analyzed for acetate ester content by vpc. The composition of the acetate fraction was shown to be 74% *syn*-7-acetoxynorbornene, 16% *anti*-7-acetoxynorbornene, 3% 7-acetoxynorbornane, and 7% 3-acetoxynortricyclene. Based on the direction of deuterium addition in forming these isomeric acetates during reduction of dienyl acetate, the mixture of norbornenyl acetates corresponded to 20% *endo,endo*-5,6-dideuterio-*anti*-7-acetoxynorbornene, 68% *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene, and 12% *endo,endo*-5,6-dideuterio-*syn*-7-acetoxynorbornene. Since it had been shown (*vide supra*) that the *anti* isomer experienced 100% *exo,cis* deuterium addition and that the *syn* isomer (over a nonprereduced catalyst) underwent 40% *endo,cis* and 60% *exo,cis* deuterium addition, the deuterium distribution of tetradeuterated 7-acetoxynorbornane was predicted to be 33.6% *endo,cis* and 66.4% *exo,cis*. The values agreed with the observed distribution of 34% and 66%, respectively.

Competitive Reduction of Norbornene and 7-Acetoxynorbornadiene.—In a gas buret apparatus 268.5 mg of 10% palladium on charcoal in 5 ml of methanol was reduced with deuterium. Into the catalyst slurry a solution of 764 mg (4.8 mmol) of 7-acetoxynorbornadiene and 990 mg (10.5 mmol) of norbornene in 5 ml of methanol was injected. The reduction reaction was sampled periodically and analyzed by vpc.[6] The composition of the acetate mixture was determined and is summarized in Table VI below.

TABLE VI

Reduction, %	Composition, %					
	Norbornene	Dienyl acetate	*syn-*	*anti-*	Satd	Nortricyclic
24	81	49	11	20	0	20
48	56	11	23	37	0	30
64	34	0	25	40	4	30
80	6	0	26	38	7	30
96	0	0	16	0	54	30
100	0	0	0	0	70	30

Determination of k_{anti}/k_{syn} for Reduction of 7-Acetoxynorbornadiene to *syn-* and *anti*-7-Acetoxynorbornenes.—In the reduction of 7-acetoxynorbornadiene, k_{anti} is derived from the rate of reduction of the *anti* double bond to yield *syn*-7-acetoxynorbornene. Conversely, k_{syn} is a measure of the rate of reduction of the *syn* double bond to produce *anti*-7-acetate. The relative rate, k_{anti}/k_{syn}, has been determined by the ratio, % *syn*-acetate produced/% *anti*-acetate produced. For palladium-on-charcoal catalysts, this ratio is readily calculated from reductions performed in the presence of excess norbornene or norbornadiene, where the subsequent conversion of *syn-* and *anti*-acetates to saturated product is effectively suppressed. In the case of a prereduced palladium-on-charcoal catalyst (norbornene present), k_{anti}/k_{syn} = 0.56–0.61 (average 0.58). In the case of a nonprereduced palladium catalyst (norbornadiene present), k_{anti}/k_{syn} = 3.22–3.52 (average 3.41).

Reductions utilizing platinum catalysts are complicated by the fact that conversion of initially formed *syn-* and *anti*-acetates to saturated ester cannot be suppressed. In these cases the assumption has been made that the saturated product formed while dienyl acetate is present arises predominately from reduction of the *anti* isomer. This rationale is predicated on the observed preference for *anti* double bond reduction in the competitive reduction of *syn-* and *anti*-acetates over platinum catalysts (see Table III). Consequently, k_{anti}/k_{syn} for dienyl acetate reductions over platinum catalysts has been estimated from the ratio, % *syn* produced/% *anti* + % saturated produced. For the platinum oxide catalyst, values of k_{anti}/k_{syn} were calculated to be 1.01–1.36 (average 1.19). A platinum-on-carbon catalyst gave an average value for k_{anti}/k_{syn} of 1.11; a prereduced platinum catalyst gave an average value of 1.81.

Registry No.—**1**, 13426-49-8; **2**, 13426-52-3; **3**, 13426-55-6; **6a**, 15649-38-4; **6b**, 20843-70-3; **7**, 20843-71-4; **8a**, 20843-72-5; **8b**, 20843-73-6; **8d**, 20843-74-7; **8e**, 20843-75-8.

