[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. XVII. Products and Rates of Solvolysis of Cycloöctenyl Derivatives[1,2]

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The study of proximity effects in cycloöctane derivatives has been extended to compounds containing double bonds in the eight-membered ring. The products of solvolysis of 4-cycloöcten-1-yl brosylate, 3-cycloöcten-1-yl brosylate, 3-bromocyclooctene and cycloöctyl brosylate in acetic acid containing sodium acetate were studied. First-order rate constants for the solvolysis of these compounds and for the solvolysis of cycloöctyl bromide were determined. 4-Cycloöcten-1-yl brosylate yielded bridged compounds having the bicyclo[3.3.0]octane ring system as the major solvolysis products, while 3-cyclo-octen-1-yl brosylate formed bicyclo[5.1.0]octan-2-ol as a principal product. Although 4-cycloöcten-1-yl brosylate gave bridged products that might arise from double bond participation, its solvolysis rate was only about one-sixtieth that of cycloöctyl brosylate. Syntheses of 3-cycloöcten-1-ol and 4-cycloöcten-1-ol were developed. The products of reaction of formic acid with 1,5-cycloöctadiene were studied, and *trans*-2-vinylcyclohexanol was identified as one of them.

Other papers in this series have described reactions in which hydrogen atoms on an eight-membered ring enter into unusual reactions because they are held in proximity to an activating group located across the ring. A somewhat comparable example of reactions influenced by the spatial proximity of an activating group is to be found in cases in which a double bond, usually in the homoallylic position, participates in carbonium ion reactions. The most familiar cases of double bond participation of this type are in the norbornenyl and cholesteryl systems, although cases of participation of double bonds more remotely situated from the initially formed carbonium ion have now been demonstrated in certain acid-catalyzed cyclization reactions.[4] In the solvolysis of homoallylic tosylates, double bond participation gives rise to enhanced rates of solvolysis and to retention of configuration in the product formed by reaction of intermediate carbonium ion with solvent,[5] while in the acid-catalyzed cyclizations referred to above steric control of the course of reaction is the only consequence of double bond participation that has been demonstrated.[4] Since the various cycloöctenols possess double bonds that are held in proximity of the hydroxyl group, it was of interest to investigate the solvolysis of the corresponding tosylates or brosylates. The present paper reports such a study for the brosylates of 3-cycloöcten-1-ol, the homoallylic alcohol in the series, and 4-cycloöcten-1-ol, in which the double bond is one carbon atom further removed from the brosylate group. Attempts to prepare the brosylate of the allylic alcohol 2-cycloöcten-1-ol using *p*-bromobenzenesulfonyl chloride in pyridine failed, probably because of reaction of the initially formed brosylate with pyridine. Since the allylic brosylate would be expected to be extremely unstable, the less reactive bromide, 3-bromocycloöctene, was studied instead. Although 3-cycloöcten-1-ol and 4-cycloöcten-1-ol have been reported,[6,7] their preparation in quantity required a new series of reactions, described below.

Addition of Formic Acid to 1,5-Cycloöctadiene; Preparation of 4-Cycloöcten-1-ol.—4-Cycloöcten-1-ol was prepared in 20% yield by addition of one mole of formic acid to *cis-cis*-1,5-cycloöctadiene in the presence of perchloric acid.[8] Success of the preparation depended upon careful distillation of the reaction mixture after saponification, to remove the lower boiling components described below, followed by separation of the 4-cycloöcten-1-ol from saturated alcohols by extraction of the former into 20% aqueous silver nitrate. Since the addition of formic acid to 1,5-cycloöctadiene may be considered to proceed *via* the same intermediate carbonium ion as the 4-cycloöcten-1-yl brosylate solvolysis described later (cf. Fig. 1), study of the reaction products other than 4-cycloöcten-1-ol was of interest.

No glycol fraction was found upon distillation of the products after saponification. Conditions presumably favored the formation of glycols, since the mixture was originally present in two phases and became homogeneous as the reaction proceeded, giving rise to a higher concentration of monoformate than of diene in the formic acid layer. Indeed, it is reported,[9] and we have verified, that the perchloric acid-catalyzed addition of formic acid to 4-vinylcyclohexene under similar conditions gives a glycol fraction, as well as an unsaturated alcohol fraction, when the saponified reaction products are distilled. It is likely that failure of the 4-cycloöcten-1-yl formate to add a second mole of formic acid is partly due to the strain attending the conversion of a cycloöctene derivative to a compound containing a completely saturated eight-membered ring, as discussed further when the solvolysis of 4-cycloöcten-1-yl brosylate is described.

Protonation of the double bond of 4-cycloöcten-1-yl formate (or the alcohol) may lead to products other than a glycol. In particular, a mixture of 1,4- and 1,5-epoxycycloöctane was isolated from the lower boiling distillation fractions of the re-

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[1] Supported in part by a research grant (NSF-G5505) of the National Science Foundation.

[2] Paper XVI, A. C. Cope, J. M. Grisar and P. E. Peterson, THIS JOURNAL, **81**, 1640 (1959).

[3] National Institutes of Health Postdoctoral Fellow, 1956–1958.

[4] A. Eschenmoser, P. A. Stadler, A. Nechvatal and A. J. Frey, *Helv. Chim. Acta*, **40**, 1373 (1957).

[5] E. M. Kosower and S. Winstein, THIS JOURNAL, **78**, 4347, 4354 (1956).

[6] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons and G. W. Wood, *ibid.*, **79**, 3900 (1957).

[7] A. C. Cope and B. C. Anderson, *ibid.*, **79**, 3892 (1957).

[8] H. B. Knight, R. E. Koos and D. Swern, *ibid.*, **75**, 6212 (1953).

[9] R. C. Kuder, U. S. Patent 2,764,610, September 25, 1956; *C. A.*, **51**, 4420 (1957).

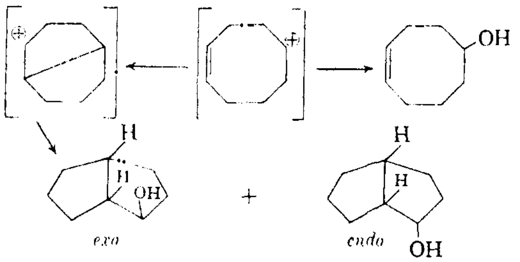

Fig. 1. Alcohols from 1,5-cycloöctadiene.

action mixture, and could arise from such a reaction path, as shown in Fig. 2. The other products are presumably a proton if the alcohol is the intermediate, or carbon monoxide and a proton

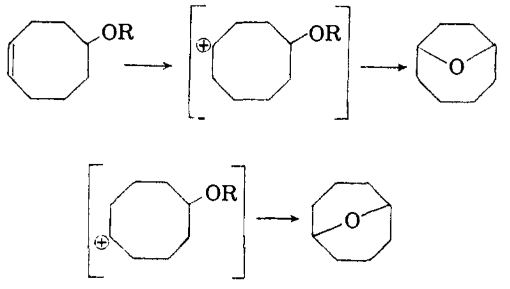

Fig. 2.—Epoxycycloöctanes from 1,5-cycloöctadiene; R = H or CHO.

