phenyl sulfone[9,10] (3 g.), sodium hydroxide (3 g.), and water (3 ml.) were boiled under reflux for 20 hr. The trapped volatile products contained 1.2 g., (90% yield) of 1,1,2,2-tetrafluoroethane, identified by mass spectroscopy.

2,2,3,3-Tetrafluorothiolane 1,1-dioxide[10] (6 g.), sodium hydroxide (4 g.), and water (9 ml.) were boiled under reflux for 6 hr. The solution was neutralized (H_2SO_4), dried, and extracted with ethanol. The extracted solids were recrystallized from ethanol to give sodium 3,3,4,4-tetrafluoro-1-butanesulfonate.

Anal. Calcd. for $C_4H_5F_4NaO_3S$: C, 20.7; H, 2.2; F, 32.7; Na, 9.9; S, 13.8. Found: C, 20.7; H, 2.3; F, 30.2; Na (ash), 9.7; S, 13.9.

Sodium 4-(Methylsulfonyl)octafluoro-1-butanesulfonate.—1,4-Bis(methylsulfonyl)octafluorobutane (50 g.), dissolved in concentrated sulfuric acid (300 g.), was heated to 190° and treated with chromium trioxide (70 g.) during 1 hr. The material was heated for a further 3 hr., cooled, diluted with water, neutralized (NaOH), dried, and extracted with ethanol. The extracted salts were crystallized twice from hot water to yield the sulfone-sulfonate.

Anal. Calcd. for $C_5H_3F_8NaO_5S_2$: C, 15.71; H, 0.79; F, 39.77; S, 16.78. Found: C, 15.5; H, 1.0; F, 38.0; S, 16.6.

Dipotassium Eicosafluoro-1,10-decanedisulfonate.—Potassium permanganate (30 g.), 1,10-bis(methylsulfonyl)eicosafluorodecane (15 g.), and water (200 ml.) were heated at 150° for 6 hr. in a 400-ml. bomb. The discharged product was boiled with ethanol under reflux to destroy excess oxidant, and the slurry was filtered hot. The residue was washed with hot water, and the combined aqueous solutions were treated with Dowex 50 resin (H^+ form) at 80° to pH 5. The solution was boiled for 5 min., filtered, and evaporated to leave the crystalline salt (13.1 g., 78%).

Anal. Calcd. for $C_{10}F_{20}K_2O_6S_2$: C, 16.3; F, 51.5; K, 10.6; S, 8.7. Found: C, 16.4; F, 51.8; K (ash), 10.3; S, 8.3.

The salts of tetrafluoro-1,2-ethane-, octafluoro-1,4-butane-, dodecafluoro-1,6-hexane-, and hexadecafluoro-1,8-octanedisulfonic acids were obtained similarly.

Dodecafluoro-1,6-hexanedisulfonyl Chloride.—Dry potassium dodecafluoro-1,6-hexanedisulfonate (100 g.) was powdered with phosphorus pentachloride–zinc chloride (270 g.)[5] and was heated vigorously in a simple still to 250° (50 mm.). Redistillation of the distillate gave the disulfonyl chloride (76 g., 82%), b.p. 138° (40 mm.).

Anal. Calcd. for $C_6Cl_2F_{12}O_4S_2$: C, 14.4; Cl, 14.2; F, 45.7; S, 12.8. Found: C, 14.1; H, <0.1; C, 14.5; F, 47.7; S, 12.6.

Acknowledgment.—The author wishes to thank Mr. Thomas E. Beukelman for n.m.r. (H^1 and F^{19}) studies and Dr. Robert K. Miller for infrared studies. Confirmatory structural proof for the described products by these two techniques was invaluable.

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[9] D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5116 (1960).

[10] C. G. Krespan, *J. Org. Chem.*, **27**, 3588 (1962).

A Novel Method for the Preparation of Bicyclooctane Systems. III.[1,2] Cyclization of Vinylcyclohexenes

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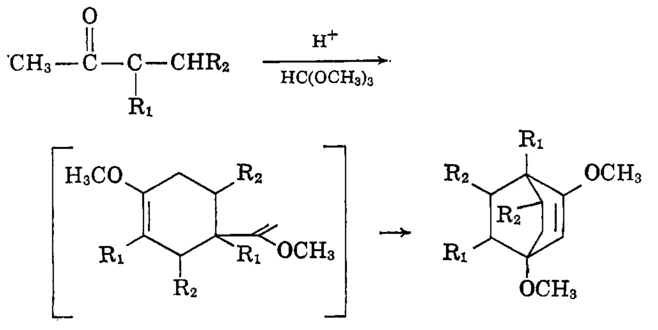
An acid-catalyzed cyclization of variously substituted 4-vinyl-1-cyclohexenes leading to bicyclooctene systems was studied. The presence of substituents such as phenyl and methoxyl groups at C-1 of vinylcyclohexenes favors the acid-catalyzed ring-closure reaction, whereas electron-attracting groups such as carbonyl, carboxyl, and cyano at C-1 resist cyclization. Mechanism of the cyclization of 1-phenyl-4-vinyl-1-cyclohexenes (**10** and **31**) might involve, in part, the anchimeric effect of a junction-forming second double bond.

Reaction of α,β-unsaturated ketones with trimethyl orthoformate in the presence of an acid catalyst affords bicyclo[2.2.2]octane systems, and the mechanism of the reaction involves the acid-catalyzed cyclization of vinylcyclohexenes derived by a condensation of enol ethers of α,β-unsaturated ketones.[1,2] It was also described in a recent paper[2a] that cyclization of 4-substituted 1-methoxy-4-(1-methoxyvinyl)-1-cyclohexenes leads to 1-substituted 2,4-dimethoxybicyclo[2.2.2]oct-2-enes and of 1,4-diphenyl-4-vinyl-1-cyclohexene (**31**) to 1,4-diphenylbicyclo[3.2.1]oct-3-ene (**14**).



Ipatieff and his colleagues[3] obtained 2,6-dimethylbicyclo[3.2.1]oct-2-ene among other products when limonene was passed over silicophosphoric acid catalyst at 210°. Wenkert[4,5] has reported transformation of the 3-vinyl-1-cyclohexene structure in the tricarbocyclic diterpene, rimurene, into the bicyclo[3.2.1]oct-6-ene system (isophyllocaladene) by treatment with formic acid. Patent literature[6] has described cyclization of 4-vinyl-1-cyclohexene with tris[2-(3-cyclohexen-1-yl)ethyl]aluminum leading to bicyclo[3.2.1]oct-2-ene.

We report herein cyclization and attempted cyclization of variously substituted vinylcyclohexenes, and discuss the effects of substituents on the cyclization. The mechanism of the reaction is also discussed.

Cyclization of 4-Methyl-1-methoxy-4-vinyl-1-cyclohexene (**6**).—The hitherto unknown 4-methyl-1-methoxy-4-vinyl-1-cyclohexene (**6**) was prepared from 4-acetyl-4-methyl-1-cyclohexanone (**1**).[7] Reaction of **1** with excess morpholine in boiling benzene afforded

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[1] K. Morita, G. Somp, and E. V. Jensen, *J. Am. Chem. Soc.*, **84**, 3779 (1962).

[2] (a) K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965); (b) K. Morita and Z. Suzuki, *Tetrahedron Letters*, No. **6**, 203 (1964).

[3] V. N. Ipatieff, J. E. Germaine, W. W. Thompson, and H. Pines, *J. Org. Chem.*, **17**, 272 (1952).

[4] E. Wenkert, *Chem. Ind.* (London), 282 (1955).

[5] *Cf.* (a) A. J. Birch, R. W. Richards, H. Smith, A. Harris, and W. B. Whalley, *Tetrahedron*, **7**, 241 (1959); (b) G. Büchi, E. Koller, and C. W. Perry, *J. Am. Chem. Soc.*, **86**, 5646 (1964).

[6] Schering A. G., French Patent, 1,351,716 ((1964); *Chem. Abstr.*, **60**, 13164*f* (1964).

