, followed by 5% sodium carbonate solution. After drying over magnesium sulfate, the extract was distilled to give 10.5 g. (71%) of the diacetate ester as a clear, colorless oil, b.p. 113–115° (1 mm.), $n^{20}\mathrm{D}$ 1.4593, $[\alpha]^{31}\mathrm{D}$ +13.65°. The infrared absorption spectrum contained bands at 5.70, 8.0, and 9.65 μ, typical of esters, but showed no hydroxyl absorption.

Anal. Calcd. for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 67.00; H, 9.66.

B. From III.—A solution of 1.0 g. of 2-methyl-5-isopropyl-7-oxabicyclo[4.2.0]octane and 2 g. of pyridine hydrochloride in 10 ml. of acetic anhydride was heated under reflux for 7 hr., followed by processing similar to that in A. The product consisted of 0.8 g. (50%) of a clear, colorless oil, b.p. 91° (0.4 mm.), $n^{20}\mathrm{D}$ 1.4665, $[\alpha]^{27}\mathrm{D}$ +38.38°. The infrared spectrum was identical in all respects to that of the diacetate of 3-hydroxymethylcarvomenthol.

Reaction of 3-Hydroxymethylcarvomenthol with Ethyl Carbonate.—A solution of 11 g. of 3-hydroxymethylcarvomenthol and 9.0 g. of ethyl carbonate, in which 0.2 g. of sodium metal had been dissolved to provide a catalyst, was heated under reflux, until the vapor temperature dropped to 80°, whereupon the ethanol formed was removed by distillation. When ethanol distillation virtually ceased, the reaction mixture was distilled under reduced temperature to give 4.0 g. (40%) of a clear, colorless liquid, b.p. 74–76° (0.1 mm.), $n^{20}\mathrm{D}$ 1.4850, and 5.0 g. (35%) of another colorless liquid, b.p. 168–175° (0.1 mm.) $n^{20}\mathrm{D}$ 1.4842. Both showed unsaturation towards bromine in carbon tetrachloride.

The lower boiling fraction had an infrared spectrum identical to that of 3-methylenecarvomenthol (IX) obtained by the lithium aluminum hydride reduction of 3-hydroxymethylenecarbomenthone (see below), and contained strong absorption bands at 2.75 μ (O—H), 5.41, and 10.95 μ ($C{=}CH_2$), 5.98 (C=C), and 9.40 μ (C=O).

The higher boiling fraction gave an infrared spectrum possessing strong bands at 5.60 μ (carbonate C=O), 6.15 μ (C=C), and 7.13 and 12.95 μ ($R_2C{=}CHR$), consistent with structure XI or XII.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: 70.02; H, 10.00.

3-Methylenecarvomenthol (IX).—A solution of 45.5 g. of 3-hydroxymethylenecarvomenthone in 250 ml. of anhydrous ether was added to a slurry of 7.0 g. of lithium aluminum hydride in 250 ml. of ether. The mixture was heated under reflux overnight, cooled, and hydrolyzed with 20% sodium carbonate solution. The ether solution was dried over magnesium sulfate and distilled to give 23 g. (55%) of 3-methylenecarvomenthol. b.p. 114–115° (17 mm.), $n^{20}\mathrm{D}$ 1.4800, with recovery of 7 g. of starting diol.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.16; H, 11.67.

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(25) J. L. Simonsen and M. G. Rae, *J. Chem. Soc.*, **121**, 881 (1922).

(26) W. Hückel and W. Doll, *Ann.*, **526**, 103 (1936).

(27) J. Read and A. Watters, *J. Chem. Soc.*, 2165 (1929).

Acknowledgment.—We are greatly indebted to Dr. George Van Dyke Tiers and Minnesota Mining and Manufacturing Co., St. Paul, Minn., for NMR spectra, to Dr. R. W. Kiser and Mr. Emilio Gallegos for a mass spectrum, and Dr. G. Dana Johnson for his comments.

