To 15 mmol of aluminum hydride dissolved in 45 ml of THF, 15 mmol of *exo*-norbornene oxide dissolved in 15 ml of THF was added at room temperature and permitted to react at room temperature. The reaction was followed by measuring the residual hydride of aliquots of the reaction mixture. After 4 days, the reduction was complete as indicated by one hydride uptake per mol of compound. To 8 ml of the reaction mixture (2 mmol of compound), 2 mmol of cyclohexanol was added as an internal standard, and the reaction mixture was hydrolyzed with the usual 1:1 mixture of THF and water. After saturating the aqueous layer with potassium carbonate, the clear THF was separated and dried over anhydrous magnesium sulfate. Glpc analysis indicated an 84% yield of alcohols which contained a 69:31 mixture of *exo*-2-norbornanol to 7-norbornanol.

At elevated temperature norbornene oxide is converted in reasonable yield to 7-norbornanol. The following describes the procedure used.

To 10.3 mmol of aluminum hydride dissolved in 30 ml of THF, 10 mmol of *exo*-norbornene oxide dissolved in 10 ml of THF was added at room temperature and refluxed for 12 hr. After adding 10 mmol of cyclohexanol as an internal standard, the reaction mixture was worked up exactly the same as above. Glpc analysis indicated no *exo*-norbornene oxide and an 80% yield of alcohols which contained a 51:48 mixture of *exo*-2-norbornanol to 7-norbornanol and contaminated with less than 1% of *endo*-2-norbornanol. Since the same sample of *exo*-norbornene oxide gave only *exo*-2-norbornanol when reduced with lithium aluminum hydride, this contamination of *endo*-2-norbornanol did not come from *endo*-norbornene oxide which might have been contaminated with *exo*-norbornene oxide.

Finally, we observed that lithium aluminum hydride in diglyme at 100° reduces norbornene oxide relatively rapidly, without rearrangement. This procedure would appear to have many advantages for the reduction of bicyclic epoxides.

To 5 mmol of lithium aluminum hydride in 15 ml of diglyme, 5 mmol of *exo*-norbornene oxide dissolved in 5 ml of diglyme was added at room temperature. The reaction mixture was kept at 100° for 24 hr. After adding 5 mmol of naphthalene as an internal standard, the reaction mixture was worked up exactly the same as above. Glpc analysis indicated 98% yield of *exo*-2-norbornanol with no contamination by 7-norbornanol.

**Reduction of Ketones.** Again, there appears to be no major advantage to the use of aluminum hydride for the reduction of ketones, except possibly in cases where it is desirable to avoid the presence of a strongly alkaline reagent. The following procedure describes the use of aluminum hydride for the reduction of camphor.

To 6.66 mmol of aluminum hydride in 15 ml of THF, 5 mmol of *d*-camphor dissolved in 5 ml of THF was added at 0°. The reaction was over in 15 min, as indicated by one hydride uptake. The reaction mixture was worked up the same as epoxides and analyzed by glpc on a 25% glycerol column on Firebrick. Isoborneol and borneol were identified by comparing with authentic samples. The ratio of isoborneol to borneol was 90:10.

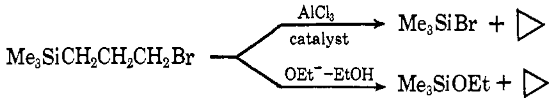
# Trimethylmetal Halide Elimination from Trimethylsilylmethyl- and Trimethyltinmethyl-Substituted *gem*-Dihalocyclopropanes

**Dietmar Seyferth and Theodore F. Jula**[1]

*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.* *Received October 6, 1967*

**Abstract:** The zinc chloride catalyzed elimination of trimethylchlorosilane or trimethyltin chloride from trimethylsilylmethyl- or trimethyltinmethyl-substituted *gem*-dihalocyclopropanes was found to give as organic products halogen-substituted 1,3-dienes. The fact that *cis*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane readily gave *cis*-3-chloropiperylene in high yield and that *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane gave a 72:28 mixture of *cis*- and *trans*-3-chloropiperylene in only 7% yield after considerably longer reaction time provided some insight into the nature of the elimination process. An explanation in terms of disrotatory, stereospecific opening of the cyclopropane ring to an allylic cation from which the trimethylmetal group is lost to give the 1,3-diene is presented. Other conversions described include: 1,1-dichloro-2-(trimethylmetalmethyl)cyclopropane (metal = Si and Sn) to 2-chloro-1,3-butadiene, 1,1-dibromo-2-(trimethylsilylmethyl)cyclopropane to 2-bromo-1,3-butadiene, 1,1-dichloro-2-methyl-2-(trimethylsilylmethyl)cyclopropane to 2-chloro-3-methyl-1,3-butadiene, and 30:70 *cis*-:*trans*-1,1-dichloro-2-methyl-3-(trimethyltinmethyl)cyclopropane to 3:1 *cis*-:*trans*-3-chloropiperylene.

