TABLE III

SUMMARY OF N.M.R. DATA FOR DIOXOLANES

Compound	C-2-Proton peak[a]	C-4,5-Protons peaks[a]
Dioxolane	5.43[b]	6.43[b]
2-Ethyl-2-methyl (5a)	...	6.08
2,2'-Bis (6)	5.08	6.03
2-Lauryl (5b)	5.18	6.10, 6.14

[a] Expressed in τ units. [b] Converted from values given in "A Catalog of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and Their Derivatives," Humble Oil and Refining Co., Baytown, Texas, 1959.

carbons 4 and 5 are not equivalent in the compounds used for this study. Inspection of models indicates that the ring is fairly rigid and that free rotation about the carbon-carbon or carbon-oxygen bonds is severely restricted. Consequently, conformational inversion of the type found in dioxane would not be expected to cause a zero average of the chemical shift. For this reason splitting of the peak for the ring protons was expected to occur, but in most cases was not observed.

The ring protons of 2,2'-bis-1,3-dioxolane (5b) (Fig. 6B) gave a series of eight peaks for the protons on carbons 4 and 5. On cooling the solution to −60°, these peaks began to merge. No splitting was observed for the single downfield

(14) J. Kalvoda, G. Anner, D. Arigoni, K. Heusler, H. Immer, O. Jeger, M. Lj. Mihailovic, K. Schaffner, and A. Wettstein, Helv. Chim. Acta, 44, 186 (1961); R. F. Zürcher and J. Kalvoda, ibid., 44, 198 (1961).

(15) E. Caspi, T. A. Wittstruck, and (Mrs.) N. Grover, to be submitted for publication.

peak which was assigned to the protons on carbons 2 and 2'. If there is no accidental superposition of the bands, then the two rings are either eclipsed or rapidly rotating about the 2-2' carbon-carbon bond.

The appearance of two bands for the protons at C-4 and C-5 of 2-lauryl-1,3-dioxolane (5b) (Fig. 6c), separated by 2.5 c.p.s., arises from the above mentioned non-equivalence of the ring protons, since two of the protons are cis to the lauryl group and two are trans. A somewhat similar situation should exist for the 2-methyl-2-ethyl-1,3-dioxolane, but here only an unsplit peak was observed for the protons at carbons 4 and 5.

Comparison of Spectra for Five- and Six-Membered Rings.—It is seen by a comparison of the spectra for dioxanes and dioxolanes that the chemical shift of the peaks for protons on carbons bearing two oxygen atoms is characteristic of the size of the ring. In the dioxolane derivative, this peak lies at lower field (ca. 5.1) than does the corresponding peak for the dioxane derivative (ca. 5.3).

The nature of the signals arising from the —O—CH₂—CH₂—O— portion of the ring is also characteristic of the size of the ring. Unless the molecule is inverting rapidly, the signal for the six-membered rings is split into a number of peaks, and the entire multiplet generally extends over a relatively wide portion of the spectrum. The signal for the analogous protons in five-membered rings is generally much narrower and often unsplit, especially when attached to steroids.

Addition Reactions with Methylenecyclodecane[1a,b]

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Addition reactions with methylenecyclodecane which presumably proceed by way of intermediates with substantial carbonium ion character lead to products which appear to have been formed by proton loss after the initial addition step. Methylenecyclodecane reacts with hydrogen bromide in acetic acid solution to give mainly 1-methylcyclodecene along with some 1-bromo-1-methylcyclodecane; with hypochlorous acid solution to give 1-(chloromethyl)cyclodecene and no chlorohydrin; with 2,4-dinitrobenzenesulfenyl chloride to give an unsaturated, chlorine-free sulfide; and with peroxybenzoic acid to give cyclodecanecarboxaldehyde instead of epoxide. However with hypobromous acid, which can form a bridged-ion intermediate, methylenecyclodecane reacts to give a high yield of a true addition product, a bromohydrin with abnormal orientation. The 1-bromocyclodecylmethanol undergoes rearrangement to 1-(bromomethyl)cyclodecene upon distillation.

Investigations in a number of laboratories have established that alicyclic compounds with medium-sized rings (eight to twelve members in the ring) exhibit features that set them apart from compounds with other ring sizes.[2] For example, chemical equilibria and relative rates of reaction involving numerous alicyclic compounds often show minima or maxima in the medium-ring range. Organic chemists have long rationalized these differences by assuming unusual nonclassical strains in the medium-ring compounds, and very recently

(2) For a summary of some of the evidence for a medium-ring effect, see V. Prelog, J. Chem. Soc., 420 (1950).

