

pressure mercury lamp (NFUV-300) through a Vycor probe. The solution was outgassed with helium for 2 hr prior to and during the irradiation. The progress of the reaction was monitored by glpc.

(a) *trans*-3-Methylenecyclodecene. The diene was irradiated under the usual conditions, and the glpc results are summarized in Figure 1.

(b) *cis*-3-Methylenecyclodecene. Irradiation of *cis*-7 gave the results summarized in Figure 2.

(c) Bicyclo[7.1.1]undec-1(10)-ene. Irradiation of the cyclohexene for 2 hr produced no change.

(d) 1-Methylcyclodeca-1,3-diene. Upon irradiation, diene 9 slowly isomerized to 10. After 334 min approximately 50% of the starting material had polymerized.

(e) 2-Methylcyclodeca-1,3-diene. After 1140 min approximately 80% of the diene had disappeared. Only 10% of the products were monomeric, and none of the components corresponded to previously identified C<sub>11</sub>H<sub>18</sub> hydrocarbons.

**Sensitized Irradiation of *cis*- and *trans*-3-Methylenecyclodecene.** Following the general procedure for analytical irradiations, a solution of 30 mg (0.20 mmol) of a mixture of *cis*- and *trans*-3-methylenecyclodecene (*cis*- and *trans*-7), 20 mg of tridecane (internal standard) and 10 mg (0.04 mmol) of triphenylene in 80 ml of diethyl ether was irradiated with a low-pressure mercury lamp through a Pyrex probe. The only observed reaction was *cis*-*trans* isomerization about the internal double bond (see Table I).

**Ozonolysis of 2-Methylcyclodeca-1,3-diene.** A room temperature solution of 35 mg (0.23 mmol) of 2-methylcyclodeca-1,3-diene in 8 ml of methylene chloride was ozonized until ozone was no longer consumed. The solution was then concentrated to 3

**Table I.** Sensitized Irradiation of *cis*- and *trans*-3-Methylenecyclodecene

|                   | Irradiation time, min |    |     |     |
|-------------------|-----------------------|----|-----|-----|
|                   | 0                     | 75 | 280 | 720 |
| % <i>cis</i> -7   | 60                    | 73 | 93  | 94  |
| % <i>trans</i> -7 | 40                    | 27 | 7   | 6   |

ml, a mixture of 0.5 ml of hydrogen peroxide (30%), 1 ml of formic acid, and 0.5 ml of water added, and the solution refluxed for 1.5 hr and then evaporated. The resulting yellow oil (56 mg) was crystallized from ethyl acetate to give 11.5 mg (30%) of colorless crystals with mp 130–136°. After recrystallization from the same solvent the mp was 137–139° (mp of authentic suberic acid was 141–142°, mmp 138–141°; the dimethyl esters, prepared with diazomethane, showed identical retention time on SE-30 and on Carbowax columns).

**Permanganate Cleavage of 1-Methylcyclodeca-1,3-diene.** Following the method of Blomquist and Goldstein,<sup>22</sup> 17 mg of 1-methylcyclodeca-1,3-diene was oxidized in aqueous potassium permanganate. After work-up, the resulting yellow oil (32 mg) was esterified with diazomethane. The main product was separated on a 20% DEGS column and showed ir and mass spectra identical with that of an authentic sample of methyl 8-oxononanoate.

(22) A. T. Blomquist and A. Goldstein, *J. Amer. Chem. Soc.*, **77**, 998 (1955).

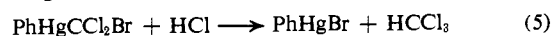
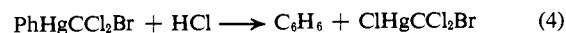
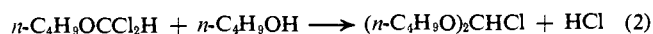
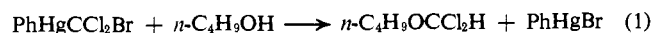
## Halomethyl Metal Compounds. XXXIX. Reactions of Phenyl(trihalomethyl)mercury-Derived Dihalocarbenes with Cyclic Allylic Alcohols, Acetates, and Methyl Ethers<sup>1</sup>

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**Abstract:** While dichlorocarbene (from thermolysis of PhHgCCl<sub>2</sub>Br) appears to react exclusively at the O–H bond of allyl alcohol, it reacts with 3-cyclooctenol to give the C=C addition product, 9,9-dichlorobicyclo[6.1.0]nonanol-2, in 70% yield. Similar reactions with 3-cycloheptenol and 3-cyclononenol gave the C=C addition products in ca. 30% yield, but with 3-cyclohexenol none of the C=C addition product was detected. The successful addition of CCl<sub>2</sub> to the C=C bond of Me<sub>2</sub>C=CHCH(Me)OH in 52% yield suggested that electronic factors are the most important in determining at which site in an unsaturated alcohol—the O–H bond or the C=C bond—dichlorocarbene attack will occur. Chemical and nmr studies indicated that in each case it was the *trans*-*x,x*-dichlorobicyclo[*n*.1.0]-alkan-2-ol which was formed. Phenyl(bromodichloromethyl)mercury-derived CCl<sub>2</sub> also was added to the C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, and C<sub>9</sub> cyclic allylic acetates and methyl ethers to give *trans* products, generally in good yield. The cyclopropanation of C<sub>7</sub>, C<sub>8</sub>, and C<sub>9</sub> cyclic allylic alcohols and methyl ethers with iodomethylzinc iodide also was studied.

We recently reported concerning a study of the reactions of phenyl(trihalomethyl)mercury compounds with alcohols.<sup>2,3</sup> For a simple saturated alcohol such as *n*-butyl alcohol the major products were *n*-butyl formate, *n*-butyl chloride, chloroform, and benzene, in addition to phenylmercuric bromide. It was proposed that these products are formed by the scheme shown in eq 1–5. In the case of allyl alcohol,



we found that such reaction at the O–H bond (eq 1) is preferred to CCl<sub>2</sub> addition to the C=C bond, the isolated products being allyl formate, allyl chloride, benzene, and chloroform.<sup>3</sup>

Our interest in PhHgCX<sub>3</sub> reactions with unsaturated alcohols revived when a report appeared which claimed that phenyl(tribromomethyl)mercury reacts with

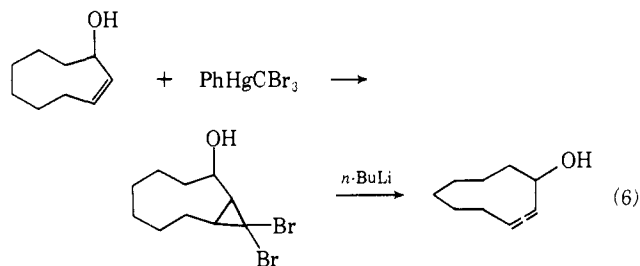
\* To whom correspondence should be addressed.

(1) Part XXXVIII: D. Seyferth, E. M. Hanson, B. Prokai, and R. J. Cross, *J. Organometal. Chem.*, **24**, 33 (1970).

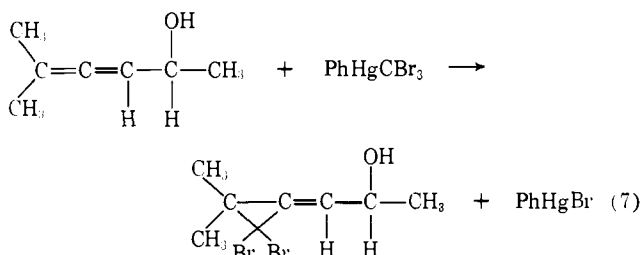
(2) D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *J. Amer. Chem. Soc.*, **86**, 2961 (1964).

(3) D. Seyferth, V. A. Mai, J. Y.-P. Mui, and K. V. Darragh, *J. Org. Chem.*, **31**, 4079 (1966).

3-cyclononanol to give the C=C addition product, 10,10-dibromobicyclo[7.1.0]decanol-2, in 88% yield. The product was not isolated or characterized, but was used in a further reaction with *n*-butyllithium to prepare 1,2-cyclodecadienol-3 (eq 6).<sup>4</sup> An allenyl alcohol also



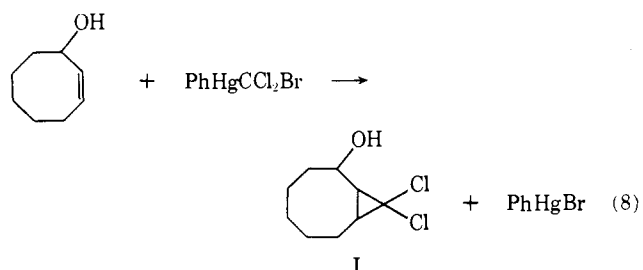
was reported by the same research group<sup>5</sup> to react with phenyl(trihalomethyl)mercury as shown in eq 7.



In view of these divergent findings, it seemed necessary to devote further attention to reactions of phenyl-(trihalomethyl)mercury compounds with unsaturated alcohols.

## Results and Discussion

Our investigation began with the eight-membered ring series. Reaction of 3-cyclooctenol with phenyl-(bromodichloromethyl)mercury in 1:1 molar ratio for 3 hr in refluxing benzene solution gave as product a white, crystalline solid in 70% yield. This product was identified as the C=C addition product, 9,9-dichlorobicyclo[6.1.0]nonanol-1 (I). Its infrared spectrum showed bands indicative of an OH group at 3600, 3400, and 1045  $\text{cm}^{-1}$ , no bands between 1800 and 1600  $\text{cm}^{-1}$ , but weak absorption at 3000  $\text{cm}^{-1}$ , indicative of a chlorine-substituted cyclopropane. No vinyl proton resonances were present in the nmr spectrum. The molecular weight, determined mass spectrometrically, was 208, with the correct isotopic distribution of the parent ion for two chlorine atoms (208:210:212::9:6:1). Carbon, hydrogen, and chlorine analyses confirmed the molecular formula  $\text{C}_9\text{H}_{14}\text{OCl}_2$ . Thus the main reaction is that indicated in eq 8. In



addition, 1,3-cyclooctadiene was formed in 4% yield. Chloroform also was a by-product.

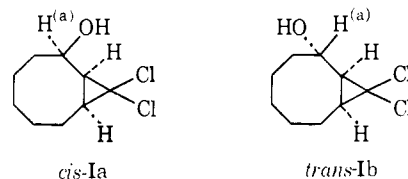
(4) M. Bertrand, M. Santelli, and R. Maurin, *Bull. Soc. Chim. Fr.*, 998 (1967).

(5) M. Bertrand and R. Maurin, *ibid.*, 2779 (1967).

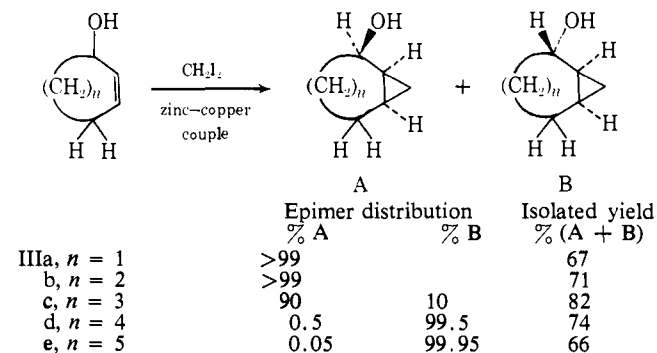
Phenyl(trihalomethyl)mercury reacted with 3-cyclooctenol to give a crystalline C=C addition product, 9,9-dibromobicyclo[6.1.0]nonanol-2 (II), in 61% yield. Again, the haloform was a minor by-product. Both 9,9-dihalobicyclo[6.1.0]nonanol-2 compounds could not be distilled or sublimed without decomposition, but they are relatively stable once they have been purified by recrystallization from hexane. They could not be isolated by glc, but analytical glc could be used to determine their yields.

In the reactions of these phenyl(trihalomethyl)mercurials with 3-cyclooctenol it appears that only one isomer of the respective 9,9-dihalobicyclo[6.1.0]nonanol-2 was formed. Examination of the products by glc suggested this, and, as discussed later, reduction of the products with lithium in *tert*-butyl alcohol and THF gave only one of the two possible bicyclo[6.1.0]nonanol-2 isomers. Both isomers of the latter are separable by glc and samples of each were available for comparison.