The elimination of trimethylhalosilane from β-haloethyl- and γ-halopropylsilicon compounds, reported first by Sommer, Whitmore, and their coworkers in the late forties, is by now a well-known reaction in organosilicon chemistry.[2] In some cases such eliminations occur simply when the compound in question is heated, *e.g.*, $Me_3SiCH_2CH_2Cl \rightarrow Me_3SiCl + CH_2{=}CH_2$, but, more generally, such reactions are promoted by Lewis acid catalysts or occur upon solvolysis (usually base catalyzed). Thus, for instance, Sommer and coworkers[3] have described the preparation of cyclopropane from γ-bromopropyltrimethylsilane in high yield.



(1)

Our recent investigation of the addition of dihalocarbenes to the C=C bonds of allyl and vinyl compounds of silicon and tin[4,5] led to an interest in the chemistry of silicon- and tin-containing *gem*-dihalocyclopropanes and suggested that a study of the elimination reactions of compounds of type I might be of interest. From such compounds γ elimination of trimethylmetal halide is in principle possible, and we report here concerning this question.

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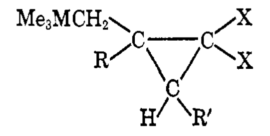
[1] National Institutes of Health Predoctoral Fellow, 1963–1967.

[2] C. Eaborn, "Organosilicon Compounds," Butterworths & Co. (Publishers) Ltd., London, 1960, pp 133–136, 139–140.

[3] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3056 (1949).

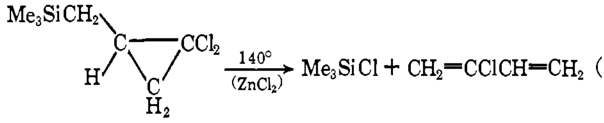
[4] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

[5] D. Seyferth, T. F. Jula, H. Dertouzos, and M. Pereyre, *J. Organometal. Chem.* (Amsterdam), **11**, 63 (1968).



I, M = Si or Sn; X = Cl or Br;
R, R' = H or CH$_3$

Silicon compounds of type I were found to be thermally quite stable. Thus 1,1-dichloro-2-(trimethylsilylmethyl)cyclopropane could be distilled (bp 185°) at atmospheric pressure without decomposition. However, trimethylchlorosilane elimination occurred readily in the presence of zinc chloride, a mild Lewis acid. When this silane was heated to 110° for 4 hr under nitrogen in the presence of 20 mol % of anhydrous zinc chloride, decomposition was complete. The volative products obtained, each in 76% yield, were trimethylchlorosilane and 2-chloro-1,3-butadiene (chloroprene) (eq 2). Similarly, pyrolysis of 1,1-dibromo-2-(trimethylsilylmethyl)cyclopropane at 140° in the presence of zinc bromide gave trimethylbromosilane (61%) and 2-bromo-1,3-butadiene (40%).



(2)

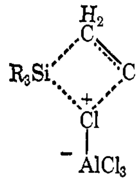
The 2-halo-1,3-butadiene produced was very sensitive to air and readily polymerized. A black, tarry residue always remained in the reaction flask at the end of the experiment. An improved procedure was developed in which a smaller amount of catalyst was used and in which the thermal decomposition was carried out at reduced pressure so that the volatile products were flash distilled into a chilled receiver as they were formed. In this manner, 1,1-dichloro-2-methyl-2-(trimethylsilylmethyl)cyclopropane was pyrolyzed in the presence of 8 mol % of zinc chloride at 130° for 4 hr (150 mm) to give trimethylchlorosilane and 2-chloro-3-methyl-1,3-butadiene, both in 85% yield.

In contrast to the thermal stability of these silicon compounds, thermal decomposition of 1,1-dichloro-2-(trimethyltinmethyl)cyclopropane occurred even in the absence of zinc chloride. When this compound was heated at 145–150° at atmospheric pressure for 90 min while the volatile products were continually being removed by means of a distillation head, extensive decomposition was noted. The volatiles consisted of chloroprene (56%) and tetramethyltin (18%). The pot residue contained trimethyltin chloride and dimethyltin dichloride. Thus this reaction is complicated by the redistribution of trimethyltin chloride (eq 3). A similar

$$2Me_3SnCl \longrightarrow Me_4Sn + Me_2SnCl_2 \qquad (3)$$

result was obtained when the pyrolysis was carried out in the presence of zinc chloride (7 mol %) at 110°. The "uncatalyzed" decomposition of this tin compound may still be considered to occur as a catalyzed reaction, since the methyltin chlorides formed themselves are weak Lewis acids,[6] and especially to be noted in this connection is the fact that $Me_3SnCl$ and $Me_2SnCl_2$ form anionic complexes of type $Me_3SnCl_2^-$ and $Me_2SnCl_4^{2-}$.[7] Thus the initial formation of a small amount of trimethyltin chloride (and by its disproportionation of the dichloride) could catalyze the decomposition of the remaining cyclopropane.