The Oxymercuration–Demercuration of Cycloalkadienes

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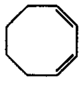
The oxymercuration–demercuration of isomeric cyclooctadienes was studied. The major product from 1,3-cyclooctadiene is 9-oxabicyclo[4.2.1]non-7-ene (2). 1,4-Cyclooctadiene yields mostly 3-cycloocten-1-ol and 1,4-epoxycyclooctane. Treatment of 3-cycloocten-1-ol with mercuric acetate, followed by reduction with sodium borohydride, is a convenient preparatory method for isomerically pure 1,4-epoxycyclooctane.

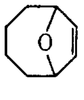
Oxymercuration–demercuration of olefins has been shown to be an excellent method for obtaining alcohols.[1] Previous studies[1,2] have shown that the direction of the addition is according to Markovnikov's rule and that the addition is controlled by steric factors. Relatively little work, however, has been done on the reactions of dienes. Bordwell[3] recently reported that the oxymercuration of 1,5-cyclooctadiene yielded a cyclization product instead of a simple addition product. We wish to report our studies on the reaction of some cyclic dienes, and related olefinic alcohols. The dienes that were chosen for our studies were 1,3-,1,4,- and 1,5-cyclooctadienes and 1,3- and 1,4-cyclohexadienes.

Results and Discussion

Treatment of 1,3-cyclooctadiene (**1**) with mercuric acetate in tetrahydrofuran (THF) and water, followed, by alkaline demercuration with sodium borohydride gave 9-oxabicyclo[4.2.1]non-7-ene (**2**) in 37% yield, in addition to **3a**, **4a**, and **5a**. When the diene was treated with mercuric nitrate instead of mercuric acetate, **2** was obtained in a lower yield.



1



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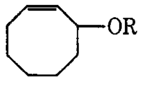

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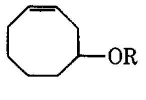
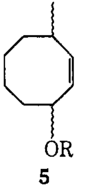


4



5

a, R = H
b, R = Ac

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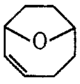
[1] For excellent review articles, see (a) J. Chatt, *Chem. Rev.*, **48**, 7 (1951); (b) N. S. Zefirove, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) W. Kitchins, *Organometal. Chem. Rev.*, **3**, 61 (1968).

[2] H. C. Brown and P. Geogegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

[3] F. G. Bordwell and M. S. Douglass, *ibid.*, **88**, 993 (1966).

The structure of **2** was assigned on the basis of elemental analysis and spectroscopic properties and by its facile conversion into 1,4-epoxycyclooctane (**9**) by hydrogenation. The nmr spectrum showed signals at τ 4.2 (s, 2) for the olefinic hydrogens, at 5.1 (d, 2) for the tertiary hydrogens, and at 8.3 (m, 8) for the methylene protons. Of the structures **2**, **2a**, and **2b**, only **2** is consistent with the nmr spectrum.



2a

2b

When the reaction product of the oxymercuration–demercuration of **1** was not washed with water, but was concentrated and treated with acetic anhydride and pyridine, four additional products were observed on gas chromatography.

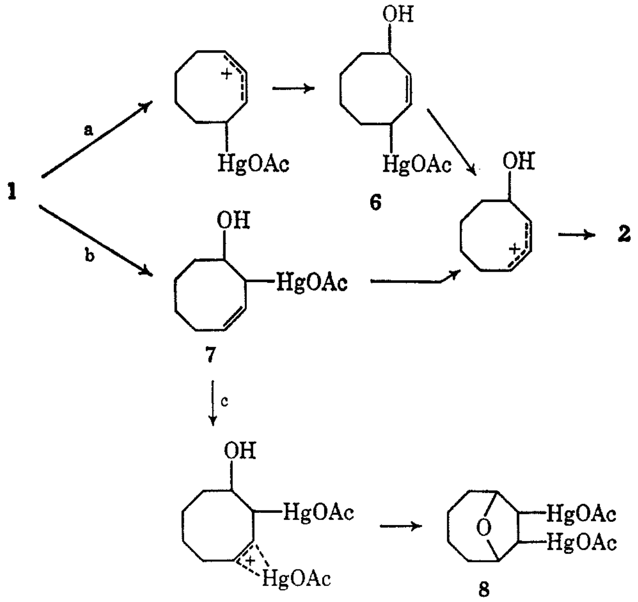
The infrared spectrum of each of the two major products, isolated by gas chromatography, indicated ester bands and olefinic hydrogens. The nmr spectrum of the mixture of the two major products showed two olefinic hydrogens, two different methyl peaks (acetates) of about equal strength, and two allyl hydrogens alpha to the acetate group. The mixture of these two compounds was hydrogenated, but the products were not separable on gas chromatography. The infrared spectrum of the hydrogenated product had all of the bands characteristic of *cis*-1,4-cyclooctanediol diacetate, plus several more. That the product was not *trans*-1,3-cyclooctanediol diacetate was indicated by comparison of its spectrum and retention time on gas chromatography with those of an authentic sample. On the basis of ir, nmr, gas chromatographic, and hydrogenation data, we believe the major products to be *cis*- and *trans*-2-cyclooctene-1,4-diol diacetates (**5b**). The configuration of **5a** and **5b** was not determined. Two minor products were identified as 3-cycloocten-1-yl acetate (**4b**, 3%) and 2-cycloocten-1-yl acetate (**2b**, 1.5%).