HBr
glacial HOAc, 10° → CH₃

HBr
pentane, -20° → Br CH₃

HOCl
H₂O-THF, 5° → CH₂Cl

2, 4-(NO₂)₂C₆H₃-S-Cl
HOAc → CH₂—S—Ar

C₆H₅CO₃H
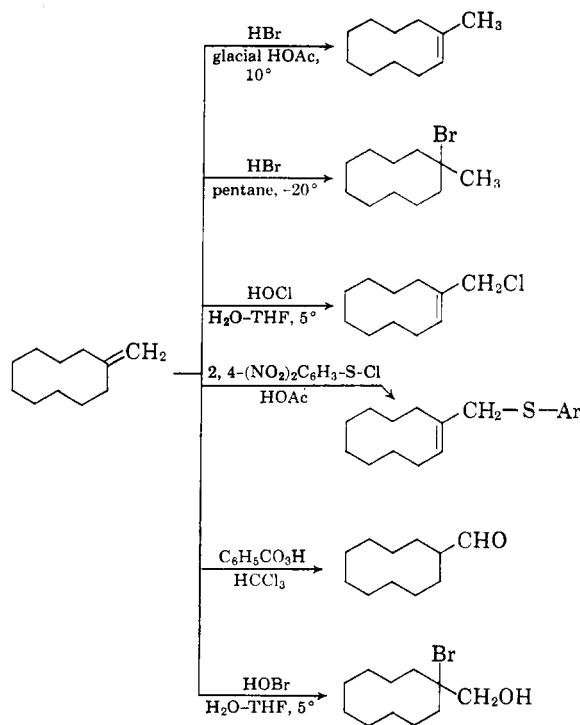HCCl₃ → CHO

HOBr
H₂O-THF, 5° → Br CH₂OH

=CH₂

Fig. 1.—Summary of reaction data.

physical data which indicate the validity of these assumptions have become available. Both thermochemical[3] and X-ray diffraction measurements[4] substantiate the presumption of strain, with the maximum effects being present in nine- and ten-membered rings. A large part of the strain in these rings stems from end-on interaction by hydrogens pointing toward each other from transannular positions.[4] Some of this strain is relieved by the introduction of trigonal carbons in the rings, and attempted substitution reactions are usually accompanied by large amounts of elimination reactions.[5] The intra-annular hydrogens are also responsible for reactions which are different in kind from those of other cyclane derivatives, namely, transannular reactions. Although transannular reactions, usually involving hydride shifts, have been described for smaller ring compounds, these reactions apparently are most favored in ten- (and nine-) membered rings.

Studies of several types of cycloalkane derivatives in the medium-ring group have been reported, but few reactions of olefins in this class have been described. For several years, we have been investigating addition reactions of cyclic olefins, and

some interesting and unexpected orientation effects have been observed. With a series of methylenecycloalkanes (ring sizes four to seven), hydrogen bromide adds only normally (tertiary bromide)[6]; hypochlorous acid gives mixtures of chlorohydrins, sometimes with abnormal orientation (tertiary chloride) predominating[7]; and hypobromous acid gives exclusively the abnormally oriented bromohydrins.[7] We wished to extend those studies to medium-ring compounds in order to investigate the possibility of transannular addition to an olefin and to delineate more precisely the nature of the intermediates in olefin addition reactions. This paper describes our studies with methylenecyclodecane.

Methylenecyclodecane was prepared from cyclodecanone by the Wittig reaction (triphenylphosphorus–methylene).[8] Poor yields of olefin contaminated with unchanged ketone were obtained in refluxing ether,[8] but good yields of ketone-free olefin were obtained when the Wittig complex was heated at 85–90° in diglyme (diethylene glycol dimethyl ether). A summary of our experiments with this olefin is presented in Fig. 1.

Additions with Elimination.—Attempted addition of anhydrous hydrogen bromide in glacial acetic acid to methylenecyclodecane gave little or no alkyl bromide; instead isomerized olefin, 1-methylcyclodecene, was isolated as the main or exclusive product, sometimes in quantitative yield. The tertiary bromide was isolated in good yield from reactions of the olefin with anhydrous hydrogen bromide in pentane solution. It slowly lost hydrogen bromide on standing at room temperature although it appeared stable for a few days in a refrigerator. Either spontaneously or on treatment with pyridine, the bromide lost hydrogen bromide to form 1-methylcyclodecane. In glacial acetic acid, 1-methylcyclodecene itself added hydrogen bromide in fairly good yields to give the same 1-bromo-1-methylcyclodecane. Since much higher yields of tertiary bromide are obtained from the endo olefin than from its exo isomer under identical conditions, and since we can isolate the relatively unstable bromide with little loss through decomposition, we suggest that isomerization of methylenecyclodecane is the primary reaction and that formation of 1-bromo-1-methylcyclodecane in those reaction mixtures involving the exo olefin is a result of relatively slow addition to the isomerization product. Support for this suggestion is found in the report that isomerization of methylenecyclodecane to 1-methylcyclodecene, catalyzed by a non-adding acid (p-toluenesulfonic acid), in glacial acetic acid solution is complete only after about four hours at

(3) H. van Kamp, thesis, Vrije Universiteit, Amsterdam, Netherlands, 1957; J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, Rec. trav. chim., 79, 1226 (1960).

(4) R. R. Bryan and J. D. Dunitz, Helv. Chim. Acta, 43, 760 (1960); J. D. Dunitz and H. M. M. Shearer, ibid., 43, 18 (1960); J. D. Dunitz and V. Prelog, Angew. Chem., 72, 896 (1960).

(5) A. C. Cope and H. E. Johnson, J. Am. Chem. Soc., 79, 3889 (1957).

(6) J. G. Traynham and O. S. Pascual, J. Org. Chem., 21, 1362 (1956).