if the formate is the intermediate. Cycloöctanone was isolated from the lower boiling distillation fractions in less than 1% yield as the 2,4-dinitrophenylhydrazone; this product may be formed by protonation of the double bond of 4-cycloöcten-1-ol or 4-cycloöcten-1-yl formate. This possibility is illustrated in Fig. 3, in which the cycloöctanone (or its enol formate) is formulated as arising from a 1,5-transannular hydride shift in the protonated intermediate. The conversion of 1-methyl-1,6-cyclodecanediol to 6-methylcyclodecanone *via* a 1,6-hydride shift has been reported, and confirmed by deuterium labeling.[10]

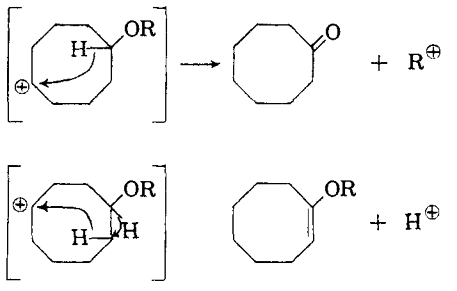

Fig. 3.—Cycloöctanone from 1,5-cycloöctadiene; R = H or CHO

In addition, a saturated alcohol mixture (16%, calculated as $C_8H_{14}O$) was formed in the addition of formic acid to 1,5-cycloöctadiene and was separated from 4-cycloöcten-1-ol by silver nitrate extraction. As described in the Experimental section, the saturated alcohol fraction was shown by gas chromatography and by oxidation to the ketone to contain *exo*-bicyclo[3.3.0]octan-2-ol (the major component), probably some *endo*-bicyclo[3.3.0]octan-2-ol, and two unidentified alcohols.

Gas chromatography of the lower boiling distillation fractions gave, in addition to the 1,4- and 1,5-epoxycycloöctane already mentioned, an unsaturated alcohol identical with the unknown unsaturated alcohol obtained earlier from the solvolysis of *cis*-cycloöctene oxide.[6] The alcohol was identified as *trans*-2-vinylcyclohexanol by catalytic addition of one mole of hydrogen, forming *trans*-2-ethylcyclohexanol, and by the absence of a C-methyl group, which is sufficient to show the position of the double bond. Further details appear in the Experimental section. The *trans*-2-vinylcyclohexanol is formulated in Fig. 4 as arising from a hydride shift in the 4-cycloöcten-1-yl carbonium ion to give an intermediate 3-cycloocten-1-yl carbonium ion. Experiments which support such a formulation will be described in a later paper.[11] It is interesting to note that the over-all process may be regarded as the conversion of one homoallylic carbonium ion to another, and that the *trans*-stereochemistry of the product would be predicted if the p-electrons of the double bond in the vinyl group "participate" in the stabilization of the carbonium ion, in a manner analogous to the participation that occurs in reactions of the norbornenyl and cholesteryl cations. The possibility that *cis*-2-vinylcyclohexanol was present in considerable amount in the original reaction mixture is unlikely as judged from gas chromatography of the product.

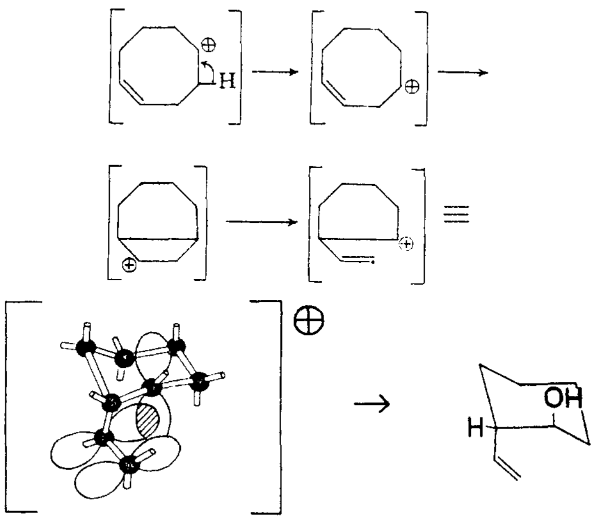

Fig. 4.—*trans*-2-Vinylcyclohexanol from 1,5-cycloöctadiene.

Preparation of 3-Cycloöcten-1-ol.—From rate data in the literature[12] it was predicted that reaction of *cis-cis*-1,3-cycloöctadiene with peracids would give a monoepoxide fairly rapidly, followed by slower reaction to give a diepoxide. The monoepoxide was prepared in this way with peracetic acid containing sodium acetate in 64% yield. Reaction of the monoepoxide with lithium aluminum hydride resulted in breaking of the allylic carbon–oxygen bond to give 3-cycloöcten-1-ol in 85% yield. The other possible product, 2-cycloöcten-1-ol, was shown to be absent or present to an extent of less than 5% by gas chromatog-

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[10] V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956).

[11] J. Martin Grisar, unpublished work.

[12] K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

raphy. The preferential breaking of the allylic carbon–oxygen bond was expected on the basis of reported reactions.[13,14]

Solvolysis Products of 4-Cycloöcten-1-yl Brosylate, 3-Cycloöcten-1-yl Brosylate, 3-Bromocyclooctene and Cycloöctyl Brosylate.—The crystalline brosylates were solvolyzed in acetic acid containing excess sodium acetate to neutralize the *p*-bromobenzenesulfonic acid formed. The solvolysis products of 4-cycloöcten-1-yl brosylate were separated by distillation into a fraction containing elimination products (hydrocarbons, 19%) and a fraction containing substitution products (acetates, 35%). The distillation fractions were analyzed by gas chromatography and the identities of the components were confirmed by infrared spectra. The hydrocarbon fraction was found to consist of *cis*-bicyclo[3.3.0]oct-2-ene (64%), 1,4-cycloöctadiene (23%) and 1,5-cycloöctadiene (13%). *cis*-Bicyclo[3.3.0]oct-2-ene has not been described previously and accordingly a sample for comparison was obtained by phosphoric acid dehydration of a mixture of *cis-exo-* and *cis-endo*-bicyclo[3.3.0]octan-2-ol. The major component from the dehydration was separated by gas chromatography and its structure was proved by ozonolysis, followed by oxidation, which gave the known *cis*-2-carboxycyclopentaneacetic acid. The acetate fraction from the solvolysis of 4-cycloöcten-1-yl brosylate consisted of approximately 20% of 4-cycloöcten-1-yl acetate and 80% of saturated acetates. Gas chromatography of the alcohols obtained by hydrolysis of the acetate fraction showed that the saturated alcohols consisted of 60% of the less stable *endo*-bicyclo[3.3.0]octan-2-ol and 40% of the more stable *exo*-bicyclo[3.3.0]octan-2-ol. As discussed below, a completely concerted reaction would be expected to give the *endo* isomer.

The solvolysis of 3-cycloöcten-1-yl brosylate gave no hydrocarbon fraction. Saponification of the acetates followed by silver nitrate extraction gave some 3-cycloöcten-1-ol and a saturated alcohol, bicyclo[5.1.0]octan-2-ol, the latter being the major product. The assignment of structure to the saturated alcohol, reported in detail in the Experimental section, rests primarily upon oxidation of the alcohol to the ketone, identical with authentic bicyclo[5.1.0]octan-2-one. The ketone has an unusual double carbonyl peak with maxima at 1700 and 1675 cm.$^{-1}$, which may be due to the presence of two different conformations, only one of which possesses the steric features necessary for lowering the carbonyl frequency by conjugation with the cyclopropane ring.