[7] J. Colonge and R. Vuillemet, *Bull. soc. chim. France*, 2235 (1961)

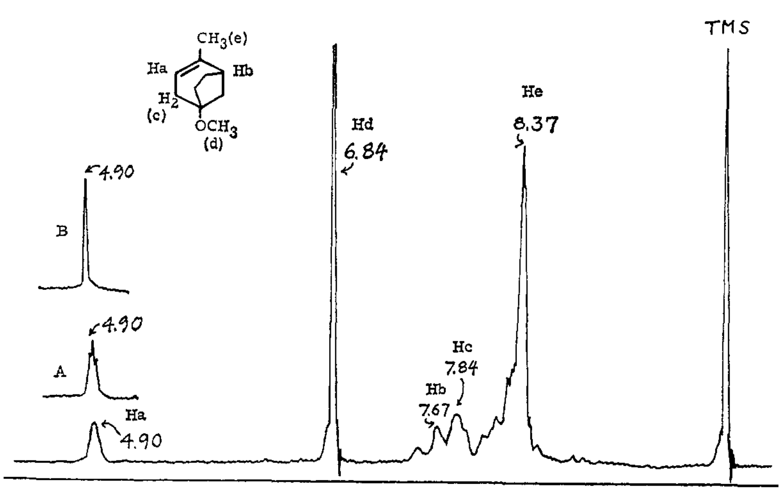
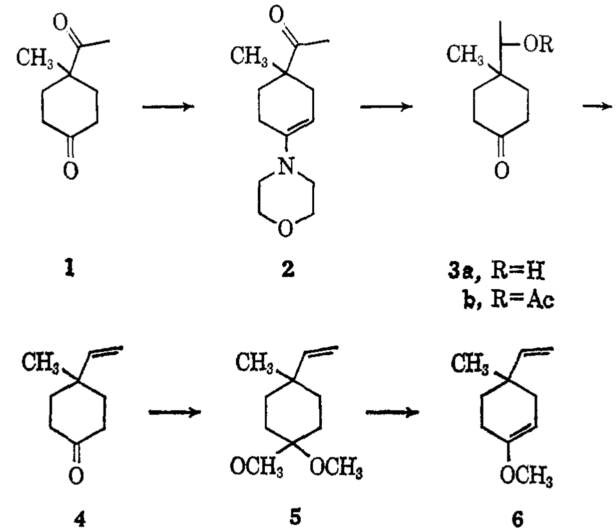
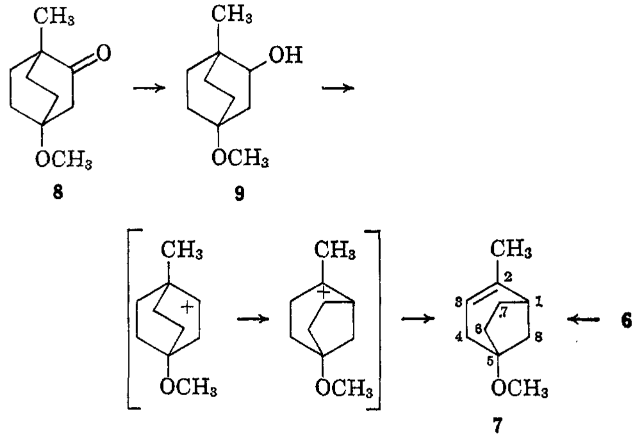


Figure 1.—N.m.r. spectrum of 5-methoxy-2-methylbicyclo[3.2.1]oct-2-ene (7) in carbon tetrachloride at 100 Mc.: A, when irradiated at τ 8.37; B, when irradiated at τ 7.84.

what is believed to be enamine 2. Lithium aluminum hydride reduction of 2 gave, after an acid hydrolysis, 4-(1-hydroxyethyl)-4-methyl-1-cyclohexanone (3a), 3,5-dinitrobenzoate m.p. 122–123°, in 87% over-all yield. Pyrolysis of the acetate 3b at 560° gave 4-methyl-4-vinyl-1-cyclohexanone (4). The n.m.r. and infrared spectra are entirely consistent with the presumed structure. The n.m.r. spectrum confirmed the existence of the vinyl side chain, showing a quartet at τ 4.08 (J = 10 and 18 c.p.s.), four peaks at τ 4.76, 4.81, 4.98 and 5.06 which may be considered as two doublets (τ 4.90, J = 10 c.p.s., and τ 4.91, J = 18 c.p.s.), and a methyl group at τ 8.87. Infrared bands were found for the vinyl group (1642, 1005, and 910 cm.$^{-1}$) and a six-membered ring ketone (1719 cm.$^{-1}$). Reaction of 4 with trimethyl orthoformate gave the corresponding ketal 5, which in turn was transformed into the desired 6 by heating in acetic anhydride–pyridine.



Reaction of a benzene solution of 6 with boron trifluoride etherate at reflux temperature gave 5-methoxy-2-methylbicyclo[3.2.1]oct-2-ene (7) in 79% yield. Conclusive proof that 7 represented the correct structure was obtained by a combination of physical and chemical methods. The n.m.r. spectrum (Figure 1) confirmed the existence of a tertiary methoxyl group, τ 6.84, methyl group on ethylenic carbon bearing no hydrogen, τ 8.37, bridgehead hydrogen, τ 7.67, and a vinyl proton, τ 4.90. When the methyl protons at τ 8.37 were irradiated, the vinyl proton at τ 4.90 was converted into a triplet (J = 2.6 c.p.s.); when allylic methylene protons at τ 7.84 were irradiated the vinyl proton was converted into a somewhat broad singlet. Those observations confirm the existence of a long-range coupling between a vinyl proton and methyl protons. Infrared spectrum of 7 was also entirely consistent with the assigned structure. Bands for methoxyl group were found at 2837 and 1114 cm.$^{-1}$.



Lithium aluminum hydride reduction of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one (8)[2] gave 4-methoxy-1-methylbicyclo[2.2.2]octan-2-ol (9), p-nitrobenzoate m.p. 119–121°. Dehydration of 9 over alumina catalyst at 200° gave 7 whose n.m.r. and infrared spectra were identical with those obtained by the cyclization of 6. As the mechanism proposed[8] for dehydration catalyzed by alumina involves carbonium ion intermediate, Wagner–Meerwein rearrangement from secondary ion to tertiary ion to form bicyclo[3.2.1] skeleton could easily be anticipated. It has been observed that hydration of bicyclo[2.2.2]octene with aqueous sulfuric acid results in rearrangement and give bicyclo[3.2.1]octan-2-ol.[9] This and other results have been quoted as evidence that bicyclo[3.2.1]octane systems

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(8) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961); M. E. Winfield, "Catalystic Dehydration and Hydration in Catalysis," Vol. IV, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 93–182.

(9) M. S. Newman and Y. T. Yer, *J. Am. Chem. Soc.*, **74**, 507 (1952).

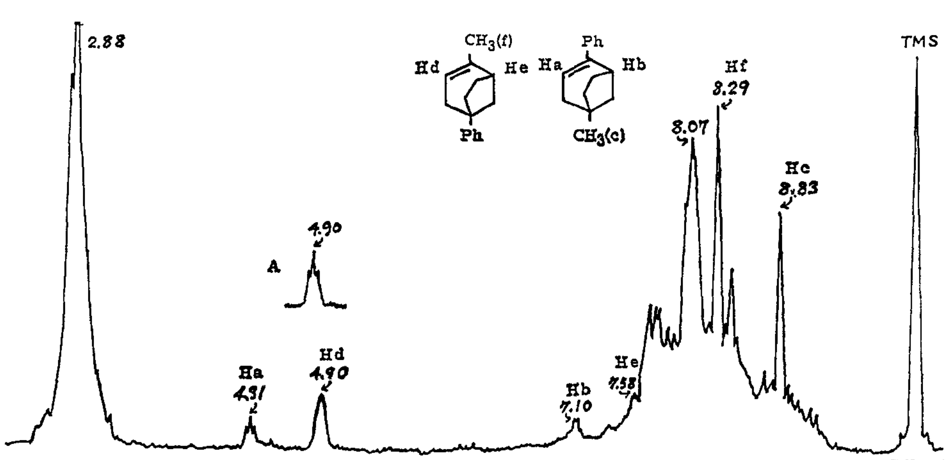
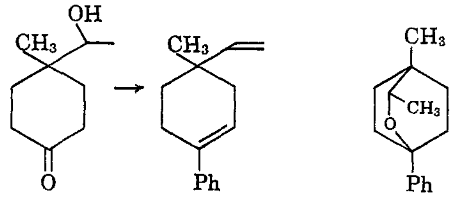