(7) J. G. Traynham and O. S. Pascual, Tetrahedron, 7, 165 (1959).

(8)(a) S. Trippett, in "Advances in Organic Chemistry," ed. by R. A. Raphael, E. C. Taylor, and H. Wynberg, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, p. 83; (b) G. Wittig and U. Schoellkopf, Org. Syn., 40, 66 (1960).

25°.[9] (We used a reaction time of four hours at 10–15°.)

No real attempt was made in our work to analyze the product 1-methylcyclodecene for cis and trans isomers, but the infrared spectra are consistent with the earlier report[9] that equilibrium mixtures of olefins formed from methylenecyclodecane contain substantial amounts of trans- as well as cis-1-methylcyclodecene.

In several experiments the yield of 1-methylcyclodecene was nearly quantitative; only small amounts of any other substances could be detected by gas chromatography, and those were of appreciably shorter retention times. Particularly notable was the absence of any detectable amount of a transannular product such as 5- or 6-methylcyclodecene, indicating that the intermediate tertiary carbonium ion fails to undergo a transannular hydride shift. Other examples, in cyclooctyl derivatives, of the exclusion of transannular reactions which would require a rearrangement from a more stable (tertiary) carbonium ion to a less stable (secondary) one have been reported.[10] This present example with a cyclodecane derivative, some of which react exclusively in the transannular manner, provides good evidence that such hydride shifts are most unlikely to be observed.

In a solvent with poor ion stabilizing ability (pentane), methylenecyclodecane reacts with hydrogen bromide to give the true addition product, 1-bromo-1-methylcyclodecane. But in a better ion stabilizing solvent, such as glacial acetic acid, the intermediate tertiary carbonium ion reacts by a different path. Apparently elimination of a proton to give the less strained olefin is the preferred path, rather than addition, once an intermediate with substantial tertiary carbonium ion character has been formed. This result suggested to us that
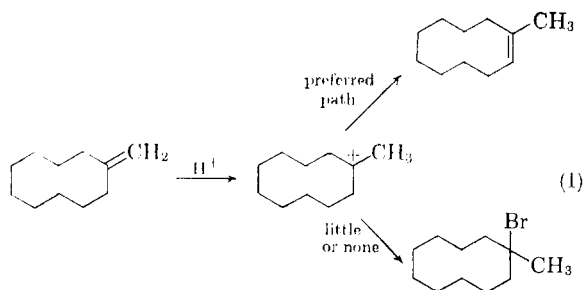

methylenecyclodecane might well afford data which will be helpful in delineating the nature of intermediates in ionic addition reactions with olefins.

A related result has been obtained in the attempted addition of hypochlorous acid to methylenecyclodecane. No chlorohydrin could be obtained, but an unsaturated chloride, shown by degradative

(9) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.*, **82**, 1750 (1960).

(10) A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **81**, 1650 (1959); A. C. Cope and P. E. Burton, *ibid.*, **82**, 5439 (1960).

oxidation to be 1-(chloromethyl)cyclodecene, was formed instead. The intermediate ion, formed in aqueous solution by attack of positive chlorine on the olefin, fails to combine with nucleophilic reagent. Product is formed by loss of proton to give the less crowded cyclodecene derivative.
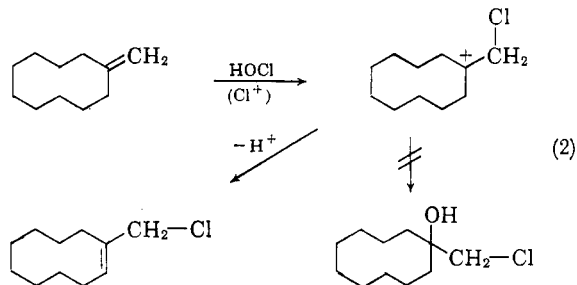
Additions of 2,4-dinitrobenzenesulfenyl chloride to unsymmetrical olefins give adducts in which chlorine is attached to the more substituted carbon, —S—Ar to the less substituted one.[11] Sometimes mixtures are formed, but in those cases which have been carefully examined the predominant product is that one expected on the assumption that initial attack on the olefin is by 2,4-dinitrobenzenesulfenylium ion.
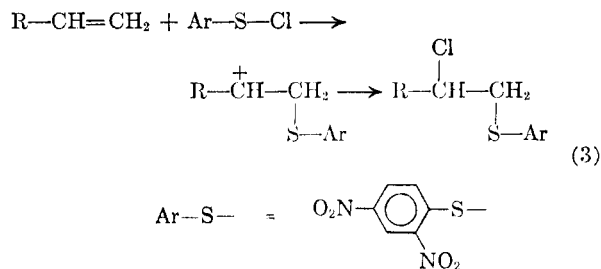
When methylenecyclodecane and 2,4-dinitrobenzenesulfenyl chloride are allowed to react under conditions which usually give high yields of addition products,[11] a chlorine-free, unsaturated product is obtained in virtually quantitative yield. So far as we know, this is the first reported instance of the formation of unsaturated sulfide rather than chloro sulfide in such an olefin reaction. Although we have not established the structure of this product unequivocally, it gives analyses for C, H, and N consistent with the formulation
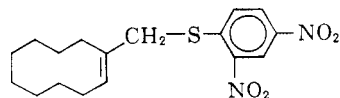
Here again, the apparent course for the reaction is formation of intermediate by attack of cationic sulfur followed by loss of proton rather than by addition of chloride.

