

**Studies on the Bromination and Acetylation
of the Isomeric Cyclooctadienes¹**

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Allylic bromination and subsequent silver acetate acetylation of 1,3-, 1,4-, and 1,5-cyclooctadiene (COD) were studied. 1,3-COD yielded bicyclo[3.3.0]oct-3-en-2-yl acetate in addition to the expected 2,4-cyclooctadien-1-yl acetate. The latter, as well as its alcohol and ketone derivatives, was found to undergo facile 1,5-hydrogen shifts under thermal conditions. 1,4-COD afforded the same bromide and acetate products as did 1,3-COD. This points to a common intermediate during bromination. 1,5-COD led to nonrearranged as well as allylic rearrangement products. Possible mechanisms for the various conversions are discussed.

In connection with projected studies, it was of interest to us to prepare various bicyclo[4.2.0]oct-7-en-2-yl derivatives. Cope and coworkers³ have reported that photolysis of 2,4-cyclooctadien-1-yl acetate (1) provides a convenient route to bicyclo[4.2.0]oct-7-en-2-yl acetate. This reaction appeared to offer a good means of entry into the systems desired in our work.

The appearance of anomalous results upon preparing 1 by Cope's procedure prompted us to reinvestigate the reaction pathways leading to 1. Described below are the results of this work as well as an extension of this research to include the corresponding reactions of the isomeric 1,4- and 1,5-cyclooctadiene.

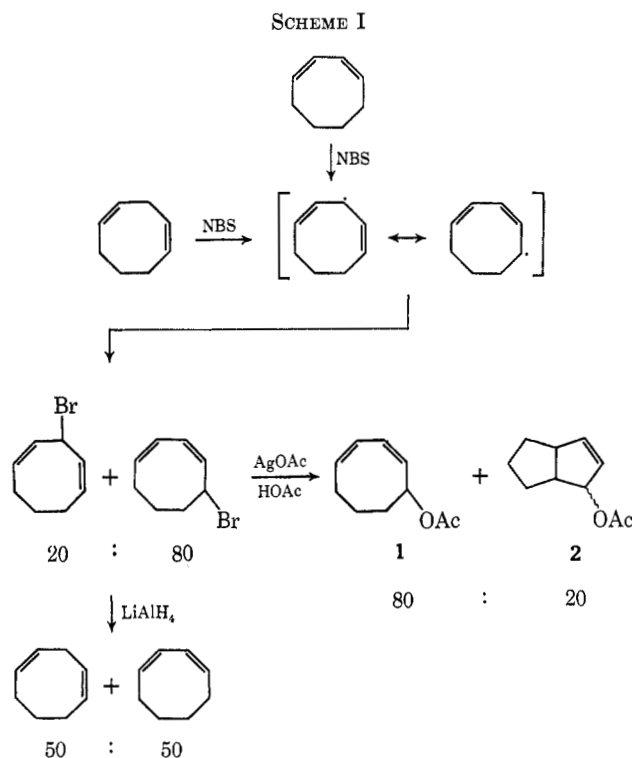
Results and Discussion

The reaction of 1,3-cyclooctadiene (COD) with N-bromosuccinimide followed by treatment of the bromination product with silver acetate in acetic acid gave two products. Gas chromatography (glpc) showed them to be in the ratio of 20:80 (Scheme I).

The major product was assigned the structure 1 by virtue of its uv, ir, and nmr spectra. The minor product was shown by its ir and nmr spectra to also be an unsaturated acetate. The absence of uv absorption above 210 m μ , however, indicated that it did not contain a conjugated diene chromophore.

The acetate mixture was subjected to catalytic hydrogenation to determine whether the minor product resulted from a simple double-bond reorganization or from a skeletal rearrangement. The appearance of two saturated acetates in the hydrogenation product

indicated that two-carbon skeletons were present. The one present in the greater amount was shown to be cyclooctyl acetate by comparison of its spectral properties with those of an authentic sample.



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Petroleum Research Fund Fellow, 1968-1969.

(3) A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Amer. Chem. Soc.*, **84**, 4865 (1962).

As will be subsequently described, the formation of the rearranged product was found to take place during the step involving the carbonium ion (acetylation). Inspection of models of 1,3-COD suggested that inter-

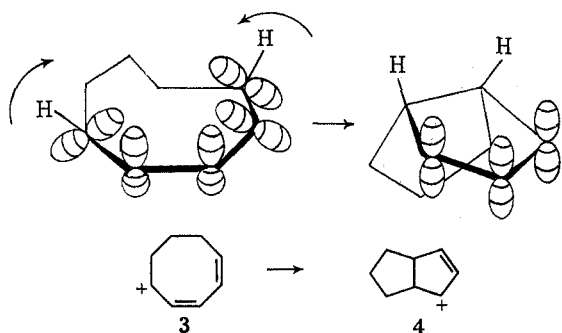


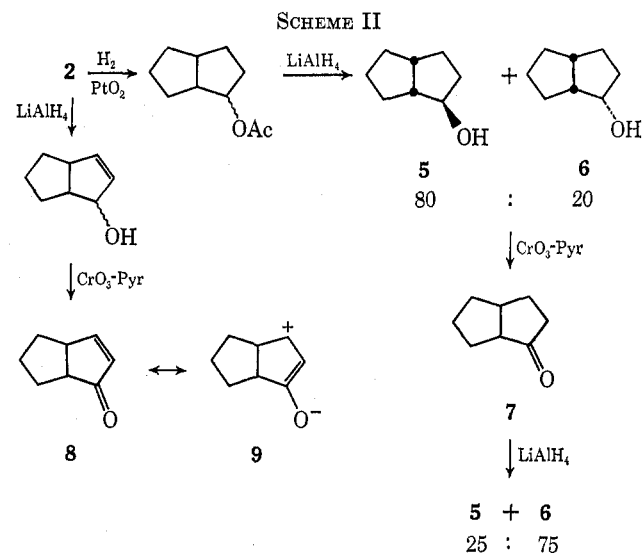
Figure 1.—Transformation of 2,4-cyclooctadien-1-yl cation to bicyclo[3.3.0]oct-3-en-2-yl cation.

action between a carbonium ion p orbital at the allylic position and the p orbital at the opposite end of the diene system was geometrically quite feasible. The bicyclo[3.3.0] system appeared, therefore, to be a likely candidate for the rearranged carbon skeleton. In addition, the nmr spectrum of the unknown unsaturated acetate was compatible with that expected for bicyclo[3.3.0]oct-3-en-2-yl acetate (2). This transformation is illustrated schematically in Figure 1.

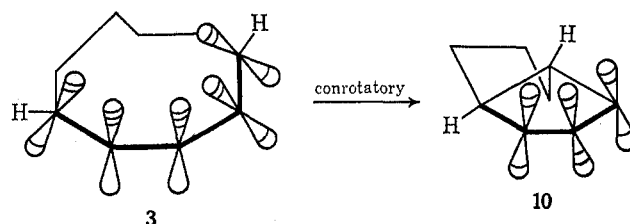
The bicyclic structure, the *cis* ring junction, and the stereochemistry of the acetate group (a mixture of *exo* and *endo* isomers) in 2 were established by conversion of the unsaturated acetate into the known saturated alcohols. Thus, hydrogenation of 2 followed by lithium aluminum hydride reduction of the resultant material afforded two alcohols. The major constituent (~80% of the mixture) was identified as *exo,cis*-bicyclo[3.3.0]octan-2-ol (5) by comparison of its ir spectrum with that of an authentic sample.⁴ The minor product could not be obtained in sufficient purity for direct characterization. However, the formation of a single ketone 7, upon oxidation of the alcohol mixture, indicated that the minor component was probably the *endo* alcohol 6. Brown and Hammar⁵ have reported that LiAlH₄ reduction of ketone 7 gives a 75:25 mixture of 6 and 5, respectively. In agreement with Brown's report, the major component (~75%) from our reduction of 7 was identified as the *endo* alcohol 6 by comparing its ir spectrum to that of an authentic sample.⁴ The retention time of this *endo* alcohol was identical with that of the minor alcohol obtained from the hydrogenation and subsequent reduction of 2. This permitted assignment of structure 6 to the minor alcohol.

Conversion of 2 into the corresponding ketone gave a product whose spectral properties (see Experimental Section) were in good agreement with those reported for 2-cyclopentenone.⁶ Of particular interest was the nmr spectrum which revealed a marked difference in the chemical shifts of the two vinyl protons (τ 2.67 vs. τ 4.05). The large downfield shift of the 3 proton can be attributed to a planar conformation of the enone ring⁷ and thus a sizable contribution of resonance form 9 to the electron distribution in 8. The formation of an

α,β -unsaturated ketone indicated that the acetate group was α to the olefinic moiety thus providing further confirmation for the structural assignment of 2. The reaction sequences used in the structure determination of 2 are outlined in Scheme II.