Figure 2.—N.m.r. spectrum of a 33:67 mixture of 5-methyl-2-phenylbicyclo[3.2.1]oct-2-ene (**12**) and 2-methyl-5-phenylbicyclo[3.2.1]oct-2-ene (**13**) in carbon tetrachloride at 100 Mc.: A, when irradiated at τ 8.29.

are more stable than the isomeric bicyclo[2.2.2]octane systems.[10] A mixture of bicyclo[2.2.2]octyl and bicyclo[3.2.1]octyl systems have been obtained in solvolysis of either 2-(3-cyclohexenyl)ethyl *p*-bromobenzenesulfonate[11] or bicyclo[2.2.2]2-octyl *p*-bromobenzenesulfonate[12] or in deamination of 2-aminobicyclo[2.2.2]octane.[13] The presence of the methyl substituent at the bridgehead in **9** undoubtedly favors the formation of a [3.2.1]bicyclic system.

Alkaline decomposition[14] of the *p*-tosylhydrazone of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one (**8**) gave a mixture of at least three compounds.

Cyclization of 4-Methyl-1-phenyl-4-vinyl-1-cyclohexene (10).—Pyrolysis of the acetylated reaction mixture, prepared from **3a** and phenylmagnesium bromide, at 550° gave 4-methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**). The n.m.r. spectrum [τ 8.95 (methyl protons), triplet centered at 3.98 (J = 2.5 c.p.s., vinyl proton in the ring), quartet centered at 4.16 (J = 9 and 15 c.p.s.), and doublets centered at 5.09 (J = 9 c.p.s.) and 5.05 (J = 15 c.p.s., vinyl protons)] and ultraviolet spectrum [λ_{max} 247 mμ (ϵ 13,500)] of this material were entirely consistent with the presented structure. Under certain conditions, pyrolysis of the acetate mixture gave 3,4-dimethyl-1-phenyl-2-oxabicyclo[2.2.2]octane (**11**). The structure of **11** was assigned by its n.m.r. spectrum (see Experimental part).



3a **10** **11**

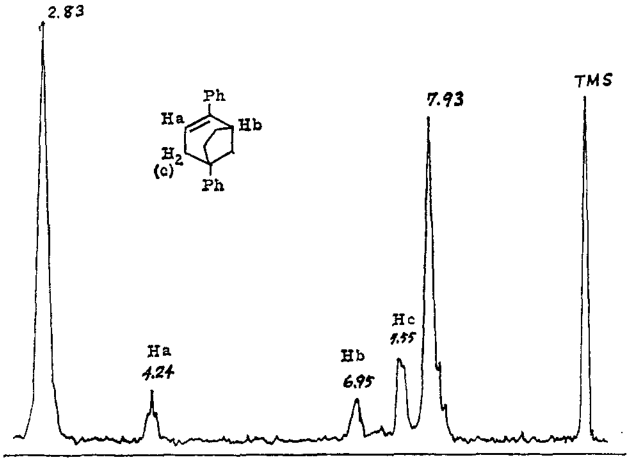


Figure 3.—N.m.r. spectrum of 2,5-diphenylbicyclo[3.2.1]oct-2-ene (**14**) in carbon tetrachloride at 60 Mc.

Reaction of a benzene solution of **10** with boron trifluoride etherate gave a 63% yield of the cyclization product. The cyclization product was found to be a mixture of two compounds, as shown by its thin layer chromatography over silicic acid coated with 10% silver nitrate and by its n.m.r. (Figure 2) and ultraviolet spectra with low extinction coefficient [λ_{max} 252 mμ (ϵ 4800)]. The structure assignment was carried out on the mixture. The elemental analysis and molecular weight determination of the mixture corresponded to the formula $C_{15}H_{18}$, isomeric with the starting hydrocarbon, and there were only vinyl protons of the type of $>C{=}CH{-}CH_2{-}$ in the mixture, shown by its n.m.r. spectrum (Figure 2). The n.m.r. peaks of a vinyl proton at τ 4.31 (triplet, J = 2.6 c.p.s.), of a bridgehead proton at τ 7.10, and of methyl protons at τ 8.83 were ascribed to those of **12**. The n.m.r. spectrum (Figure 3) of 2,5-diphenylbicyclo[3.2.1]oct-2-ene (**14**),[2a] obtained by the cyclization of 1,4-diphenyl-4-vinyl-1-cyclohexene, showed a vinyl proton at τ 4.24 and a bridgehead proton at τ 6.95. The peaks of a vinyl proton at τ 4.90, of a bridgehead proton at τ 7.58, and of methyl protons at τ 8.29 were assigned for those of **13**. When methyl protons at τ 8.29 were irradiated, the vinyl proton at τ 4.90 was converted into a triplet (J = 2.7 c.p.s.). Ultraviolet absorption maxima of the reaction product (λ_{max} 252 mμ) and of **14** [λ_{max} 249 mμ (ϵ 13,600)] are comparable. The mass spectrum (Figure 4) of the cyclization mixture, which showed the peaks at *m/e* 143 and 81 ascribable to the fragments shown, confirmed the assigned structures (*cf.* Figure 5). Reductive ozonolysis of the mixture gave a product, in which benzoyl and acetyl moieties were found to be present, shown by its ultraviolet spectrum [λ_{max} 242.5 mμ (ϵ 2700)] and by the iodoform

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[10] H. L. Goering and M. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

[11] G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

[12] S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

[13] H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

[14] *Cf.* W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

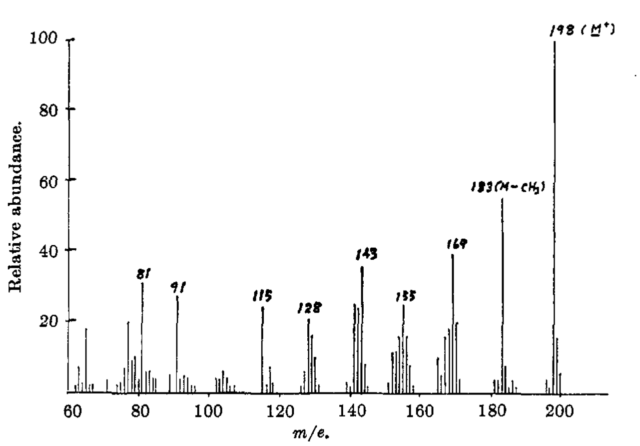
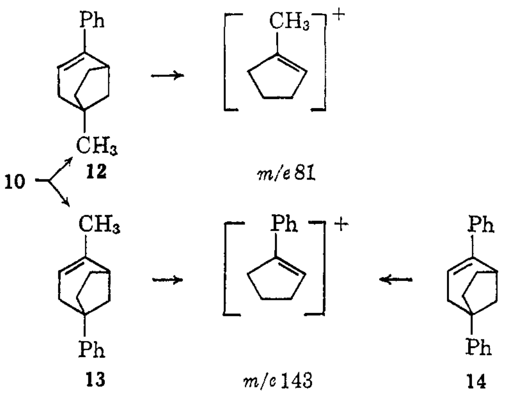
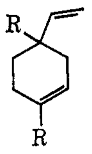


Figure 4.—Mass spectrum of a 33:67 mixture of 5-methyl-2-phenylbicyclo[3.2.1]oct-2-ene (**12**) and 2-methyl-5-phenylbicyclo[3.2.1]oct-2-ene (**13**).

test of the crude reaction mixture, respectively. Thus we concluded that the cyclization mixture was a 33:67 mixture (determined by n.m.r. peaks of vinyl protons) of 5-methyl-2-phenylbicyclo[3.2.1]oct-2-ene (**12**) and 2-methyl-5-phenylbicyclo[3.2.1]oct-2-ene (**13**).