Attempted additions of hydrogen bromide, hypochlorous acid, and 2,4-dinitrobenzenesulfenyl

(11) For a review and references, see N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956).

chloride all apparently follow this half-addition, elimination course involving an intermediate with substantial tertiary carbonium ion character. One further example may provide information of particular diagnostic value, so far as mechanisms are concerned.

In an attempted epoxidation of methylenecyclodecane with peroxybenzoic acid in chloroform solution, no epoxide at all could be found in the product mixture. Instead, the yield of cyclodecanecarboxaldehyde is nearly quantitative. Some descriptions of the mechanisms of olefin epoxidations by peroxy acids include an intermediate carbonium ion formed by addition of OH^+ to the less substituted olefinic carbon (equation 4).[12]

$$R—CH=CH_2 + C_6H_5—CO_3H \longrightarrow$$
$$R—\overset{+}{C}H—CH_2 \longrightarrow R—CH—CH_2 + H^+ \quad (4)$$
$$\underset{OH}{\longleftarrow}$$
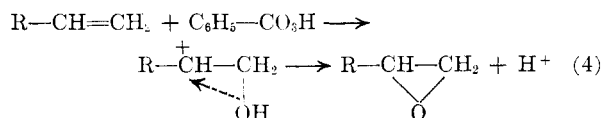
If such a carbonium ion is indeed an important part of the reaction, proton loss should intervene before epoxide formation is complete when methylenecyclodecane is used as olefin. Apparently elimination of proton does indeed occur, but not to give the *endo* olefin obtained from the hydrogen bromide reaction. Proton from the exocyclic carbon is lost to give presumably an enol, and then aldehyde (equation 5).


(5)
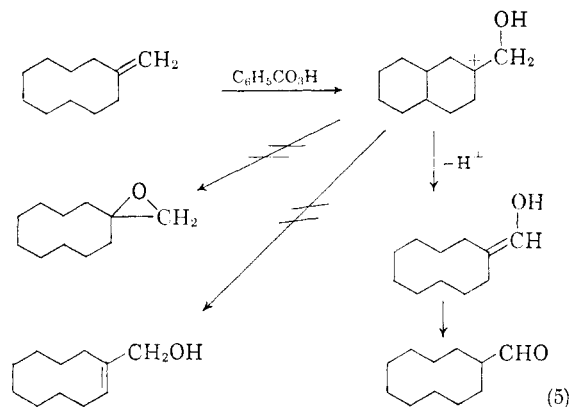
The direction of elimination in this case is interesting. The equilibrium between the isomers methylenecyclodecane and 1-methylcyclodecene has been studied, and the *endo* olefin is favored by a factor of at least 1000.[9] This amounts to a stabilization energy of about 3.5–4 kcal./mole, roughly the same as the resonance energy in ethyl vinyl ether,[13] which the enol intermediate might be expected to resemble in terms of stabilization energy. In other words, the usual preference for formation of the *endo* olefin is balanced in this case by the resonance energy contribution by the substituent

(12) W. A. Waters, "Oxidation Processes," in Gilman's "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1165.
(13) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 85.

oxygen, and subsequent formation of aldehyde may well provide the deciding driving force. Alternatively, aldehyde formation may be pictured as an example of a pinacol-type rearrangement, with hydride migrating from exocyclic carbon to the electron-deficient ring carbon.

The isolation of aldehyde rather than epoxide may be indicative simply of the instability of the epoxide rather than of mechanistic details. Other epoxides rearrange under the influence of acid catalysis to aldehydes, and in certain cases the epoxide has indeed been shown to be incapable of isolation from peroxy acid oxidation mixtures.[14] We intend to acquire data bearing on this point by attempting to prepare methylenecyclodecane oxide by other routes.

Additions without Elimination.—If an intermediate with substantial tertiary carbonium ion character could be avoided, addition might be expected to continue and be unaccompanied by elimination. Such a result has been realized in the addition of hypobromous acid. Attack by Br^+ or its kinetic equivalent leads to pi-complex and then to bridged bromonium ion, which suffers attack by water at the primary position to give abnormally oriented bromohydrin (tertiary bromide) (equation 6). This 1-bromo-1-cyclodecylmethanol, which

(6)
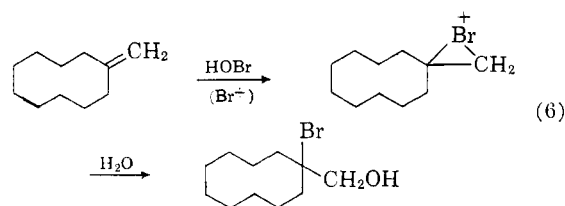
was obtained in 88% yield, gives infrared absorptions and chemical classification tests characteristic of tertiary bromide, primary alcohol rather than those for the isomeric primary bromide, tertiary alcohol. Similar abnormal addition of hypobromous acid has been found for methylenecycloalkanes with smaller rings, and it was attributed to bridged ion formation.[7] The present case seems to provide unusually good evidence for the bridged-ion intermediate, since elimination is apparently the preferred path for reaction involving an intermediate with substantial tertiary carbonium ion character.