The question of the mechanism of these elimination reactions now arises. Although the Lewis acid catalyzed elimination of trimethylhalosilane from $\beta$-haloethyl- and $\gamma$-halopropylsilanes had once been considered to proceed *via* siliconium ion intermediates, recent work by Bott, Eaborn, and Rushton[8] appears to speak in favor of an intramolecular exchange of halogen from carbon to silicon (transition state II) in such processes. The exclusive formation of 2-halo-1,3-butadiene in the $\gamma$ eliminations described above suggested that loss of trimethylhalosilane was concerted with the cleavage of the cyclopropane ring. However, the intermediate formation of a bicyclo[1.1.0]butane could not be excluded, since under the reaction conditions further rearrangement could occur, giving finally the butadiene product, eq 4. Such thermally induced rearrangements of 1,3-disubstituted bicyclo[1.1.0]butanes are known.[9] However, two positional isomers should be obtained from a 1,2-disubstituted bicyclobutane. To obtain more information concerning this possibility, a mixture of *cis*- and *trans*-1,1-dichloro-2-methyl-3-(trimethyltinmethyl)cyclopropane (obtained *via* CCl$_2$ addition to 3:7 *cis*-:*trans*-crotyltrimethyltin) was pyrolyzed in the presence of zinc chloride at 80° (40 mm). In addition to tetramethyltin, there was obtained a 3:1 mixture of two other volatile products. Analysis of the nmr spectra of these compounds clearly indicated that they were the *cis* and *trans* isomers of 3-chloro-1,3-pentadiene (3-chloropiperylene) and not positional isomers. The distinction between *cis*- and *trans*-3-chloropiperylene could not be made on the basis of nmr evidence alone. Conclusive identification of the structure of each isomer was obtained by allowing the mixture of isomers to react with maleic anhydride. The steric hindrance of the *trans*-methyl group in the cisoid configuration required for the Diels–Alder reaction to occur[10] should re-



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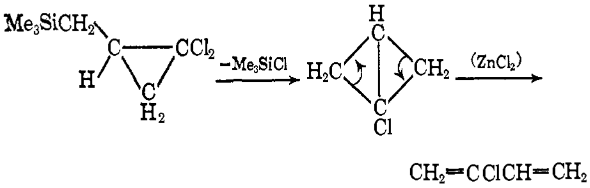

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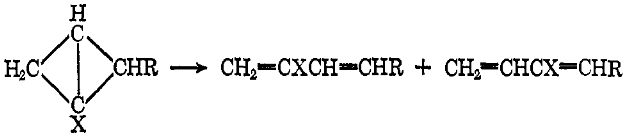

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(6) I. R. Beattie, *Quart. Rev.* (London), **17**, 382 (1963).

(7) (a) P. Pfeiffer, *Ann.*, **376**, 310 (1910); (b) A. Cassol and R. Barbieri, *Ann. Chim.* (Rome), **55**, 606 (1965); D. Seyferth, U. S. Patent 3,070,615 (Dec 25, 1962).

(8) R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometal. Chem.* (Amsterdam), **3**, 455 (1965).

(9) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

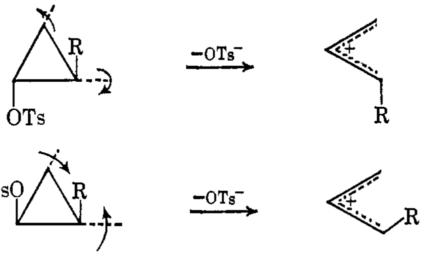
(10) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 540 (1961).

duce the rate of reaction of the *trans* isomer with maleic anhydride. The methyl group in the parent compound, *trans*-piperylene, has been shown to reduce the rate of reaction of this isomer with maleic anhydride relative to *cis*-piperylene.[11] In the present case, the initial ratio of isomers was determined by gas–liquid partition chromatography (glpc) as 3:1, in order of increasing retention time, but after the isomer mixture had been treated with maleic anhydride (to partial conversion), the remaining 3-chloropiperylene isomers were eluted in a ratio of 1:3. Therefore, it was concluded that the first isomer to be eluted was the *cis*-diene and the second the *trans*-diene. The initial ratio of *cis*- and *trans*-3-chloropiperylene obtained from the 1,1-dichloro-2-methyl-3-(trimethyltinmethyl)cyclopropane (3:1) was quite close to the ratio of the *cis*- and *trans*-crotyltrimethyltin isomers from which the cyclopropane was prepared (*ca.* 1:3), which suggested that the *cis*-3-chloropiperylene was obtained from the *trans*-cyclopropane isomer. This point could not be examined further with organotin compounds, so the *gem*-dichlorocyclopropanes were prepared from *cis*- and *trans*-crotyltrimethylsilane. Conditions for the resolution of the *cis* and *trans* isomers of 1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane by glpc were found, so that the isomeric purity of the starting materials could be established.