The solvolysis products of cycloöctyl brosylate and 3-bromocycloöctene were the expected acetates and hydrocarbons. Cycloöctyl brosylate gave cycloöctanol (after saponification) and *cis*-cycloöctene containing less than 0.1% of *cis*-bicyclo[3.3.0]octane, which could arise from the influence of proximity effects in the saturated system. The products from 3-bromocycloöctene were 2-cycloöcten-1-ol and *cis-cis*-1,3-cycloöctadiene.

Rate Measurements.—The rate data obtained in the present investigation are summarized in Table I. The rates were determined under conditions similar to those used for the product studies, except that lower concentrations were employed. The added sodium acetate was shown to be necessary to prevent acid-catalyzed transformations of the primary solvolysis products in the case of 4-cycloöcten-1-yl brosylate.

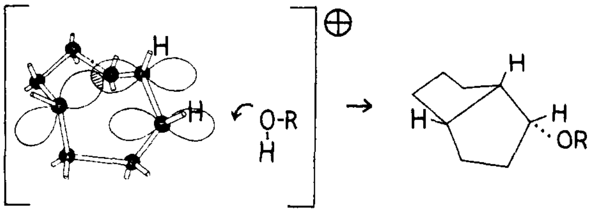
TABLE I

RATE CONSTANTS AND DERIVED DATA FOR SOLVOLYSIS OF BROSYLATES AND BROMIDES IN ACETIC ACID CONTAINING SODIUM ACETATE AND WATER

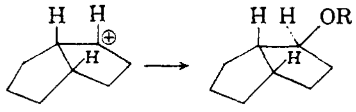
Compound	T, °C.	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$, at 70° (calcd.)	k/k cyclohexyl (70°)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
4-Cycloöcten-1-yl brosylate	37.4	0.349				
	54.4	3.20	23.22	2.9	26.6	+ 2.0
	73.4	34.4				
3-Cycloöcten-1-yl brosylate	24.9	41.7				
	37.4	154	2970	370	19.0	−13.4
Cycloöctyl brosylate	24.9	12.2				
	37.4	53.8	1484	185	21.0	− 3.9
	54.4	328				
3-Bromocyclooctene	37.4	0.283				
	73.4	22.2	15.3		25.2	− 2.9
	90.0	123				
Cycloöctyl bromide	73.4	0.384				
	90.0	2.56	0.255[a]		27.8	− 3.2
Cyclohexyl brosylate[b]	70.0	8.02	8.02		26.8	−10.4

[a] k (sec.$^{-1}$) at 100° was calculated to be 7.39 (10^{-5}).
[b] Data from ref. 17.

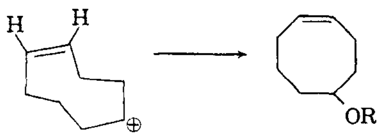
Discussion of Solvolysis Products and Rates.—As illustrated in Fig. 5, *trans* addition of acetic acid and of the positive center in the 4-cycloöcten-1-yl carbonium ion to the *cis* double bond already present in the molecule would give *endo*-bicyclo[3.3.0]oct-2-yl acetate as the bridged product. On the other hand, a planar bicyclo[3.3.0]oct-2-yl carbonium ion would be more likely to give the corresponding *exo*-acetate by approach of acetic acid from the less hindered *exo* position. The production



Non-classical ion or concerted cyclization *via* boat conformation; *cf.* Fig. 1.



planar carbonium ion



chair conformation

Fig. 5—Solvolysis of 4-cycloöcten-1-yl brosylate; R = CH_3CO.

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[13] T. A. Crabb and K. Schofield, *Chemistry & Industry*, 102 (1958).

[14] C. A. VanderWerf, R. Y. Heisler and W. E. McEwen, THIS JOURNAL, 76, 1231 (1954).

of a preponderance of the less stable[15] *endo* isomer in the solvolysis reported in this paper accordingly can best be interpreted as evidence for participation of the double bond in a concerted addition reaction or in formation of a bridged ion.

Rate measurements were made in order to determine whether such participation by the double bond would give rise to a pronounced enhancement of solvolysis rate as has been observed in various homoallylic systems. In fact, as seen from Table I, 4-cycloöcten-1-yl brosylate solvolyzed at a rate only one-sixtieth as fast as cycloöctyl brosylate. These results become meaningful only when allowance is made for the fact that the solvolysis rate of cycloöctyl brosylate is itself strongly enhanced over that of cyclohexyl brosylate, the latter being a suitable reference standard whose rate of solvolysis is comparable to that of acyclic brosylates. Although the possibility that the cyclooctyl brosylate rate enhancement is electronic in origin has been considered,[16] the alternative explanation[16,17] that the enhancement is due to relief of steric strain in the transition state for formation of a planar carbonium ion provides a good basis for explanation of our results. (In the discussion which follows a number of factors which must affect the solvolysis rates to some extent, such as inductive effects of double bonds and detailed conformational effects, have been ignored.) Thus it appears that introduction of only one double bond into a cycloöctane derivative is sufficient to relieve much of the strain in the molecule (part of which arises from several eclipsed hydrogen interactions). Accordingly, the solvolysis rate of 4-cycloöcten-1-yl brosylate would be similar to the rate for cyclohexyl brosylate in the absence of rate enhancement due to double bond participation. The relative rate of 2.9 reported in Table I indicates that little if any rate enhancement is found, which is in accord with the fact that the reaction is relatively non-stereospecific. However, addition of formic acid to 1,5-cycloöctadiene, which could proceed *via* a similar bridged ion or by concerted addition, did not exhibit even the partial stereospecificity found in the brosylate solvolysis, although other acid-catalyzed additions of formic acid are known to be stereospecific.[4]

Examination of models shows that the distances between the leaving brosyl group and the double bond may be almost the same for the brosylates of 3-cycloöcten-1-ol and of 4-cycloöcten-1-ol. Although a considerable fraction of the 4-cyclooctenl-1-yl brosylate in solution would presumably exist in a chair or crown conformation unsuitable for participation (*cf.* Fig. 5), the boat-like conformation shown in Fig. 5 also appears to be a favorable one. The chair forms might solvolyze to give 4-cycloöcten-1-yl acetate, as shown, but they presumably would be converted rapidly to the boat form if the latter disappeared in a fast reaction. From the data in Table I, 3-cycloöcten-1-yl brosylate solvolyzed 130 times more rapidly than the 4-cycloöcten-1-yl derivative at 70°. As in the case of 4-cycloöcten-1-yl brosylate solvolysis, the rate unassisted by double bond participation may be considered to be approximately the same as for cyclohexyl brosylate. The amount of double bond participation is then indicated by the rate enhancement by a factor of approximately 370 compared to cyclohexyl brosylate. Although the stereochemistry of the alcohol formed was not determined in this case, models again indicated that the *endo* isomer, *endo*-bicyclo[5.1.0]octan-2-ol is the predicted product from a concerted reaction (*cf.* Fig. 6).

Since the entire discussion of rates is based upon the assumption that an eight-membered ring containing one double bond has much of its medium-sized ring strain relieved, it should be stated that other chemical evidence also favors such a hypothesis. Thus it is possible to prepare 4-cycloöcten-1-yl bromide in good yield by addition of hydrogen bromide to 1,5-cycloöctadiene,[12] indicating that addition of a second mole of hydrogen bromide to the 5-bromocycloöctene is somewhat slower, presumably because of the strain attending the formation of the completely saturated compound. Other reactions of 1,5-cycloöctadiene appear to follow the same pattern, including hydrogenation in the presence of palladium,[12,18] epoxidation,[19] and the addition of formic acid, mentioned earlier in this paper.