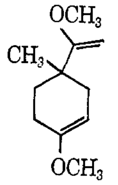


Scope and Limitations.—Efforts to cyclize 1,4-diformyl-4-vinyl-1-cyclohexene (**15**),[15] the semicarbazone (**16**)[15] and the oxime (**17**)[15] of **15**, 1,4-dicarboxy-4-vinyl-1-cyclohexene (**18**),[16] 1,4-dicarboethoxy-4-vinyl-1-cyclohexene (**19**),[16] and 1,4-dicyano-4-vinyl-1-cyclohexene (**20**)[16] so far have not proved successful.



15, R = CHO
16, R = CH=N—NHCONH$_2$
17, R = CH=NOH
18, R = CO$_2$H
19, R = CO$_2$C$_2$H$_5$
20, R = CN

It appears that presence of substituents such as methoxyl and phenyl groups which are capable of stabilizing carbonium ions generated at C-1 of vinylcyclohexenes favors the ring-closure reaction, whereas substituents such as carbonyl and cyano groups which destabilize carbonium ions generated at C-1 of vinylcyclohexenes are unfavorable for the cyclization reaction.[17] Another factor influencing the ring-closure reaction of vinylcyclohexenes is a conformational one as already discusssed in a previous paper,[2a] *i.e.*, the bulkier the substituents at C-4 is, the easier the cyclization.



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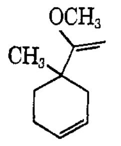

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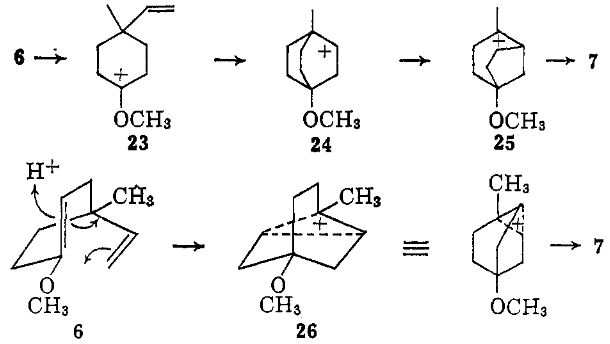
Presence of methoxyl at the α position of the vinyl side chain seems to favor the cyclization. No cyclization of 1-methoxy-4-methyl-4-vinyl-1-cyclohexene (**6**) occurred with boron trifluoride etherate in ether at room temperature, whereas cyclization of 1-methoxy-4-(1-methoxyvinyl)-4-methyl-1-cyclohexene (**21**) took place smoothly under similar conditions. It seems, however, that the presence of a methoxyl group in the vinyl side chain favors cyclization better when accompanied by the presence of a methoxyl group at C-1. Preliminary examination revealed that 4-(1-methoxyvinyl)-4-methyl-1-cyclohexene (**22**) prepared from 4-acetyl-4-methyl-1-cyclohexene did not cyclize under the similar conditions.

Mechanism of Cyclization.—Cyclization of acylic 1,5-dienes has extensively been studied,[18,19] partly because the cyclization plays an important role in the biogenesis of many terpenoid compounds.[20,21] The mechanism and stereochemical implications of olefin cyclization have been discussed.[19c,d,f,22,23]

Cyclization of **6** might proceed as depicted below. Thus, proton addition at the enol ether double bond to give an alkoxy carbonium ion **23** which cyclizes to the secondary ion **24**, followed by Wagner–Meerwein rearrangement leading to the tertiary ion **25** might be



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[15] R. Pummer, F. Aldebert, F. Büttner, F. Graser, E. Pirson, H. Rick, and H. Sperber, *Ann.*, **583**, 161 (1953).

[16] C. S. Marvel and N. O. Brace, *J. Am. Chem. Soc.*, **71**, 37 (1949).

[17] For more complicated effects of substituents for the cyclization, see later discussion.

[18] *Inter alia:* (a) J. L. Simonsen and L. N. Owen, "The Terpenes," Vol. 1, Cambridge University Press, London, 1947; (b) J. F. King and P. de Mayo, "Molecular Rearrangements," part 2, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p. 834; (c) J. H. Richard and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpene, and Acetogenins," W. A. Benjamin, Inc., New York, N. Y., 1964, pp. 257–263.

[19] *Inter alia:* (a) R. Helg and H. Schinz, *Helv. Chim. Acta*, **35**, 2406 (1952); (b) G. Gamboni, H. Schinz, and A. Eschenmoser, *ibid.*, **37**, 964 (1954); (c) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *ibid.*, **38**, 1890 (1955); (d) G. Stork and A. W. Burgstahler, *J. Am. Chem. Soc.*, **77**, 5068 (1955); (e) P. A. Stadler, A. Nechvatel, A. Frey, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1373 (1957); (f) H. E. Ulery and J. H. Richards, *J. Am. Chem. Soc.*, **86**, 3113 (1964); (g) V. A. Smith, A. V. Semenovskii, and V. F. Kucherov, *Bull. Acad. Sci. (USSR)*, 435 (1962).

[20] (a) J. B. Hendrickson, *Tetrahedron*, **7**, 82 (1959); (b) ref. 18c, pp. 240–276.

[21] T. T. Tchen and K. Bloch, *J. Biol. Chem.*, **226**, 921 (1957).

[22] A. V. Semenovsky, V. A. Smith, and V. F. Kucherov, presented at the International Symposium on the Chemistry of Natural Products, Kyoto, Japan, April 1964.

[23] W. S. Johnson, D. M. Baily, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 1959 (1964).

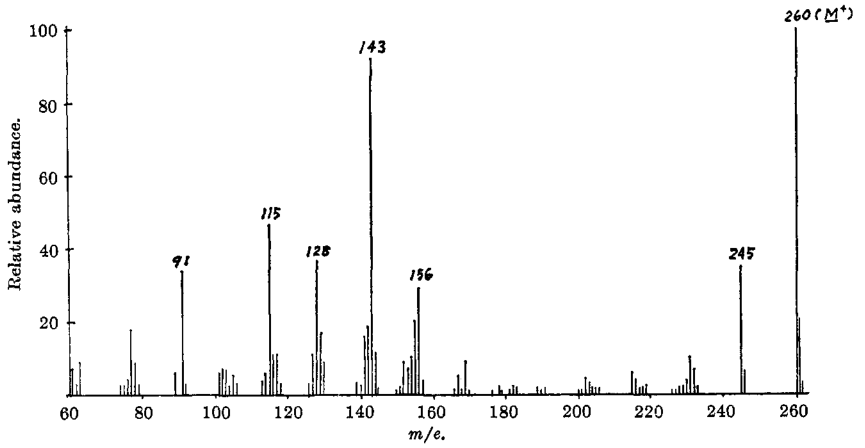
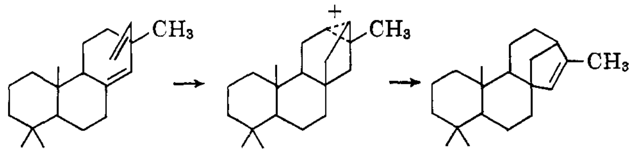


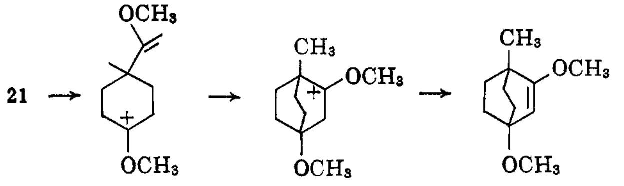
Figure 5.—Mass spectrum of 2,5-diphenylbicyclo[3.2.1]oct-2-ene (**14**).

envisioned; this then transforms into **7**, or a transition state or an intermediate of the reaction might be a bicyclooctyl bridged ion **26** as was suggested by Wenkert[4] for cyclization of rimurene (**27**) leading to tetracyclic isophyllocaladene (**28**).