As far as can be determined, a ring closure of carbonium ion 3 to cation 4 is without literature precedent. A possible reason for this is the fact that the formation of a *cis* ring junction, as in 4, is contrary to that predicted by orbital symmetry considerations.⁸ Thus the conversion of the pentadienyl carbonium ion to the cyclopentenyl cation is expected to proceed in a conrotatory manner. It is readily seen that an analogous conrotatory ring closure in 3 would lead to a strained *trans* ring junction.



Several lines of reasoning can be used to interpret the observed contradiction. The basis for the first of these is a corollary to the Woodward-Hoffmann Rules which asserts that, if a symmetry-allowed product is geometrically of high energy, as is 10, then the symmetry rules may be overcome and formation of the forbidden product may be possible.⁹ This, however, usually requires much more energetic conditions than those necessary for the allowed process. Since the formation of 2 occurs at room temperature, an explanation based on this postulate becomes somewhat tenuous.

A second rationale for the observed phenomenon can be found in the fact that a reaction must be concerted in order to be governed by the orbital symmetry rules.⁸ Inspection of a molecular model of 3 indicates that a good deal of ring strain as well as several unfavorable nonbonded interactions exist when the double bonds and the carbonium ion center are made coplanar. This

(4) A. C. Cope, R. W. Gleason, S. Moon, and C. H. Park, *J. Org. Chem.*, **32**, 942 (1967).

(5) H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 1524 (1967).

(6) (a) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 12, 41; (b) J. Wieman, P. F. Casals, and S. Resse, *Bull. Soc. Chim. Fr.*, 1281 (1963).

(7) (a) N. Heap and G. H. Whitman, *J. Chem. Soc.*, **B**, 164 (1966);

(b) H. L. Goering, R. W. Greener, and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1391 (1961).

(8) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(9) G. B. Gill, *Quart. Rev. (London)*, **22**, 338 (1968).

factor could cause a concerted reaction, involving overlap of the five p orbitals, to be somewhat difficult in which case the Woodward-Hoffmann Rules may no longer apply. On the other hand, Stapp and Kleinschmidt¹⁰ have found that the 2,4-cyclooctadien-1-yl anion is converted, in good yield, by a symmetry-allowed disrotatory process, into the *cis*-bicyclo[3.3.0]oct-3-en-2-yl anion. It therefore appears that 1,3-cyclooctadienyl systems may be capable of concerted reactions in spite of adverse geometric requirements.

Although the above explanations cannot be completely rejected, it is most tempting to view the formation of cation 4 as resulting from the presence of silver ion in the reaction medium. It has been demonstrated¹¹ that transition metal ions may, through mixing of substrate and metal energy levels, cause a symmetry-forbidden process to become symmetry allowed. Of particular note is the work of Merk and Pettit¹² in which added silver ion was shown to make a thermally disallowed reaction facile, even at room temperature. In addition, as will be noted below, there is some evidence that 2 will not form in the absence of silver ion.

Throughout the foregoing discussion it was assumed that rearrangement to the bicyclo[3.3.0] system occurred in the carbonium ion step (acetylation) and not in the radical step (bromination). Somewhat surprisingly, careful examination of the nmr spectrum of the bromination product indicated that the signal at τ 5.15, presumably due to an allylic proton on a bromine-bearing carbon, integrated for less than the expected one proton. It was assumed that this signal was due to 2,4-cyclooctadien-1-yl bromide and it was thereby calculated that the mixture was comprised of only about 80% of this material. No nmr signal consistent with either of the bridgehead protons in bicyclo[3.3.0]oct-3-en-2-yl bromide could be found.

Removal of both allylic and nonallylic bromines, in good yield, by reduction with LiAlH₄, is well documented.¹³ This method offered a possible means of identifying the unknown bromides through the corresponding olefins, provided that the latter could be separated.

Treatment of the bromination product with LiAlH₄ yielded approximately a 50:50 mixture of two olefins. One of the products was identified as 1,3-COD. The nmr spectrum of the second olefin indicated that it was not bicyclo[3.3.0]oct-2-ene but rather 1,4-COD. Comparison of the latter with an authentic sample¹⁴ confirmed this belief.

The formation of 1,4-COD can be explained by invoking an allylic rearrangement of the initially formed radical from the NBS reaction¹⁵ (see Scheme I). Winstein and coworkers¹⁶ have carried out the bromina-

tion and LiAlH₄ reduction of 1,3-COD with similar results. Winstein's group contends, however, based on a publication by Jefford, *et al.*,¹⁷ that the rearrangement is an S_N2' process which occurs during LiAlH₄ reduction. From the product ratios found in our bromide mixture and then in our olefin mixture, it now appears that both a free-radical allylic rearrangement and an S_N2' reaction are operating here. The allylic rearrangement is apparent, not only from nmr evidence, but also from the fact that NBS bromination of 1,4-COD gave a bromide mixture whose nmr spectrum was identical with that of the bromides obtained from 1,3-COD. Conversion of the 1,4-COD bromide mixture into the corresponding acetates, with silver acetate and acetic acid, as well as to the olefins with LiAlH₄ afforded essentially the same product mixtures as those derived from 1,3-COD. Both of these reactions provide further confirmation that the two bromide products were the same. Furthermore, the change in product ratios going from the bromides to the olefins is indicative of an S_N2' process during LiAlH₄ reduction.

From the preceding it is clear that the bicyclo[3.3.0] system was not formed during the NBS bromination. It is interesting that no acetate corresponding to 2,7-cyclooctadien-1-yl bromide was found in the acetylation product. This difference between the free-radical and carbonium ion reactions may simply reflect different conformational requirements for stabilization of the two species.¹⁸ However, there is not sufficient evidence available to make a definitive statement with regard to more subtle factors which may be operating here.

An investigation of the properties of 2,4-cyclooctadien-1-yl acetate (1) and its analogs (see Scheme III) demonstrated that facile thermal rearrangements occurred in virtually all of the dienes studied. In fact this portion of our study was initiated by just such a finding in the dienyl acetate system. Thus, the mixture of 1 and 2 was distilled through a spinning-band column. An nmr spectrum of the fraction presumably containing 1, however, revealed an absorption (τ 5.2, triplet of triplets) not previously present in the nmr spectrum of 1 or 2. In addition subtle changes in the multiplet structure of the other absorption bands were evident. Crandall¹⁹ has suggested that cyclooctadienyl acetates can undergo thermal 1,5-hydrogen shifts. In order to explore the possibility that thermal conversions could account for the observed changes in the nmr spectrum, a carbon tetrachloride solution of 1 (isolated by glpc at 90°, prior to spinning-band distillation, and later found to contain 30% of 11) was placed in a sealed nmr tube and heated at about 110°. Periodic recordings of the nmr spectrum of the solution showed an increase in the relative area of the τ 5.2 absorption, thereby confirming that a thermal rearrangement was indeed taking place. The product mixture, however, showed only a single peak on gas chromatography (EGA) with the same retention time as 1.

Comparison of the chemical shift of the τ 5.2 absorp-

(10) P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965).

(11) (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967).

(12) W. Merk and R. Pettit, *ibid.*, **89**, 4787, 4788 (1967).

(13) (a) C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 34.

(14) We wish to thank Dr. E. Ciganek for supplying the spectra of 1,4-cyclooctadiene.

(15) S. Moon and C. Ganz, *J. Org. Chem.*, **34**, 465 (1969).

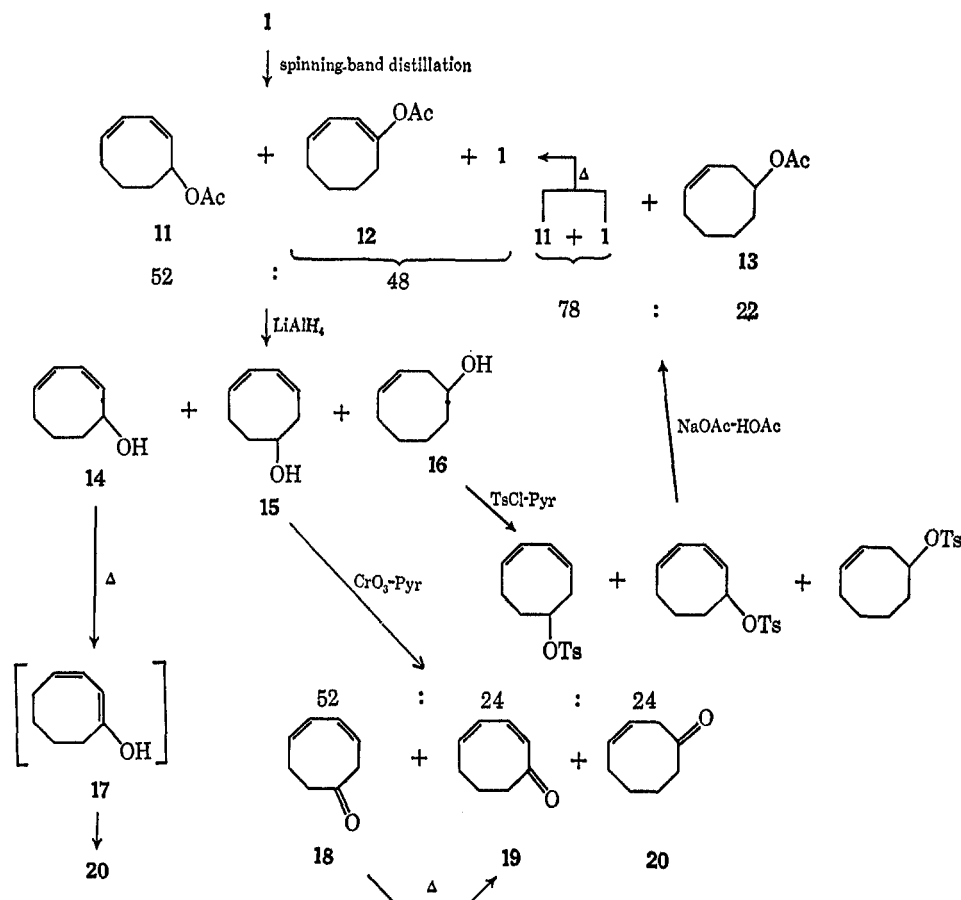
(16) D. S. Glass, R. S. Boicess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

(17) C. W. Jefford, S. Maksjan, J. Gunsher, and B. Waegell, *ibid.*, 2333 (1965).