Although the heats of hydrogenation of the cycloöctadienes are not available, the heat of hydrogenation of cycloöctatetraene is much greater than four times the heat of hydrogenation of *cis*-cycloöctene, probably because of the strain involved in converting cycloöctene to cycloöctane.[20] It is of interest to note that a similar stabilization of other medium-sized rings might occur upon introduction of one double bond. A possible example is *cis*-5-cyclodecen-1-yl tosylate whose solvolysis rate is enhanced by a factor of seven over the rate for cyclodecyl tosylate.[21] The present study suggests that the solvolysis rate of a hypothetical cyclodecene derivative with a non-participating double bond might be slower than that of the cyclodecane derivative, in which case the factor by which the solvolysis rate of *cis*-5-cyclodecen-1-yl tosylate is enhanced by double bond participation could be considered to be greater than seven.

Examination of models indicates that the greater rate enhancement for solvolysis of 3-cycloöcten-1-yl brosylate compared to solvolysis of 4-cyclooctenl-1-yl brosylate may be due to the unfavorable angle for overlap of the p-orbital of the 4-cyclooctenl-1-yl cation with the orbitals of the double bond. Another possible contributing factor is the strain in bicyclo[3.3.0]octane derivative and in *cis*-bicyclo[5.1.0]octane derivatives formed as products of the reactions, since some of the strain will be present in the transition states. Although carbonium ions may react with solvent to give the less stable of two possible products, the absence

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(15) A. C. Cope, M. Brown and H. E. Petree, THIS JOURNAL, **80**, 2852 (1958).

(16) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1511 (1955).

(17) H. C. Brown and G. Ham, THIS JOURNAL, **78**, 2735 (1956).

(18) Victor Seemann, unpublished work.

(19) Bruce S. Fisher, unpublished work.

(20) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, THIS JOURNAL, **79**, 4127 (1956).

(21) H. L. Goering, H. E. Espy and W. D. Closson, *ibid.*, **81**, 329 (1959).

of several possible reaction products in the present study may be due to unusual amounts of strain in the corresponding transition states. Such products include compounds with the *trans*-bicyclo[3.3.0]-octane and *cis*-bicyclo[4.2.0]octane ring systems, the latter ring system being a possible product from both brosylates. The slow solvolysis rate of 4-cycloöcten-1-yl brosylate is also in contrast with that of *cis*-5-cyclodecen-1-yl tosylate where the products may have the relatively unstrained decalin ring system.[21]

The fact that the allylic bromide, 3-bromocyclooctene, solvolyzed 60 times faster than cyclooctyl bromide at 70° makes the failure of the preparation of the allylic brosylate readily understandable, since crystalline cycloöctyl brosylate could be obtained only if it was isolated at low temperatures. As expected, cycloöctyl bromide shows the same medium-sized ring enhancement in its solvolysis rate as cycloöctyl brosylate and tosylate, although the bromide solvolysis is many times less rapid. Few secondary bromide solvolysis rates in acetic acid have been reported, no doubt because of the inconveniently slow rates, but a rate ratio of 83 can be calculated for comparison of the cycloöctyl bromide rate with that of isopropyl bromide at 100°.[22]

Experimental[23]

Addition of Formic Acid to 1,5-Cycloöctadiene.—*cis-cis*-1,5-Cycloöctadiene (46.3 g.) was stirred vigorously with 100 ml. of 98–100% formic acid and 0.5 ml. of 70% perchloric acid. The reaction mixture was heated to about 90°, at which point an exothermic reaction occurred, giving a single-phase, deep red solution. Enough sodium bicarbonate was added to neutralize the perchloric acid present, and the excess formic acid was removed by distillation under reduced pressure (head temperature 60°). The residual liquid, which at this point had become light brown, was saponified by stirring vigorously and heating at 90° for 20 min. with 100 ml. of water containing 50 g. of sodium hydroxide. Extraction with 100 ml. of chloroform followed by distillation through a spinning band column (46 × 1.5-cm.) gave 33.0 g. (61% calculated as $C_{18}H_{14}O$) of material, b.p. 45–71° (2.4 mm.). No glycol fraction could be distilled; there was a non-volatile residue of 5.5 g.

Isolation of Bicycloöctanols and 4-Cycloöcten-1-ol.—The later distillation fractions (27 g.), b.p. 69–71° (2.4 mm.), were shaken with 150 ml. of 20% silver nitrate and 50 ml. of ether in order to separate saturated alcohols from the 4-cycloöcten-1-ol. Addition of the silver nitrate layer to an equal volume of cold, concentrated ammonium hydroxide liberated the 4-cycloöcten-1-ol from its silver nitrate complex. Ether extraction and distillation gave 4-cycloöcten-1-ol (12.3 g., 23%), b.p. 73° (3.3 mm.). Gas chromatography on Silicone oil[24] showed that no saturated alcohols (described below) were present. The unsaturated alcohol gave a phenylurethan which was recrystallized from methanol–water, m.p. 90–92°. The infrared spectrum of the crude phenylurethan and a mixed melting point of the recrystallized product with authentic 4-cycloöcten-1-yl phenylurethan[25] indicated that the unsaturated alcohol was 4-cycloöcten-1-ol. The infrared spectrum of the alcohol showed that little if any 3-cycloöcten-1-ol or 2-cycloöcten-1-ol was present.

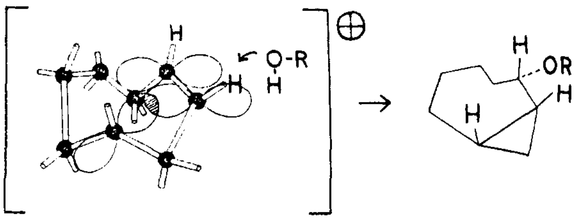

Fig. 6.—Solvolysis of 3-cycloöcten-1-yl brosylate; R = CH_3CO.

The ether layer from the silver nitrate extraction was shaken with two additional 20-ml. portions of 20% silver nitrate. The ether layer yielded 7.7 g. (16%) of saturated alcohols, b.p. 72–74° (3–4 mm.), shown to be free of 4-cycloöcten-1-ol by gas chromatography on Silicone oil.[24] The gas chromatogram showed a peak with a shoulder. The peak was found to be attributable to *endo*- or *exo*-bicyclo-[3.3.0]octan-2-ol by comparison with the gas chromatograms of authentic samples.[15,26] Since it was likely that both epimers were present, the alcohol mixture was oxidized with chromic anhydride–pyridine complex[27] to a ketone mixture which also showed a peak and a shoulder on gas chromatography. The infrared spectrum of the ketone mixture was essentially identical with the spectrum of authentic bicyclo-[3.3.0]octan-2-one,[28] except for shoulders at 1710 and 1765 $cm.^{-1}$ on the main carbonyl band (1735 $cm.^{-1}$). Further evidence that the ketone was principally bicyclo[3.3.0]octan-2-one was obtained by preparation of a 2,4-dinitrophenylhydrazone. Chromatography on silicic acid–Hi-flo Supercel gave a single band. The central portion of this band formed a derivative that melted at 134.0–135.5° after recrystallization from ethanol–water. Authentic bicyclo-[3.3.0]octan-2-one 2,4-dinitrophenylhydrazone[28] was purified in the same manner, m.p. 137–139°. A mixed melting point showed no depression and the infrared spectra of the derivatives were almost identical. Gas chromatography of the mixture of saturated alcohols on 1,2,3-tris-(2-cyanoethoxy)-propane[24] at 180° gave a symmetrical peak attributable to *endo*-bicyclo[3.3.0]octan-2-ol (20%) followed by a larger peak with a shoulder, attributable to *exo*-bicyclo-[3.3.0]octan-2-ol (45%) and an unknown component (35%). The identification of *endo*-bicyclo[3.3.0]-octan-2-ol was confirmed by collection of a sample from the effluent gas from the gas chromatogram and comparison of its infrared spectrum with the spectrum of an authentic sample.