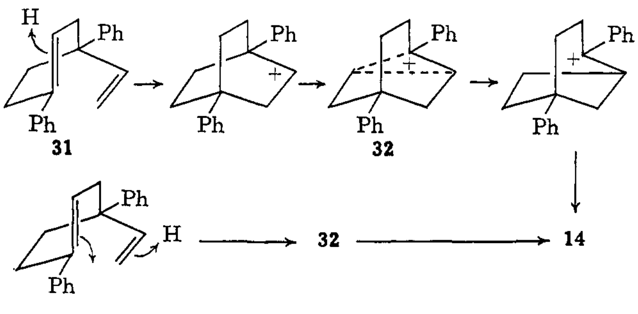
27 **28**

Formation[2] of a bicyclo[2.2.2]octene system rather than a [3.2.1] bicyclic system by the cyclization of **21** might be associated with the effect of the methoxyl group that can stabilize the intermediate carbonium ion **29**, preventing rearrangement.

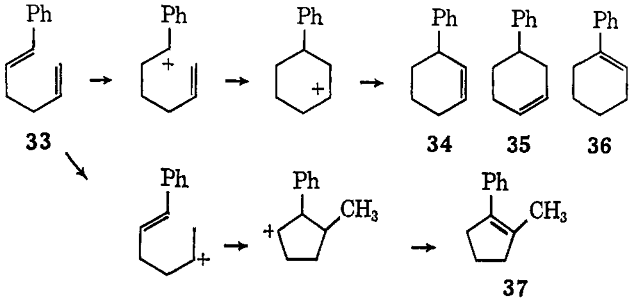


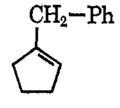
29 **30**

In a previous paper,[2a] it was reported that an acid-catalyzed cyclization of 1,4-diphenyl-4-vinyl-1-cyclohexene (**31**) furnished 2,5-diphenylbicyclo[3.2.1]oct-2-ene (**14**). The reaction could proceed in the same way as assumed for the cyclization of **6** by a stepwise classical carbonium ion process or *via* the nonclassical bicyclooctyl bridged ion **32**. In contrast to the cyclization of **6**, reaction of **31** could proceed alternatively. Thus, anti-Markovnikov addition[24] of a proton at a terminal double bond of **31** could lead to the ion **32**, which would then transform into **14**. In order to distinguish two possible routes, an acid-catalyzed cyclization of 4-methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**) was carried out, yielding a 33:67 mixture of 5-methyl-2-phenylbicyclo[3.2.1]oct-2-ene (**12**) and 2-methyl-5-phenylbicyclo[3.2.1]oct-2-ene (**13**) as already described.



In order to see whether protonation could occur at the terminal double bond in a system like 4-methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**), the cyclization of the simplest model 1-phenyl-1,5-hexadiene (**33**) was carried out. Reaction of a benzene solution of **33**[25] with boron trifluoride etherate gave a mixture, b.p. 94–99.5° (12 mm.), in 62% yield, the elemental analysis and molecular weight determination of which were compatible with the formula $C_{12}H_{14}$. The mixture was analyzed by vapor phase chromatography over a polyethylene glycol 6000 column and the peaks were compared with those of authentic substances. The mixture consisted of (retention times at 203°) 1-methyl-2-phenyl-1-cyclopentene (**37**) (8.8 min.), 3-phenyl-1-cyclohexene (**34**) (9.8 min.), 4-phenyl-1-cyclohexene (**35**) (11.0 min.), 1-phenyl-1-cyclohexene (**36**) (14.5 min.), and unidentified material that could be the double-bond isomer of the starting material presumably derived by isomerization prior to the cyclization. No hydrocarbon fractions which correspond to 1-benzyl-1-cyclopentene (**38**) (retention time, 8.2





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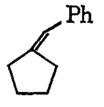

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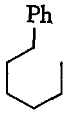

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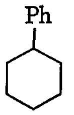

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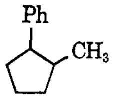

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[24] Anti-Markovnikov protonation might be occurring in the biogentic cyclization.[20]

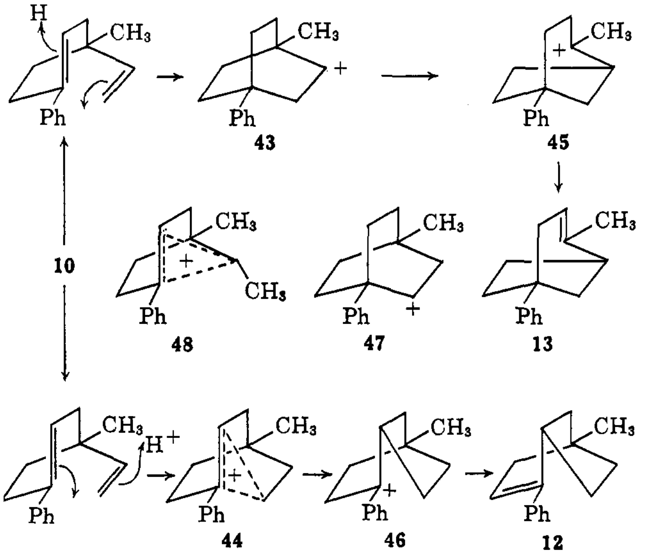
[25] H. Levy and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 1684 (1944).

min.) or benzylidenecyclopentane (**39**) (retention time, 15.1 min.) were detected. The mixture was hydrogenated over Urushibara nickel catalyst and the product was analyzed quantitatively by vapor phase chromatography over an Apiezon L column to have the following composition (together with retention times at 210°): 65% of 1-phenylhexane (**40**) (7.0 min.), 9% of 1-methyl-2-phenylcyclopentane (**42**) (9.3 min.), and 26% of 1-phenylcyclohexane (**41**) (11.1 min.). The identities of hydrocarbons **40**, **41**, and **42** were confirmed by isolation of the appropriate fractions by preparative vapor phase chromatography and comparison of their infrared spectra and other physical constants with those of authentic specimens. 1-Phenyl-1-cyclohexene (**36**) was presumably produced not directly from **33** but either from **34** or **35**.

It is well known[18] that an acid-catalyzed cyclization of 1,5-dienes generally gives a six-membered ring. Proton addition at C-2 of 1-phenyl-1,5-hexadiene (**33**) would result in the formation of a mixture of 3-phenyl-1-cyclohexene (**34**) and 4-phenyl-1-cyclohexene (**35**). It is mechanistically significant, however, that the cyclization of 1-phenyl-1,5-hexadiene (**33**) afforded 1-methyl-2-phenyl-1-cyclopentene (**37**). First of all, the formation of **37** evidenced that the cyclization was, in part, initiated by the protonation of a terminal double bond of **33**, and, secondly, a five-membered ring was formed.

The dependence on ring size in the cyclization reaction is determined by an interplay of several quantities[19d,26] and in the over-all result the acid-catalyzed cyclization of 1,5-dienes generally leads to the formation of six-membered rings.[18,19] It should be noted, however, that, if the electronic effect of stabilizing the intermediate carbonium ions is favorable for the formation of a five-membered ring in an acid-catalyzed cyclization of 1,5-dienes, the over-all ease of ring formation as a function of ring size (six *vs.* five) may be reversed and results in the predominant formation of five-membered rings.[27] Five-membered rings have been obtained in the acid-catalyzed cyclization of 1,5-hexadien-3-ones[31] (Nazarov cyclization), of 2,7-dimethyl-2,6-octadiene,[32] of artemisia ketone,[33] and of allene derivatives.[34] In all cases the intermediate cyclopentyl carbonium ions are electronically stabilized. A mechanism of the formation of five-membered rings in the cyclization of 1-phenyl-1,5-hexadiene (**32**) and in the Nazarov cyclization could be rationalized which simply involves the Markovnikov addition of a proton to a terminal double bond.