Pyrolysis of pure *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane in the presence of zinc chloride (125° (80 mm)) for 24 hr gave only a small amount of volatile material, which was shown to contain trimethylchlorosilane and a 3:1 mixture of *cis*- and *trans*-3-chloropiperylene (7% total yield). The unconverted cyclopropane was shown by glpc to contain only the *trans* isomer, which suggests at first sight that both isomers were formed directly from the *trans*-cyclopropane. However, the possibility of a slow rearrangement of the *trans*-cyclopropane to the *cis* isomer, followed by rapid elimination of trimethylchlorosilane from the latter, or of the isomerization of the chloropiperylene isomers under the reaction conditions could not be overlooked.

When pure *cis*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane was heated in the presence of zinc chloride under the same conditions, volatiles were evolved at a much faster rate. After only 6 hr, *cis*-3-chloropiperylene (containing less than 1% of the *trans* isomer) had been produced in 78% yield. In an experiment in which the heating period was only 3 hr, it was established that the unconverted starting material was still pure *cis*-cyclopropane. This experiment provided several valuable pieces of information concerning the mechanism of the $\gamma$ elimination of trimethylchlorosilane in these systems. The formation of only one isomer of 3-chloropiperylene established that the 3:1 ratio of *cis*:*trans* isomers obtained in the case of *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane did not arise from the isomerization of the elimination product under the reaction conditions. The failure of the remaining *cis*- or *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane in these two experiments to isomerize under the reaction conditions implied that the mixture of *cis*- and *trans*-3-chloropiperylene formed from the *trans*-cyclopropane was obtained by a direct elimination of trimethylchlorosilane from the *trans*-cyclopropane. Finally, the much faster elimination of trimethylchlorosilane from the *cis*-cyclopropane (as compared to the *trans* isomer) under the same reaction conditions suggested that a very specific steric factor was involved.

An explanation of these results was provided by previous work of De Puy and coworkers,[12] who had studied the solvolysis of a series of 2-arylcyclopropyl tosylates. It was found that the rate of solvolysis was dependent upon the relative stereochemistry of the leaving group, and these authors developed an explanation based upon the direction of rotation of the substituents on the cyclopropane ring in a concerted transformation to an allylic cation as the carbon–tosylate bond ionized,[12b] in good agreement with the predictions of Woodward and Hoffmann[13] for such electrocyclic transformations. The slow rate of solvolysis of *cis*-2-phenylcyclopropyl tosylate was explained by the inward rotation of the *cis* substituent to give a sterically hindered allylic cation, while in the case of *trans*-2-phenylcyclopropyl tosylate the ionization of the C–O bond resulted in an outward rotation.[12b]



Thus the solvolysis of a substituted cyclopropane to give an allylic intermediate was postulated to be a concerted, highly stereospecific transformation.

The results obtained in this study of the Lewis acid catalyzed $\gamma$ elimination of trimethylmetal halide from 1,1-dihalo-2-(trimethylmetalmethyl)cyclopropanes also are consistent with this picture. Although this elimination involves the use of a heterogeneous catalyst without any solvent, the only requirement is the transient existence of an allylic cation formed by the ionization of the carbon–halogen bond prior to the transfer of halogen to the trimethylmetal group. Since there is no solvent present other than the cyclopropane compound, this transfer is most likely an intramolecular process. A direct transfer of halogen with the concerted loss of trimethylmetal halide cannot readily occur, however, since the U arrangement required for a cyclic transition state[14] cannot be realized due to severe steric interactions between methyl groups on the metal and the *cis*-chlorine atom. The U arrangement for a 1,3 elimination is also the only configuration in which both centers undergo formal retention of configuration.[14] Thus the failure to obtain evidence for an intermediate bicyclo[1.1.0]butane is not surprising, since inversion of configuration precludes ring closure in this system.

Since the concerted loss of trimethylmetal halide is not likely, a stepwise 1,3 elimination must be considered.

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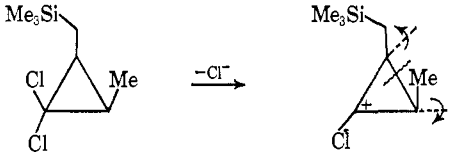
(11) D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

(12) (a) C. H. De Puy, L. G. Swnack, J. W. Hausser, and W. Wiedman, *ibid.*, 87, 4006 (1965); (b) C. H. De Puy, L. G. Swnack, and J. W. Hausser, *ibid.*, 88, 3343 (1966).

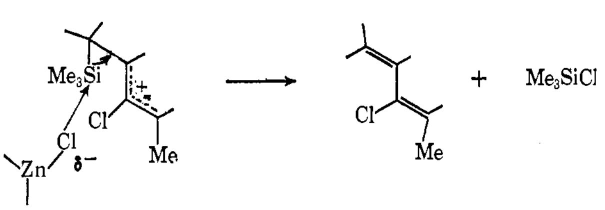
(13) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395 (1965).

(14) A. Nickon and N. H. Werstiuk, *ibid.*, **89**, 3914 (1967).