Identification of Epoxycycloöctanes and *trans*-2-Vinylcyclohexanol.—The earlier distillation fractions from the addition of formic acid to 1,5-cycloöctadiene were shown by gas chromatography on Silicone oil[24] to contain two major components in addition to 4-cycloöcten-1-ol and bicyclooctanols. Comparison with the gas chromatograms of the lowest boiling fraction from solvolysis of *cis*-cycloöctene oxide[6] indicated that they were composed of 1,4- or 1,5-epoxycycloöctane or a mixture of the two. The infrared spectrum of a sample collected from the effluent gas of the gas chromatogram showed that the sample was composed principally of 1,5-epoxycycloöctane[29] containing some 1,4-epoxycycloöctane.[7] The proportion of 1,5-epoxycycloöctane was greater than that found in the solvolysis of *cis*-cycloöctene oxide.

Comparison of the respective gas chromatograms and infrared spectra showed that the second component of the early distillation fractions was identical with the unidentified unsaturated alcohol obtained in the solvolysis of *cis*-cycloöctene oxide.[6] In a later, large-scale preparation of 4-cycloöcten-1-ol this unsaturated alcohol was obtained free of contaminants (except for a small amount of epoxycycloöctanes) by distillation through a spinning band column (46 × 1.5-

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(22) W. C. Coburn, Jr., E. Grunwald and H. P. Marshall, THIS JOURNAL, **75**, 5735 (1953).

(23) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

(24) Gas chromatography columns were 8-mm. Pyrex tubes of 190-cm. length containing 30% by weight of liquid phase absorbant on a 48–80 mesh firebrick support. The liquid phase absorbants employed were the following: Dow-Corning Silicone oil no. 550; Dow tetraethylene glycol containing about 30% by weight of dissolved silver nitrate; Carbide and Carbon polyethylene glycol no. 400; 1,2,3-tris-(2-cyanoethoxy)-propane prepared from glycerol and acrylonitrile by the method of H. A. Bruson and T. W. Riener, THIS JOURNAL, **65**, 23 (1943); *cf. C. A.*, **40**, 5450 (1946), omitting distillation; tetrahydroxyethylethylenediamine, Visco Products Co., Inc., Houston, Texas. Eight-carbon alcohols were chromatographed at temperatures of 150–190° and eight-carbon hydrocarbons at 90–110°. Helium at 10–15 p.s.i. was the carrier gas and thermistors were employed for detecting sample peaks.

(25) A. C. Cope and G. W. Wood, THIS JOURNAL, **79**, 3885 (1957).

(26) A. C. Cope, H. H. Lee and H. E. Petree, *ibid.*, **80**, 2849 (1958).

(27) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *ibid.*, **75**, 422 (1953).

(28) A. C. Cope and W. R. Schmitz, *ibid.*, **72**, 3060 (1950).

(29) A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957).

cm.). The following experiments showed that the alcohol was *trans*-2-vinylcyclohexanol. The presence of a vinyl group was shown by bands in the infrared spectrum at 3060, 1845 (weak), 1640 (strong), 990–995 (strong) and 910–920 cm.$^{-1}$ (strong), all of which disappeared on hydrogenation of the alcohol. The unsaturated alcohol formed a phenylurethan, m.p. 78.2–79.2°, after recrystallization from ethanol, now known to be *trans*-2-vinylcyclohexyl phenylurethan.

Anal. Calcd. for $C_{16}H_{19}O_2N$: C, 73.44; H, 7.81; N, 5.71; C-methyl, 0.0. Found: C, 73.66; H, 8.04; N, 5.65; C-methyl, 0.0.

Hydrogenation using platinum oxide of a sample of the unsaturated alcohol purified by gas chromatography resulted in the uptake of 98% of one molar equivalent of hydrogen to form an alcohol now known to be *trans*-2-ethylcyclohexanol.

Anal. Calcd. for $C_8H_{14}O$: C, 74.94; H, 12.58. Found: C, 74.70; H, 12.39.

Oxidation of the hydrogenated alcohol with chromic anhydride–pyridine complex[27] gave a ketone with a carbonyl band at 1708 cm.$^{-1}$, showing the alcohol to be secondary. The above results showed that the unknown alcohol contained one carbocyclic ring having a single side chain terminated by a vinyl group; furthermore, the carbonyl frequency of the ketone suggested that the hydroxyl group of the alcohol was attached to a six-membered ring. Comparison of the ketone with a sample of 2-ethylcyclohexanone prepared by hydrogenation of *o*-ethylphenol and subsequent oxidation[30] showed that the two ketones were identical, as judged from their infrared spectra and a mixed melting point of the 2,4-dinitrophenylhydrazones.[31] That the hydrogenated alcohol described above was *trans*-2-ethylcyclohexanol was established by preparation of a sample of *cis*-2-ethylcyclohexanol for comparison. Hydrogenation of 2-ethylcyclohexanone with platinum oxide in acetic acid containing a few drops of concentrated hydrochloric acid gave *cis*-2-ethylcyclohexanol as reported,[32] containing some acetate, as shown by the infrared spectrum. The alcohol was purified by regeneration from the phenylurethan, m.p. 102–103° (reported[32] 101.5°), giving a product whose infrared spectrum differed greatly from the spectrum of the product obtained by hydrogenation of *trans*-2-vinylcyclohexanol, described above. On the other hand, the 2-ethylcyclohexanol obtained by hydrogenation of *o*-ethylphenol in the presence of Raney nickel in methylcyclohexane at 200° and 1500 p.s.i. contained both isomers, as shown by its infrared spectrum. This was confirmed by gas chromatography of all three samples of 2-ethylcyclohexanol on polyethylene glycol.[14] The product from hydrogenation of 2-vinylcyclohexanol was the pure *trans* isomer; the product from platinum–acetic acid reduction of 2-ethylcyclohexanone was the pure *cis* isomer; the product from Raney nickel hydrogenation of *o*-ethylphenol was a mixture of the two isomers with *trans*-2-ethylcyclohexanol predominating, as expected for a reduction under equilibrating conditions.[33] The *trans* configuration of the 2-vinylcyclohexanol is inferred from the demonstration that the hydrogenation product possessed a *trans* configuration. The alcohol from hydrogenation of *trans*-2-vinylcyclohexanol gave a phenylurethan which melted sharply at 61–62° after recrystallization from ethanol–water. The same phenylurethan could be obtained by hydrogenation of *trans*-2-vinylcyclohexyl phenylurethan with platinum oxide in ethanol. The *trans*-2-ethylcyclohexylphenylurethan prepared *via* the reaction of cyclohexene oxide with diethyl magnesium has been reported to have m.p. 63°,[34] while that obtained *via* the reduction of 2-ethylcyclohexanone with sodium in alcohol had m.p. 82–83.°[32]

3,4-Epoxycycloöctene.—Peracetic acid (40%, 101 g., to which 18.4 g. of sodium acetate trihydrate had been added to neutralize the sulfuric acid present) was added with stirring over the course of 1 hr. to 41 g. of *cis-cis*-1,3-cycloöctadiene maintained at 20–35° by means of an ice-bath. After 15 min. of additional stirring, 100 ml. of 40% sodium hydroxide was added slowly with cooling, taking care to avoid foaming due to rapid neutralization of excess peracetic acid. Extraction with 100- and 50-ml. portions of ether and distillation of the ether extract after drying over magnesium sulfate gave 30.0 g. (64%) of 3,4-epoxycycloöctene, b.p. 81–87° (22 mm.), n^{25}D 1.4863.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.13; H, 9.68.