The stereochemistry of these additions was of obvious interest. We were interested in determining not only why the double bond of 3-cyclooctenol was so much more reactive than the C=C bond of allyl alcohol, but also which isomer, Ia or Ib, was the one formed and why. An overwhelming preference for one isomer generally is the consequence of an electronic effect, a



steric effect, or an intramolecular "directing" effect. It had been established that the cyclopropanation of 3-cycloalkenols (five, six-, seven-, eight-, and nine-membered rings) by iodomethylzinc iodide occurs stereospecifically, presumably due to prior coordination of the zinc reagent by the OH oxygen lone pair<sup>6</sup>

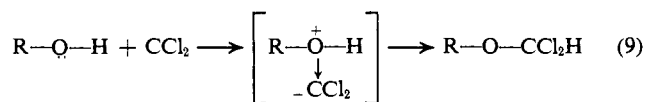


The observed abrupt switch from *cis* stereochemistry to *trans* is in line with expectations: in the case of the larger rings the stable conformations are such that the nearest face of the double bond available for attack by the zinc reagent complexed to the neighboring OH group is that which leads to formation of the *trans* isomer. The reactivity of the C=C bond of 3-cyclohexenol toward  $\text{ICH}_2\text{ZnI}$  is greatly enhanced by the proximity of the OH substituent. When 3-cyclohexenol and cyclohexene were allowed to compete for

(6) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 91, 6892 (1969), and prior references cited therein.

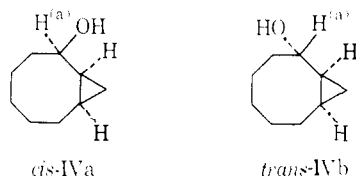
a limited amount of iodomethylzinc iodide, the *only* product obtained was *cis*-bicyclo[4.1.0]heptanol-2.<sup>7</sup>

It was possible that a similar type of steering effect by the OH function could be responsible for both the observed stereospecificity of the PhHgCX<sub>2</sub>-3-cyclooctenol reaction and the heightened reactivity of the C=C bond of this alcohol. We had shown that fluorine substitution in aliphatic alcohols greatly reduces the reactivity of their O-H bonds toward phenyl(bromodichloromethyl)mercury, and we suggested that a plausible explanation of this observation involved initial attack by the electrophilic CCl<sub>2</sub> at the oxygen atom (eq 9).<sup>8</sup> Thus it seemed entirely possible that the



geometry of medium-ring allylic alcohols could be favorable for direction of the attacking dichlorocarbene stereospecifically to the C=C bond by the nearby OH group to produce a single 9,9-dichlorobicyclo[6.1.0]nonanol-2 isomer. This was only conjecture and so it was of some importance to determine the stereochemistry of I or II.

To accomplish this, the product from the 3-cyclooctenol-PhHgCCl<sub>2</sub>Br reaction, I, was reduced with lithium and *tert*-butyl alcohol in THF. The reduction gave only one compound, IV, a liquid, bicyclo[6.1.0]nonanol-2. This compound was identical in all respects with the product obtained by the reaction of iodomethylzinc iodide with 3-cyclooctenol, first prepared by Cope and Woo<sup>8</sup> and shown by Winstein, *et al.*,<sup>6</sup> to be the *trans* isomer IVb. We felt this point to be of sufficient importance to prepare the other isomeric alcohol, IVa, for comparison. Bicyclo[6.1.0]nonanol-2



was oxidized with chromic oxide in dilute sulfuric acid in ether solution to bicyclo[6.1.0]nonanone-2. This ketone then was reduced with lithium aluminum hydride. The product had the same glc retention time as IVb on a 10% Dow Corning DC-200 silicone oil column at 150°; however, it was a low-melting solid, and its infrared and nmr spectra were different from those of IVb. Reduction of bicyclo[6.1.0]nonanone-2 with the extremely hindered diisopinocampheylborane<sup>9</sup> gave an alcohol identical with that produced in the lithium aluminum hydride reduction. The boron hydride used is so hindered that it must deliver the hydride from the least-hindered side of the molecule, producing *cis*-bicyclo[6.1.0]nonanol-2 (IVa). In no case studied previously has the reagent not yielded the most hindered (*cis*) cyclic alcohol as the major product by a large margin.<sup>10</sup> In particular, this reagent has yielded *cis* alcohols in the reduction of four- to eight-membered 2-methylcycloalkanones.

(7) W. C. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

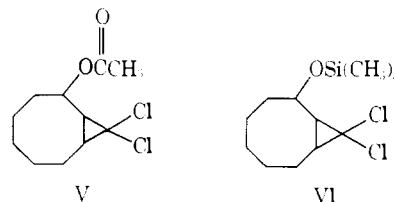
(8) A. C. Cope and G. L. Woo, *ibid.*, **85**, 3601 (1963).

(9) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 3166 (1961).

(10) H. C. Brown and V. Varma, *ibid.*, **88**, 2871 (1966).

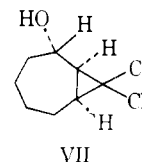
It is thus established (making the reasonable assumption that no change in stereochemistry occurred in the conversion of I to IV) that phenyl(bromodichloromethyl)mercury-derived dichlorocarbene adds to the C=C bond of 3-cyclooctenol to give the *trans* isomer, Ib. It would, at first sight, appear that a "directing" effect of the OH group in 3-cyclooctenol does occur during CCl<sub>2</sub> addition to the C=C bond, since, as in the case of the ICH<sub>2</sub>ZnI reaction, *trans* cyclopropanation did indeed take place. However, it was thought worthwhile to try to obtain similar stereochemical information for the corresponding six-, seven-, and nine-membered cyclic allylic alcohols as well before accepting this as a general conclusion.

3-Cyclooctenyl acetate and 3-trimethylsilyloxyoctene also were allowed to react with phenyl(bromodichloromethyl)mercury. In both cases a product of CCl<sub>2</sub> addition to the C=C bond was obtained in good yield. Hydrolysis of the respective products, V and VI, in each case gave a single 9,9-dichlorobicyclo[6.1.0]nonanol-2, the isomer to which we have assigned the *trans* structure Ib.

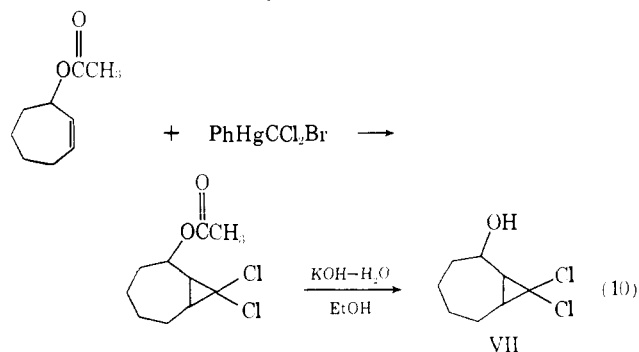


The reactions of the six-, seven-, and nine-membered cyclic allylic alcohols with phenyl(bromodichloromethyl)mercury proceeded considerably less well; the yields of C=C addition product were not as good as that obtained with 3-cyclooctenol and a greater proportion of reaction at the O-H bond seemed to occur than was observed with 3-cyclooctenol. In fact, the reactions were so complex that the respective dichlorobicyclo[*n*.1.0]alkan-2 products could not be isolated in pure form from the reaction mixtures.

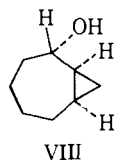
3-Cycloheptenol reacted with phenyl(bromodichloromethyl)mercury to give *trans*-8,8-dichlorobicyclo[5.1.0]octanol-2 (VII) in 31% yield, together with



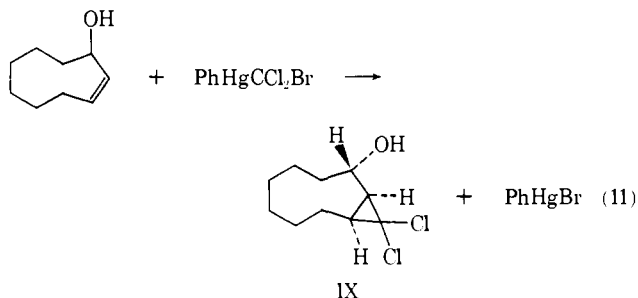
1,3-cycloheptadiene (30%) and chloroform (30%). The dichlorocarbene adduct was identified by comparison of its glc retention time and infrared spectrum with those of authentic *trans*-8,8-dichlorobicyclo[5.1.0]octanol-2 prepared by the route shown in eq 10.



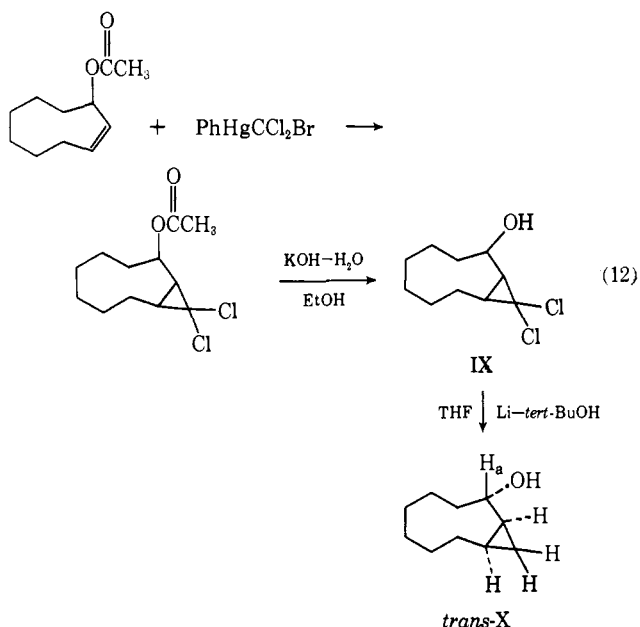
The stereochemistry of the product of the latter reaction was determined by means of its reduction with lithium and *tert*-butyl alcohol in THF to the known<sup>6,11</sup> *trans*-bicyclo[5.1.0]octanol-2 (VIII).



3-Cyclononenol reacted with phenyl(bromodichloromethyl)mercury to give *trans*-10,10-dichlorobicyclo[7.1.0]decanol-2 (IX) in 28% yield. The product



could not be isolated in pure form from the reaction mixture—it decomposed upon attempted sublimation, distillation, and preparative glc, and the contaminants were of like solubility so that crystallization procedures were unsuccessful. A pure sample of IX was prepared by the reaction of 3-cyclononenyl acetate with phenyl(bromodichloromethyl)mercury, followed by alkaline hydrolysis of the 10,10-dichlorobicyclo[7.1.0]decanol-2-acetate thus produced. The glc retention times and the infrared spectra of the two alcohols were identical. Lithium and *tert*-butyl alcohol served to reduce the IX

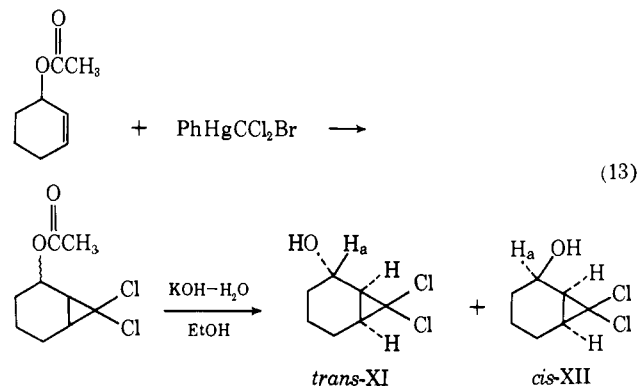


from the sequence shown (eq 12) to bicyclo[7.1.0]decanol-2 (X), a solid with mp 54–55°. An identical product (melting point and spectroscopic properties) was obtained by the reaction of  $\text{ICH}_2\text{ZnI}$  with 3-cyclononenol. Winstein, *et al.*,<sup>6</sup> reported obtaining a product with mp 54.5–55.5° from the 3-cyclononenol-

(11) A. C. Cope, S. Moon, and P. E. Peterson, *J. Amer. Chem. Soc.*, 84, 1935 (1962).

$\text{ICH}_2\text{ZnI}$  reaction and, as mentioned, assigned it the stereochemistry shown in X.