An attractive rationale[4] for the formation of **2** from **1** would involve the addition of mercuric acetate to **1**, yielding, by path a or b, respectively, either **6** or **7**, which may solvolyze to give **2** (Scheme I), as allylic mercurials would be expected to solvolyze rapidly. Formation of **6** implies a 1,4 addition of mercuric acetate to **1**. We know of no reported case of the 1,4 addition of mercuric acetate to dienes. The addition of mercuric acetate to 1,3-butadiene gave only 1,2-addition product.[5] The product obtained from norbornadiene appeared to involve 1,4 addition, but it was later found that the initial intermediate resulted from 1,2 addition.[6]

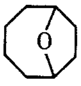
Alternatively, the dimercurial acetate **8** can be envisioned as a possible intermediate (path c). The reduction of **8** to **2** with sodium borohydride could be rationalized along the path similar to one suggested by Bordwell[3] for the demercuration of 2-acetoxymercuri-2-oxabicyclo[4.2.1]nonane to 4-cycloocten-1-ol in acidic media. Definite choice between these mechanisms must await further work.

Since the acetoxymercurial **7** was thought to be one of the possible intermediates in the formation of **2** from **1**, we investigated the reaction of 3-cycloocten-1-ol (**4**). Treatment of **4** with mercuric acetate in THF–water mixture gave 1,4-epoxycyclooctane (**9**) in 64% yield based on distilled product. Since **9** obtained in this manner was not contaminated by 1,5-epoxycyclooctane (**10**) and no by-product was detected, this procedure constitutes a convenient synthesis of **9**.

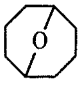
Scheme I



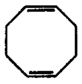
Bordwell[3] reported that the oxymercuration of 1,5-cyclooctadiene (**11**) with mercuric nitrate followed by demercuration with sodium borohydride yielded **10** uncontaminated by the 1,4 isomer **9**. We reinvestigated this reaction and our results confirmed those of Bordwell (see Table I). We also treated **11** with mercuric acetate and obtained, after demercuration with sodium borohydride, a mixture of **9** and **10** in a ratio of 55:45. Variation of conditions (see Table I) did not have any appreciable effect on the ratio of **9** and **10**. The results were surprising, as we expected the oxymercuration–demercuration of **11** to closely parallel the oxymercuration–demercuration of 4-cycloocten-1-ol (**12**), since the oxymercuration–demercuration of **11** probably proceeds through the hydroxyacetoxymercurial **13**.



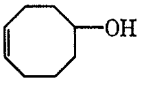
9



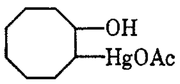
10



11



12



13

In as much as Bordwell[3] reported that the oxymercuration and demercuration of **12** in acidic media resulted in the 1,5-epoxide, and, in basic media, the 1,4-epoxide, we had hoped to prepare the 1,4-epoxide isomerically pure by the oxymercuration of much more readily available **11** with mercuric acetate. As our results indicate, the reaction is not selective. Owing to the contradiction in predicted and realized results we reinvestigated the oxymercuration of **12**. In our hands, the epoxycyclooctane **9**, obtained from the alcohol **12** under the same reaction conditions, was contaminated by 15% **10**. The discrepancy could possibly be due to the method of analysis. Gas chromatography[7] and infrared spectroscopy[3] were used for analysis of the relative amounts of **9** and **10**. We found

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[4] This is a modification of a mechanism proposed by one of the referees.

[5] K. H. McNeely and G. F. Wright, *J. Amer. Chem. Soc.*, **77**, 2553 (1955).

[6] K. C. Paude and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[7] A. C. Cope, M. Gordon, S. Moon and C. H. Park, *J. Amer. Chem. Soc.*, **87**, 3119 (1965).