(18) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill Book Co., New York, N. Y., 1965, pp 129, 155.

(19) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 532 (1967).

SCHEME III



tion with that exhibited by the allylic 2 proton (τ 4.75) in the bicyclic acetate 2 suggested that the unknown signal was due to a proton α to an acetoxy group but not allylic. Of the isomers of 1, derived from a 1,5-hydrogen shift, only 3,5-cyclooctadien-1-yl acetate (11) has a proton which would be expected to appear at about τ 5.2. Additional support for the homoallylic structure can be found in the triplet of triplets exhibited by the absorption in question. This multiplet structure is indicative of a proton flanked on either side by methylene groups with different chemical shifts and is thus quite compatible with 11.

The approximate percentage of 11 present at various time intervals during the thermal study was calculated by comparing the relative integrated area of the τ 5.2 absorption with that of the entire spectrum. It was thereby calculated that the fraction of 11 reached a value of about 60% after 26 hr of heating. Further heating showed only a slight change in this percentage. In a similar manner it was calculated that the spinning-band distillate (heated for 7 days at $\sim 80^\circ$) contained about 52% of 11.

From spectral analysis alone it was extremely difficult to obtain the structural details of all the compounds, other than 11, which were present in the thermally rearranged product. The single glpc peak obtained from the thermolysis mixture, however, indicated that the isomeric acetates 1 and 12 were likely prospects for the other components. The spinning-band distillate was subjected to LiAlH_4 reduction in an attempt to identify the unknown acetates through their corresponding alcohols. The

nmr spectrum of the crude reduction product clearly showed signals due, mainly, to homoallylic alcohols. No signal consistent with a proton both allylic and α to a hydroxyl group was visible. However, it is quite probable that an absorption of this type may well have been obscured by the vinyl signal (τ 3.9–5.1). In the first place, a marked downfield shift would be expected for a proton on the hydroxyl-bearing carbon going from a homoallylic to an allylic alcohol. Secondly, a model of 2,4-cyclooctadien-1-ol (14) strongly suggests that the allylic proton is thrust into the deshielding region of the 4,5 double bond. This would lower still further the expected chemical shift of the allylic proton. Nevertheless, it could be discerned that the homoallylic alcohol 15 was the major component due to the fact that certain features of the crude nmr spectrum were quite compatible with those reported by Crandall¹⁹ for a compound to which he assigned the structure 3,5-cyclooctadien-1-ol (15).

Gas chromatographic analysis of the crude alcohol mixture gave three components which were identified by comparison with authentic samples as 3-cycloocten-1-one (20), 3-cycloocten-1-ol (16), and a mixture of 20 and unidentified alcohols. Crandall and Chang¹⁹ have reported that 14 undergoes a thermal 1,5-hydrogen shift to afford 20. Since an ir spectrum of the crude alcohols showed essentially no carbonyl band, 20 and the mixture of 20 and the unknown alcohols were presumed to have resulted from thermal 1,5-hydrogen shifts upon gas chromatography. Thus alcohol 15 was converted into alcohol 14 and then into ketone 20 (via 17). Also, any 14 which was already present was

changed to 17 and then to 20. Reinjection of the mixture of 20 and the alcohols converted the latter almost completely into the ketone.

The presence of 16 in the LiAlH_4 reaction mixture can be explained by assuming that the enol acetate 12 was present in the acetate mixture and was reduced to 16 by LiAlH_4 . Such a reaction has ample precedent.²⁰ In addition, close inspection of an ir spectrum of the spinning-band fraction, containing the dienyl acetate mixture, revealed a weak shoulder on the major carbonyl band at approximately 1755 cm^{-1} . The position of this absorption is compatible with those reported²¹ for enol acetate carbonyl groups. This lends support to the proposed mechanism.

It was of interest to determine the relative amounts of the alcohols 14, 15, and 16 present in the reduction mixture. However, owing to the thermal interconversions of the dienols and ketone 20, a direct glpc estimate was not feasible. An attempt to overcome this difficulty was made, by oxidizing the alcohol mixture to the corresponding ketones with chromic trioxide-pyridine complex. The product was shown (glpc) to be a 24:76 mixture of two constituents. The minor component was identified as ketone 20, while uv, ir, and nmr data from the remaining glpc-isolated material suggested it to be about a 30:70 mixture of a nonconjugated and a conjugated dienone, respectively. Surprisingly, it was found, by ir and nmr spectral analysis, that the ratio of nonconjugated to conjugated dienone in the crude mixture was in direct contrast to that indicated by the spectra of the material exposed to the glpc. Thus, apparent in the nmr spectrum of the crude ketone product was a large doublet at about τ 7.0. This absorption is characteristic of a methylene group both allylic and α to a carbonyl group. The relative area of the τ 7.0 signal demonstrated that the major product in the crude material was the homoallylic rather than the allylic dienone. The same doublet was also noticeable in the nmr spectrum of the material isolated by gas chromatography but at greatly diminished relative intensity. That these results were due to another thermal rearrangement on the gas chromatograph was confirmed by heating a solution of the sample isolated by gas chromatography in carbon tetrachloride in a sealed nmr tube (110°). A recording of the nmr spectrum, after 6 hr of heating, showed a decrease of almost 50% in the relative area of the τ 7.0 doublet. It was also clear, from comparing the spectra of the crude product with those of the sample isolated by gas chromatography and the heated sample, that the characteristics of the nmr spectrum were progressively approaching those reported by Heap and coworkers²² for pure 2,4-cyclooctadien-1-one. By analogy to our previous findings, a 1,5-hydrogen shift, transforming 18 to 19, can be invoked to explain the observed thermal rearrangement.

(20) (a) W. G. Dauben and J. F. Eastham, *J. Amer. Chem. Soc.*, **73**, 3260 (1951); (b) W. G. Dauben and J. F. Eastham, *ibid.*, **75**, 1718 (1953); (c) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Wiley-Interscience, New York, N. Y. 1956, pp 533, 963; (d) one of the referees pointed out that the formation of 16 does not necessarily indicate the existence of 12, since the formation can be explained by the route $14 \rightarrow 17 \rightarrow 20 \rightarrow 16$.

(21) (a) N. J. Leonard and F. H. Owens, *J. Amer. Chem. Soc.*, **80**, 6039 (1958); (b) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 44.

(22) N. Heap, G. E. Green, and G. H. Whitham, *J. Chem. Soc., C*, 160 (1969).

The approximate percentages of ketones 18, 19, and 20 present in the crude mixture, were calculated from both gas chromatographic data as well as from well-separated nmr signals which could now be assigned, with some confidence, to 18 and 19. The nmr absorptions used to calculate 18 and 19 were a two-proton doublet at τ 6.96 and a three-proton vinyl signal centered at τ 3.83, respectively. It was thus determined that the ratio of 18 to 19 to 20 was 52:24:24. The 52% calculated for the homoallylic dienone 18 is in close agreement with that previously calculated for the corresponding homoallylic acetate 11, directly from an nmr spectrum of the spinning-band-isolated dienyl acetate mixture. Thus the ketone mixture appears to reflect the product ratios present in the acetate mixture from which it was derived.

Conversion of the alcohol mixture into the corresponding tosylates followed by solvolysis of the latter in sodium acetate buffered acetic acid afforded two major products in a 22:78 ratio. An ir spectrum of the minor product was identical with that of 3-cycloocten-1-yl acetate (13). Spectral analysis of the major glpc constituent showed it to be very similar to the spinning-band material containing the dienyl acetate mixture but slightly less abundant in acetates 11 and 12. Apparently, partial thermal equilibrium between the isomeric dienyl acetates was reestablished during isolation of the solvolysis products by gas chromatography. The product ratios found here are in good agreement with those of the ketones obtained from oxidation of the same alcohol mixture.

Noteworthy is the fact that, even though the alcohol mixture appears to have contained about 24% of 14, none of the bicyclic acetate 2 could be detected in the tosylate solvolysis product. This finding tends to support the proposed role of added silver ion in the formation of 2.