A related situation may be found in the reaction between cyclodecanone and triphenylphosphorusmethylene. The fact that high yields of methylenecyclodecane were obtained in that reaction provides, we feel, additional evidence for the accepted 4-center type mechanism of the Wittig reaction.[8a] Intermediates with substantial electron-deficiency on carbon are not formed.

(14) S. W. Tinsley. J. Org. Chem., 24, 1197 (1959). The olefins which gave ketones rather than epoxides in this study are ones which would be expected to form more stable carbonium ion intermediates than the olefins which did give epoxides.

Substituents with divalent sulfur in appropriate position frequently exhibit good neighboring group participation, and an attack on methylenecyclodecane by arenesulfenyl cation might be expected to form a bridged-ion intermediate rather than a conventional carbonium ion, described earlier. We attribute the lack of bridged-ion formation to the relatively high electron deficiency on sulfur, induced by electron withdrawal by the dinitro substituents.

Rearrangement of Bromohydrin.—Characterization of methylenecyclodecane bromohydrin was based on experiments with undistilled material.[15] During vacuum distillation of the bromohydrin, an interesting and surprising rearrangement occurred which led to the formation of hydroxyl-free, unsaturated bromide. Oxidative degradation established the identity of the distillate as 1-(bromomethyl)cyclodecene. Since the distillation system was evacuated before heating was begun, a mechanism solely involving dehydrobromination to allylic alcohol followed by reaction between the alcohol and hydrogen bromide (equation 7) seems

$$+ H_2O \qquad (7)$$
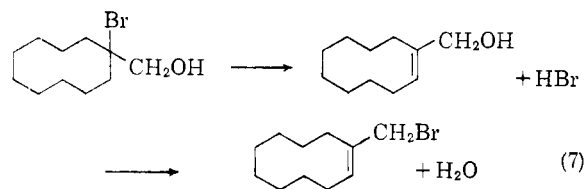
unlikely. Most probably substantial amounts, if not all, of the hydrogen bromide would be lost through the evacuating system and some allylic alcohol would remain unconverted. No alcohol could be found in the product distillate. We suggest a mechanism represented by equation 8. A

$$(8)$$
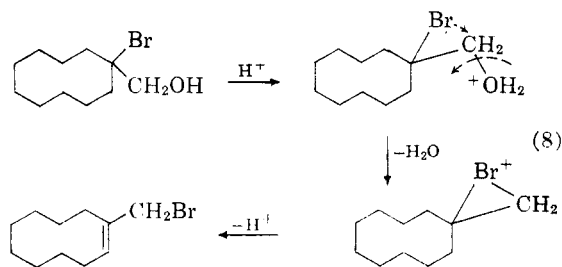
trace of acid, perhaps from dehydrobromination of a few molecules of bromohydrin, protonates the hydroxyl group of a bromohydrin molecule. Assistance by neighboring bromine leads to loss of water and to formation of the same bridged-ion intermediate involved in bromohydrin formation (equation 6). In the absence of a good nucleophilic reagent, however, displacement of the bromine in this bridged-ion intermediate does not occur, and an alternate course—migration of bromine and loss of proton—leads to product. The proton can be

(15) Some samples were chromatographed on alumina without noticeable change in chemical behavior or in infrared spectra.

lost directly to another bromohydrin molecule to continue the reaction sequence. In this scheme, hydrogen bromide molecules are never formed beyond the initial trace amounts required, and no products other than 1-(bromomethyl)cyclodecene and water are formed during the process.[16]

Studies of the chemistry of medium-ring olefins are being continued in our laboratory.

Experimental[17]

Preparation of Methylenecyclodecane.—To 31 g. (0.087 mole) of methyltriphenylphosphonium bromide in a nitrogen-filled three-neck flask was added 100 ml. of 0.88 M phenyllithium solution (0.088 mole). After the reaction mixture had been stirred vigorously for 3.5 hr., a solution of 13.5 g. (0.0875 mole) of cyclodecanone in 20 ml. of anhydrous ethyl ether was added slowly by drops. The react'on mixture was stirred under a nitrogen atmosphere for 24 hr. The ether was removed by distillation, 100 ml. of anhydrous diglyme was added, and the mixture was stirred and heated at 80–90° for 5 hr. The mixture was cooled and filtered. The filter cake was washed with five 50-ml. port ons of pentane, and the pentane washings were used to extract the filtrate, which had been diluted with 250 ml. of water. The combined pentane extracts were washed with five 50-ml. portions of water to remove all diglyme, and the aqueous washings were extracted once with 25 ml. of pentane. The total pentane solution was dried over magnesium sulfate, and the solvent was removed by distillation through a 30-cm. Vigreux column. The residue was distilled at reduced pressure to yield 11.2 g. (84%) of methylenecyclodecane[9]: b.p. 103–111° (29 mm.), $n^{25}D$ 1.4819–1.4822. Analysis by gas chromatography (6-ft. silicone column) indicated purity of 93–99% in different preparations. Definitive infrared absorptions: 3050 (=CH$_2$), 1630 (olefin, =CH$_2$?), and 883 (=CH$_2$) cm.$^{-1}$.