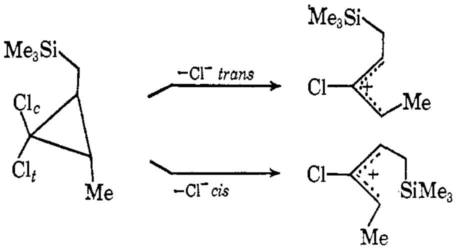
In *cis*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane the chlorine atom *trans* to the $Me_3SiCH_2$ substituent is much less sterically hindered than the *cis*-chlorine atom. Ionization of the *trans* C–Cl bond with a concerted transformation to an allylic cation should result in an outward, disrotatory[13] motion of the *cis* substituents, in analogy with the postulates of De Puy, *et al.*[12] It can be seen that such an outward disrotatory motion would lead to the stereospecific formation of the observed elimination product, *cis*-3-chloropiperylene, as the *trans* C–Cl bond is ionized.



The initial ionization of the *trans* C–Cl would lead to the formation of an allylic cation from which the butadiene structure could be obtained (with a semi-U elimination[14] of the trimethylsilyl group) as the transfer of the chlorine to the silicon is completed.



In the case of *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane and the analogous tin compound, both of the chlorine atoms are somewhat hindered. Application of the same postulates to the *trans*-cyclopropane shows that the ionization of either C–Cl bond would also lead to the formation of a sterically hindered intermediate.



Thus the low reactivity of this isomer toward the elimination of trimethylmetal halide, as well as the formation of a mixture of *cis*- and *trans*-3-chloropiperylene, also may be explained by the stereospecific opening of the cyclopropane ring during a concerted intramolecular transfer of halide ion.

The application of the postulates of De Puy, *et al.*, and of the more generalized predictions of Woodward and Hoffmann to these systems must, however, be treated with caution. As mentioned above, the reaction is heterogeneous and no solvent is present. While the transient formation of an ionic species is necessary for the elimination to occur at all by this mechanism, the only requirement is that the ionization of the carbon–halogen bond occur prior to the transfer of the halogen to the trimethylmetal group. The existence of a free ionic intermediate is not necessary for the elimination to occur, provided that the halogen is transferred in an intramolecular process. The proposed mechanism can be regarded only as a working hypothesis to explain the stereochemistry of the final products, and further study is required to define the exact mechanism which is operative in this heterogeneous system.

In conclusion, mention also must be made of some related studies by other workers. Thus Engelsma[15] has reported the pyrolysis (at 450°) of 1,1-dichloro-2,2-dimethylcyclopropane, which gave 2-chloro-3-methylbutadiene in 40% yield, together with a 57% yield of polymer. *gem*-Dichlorocyclopropane synthesis and pyrolysis could be effected in one experimental operation, *i.e.*, by pyrolysis of chloroform at 450° in the presence of appropriate olefins. Three other groups have published reports in 1967[16–19] of similar effects of the configuration about the cyclopropane ring in the thermal and Lewis acid catalyzed ring expansions of halo- and dihalocyclopropanes. These studies all showed that the stereochemistry of the rearrangement products as well as the rate of reaction for isomeric halocyclopropanes is directly related to the *cis*:*trans* geometry of the cyclopropane ring substituents.

## Experimental Section

**Starting Materials.** The preparation of the trimethylsilylmethyl- and trimethyltinmethyl-substituted *gem*-dihalocyclopropanes has been described in a previous publication from this laboratory.[5] The catalyst was prepared by heating the flask containing the zinc halide to 100° (0.1 mm) overnight, or until constant weight was reached. An alternate procedure involved heating the flask containing the zinc halide with a low bunsen flame (0.1 mm) until it began to sublime onto the wall of the flask. Both methods gave identical results, although in the second method some care was necessary to prevent decomposition of the zinc halide due to overheating.

**General Comments Concerning the Elimination Reactions.** The elimination reactions were carried out under nitrogen in a dry, 25-ml round-bottomed flask fitted with a short-path distillation head, condenser, and a tared receiver. The zinc halide catalyst, if used, was present in 7–10 mol % of the amount of cyclopropane used. The flask containing the cyclopropane (and catalyst) was immersed in an oil bath and heated to the required temperature. Generally, the zinc halide, when present, began to darken at about 80–100°, and the decompositions generally were carried out between 120 and 140°. In the early experiments the reactions were carried out at atmospheric pressure, but later it was found that better yields were obtained by evacuating the system to 40–80 mm (depending upon the boiling point of the cyclopropane) and cooling the receiver to −78°, so that the volatile decomposition products were flash distilled into the receiver as formed. A small amount (*ca.* 5–10 mg) of *p*-dinitrobenzene was placed in the receiver in order to inhibit the polymerization of the dienes produced.

The product mixtures were analyzed by glpc using an MIT isothermal unit. Samples of the products were collected by trapping the eluted component in U-shaped, 6-mm glass tubes equipped with a no-air stopper and a short, Drierite-filled tube. The sample collectors were swept with nitrogen immediately before use, since the reaction products were in general very sensitive to air, and samples were handled exclusively in glass syringes under nitrogen. The spectral data were recorded using only freshly collected samples. The yields were determined by the internal standard method or from the actual weights of the elimination products. The relative amounts of the elimination products in the mixture in the latter case were determined by the external standard method.