The reaction of 3-cyclohexenol with phenyl(bromodichloromethyl)mercury produced a highly colored reaction mixture—generally blue. A similar color phenomenon, “halochromism,” has been reported to take place in solutions containing mercuric chloride and 3-chlorocyclohexene.<sup>12</sup> The compound responsible for the color changes observed (colorless to yellow to orange to red to dark blue) is thought to be a cyclohexadiene polymer that incorporates the mercuric salt and hydrogen chloride, with a degree of polymerization of 7–10.<sup>12</sup> It was obvious upon examination of our reaction mixture that major decomposition had taken place. Three major high boiling compounds were evident in the mixture. 3-Chlorocyclohexene (31%) was present. Benzene (15%) and chloroform (25%), products derivable from the reaction of phenyl(bromodichloromethyl)mercury with hydrogen chloride (eq 4 and 5), also were identified. *trans*-7,7-Dichlorobicyclo[4.1.0]heptanol-2 (XI), one of the expected products in this reaction, and which was not found, was prepared by the reactions shown in eq 13. Some of the *cis* isomer was formed as well and analytical glc established a *trans/cis* ratio of 7. The reaction product

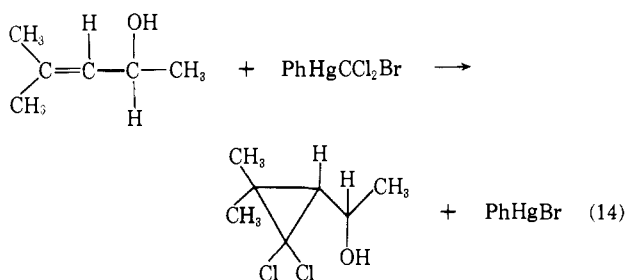


mixture of XI and XII decomposed during attempted glc isolation; its reduction with lithium and *tert*-butyl alcohol yielded a mixture containing mostly *trans*-bicyclo[4.1.0]heptanol-2, together with a small amount of the *cis* isomer. Both of these isomers are known compounds.<sup>7</sup>

Before considering the implications of our finding of *trans* stereochemistry for the products of dichlorocarbene addition to the C=C bonds of the seven-, eight-, and nine-membered ring 3-cycloalkenols, we wish to inquire more deeply into the question of why the C=C bonds in these compounds are so much more reactive than the C=C bond of allyl alcohol. Facilitation of reagent approach by the OH group certainly is one possible explanation, but electronic effects should not be neglected. For instance, available data suggest that the C=C bonds of allyl alcohol and 3-cyclooctenol should differ considerably in reactivity toward  $\text{PhHgCCL}_2\text{Br}$ -derived dichlorocarbene on the basis of electronic effects alone. Relative rate studies have shown that the C=C bond of cyclooctene is 1.24 times more reactive than that of cyclohexene toward dichlorocarbene generated from phenyl(bromodichloromethyl)mercury in benzene at 80°, while the C=C bond of a terminal olefin, 1-heptene, is only 0.24

(12) H. Böhme and G. Peters, *Z. Naturforsch. B*, 12, 5 (1957).

times as reactive as that of cyclohexene under the same conditions.<sup>13,14</sup> Thus in the case of 3-cyclooctenol *vs.* allyl alcohol, one would expect (in the absence of other factors) the former to be some five times more reactive than the latter with respect to  $\text{CCl}_2$  addition to the  $\text{C}=\text{C}$  bond. Is this difference sufficient to cause a complete changeover in the nature of the reaction observed— $\text{C}=\text{C}$  addition with the cyclic alkenol, O—H insertion with allyl alcohol? In the absence of quantitative information concerning the reactivity of the alcohol O—H bond toward dichlorocarbene one cannot answer this question. However, this idea could be tested by increasing the nucleophilicity of the  $\text{C}=\text{C}$  bond of allyl alcohol by appropriate alkyl substitution. In our relative rate study<sup>14</sup> we noted the following relative rate constant sequence for selected olefin— $\text{PhHgCCl}_2\text{Br}$  reactions:  $\text{Me}_2\text{C}=\text{CMeEt}$ , 22.5;  $\text{Et}_2\text{C}=\text{CHMe}$ , 3.54; *n*-Pr(Et) $\text{C}=\text{CH}_2$ , 2.06; cyclohexene, 1.00; *n*- $\text{C}_5\text{H}_{11}\text{CH}=\text{CH}_2$ , 0.24. Thus a comparison of the reactions of allyl alcohol and 1,3,3-trimethylallyl alcohol,  $\text{Me}_2\text{C}=\text{CHCHMeOH}$ , would be instructive, since in the case of the latter we are dealing with a  $\text{C}=\text{C}$  bond that should be *ca.* 3.5 times more reactive than that of allyl alcohol. (We assume that the electron-withdrawing effect of the OH group will to a large extent be cancelled out by the electron-releasing effect of the  $\alpha$ -methyl substituent.) When the reaction of phenyl(bromodichloromethyl)mercury with  $\text{Me}_2\text{C}=\text{CHCHMeOH}$  was carried out, it was found that the major product (52% yield) was the  $\text{C}=\text{C}$  addition product (eq 14). It is not certain that any reaction at the



O—H bond had occurred since chloroform was not present. Thus electronic effects are important and possibly could serve to explain the  $\text{C}=\text{C}$  *vs.* O—H discrimination by  $\text{CCl}_2$  found in our investigation of these cyclic allylic alcohols. Electronic effects also explain the results obtained by Bertrand and Maurin<sup>5</sup> which are shown in eq 7.

To obtain further information concerning the question of possible effects of the OH substituent in reactions of the medium-ring allylic alcohols with dichlorocarbene, a reaction was carried out in which a mixture of 7.5 mmol each of cyclooctene and 3-cyclooctenol was treated with 1.5 mmol of phenyl(bromodichloromethyl)mercury in benzene at 80°. Glc analysis of the filtered reaction mixture showed the presence of 9,9-dichlorobicyclo[6.1.0]nonane (36% yield) and 9,9-dichlorobicyclo[6.1.0]nonanol-2 (44% yield). A similar experiment with phenyl(tribromomethyl)mercury gave 9,9-dibromobicyclo[6.1.0]nonane (40%) and 9,9-dibromobicyclo[6.1.0]nonanol-2 (52%).

(13) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 4953 (1967).

(14) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

Although it is dangerous to equate product yields with relative reactivities, the results obtained in our investigation of the reactions of cyclic allylic alcohols with  $\text{PhHgCCl}_2\text{Br}$ -derived dichlorocarbene (70%  $\text{C}=\text{C}$  addition with the  $\text{C}_8$  alcohol, ~30%  $\text{C}=\text{C}$  addition with  $\text{C}_7$  and  $\text{C}_9$  alcohols, no detectable  $\text{C}=\text{C}$  addition with 3-cyclohexenol) are in line with the known relative reactivities of medium-ring olefins toward a variety of reagents:  $\text{C}_8 > \text{C}_7 \sim \text{C}_9 \gg \text{C}_6$ .<sup>15</sup> References 15b and 15c, dealing with epoxidation and silver ion complexation, respectively, are the most pertinent. We conclude that the  $\text{C}=\text{C}$  bond reactivity toward dichlorocarbene in the cyclic allylic alcohols studied is determined by those electronic, steric, and ring-associated factors (torsional strain, angle bending<sup>15a</sup>) which normally determine reactivities of cyclic olefins, and that an explanation for the  $\text{C}=\text{C}$  reactivity toward  $\text{CCl}_2$  of 3-cyclooctenol involving facilitation of reagent approach by the OH substituent is not necessary.

We now direct our attention to the question of the stereochemistry of the 3-cycloalkenol— $\text{PhHgCCl}_2\text{Br}$  reactions. In order to study a system in which dichlorocarbene insertion into an O—H bond would not be a complicating feature, we examined the reactions of phenyl(bromodichloromethyl)mercury with the methyl ethers of the six-, seven-, eight-, and nine-membered ring 3-cycloalkenols. It was known that iodomethylzinc iodide reacts stereospecifically with the methyl ether of 3-cyclohexenol,<sup>7</sup> presumably *via* OH oxygen-to-zinc reagent coordination, and thus one might anticipate that if such a “steering” effect does indeed occur in dichlorocarbene reactions with the cyclic allylic alcohols studied, it should also be operative in the case of their methyl ethers. Accordingly, the reactions of phenyl(bromodichloromethyl)mercury with the 3-methoxy derivatives of cyclohexene, cycloheptene, cyclooctene, and cyclononene were carried out. In each case there was formed one major product by far. As in the case of the alcohols, the stereochemical assignments for these products were made by reducing them to the corresponding 2-methoxybicyclo[*n*.1.0]alkanes with lithium and *tert*-butyl alcohol in THF; nmr studies of the latter as well as comparison with data for those compounds which already were known followed. The results of the  $\text{CCl}_2$  addition reactions are presented in Table I. The nmr data on the basis of which the stereochemical assignments were made are given in Table II. The *cis* and *trans* isomers of 2-methoxybicyclo[4.1.0]heptane were known,<sup>7</sup> but the other 2-methoxybicyclo[*n*.1.0]alkanes in Table II were not.

Lemieux, *et al.*,<sup>16</sup> showed that for a proton bonded to a carbon with an oxygen substituent, if the hydrogen was axial, the signal would be relatively broad and upfield (toward tetramethylsilane) with respect to that of an equatorial proton. The axial proton signal should be broad because axial-axial coupling is larger (6–8 Hz) than equatorial-equatorial coupling (2–3 Hz). The magnitude of axial-equatorial coupling is generally 0.5–1.5 Hz. The axial signal should be upfield because the proton is not shielded by the ring C—C bonds as

(15) (a) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965), and references therein; (b) B. Rickborn and J. H. Chan, *J. Org. Chem.*, **32**, 3576 (1967); (c) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

(16) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *ibid.*, **80**, 6098 (1958).

Table I. Reactions of Methyl Ethers with  $C_6H_5HgCX_2Br$  (80°, 3 hr)

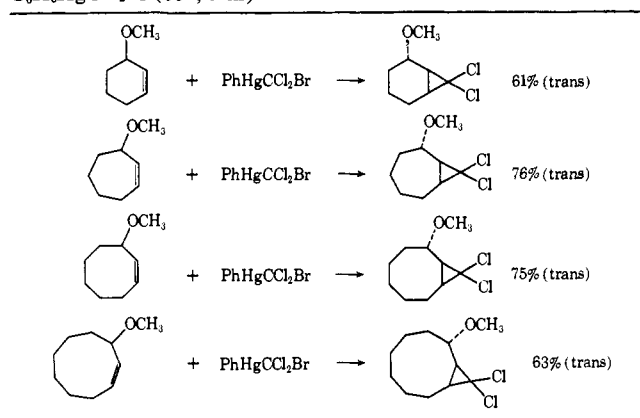


Table II. Nmr Data for  $H_a$

| A-ring size | Alcohol             |                          | Methyl ether        |                          |
|-------------|---------------------|--------------------------|---------------------|--------------------------|
|             | Chemical shift, ppm | Width at half-height, Hz | Chemical shift, ppm | Width at half-height, Hz |
| 6           | cis                 | 4.5 <sup>a</sup>         | 3.65 <sup>a</sup>   | 11                       |
|             | trans               | 4.2 <sup>a</sup>         | 3.35 <sup>a</sup>   | (16)                     |
| 7           | cis                 | 4.2 <sup>a</sup>         | 3.92                | 12                       |
|             | trans               | 3.25 <sup>a</sup>        | 2.8                 | 15                       |
| 8           | cis                 | 4.45                     |                     |                          |
|             | trans               | 3.32                     | 2.6                 | 22                       |
| 9           | cis                 |                          |                     |                          |
|             | trans               | 3.45                     | 2.9                 | 18                       |

<sup>a</sup> Stereochemistry previously determined.

the equatorial proton is, and thus more "aliphatic" in nature. We had found such a relationship to hold in the cases of bicyclo[*n*.1.0]alkan-2-ol compounds prepared in this study. For instance, for the bicyclo[6.1.0]nonan-2-ol assigned the trans configuration IVb (equatorial hydroxyl, equatorial cyclopropyl, axial  $H_a$ ) the  $H_a$  signal was observed at 3.32 ppm and the signal width at half-height was 22 Hz. For the cis isomer IVa (axial hydroxyl, equatorial cyclopropyl, equatorial  $H_a$ ), the  $H_a$  signal was seen at 4.45 ppm and the signal width at half-height was 8 Hz. These findings are in excellent accord with Lemieux's work. In addition, Cope, Moon, and Park<sup>17</sup> have shown that the nmr relationship holds for *cis*- and *trans*-bicyclo[5.1.0]octan-2-ol: the *trans* isomer's (VIII)  $H_a$  signal (axial proton) was at 3.3 ppm (width at half-height = 15 Hz), while the *cis* isomer's  $H_a$  signal occurred at 4.2 ppm (width at half-height = 11 Hz). These relationships involving  $H_a$  resonances and signal widths appeared to apply in the case of the methyl ethers (Table II) and, in addition, the nmr spectrum in each case was very similar to that of the respective bicyclo[*n*.1.0]alkan-2-ol in the  $CH(OH)$  and cyclopropyl hydrogen region. The *cis* isomer of 2-methoxybicyclo[5.1.0]octane was prepared by the action of iodomethylzinc iodide on 3-methoxycycloheptene.

(17) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4843 (1962).