3-Cycloöcten-1-ol.—3,4-Epoxycycloöctene (29 g.) in ether was added slowly with stirring to a suspension of 10 g. of lithium aluminum hydride in 500 ml. of dry ether. The mixture was heated under reflux for 4 hr., and the excess lithium aluminum hydride was destroyed by slow addition of 100 ml. of 6 *N* hydrochloric acid and 150 ml. of water. The ether layer was separated, washed with 5% sodium bicarbonate, and dried. Distillation gave 24.6 g. (85%) of 3-cycloöcten-1-ol, b.p. 74.5–76.0° (3.1 mm.), n^{25}D 1.4968. The infrared spectrum of the alcohol was identical with the spectrum of 3-cycloöcten-1-ol previously obtained by regeneration from the phenylurethan[6] except for the presence of a weak band at 723 cm.$^{-1}$ in the latter, indicating slight contamination by 4-cycloöcten-1-ol in the alcohol regenerated from the phenylurethan. The infrared spectrum of the crude phenylurethan, m.p. 96–101°, freed of diphenylurea by dissolving in pentane, was identical with the spectrum of authentic 3-cycloöcten-1-yl phenylurethan obtained earlier.[6]

4-Cycloöcten-1-yl Brosylate.—4-Cycloöcten-1-ol (11.0 g.) in 50 ml. of pyridine was cooled in a refrigerator and added to a solution prepared by dissolving 44.4 g. of *p*-bromobenzenesulfonyl chloride in 100 ml. of cold pyridine. After 20 hrs. at 5° the excess *p*-bromobenzenesulfonyl chloride was hydrolyzed by addition of small portions of water, while the temperature was maintained below 20° by means of an ice-bath. Finally 500 ml. of water was added and the mixture was extracted with 300 ml. of ether. The ether layer was washed twice with 100-ml. portions of 6 *N* hydrochloric acid and three times with 50-ml. portions of 5% sodium carbonate. The ether layer was dried with magnesium sulfate, without a final washing with water because the presence of a small amount of magnesium carbonate would help prevent acid-catalyzed decomposition of the brosylate. After filtration, an equal volume of pentane was added to the dried ether solution. On cooling, crystals of 4-cycloöcten-1-yl *p*-bromobenzenesulfonate formed, 18.36 g. (61.3%), m.p. 67–70° dec. After recrystallization from ethanol–water without heating, the m.p. was 68.5–71.0° dec.

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96. Found: C, 48.64; H, 4.96.

4-Cycloöcten-1-yl brosylate was considerably more stable than 3-cycloöcten-1-yl brosylate, but on standing for several days at room temperature an autocatalytic decomposition occurred with formation of a black, tarry residue.

3-Cycloöcten-1-yl Brosylate.—The preparation was similar to that of 4-cycloöcten-1-yl brosylate, except that the ether solution was evaporated on a rotary evaporator to give a clear, viscous liquid that solidified on cooling at −10°. The product from 11.0 g. of 3-cycloöcten-1-ol was triturated with pentane and separated by filtration to give 18.6 g. (61%), m.p. 50–53°. Because the compound tended to undergo rapid autocatalytic decomposition at room temperature, the brosylate was solvolyzed without recrystallization. Attempted recrystallization from methanol–water appeared to result in rapid solvolysis, but the product could be recrystallized from ether–pentane.

Anal. Calcd. for $C_{14}H_{17}O_3SBr$: C, 48.70; H, 4.96. Found: C, 48.40; H, 5.01.

Solvolysis of 4-Cycloöcten-1-yl Brosylate.—4-Cycloöcten-1-yl brosylate (18.36 g.) was dissolved in 120 ml. of acetic acid solution, 0.5 molar in sodium acetate (prepared by dissolving sodium carbonate in acetic acid) and 80 ml. of acetic acid. The solution was heated to 80° for 4–5 hr., during which time white crystals of sodium *p*-bromobenzenesulfonate separated. The sodium salt was separated by filtration and the filtrate was poured into 1 l. of water and 400 ml. of ether. The ether layer was washed with sodium carbonate solution until the aqueous washings were basic. Distillation of the dried (magnesium sulfate) ether layer, using a large flask because of foaming, gave a hydrocarbon fraction, 1.25 g., b.p. 94° (220 mm.), an intermediate fraction (0.40 g.) and an acetate fraction, 3.45 g., b.p. 68–74° (3.3 mm.).

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(30) The *o*-ethylphenol was obtained from Distillation Products Industries.

(31) Our melting point was 161.5–162.5°, in agreement with the value of 162.0°, reported by F. E. King, J. A. Barltrop and R. J. Walley, *J. Chem. Soc.*, 277 (1945).

(32) G. Vavon and V. M. Mitchovitch, *Bull. soc. chim.*, [4] **45**, 961 (1929).

(33) R. J. Wicker, *J. Chem. Soc.*, 2165 (1956).

(34) P. D. Bartlett and C. M. Berry, THIS JOURNAL, **56**, 2683 (1934).

Identification of the Hydrocarbon Components.—Gas chromatography on Silicone oil[24] of the hydrocarbon fraction showed that three major components were present, later identified as 1,5-cycloöctadiene, 1,4-cycloöctadiene and bicyclo[3.3.0]oct-2-ene. The respective percentages of these components were estimated from the peak areas to be 13, 23 and 64%. The three hydrocarbons were collected separately from the gas chromatography column and identified by comparison of their infrared spectra with the spectra of authentic samples.

The authentic 1,5-cycloöctadiene was already available from catalytic dimerization of 1,3-butadiene according to the method of Reed.[35] 1,4-Cycloöctadiene was obtained by repeating the dehydrobromination of 5-bromocycloöctene by the method of Ziegler and Wilms.[12] In addition to 1,5-cycloöctadiene and 1,4-cycloöctadiene, considerable bicyclo-[3.3.0]oct-2-ene was present in the early distillation fractions of the hydrocarbon prepared in this way. The bicyclic hydrocarbon probably arose from 2-bromobicyclo[3.3.0]-octane in the 5-bromocycloöctene. Pure 1,4-cycloöctadiene could not readily be separated by distillation, but a sample for infrared comparison was obtained by collection from a silver nitrate–tetraethylene glycol gas chromatography column.[24] On exposure to air for several days the hydrocarbon formed a hydroperoxide, as shown by a peak in the hydroxyl stretching region of the infrared spectrum and by liberation of iodine from potassium iodide. The preparation of authentic bicyclo[3.3.0]oct-2-ene is described later in this paper.