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(15) J. W. Engelsma, *Rec. Trav. Chim.*, 84, 187 (1965).

(16) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, 32, 924 (1967).

(17) T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *Tetrahedron Letters*, 1123 (1967).

(18) L. Ghosez, P. Laroche, and G. Slinckx, *ibid.*, 2767 (1967).

(19) L. Ghosez, G. Slinckx, M. Glineur, P. Hoet, and P. Laroche, *ibid.*, 2773 (1967).

Infrared spectra were determined using a Perkin-Elmer Model 237 or 337 spectrophotometer, generally in carbon tetrachloride solution. Nmr spectra were determined with a Varian Associates A-60 nmr spectrometer; chemical shifts are given in ppm downfield from internal tetramethylsilane.

**Elimination Reactions. 1. 1,1-Dichloro-2-(trimethylsilylmethyl)-cyclopropane.** A 10.0-g (50.1 mmol) sample containing 1.36 g (10 mmol) of zinc chloride was heated at atmospheric pressure to 110° for 4 hr. During this time a clear liquid slowly distilled into the receiver; a total yield of 8.76 g was obtained. Analysis by glpc (25% Dow Corning 710 Silicone Fluid on Chromosorb P at 68° and 15 psi helium) showed the presence of approximately equal amounts of two products. The second component to be eluted was identified as 2-chloro-1,3-butadiene (chloroprene) by comparison of its ir and nmr spectra with those reported in the literature.[20,21] The first component had a glpc retention time identical with that of trimethylchlorosilane. Its identity was confirmed by its hydrolysis to hexamethyldisiloxane and identification of the latter by means of its ir spectrum and glpc retention time.

The yield of chloroprene was 76%, based on starting cyclopropane, and the molar ratio of chloroprene to trimethylchlorosilane was 1:1.

In a separate experiment, 1,1-dichloro-2-(trimethylsilylmethyl)-cyclopropane was distilled in the absence of zinc chloride under nitrogen at atmospheric pressure (184–185°) without any evidence of decomposition.

**2. 1,1-Dibromo-2-(trimethylsilylmethyl)cyclopropane.** A 15.05-g (52.5 mmol) sample, in the presence of 2.47 g (11.0 mmol) of zinc bromide, was heated to 140°. A clear liquid, bp 70–80°, slowly distilled into the receiver. At the end of 4.5 hr, a black, solid residue remained, and 7.89 g of faintly yellow liquid had been collected. Glpc analysis (76°, 23 psi helium) showed only two peaks with retention times of 7.5 and 12.7 min in a ratio of 3:2. The first component was identified as trimethylbromosilane by glpc retention time and conversion to hexamethyldisiloxane. The second was shown to be 2-bromo-1,3-butadiene by comparison of its ir spectrum with that reported for this compound[22] and by means of its nmr spectrum, which showed a complex pattern from 5.15 to 5.85 ppm (4 H) and a four-line pattern centered at 6.28 ppm (1 H). The splitting pattern and relative chemical shifts were nearly identical with those in the nmr spectrum of 2-chloro-1,3-butadiene. The yields of bromoprene and trimethylbromosilane were 40 and 61%, respectively.

**3. 1,1-Dichloro-2-(trimethyltinmethyl)cyclopropane.** A flask containing 8.87 g (31 mmol) of the cyclopropane was immersed in an oil bath and heated (with stirring) to 120° without any noticeable reaction. As the temperature increased to 140°, the liquid began to reflux vigorously, and the head temperature fluctuated 55–60°. The bath was maintained at 140° for 90 min until the head temperature began to drop. The oil bath temperature was raised to 170°, and the remaining liquid began to distil over. The condenser became clogged with white, needle-like crystals, requiring the use of an infrared lamp, and the distillation was continued to dryness. A pale yellow liquid (7.10 g) was collected in the receiver, and about 1 g of black tarry residue remained in the flask. The distillate was analyzed by glpc at 72°, 10 psi helium. Two peaks with retention times of 9.2 and 11.1 min were eluted in a ratio of about 1:3, respectively, and a third broad peak with a retention time of 30 min also was observed.

The products were identified by repeating the above experiment with 9.34 g of the cyclopropane. The bath temperature was kept at 145–150° for 90 min, so that only the two lower boiling components distilled over. Glpc analysis of the distillate (2.98 g) showed the volatiles to be tetramethyltin and 2-chloro-1,3-butadiene, in order of increasing retention time. The glpc retention times and infrared spectra of collected samples were identical with those of authentic samples. The molar ratio of tetramethyltin to 2-chloro-1,3-butadiene was 1:3, and the yield of the latter was determined to be 56%. The residue (3.5 g) was analyzed by glpc using a short column (Dow Corning 710 Fluid). The major component was trimethyltin chloride, a collected sample of which showed no melting point depression with authentic material. A small amount of dimethyltin dichloride also was present; it was identified by peak enhancement with an authentic sample.