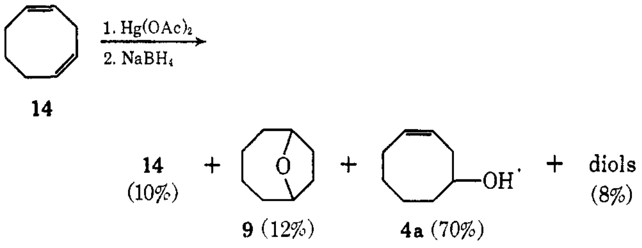
TABLE I
COMPOSITION OF CYCLIC ETHERS OBTAINED FROM CYCLOOCTENOLS AND CYCLOOCTADIENES

Starting material	Solvent	Mercuric salt	Products,[a] % 9	10
12	H_2O	Hg(OAc)$_2$[b]	86	14
12	H_2O-THF	Hg(OAc)$_2$[b]	85	15
11	H_2O-THF	Hg(OAc)$_2$	54	46
11	H_2O-THF	Hg(OAc)$_2$[b]	56	44
11	H_2O-THF	Hg(NO$_3$)$_2$	0	100
4a	H_2O-THF	Hg(OAc)$_2$	100	0

[a] Ratio of ether isomers as determined by nmr analysis. [b] Sodium acetate added to water before mercuric acetate.

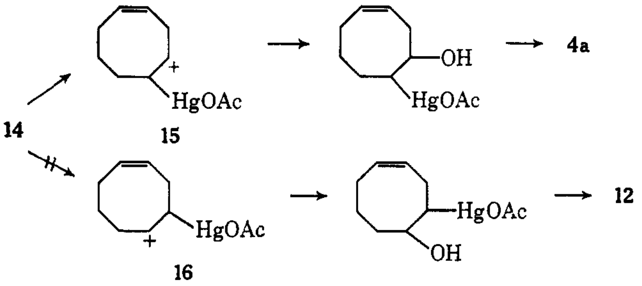
that nmr spectroscopy was superior to either of these methods. In nmr analysis, advantage was taken of the fact that **9** has a signal at τ 5.7 for the tertiary hydrogens, whereas **10** has a signal at 6.2. The infrared spectrum of **9**, contaminated with 15% **10**, as shown by nmr analysis, was practically the same as that of pure **9**. Thus we conclude that infrared sepctroscopy cannot detect less than 10% **10** which might be present in **9**.

The major product from 1,4-cyclooctadiene[8] on oxymercuration–demercuration was 3-cycloocten-1-ol. The addition of mercuric acetate is specific, for the isomeric 4-cycloocten-1-ol was not detected. There was only a small amount of cyclization product, namely, 1,4-epoxycyclooctane **9**, which was not contaminated by the 1,5 isomer.

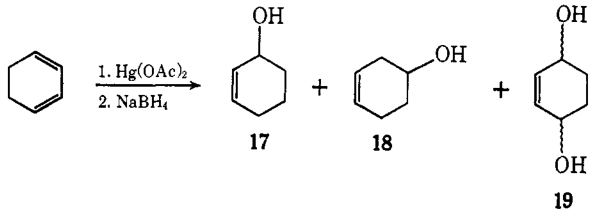


Since the diacetates were more readily detected on gas chromatography, the above reaction mixture was treated with acetic anhydride to determine the amount of diols formed. The diacetates formed were less than 8% of the total mixture, and no further attempts were made to identify them.

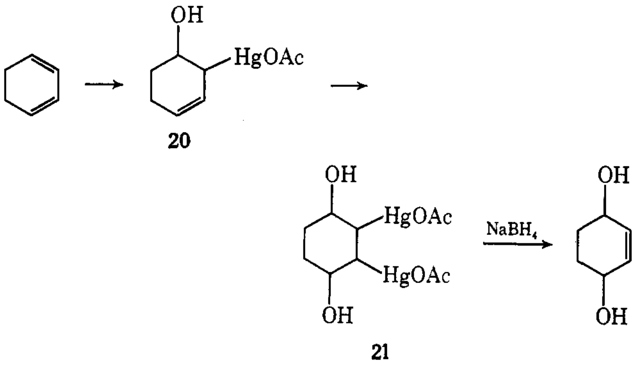
Specific addition of mercuric acetate to 1,4-cyclooctadiene may be rationalized on the basis of the stability of the mercuric acetate addition intermediate in terms of carbonium-ion character. It has been shown[9] that no rearrangement occurs during the addition of mercuric acetate to olefins, indicating that the intermediate does not involve a free carbonium ion. However, the intermediate might have enough ionic character to cause the selective addition of mercuric acetate to 1,4-cyclooctadiene. The intermediate **15** is a homoallylic carbonium ion, which is expected to be more stable than the intermediate **16**. An alternative explanation for the selective addition may be based on coordination between the mercuric acetate and one of the double bonds, thus directing the addition of the mercuric acetate to the second double bond. We have previously shown[10] that a hydroxyl group in a position allylic to a double bond directs the addition of mercuric acetate. Thus, cyclohexen-1-ol gave mainly *trans*-1,3-cyclohexanediol. There may be an analogous coordination between mercury and a double bond. However, a study of a molecular model of 1,4-cyclooctadiene does not show clearly why the mercury coordinated with a double bond in the 1,2 position should add to the 4 position exclusively.