If one assumes that the cyclization of 4-methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**) is initiated by the protonation at both double bonds as was the case in the cyclization of 1-phenyl-1,5-hexadiene (**32**) as described above, that an electronic delocalization from a junction-forming ring double bond can stabilize the developing primary carbonium ion at the terminal carbon atom leading to bicyclo[2.2.2]octyl bridged ion (**44**) as Winstein[12] suggested in the case of the acetolysis of 2-(3-cyclohexenyl)ethyl *p*-bromobenzenesulfonate,[35-38] and that an alternative cation **48** that could be derived by a Markovnikov addition of a proton to the terminal double bond of **10** requires greater activation energy because of increased ring strain,[39] then one might illustrate a mechanism as depicted below.



Alternative mechanisms involve 1,2-hydride shift of cation **43**, *i.e.*, **10** → **43** → **47** → **46** → **12**, or Cope rearrangement prior to the cyclization. Those mechanisms would not account for the formation of 5-

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(26) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(27) Although relative ease of ring formation as a function of ring size (six *vs.* five) are somewhat different in radical and cationic cylizations, *e.g.*, cyclization of the 5-hexen-1-yl radicals[28] yielded five-membered rings, whereas cyclization of the 5-hexen-1-yl cation[29] gave a cyclohexane ring, a similar electronic effect stabilizing the intermediate radicals appears to be important in determining the ring size in radical cyclization.[30]

(28) C. Walling and M. S. Pearson, *J. Am. Chem. Soc.*, **86**, 2262 (1964); R. C. Lamb, P. W. Ayers, and M. K. Joney, *ibid.*, **85**, 3483 (1963); N. O. Brace, *ibid.*, **86**, 523 (1964).

(29) P. D. Bartlett, *Ann. Chem.*, **653**, 45 (1962).

(30) M. Julia, J. M. Surzm, and L. Katg, *Compt. rend.*, **251**, 1030 (1960); M. Julia and F. Legoffice, *ibid.*, **255**, 714 (1962); M. Julia, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 3 (1964).

(31) I. N. Nazarov and L. N. Pinkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 633 (1964); *Chem. Abstr.*, **42**, 7731 (1948). For the mechanism of the Nazarov cyclization, see I. N. Nazarov, I. I. Zaretskaya, Z. N. Parnes, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 519 (1953); *Chem. Abstr.*, **48**, 9930 (1954); E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1430 (1952).

(32) P. G. Stevens and S. C. Spalding, Jr., *J. Am. Chem. Soc.*, **71**, 1687 (1949).

(33) A. Eschenmoser, H. Schinz, R. Fischer, and J. Colonge, *Helv. Chim. Acta*, **34**, 2329 (1951).

(34) W. Kimel, *et al.*, *J. Org. Chem.*, **22**, 1611 (1957); **23**, 153 (1958); O. Isleu, *et al.*, *Helv. Chim. Acta*, **41**, 160 (1958); Y. R. Naves, *et al.*, *Bull. soc. chim. France*, 1213 (1957).

(35) The evidence for the existence of the bicyclo[2.2.2]octyl bridged ion[36] has been reported by Walborsky[37a] and Berson,[37b] and their associates. P. v. R. Schleyer [*J. Am. Chem. Soc.*, **86**, 1856 (1964)] predicted that bicyclo-[2.2.2]octyl bridged ion must be of energy nearly comparable with a corresponding classical ion.

(36) This concept has been questioned and an alternative structure of rapidly equilibrating simple ions have been advanced: H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–158, 174–178 [*cf.* however, S. Winstein and R. Baker, *J. Am. Chem. Soc.*, **86**, 2071 (1964)]; H. C. Brown and F. J. Chloupek, *ibid.*, **85**, 2322 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963) [*cf.* however, S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963)]; H. C. Brown, F. J. Chloupek, and M. H. Rei, *ibid.*, **86**, 1246, 1247, 1248, 5004, 5008 (1964).

(37) (a) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3214 (1963); (b) J. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

(38) The fact that acetolysis of 2-(3-cyclohexenyl)ethyl *p*-bromobenzenesulfonate gave 80% of cyclization products and 20% of the product of direct substitution,[11,12] while acetolysis of 5-hexen-1-yl *p*-nitrobenzenesulfonate furnished a mixture consisting of 25% of cyclohexylacetate and 75% of hexenylacetate[29] might suggest that the double-bond participation in cyclohexenylethyl system would be greater than that in hexenyl system.

(39) For the similar steric effects, see J. A. Berson, "Molecular Rearrangements," part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, 1963, pp. 120, 183.

methoxy-2-methylbicyclo[3.2.1]oct-2-ene (7) as a sole product in the case of cyclization of 1-methoxy-4-methyl-4-vinyl-1-cyclohexene (6). The mechanism of cyclization of 6 would not involve the protonation at the terminal double bond, since the proton would preferentially add to the strongly nucleophilic center in an enol ether group.

Experimental[40]

4-(1-Hydroxyethyl)-4-methyl-1-cyclohexanone (3a).—A mixture of 15.4 g. (0.1 mole) of 4-acetyl-4-methyl-1-cyclohexanone (1),[7] 17.4 g. (0.2 mole) of morpholine, and 50 ml. of benzene was heated at reflux using a Bidwell–Sterling moisture trap to collect the water of reaction. After 16 hr., the slight excess of the calculated amount of water had collected in the trap. The solvent and excess morpholine was evaporated and the residue was distilled *in vacuo*, giving 21.7 g. (97.4%) of monoenamine, b.p. 130–135° (1 mm.), $\nu_{\max}^{\text{film}}$ 1650 cm.$^{-1}$. To a suspension of 1.4 g. (1.5 molar equiv.) of lithium aluminum hydride in 230 ml. of dry ether was added dropwise 21.7 g. of the enamine prepared above in 200 ml. of dry ether under a nitrogen atmosphere with stirring during a period of 0.5 hr. After the completion of the addition, stirring was continued further for 24 hr. The reaction mixture was decomposed by the addition of 50 ml. of water followed by that of 50 ml. of 6 *N* sulfuric acid and the mixture was stirred for 10 min. The ethereal layer was separated and the water layer was extracted with ether. The combined ethereal extracts were dried over anhydrous sodium sulfate and the solvent was evaporated. Distillation of the residue *in vacuo* afforded 13.5 g. (89%) of 4-(1-hydroxyethyl)-4-methyl-1-cyclohexanone (3), b.p. 103–104° (1 mm.), $n^{20}\mathrm{D}$ 1.4870, $\nu_{\max}^{\text{film}}$ 3445 (OH) and 1709 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.12; H, 10.42.

The **3,5-dinitrobenzoate** melted at 122–123° (from ethanol).

Anal. Calcd. for $C_{16}H_{18}N_2O_7$: C, 54.84; H, 5.18; N, 8.00. Found: C, 54.94; H, 5.34; N, 7.74.

4-(1-Acetoxyethyl)-4-methyl-1-cyclohexanone (3b).—To 20 g. of 4-(1-hydroxyethyl)-4-methyl-1-cyclohexanone (3a) was added 120 ml. of acetic anhydride and 12 ml. of dry pyridine and the mixture was heated at 100° for 12 hr. Distillation of the reaction mixture *in vacuo* furnished 24 g. (94.5%) of **3b**, b.p. 113° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4662, $\nu_{\max}^{\text{film}}$ 1715–1735 and 1243 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.40; H, 9.35.

4-Methyl-4-vinyl-1-cyclohexanone (4).—Twenty grams of 4-(1-acetoxyethyl)-4-methyl-1-cyclohexanone (3b) was dropped into a 1-cm.-diameter quartz tube heated with a 30-cm.-long electric furnace at 560° during a period of 28 min. with a nitrogen stream of 100 cc./min. The decomposition product was diluted with 50 ml. of ether, washed successively with saturated sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation of the residue *in vacuo* gave 5.7 g. (42%) of 4-methyl-4-vinyl-1-cyclohexanone (4): b.p. 114–118° (40 mm.); $n^{20}\mathrm{D}$ 1.4710; $\nu_{\max}^{\text{film}}$ 1719 (C=O), 1644, 1009, and 913 cm.$^{-1}$ (—CH=CH$_2$).

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.16.