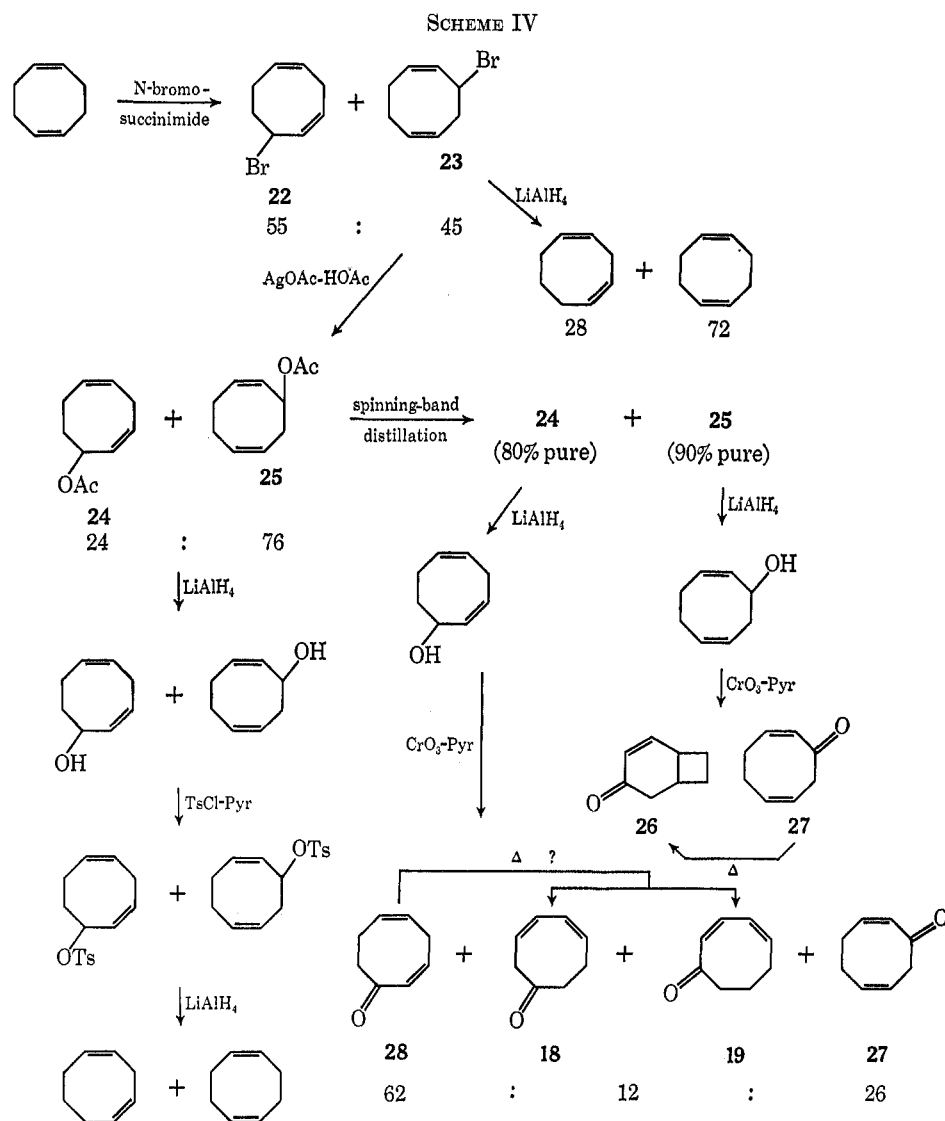
The results obtained from the 1,3-cyclooctadienyl systems prompted us to investigate the same reaction sequences in the isomeric 1,4- and 1,5-cyclooctadienes.

As described above, 1,4-COD gave, upon NBS bromination and subsequent acetylation, bromide and acetate mixtures identical with those obtained from 1,3-COD.

As previously reported by Cope,²³ bromination of 1,5-COD (21) afforded two isomeric bromides. A characteristic distorted triplet, similar to the one exhibited by the diallylic protons of 1,4-COD, was clearly visible at τ 7.2 in the nmr spectrum of the bromide mixture. This enabled one of the isomers to be tentatively assigned the structure of the allylic rearrangement product, 2,5-cyclooctadien-1-yl bromide (22). A calculation based on the relative area of this absorption indicated that the mixture was made up of approximately 55% of 22 and 45% of another bromide which was assumed to be 2,6-cyclooctadien-1-yl bromide (23).

Spectral analysis of a variety of derivatives obtained from the components of the bromide mixture (see Scheme IV) lent considerable support to the assignments of 22 and 23. In particular, two different routes from 22 and 23 to the parent olefins gave only 1,4- and 1,5-cyclooctadiene.

(23) A. C. Cope and F. Hochstein, *J. Amer. Chem. Soc.*, **72**, 2510 (1950).



In all of the isolated derivatives of **22** the distinctive absorption at about τ 7.2 firmly established that the diallylic methylene group of the 1,4-cyclooctadienyl system was present and unsubstituted. That the substituent was also not at the 7 position of 1,4-COD was confirmed by differences found in comparing the nmr spectrum reported²⁴ for 3,6-cyclooctadien-1-ol with that of the alcohol derived from **22**.

The nmr spectra of the analogs of **23** were compatible with the expected structures. In particular the ketone derivative **27** exhibited a doublet at τ 6.75, characteristic of a methylene group α to a carbonyl group and also allylic.^{7a} Uv data (λ_{max} 223, 310 m μ) indicated that the carbonyl group was also α,β -unsaturated and thus permitted the assignment of the expected 2,6-cyclooctadien-1-one (**27**) to the ketone. Fariessey and coworkers²⁵ have assigned the structures **27** and 2,5-cyclooctadien-1-one (**28**) to a pair of ketones derived from air oxidation of 1,5-COD followed by hydrolysis of the resultant hydroperoxides. These workers did not separate these products. They did find, however, that the compound thought to be **27** was converted, upon heating, into bicyclo[4.2.0]oct-2-en-4-

one (**26**). Interestingly, in our hands, gas chromatographic isolation of **27** gave rise to a smaller second peak of slightly shorter retention time than **27**. The uv and ir spectra of this material were in good agreement with those expected from **26**. This suggested that the thermal rearrangement found by Fariessey may have occurred to some extent on the gas chromatograph.

It is noteworthy that the isomer ratios changed in favor of the 1,5-COD system going from the bromides directly to either the olefins or the acetates. In the former case, by analogy to the LiAlH₄ reduction of the bromides derived from 1,3-COD, an S_N2' process can be invoked. Probably owing to variations in steric factors about the bromine-bearing carbon, this type of attack occurs preferentially on the 1,4-diene. On the other hand, the acetate results again appear to reflect differences in the environmental conditions necessary for stabilization of a free radical and a carbonium ion.

The diminished relative concentration of 2,5-cyclooctadien-1-yl acetate (**24**) compared with its bromide counterpart, in addition to the very close boiling points of **24** and its 2,6 isomer (**25**), allowed spinning-band separation of only a small sample of acetate **24** (contaminated with about 15–20% of **25**). A crude mixture of the corresponding alcohols, obtained from LiAlH₄ reduction of the impure **24**, exhibited an nmr spectrum,

(24) P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 1866 (1964).

(25) W. J. Fariessey, Jr., R. H. Perry, Jr., F. C. Stehling, and N. F. Chamberlain, *Tetrahedron Lett.*, 3635 (1964).

the gross features of which were quite consistent with that expected for 2,5-cyclooctadien-1-ol. Attempted conversion of this crude material into the ketones yielded a mixture which, when analyzed by gas chromatography, showed a marked decrease in the anticipated amount of ketone **28** relative to **27**. In addition, there appeared a third component ($\sim 12\%$) which was identified as a mixture of **18** and **19** ($\sim 30:70$, respectively). Several mechanisms for this transformation can be envisioned. A thermal conversion may again be operating since an ir spectrum of a small sample of **28**, collected by gas chromatography, exhibited a carbonyl band (1705 cm^{-1}) compatible with that found for ketone **18**. Unfortunately, difficulties encountered in isolating **28** did not permit either elucidation of its structure or confirmation of its involvement in the formation of **18** and **19**.

Experimental Section²⁶

Bromination of 1,3-Cyclooctadiene.—This bromination procedure has been described previously.¹⁵ The nmr spectrum of the distillate showed the following signals:¹⁶ τ 4.25 (m, =CH), 5.15 (m, =CCHBr), 7.8 (m, =CCH₂), and 8.0–8.8 (m, CH₂). A calculation of the area of the τ 5.15 absorption relative to the rest of the spectrum showed that it was equivalent to approximately 0.8 proton. On this basis the mixture was assumed to contain $80 \pm 5\%$ of 2,4-cyclooctadien-1-yl bromide.

Lithium Aluminum Hydride Reduction of the 1,3-Cyclooctadiene Bromination Product.—The bromination product was treated with lithium aluminum hydride as described previously.¹⁶ The product was found to be a 50:50 mixture of 1,3- and 1,4-cyclooctadiene.