Identification of the Alcohol Components.—Gas chromatography of the acetate fraction on polyethylene glycol[24] at 115° showed the presence of two components, later shown to be 4-cycloöcten-1-yl acetate (20%) and bicyclo[3.3.0]oct-2-yl acetate (80%). A sample of the acetate was saponified by refluxing with 40% sodium hydroxide for 1 hr. The 4-cycloöcten-1-ol was separated from the bicycloöctanol by the silver nitrate extraction method already described for the preparation of 4-cycloöcten-1-ol. The 4-cycloöcten-1-ol was identified by comparison of its infrared spectrum with that of authentic 4-cycloöcten-1-ol already described, and by a mixed melting point of the phenylurethan with 4-cycloöcten-1-yl phenylurethan. The saturated alcohol fraction appeared from its infrared spectrum to be principally *endo*-bicyclo[3.3.0]octan-2-ol containing the *exo* isomer, both of which were available from another study.[28] Gas chromatography on polyethylene glycol at 115° indicated the composition to be 60% *endo* and 40% *exo* isomer. The saturated alcohol mixture yielded a phenylurethan, m.p. 86–87°, which showed no depression in a mixed melting point with *endo*-bicyclo [3.3.0]oct-2-yl phenylurethan[28] of m.p. 88–89°.

Solvolysis of 3-Cycloöcten-1-yl Brosylate.—3-Cycloöcten-1-yl brosylate (16.1 g.) was dissolved in 106 ml. of acetic acid, 0.5 molar in sodium acetate (prepared by dissolving sodium carbonate in acetic acid) and 70 ml. of acetic acid. The solution was allowed to stand at room temperature for 13 hr., after which the crystalline precipitate of sodium *p*-bromobenzenesulfonate was removed by filtration, and the products were isolated from the filtrate as described for 4-cycloöcten-1-yl brosylate. Gas chromatography showed that no hydrocarbon was present, contrary to the results obtained with 4-cycloöcten-1-yl brosylate. The yield of crude acetates was 7.57 g. (89%). The crude acetates (6.57 g.) were saponified by refluxing for 10 min. with 50 ml. of 40% sodium hydroxide.

Isolation of 3-Cycloöcten-1-ol and Bicyclo[5.1.0]octan-2-ol.—A solution of the saponification products in 12 ml. of ether was extracted with one 30-ml. and two 4-ml. portions of 20% silver nitrate. Addition of an equal volume of cold, concentrated ammonium hydroxide to the silver nitrate layer gave 0.81 g. of 3-cycloöcten-1-ol, identified by comparison of its infrared spectrum with that of an authentic sample[6] and by a mixed melting point of the phenylurethan.

Evaporation of the ether layer from the silver nitrate extraction gave 2.2 g. of the saturated alcohol, later shown to be bicyclo[5.1.0]octan-2-ol.

Anal. Calcd. for $C_8H_{14}O$: C,76.14; H, 11.18. Found: C,75.88; H, 11.27.

The alcohol showed bands in the infrared spectrum at 3070 and 2990 cm.$^{-1}$, known to be characteristic of a methylene group in a cyclopropane ring,[36] but contained no other strong bands attributable to double bonds. The alcohol formed a phenylurethan which melted at 92–94° after recrystallization from pentane. Five additional recrystallizations from pentane or alcohol-water raised the melting point to 102.5–105.0°, suggesting that the phenylurethan was a mixture of stereoisomers. A mixed melting point with 3-cycloöcten-1-yl phenylurethan was depressed at least 10 degrees, showing that the impurity was not the latter phenylurethan. The highest melting material was analyzed.

Anal. Calcd. for $C_{16}H_{19}O_2N$: C, 73.44; H, 7.81. Found: C, 73.07; H, 7.96.

Bicyclo[5.1.0]octan-2-one.—The bicyclo[5.1.0]octan-2-ol from the 3-cycloöcten-1-yl brosylate solvolysis (0.84 g.) in 10 ml. of pyridine was oxidized with the preformed complex prepared from 1.54 g. of chromium trioxide and 15 ml. of pyridine.[27] After 24 hr., 100 ml. of water and 100 ml. of ether were added. From the ether layer 0.26 g. (31%) of bicyclo[5.1.0]octan-2-one was obtained, b.p. 62° (2.5 mm.), $n^{25}\text{D}$ 1.4909.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 76.83; H, 10.00.

The infrared spectrum showed two carbonyl peaks at 1700 (medium) and 1675 cm.$^{-1}$ (strong), suggesting that two ketones might be present. However, two likely impurities appeared to be absent, from the following evidence: 2-Cycloöcten-1-one was not present because the ketone showed only end absorption in the ultraviolet spectrum, recorded on a Cary model 11MS instrument (reported[37] for 2-cycloöcten-1-one, λ_{max} 230 mμ, ϵ 7700). The possibility of the presence of 3-cycloöcten-1-one as a major impurity was eliminated by a comparison of the infrared spectra of the ketones.[38] Gas chromatography of the ketone on Silicone oil[24] gave a single peak.

The ketone (0.034 g.) gave a 2,4-dinitrophenylhydrazone (0.074 g., 89%) which without recrystallization melted at 189–190°, compared to an m.p. of 195–196° after three recrystallizations from methanol.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.38. Found: C, 55.45; H, 5.38.

Bicyclo[5.1.0]octan-2-one from 2-Cyclohepten-1-yl Acetate.—A mixture of 2-cyclohepten-1-yl acetate and bicyclo-[5.1.0]oct-2-yl acetate (0.70 g.)[39] was converted to the alcohols by reaction with 0.16 g. of lithium aluminum hydride in ether. Addition of a few drops of water and stirring for 30 min. followed by filtration and drying gave an ether solution which was extracted with silver nitrate as described for the solvolysis product from 3-cycloöcten-1-yl brosylate. The resulting 0.085 g. of alcohol was free of 2-cyclohepten-1-ol according to infrared analysis. The alcohol possessed the same bands at 3070 and 2990 cm.$^{-1}$ in the infrared spectrum as the bicyclo[5.1.0] octan-2-ol already described, but the infrared spectra of the two alcohols were not identical, suggesting that the alcohols were epimers. Oxidation of 0.085 g. of the alcohol with chromic oxide–pyridine gave 0.011 g. of ketone whose infrared spectrum was identical with that of the ketone obtained earlier, including the double carbonyl peak. The ketone gave a 2,4-dinitrophenylhydrazone which after one recrystallization melted 3 degrees lower than the derivative obtained earlier and showed no depression in mixed melting point.

***cis*-Bicyclo[3.3.0]oct-2-ene.**—A mixture of *exo*- and *endo*-*cis*-bicyclo[3.3.0]octan-2-ols was prepared by hydrogenation of *cis*-bicyclo[3.3.0]-octan-2-one[28] with Raney nickel in ethanol at 180° and 1500 p.s.i. Dehydration of the mixed alcohols (8.20 g.) was accomplished by heating with 80% phosphoric acid (1.4 g.) at 180–230°[40] and collecting the distillate of hydrocarbon and water. Addition of magnesium sulfate and decantation of the dried product gave 4.64 g. (66%) of hydrocarbon, which was further purified by dis-

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[35] H. W. B. Reed, *J. Chem. Soc.*, 1931 (1954).

[36] C. F. H. Allen, T. J. Davis, W. J. Humphlett and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957), and references cited therein.

[37] A. C. Cope, M. R. Kinter and R. T. Keller, THIS JOURNAL, **76**, 2757 (1954).