The notable feature of the results shown in Table I is that dichlorocarbene addition to all four 3-methoxycycloalkenes gave as major (if not exclusive) product the *trans*-dichloro-2-methoxybicyclo[*n*.1.0]alkane. Table III compares the stereochemical results obtained in

Table III. Stereochemistry of Products of the Reactions of  $PhHgCCl_2Br$  and  $ICH_2ZnI$  with Five-, Six-, Seven-, Eight-, and Nine-Membered Cyclic Allylic Alcohols and Methyl Ethers

| Alcohol | Stereochemistry in reaction with |                                 |
|---------|----------------------------------|---------------------------------|
|         | $PhHgCCl_2Br$                    | $ICH_2ZnI$                      |
|         |                                  | Cis <sup>a</sup>                |
|         |                                  | Cis <sup>b</sup>                |
|         | Trans                            | Cis <sup>b</sup>                |
|         | Trans                            | 90% cis, 10% trans <sup>c</sup> |
|         | Trans                            | Predominantly cis <sup>d</sup>  |
|         | Trans                            | Trans <sup>c,d</sup>            |
|         | Trans                            |                                 |
|         | Trans                            | Trans <sup>c,d</sup>            |
|         | Trans                            |                                 |

<sup>a</sup> E. J. Corey and D. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963). <sup>b</sup> Reference 7. <sup>c</sup> Reference 6. <sup>d</sup> This work.

the cyclopropanation of the six-, seven-, eight-, and nine-membered cyclic allylic alcohols and methyl ethers. With phenyl(bromodichloromethyl)mercury, *in all cases* trans products were obtained. With iodomethylzinc iodide, where the evidence for facilitation of reagent approach *via* complexation of the OH oxygen atom with the metal atom of the attacking reagent is well documented (a complete list of references is given by Winstein, *et al.*<sup>6</sup>), there is a fairly abrupt change from *cis* to *trans* stereochemistry as the ring size increases from seven carbons to eight.

The absence of such an abrupt switch in stereochemistry in the phenyl(bromodichloromethyl)mercury-derived dichlorocarbene reactions listed in Table III suggests to us that the OH and OMe substituents *do not* facilitate  $CCl_2$  approach to the  $C=C$  bond through complexation of the type indicated in eq 9, rather that the preferred *trans* stereochemistry simply reflects reagent approach to the less-hindered face of the  $C=C$  bond, *i.e.*, a steric factor. One other major difference between the reactions of  $ICH_2ZnI$  and  $PhHgCCl_2Br$  with medium-ring allylic alcohols is in line with this idea. In the competition of 3-cyclohexenol and cyclohexene for a deficiency of  $ICH_2ZnI$ , the unsaturated alcohol was favored by an overwhelming margin. In contrast, when 3-cyclooctenol and cyclooctene com-

Table IV. 2-Hydroxy-, 2-Methoxy-, and 2-Acetoxy-Substituted Bicyclo[*n*.1.0]alkanes Prepared during This Study



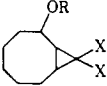
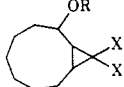
| Compd   | Procedure (yield, %)  | Bp, °C (mm)  | Mp, °C  | <i>n</i> <sup>25D</sup>  | —Anal. <sup>a</sup> found (calcd)— |                  |                     |
|---|---|--------------|---|--|------------------------------------|------------------|---------------------|
|   |   |              |   |  | C                                  | H                | Cl                  |
|   |   |              |    |  |                                    |                  |                     |
| R = Ac; X = Cl<br>(trans:cis = 7)                     | Via PhHgCCl <sub>2</sub> Br<br>(84%)                        | Glc          |   |  | 48.93 (48.44)                      | 5.41 (5.42)      | 31.43 (31.78)       |
| R = H; X = Cl<br>(predominantly trans)                | Via hydrolysis of<br>R = Ac compd                           | Oil          |   |  | (Partial decomposition on glc)     |                  |                     |
| R = H; X = H<br>(predominantly trans)                 | Via reduction of<br>R = OH, X = Cl<br>compd                 |              |   |  | (Known compd) <sup>a</sup>         |                  |                     |
| R = CH <sub>3</sub> ; X = Cl<br>(predominantly trans) | Via PhHgCCl <sub>2</sub> Br<br>(78%)                        | 64 (1.7)     |   | 1.4942   | 49.29 (49.25)                      | 6.17 (6.20)      |                     |
| R = CH <sub>3</sub> ; X = H<br>(trans)                | Via reduction of R =<br>CH <sub>3</sub> , X = Cl compd      | 46 (9.0)     |   | 1.4567   | 76.72 (76.14)                      | 11.14 (11.18)    |                     |
| R = CH <sub>3</sub> ; X = H<br>(cis)                  | Via ICH <sub>2</sub> ZnI                                    | Glc          |   | 1.4581   | (Known compd) <sup>a</sup>         |                  |                     |
|   |   |              |    |  |                                    |                  |                     |
| R = H; X = Cl<br>(trans)                              | Via PhHgCCl <sub>2</sub> Br<br>(31%)                        |              |   |  | (Decomposition on preparative glc) |                  |                     |
| R = Ac; X = Cl<br>(trans)                             | Via hydrolysis of R =<br>Ac, X = Cl compd                   |              | 75–75.5   |  | 49.38 (49.25)                      | 6.17 (6.20)      | 36.53 (36.34)       |
| R = H; X = H<br>(trans)                               | Via PhHgCCl <sub>2</sub> Br<br>(71%)                        | 78–80 (0.2)  |   | 1.4926   | 50.40 (50.65)                      | 5.86 (5.95)      |                     |
| R = H; X = H<br>(trans)                               | Via reduction of R =<br>H, X = Cl compd                     | Glc          |   | 1.4858 <sup>b</sup><br>(at 25.5°)  | (Known compd) <sup>d</sup>         |                  |                     |
| R = H; X = H<br>(cis)                                 | Via ICH <sub>2</sub> ZnI                                    |              | 41–42 <sup>e</sup>  |  | (Known compd) <sup>d</sup>         |                  |                     |
| R = CH <sub>3</sub> ; X = Cl<br>(trans)               | Via PhHgCCl <sub>2</sub> Br<br>(76%)                        | Glc          |   | 1.4959   | 51.38 (51.69)                      | 6.66 (6.75)      |                     |
| R = CH <sub>3</sub> ; X = H<br>(trans)                | Via reduction of R =<br>CH <sub>3</sub> , X = Cl compd      | 60 (8.0)     |   | 1.4600<br>(at 27.5°)   | 76.81 (77.09)                      | 11.39 (11.50)    |                     |
| R = CH <sub>3</sub> ; X = H<br>(cis)                  | Via ICH <sub>2</sub> ZnI                                    | Glc          |   | 1.4666   | 76.95 (77.09)                      | 11.39 (11.50)    |                     |
|   |   |              |  |  |                                    |                  |                     |
| R = H; X = Cl<br>(trans)                              | Via PhHgCCl <sub>2</sub> Br<br>(70%)                        |              | 87.5–89   |  | 51.59 (51.69)                      | 6.69 (6.75)      | 34.01 (33.91)       |
| R = H; X = Br<br>(trans)                              | Via PhHgCBr <sub>3</sub><br>(61%)                           |              | 82–83.5   |  | 36.24 (36.27)                      | 4.60 (4.74)      | Br 53.67<br>(53.61) |
| R = H; X = H<br>(trans)                               | Via reduction of R =<br>H, X = Cl compd                     |              |   | 1.4932 <sup>e</sup>  | 76.95 (77.09)                      | 11.43 (11.50)    |                     |
|   | Via ICH <sub>2</sub> ZnI (65%)                              | 58–60 (0.5)  |   | 1.4928<br>(at 27°)   |                                    |                  |                     |
| Bicyclo[6.1.0]-<br>nonanone-2                         | Via oxidation of R =<br>H, X = H compd<br>(87%)             | Glc          |   | 1.4836<br>(at 26°)   | 78.36 (78.21)                      | 10.16 (10.21)    |                     |
| R = H; X = H<br>(cis)                                 | Via LiAlH <sub>4</sub> reaction<br>with the ketone<br>(86%) | Glc          | 38–40   |  | 77.43<br>(77.09)                   | 11.84<br>(11.50) |                     |
| R = Ac; X = Cl<br>(trans)                             | Via PhHgCCl <sub>2</sub> Br<br>(64%)                        | 87 (0.23)    |   | 1.4962<br>(at 27.5°)   | 52.12 (52.60)                      | 6.32 (6.42)      | 28.18 (28.23)       |
| R = SiMe <sub>3</sub> ; X = Cl<br>(trans)             | Via PhHgCCl <sub>2</sub> Br                                 |              |   | Reaction mixture hydrolyzed to obtain alcohol (R = H; X = Cl),<br>mp 86–88.5°, in 59% recrystallized yield |                                    |                  |                     |
| R = CH <sub>3</sub> ; X = Cl<br>(trans)               | Via PhHgCCl <sub>2</sub> Br<br>(75%)                        | 57–58 (0.02) |   | 1.4931   | 54.08 (53.83)                      | 7.27 (7.23)      |                     |
| R = CH <sub>3</sub> ; X = H<br>(trans)                | Via reduction of R =<br>CH <sub>3</sub> , X = Cl compd      |              |   | 1.4683<br>(at 25.4°)   | 77.70 (77.87)                      | 11.56 (11.76)    |                     |
|   | Via ICH <sub>2</sub> ZnI                                    |              |   | 1.4708<br>(at 20°)   |                                    |                  |                     |
|   |   |              |  |  |                                    |                  |                     |
| R = H; X = Cl<br>(trans)                              | Via PhHgCCl <sub>2</sub> Br<br>(28%)                        |              |   |  |                                    |                  |                     |
|   | Via hydrolysis of R =<br>Ac, X = Cl compd                   |              | 65.5–66.0   |  | 53.76 (53.83)                      | 7.21 (7.23)      | 31.70 (31.78)       |

Table IV (Continued)

| Compd                                   | Procedure (yield, %)  | Bp, °C (mm)  | Mp, °C | $n_D^{25}$           | Anal. <sup>a</sup> found (calcd)        |               |    |
|---|---|--------------|--------|----------------------|---|---------------|----|
|   |   |              |        |                      | C                                       | H             | Cl |
| R = Ac; X = Cl<br>(trans)               | Via PhHgCCl <sub>2</sub> Br<br>(64%)  | 101 (0.2)    |        |                      | 92% pure; decomposed on preparative glc |               |    |
| R = H; X = H<br>(trans)                 | Via ICH <sub>2</sub> ZnI<br>(50%)   |              | 54-55  |                      | 77.58 (77.87)                           | 11.71 (11.76) |    |
| R = CH <sub>3</sub> ; X = Cl<br>(trans) | Via reduction of R =<br>H, X = Cl compd<br>Via PhHgCCl <sub>2</sub> Br<br>(63%) | 87-88 (0.35) |        |                      | Impure, decomposed on preparative glc   |               |    |
| R = CH <sub>3</sub> ; X = H<br>(trans)  | Via reduction of crude<br>R = CH <sub>3</sub> , X = Cl<br>compd                 | Glc          |        | 1.4762<br>(at 25.5°) | 78.21 (78.51)                           | 11.83 (11.98) |    |

<sup>a</sup> Reference 7. <sup>b</sup> Lit.<sup>9</sup>  $n_D^{25}$  1.4870. <sup>c</sup> Lit.<sup>9</sup> mp 42.8-43.6°; 39-40°. <sup>d</sup> Reference 9. <sup>e</sup> Lit.<sup>8</sup>  $n_D^{25}$  1.4942.

peted for a deficiency of PhHgCCl<sub>2</sub>Br-derived CCl<sub>2</sub>, the unsaturated alcohol was only very slightly more reactive than the unsubstituted olefin.

In summary, this study has shown that in the intramolecular competition of a C=C bond and an O-H bond in an allylic alcohol for dichlorocarbene the final outcome—C=C addition or O-H insertion—is determined by the extent of alkyl substitution of the C=C bond (*i.e.*, its nucleophilicity). From the results of this investigation one may conclude that an O-H group in the allylic position is slightly more reactive toward CCl<sub>2</sub> than the double bond in cyclohexene. Thus a definite limit is placed on the scope of the dihalocyclopropanation of allylic alcohols. Especially to be noted are the good dichlorocyclopropane yields obtained in reactions of PhHgCCl<sub>2</sub>Br with these cyclic allylic acetates and methyl ethers. Indeed, the method of choice for the preparation of the *trans*-bicyclo[*n*.1.0]-alkan-2-ol compounds ( $n = 3, 4, 5$ ) is by addition of CCl<sub>2</sub> to the corresponding acetates followed by reduction of the C-Cl linkages.

## Experimental Section

**General Comments.** All reactions except for the acetate ester hydrolyses were carried out under an atmosphere of dry nitrogen in flame-dried glassware. The standard reaction apparatus was a three-necked round-bottomed flask of appropriate size equipped with a reflux condenser, a magnetic stirring assembly, a dropping funnel if needed, and a nitrogen inlet tube.