Acetylation of the 1,3-Cyclooctadiene Bromination Product (Formation of 1 and 2).—To 72.8 g (0.39 mol) of the bromide mixture in 170 ml of glacial acetic acid was added, with stirring and external cooling, a slurry of 85 g (0.51 mol) of silver acetate in 170 ml of glacial acetic acid. The mixture was stirred in the dark at room temperature for 48 hr. After filtration, the supernatant liquid was diluted with 50 ml of water. The resultant mixture was extracted with one 400-ml portion and then two 300-ml portions of ether. The combined extracts were washed with two 1-l. portions of water, 1 l. of 10% sodium bicarbonate solution, and water again, and dried (MgSO₄). The ether was removed, under reduced pressure, on a rotary evaporator and the residue was distilled through a short-path distillation column to give 46.3 g (72%) of an acetate mixture, bp 42–47° (0.08–0.12 mm). The distillate showed two components on glpc (EGA, 2 ft, 110°) in a ratio of 20:80. The minor component was assigned the structure bicyclo[3.3.0]oct-3-en-2-yl acetate (**2**) and exhibited the following spectral properties: uv: no absorptions above 210 m μ ; ir (CS₂): 3040, 2930, 1725, 1250, 1110, 1020, 942, 900, 810, and 730 cm⁻¹; nmr: τ 4.25 (m, 2, =CH), 4.75 (doublet of doublets, 1, $J = 5\text{ Hz}$, $J = 2\text{ Hz}$, =CCHOAc), 6.70 (m, 1, bridgehead =CCH), 7.55 (m, 1, bridgehead CH), 8.03 (s, 3, O=CCH₃), 8.45 (m, 6, CH₂). The major component was assigned the structure 2,4-cyclooctadien-1-yl acetate (**1**): uv: λ_{max} (95% ethanol) 222 m μ (ϵ 6225); ir (CS₂): 3000, 2910, 1730, 1250, 1165, 1030, 970, 950, 910, 800, and 690 cm⁻¹; nmr: τ 3.9–4.5 (m, 4, =CH), 4.7 (m, 1, =CCHOAc), 7.4–8.0 (m, 2, =CCH₂), 8.01 (s, 3, O=CCH₃), 8.1–8.8 (m, 4, CH₂).

Hydrogenation of the Acetylation Product (Formation of Bicyclo[3.3.0]octan-2-yl Acetate and Cyclooctyl Acetate).—A mixture of 1 g (6 mmol) of the acetylation product, 100 mg of platinum oxide, and 50 ml of glacial acetic acid was shaken in an atmospheric pressure hydrogenation apparatus for 24 hr. After

removal of the catalyst by filtration, the liquid was diluted with water and extracted with ether. The ether extracts were washed with water, 5% sodium carbonate solution, and saturated sodium chloride solution, and dried (MgSO₄). Glpc analysis (EGA, 4 ft, 110°) of the residue, after removal of ether under reduced pressure, showed two components in a 13:87 ratio. The disappearance of the ir absorptions in the 3000-cm⁻¹ region showed both to be saturated acetates. Based on spectral analysis and the structure proof described below, the minor product was assigned the structure bicyclo[3.3.0]octan-2-yl acetate: ir (CCl₄): 1735 (C=O), 1250 cm⁻¹ (CO); nmr: τ 5.3 (m, 1, CHOAc), 7.55 (m, 2, bridgehead CH), 8.07 (s, 3, O=CCH₃), 7.8–8.9 (m, 10, CH₂). The ir and retention time of the major product were identical with those of an authentic sample of cyclooctyl acetate prepared from cyclooctanol.

Teflon Spinning-Band Distillation of the Acetylation Product.—The acetylation product (46.3 g) was slowly distilled, over 7 days, on a Teflon spinning-band column. Two major fractions, SB-F-1 (7.5 g), bp 56–58° (1.6–1.7 mm), and SB-F-2 (24.4 g), bp 65.5° (2.1 mm), both of which were homogeneous on gas chromatography (EGA, 2 ft, 110°), were isolated. The ir and nmr spectra of SB-F-1 were identical with those of the minor acetylation product, **2**. However, SB-F-2 was different from the major acetylation product and showed the following spectral data: nmr: τ 4.35 (m, =CH and =CCHOAc), 5.2 (triplet of triplets, $J = 7\text{ Hz}$, $J = 5\text{ Hz}$, CH₂CHOAcCH₂), 7.0–8.8 (m, =CCH₂ and CH₂), 8.07 (s, O=CCH₃); ir (CCl₄): 3005 (=CH), 1755 (=COC=O), 1735 (C=O), 1240 cm⁻¹ (CO). Integration of the nmr spectrum showed, based on the τ 5.2 absorption, that this fraction contained about 52% of a compound assigned the structure 3,5-cyclooctadien-1-yl acetate (**11**) and 48% of a mixture of two acetates which were subsequently assigned the structures **1** (24%) and 1,3-cyclooctadien-1-yl acetate (**12**) (24%).
Anal. Calcd for C₁₀H₁₄O₂: C, 72.24; H, 8.49. Found (SB-F-1; **2**): C, 72.14; H, 8.40. Found (SB-F-2): C, 72.08; H, 8.45.

Thermal Rearrangement of 1.—Approximately a 10% carbon tetrachloride solution of **1**, isolated by gas chromatography (EGA, 2 ft, 110°), and shown, by the τ 5.2 absorption in the nmr, to contain about 31% of **11**, was sealed in an nmr tube and heated in an oil bath at $108 \pm 4^\circ$. Periodic recordings of the nmr spectrum of the solution showed that, after 26 hr, the fraction of **11**, based on the area of the τ 5.2 signal, reached a value of about 60%. Additional heating to a total of 72 hr brought this value to approximately 70%. The final solution showed only a single homogeneous peak on gas chromatography (EGA, 4 ft, 150°) and an ir spectrum very similar to that of the spinning-band fraction, SB-F-2.

Lithium Aluminum Hydride Reduction of Spinning-Band Fraction SB-F-2 (Formation of 14, 15 and 16).—A 2-g sample (12 mmol) of SB-F-2 was treated with 0.6 g (0.16 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether in the manner described above. The crude product (1.15 g, 78%) showed the following spectral properties: ir (CCl₄): 3600 (OH), 3325 (OH), 3000 (=CH), 1060 cm⁻¹ (CO); no carbonyl band was present; nmr (external TMS): τ 3.9–5.1 (m, =CH and =CHCHOH), 5.7 (s, OH), 5.9 (s, OH), 6.1 (s, OH), 6.33 (quintet, $J = 5.5\text{ Hz}$, CHOH), 7.3–8.1 (m, =CHCH₂), 8.1–8.8 (m, CH₂). From integration of the nmr spectrum and by comparison of it with that reported for 3,5-cyclooctadien-1-ol¹⁹ (**15**), it was discerned that the major alcohol component was **15**. Gas chromatographic analysis (EGA, 4 ft, 150°) showed three constituents which were identified, by comparison with authentic samples, as **20** ($\sim 31\%$), 3-cycloocten-1-ol ($\sim 14\%$), and a mixture of **20** and unidentified alcohols ($\sim 55\%$). Reinjection of **20** and 3-cycloocten-1-ol into the glpc showed no apparent changes. Reinjection of the mixture of **20** and the alcohols converted the latter almost completely into **20**. It was thus apparent that the dienols were thermally converted into **20**.

Conversion of the Crude Alcohol Mixture into the Tosylates.—To 0.5 g of the crude alcohol mixture derived from SB-F-2, in 10 ml of pyridine, was added, with external cooling, 1.55 g of toluenesulfonyl chloride. After standing in a refrigerator overnight, the mixture was poured into ice and the resultant solution extracted with ether. The combined extract was washed with water, 3 N hydrochloric acid, and 10% sodium bicarbonate solution, dried (MgSO₄), and concentrated. The resultant tosylate mixture (0.59 g, 22%) was used without further purification.

Solvolysis of the Crude Tosylates (Formation of 1, 11, and 13).—To 0.4 g of the crude tosylate mixture was added a solution of

(26) Nmr spectra were determined on a Varian A-60 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Ultraviolet spectra were obtained from a Cary-14 recording spectrophotometer. Gas chromatography was performed on an F & M Model 720 thermal conductivity gas chromatograph using 2- or 4-ft columns containing either 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P or 20% ethylene glycol adipate (EGA) on Chromosorb W. Boiling points are uncorrected. Unless otherwise specified, nmr spectra were determined as carbon tetrachloride solutions containing tetramethylsilane (TMS) as an internal standard.