Reaction of Methylenecyclodecane with HBr. I. In Glacial Acetic Acid.—A. A solution of methylenecyclodecane (1.0 g., 0.0066 mole) in 15 ml. of glacial acetic acid, chilled to 10–15°, was added to a chilled solution of anhydrous hydrogen bromide (0.57 g., 0.0070 mole) in glacial acetic acid (6.5 ml.), and the mixture was stirred at 10–15° for 4 hr. After being poured into 100 ml. of ice water, the mixture was extracted four times with 25-ml. portions of pentane. The combined organic solution was washed once with 25 ml. of 5% sodium bicarbonate solution and twice with 25-ml. portions of water. After drying and removal of solvent at reduced pressure at room temperature, 1.0 g. (100%) of 1-methylcyclodecene[9] remained; $n^{25}D$ 1.4840; 95% purity indicated by gas chromatography (6-ft. silicone column; most of the remaining 5% was material with short retention time). The infrared spectrum of this olefin, with relatively strong absorptions at 1660 (olefin), 1372 (CH$_3$), 855 (internal C=C) 824 (internal C=C) and 788 (R$_2$C=CHR) cm.$^{-1}$, is clearly distinguishable from that of methylenecyclodecane. Several weaker absorptions (at 1319, 987, and 965 cm.$^{-1}$) can be

attributed to the presence of *trans* olefin.[18] Isomerization of methylenecyclodecane in acetic acid containing *p*-toluenesulfonic acid has previously been shown to yield appreciable amounts of *trans*-1-methylcyclodecene along with the principal product, *cis*-1-methylcyclodecene.[9] The spectra of our 1-methylcyclodecene products are entirely consistent with that report.

Identity of the 1-methylcyclodecene was established by ozonolysis of the olefin in methanol solution at −78°. After removal of methanol solvent, decomposition of the ozonide in 90% formic acid solution with 30% hydrogen peroxide gave an 88% yield of the known 10-ketoundecanoic acid, m.p. 57.5–58°.[19] The keto acid was converted to its semicarbazone, m.p. 133.5–134°.[19] We were unable to obtain any evidence for the presence of any isomeric olefin, such as 4- or 5-methylcyclodecene, which would have been formed by a transannular hydride shift.

When a solution of methylenecyclodecane (0.59 g.) in glacial acetic acid (10 ml.) was stirred at 10–15° for 4 hr., the recovered olefin gave an infrared spectrum identical with that of starting methylenecyclodecane (different from isomeric 1-methylcyclodecene). Apparently no isomerization occurs under these conditions in the absence of hydrogen bromide.

B. In a later experiment, after 1-bromo-1-methylcyclodecane had been isolated from the addition in pentane (II below), particular care was used to ensure that any *t*-bromide formed would not be lost during work-up. From 1.0 g. (0.0066 mole) of methylenecyclodecane and 0.64 g. (0.0072 mole) of anhydrous hydrogen bromide in 13 ml. of glacial acetic acid was obtained, by the same procedure, 1.11 g. of a mixture of olefin and *t*-bromide: n^{25}D 1.4868. On the basis of refractive index and weight of material, this mixture was estimated to be about 85–95% 1-methylcyclodecene and about 15–5% 1-bromo-1-methylcyclodecane.

II. **In Pentane.**—A. A slow stream of anhydrous hydrogen bromide was passed for 2 hr. into a solution of methylenecyclodecane (1.11 g., 0.0072 mole) in 50 ml. of pentane, chilled to −20° in a nitrogen-filled flask. The pentane solution was washed twice with 10-ml. portions of 10% sodium bicarbonate solution and twice with 25-ml. portions of water, it was dried over magnesium sulfate, and the solvent was removed under vacuum at room temperature to give 1.53 g. (91%) of crude bromide. Vacuum distillation of the product gave 1.11 g. (66%) of 1-bromo-1-methylcyclodecane; b.p. 78–80° (0.4 mm.), n^{22}D 1.5096, infrared absorptions at 1370 (CH₃) and 1090 cm.⁻¹. The *t*-bromide gave an immediate precipitate with silver nitrate and slowly lost hydrogen bromide at room temperature to form 1-methylcyclodecene. Because of the instability of the 1-bromo-1-methylcyclodecane, we did not obtain microanalytical data for this compound.

B. In another experiment, an attempt was made to add hydrogen bromide under free radical conditions. A solution of methylenecyclodecane (1.93 g., 0.0127 mole) in 50 ml. of pentane was irradiated in a quartz reaction flask with a GE 250-watt Type H lamp while a slow stream of anhydrous hydrogen bromide was passed through the solution for 2 hr. Work-up very similar to that above gave 2.81 g. (95%) of crude 1-bromo-1-methylcyclodecane, n^{23}D 1.5089, which was vacuum distilled; yield, 2.12 g. (72%); b.p. 75–77° (0.3 mm.); n^{23}D 1.5108. The infrared spectrum was identical with that obtained for the sample of 1-bromo-1-methylcyclodecane prepared in the absence of irradiation. No evidence could be obtained for the formation of the isomer, (bromomethyl)cyclodecane. A control experiment with 1-octene under identical reaction conditions gave a 76% yield of 1-bromoöctane, b.p. 109–110° (40 mm.), n^{25}D 1.4523.