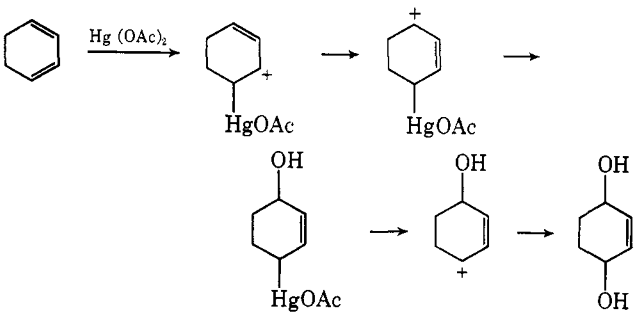
Similar treatment of 1,3-cyclohexadiene did not yield any cyclization product, but gave the alcohols **17**, **18**, and **19**. To better estimate the relative amounts, the alcohol mixture was converted into the corresponding acetates. The relative ratio of the acetates of **17**, **18**, and **19** was 13:13:74.



The formation of **19** may be rationalized as the addition of 2 mol of mercuric acetate, followed by reduction of the dimercurial to form the double bond, as shown below.



Alternatively, the formation of **19** may be envisioned as a product of 1,4 addition of mercuric acetate, followed by solvolysis of the allyl mercurial. We favor



this mechanism over the first one for the following reasons. First, only a 1:1 molar ratio of mercuric acetate to diene was used. It is therefore unlikely that a

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[8] We are grateful to Mr. Charles Ganz for a sample of 1,4-cyclooctadiene

[9] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967).

[10] S. Moon and B. H. Waxman, *Chem. Commum.*, 1283 (1967).

two-step mechanism should provide a predominance of diol. Halpern[11] indicates that the addition of a hydroxy group to the 4 position of 1-butene slows the addition of mercuric acetate to the carbon–carbon double bond by a factor of ten. We therefore suggest that the first mechanism should yield little or no diol. Second, while Henbest[12] demonstrated that 3-cyclohexen-1-ol, which is similar to **20**, adds mercuric acetate selectively yielding only the 1,4-diol, he also demonstrated that the reaction gives only the *trans* product. Our results indicate that both the *cis*- and *trans*-diols are present. Third, it is known that mercuric chloride adds across norbornadiene, yielding the tricyclic derivative.[13] The reaction shows no rearrangement products characteristic of a free carbonium intermediate and suggests a molecular rather than an ionic addition. 1,3-Cyclohexadiene should be prone to a similar attack. Finally it was suggested above that allylic mercurials solvolyze rapidly. Upon the addition of sodium hydroxide, prior to sodium borohydride reduction, a black suspension formed, indicative of free mercury. Such evidence is suggestive of solvolysis of the mercurial acetate group.

1,4-Cyclohexadiene also did not give any cyclization product, but gave 4-cyclohexen-1-ol and a diol. The alcohols were converted into the corresponding acetates. The diacetate peaks on gas chromatography were separated into three small peaks. Attempts to separate these peaks were unsuccessful and no further work was done to identify them individually.

Experimental Section[14]

3,4-Epoxycyclooctene.—The monoepoxide was prepared by the method of Crandall.[15] Treatment of 73.5 g of 1,3-cyclooctadiene with 126 g of 40% peracetic acid in 750 ml of dichloromethane and 290 g of powdered anhydrous sodium carbonate gave 61.3 g (73%) of 3,4-epoxycyclooctene: bp 69–71° (18 mm) [lit.[16] bp 81–87° (22 mm)]. It was noted that, when the crude epoxycyclooctene was injected on a gas chromatograph (silicone oil), it partially rearranged to 3-cycloocten-1-one, probably owing to the high temperature at the injection port (over 200°).