0.3 g of sodium acetate in 25 ml of acetic acid. The solution was stirred at room temperature for 18 hr and then poured into 100 ml of water. The resultant mixture was extracted with two 75-ml portions of ether. The combined ether extracts were washed with two 150-ml portions of water, 150 ml of 10% sodium bicarbonate solution, and water again, dried (MgSO_4), and concentrated. Gas chromatography (EGA, 4 ft, 175°) showed two major product peaks in the ratio of 22:78 in addition to several components each of which had an area equivalent to less than 5% of the major peak. The smaller of the major components was isolated by gas chromatography and its ir was found to be identical with that of an authentic sample of 3-cycloocten-1-yl acetate (13). The major component, also isolated from the glpc, exhibited an nmr spectrum very similar to that of SB-F-2. It was determined, from the τ 5.2 absorption, that this mixture of dienyl acetates contained about 40% of 11. Partial thermal re-equilibration during isolation of the major component appears to have taken place. One of the trace components had a retention time which was compatible with that expected from the bicyclic acetate, 2. An ir spectrum of this material demonstrated that it was not 2, thus precluding the formation of 2 during the solvolysis.

Conversion of the Crude Alcohol Mixture into the Ketones (Formation of 18, 19, and 20).—To 15 ml of pyridine was added, with external cooling, 2 g of chromium trioxide and then 0.5 g of the crude alcohol mixture from SB-F-2. The resultant brown suspension was stirred overnight at room temperature and then poured onto 50 ml of ice. After extraction of the solution with two 75-ml aliquots of ether, the ether layers were combined and washed with two 150-ml portions of water, 150 ml of 3 *N* hydrochloric acid, and water again, and dried (MgSO_4). The ether was removed under reduced pressure to give 0.23 g (~47%) of a crude ketone mixture which had the following spectral properties: ir (CCl_4): 3000 ($=\text{CH}$), 1705 ($\text{C}=\text{O}$, strong), 1665 cm^{-1} ($=\text{C}-\text{C}=\text{O}$, medium intensity); nmr: τ 3.5–3.95 (m, $=\text{CH}$), 3.95–4.9 (m, $=\text{CH}$), 6.96 (d, $J = 6$ Hz, $=\text{CCH}_2\text{C}=\text{O}$), 7.05 (d, $J = 4$ Hz, $=\text{CCH}_2\text{C}=\text{O}$), 7.15–8.8 (m, $\text{CH}_2\text{C}=\text{O}$, $=\text{CCH}_2$ and CH_2). Gas chromatography (EGA, 4 ft, 175°) showed two product peaks in a ratio of 24:76. The minor constituent had the shorter retention time, and, upon isolation by gas chromatography, was found to be identical with an authentic sample of enone 20. The major glpc-isolated peak gave the following spectral data: uv: λ_{max} (95% ethanol) 220, 274 $\text{m}\mu$; ir (CCl_4): 3005 ($=\text{CH}$), 1705 ($\text{C}=\text{O}$, medium intensity), 1665 cm^{-1} ($=\text{C}=\text{O}$, strong); nmr: τ 3.5–4.0 (m, $=\text{CH}$), 4.0–4.5 (m, $=\text{CH}$), 6.96 (d, $J = 6$ Hz, $=\text{CCH}_2\text{C}=\text{O}$), 7.2–7.7 (m, $\text{CH}_2\text{C}=\text{O}$), 7.7–8.3 (m, $=\text{CCH}_2$ and CH_2). By comparing the area of the τ 6.96 doublet with that of the total spectrum it was calculated that the major product contained approximately 30% of 3,5-cyclooctadien-1-one (18). By comparison with the nmr spectrum reported²² for 2,4-cyclooctadien-1-one (19), the other component (70%) of the major peak was assigned structure 19. On the other hand, from the relative areas of the τ 3.5–3.95 (assigned to 19) and the τ 6.96 (assigned to 18) absorptions in the nmr of the crude ketone mixture, it was determined that, of the 76% of the mixture found by glpc to be dienones, about 52% was 18 and 24% was 19. Thus the crude mixture was approximately a 52:24:24 mixture of 18, 19, and 20, respectively.

Thermal Rearrangement of 3,5-Cyclooctadien-1-one (18).—A carbon tetrachloride solution of a glpc-isolated sample of the major ketone peak from the alcohol oxidation was sealed into an nmr tube and heated in an oil bath at 110° . After 6 hr of heating, the τ 6.96 doublet, which had already markedly diminished in relative intensity going from the crude to the glpc-isolated material, showed a still further decrease in relative area. In addition the characteristic features of the nmr reported²² for 19 had become more clearly defined while signals, other than the τ 6.96 doublet, not compatible with structure 19, seemed to be disappearing. From this evidence it was apparent that ketone 18 was being thermally converted into ketone 19.

Lithium Aluminum Hydride Reduction of the Spinning-Band Fraction SB-F-1 (Formation of Bicyclo[3.3.0]oct-3-en-2-ol).—The spinning-band fraction assigned structure 2 (SB-F-1) (1 g, 6 mmol) was treated with a suspension of 0.85 g (22 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether as described above. Glpc analysis (EGA, 4 ft, 130°) of the crude product (0.35 g, 54%) yielded a broad major peak. Preparative glpc, isolating either the front or the tail end of this peak, gave materials whose ir spectra were indistinguishable: ir (CCl_4): 3590, 3310, 3040, 1115, 1040, 1010 and 930 cm^{-1} ; nmr (crude

product): τ 4.42 (m, 2, $=\text{CH}$), 5.75 (doublet of doublets, $J \sim 3$ Hz, $J \sim 1$ Hz, CHOH), 6.0 (s, 1, OH), 6.80 (m, 1, bridgehead $=\text{CCH}$), 7.67 (m, 1, bridgehead CH), 8.58 (m, 6, CH_2). On the basis of spectral data, the major product was assigned the structure bicyclo[3.3.0]oct-3-en-2-ol.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{O}$: C, 77.37; H, 9.71. Found: C, 77.05; H, 9.61.

Oxidation of the Crude Alcohol from SB-F-1 (Formation of Bicyclo[3.3.0]oct-3-en-2-one).—To 40 ml of pyridine was added 4 g of chromium trioxide, the crude bicyclo[3.3.0]oct-3-en-2-ol, and then an additional 8 ml of pyridine. After stirring at room temperature overnight, the mixture was poured onto 50 ml of ice and the resultant liquid extracted with two 150-ml portions of ether. The combined ether layers were washed with 150-ml portions of water, 3 *N* hydrochloric acid, and water, then dried (MgSO_4), and concentrated. Glpc analysis (EGA, 4 ft, 170°) showed a single major product. A sample of this product, isolated by glpc, exhibited the following spectral properties: uv: λ_{max} (95% ethanol) 218 $\text{m}\mu$ (ϵ 9300), 310 (46); ir (CCl_4): 3040, 2950, 1710, 1265 cm^{-1} ; nmr: τ 2.67 (doublet of doublets, 1, $J = 6$ Hz, $J = 3$ Hz, $\text{HC}=\text{C}=\text{O}$), 4.05 (doublet of doublets, 1, $J = 6$ Hz, $J = 2$ Hz, $=\text{CHC}=\text{O}$), 6.77 (m, 1, bridgehead $\text{CHC}=\text{O}$), 7.50 (m, 1, bridgehead $=\text{CCH}$), 7.8–8.9 (m, 6, CH_2). These data were compatible with the structure *cis*-bicyclo[3.3.0]oct-3-en-2-one (8).

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}$: C, 78.55; H, 8.23. Found: C, 78.61; H, 8.35.

Hydrogenation of the Spinning-Band Fraction SB-F-1 (Formation of Bicyclo[3.3.0]octan-2-yl Acetate).—A mixture of 1 g (6 mmol) SB-F-1, 100 mg of platinum oxide, and 50 ml of glacial acetic acid was stirred for 22 hr in an atmospheric pressure hydrogenation apparatus. The catalyst was removed by filtration and the supernatant liquid diluted with 150 ml of water. After extraction with two 200-ml portions of ether, the ether layers were combined, washed with two 300-ml aliquots of water, 100 ml of 10% sodium bicarbonate solution, and again water, dried (MgSO_4), and concentrated. Glpc analysis of the residue (0.49 g, 49%) displayed a single major product which was collected from the glpc (EGA, 4 ft, 130°). The component acetates of this peak were assigned the structures *endo*- and *exo*-bicyclo[3.3.0]octan-2-yl acetate based on the fact that conversion into the corresponding alcohols gave compounds whose ir spectra were identical with those of authentic *endo*- and *exo*-bicyclo[3.3.0]octan-2-ol. The ir and nmr spectra of the product were identical with that of the minor acetate isolated from the hydrogenation of the acetate mixture of 1 and 2.

Lithium Aluminum Hydride Reduction of the Hydrogenation Mixture (Formation of 5 and 6).—To a suspension of 0.6 g (16 mmol) of lithium aluminum hydride in 20 ml of anhydrous ether was added 0.25 g (1.5 mmol) of the compound assigned the structure bicyclo[3.3.0]octan-2-yl acetate. The resultant mixture was treated in the usual manner. Glpc (EGA, 4 ft, 130°) of the crude product showed two overlapping peaks in an approximate ratio of 20:80. The minor peak which had the shorter retention time could not be isolated in sufficient purity for positive identification. The major peak, collected from the gas chromatograph, exhibited an ir spectrum identical with that of an authentic sample⁴ of *exo,cis*-bicyclo[3.3.0]octan-2-ol (5); nmr: τ 6.23 (m, 1, CHOH), 7.6 (m, 2, bridgehead CH), 7.6 (s, 1, OH), 7.9–9.0 (m, 10, CH_2).