Infrared spectra were recorded using a Perkin-Elmer infracord 237B or 337 grating spectrophotometer, nmr spectra with a Varian A60 or T60 nmr spectrometer. Chemical shifts are given in units downfield from internal tetramethylsilane. Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU6D mass spectrometer. Gas-liquid partition chromatography (glc) was used extensively for the separation and purification of products and for yield determinations. The instruments used included the MIT isothermal unit and F & M Model 700, 720, and 5754 gas chromatographs. The internal standard method was used in yield determinations. The glc columns used included the following: column A, 10% Dow Corning DC-200 silicone oil, 6 ft × 1/4 in., F & M 5754; B, 20% DC-200, 6 ft × 1/4 in., F & M 700; C, 10% Carbowax 20M, 6 ft × 1/4 in., F & M 5754; D, 10% diethylene glycol succinate, 10 ft × 1/8 in., F & M 5754; E, 20% LAC 728, 4 ft × 1/4 in., F & M 700; F, 10% UC-W98, 4 ft × 1/4 in., F & M 5754; G, 20% UC-W98, 4 ft × 1/4 in., F & M 720; H, 25% General Electric Co. SE-30 silicone rubber gum, 8 ft × 1/4 in., MIT isothermal, all using 80-100 mesh, acid-washed Chromosorb W as solid support.

All solvents were dried prior to use, benzene by distillation from calcium hydride, diethyl ether and tetrahydrofuran by distillation from lithium aluminum hydride.

**Preparation of Starting Materials.** Phenyl(bromodichloromethyl)mercury and phenyl(tribromomethyl)mercury were prepared using first the procedure in which benzene was used as solvent,<sup>18a</sup> later our improved procedure in which THF replaces benzene.<sup>18b</sup>

3-Cyclohexenyl acetate,<sup>19</sup> 3-methoxycyclohexene,<sup>19</sup> 3-cycloheptenyl acetate,<sup>20</sup> 3-cycloheptenol,<sup>20</sup> 3-cyclooctenol,<sup>21</sup> 3-cyclooctenyl acetate,<sup>21</sup> 3-cyclononenol,<sup>22</sup> and 3-methoxycyclononenol<sup>22</sup> were prepared by known procedures as referenced.

3-Methoxycycloheptene and 3-methoxycyclooctene were prepared by converting the respective cycloalkenol to the sodium cycloalkenoxide with NaH in diethyl ether and then adding methyl iodide in excess and stirring at room temperature for 2 days.

**3-Methoxycycloheptene** exhibited the following characteristics: bp 56° (18 mm);  $n_D^{25}$  1.4586; ir  $\nu_{C=C}$  1650 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  5.65 (m, 2 H, HC=CH), 3.7 (m, 1 H, H-C-OMe), 3.2 (s, 3 H, OCH<sub>3</sub>), 2.2-1.0 ppm (m, 10 H). Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O: C, 76.14; H, 11.18. Found: C, 76.07; H, 11.04.

**3-Methoxycyclooctene** showed the following: bp 60-62° (6-6.5 mm);  $n_D^{25}$  1.4660; ir  $\nu_{C=C}$  1650 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  5.9-5.25 (m, 2 H, HC=CH) 4.2-3.8 (m, 1 H, H-C-OMe), 3.2 (s, 3 H, OCH<sub>3</sub>), 2.4-1.05 ppm (m, 10 H). Anal. Calcd for C<sub>9</sub>H<sub>16</sub>O: C, 77.09; H, 11.50. Found: C, 77.31; H, 11.54.

**3-Trimethylsilyloxycyclooctene**, bp 42° (0.55 mm),  $n_D^{25}$  1.4530, was prepared by the usual Me<sub>3</sub>SiCl-catalyzed reaction of 3-cyclooctenol and hexamethyldisilazane: ir (liquid film)  $\nu_{C=C}$  1635 cm<sup>-1</sup>; Me<sub>3</sub>Si vibrations: 1250, 840, 750 cm<sup>-1</sup>. Anal. Calcd for C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>Si: C, 66.60; H, 11.18. Found: C, 66.24; H, 11.05.

**3-Cyclononenyl acetate**, bp 79-81° (2.5 mm),  $n_D^{25}$  1.4732, was prepared by the HgSO<sub>4</sub>-catalyzed reaction of 1,2-cyclononadiene<sup>23</sup> with glacial acetic acid (6 days at room temperature): ir (liquid film)  $\nu_{C=O}$  1740,  $\nu_{C=C}$  1660 cm<sup>-1</sup>. Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>: C, 72.49; H, 9.95. Found: C, 72.59; H, 9.87.

**Bicyclo[6.1.0]nonanone-2** was prepared by oxidizing with CrO<sub>3</sub> in aqueous H<sub>2</sub>SO<sub>4</sub><sup>24</sup> 6.5 mmol of *trans*-bicyclo[6.1.0]nonanol-2 (obtained *via* ICH<sub>2</sub>ZnI) in ether at 10-15°. The organic layer was treated with aqueous NaHCO<sub>3</sub>, washed, and dried. Evaporation of solvent left the product (87% yield) as a clear oil. Glc gave a pure sample.

**Reaction of Phenyl(bromodichloromethyl)mercury with 3-Cycloalkenols.** (a) **3-Cyclooctenol.** A benzene (15 ml) solution of 1.26 g (0.01 mol) of 3-cyclooctenol and 4.8 g (0.011 mol) of the mercurial was stirred and heated at reflux under nitrogen for 3 hr (oil bath temperature, 90-100°). Five to ten minutes after the heating had begun, a large quantity of white crystals formed, and vigorous frothing was observed. The yellow-gray reaction mixture was allowed to cool and then 3.69 g (95%, mp 274-278°) of phenylmercuric bromide was filtered. The filtrate was trap-to-trap distilled at 0.25 mm (no heating above room temperature) into a re-

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(25) The products of these reactions, their yields (when determined), physical constants, and analytical data are given in Table IV, their nmr, ir, and mass spectra (when determined) in Table V.



Table V. 2-Hydroxy-, 2-Methoxy-, and 2-Acetoxy-Substituted Bicyclo[*n*.1.0]alkanes. Nuclear Magnetic Resonance, Infrared, and Mass Spectra

| Compd                                  | Nmr, in $\delta$ units, ppm downfield from internal TMS  | Ir, principal bands in $\text{cm}^{-1}$   | Mass spectrum, $m/e$ (rel intensity)  |
|--|--|---|---|
|  |  |   |   |
| R = Ac; X = Cl<br>(trans:cis = 7)      | ( $\text{CCl}_4$ ) 4.9 (m, 1 H, $W_{1/2}$ = 14 Hz, $H_a$ ), with small shoulder at 5.2, 2.3–1.1 (m, with superimposed singlet at 2.1, 11 H)    | (Liq film) 3030 (m), 2965 (s), 2830 (sh), 1740 (vs), 1245 (vs), 1030 (s), 800 (s)   |   |
| R = H; X = Cl<br>(predominantly trans) | ( $\text{CDCl}_3$ ) 3.95 (m, 1 H, $W_{1/2}$ = 14 Hz, $H_a$ ), with small shoulder at 4.3, 3.55 (s, 1 H, OH), 2.25–1.1 (m, 8 H)                 | (Liq film) 3590 (m), 3450 (s, broad), 3030 (m), 2950 (s), 2870 (s), 1470 (s), 1455 (s), 1390 (m), 1350 (m), 1135 (m), 1115 (m), 1060 (s), 1035 (s), 995 (s), 800 (s)  |   |
| R = H; X = H<br>(predominantly trans)  | ( $\text{CDCl}_3$ ) 4.2 (m, 1 H, $W_{1/2}$ = 18 Hz, $H_a$ ), with small shoulder at 4.5, 3.8 (s, 1 H, OH), 2.8–0.6 (m, 9 H), 0.55–0.5 (m, 1 H) | ( $\text{CS}_2$ ) 3610 (m), 3450 (s, broad), 3070 (m), 3000 (m), 2940 (s), 2860 (s), 1100 (m), 1050 (s), 1020 (s), 975 (s), 895 (m), 825 (m)  |   |
| R = $\text{CH}_3$ ; X = Cl<br>(trans)  | ( $\text{CCl}_4$ ) 3.5 (s, 3 H, $\text{OCH}_3$ ), 3.36 (m, 1 H, $H_a$ ), 2.14–1.0 (m, 8 H)   | (Liq film) 3010 (s), 2990 (sh), 2940 (s), 2870 (s), 2820 (m), 1460 and 1450 (s), 1380 (m), 1355 (m), 1340 (m), 1330 (m), 1310 (m), 1085 (s), 790 (s)  | 71 (100) [ $\text{C}_6\text{H}_{11}$ ], 79 (49) [ $\text{C}_6\text{H}_8$ ], 91 (38) [ $\text{C}_7\text{H}_7$ ], 127 (53) [ $\text{M} - \text{Cl} - \text{CH}_2\text{OH}$ ], 139 (53) [ $\text{C}_6\text{H}_8\text{Cl}_2$ ], 194 (2) [parent ion, 2 Cl's, 194:196:198 = 9:6:1]   |
| R = $\text{CH}_3$ ; X = H<br>(trans)   | ( $\text{CCl}_4$ ) 3.35 (m, 1 H, $W_{1/2}$ = 16 Hz, $H_a$ ), 3.25 (s, 3 H, $\text{OCH}_3$ ), 0.7–1.8 (m), 0.5 (m, 1 H), 0.2 (m, 1 H)           | (Liq film) 3060 (m), 2995 (s), 2975 (sh), 2930 (s), 2860 (s), 1455 (s), 1385 (m), 1370 (m), 1195 (m), 1100 (vs), 1050 (sh), 1015 (m), 895 (m), 825 (m)  | 71 (72) [ $\text{C}_4\text{H}_7\text{O}$ ], 84 (67), 94 (100) [ $\text{C}_6\text{H}_8\text{O}$ ], 96 (45) [ $\text{M} - \text{CH}_2\text{O}$ ], 111 (9) [ $\text{M} - \text{CH}_3$ ], 126 (27) [parent ion]   |
| R = $\text{CH}_3$ ; X = H<br>(cis)     | ( $\text{CCl}_4$ ) 3.65 (m, 1 H, $W_{1/2}$ = 11 Hz, $H_a$ ), 3.25 (s, 3 H, $\text{OCH}_3$ ), 0.8–1.8 (m, 8 H), 0.2–0.65 (m, 2 H)               | (Liq film) 3065 (m), 3000 (s), 2970 (sh), 2930 (s), 2860 (s), 2815 (s), 1465 and 1450 (s), 1385 (m), 1350 and 1340 (s), 1215 (m), 1190 (s), 1100 (vs), 1065 (sh), 1035 (m), 1020 (m), 970 (s), 900 (m), 875 (m), 735 (m)        | 71 (100) [ $\text{C}_4\text{H}_7\text{O}$ ], 84 (90), 94 (61) [ $\text{C}_6\text{H}_8\text{O}$ ], 96 (61) [ $\text{M} - \text{CH}_2\text{O}$ ], 111 (21) [ $\text{M} - \text{CH}_3$ ], 126 (27) [parent ion]  |
|  |  |   |   |
| R = H; X = Cl<br>(trans)               | ( $\text{CDCl}_3$ ) 3.64 (m, 1 H, $W_{1/2}$ = 20 Hz, $H_a$ ), 2.46 (s, 1 H, OH), 2.7–0.9 (m, 10 H)   | ( $\text{CS}_2$ ) 3600 (m), 3380 (m, broad), 2980 (s), 1135 (m), 1050 (s), 1010 (s), 975 (m), 945 (m), 915 (m), 855 (m), 830 (m), 795 (s), 770 (m)  | 43 (100) [ $\text{C}_3\text{H}_7$ ], 55 (26) [ $\text{C}_4\text{H}_7$ ], 57 (37) [ $\text{C}_5\text{H}_6\text{O}$ ], 63 (43), 105 (6) [ $\text{M} - \text{H}_2\text{OCl}_2$ ], 113 (10) [ $\text{M} - \text{CCl}_2\text{H}$ ], 176 (2) [ $\text{M} - \text{H}_2\text{O}$ ], 194 (6) [parent ion, 2 Cl's, 194:196:198 = 9:6:1] |
| R = Ac; X = Cl<br>(trans)              | ( $\text{CCl}_4$ ) 4.45 (m, 1 H, $W_{1/2}$ = 20 Hz, $H_a$ ), 2.4–0.8 (m, 13 H, with superimposed singlet at 1.9)                               | (Liq film) 3010 (w), 2930 (s), 2870 (sh), 2860 (m), 1740 (s), 1455 (m), 1370 (s), 1245 (vs), 1205 (s), 1150 (m), 1045 and 1025 (s), 990 (m), 970 (m), 960 (m), 900 (m), 855 (m), 830 (m), 800 (s)                               | 43 (100) [ $\text{COCH}_3$ ], 71 (18) [ $\text{C}_3\text{H}_7$ ], 123 (15) [ $\text{M} - 2\text{Cl} - \text{COCH}_3$ ], 141 (7) [ $\text{M} - \text{H} - \text{Cl} - \text{OCOCH}_3$ ], 194 (3) [ $\text{M} - \text{Cl}$ ], 236 (0.8) [parent ion, 2 Cl's, 236:238:240 = 9:6:1]   |
| R = H; X = H<br>(trans)                | ( $\text{CCl}_4$ ) 4.3 (s, 1 H, OH), 3.25 (m, 1 H, $W_{1/2}$ = 16 Hz, $H_a$ ), 2.5–1.0 (m, 10 H), 0.8 (m, 3 H), 0.2 (m, 1 H)                   | (Liq film) 3620 (w), 3360 (s, broad), 3065 (m), 3000 (s), 2930 (s), 2830 (s), 1455 (s), 1350 (m), 1260 (m), 1200 (m), 1110 (m), 1020 (s), 960 (m), 935 (m), 920 (m), 865 (m), 835 (m), 790 (s), 740 (m)                         |   |
| R = H; X = H<br>(cis)                  | ( $\text{CCl}_4$ ) 4.2 (m, 1 H, $W_{1/2}$ = 8 Hz, $H_a$ ), 2.8 (s, 1 H, OH), 2.2–1.2 (m, 8 H), 1.2–0.8 (m, 2 H), 0.7–0.2 (m, 2 H)              | ( $\text{CS}_2$ ) 3600 (m), 3060 (m), 2990 (s), 2910 (s), 2840 (s), 1070 (m), 1035 (s), 1005 (m), 970 (m), 885 (m), 875 (sh)  |   |
| R = $\text{CH}_3$ ; X = Cl<br>(trans)  | ( $\text{CCl}_4$ ) 3.34 (s, 3 H, $\text{OCH}_3$ ), 3.1 (m, 1 H, $W_{1/2}$ = 14 Hz, $H_a$ ), 2.4–0.8 (m, 10 H)                                  | (Liq film) 3010 (sh), 2985 (sh), 2935 (s), 2860 (s), 2825 (m), 1450 (s), 1400 (m), 1365 (m), 1180 (m), 1130 (m), 1095 and 1085 (s), 970 (m), 945 (m), 910 (m), 850 (m), 795 (s)   | 41 (30) [ $\text{C}_3\text{H}_5$ ], 43 (17) [ $\text{C}_3\text{H}_7$ ], 71 (68) [ $\text{C}_4\text{H}_7\text{O}$ ], 97 (100) [ $\text{C}_6\text{H}_8\text{O}$ ], 141 (8) [ $\text{M} - \text{HCl} - \text{CH}_2\text{O}$ ], 208 (14) [parent ion, 2 Cl's, 208:210:212 = 9:6:1]  |
| R = $\text{CH}_3$ ; X = H<br>(trans)   | ( $\text{CCl}_4$ ) 5.3 (s, 3 H, $\text{OCH}_3$ ), 2.8 (m, 1 H, $W_{1/2}$ = 15 Hz, $H_a$ ), 2.4–0.6 (m, 10 H), 0.3 (m, 2 H)                     | (Liq film) 3065 (m), 2990 (m), 2920 (s), 2850 (s), 2815 (m), 1455 (s), 1375 (m), 1360 (m), 1255 (m), 1215 (m), 1195 (m), 1185 (m), 1130 (s), 1095 and 1080 (s), 1045 (m), 1025 (m), 985 (s), 945 (s), 940 (m), 915 (m), 835 (m) |   |