The **semicarbazone** had m.p. 191°.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.40; H, 8.85; N, 21.45.

1,1-Dimethoxy-4-methyl-4-vinylcyclohexane (5).—To a stirred mixture of 4.64 g. (33.6 mmoles) of 4-methyl-4-vinyl-1-cyclohexanone (4), 6.88 g. (64.8 mmoles) of trimethyl orthoformate, and 30 ml. of methanol was added 3 drops of concentrated sulfuric acid. The reaction was exothermic and a red color developed. Stirring was continued at room temperature for 1 hr. and then sodium methoxide in methanol was added until the red color disappeared. After the removal of methanol and methyl formate *in vacuo*, ether was added and the precipitated solid was removed by filtration. Evaporation of the solvent and distillation of the residue *in vacuo* afforded 5.07 g. (82%) of **5**: b.p. 92–95° (16 mm.) or 212–213° (760 mm.); $\nu_{\max}^{\text{film}}$ 2850, 1109, 1062 (OCH$_3$), 1643, 1003, and 916 cm.$^{-1}$ (—CH=CH$_2$).

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94; mol. wt., 184. Found: C, 71.65; H, 10.93; mol. wt., 184.5.

1-Methoxy-4-methyl-4-vinyl-1-cyclohexene (6).—A mixture of 2.64 g. (14.3 mmoles) of 5, 10.6 ml. of acetic anhydride, and 3.6 ml. of pyridine was heated at reflux for 15 hr. and then slowly distilled until the boiling point reached 130° and distillation ceased. It took about 5 hr. The residue was distilled *in vacuo* to furnish 1.16 g. (53%) of **6**: b.p. 92° (30 mm.); $\nu_{\max}^{\text{film}}$ 2840 (OMe), 1672 (enol ether double bond), 1001, and 915 cm.$^{-1}$ (—CH=CH$_2$). This material was contaminated with a trace of ketone 4 (shown by v.p.c.).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59; mol. wt., 152. Found: C, 78.06; H, 10.43; mol. wt., 163.

Cyclization of 1-Methoxy-4-methyl-4-vinyl-1-cyclohexene (6).—To a stirred mixture of 801 mg. (5.64 mmoles) of boron trifluoride etherate in 40 ml. of dry benzene was added a solution of 398 mg. (2.62 mmoles) of 6 in 40 ml. of benzene during a period of 40 min. The mixture was heated at reflux for 20 hr. and then sodium methoxide in methanol was added until the red color disappeared. The precipitated solid was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was distilled *in vacuo* to furnish 313 mg. (79%) of 5-methoxy-2-methylbicyclo[3.2.1]oct-2-ene (7): b.p. 102–103° (42 mm.), 94–95° (28 mm.); $n^{20}\mathrm{D}$ 1.4800; $\nu_{\max}^{\text{film}}$ 2839 and 1114 (OMe) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59; mol. wt., 152. Found: C, 78.84; H, 10.60; mol. wt., 152 (mass spectrometry).

4-Methoxy-1-methylbicyclo[2.2.2]octan-2-ol (9).—To a solution of 3.0 g. of lithium aluminum hydride in 300 ml. of dry ether was added a solution of 20.0 g. of 4-methoxy-1-methylbicyclo-[2.2.2]octan-2-one (8) during a period of 3 hr. and the mixture was heated at reflux for 45 min. After the usual work-up, the residue was distilled *in vacuo* to give 18.4 g. (91%) of 9, b.p. 118.5° (4 mm.), $n^{20}\mathrm{D}$ 1.4910.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.25; H, 10.72.

The **acetate** had b.p. 119–121° (7 mm.), $n^{20}\mathrm{D}$ 1.4690.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.75; H, 9.54.

The ***p*-nitrobenzoate** had m.p. 137.5°.

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 63.93; H, 6.63; N, 4.39. Found: C, 63.99; H, 6.69; N, 4.40.

4-Methoxy-1-phenylbicyclo[2.2.2]octan-2-ol.—Lithium aluminum hydride reduction of 4-methoxy-1-phenylbicyclo[2.2.2]-octan-2-one[2] was carried out in the same way as described above to afford 93% of 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-ol, m.p. 122–123° [from ether–petroleum ether (b.p. 35–45°)].

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.65.

Dehydration of 4-Methoxy-1-methylbicyclo[2.2.2]octan-2-ol (9).—4-Methoxy-1-methylbicyclo[2.2.2]octan-2-ol (9, 1.6 g.) was dropped into a 1-cm.-diameter quartz tube filled with activated alumina pellets and heated with a 30-cm.-long electric furnace at 200° during a period of 2 min. with a nitrogen flow of 150 cc./min. The decomposition product was diluted with petroleum ether (b.p. 35–45°), dried over anhydrous sodium sulfate, and concentrated. The residue was chromatographed on 100-mesh silicic acid (Mallinckrodt Chemical Works). Elution with chloroform and distillation gave 5-methoxy-2-methylbicyclo[3.2.1]oct-2-ene (7), b.p. 102° (41 mm.). The n.m.r. and infrared spectra were identical with those of material obtained by cyclization of 6.

4-Methoxy-1-methylbicyclo[2.2.2]octan-2-one Tosylhydrazone.—To a mixture of 2.417 g. (14.4 mmoles) of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one and 2.679 g. (14.4 mmoles) of *p*-toluenesulfonylhydrazine in 10 ml. of ethyl alcohol was added 20 ml. of ethyl alcohol containing 1% of concentrated hydrochloric acid, and the mixture was heated at reflux for 30 min. After cooling, crystalline material was collected by filtration. Recrystallization from ethyl alcohol furnished 3.968 g. of the tosylhydrazone, m.p. 195.5–196°.

Anal. Calcd. for $C_{17}H_{24}N_2O_3S$: C, 60.68; H, 7.18; N, 8.37. Found: C, 60.48; H, 7.20; N, 8.38.

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[40] All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer. Ultraviolet spectra were recorded on a Cary 14 recording spectrophtometer. N.m.r. spectra were obtained with either a Varian DP-60, A-60, or HR-100 *instrument using carbon tetrachloride as a solvent and tetramethylsilane as* the internal standard. Vapor chromatography was performed with a Yanagimoto GCG 220 for the analytical and with a Beckman Megachrom GC-100 for the preparative purpose. Molecular weight was determined with Mechrolab vapor pressure osmometer, Model 301. Mass spectra were recorded on a Hitachi Model RMU-6A mass spectrophotometer.

Other tosylhydrazones were prepared in a same way as described above. **4-Isopropoxybicyclo[2.2.2]octan-2-one tosylhydrazone**[41] had m.p. 175.5–176.5° (from ethanol).

Anal. Calcd. for $C_{18}H_{26}N_2O_3S$: C, 61.69; H, 7.48; N, 7.99. Found: C, 61.76; H, 7.52; N, 7.99.

4-Methoxy-1-phenylbicyclo[2.2.2]octan-2-one tosylhydrazone had m.p. 187° (from ethanol).

Anal. Calcd. for $C_{22}H_{26}N_2O_3S$: C, 66.30; H, 6.58; N, 7.03. Found: C, 66.21; H, 6.56; N, 7.11.

4-Methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**).—To a vigorously stirred solution of phenylmagnesium bromide in tetrahydrofuran, prepared from 9.1 g. (0.373 g.-atom) of magnesium ribbon, 58.5 g. (0.373 mole) of phenyl bromide, and 150 ml. of dry tetrahydrofuran, was added dropwise 23.2 g. (0.149 mole) of **3a** in 30 ml. of dry tetrahydrofuran during a period of 1 hr. with ice-bath cooling. Being stirred further for 1 hr., the reaction mixture was decomposed by the addition of 100 ml. of saturated ammonium chloride solution and 100 ml. of water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and concentrated. Distillation of the residue *in vacuo* gave 20.8 g. of a colorless liquid, b.p. 132–167° (2 mm.), which was presumably a mixture of 4-(1-hydroxyethyl)-4-methyl-1-phenyl-1-cyclohexanol and 4-(1-hydroxyethyl)-4-methyl-1-phenyl-1-cyclohexene, deduced from the analytical data.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 80.07; H, 9.47.