Dehydrobromination of 1-Bromo-1-methylcyclodecane.—A solution of 1-bromo-1-methylcyclodecane (0.64 g., 0.0027

mole) in 10 ml. of anhydrous pyridine was permitted to stand at room temperature for 1 hr. with occasional shaking and was then heated on a steam bath for 1 hr. The solution was poured into 100 ml. of ice water, the mixture was extracted with three 20-ml. portions of pentane, and the pentane solution was washed with 10% hydrochloric acid and twice with water. After the solution had been dried over magnesium sulfate, the solvent was evaporated to leave 0.39 g. (95%) of 1-methylcyclodecene. Other experiments gave yields of 87 and 98%. Distillation afforded olefin shown to be at least 98% pure by gas chromatography; b.p. 120–123° (40 mm.), n^{24}D 1.4858.

Reaction of 1-Methylcyclodecene with Hydrogen Bromide. —1-Methylcyclodecene (0.0066 mole) and anhydrous hydrogen bromide (0.0072 mole) were allowed to react in glacial acetic acid (15.8 ml.) under the same conditions as were used for methylenecyclodecane. After evaporation of solvent, there remained 1.3 g. (86%) of a mixture of 1-bromo-1-methylcyclodecane and 1-methylcyclodecene; n^{24}D 1.5024. On the basis of weight of material and refractive index, the composition of the mixture was estimated to be about 55–70% *t*-bromide, 45–30% olefin.

Reaction of Methylenecyclodecane with Hypochlorous Acid.—A suspension of methylenecyclodecane (1.35 g., 0.0089 mole) in a mixture of 50 ml. of tetrahydrofuran and 25 ml. of water was cooled to 5°. A solution prepared from 5 ml. of 2.15 M (0.0108 mole) hypochlorous acid and 15 ml. of water was added to the stirred, chilled olefin suspension in 5-ml. portions at 10–15-min. intervals. The mixture was then stirred for 1 hr. at 5–10°, diluted with 100 ml. of water, and extracted three times with 30-ml. portions of ether. The combined ether solution was washed with 15 ml. of dilute potassium iodide solution, with 15 ml. of 10% potassium carbonate solution, and three times with 20-ml. portions of water. The wash solutions were extracted with two 25-ml. portions of ether and the combined ether solution was dried over magnesium sulfate. Removal of the solvent under vacuum at room temperature left 1.33 g. of chlorine-containing liquid which quickly gave a precipitate with silver nitrate solution at room temperature and decolorized potassium permanganate solution. Vacuum distillation gave 0.67 g. (40.5%) of 1-(chloromethyl)cyclodecene, b.p. 65–68° (0.2 mm.), n^{25}D 1.5090, infrared absorptions at 1670 (olefin), 1260, 885, and 855 (internal C=C) cm.⁻¹.

Anal. Calcd. for C₁₁H₁₉Cl: C, 70.80; H, 10.26. Found: C, 70.86; H, 10.14.

Oxidation of 1-(Chloromethyl)cyclodecene.—The structure of the product from the reaction of methylenecyclodecane and hypochlorous acid was established by sequential oxidation with ozone and hypobromite to sebacic acid. A solution of 0.67 g. (0.0036 mole) of 1-(chloromethyl)cyclodecene in 30 ml. of absolute methanol was saturated with ozone at −78°. The alcohol solvent was removed under vacuum, and the ozonide residue was decomposed in 10 ml. of 90% formic acid with 7 ml. of 30% hydrogen peroxide. After the reaction mixture had been poured into ice water and the aqueous solution had been extracted with three 15-ml. portions of ether, the ether solution was extracted twice with 10-ml. portions of 5% sodium hydroxide solution and once with water. To the combined, alkaline aqueous solution, chilled to 0–5°, was added a chilled solution of sodium hypobromite (prepared from 1 g. of sodium hydroxide, 0.58 ml. of bromine, and 20 ml. of water; 0.011 mole). This mixture was stirred at 0–5° for 30 min. and then at room temperature for 2 hr. After extraction with carbon tetrachloride and subsequent acidification with hydrochloric acid, the aqueous mixture was extracted continuously with ether overnight. The ether extract was dried over magnesium sulfate and evaporated to give 0.4 g. (55%) of sebacic acid. After one recrystallization from water and vacuum sublimation, the material melted at 129–131° and did not depress the melting point of authentic sebacic acid.

The ether extract of the ozonolysis reaction mixture yielded 0.11 g. of neutral material which was not identified.

(18) In addition to the book by L. J. Bellamy,[17] see M. Jacobson, M. Beroza, and W. A. Jones, *J. Am. Chem. Soc.*, **83**, 4820 (1961).

(19) W. W. Myddleton and A. W. Barrett, *ibid.*, **49**, 2263 (1927).