Table V (Continued)

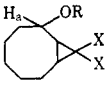

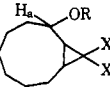
| Compd                                 | Nmr, in $\delta$ units, ppm downfield from internal TMS  | Ir, principal bands in $\text{cm}^{-1}$   | Mass spectrum, $m/e$ (rel intensity)  |
|---------------------------------------|--|---|---|
| R = $\text{CH}_3$ ; X = H<br>(cis)    | ( $\text{CCl}_4$ ) 3.92 (m, 1 H, $W_{1/2}$ = 12 Hz, $H_a$ ), 3.52 (s, 3 H, $\text{OCH}_3$ ), 2.2-1.4 (m, 8 H), 1.2-0.5 (m, 4 H)                        | (Liq film) 3060 (m), 2990 (s), 2900 (s), 2835 (s), 2810 (s), 1450 (s), 1370 (m), 1355 (m), 1195 (m), 1120 (m), 1100 (s), 1030 (s), 920 (m), 865 (s), 845 (m), 750 (m)   | 41 (40) [ $\text{C}_8\text{H}_5$ ], 67 (22), 71 (100) [ $\text{C}_4\text{H}_5\text{O}$ ], 79 (19), 80 (22), 97 (19) [ $\text{C}_8\text{H}_5\text{O}$ ], 108 (30) [ $\text{M} - \text{CH}_2\text{OH}$ ], 125 (0.7) [ $\text{M} - \text{CH}_3$ ], 140 (3.7) [parent ion]  |
|                                       |   |   |   |
| R = H; X = Cl<br>(trans)              | ( $\text{CDCl}_3$ ) 3.9 (m, 1 H, $W_{1/2}$ = 20 Hz, $H_a$ ), 2.7 (s, 1 H, OH), 2.5-1.0 (m, 12 H)   | ( $\text{CS}_2$ ) 3600 (m), 3460 (m), 2920 (s), 2850 (s), 1260 (m), 1210 (m), 1165 (s), 1070 (m), 1045 (s), 1000 (s), 920 (m), 840 (m), 815 (s), 780 (m), 760 (m), 735 (m)  | 41 (46) [ $\text{C}_8\text{H}_5$ ], 43 (33) [ $\text{C}_7\text{H}_7$ ], 55 (42) [ $\text{C}_4\text{H}_7$ ], 57 (100) [ $\text{C}_8\text{H}_5\text{O}$ ], 61 (33), 67 (27), 68 (26), 81 (44), 83 (64) [ $\text{C}_8\text{H}_{11}$ ], 122 (26), 125 (15) 127 (10), 190 (0.8) [ $\text{M} - \text{H}_2\text{O}$ ], 208 (5.7) [parent ion, 2 Cl's, 208:-210:212 = 9:6:1]                                    |
| R = Ac; X = Cl<br>(trans)             | ( $\text{CCl}_4$ ) 4.7 (m, 1 H, $W_{1/2}$ = 22 Hz, $H_a$ ), 2.4-1.2 (m, 13 H, with superimposed singlet at 2.1)  | (Liq film) 3010 (sh), 2940 (s), 2875 (s), 1735 (s), 1630 (m), 1455 and 1445 (s), 1365 (s), 1235 (s), 1170 (m), 1070 (m), 1015 (s), 955 (m), 937 (m), 875 (m), 855 (m), 815 (s), 740 (m)                               | 43 (100) [ $\text{COCH}_3$ ], 137 (20) [ $\text{C}_9\text{H}_{13}\text{O}$ ], 155 (6), 190 (3) [ $\text{M} - \text{HCO}_2\text{CH}_3$ ], 208 (7) [ $\text{M} - \text{COCH}_2$ ], 215 (2) [ $\text{M} - \text{Cl}$ ], 250 (2) [parent ion, 2 Cl's, 250:252:254 = 9:6:1]  |
| R = H; X = H<br>(trans)               | ( $\text{CCl}_4$ ) 3.32 (m, 1 H, $W_{1/2}$ = 22 Hz, $H_a$ ), 2.85 (s, broad, 1 H, OH), 1.6 (m, 10 H), 0.8 (m, 3 H), 0.1 (m, 1 H)                       | (Liq film) 3600 (sh), 3400 (s, broad), 3000 (sh), 2960 (s), 2870 (s), 1455 (s), 1420 (s), 1150 (m), 1040 (s), 1000 (s), 960 (s), 925 (m), 910 (m), 850 (m)  | 55 (82), 57 (100) [ $\text{C}_8\text{H}_5\text{O}$ ], 67 (73), 70 (47), 83 (87), 93 (35), 96 (66), 107 (20), 122 (26), 140 (3) [parent ion]   |
| R = H; X = H<br>(cis)                 | ( $\text{CCl}_4$ ) 4.45 (m, 1 H, $W_{1/2}$ = 11 Hz, $H_a$ ), 2.25 (s, 1 H, OH), 1.65 (m, 10 H), 1.0-0.5 (m, 4 H)                                       | (Liq film) 3600 (sh), 3400 (s), 3065 (m), 2990 (s), 2920 (s), 2860 (s), 1455 (s), 1140 (m), 1015 (s), 845 (s)   | 55 (76), 57 (100), 67 (54), 70 (51), 81 (47), 83 (96), 122 (88), 140 (2)  |
| R = H; X = Br<br>(trans)              | ( $\text{CDCl}_3$ ) 3.7 (m, 1 H, $W_{1/2}$ = 22 Hz, $H_a$ ), 2.6 (s, 1 H, OH), 2.4-1.0 (m, 12 H)   | ( $\text{CCl}_4$ ) 3600 (m), 3450 (m), 2930 (m), 2860 (m), 1520 (m), 1460 (s), 1410 (m), 1202 (m), 1000 (s), 965 (m), 720 (m)   | 39 (40), 41 (49), 43 (30), 53 (28), 55 (43), 57 (100) [ $\text{C}_4\text{H}_5$ ], 67 (40), 68 (23), 70 (25), 79 (34), 81 (66), 82 (25), 83 (83) [ $\text{C}_8\text{H}_{11}$ ], 84 (26), 91 (25), 93 (26), 95 (23), 97 (25), 119 (55) [ $\text{C}_8\text{H}_{11}$ ], 137 (34), 210 (21), 212 (40), 213 (13), 214 (21), 215 (22), 217 (17), 219 (11), 296 (7.5) [parent ion, 2 Br's], 298 (15); 300 (7.5) |
| R = $\text{CH}_3$ ; X = Cl<br>(trans) | ( $\text{CCl}_4$ ) 3.4 (s, 3 H, $\text{OCH}_3$ ), 3.12 (m, 1 H, $W_{1/2}$ = 22 Hz, $H_a$ ), 2.24-1.0 (m, 12 H)   | (Liq film) 2995 (sh), 2960 (vs), 2865 (sh), 2820 (m), 1410 (m), 1370 (m), 1350 (m), 1230 (m), 1190 (m), 1170 (s), 1150 (m), 1100 (vs), 1040 (m), 1025 and 1015 (s), 1000 (m), 770 and 760 (m), 745 (m)                | 71 (100) [ $\text{C}_8\text{H}_{11}$ ], 97 (62) [ $\text{C}_7\text{H}_{13}$ ], 122 (21) [ $\text{C}_8\text{H}_{14}$ ], 139 (16) [ $\text{M} - \text{CCl}_2$ ], 141 (12) [ $\text{M} - \text{CH}_2\text{Cl}_2$ ], 155 (9) [ $\text{M} - \text{HCl} - \text{CH}_2\text{OH}$ ], 187 (15) [ $\text{M} - \text{HCl}$ ], 190 (3) [ $\text{M} - \text{CH}_2\text{OH}$ ], 222 (17) [parent], 224 (11), 226 (2)  |
| R = $\text{CH}_3$ ; X = H<br>(trans)  | ( $\text{CCl}_4$ ) 3.22 (s, 3 H, $\text{OCH}_3$ ), 2.6 (m, 1 H, $W_{1/2}$ = 22 Hz, $H_a$ ), 2.2-1.0 (m, 10 H), 0.95-0.3 (m, 3 H), 0.15-(-0.5) (m, 1 H) | (Liq film) 3080 (m), 3000 (s) 2960 (s), 2880 (sh), 1458 (s), 1405 (m), 1353 (m), 1302 (m), 1255 (m), 1185 (m), 1150 (m), 1100 (vs), 1035 (m), 1010 (m), 990 (m), 950 (s), 910 (m), 850 (m)                            | 67 (35), 93 (24), 97 (100), 107 (26), 122 (45), 154 (23) [parent ion]   |
|                                       |   |   |   |
|                                       | ( $\text{CCl}_4$ ) 3.2-0.8 (m)   | (Liq film) 3080 (w), 3000 (m), 2940 (s), 1700 (s), 1450 (s), 1390 and 1375 (s), 1315 (m), 1260 (m), 1225 (m), 1205 (m), 1180 (m), 1150 (m), 1135 (m), 1040 (m), 1000 (m), 905 (s), 880 (m), 845 (s), 815 (m), 735 (m) |   |
|                                       |   |   |   |
| R = Ac; X = Cl<br>(trans)             | ( $\text{CDCl}_3$ ) 4.75 (m, 1 H, $W_{1/2}$ = 18 Hz, $H_a$ ), 2.3-1.0 (m, with superimposed singlet at 2.1, 17 H)                                      | (Liq film) 3010 (sh), 2940 (s), 2870 (s), 1740 (s), 1475 (s), 1450 (s), 1370 (s), 1240 (vs), 1020 (s), 980 (m), 820 (s), 725 (m), 710 (m), 655 (m)  |   |