This experiment was repeated with 5.76 g (20 mmol) of 1,1-dichloro-2-(trimethyltinmethyl)cyclopropane, but with 0.20 g (1.46 mmol) of added zinc chloride. The mixture was heated to 70°; it became cloudy and the zinc chloride darkened. As the temperature was increased to 110°, a clear liquid began to distil, bp 58–59°. Glpc analysis of the distillate demonstrated the presence of a nearly equimolar mixture of tetramethyltin and 2-chloro-1,3-butadiene.

**4. 1,1-Dichloro-2-methyl-2-(trimethylsilylmethyl)cyclopropane.** The cyclopropane (12.68 g, 61.0 mmol) and 0.830 g (6.1 mmol) of zinc chloride were heated to 130° for 5 hr until only a black, tarry residue remained in the flask. Glpc analysis of the distillate showed the presence of only two components: trimethylchlorosilane and 2-chloro-3-methyl-1,3-butadiene, in order of increasing retention time. The latter was identified by means of its infrared spectrum, which was identical with that reported for this compound,[23] and of its nmr spectrum, which showed a partially resolved doublet at 1.95 ppm (3 H, $J$ = 2 cps) and three peaks showing considerable fine splittihg at 5.18, 5.40, and 5.60 ppm (4 H total).

Since the yield of the butadiene was low (no more than 20% of the amount of trimethylchlorosilane formed), the decomposition was repeated (25.6 mmol of the cyclopropane, 3.0 mmol of $ZnCl_2$) in a system evacuated to 150 mm under nitrogen. The receiver was connected to the reaction flask through a curved, 10-mm tube with ground-glass joints and was cooled to −78°. The reaction mixture was heated to 125–130° for 4 hr to give 4.60 g of clear liquid and 0.42 g of black solid residue. Glpc analysis at 110°, 20 psi helium, showed the distillate to contain trimethylchlorosilane and 2-chloro-3-methyl-1,3-butadiene in 1:1 molar ratio. The yield of products calculated from the weight of distillate was 85%, based on starting cyclopropane.

**5. *cis*- and *trans*-1,1-Dichloro-2-methyl-3-(trimethyltinmethyl)-cyclopropane.** A mixture of the cyclopropane (isomeric mixture, prepared from a 30:70 mixture of *cis*- and *trans*-crotyltrimethyltin) (2.77 g, 9.2 mmol) and zinc chloride (0.98 g, 6.8 mmol) was heated to 80° (40 mm) for 4 hr. Clear liquid, 1.45 g, distilled into the −78° receiver and white, crystalline solid sublimed into the connecting tube. This was identified as dimethyltin dichloride by means of its melting point and infrared spectrum.[24] The distillate was analyzed by glpc at 103° and 18 psi helium. Three components were eluted within 15 min, and a fourth (in small amount) appeared at about 25 min. The latter was identified as trimethyltin chloride. The first component to be eluted was tetramethyltin. The second and third components were present in 3:1 ratio, respectively. Their infrared and nmr spectra indicated that they were the *cis* and *trans* isomers of 3-chloropiperylene.

The isomer to be eluted first from a Dow Corning 710 column had the following infrared spectrum: 3110 (m), 3025 (s), 2920 (s), 2855 (m), 1820 (m), 1645 (s), 1610 (s), 1440 (m), 1420 (m), 1400 (m), 1380 (m), 1315 (m), 1282 (s), 1186 (s), 1017 (m), 978 (s), 933 (m), 915 (s), 605 (s), and 550 (m) cm$^{-1}$. Chemical evidence (see below) showed this to be the *cis* isomer. The other isomer showed absorption at 3108 (m), 3030 (m), 2920 (s), 1840 (m), 1640 (m), 1590 (s), 1445 (m), 1420 (s), 1380 (m), 1340 (m), 1165 (s), 1081 (m), 974 (s), 937 (s), 920 (s), 704 (m), and 660 (m) cm$^{-1}$.

The nmr spectrum of the *cis* isomer (in $CCl_4$) showed a sharp doublet centered at 1.84 ppm (3 H, $J$ = 7 cps), a doublet showing further fine splitting centered at 5.08 ppm (1 H, $J$ = 10 cps), a quartet centered at 5.75 ppm ($J$ = 7 cps), the high-field member of which overlapped with a resonance at about 5.62 ppm and another resonance at 5.36 ppm (total 2 H), and a pair of doublets ($J$ = 10 cps for each) separated by 17 cps and centered at 6.31 ppm (1 H). The nmr spectrum of the *trans* isomer showed a sharp doublet at 1.82 ppm (3 H, $J$ = 7.5 cps), a complex pattern of resonances (5.18, 5.26, 5.50, 5.63, 5.78, and 5.88 ppm) all showing further fine splitting (3 H total), and a pair of doublets ($J$ = 10 cps for each) separated by 16 cps and centered at 6.66 ppm (1 H). These data clearly indicated that the products were the *cis* and *trans* isomers of 3-chloropiperylene and not positional isomers. The methyl resonance in the spectrum of each isomer appeared as a sharp doublet. If these compounds were of the type $CH_2{=}CClCH{=}CHCH_3$, the methyl resonance would be split further by the adjacent $\alpha$-vinylic proton as well as by the $\beta$ proton to give a quartet similar to that reported for the methyl resonance in crotonic acid, $CH_3CH{=}CH$-