3-Cycloocten-1-ol.—Treatment of 44.6 g of 3,4-epoxycyclooctene with 7.65 g of lithium aluminum hydride in ether according to the method of Cope and Peterson[16] gave 36 g (71%) of the alcohol **4a**: bp 82–84° (13 mm) [lit.[16] 74.5–76.0° (3.1 mm)].

5,6-Epoxycyclooctene.—1,5-Cyclooctadiene (54 g) was treated with 40% peracetic acid by the method of Cope[16] and yielded 28.0 g (46%) of 5,6-epoxycyclooctene: bp 98° (11 mm).

4-Cycloocten-1-ol.—Treatment of 26 g of 5,6-epoxycyclooctene with 2.2 g of lithium aluminum hydride in THF gave[14] 16 g (61%) of 4-cycloocten-1-ol: bp 110° (10 mm).

Oxymercuration–Demercuration of 1,3-Cyclooctadiene with Mercuric Acetate.—To a yellow suspension of 288 g (0.9 mol) of mercuric acetate, 500 ml of THF, and 500 ml of water, 33 g (0.3 mol) of 1,3-cyclooctadiene was added and the mixture was stirred for 4 days at room temperature. To this white-yellow mixture, 390 ml of 3 *M* sodium hydroxide was added and the mixture acquired a brown-green color; the mixture, on stirring for 10 min, became black. The black mixture was then treated with 24 g of sodium borohydride in 390 ml of 3 *M* sodium hydroxide solution; the reaction was exothermic. Metallic mercury was formed at the bottom. The mixture was saturated with sodium chloride and extracted with ether. The organic layer was washed twice with water and dried ($MgSO_4$). The solution was concentrated by distillation and the crude product was distilled through a Vigreux column giving 12.5 g (37%) of 9-oxabicyclo[4.2.1]non-7-ene (**2**): bp 74° (10 mm); ir (CS_2) 3050, 1115, 1090, 1020, 975, 950, 880, 825, 805, 765, and 695 cm^{-1}; nmr (CCl_4) τ 4.2 (s, 2), 5.1 (d, 2), and 8.3 (m, 8).

Anal. Calcd for $C_8H_{12}O_1$: C, 77.28; H, 9.85. Found: C, 77.22; H, 9.65.

When 1,3-cyclooctadiene was treated with mercuric nitrate, it gave **2** only in 15% yield.

The reaction of 1,3-cyclooctadiene with mercuric acetate was repeated in the same way as above, except that the ether–THF layer was not washed with water to avoid the loss of the diols which are water soluble. Thus, from 2.2 g of 1,3-cyclooctadiene was obtained 2.1 g of a crude product. This was treated with acetic anhydride in pyridine. Gas chromatographic analysis (silicone oil) indicated four peaks. The first peak was 1,3-cyclooctadiene (4%), the second peak the unsaturated ether **2** (49%), and the third peak a mixture of 3- and 4-cycloocten-1-yl acetates (6%). The infrared spectrum of the third peak indicated that the two isomeric acetates were present in about equal amount. The fourth peak (41%) was further separated into two peaks, which are believed to be a mixture of *cis*- and *trans*-2-cyclooctene-1,4-diol diacetates.

Oxymercuration–Demercuration of 3-Cycloocten-1-ol.—To a yellow suspension of 63.7 g (0.2 mol) of mercuric acetate, 150 ml of THF, and 150 ml of water, 12.6 g (0.1 mol) of 3-cycloocten-1-ol was added and the mixture was stirred overnight at room temperature. The yellow color persisted owing to the excess mercuric acetate. The mixture was then treated with 150 ml of 3 *M* sodium hydroxide solution and the yellow color intensified to darker yellow. The mixture was then treated with 5 g of sodium borohydride in 150 ml of 3 *M* sodium hydroxide solution (the reaction was exothermic) and after it stirred for 30 min metallic mercury, a gray suspension, and a THF layer at the bottom were observed. The resulting mixture was saturated with sodium chloride and extracted with 300 ml of ether. The combined ether extracts were washed with water, dried ($MgSO_4$), concentrated, and distilled through a Vigreux column giving 8.0 g (63%) of 1,4-epoxycyclooctane (**9**), a camphorlike waxy solid: mp 31.5–32.5° (lit.[17] mp 30.8–32.2°); nmr (CCl_4) τ 5.7 (s, 2) and 8.3 (m, 12).

Oxymercuration–Demercuration of 1,5-Cyclooctadiene.—1,5-Cyclooctadiene (11 g, 0.1 mol) was treated with mercuric acetate (70 g, 0.22 mol) in 100 ml of water and 100 ml of THF. The reaction was fast, as indicated by the change of color from yellow to colorless in 40 sec. The product was isolated as described above, and 8.0 g (63%) of a mixture of 1,4- and 1,5-epoxycyclooctanes was obtained. Nmr analysis indicated that the mixture contained **9** and **10** in a ratio of 55:45.