Table V (Continued)

| Compd                                 | Nmr, in $\delta$ units, ppm downfield from internal TMS   | Ir, principal bands in $\text{cm}^{-1}$   | Mass spectrum, $m/e$ (rel intensity) |
|---------------------------------------|---|---|--------------------------------------|
| R = H; X = Cl<br>(trans)              | ( $\text{CDCl}_3$ ) 3.8 (m, 1 H, $W_{1/2}$ = 18 Hz, $H_a$ ), 2.6–0.8 (m, with superimposed singlet (OH) at 2.1, 15 H)                     | ( $\text{CS}_2$ ) 3600 (s), 3460 (s, broad), 2930 (s), 2860 (m), 1380 (m), 1275 (m), 1265 (m), 1240 (m), 1205 (m), 1185 (m), 1135 (s), 1065 (m), 1040 (m), 1015 (s), 930 (m), 900 (m), 825 (s), 710 (m) |                                      |
| R = H; X = H<br>(trans)               | ( $\text{CDCl}_3$ ) 3.45 (m, 1 H, $W_{1/2}$ = 19 Hz, $H_a$ ), 2.4–1.2 (m, 12 H), 0.8 (m, 3 H), 0.1 (m, 1 H)                               | ( $\text{CS}_2$ ) 3600 (m), 3400 (m, broad), 3050 (m), 2990 (s), 2920 (s), 2850 (s), 1070 (m), 1035 (s), 1010 (s), 970 (m), 885 (m), 850 (m), 700 (m)   |                                      |
| R = $\text{CH}_3$ ; X = Cl<br>(trans) | ( $\text{CCl}_4$ ) 3.5 (s, 3 H, $\text{OCH}_3$ ), 3.25 (m, 1 H, $W_{1/2}$ = 16 Hz, $H_a$ ), 2.4–1.2 (m, 14 H)                             | (Liq film) 2940 (s), 1470 and 1450 (s), 1135 (s), 1090 (s), 810 (s)   |                                      |
| R = $\text{CH}_3$ ; X = H<br>(trans)  | ( $\text{CCl}_4$ ) 3.38 (s, 3 H, $\text{OCH}_3$ ), 2.9 (m, 1 H, $W_{1/2}$ = 18 Hz, $H_a$ ), 2.4–1.2 (m, 12 H), 0.8 (m, 3 H), 0.1 (m, 1 H) | (Liq film) 3065 (m), 3000 (sh), 2920 (s), 2860 (m), 1450 (s), 1350 (m), 1180 (m), 1150 (m), 1090 (s), 970 (s), 900 (m), 845 (m), 695 (m)  |                                      |

ceiver at  $-78^\circ$ . The nonvolatile residue (2.21 g) was treated with hexane to extract 0.44 g of a substance that crystallized in white needles, mp  $83\text{--}85.5^\circ$ . Upon recrystallization from hexane, pure 9,9-dichlorobicyclo[6.1.0]nonanol-2, mp  $87.5\text{--}89^\circ$ , was obtained. A similar reaction was carried out, and glc analysis of the filtrate (column A,  $180^\circ$ , ethyl cinnamate internal standard) showed the product yield to be 70%.

The volatile portion from the trap-to-trap distillation was analyzed by glc and shown to contain 3-cyclooctenol (5%) and 1,3-cyclooctadiene (4%) (column A;  $60\text{--}180^\circ$ ,  $6^\circ/\text{min}$  program, *n*-dodecane internal standard). These products were identified by comparison of their glc retention times and ir spectra with those of authentic samples.

A similar reaction between 0.01 mol of 3-cyclooctenol and phenyl-(tribromomethyl)mercury (0.011 mol) gave  $\text{PhHgBr}$  in quantitative yield and 9,9-dibromobicyclo[6.1.0]nonanol-2 in 61% yield (column A,  $180^\circ$ , 1-chloronaphthalene internal standard). A pure sample was isolated by distillation and subsequent recrystallization from *n*-hexane. Bromoform (21%) also was produced in this reaction.

(b) **3-Cycloheptenol.** A similar procedure was followed in the reaction of 0.01 mol of 3-cycloheptenol with 0.011 mol of  $\text{PhHgCCl}_2\text{Br}$  in 15 ml of benzene for 3 hr. Phenylmercuric bromide was recovered in 94% yield. Glc analysis (column A,  $180^\circ$ , 9,9-dibromobicyclo[6.1.0]nonane internal standard) showed that *trans*-8,8-dichlorobicyclo[5.1.0]octanol-2 was present in 31% yield. Two other higher boiling compounds, one of which was identified (ir and glc) as 1,3-cycloheptadiene, also were present in lesser amounts. Attempts to isolate pure product were not successful; it decomposed on attempted preparative glc and distillation and attempted crystallization did not succeed. Identification of the product was based upon comparison of its glc retention time with that of an authentic sample obtained by alkaline hydrolysis of *trans*-8,8-dichlorobicyclo[5.1.0]octyl 2-acetate and by comparison of the ir and nmr spectra of the crude product with those of an authentic sample.

In another reaction carried out on the same scale in *n*-heptane at reflux, chloroform (30% yield) was identified as an additional product.

(c) **3-Cyclononenol.** A reaction of 0.011 mol of the mercurial and 1.4 g (0.01 mol) of the alkenol in 15 ml of benzene for 4 hr gave phenylmercuric bromide in 92% yield. Analysis of the filtrate by glc (column A,  $180^\circ$ , 1-chloronaphthalene internal standard) showed that 10,10-dichlorobicyclo[7.1.0]decanol-2 was present in 28% yield. Chloroform also was present, as was another higher boiling compound whose presence made impossible the purification of the product by crystallization. The product decomposed on attempted preparative glc and on attempted distillation at  $10^{-6}$  mm. It was identified by comparison of its glc retention time and of the ir and nmr spectrum of the crude product with those of authentic material obtained by alkaline hydrolysis of 10,10-dichlorobicyclo[7.1.0]decyl 2-acetate.

(d) **3-Cyclohexenol.** The mercurial (0.01 mol) and the alkenol (0.01 mol) in 15 ml of toluene were heated for 1 hr in an oil bath at  $80\text{--}90^\circ$ . Five minutes after the mercurial had dissolved, white flakes began to form very rapidly and much frothing was noticed. The yellow reaction mixture was allowed to cool, and phenyl-

mercuric bromide (91%) was filtered. The filtrate was trap-to-trap distilled at room temperature and 0.15 mm. The oily nonvolatile portion turned dark yellow, and as it became more concentrated, dark blue. The residue turned blue-black on standing overnight. Glc analysis of the distillate revealed the presence of chloroform (25%), benzene (15%), and 3-chlorocyclohexene (31%).

**Reaction of Phenyl(bromodichloromethyl)mercury with 3-Cycloalkenyl Acetates.**<sup>25</sup> (a) **3-Cyclooctenyl Acetate.** The mercurial (0.01 mol) and 1.68 g (0.01 mol) of the acetate in 15 ml of benzene were heated at reflux for 3 hr. Filtration gave  $\text{PhHgBr}$  in 94% yield. Glc analysis of the filtrate showed *trans*-9,9-dichlorobicyclo[6.1.0]nonyl 2-acetate to be present in 64% yield (column A,  $180^\circ$ , 1-chloronaphthalene internal standard). The solution was concentrated and distilled (short path) to give 1.4 ml of liquid, bp  $87^\circ$  (0.23 mm), 95% pure by glc. An analytical sample was collected by glc (column A,  $180^\circ$ ).

(b) **3-Cycloheptenyl Acetate.** A similar procedure was used to prepare *trans*-8,8-dichlorobicyclo[5.1.0]octyl 2-acetate in 71% yield.

(c) **3-Cyclononenyl Acetate.** A similar reaction on the same scale was carried out. Phenylmercuric bromide was isolated in 95% yield. Glc analysis of the filtrate showed the presence of 10,10-dichlorobicyclo[7.1.0]decyl 2-acetate in 64% yield, but the material obtained on subsequent distillation of the filtrate, bp  $101^\circ$  (0.2 mm), was contaminated with 6–8% of starting material. Attempted purification by preparative glc resulted in partial decomposition and thus the crude product was only characterized spectroscopically and then was hydrolyzed to the corresponding alcohol, which was obtained in good purity.

(d) **3-Cyclohexenyl Acetate.** A 0.01-mol scale reaction was carried out using the same procedure. After removal of  $\text{PhHgBr}$  (97%), the filtrate was examined by glc (column A,  $140^\circ$ ). Two principal high-boiling products were present in a 1:7 ratio, with retention times of 19.5 and 22 min, respectively. Their separation by glc without partial decomposition proved to be impossible. Spectral evidence suggested that they were the *cis* and *trans* isomers, respectively, of 7,7-dichlorobicyclo[4.1.0]heptyl 2-acetate. Their combined yield, determined by glc (column A,  $140^\circ$ , *n*-dodecane internal standard), was 84%. The analysis given in Table IV was obtained for the combined isomers. The *trans* isomer was the major product, as the nmr spectrum showed a wide axial proton signal for  $H_a$  (Table V), and reduction of the 7,7-dichlorobicyclo[4.1.0]heptanol-2 formed upon alkaline hydrolysis of this isomer mixture led chiefly to the known *trans*-bicyclo[4.1.0]heptanol-2.

**Reaction of Phenyl(bromodichloromethyl)mercury with 3-Methoxycycloalkenes.**<sup>25,25a</sup> (a) **3-Methoxycyclooctene.** A benzene

(25a) NOTE ADDED IN PROOF. In these reactions with 3-methoxycycloalkenes, the  $\text{C}=\text{C}$  addition compounds were the major products, but other products were formed as well. These were not characterized, but the presence of chlorine and olefinic unsaturation (by ir) would suggest that these are the products of  $\text{CCl}_2$  insertion into the C–H bond that is both allylic and  $\alpha$  to the methoxy function. Such insertions have been noted previously in the case of 2,5-dihydrofuran and allyl ethyl ether: D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, 87, 4259 (1965).

solution (15 ml) of 0.011 g of the mercurial and 1.68 g (0.012 mol) of the olefin was stirred and heated at reflux under nitrogen for 4 hr. Phenylmercuric bromide was obtained in 97% yield. Glc analysis of the filtrate (column A, 180°, 1-chloronaphthalene internal standard) showed the presence of only one major product, *trans*-9,9-dichloro-2-methoxybicyclo[6.1.0]nonane, in 75% yield. Distillation of the filtrate gave 1.1 ml of liquid, bp 57–58° (0.02 mm), 99% pure by glc.

(b) **3-Methoxycycloheptene.** Using this procedure, this olefin was converted to *trans*-8,8-dichloro-2-methoxybicyclo[5.1.0]octane in 76% yield.

(c) **3-Methoxycyclononene.** Application of this procedure to this olefin gave a colorless oil, bp 87–88° (0.35 mm), which glc (column A, 180°) showed to be a 5.5:1 mixture of two components. Attempted isolation of the major product by glc (165°, column E) was not successful. Spectroscopic examination of the distillate showed it to be primarily *trans*-10,10-dichloro-2-methoxybicyclo[7.1.0]decane (wide axial proton signal for H<sub>a</sub>), a conclusion confirmed by its reduction to give mainly *trans*-2-methoxybicyclo[7.1.0]decane. Glc yield determination showed the major product to be present in 63% yield, the minor product in *ca.* 11% yield (column A, 180°, ethyl cinnamate internal standard).

(d) **3-Methoxycyclohexene.** The same procedure gave two products. The major product (61% yield) was identified as *trans*-7,7-dichloro-2-methoxybicyclo[4.1.0]heptane and was isolated in pure form by glc (column E, 100°). The minor product, present in *ca.* 17% yield, was not identified.

(e) **3-Trimethylsilyloxycyclooctene.** The reaction was carried out in a similar manner on a 0.01-mol scale. After removal of phenylmercuric bromide (100% yield), the filtrate was concentrated and the residue treated with 0.2 ml of water and 5 ml of methanol, at reflux for 11 hr. The reaction mixture was poured into 40 ml of water and extracted with ether. The dried ether extracts were concentrated and chilled to give white solid. Recrystallization from *n*-hexane gave 1.24 g (59%) of white crystals, mp 86–88.5°, which showed an undepressed mixture melting point with authentic *trans*-9,9-dichlorobicyclo[6.1.0]nonanol-2, and infrared spectrum identical with that of that compound.

**Reduction of Dichlorocyclopropanes.**<sup>25</sup> The reduction of 9,9-dichlorobicyclo[6.1.0]nonanol-2 is described as an example of the procedure used throughout.

A THF (6 ml) solution of 9,9-dichlorobicyclo[6.1.0]nonanol-2 (0.459 g, 2.2 mmol) was treated under nitrogen with lithium wire (0.3 g, cut into small pieces) and 12 ml of dry *tert*-butyl alcohol. The mixture was stirred at room temperature for 2 days. After *cautious* quenching of the orange-brown solution with 50 ml of water, the reaction mixture was extracted with diethyl ether. The dried (MgSO<sub>4</sub>) ether extracts were concentrated at reduced pressure. Glc examination of the residue showed the presence of the desired bicyclo[6.1.0]nonanol-2, together with a lesser amount of what probably was the monochloro compound. The bicyclo[6.1.0]nonanol-2 was isolated by glc (column B, 150°). It was identical in all respects with the isomer produced in the 3-cyclooctenol-ICH<sub>2</sub>ZnI reaction<sup>8</sup> but not with the isomer obtained in the reduction of bicyclo[6.1.0]nonanone-2 with LiAlH<sub>4</sub> or diisopinocampheylborane, and on this basis and on the basis of its nmr spectrum was assigned the *trans* configuration.