Oxidation of the Alcohol Mixture Containing 5 and 6.—To 10 ml of pyridine was added, with stirring, 1 g of chromium trioxide and the crude alcohol mixture derived from 2 by hydrogenation and lithium aluminum hydride reduction. The resultant mixture was treated in the manner previously described to give a homogeneous product on glpc (EGA, 4 ft, 125°). The nmr spectrum of the product showed bands centered at τ 7.3 (m, 1, bridgehead $\text{CHC}=\text{O}$), 7.3–8.75 (m, 11, CH_2 and bridgehead CH).

Regeneration of Alcohols 5 and 6 from Oxidation Product.—The crude alcohol oxidation product was treated with a suspension of 0.3 g of lithium aluminum hydride in 10 ml of anhydrous ether in the usual way. Glpc of the product showed two overlapping product peaks in about a 75:25 ratio in order of their respective retention times. The retention time of the major peak was identical with that of the unidentified minor peak in the alcohol mixture from which the oxidation product was derived. In addition the ir spectrum of this major peak was identical to that of an authentic sample⁴ of *endo,cis*-bicyclo[3.3.0]octan-2-ol (6). The minor constituent had a retention time identical with

that of 5. However it could not be isolated in sufficient purity for positive identification.

Bromination of 1,4-Cyclooctadiene.—A mixture of 2 g (18.5 mmol) of 1,4-cyclooctadiene,¹⁵ 3.5 g (19.7 mmol) of N-bromosuccinimide, 30 mg of benzoyl peroxide, and 30 ml of carbon tetrachloride was refluxed in a nitrogen atmosphere for 3 hr. The reaction mixture was cooled in a refrigerator, filtered, washed with 50-ml portions of water, 10% sodium bicarbonate solution, and water, and dried (MgSO₄). The carbon tetrachloride was removed by distillation under reduced pressure and the residue then distilled to give 1.64 g (49%) of a bromide mixture: bp 25–34° (0.07 mm). The nmr spectrum of this product was identical with that of the bromide mixture obtained by similar treatment of 1,3-cyclooctadiene.

Lithium Aluminum Hydride Reduction of the 1,4-Cyclooctadiene Bromination Product.—The bromination product (0.5 g, 2.7 mmol) and a suspension of 0.15 g (4.0 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether were treated in the manner described above. The product showed two peaks in about a 40:60 ratio in order of their retention times. These products were identified as 1,3- and 1,4-cyclooctadiene, respectively, by comparison of their retention times with those of authentic samples.

Acetylation of the 1,4-Cyclooctadiene Bromination Product.—To 1 g (5.4 mmol) of the bromination product in 2 ml of glacial acetic acid was added a slurry of 1.35 g (8.1 mmol) of silver acetate in 5 ml of acetic acid. After stirring in the dark overnight, the mixture was filtered and the filtrate added to 75 ml of water. The resultant solution was extracted with 75- and 25-ml portions of ether; the combined ether layers were washed with 100-ml portions of water, 10% sodium bicarbonate solution, and water, dried (MgSO₄), and concentrated with a rotary evaporator. The product (0.67 g, 75%) showed two major product peaks on glpc (EGA) in the approximate ratio of 15:85. The ir spectra and retention times of these materials were identical with those of the acetates 1 and 2 derived from 1,3-cyclooctadiene.

Bromination of 1,5-Cyclooctadiene (Formation of 22 and 23).—A mixture of 108.5 g (1.01 mol) of 1,5-cyclooctadiene, 180 g (1 mol) of N-bromosuccinimide, 0.95 g benzoyl peroxide, and 400 ml of carbon tetrachloride was refluxed, under nitrogen, for 2 hr. The reaction mixture was then cooled in an ice bath and filtered. The filtrate was washed with 600-ml portions of water, 10% sodium bicarbonate solution (twice), and water, and then dried by stirring with MgSO₄ for 2 hr. The carbon tetrachloride and unchanged diene were removed by distillation under reduced pressure and the residue was then distilled to give 106 g (57%) of a bromide mixture: bp 27–67° (0.1 mm); nmr: τ 4.1–4.7 (m, =CH), 4.7–5.5 (m, =CCHBr), 7.2 (t, $J = 4$ Hz, =CCH₂C=), 7.3–8.4 (m, =CCH₂ and CH₂). By comparison of the integrated area of the τ 7.2 absorption with that of the total spectrum it was discerned that the mixture comprised about 55% of the allylic rearrangement product, 2,5-cyclooctadien-1-yl bromide. The remaining 45% was assumed to be the expected 2,6-cyclooctadien-1-yl bromide.

Lithium Aluminum Hydride Reduction of the 1,5-Cyclooctadiene Bromination Product.—A mixture of 2 g (10.8 mmol) of the 1,5-cyclooctadiene bromination product and a suspension of 0.75 g (19.8 mmol) of lithium aluminum hydride in 25 ml of anhydrous ether was treated in the usual manner. The product showed two glpc peaks in a 28:72 ratio in order of their retention times. These components were respectively identified as 1,4- and 1,5-cyclooctadiene by comparison of their ir spectra and retention times with those of authentic samples.

Acetylation of the 1,5-Cyclooctadiene Bromination Product (Formation of 24 and 25).—The bromination product (43 g, 0.23 mol) in 100 ml of glacial acetic acid was treated with a slurry of 57 g (0.34 mol) of silver acetate in 125 ml of glacial acetic acid in the manner described above to afford 18.2 g (48%) of an acetate mixture (bp 52–57° at 0.1 mm) found by glpc (EGA, 4 ft, 150°) to contain two major components in a 24:76 ratio in order of their retention times. A sample of the major product, isolated by glpc, displayed the following spectral data: ir (CCl₄): 3005, 1740, 1250, 1025, 955, 685, and 650 cm⁻¹; nmr: τ 3.9–4.2 (m, 1, =CCHOAc), 4.2–4.9 (m, 4, =CH), 7.1–8.0 (m, 6, =CCH₂), 8.01 (s, 3, O=CCH₂). Based on the spectral results, the major acetate was assigned the structure 2,6-cyclooctadien-1-yl acetate (25).

Anal. Calcd for C₁₀H₁₄O₂ (25): C, 72.24; H, 8.49. Found: C, 72.47; H, 8.58.

Similarly, the minor acetate exhibited ir (CCl₄): 3005, 1735, 1250, 1040, 870, 720, and 675 cm⁻¹; nmr: τ 4.0–5.0 (m, 5, =CH and =CCHOAc), 7.17 (m, 2, =CCH₂C=), 7.2–8.9 (m, 4, =CCH₂ and CH₂). This isomer was assigned the structure 2,5-cyclooctadien-1-yl acetate (24).

Anal. Calcd for C₁₀H₁₄O₂ (24): C, 72.24; H, 8.49. Found: C, 71.94; H, 8.45.

Distillation of 13.3 g of the acetate mixture through an 18-in. Teflon spinning-band column separated it into two major fractions: SB-F-3 (0.73 g, bp 54° at 0.7 mm) and SB-F-4 (9.20 g, bp 62–64° at 0.8 mm). Glpc (EGA, 4 ft, 150°) showed SB-F-3 to contain about 83% of the minor acetate product 2,5-cyclooctadien-1-yl acetate while SB-F-4 contained about 91% of the major acetate product 25. A trace product (about 1%) appeared in the glpc of SB-F-3 with a slightly shorter retention time than the two identified acetates. This product could not be isolated in sufficient quantity for identification.

Lithium Aluminum Hydride Reduction of SB-F-4 (Formation of 2,6-Cyclooctadien-1-ol).—To a suspension of 0.6 g (16 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether was added 2 g (12 mmol) of SB-F-4. The resultant mixture was treated in the usual manner to give 0.8 g (54%) of a mixture containing about 90% of one alcohol. A glpc-isolated sample (EGA, 4 ft, 175°) of this alcohol showed the following spectral properties: ir (CCl₄): 3600, 3325, 3000, 1080, 1040, 1015, 980, 900, 720, and 650 cm⁻¹; nmr (external TMS): τ 4.2–4.9 (m, 4, =CH), 5.1–5.5 (m, 1, =CCHOH), 7.1–8.1 (m, 6, =CCH₂), 8.13 (s, 1, OH). This spectral data is compatible with the structure 2,6-cyclooctadien-1-ol.

Anal. Calcd for C₈H₁₂O: C, 77.37; H, 9.71. Found: C, 77.67; H, 9.70.