Oxymercuration–Demercuration of 1,4-Cyclooctadiene.—1,4-Cyclooctadiene (3.0 g, 0.028 mol) was treated with mercuric acetate (8.9 g, 0.028 mol) in 20 ml of water and 30 ml of THF. The yellow color disappeared after 3 min. The mixture was stirred for 0.5 hr. A test with 3 *M* sodium hydroxide for mercuric ion was negative. The mixture was treated with 20 ml of 3 *M* sodium hydroxide, followed by addition of 2 g of sodium borohydride in 20 ml of 3 *M* sodium hydroxide. The mixture was stirred for 20 min and then saturated with sodium chloride. The solution was extracted with ether and the ethereal extract was dried ($MgSO_4$) and concentrated. The products were identified as **14** (13%), **9** (12%), **4a** (70%), and unidentified diols (8%). The reaction mixture was treated with acetic anhydride in pyridine. Gas chromatography and ir analysis showed that, in addition to **9** and **4b** (70%), unidentified acetates (8%) were also present.

Oxymercuration–Demercuration of 1,3-Cyclohexadiene.—A yellow mixture of mercuric acetate (11.5 g, 0.036 mol), 25 ml of water, and 30 ml of THF was treated with cold 1,3-cyclohexadiene (3.0 g, 0.036 mol). The reaction was fast, since the yellow color disappeared in 10 sec, giving a white color to the solution; slight precipitation was also observed. The mixture was stirred until a negative mercuric ion test was obtained on addition of 3 *M* sodium hydroxide. Sodium hydroxide (3 *M*, 20 ml) was added to the mixture, producing a black suspension

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[11] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

[12] H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959).

[13] S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

[14] For gas chromatographic analysis, an F & M Model 720 gas chromatograph was used. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 337, and a Varian A-60 nmr spectrometer was used to record the nmr spectra. The chemical shifts are shown in τ units with tetramethylsilane as an internal standard.

[15] J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).

[16] A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959).

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

which was treated with 2.0 g of sodium borohydride in 25 ml of 3 *M* sodium hydroxide. Mercury metal was observed after the reduction. The suspension was then saturated with sodium chloride and the product was extracted with 100 ml of ether. The ethereal extract was dried ($MgSO_4$) and the solvent was removed by distillation through a Vigreux column. The mixture contained 2-cyclohexen-1-ol (13%), 3-cyclohexen-1-ol (13%), and a fraction which is believed to be *cis*- and *trans*-2-cyclohexene-1,4-diols (74%).

About 1 g of the reaction mixture was treated with acetic anhydride in pyridine. The resulting acetate mixture was shown to be 2-cyclohexen-1-yl acetate (13%), 3-cyclohexen-1-yl acetate (13%), and a diacetate fraction (74%). The infrared spectrum of the diacetate indicated unsaturation, and its nmr had absorptions at τ 4.25 (d, 2 olefinic hydrogen), 5.0 (m, 2, tertiary hydrogen), 8.03 (m, 6 acetoxymethyl hydrogen), and 8.3 (m, 4 H).

About 0.5 g of the above mixture was hydrogenated in acetic acid under atmospheric pressure using platinum oxide as a catalyst. The mixture contained cyclohexyl acetate (26%) and diacetates. Comparison of the infrared spectrum and nmr spectrum of the diacetate with those of authentic samples of *cis*- and *trans*-1,4-cyclohexanediol diacetates indicated that the diacetate was a mixture of the latter two compounds, perhaps with a different isomeric ratio.

Oxymercuration–Demercuration of 1,4-Cyclohexadiene.—1,4-Cyclohexadiene (2 g, 0.025 mol) was treated with mercuric acetate (8 g, 0.025 mol) in 15 ml of water and 25 ml of THF. The reaction color changed from yellow to clear in 50 sec. The product was isolated as described for oxymercuration–demercuration of 1,3-cyclohexadiene and was shown to be 3-cyclohexen-1-ol (67%) and unidentified diol (33%). The mixture was converted into the corresponding acetates by treatment with acetic anhydride in pyridine.