[38] 3-Cycloöcten-1-ol was oxidized to the ketone with chromic oxide-pyridine; M. Brown, Ph.D. Thesis, M.I.T., 1957.

[39] The bicyclo[5.1.0]oct-2-yl acetate, kindly supplied by Dr. Howard E. Simmons, was prepared from 2-cyclohepten-1-yl acetate by a method described by H. E. Simmons and R. D. Smith, THIS JOURNAL, **80**, 5323 (1958).

[40] A repetition of unpublished work by Albert Fournier, Jr.

tillation and separated into two components by gas chromatography on a silver nitrate–tetraethylene glycol column.[24] The major component showed strong bands at 700 and 3080 cm.$^{-1}$ in the infrared spectrum suggesting that the hydrocarbon contained a *cis*-disubstituted double bond and was therefore *cis*-bicyclo[3.3.0]oct-2-ene.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.86; H, 11.26.

The position of the double bond was confirmed by ozonolysis of a sample (0.20 g.) in 2 ml. of ethyl acetate and 8 ml. of acetic acid at 0° with one molar equivalent of ozone. Hydrogen peroxide (1 ml. of a 30% solution) was added to the cold solution of ozonide, and the mixture was warmed to 45° for 3 days. After addition of platinum black to destroy any remaining hydrogen peroxide, the acetic acid was removed on a rotary concentrator under reduced pressure. The product was shaken with sodium bicarbonate solution and ether. Ether extraction of the acidified bicarbonate layer gave 0.17 g. of acid (53%), which partially solidified. Three recrystallizations from benzene–pentane gave a product with m.p. 90.5–93.0°, which did not depress the melting point of authentic *cis*-2-carboxycyclopentaneacetic acid, m.p. 91.0–93.5°, prepared by nitric acid oxidation of *cis*-bicyclo[3.3.0]octan-2-one.[41] Gas chromatography of the phosphoric acid dehydration product also gave a second hydrocarbon which may have been the expected bicyclo[3.3.0]oct-1-ene, as indicated by the presence of a peak of medium intensity in the infrared spectrum at 788 cm.$^{-1}$, attributable to a trisubstituted double bond.

Solvolysis of 3-Bromocycloöctene.—3-Bromocycloöctene (17 g.) in 200 ml. of acetic acid, 0.5 molar in sodium acetate was allowed to react at 75° for 100 hr. The reaction mixture was poured into 1 l. of water and 400 ml. of ether, and the ether layer was washed with sodium bicarbonate solution until the aqueous layer was basic. Distillation of the ether extract gave 4.6 g. (47%) of 1,3-cycloöctadiene, b.p. 83° (110 mm.), and 4.0 g. (27%) of 2-cycloöcten-1-yl acetate, b.p. 70° (3.5 mm.). The 1,3-cycloöctadiene was identified by comparison of its infrared spectrum with the spectrum of an authentic sample.[42] Gas chromatography of the diene using a silver nitrate–tetraethylene glycol column[24] showed that there was less than 1% of 1,4-cycloöctadiene or 1,5-cycloöctadiene present. The infrared spectrum of the acetate showed no hydroxyl peak. Conversion of the acetate to the alcohol with lithium aluminum hydride gave 2-cycloöcten-1-ol with an infrared spectrum identical with the spectrum of an authentic sample.[37]

Preparation and Solvolysis of Cycloöctyl Brosylate.—Cycloöctanol (6.23 g.) was allowed to react with *p*-bromobenzenesulfonyl chloride as described for the preparation of 3-cycloöcten-1-yl brosylate. Crystallization from ether and pentane at −10° gave 10.78 g. of crystalline brosylate, m.p. 24.5–25.0°. After a second crystallization the melting point was 25.3–25.7°, but the twice recrystallized material had a greater tendency to decompose, probably because of accumulation of trace amounts of *p*-bromobenzenesulfonic acid which catalyzes further decomposition. Because of the tendency for rapid decomposition at room temperature, the crystalline brosylate (7.78 g.) was solvolyzed immediately without being analyzed. The brosylate was solvolyzed in 50 ml. of acetic acid containing somewhat less than one molar equivalent of sodium acetate. The solvolysis yielded 0.95 g. (39%) of *cis*-cycloöctene, b.p. 105–115° (210 mm.), and 0.38 g. (10%) of cycloöctyl acetate, b.p. 71° (7 mm). The low yields can be attributed partly to the use of a large distillation flask, necessary because of excessive foaming during the distillation. The *cis*-cycloöctene, after being freed from some acetate by gas chromatography on Silicone oil,[24] had an infrared spectrum identical with the spectrum of an authentic sample. The gas chromatogram indicated that 0.07% of *cis*-bicyclo[3.3.0]octane was present. The cycloöctyl acetate was converted to cycloöctanol by lithium aluminum hydride reduction, and the cycloöctanol was identified by its infrared spectrum.

Rate Measurements.—Sodium acetate (0.0490 mole/liter) in acetic acid was prepared by dissolving anhydrous sodium carbonate in Mallinckrodt glacial acetic acid. The resulting solution therefore contained the half mole of water per mole of sodium acetate formed in the neutralization reaction, but studies in the literature suggest that the water had no important effect on the rates of solvolysis.[43] For convenience our product studies were carried out at higher concentrations than our rate studies, although it is possible that the reaction products may be somewhat dependent upon the concentration of sodium acetate or water. For a rate determination the amount of brosylate or bromide required to make up a 0.0450 molar solution was placed in a 50- or 100-ml. volumetric flask. The 0.0490 molar sodium acetate solution was added from a buret to make a 0.0450 molar solution of brosylate or bromide (slightly less than 50 or 100 ml. was required because of the volume occupied by the brosylate or bromide). The resulting solution was placed in stoppered test-tubes or sealed in ampoules and placed in a bath maintained at a constant temperature ±0.1°. Tubes were removed at intervals and the sodium acetate concentration was determined by titration with 0.0504 molar perchloric acid in acetic acid using bromophenol blue as the indicator. The actual concentrations of bromide or brosylate originally present were determined from the total changes in sodium acetate concentration; these in some cases were several per cent less than expected from the weights of material used. However, first-order plots were linear to more than 80% completion.

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Proximity Effects. XVIII. Solvolysis of Ditosylates and an Acetoxy Tosylate in the Cycloöctane Series[1,2]

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The products of solvolysis of *cis*-1,2-cycloöctanediol ditosylate, *trans*-1,2-cycloöctanediol ditosylate, *cis*-1,4-cycloöctanediol ditosylate and *trans*-2-acetoxycycloöctyl tosylate in acetic acid containing sodium acetate and water have been studied. Products formed by transannular hydride shifts were formed from *cis*-1,2- and *trans*-1,2-cycloöctanediol ditosylate, while normal elimination and displacement products were obtained from the solvolysis of *cis*-1,4-cycloöctanediol ditosylate. Solvolysis of *trans*-2-acetoxycycloöctyl tosylate gave products formed both by transannular hydride shifts and by normal elimination and substitution reactions.

Several reactions of medium-sized ring compounds have been reported[2] in which abnormal products are formed by transannular hydride shifts. This paper reports a series of reactions in which substituted cycloöctyl carbonium ions of varying stability are the expected intermediates.

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(2) Paper XVII, A. C. Cope and P. E. Peterson, THIS JOURNAL, **81**, 1643 (1959).

(3) National Institutes of Health Postdoctoral Fellow, 1956–1958.