Oxidation of the Alcohol Mixture from SB-F-4 (Formation of 27).—To 15 ml of pyridine was added 2 g of chromium trioxide and a solution of 0.5 g of the alcohol mixture from SB-F-4 in 8 ml of pyridine. The resultant mixture was treated in the usual manner to give a crude ether solution, the glpc (EGA, 4 ft, 160°) of which showed two products in a 15:85 ratio in order of their retention times. Based on spectral data, the major product was assigned the structure 2,6-cyclooctadien-1-one (27): ir (CCl₄): 3010, 2950, 1670, 1650, 1235, 1220, 1125, 1080, 830, and 670 cm⁻¹; uv: λ_{\max} (95% ethanol) 223 m μ (ϵ 7700), 321 (110); nmr (external TMS): τ 3.4–4.9 (m, 4, =CH), 6.76 (d, 2, $J = 6$ Hz, =CCH₂C=O), 7.1–8.0 (m, 4, =CCH₂).

Anal. Calcd for C₈H₁₀O (27): C, 78.55; H, 8.23. Found: C, 78.37; H, 8.20.

The minor glpc-isolated product exhibited the following spectral properties: ir: 3030 (=CH), 1675 (=CC=O); uv: λ_{\max} (95% ethanol) 233 m μ (ϵ 5000), 317 (s, ϵ 38). The low degree of unsaturation (as determined from the ir spectrum) in addition to the uv data are compatible with the structure bicyclo[4.2.0]oct-3-en-2-one. This may be a product of thermal isomerization²⁵ on the glpc. A complete structure proof was not carried out.

Lithium Aluminum Hydride Reduction of SB-F-3 (Formation of 2,5-Cyclooctadien-1-ol).—The spinning-band fraction containing mostly 2,5-cyclooctadien-1-yl acetate (SB-F-3, 0.5 g, 3 mmol) was reduced with a suspension of 0.6 g (16 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether, in the usual manner, to afford 0.22 g (59%) of a crude alcohol mixture. Glpc (EGA, 4 ft, 175°) indicated that the product contained about 90% of a single component which was collected from the glpc and showed ir absorptions (CCl₄) at 3600 (OH), 3325 (OH), 3005 (=CH), 1055 cm⁻¹ (CO). An nmr spectrum of the crude alcohol mixture showed signals at τ 4.0–5.0 (m, 5.1, =CH), 5.3 (quintet, 1, $J = 5$ Hz, =CCHOH), 6.2 (s, 1, OH), 7.23 (t, 2, $J = 4$ Hz, =CCH₂C=), 7.0–9.0 (m, 5.7, =CCH₂ and CH₂). The somewhat larger than expected integrated areas for the vinyl and methylene regions can be traced to impurities present in the crude material. In general, the ir and nmr spectra are in good agreement with those expected for the anticipated major product, 2,5-cyclooctadien-1-ol.

Attempted Oxidation of the Crude Alcohol Mixture from SB-F-3.—To 10 ml of pyridine was added 1 g of chromium trioxide and a solution of 0.2 g of the crude alcohol mixture in 2 ml of pyridine. The mixture was treated in the usual manner to afford about 50 mg (25%) of a ketone mixture, the glpc (EGA, 4 ft, 140°) of which showed three product peaks in the approximate ratio of 12:62:26 in order of their retention times. The smallest component exhibited an ir spectrum identical with that of the 30:70 mixture of 18 and 19 described above. The peak of longest retention time had an ir spectrum identical with that of

dienone 27. Only about 1 mg of the major product could be isolated from glpc owing to the significant overlap of this peak and that of 27. A capillary tube nmr²⁷ of this sample, after standing at room temperature for several days, showed absorption regions at τ 3.4–4.9 (~ 4 , =CH) and 6.7–8.2 (~ 6 , CH₂C=O, =CCH₂, and =CCH₂C=). The fine structure of the nmr signals was not discernible. An ir spectrum of this sample displayed bands at 3020 (=CH), 1705 (C=O), and 1665 cm⁻¹ (=CC=O). The absorption at 1705 cm⁻¹ may indicate that some of 18 was present and was formed either on standing at room temperature or upon collection from the glpc. Since 18 was also found upon glpc analysis, it appears that the latter explanation is more plausible.

Lithium Aluminum Hydride Reduction of the Crude Acetate Mixture from 1,5-Cyclooctadiene (Formation of 2,5- and 2,6-Cyclooctadien-1-ol).—The crude acetate mixture (2 g, 12 mmol) derived from the 1,5-cyclooctadiene bromination product was reduced with a suspension of 0.6 g (15 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether to give 0.72 g (48%) of a crude alcohol product which showed two major glpc components (EGA, 4 ft, 175°) in a 45:55 ratio, in order of their retention times. The ir spectra of samples of the minor and major peaks, collected from the glpc, were identical with those of compounds

(27) L. R. Provost and R. V. Jardine, *J. Chem. Educ.*, **45**, 675 (1968).

previously assigned the structures 2,5-cyclooctadien-1-ol and 2,6-cyclooctadien-1-ol, respectively.

Conversion of the Crude Alcohol Mixture into the Tosylates.—To a solution of the crude alcohol mixture (0.5 g) in 10 ml of cold pyridine was added 1.55 g of tosyl chloride. The mixture was isolated as described above to afford an ether solution of a crude tosylate mixture which was not further purified.

Lithium Aluminum Hydride Reduction of the Crude Tosylates.—The crude tosylate mixture was treated with a suspension of 0.3 g of lithium aluminum hydride in 10 ml of anhydrous ether in the usual way to afford two major products in a 56:44 ratio, in order of their retention times. The ir spectra of the major and minor products were identical with those of authentic samples of 1,4- and 1,5-cyclooctadiene, respectively.

Registry No.—1, 10095-82-6; 2, 23346-35-2; 5, 23359-88-8; 8, 1122-07-2; 11, 10095-81-5; 12, 23346-37-4; 15, 10095-79-1; 20, 4734-90-1; 22, 23359-89-9; 23, 23346-40-9; 24, 23346-41-0; 25, 23346-42-1; 27, 1460-21-5; bicyclo[3.3.0]octan-2-yl acetate, 23346-44-3; bicyclo[3.3.0]oct-3-en-2-ol, 23346-45-4; 2,6-cyclooctadien-1-ol, 10017-18-2; 2,5-cyclooctadien-1-ol, 10054-74-7.

Molecular Rearrangements. IX.^{1a} The Synthesis and Rearrangements of 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide

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The synthesis of 2-chlorobicyclo[2.2.2]oct-2-ene oxide (4) is reported. Neat, thermal rearrangement of 4 produces 89% 3-chlorobicyclo[2.2.2]octan-2-one (8) in addition to nine minor products. Acetolysis of 4 gives as major products 8 (45%) and 3-acetoxycyclo[2.2.2]octan-2-one (11, 40%). Reaction of 4 with anhydrous hydrogen chloride in ether leads to the formation of 8 and 3,3-dichlorobicyclo[2.2.2]octan-2-ol (10). The formation of these products is compared with and contrasted to the results from similar studies with 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide.

Our previous investigations of the mechanism of the epoxide-carbonyl rearrangements of α -chloro epoxides have involved peroxidations of α -chlorostilbenes,² the intermediacy of α -chloro epoxides being assumed, and studies with the relatively stable α -chloro epoxides, 1-chloro-*cis*- (1) and -*trans*-4-methylcyclohexene oxide (2),³ and 2-chloronorbornene *exo*-oxide (3).^{4,5} The results obtained from these latter α -chloro epoxides have led us to suggest that α -ketocarbenium ion-chloride ion pairs are the principal intermediates in their neat, thermal rearrangements.

A goal of our program in this area of molecular rearrangements has been to study the kinetics of rearrangement of a number of α -chloro epoxides as a function of solvent, added salts, etc., to help us to substantiate or refute the idea of such ion-pair intermediates. The mixture of 1 and 2 did not appear to be suitable for such kinetic studies, since we have been unable to rule out the possibility of a chloronium ion intermediate for the rearrangement of 1.³ α -Chloro epoxide 3 was also less suitable than desired, since in

neat, thermal rearrangements *ca.* 40% was converted into polymeric material.⁴

The present work reports the synthesis and certain rearrangement studies of 2-chlorobicyclo[2.2.2]octene oxide (4), which appears to be a reasonable candidate for the proposed kinetic studies. Epoxide 4 might also allow us to determine the effect of the bicyclic framework on the rearrangement of the analogous bicyclic epoxide, 3, since 4 has considerably less angle strain than 3.⁶ The *exo-endo* geometric relationship present in 3 is absent in 4.

Results

The synthesis of 4 began with the Diels-Alder reaction of cyclohexadiene and *trans*-1,2-dichloroethylene. This reaction had been reported by Hine, *et al.*,⁷ who stated that "from the boiling point, method of preparation, and analysis, the mixture appeared to contain 5,6-dichlorobicyclo[2.2.2]oct-2-ene (5) and a somewhat larger amount of cyclohexadiene dimer." Indeed, separation of 5 from cyclohexadiene dimer was effected only after a careful distillation, and yields of 5 averaged *ca.* 20%. The halogens are believed to be *trans* by analogy to the stereochemistry of the product

(1) (a) Part VIII: R. N. McDonald and D. G. Hill, *Chem. Commun.*, 671 (1969). (b) NDEA Fellow, 1964–1967; NSF Cooperative Fellow, 1967–1968. (c) Taken from the Ph.D. Thesis of R. N. Steppel.

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