Registry No.—1, 1700-10-3; 2, 20642-83-5; 11, 111-78-4; 12, 4277-34-3; 14, 1073-07-0; 5,6-epoxycyclooctene, 637-90-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

The Base-Catalyzed Reaction of Hydrogen Sulfide with α-Chloromethyl Acrylate and α-Chloroacrylonitrile

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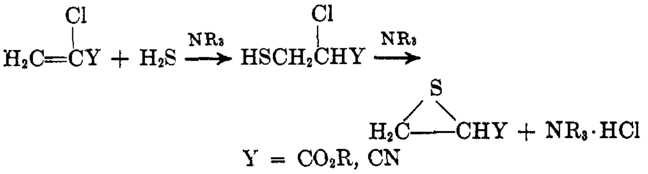
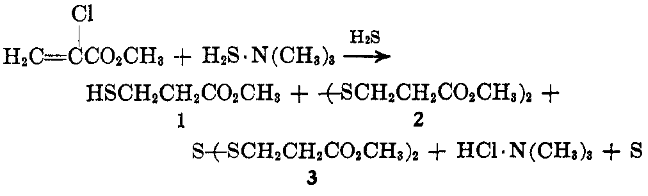
The amine-catalyzed reaction of hydrogen sulfide with α-chloromethyl acrylate produced β-mercaptomethyl propionate, di(β-carbomethoxyethyl) disulfide, di(β-carbomethoxyethyl) trisulfide, trimethylamine hydrochloride, and sulfur. Analogous products were obtained from α-chloroacrylonitrile. These unexpected products are explained by thiirane intermediates which spontaneously expel sulfur.

Base-catalyzed Michael addition of hydrogen sulfide to α-chloroacrylates, followed by the well-established internal displacement of the chloride,[1] was considered to be a convenient one-step synthetic route to apparently unknown thiiranes.[2]



The occurrence of unexpected products and their mode of formation is the topic of the present paper.

α-Chloromethyl Acrylate.—Reaction of equimolar amounts of α-chloromethyl acrylate and trimethylamine–hydrogen sulfide complex dissolved in an excess of liquid hydrogen sulfide at − 78° resulted in five identified products.



$$H_2C{=}\overset{Cl}{\overset{|}{C}}CO_2CH_3 + H_2S\cdot N(CH_3)_3 \xrightarrow{H_2S} \underset{1}{HSCH_2CH_2CO_2CH_3} + \underset{2}{(SCH_2CH_2CO_2CH_3)_2} + \underset{3}{S(SCH_2CH_2CO_2CH_3)_2} + HCl\cdot N(CH_3)_3 + S$$

The solid products, trimethylamine hydrochloride and sulfur, were isolated in 91 and 22% yield, respectively. These yields are based on molar equivalents of amine or α-chloromethyl acrylate used in the reaction.

Glpc analysis of the liquid product showed three major components, β-mercaptomethyl propionate, **1** (15%), di(β-carbomethoxyethyl) disulfide, **2** (61%), and di(β-carbomethoxyethyl) trisulfide, **3** (19%). In addition, several minor unidentified impurities (5%) were present. A mixture of disulfide **2** and trisulfide **3** was obtained on removal of the volatile impurities and the mercaptan **1** at high vacuum and elevated temperature. Attempts to separate **2** from **3** by fractional distillation failed, owing to substantial sulfur extrusion which converted trisulfide **3** into disulfide **2**. A similar situation was experienced with independently synthesized **3**. It was also observed that invariably 10–20% disulfide **2** was formed upon glpc analysis of **3**. This finding made it necessary to deduce a 7:3 ratio as a more realistic product ratio for compounds **2** and **3** from elemental analysis data and molecular weight determination of the mixture. The presence of minor amounts of polysulfides containing more than three sulfurs, however, cannot be excluded in view of the observed disproportionation of trisulfide **3** during glpc analysis.

The structure elucidation of products **1**, **2**, and **3** is based on comparison of spectral data and glpc retention times with those of independently synthesized compounds (Scheme I). Amine-catalyzed addition of H_2S to methyl acrylate afforded the β-mercaptomethyl propionate, **1**, which was oxidized with dimethyl sulfoxide to the corresponding disulfide **2**. Chlorination of this disulfide with sulfuryl chloride resulted in the β-carbomethoxyethanesulfenyl chloride, **4**. The compound's nmr spectrum is consistent with its structure; however, positive identification of this thermally labile sulfenyl chloride was achieved through its stable ethylene adduct **5**. Reaction of sulfenyl chloride **4** with

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[1] W. Coltof, U. S. Patent 2,183,860 (1939); British Patent 508,932 (1939); Dutch Patent 47,835 (1940).

[2] M. Sanders, *Chem. Rev.*, **66**, 297 (1966).