A Study of the Thermal Cyclization of 1,7-Alkadienes and Monocyclic Dienes[1]

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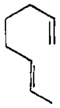
8-Methyl-1,7-nonadiene fails to cyclize at 440°, but does cyclize to an appreciable extent at 490° giving 1-methyl-2-isopropenylcyclohexane. The carbomethoxy group facilitates thermal cyclization as shown by the fact that methyl 5,9-dimethyl-2,8-decadienoate (X) cyclizes rapidly at 400°. The products are three diastereomeric methyl 8-*p*-menthene-3-acetates (XI), the major one of which is believed to be the most stable diastereomer, XII.

Monocyclic diolefins in which one double bond is contained in a six-membered ring fail to give bicyclic compounds at temperatures as high at 500°.

It was shown recently that suitably constituted 1,6-alkadienes undergo cyclization at 450° to give cyclopentane derivatives.[2] For example, 1,6-octadiene (I) gives 1-methyl-2-vinylcyclopentane (II), and 7-methyl-1,6-octadiene (III) gives 1-methyl-2-isopropenylcyclopentane (IV). Evidence has been presented which indicates that these thermal cyclizations proceed by an intramolecular mechanism.[3]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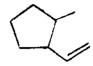
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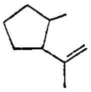
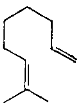
III

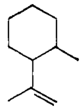

IV

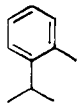
We were interested in extending this study (1) to see if cyclohexane derivatives could be obtained from 1,7-alkadienes, (2) to determine the effect of substituents other than alkyl groups, and (3) to determine if bicyclic compounds could be obtained from monocyclic dienes.

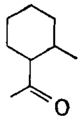
Results and Discussion

8-Methyl-1,7-nonadiene (V) was chosen for the first part of the study. No change occurred when this compound was heated at 440°, but when the temperature was increased to 490°, cyclization occurred to a significant extent. Quantitative hydrogenation indicated that the pyrolysate consisted of 25% monoolefin and 75% diolefin. The mixture was separated by chromatography over silica gel, and the diolefin was identified as unchanged starting material (V), while the monoolefin was shown to be 1-methyl-2-isopropenylcyclohexane (VI) by the following evidence.


V


VI


VII


VIII

The results of elemental analysis agreed with the formula $C_{10}H_{18}$. Strong infrared bands at 6.05 and 11.26 μ indicated a double bond of the type $R_2C{=}CH_2$.[4] *o*-Cymene (VII) was obtained when a sample of the pyrolysate was hydrogenated and then dehydrogenated over platinum-alumina. Ozonolysis gave a ketone $C_9H_{16}O$ (analyzed as the semicarbazone) which gave a positive iodoform test. Comparison of the infrared spectrum with those of authentic samples revealed that this ketone was a mixture of methyl *cis*- and methyl *trans*-2-methylcyclohexyl ketone (VIII).[5]

Methyl 5,9-dimethyl-2,8-decadienoate (X) was chosen for the study of the effect of substituents other than alkyl groups. In contrast to the behavior of V, extensive reaction occurred when X was heated at 400°, and the gas chromatography tracing of the product showed three peaks; the components are designated A, B, and C in the order of increasing retention times in the following discussion. Calculation of the approximate composition from the peak areas indicated 53% A, 29% B, and 18% C. Component C possessed a retention time identical with that of X, and was subsequently shown to be identical with it. Careful fractional

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[1] Financial support by the National Science Foundation (G7379) and the Ohio University Research Fund is gratefully acknowledged.

[2] H. Pines, N. E. Hoffman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 4412 (1954); W. D. Huntsman, V. C. Solomon, and D. Eros, *ibid.*, **80**, 5455 (1958).

[3] W. D. Huntsman and T. H. Curry, *ibid.*, **80**, 2252 (1958).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1958, p. 34.

[5] It is possible that some epimerization occurred during the degradation, *e.g.*, see ref. 2. Unfortunately, a gas chromatography instrument suitable for checking the homogeneity of the cyclic olefin was not available to us at the time this work was done.