All other reductions of dichlorocyclopropanes were carried out in this manner. Since the only object of these experiments was the isolation and structural characterization of the products, no attempts were made to optimize reaction conditions or to determine yields.

**Hydrolysis of Dichlorobicyclo[*n*.1.0]alkyl 2-Acetates.**<sup>25</sup> The hydrolysis of 9,9-dichlorobicyclo[6.1.0]nonyl 2-acetate is described as an example of the procedure used. The acetate (0.5 ml) was stirred overnight in a solution of 0.4 ml of water, 0.8 ml of ethanol, and 0.3 g of KOH. The yellow reaction mixture then was poured into water and extracted with diethyl ether. The ether extracts were dried (MgSO<sub>4</sub>), concentrated, and examined by glc (column A, 180°). Only one component was present. Complete evaporation of the ether left white crystals. Recrystallization from *n*-hexane gave material with mp 86–88° which was identified as *trans*-9,9-dichlorobicyclo[6.1.0]nonanol-2 by mixture melting point and ir.

**Reactions of 3-Cycloalkenols and 3-Methoxycycloalkenes with Iodomethylzinc Iodide.**<sup>25</sup> The reaction of 3-cyclooctenol with iodomethylzinc iodide is described as an example of the general procedure used.

The Le Goff procedure<sup>26</sup> was used to prepare the zinc-copper

couple. To an ethereal (20 ml) suspension of Zn–Cu (from 0.04 g-atom of zinc dust and 0.11 g of copper(II) acetate monohydrate) under nitrogen was added a few drops of methylene iodide to initiate the reaction. Dropwise addition of a solution of 0.02 mol of 3-cyclooctenol and 0.26 mol of methylene iodide was followed by a 3.5-day period of stirring and reflux. The orange-brown reaction mixture was filtered and washed with 25 ml of 3% HCl, saturated aqueous NaHCO<sub>3</sub>, and finally saturated aqueous NaCl solution. Glc examination (column B, 150°, 1-chloronaphthalene internal standard) of the dried organic layer showed that *trans*-bicyclo[6.1.0]nonanol-2 was present in 65% yield. Short-path distillation gave 1 ml of liquid, bp 58–60° (0.5 mm), *n*<sub>D</sub><sup>20</sup> 1.4928. The nmr and ir spectra and its glc retention time established its identity as the *trans* isomer and to the product obtained in a similar reaction by Cope and Woo.<sup>8</sup>

In some of the other reactions carried out during the course of this study yields were not determined since the purpose of these experiments was to obtain compounds for comparison with products of other reactions.

**Reduction of Bicyclo[6.1.0]nonanone-2.** (a) **With Lithium Aluminum Hydride.** Lithium aluminum hydride (0.16 g, 4 mmol) was placed in a dry 50-ml flask together with 20 ml of dry diethyl ether. An ether solution of the ketone (4 mmol) was slowly dripped into the stirred hydride solution. The reaction mixture was stirred for 1 hr at room temperature and 2 hr at reflux, then was quenched (cautiously) with 1:1 methanol-ether. Addition of saturated NH<sub>4</sub>Cl solution was followed by separation of the organic layer. The dried ether solution was evaporated at reduced pressure to leave 0.50 g of clear oil. The latter crystallized on being chilled to –78°, giving oily crystals, mp 34–37°. Two recrystallizations from cold hexane gave white crystals, mp 38–40°. The nmr spectrum of the product indicated it to be the *cis*-bicyclo[6.1.0]nonanol-2 (see Discussion). The glc retention time of this alcohol on column D at 150° was 19 min, that of the *trans* isomer was 23 min, and in the initially obtained crystals (above) *ca.* 5% of the *trans* isomer could be detected by glc.

(b) **With Diisopinocampheylborane.** The borane<sup>27</sup> was prepared by treating 5 mmol of NaBH<sub>4</sub> and 10 mmol of  $\alpha$ -pinene in 5 ml of diglyme at 0° under nitrogen with 5 mmol of BF<sub>3</sub>·Et<sub>2</sub>O in diglyme. After 15 min, 5 mmol of the ketone was added; a vigorous reaction resulted. After the addition had been completed, the solution was stirred for 4 hr at 0–3°, then overnight at room temperature. Cooling to 0° was followed by cautious, dropwise addition of 1.5 ml of 3 *N* NaOH, then of 1.5 ml of 30% hydrogen peroxide. The reaction mixture was poured into water and extracted with ether, and the dried ether layer (MgSO<sub>4</sub>) was concentrated. Glc examination of the residue showed the presence of solvents and 2,6,6-trimethylbicyclo[3.1.0]heptanol-3 and bicyclo[6.1.0]nonanol-2. Both were collected using preparative glc (column B, 150°). The first had mp 53–54° (lit.<sup>28</sup> for isopinocampheol, 55–56°); the second, mp 35–36°, had glc retention time (column D, 150°) and nmr and ir spectra identical with those of the product of the lithium aluminum hydride experiment in a above.

**Competition of Cyclooctene and 3-Cyclooctenol for a Deficiency of Phenyl(bromodichloromethyl)mercury.** A benzene (15 ml) solution containing 7.5 mmol each of the two olefins and 1.5 mmol of the organomercury compound was stirred and heated at reflux for 4 hr. After filtration of phenylmercuric bromide (95%), glc analysis of the filtrate (column A, 180°, ethyl cinnamate internal standard) showed that the yields of 9,9-dichlorobicyclo[6.1.0]nonane and 9,9-dichlorobicyclo[6.1.0]nonanol-2 were 36 and 44%, respectively.

A similar experiment with 7.5 mmol each of the same olefins and 1.5 mmol of phenyl(tribromomethyl)mercury gave 9,9-dibromobicyclo[6.1.0]nonane in 50% yield and 9,9-dibromobicyclo[6.1.0]nonanol-2 in 52% yield.

**Reaction of Phenyl(bromodichloromethyl)mercury with 2-Methyl-2-penten-4-ol.** Phenyl(bromodichloromethyl)mercury (4.84 g, 0.011 mol) and 1.00 g (0.01 mol) of 2-methyl-2-penten-4-ol (Aldrich Chemical Co., *n*<sub>D</sub><sup>20</sup> 1.4351; lit.<sup>29</sup> *n*<sub>D</sub><sup>20</sup> 1.4318) in 15 ml of dry benzene were stirred and heated at reflux for 3 hr. Filtration of phenylmercuric bromide (94%) was followed by glc analysis of the filtrate (column A, 140°, *n*-dodecane internal standard). The major product (52% yield) was 2,2-dichloro-3,3-dimethylcyclo-

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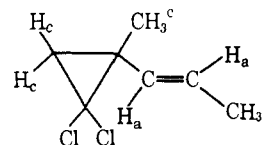
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propylmethylcarbinol, which was isolated as a white solid after removal of solvents. Recrystallization from pentane, sublimation at 0.3 mm and room temperature, and recrystallization from pentane to a constant mp of 73–73.5° gave pure material: nmr (CDCl<sub>3</sub>) δ 3.8 (m, 1 H, CH<sub>2</sub>-CH-OH), 2.2 (s, 1 H, OH), 1.8–1.2 ppm (m, with two singlets and one doublet (*J* = 8 Hz) visible, 10 H); ir (CS<sub>2</sub>) 3615 s, 3480 m, broad, 3000 sh, 2980 and 2965 s (doublet), 2935 s, 2875 m, 1390 sh, 1380 m, 1360 sh, 1325 w, 1255 s, 1235 w, 1165 s, 1135 s, 1110 s, 1095 sh, 1050 s, 1030 m, 1000 w, 980 s, 940 m, 890 s, 855 m, 830 s, 810 sh, and 730 m cm<sup>-1</sup>; mass spectrum 45 (100) [HOCHCH<sub>3</sub>], 67 (10) [C<sub>3</sub>H<sub>7</sub>], 103 (11) (M - ClC<sub>2</sub>H<sub>4</sub>O), 138 (8) [M - C<sub>2</sub>H<sub>4</sub>O], 182 (parent ion, not seen, as is usual for secondary and tertiary alcohols). *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>OCl<sub>2</sub>: C, 45.92; H, 6.61; Cl, 38.73. Found: C, 45.61; H, 6.69; Cl, 38.34.

A by-product (14% yield) in this reaction was 1-(1-methyl-2,2-dichlorocyclopropyl)propene-1: nmr (CCl<sub>4</sub>) δ 5.8 (m, 2 H<sub>a</sub>), 2.1 (d, 3 H, *J* = 5 Hz, H<sub>b</sub>), 1.75 ppm (m, 5H<sub>c</sub>). *Anal.* Calcd for



C<sub>7</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 50.94; H, 6.11; Cl, 42.96. Found: C, 51.07; H, 6.60; Cl, 42.64. This product is derived from CCl<sub>2</sub> addition to 2-methyl-1,3-pentadiene. The latter most probably was formed by acid-catalyzed dehydration of the starting alcohol, the acid (HCl) arising from that portion of CCl<sub>2</sub> attack on the alcohol which occurs at the O-H bond.

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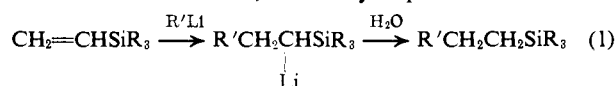
## Addition of Grignard Reagents to Vinylsilanes

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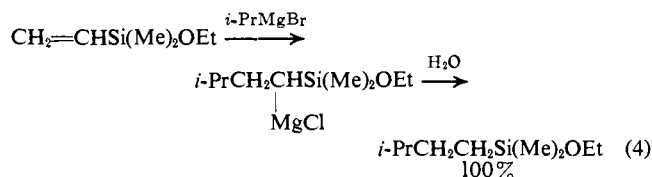
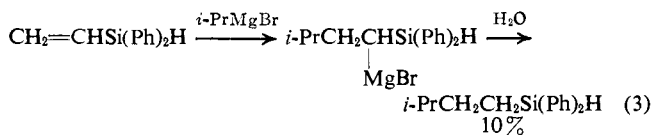
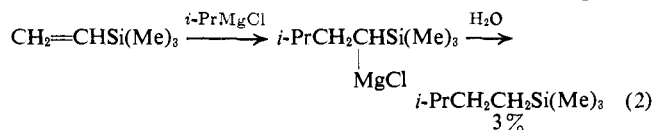
Contribution from the Chemistry Research Laboratory, Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson AFB, Ohio 45433, and Laboratoire de Chimie Organique Physique, Faculte des Sciences, 86-Poitiers, France. Received March 26, 1970

**Abstract:** The addition of Grignard reagents to vinylsilanes has been investigated with respect to the nature of the Grignard and to the substituents attached to the silicon atom. Alkoxy and chloro groups were found to exert an activating effect to the extent that quantitative yields of addition products frequently are observed. The structure of the Grignard reagent was found to have a pronounced effect, the order of reactivity being tertiary > secondary > primary.

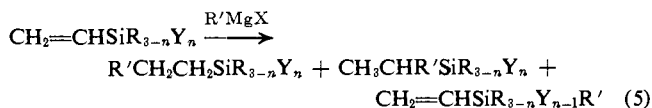
The addition of organolithium compounds to the double bond of vinylsilanes (eq 1) is well documented.<sup>2–5</sup> In contrast, the only report of an analog-



gous addition reaction with Grignard reagents is between phenylmagnesium bromide and triethylperfluorovinylsilane.<sup>4,5</sup> Reinvestigation has shown that numerous Grignard reagents add to the vinyl group of vinylsilanes and that the extent of the reaction is sensitive to the substituents attached to the silicon atom (eq 2–4).



When vinylsilanes containing labile groups on silicon (e.g., chloro, alkoxy) are allowed to react with a Grignard reagent, one can envision two possible modes of reaction: (a) addition to the α- or β-carbon of the vinyl group, or (b) displacement of the labile group from the silicon atom (eq 5). Examination of the reaction



mixtures have shown that the only major products originated from addition to the β-carbon of the vinyl group and displacement of the labile group from silicon. Authentic samples of the possible addition products were prepared by independent synthesis; the products of the reactions were separated and identified by comparison (nmr, ir, gc retention time) to the authentic samples. Indeed, groups such as alkoxy and halogen which normally are displaced by Grignard reagents activate the addition reaction to such an extent that the displacement reaction is often completely suppressed. This observation is in agreement with the activating

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