A stirred mixture of 18.1 g. of material obtained above, 120 ml. of acetic anhydride, and 2 g. of *p*-toluenesulfonic acid was heated at 95–100° overnight. Distillation of the reaction mixture *in vacuo* gave 19.2 g. of an acetylated mixture, b.p. 122–139° (1 mm.), which was thermally decomposed. The material was dropped into a 1-cm.-diameter quartz tube heated with a 30-cm.-long electric furnace at 550° during a period of 18 min. with a nitrogen stream of 140 cc./min. The decomposition product was diluted with 50 ml. of ether and washed successively with saturated sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation of the residue *in vacuo* gave a product with b.p. 95–107° (1 mm.). This was chromatographed over activated 100-mesh alumina (Sumitomo Chemical Co.) prepared in petroleum ether. Elution with petroleum ether gave 5.74 g. of crude **10**. Distillation of it gave pure **10** with b.p. 109–110° (3 mm.), $n^{25}{}_D$ 1.5532.

Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.73; H, 9.11.

Pyrolysis of the corresponding xanthate gave lower yields of the desired **10**.

When 20.8 g. of the acetylated mixture was decomposed at 500° during a period of 3 hr. and the product was chromatographed, **11** was obtained. The fractions (3.2 g.) eluted with petroleum ether were a mixture of at least six compounds. Fractions (1.8 g.) eluted with ether consisted mainly of **3,4-dimethyl-1-phenyl-2-oxabicyclo[2.2.2]octane** (**11**). Distillation of the crude material gave 1.2 g. of pure **11**, b.p. 110–113° (3 mm.), $n^{25}{}_D$ 1.5350.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32; mol. wt., 216. Found: C, 83.66; H, 9.13; mol. wt., 213.

The structure of **11** was assigned by its n.m.r. spectrum [τ 9.24 (bridgehead methyl protons), 8.85 (doublet, J = 9 c.p.s., methyl protons), and quartet centered at 6.15 (J = 6 c.p.s., a proton on a carbon atom adjacent to an oxygen atom)].

Cyclization of 4-Methyl-1-phenyl-4-vinyl-1-cyclohexene (**10**).—To a solution of 0.8 g. (0.004 mole) of **10** in 40 ml. of dry benzene, was added 2 g. (0.013 mole) of boron trifluoride etherate and the mixture was heated at reflux for 3 hr. Then the mixture was cooled and washed successively with water, saturated sodium bicarbonate solution, and water, and dried over anhydrous sodium sulfate. Evaporation of the solvent and distillation of the residue *in vacuo* afforded 0.5 g. of a mixture of **12** and **13**, b.p. 110–111° (3 mm.), $n^{20}{}_D$ 1.5575. Its n.m.r. and mass spectra are reproduced in Figures 2 and 4, respectively. The infrared spectrum of the product shows the disappearance of the terminal double bond (907 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15; mol. wt., 198. Found: C, 90.62; H, 9.10; mol. wt., 193 (osmometry).

Thin layer chromatography of the product over silicic acid coated with 10% silver nitrate (elution with petroleum–ether, b.p. 35–55°) showed two spots, R_f 0.88 (pink) and 0.80 (brown) (50% sulfuric acid as a spray reagent).

Ozonolysis of the Cyclization Product of 10.—Ozone was passed through a solution of 0.22 g. of the cyclization product described above in 80 ml. of methylene chloride at −78° for 15 min. The ozonized mixture was added to a stirred suspension of 2 g. of zinc dust in 50 ml. of acetic acid and the mixture was stirred at room temperature for 1 hr. Solid was removed by filtration and the cake was washed with methylene chloride. The combined filtrate and washings were washed successively with water, saturated bicarbonate solution, and water. The organic layer was dried over anhydrous sodium sulfate. Removal of the solvent gave 0.15 g. of a yellow oil, λ^{EtOH}_{max} 242.5 mμ, (ϵ 2700), ν^{film}_{max} 1693 (shoulder) and 1718 cm.$^{-1}$. An iodoform test of the product was positive.

Cyclization of 1-Phenyl-1,5-hexadiene (**33**).—To a solution of 10 g. (0.063 mole) of **33**[25] in 2 l. of dry benzene, was added 10.8 g. (0.076 mole) of boron trifluoride etherate, and the mixture was heated at reflux for 24 hr. Then, the benzene solution was concentrated to *ca.* 500 ml. and a further 10.8 g. (0.076 mole) of boron trifluoride etherate was added to the concentrate. The mixture was heated at reflux for a further 16 hr. After cooling, the mixture was poured onto ice–water and extracted with ether. The ether extract was washed successively with saturated sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled *in vacuo*, giving 6.19 g. of material, b.p. 94–99.5° (12 mm.), $n^{20}{}_D$ 1.5490. The balance of the product was of higher boiling material.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92; mol. wt., 158.2. Found: C, 90.87; H, 8.82; mol. wt., 158.3 (osmometry).

It was analyzed by vapor phase chromatography over a polyethylene glycol 6000 column at 203°, and peaks were compared with those of authentic specimens, prepared by known procedures.[42-46] The product consisted of 1-methyl-2-phenyl-1-cyclopentene (**37**),[42] 3-phenyl-1-cyclohexene (**34**),[44] 4-phenyl-1-cyclohexene (**35**),[45] 1-phenyl-1-cyclohexene (**36**),[46] and unidentified material. Neither 1-benzyl-1-cyclopentene (**38**)[44] nor benzylidenecyclopentane (**39**)[44] was detected in the product.

Reduction of the Cyclization Mixture.—To a solution of 5.58 g. of the cyclization product of the experiment described above in 100 ml. of ethanol was added Urushihara nickel (U-Ni-A), prepared[47] from 4 g. of $NiCl_2 \cdot 6H_2O$ and 10 g. of zinc dust and digested with 20% acetic acid, and the mixture was hydrogenated at room temperature and at slightly above atmospheric pressure. After 5 hr. 1456 cc. (1.66 molar equiv.) of hydrogen gas was absorbed. The catalyst was removed by filtration and the mixture was concentrated. Distillation of the residue *in vacuo* gave 4.80 g. of a fraction boiling at 83–88° (2 mm.). This was analyzed by vapor phase chromatography over an Apiezon L column at 210° and the peaks were compared with those of the authentic substances. The yields of products were 65% of 1-phenylhexane (**40**),[48] 9% of 1-methyl-2-phenylcyclopentane (**42**),[43] and 26% of phenylcyclohexane (**41**).[49] The separation of the mixture by a preparative vapor phase chromatography afforded 2.30 g. of 1-phenylhexane (**40**), $n^{20}{}_D$ 1.4873 (lit.[48] $n^{25}{}_D$ 1.4872); 0.18 g. of 1-methyl-2-phenylcyclopentane (**42**), $n^{20}{}_D$ 1.5239 (lit.[43] $n^{20}{}_D$ 1.5238); and 0.87 g. of phenylcyclohexane (**41**), $n^{20}{}_D$ 1.5261 (lit.[49] $n^{18}{}_D$ 1.5274). Identities were established by comparison of the infrared spectra and v.p.c. retention times of those with authentic specimens.

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(41) 4-Isopropoxybicyclo[2.2.2]octan-2-one was prepared by an acid-catalyzed cyclization of 4-acetyl-1-methoxy-1-cyclohexene in isopropyl alcohol. The detail of this and related reactions will be reported shortly by K. Morita and T. Kobayashi.

(42) Prepared according to the method of Plate,[43] *et al.*, and purified by a preparative vapor phase chromatography. It exhibited $n^{20}{}_D$ 1.5622 (no refractive index was given in ref. 43). Its structure was confirmed by n.m.r. spectrum (no olefinic proton).

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(47) S. Taira, *Bull. Chem. Soc. Japan.*, **34**, 1294 (1961).

(48) I. Simon, *Bull. soc. chim. Belges*, **38**, 53 (1929); *Chem. Abstr.*, **23**, 4440 (1929).

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