Reaction of Methylenecyclodecane with 2,4-Dinitrobenzenesulfenyl Chloride.—A mixture of methylenecyclodecane (1.0 g., 0.0066 mole) and 2,4-dinitrobenzenesulfenyl chloride (1.57 g., 0.0067 mole) in 30 ml. of glacial acetic acid was warmed on a steam bath for 30 min., during which time hydrogen chloride was evolved. After the mixture had been chilled in a refrigerator overnight, the precipitated solid (1.37 g.) was collected. The filtrate was poured over crushed ice, and the aqueous solution was extracted with three 50-ml. portions of pentane. After being washed and dried, the pentane solution yielded an additional 0.81 g. of yellow solid; total yield, 2.18 g. (93%); m.p. 94–96°. A single recrystallization from ethyl alcohol raised the m.p. to 99.5–101°; when the product was mixed with 2,4-dinitrobenzenesulfenyl chloride (m.p. 95–96°), the melting point was depressed to 60°.

The product was chlorine-free and gave a positive test for unsaturation with potassium permanganate. The infrared spectrum contained a shoulder at about 1635 cm.$^{-1}$ suggesting olefinic unsaturation but lacked the several bands usually associated with *trans* olefins.

Anal. Calcd. for $C_{17}H_{22}N_2O_4S$: C, 58.27; H, 6.33; N, 8.00. Found: C, 58.57; H, 6.44; N, 7.94.

Attempts to oxidize the unsaturated sulfide to known compounds with ozone, potassium permanganate and chromic acid all were unsuccessful: only oils or solids which have not yet been characterized were obtained. We were unable to find any cyclodecanone among the oxidation products. This, together with the appearance of a medium-intensity absorption band at 665 cm.$^{-1}$ (in addition to a stronger one at 677 cm.$^{-1}$ for Ar—S) which suggests CH_2—S rather than =CH—S, leads us to suggest tentatively that the sulfide product is 1-cyclodecenylmethyl 2,4-dinitrophenyl sulfide.

Reaction of Methylenecyclodecane with Peroxybenzoic Acid.—A mixture of methylenecyclodecane (1.0 g., 0.0066 mole) and an anhydrous chloroform solution of peroxybenzoic acid (0.48 M, 18 ml., 0.0087 mole) was chilled to 0°, shaken frequently during 45 min., and then placed in a refrigerator for 48 hr. The chloroform solution was washed twice with 10-ml. portions of 10% sodium hydroxide solution and three times with 25-ml. portions of water. The organic layer was dried over magnesium sulfate, and the chloroform was removed under vacuum at room temperature. Distillation of the residue (1.24 g.) gave 1.0 g. (90%) of cyclodecanecarboxaldehyde; b.p. 62–63.5° (0.3 mm.); n^{25}D 1.4830;

infrared absorptions at 3450 (enol) and 1725 (—CHO) cm.$^{-1}$ but none at 1250 (epoxide) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.50; H, 11.98. Found: C, 78.79; H, 11.85.

A sample of the aldehyde was converted to its 2,4-dinitrophenylhydrazone, m.p. 131–132°.

Anal. Calcd. for $C_{17}H_{24}N_4O_4$: C, 58.60; H, 6.94; N, 16.08. Found: C, 58.94; H, 6.80; N, 16.04.

Reaction of Methylenecyclodecane with Hypobromous Acid.—By essentially the same procedure described for the reaction with hypochlorous acid above, reaction between methylenecyclodecane (1.0 g., 0.0066 mole) in 50 ml. of 50% aqueous tetrahydrofuran and hypobromous acid (28 ml. of aqueous solution containing 0.008 mole of hypobromous acid) was carried out. Final removal of ether solvent at room temperature under vacuum gave 1.44 g. (88%) of methylenecyclodecane bromohydrin; n^{25}D 1.5429. Infrared absorptions at 3400, 1080, and 1045 cm.$^{-1}$ strongly suggest primary alcohol; there was no tertiary alcohol absorption in the region 1410–1310 cm.$^{-1}$. The bromohydrin gave positive tests for tertiary bromide with silver nitrate and for primary alcohol with potassium permanganate and Nessler's reagent. It did not react with bromine in carbon tetrachloride. The bromohydrin was oxidized by chromic anhydride in acetic acid at 0–5° to carboxylic acid and by aqueous permanganate (calculated quantity) to a carbonyl compound which gave a positive test with 2,4-dinitrophenylhydrazine. On the basis of these data, we assign the structure of 1-bromocyclodecylmethanol to the bromohydrin.

Attempted vacuum distillation of 1-bromocyclodecylmethanol gave only 1-(bromomethyl)cyclodecene, b.p. 83–85° (0.3 mm.), n^{25}D 1.5323. The distillate gave positive tests for reactive bromine with alcoholic silver nitrate and for unsaturation with aqueous potassium permanganate. Its infrared spectrum contained absorption bands at 1690 (olefin), 1205, 890, 851 (internal C=C), and 822 (internal C=C) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{19}Br$: C, 57.15; H, 8.28. Found: C, 56.99; H, 8.17.

The structure of the 1-(bromomethyl)cyclodecene product (0.84 g., 0.0036 mole) was established by its oxidation to sebacic acid in 85% yield by essentially the same procedure used for the oxidation of 1-(chloromethyl)cyclodecene. The intermediate α-bromoketo acid was isolated in crude yield of 1.11 g.