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$CO_2H$.[25] Further evidence for the 3-chloropiperylene structure was given by the presence of a low-field quartet in the spectrum of each isomer, centered at 6.31 and 6.66 ppm, respectively, which integrated for 1 H relative to the methyl group resonance. Each of these quartets consisted of a pair of doublets ($J$ = 10 cps for each), whose centers were separated by 17 and 16 cps, respectively, which is very similar to that observed for the internal proton in chloroprene (=C*H*CCl=). The observed coupling constants for this pattern are very close to the reported values for this quartet in the spectrum of chloroprene ($J$ = 10.51 and 16.54 cps).[21]

**6. Reaction of *cis*- and *trans*-3-Chloropiperylene with Maleic Anhydride.** A mixture of *cis*- and *trans*-3-chloropiperylene was prepared by pyrolysis of 4.88 g (16.2 mmol) of 1,1-dichloro-2-methyl-3-(trimethyltinmethyl)cyclopropane for 3 hr at 80° (60 mm) with anhydrous zinc chloride (1.40 g, 10.3 mmol) following the procedure described above. A small amount of *p*-dinitrobenzene was added to the receiver as a stabilizer. The distillate was analyzed by glpc and found to contain, in order of increasing retention time, tetramethyltin and the isomers of 3-chloropiperylene, the latter in 3:1 ratio.

Reagent grade maleic anhydride (1.94 g, 19.8 mmol) was placed in a 25-ml, pear-shaped flask with a no-air stoppered side arm, equipped with a reflux condenser and nitrogen inlet tube. The flask was evacuated and flushed with nitrogen several times, and then warmed to 70°. The distillate from the pyrolysis above was transferred in a glass syringe, and 1.0 ml was added to the maleic anhydride at 70°. The flask was shaken for about 5 min at this temperature and then was cooled to room temperature. The unconverted maleic anhydride solidified, leaving about 0.60 g of clear liquid which was removed *via* syringe into a no-air stoppered vial which had been purged with nitrogen. The liquid was analyzed by glpc immediately. The relative amounts of the two 3-chloropiperylene isomers had changed from the original 3:1 to a 1:3 ratio. Thus the first isomer to be eluted is more reactive toward maleic anhydride than is the second and this leads to the assignment of the *cis* configuration to the first isomer.

**7. *trans*-1,1-Dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane.** The pyrolysis of 2.39 g (11.3 mmol) of *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane with 0.244 g (1.8 mmol) of zinc chloride at 125° (80 mm) for 24 hr gave only 0.256 g of distillate.

A small portion of the liquid pot residue was washed with water and analyzed by glpc (124°, 15 psi helium). Only starting material (and none of the corresponding *cis* isomer) could be detected. Under these glpc conditions a mixture of *cis*- and *trans*-1,1-dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane can be resolved. The distillate was analyzed by glpc Dow Corning 710, 95°, 15 psi helium). In addition to trimethylchlorosilane, both *cis*- and *trans*-3-chloropiperylene (identified by their infrared spectra) were present, in an area ratio of about 3:1, respectively. The yield was determined to be 7.0%, with a *cis*:*trans* molar ratio of 72:28.

**8. *cis*-1,1-Dichloro-2-methyl-3-(trimethylsilylmethyl)cyclopropane.** The pyrolysis of 1.94 g (9.20 mmol) of this compound in the presence of 0.176 g (1.29 mmol) of zinc chloride at 125° (80 mm) for 6 hr gave 1.57 g of clear distillate. Analysis of the latter by glpc showed it to contain trimethylchlorosilane and *cis*-3-chloropiperylene (identified by its infrared and nmr spectra) in approximately equal amounts. A yield determination showed that the diene had been formed in 78% yield and that less than 1% of the *trans* isomer (identified by retention time only) was present.

*Anal.* Calcd for $C_5H_7Cl$: C, 58.45; H, 6.88. Found: C, 58.65; H, 6.08.

In a separate experiment a sample of 1.82 g of the *cis*-cyclopropane containing 0.112 g of zinc chloride was heated at 125° (80 mm) for 3 hr. A sample of the residue was analyzed by glpc and found to contain only *cis*-cyclopropane and none of the *trans* isomer. Analysis of the distillate showed the presence only of trimethylchlorosilane and *cis*-3-chloropiperylene.

**9. *trans*-1,1-Dichloro-2-methyl-3-(trimethyltinmethyl)cyclopropane.** The same procedure was used in the pyrolysis of 2.03 g (6.72 mmol) of this compound in the presence of 0.197 g of zinc chloride at 125° (60 mm) for 90 min. The 0.97 g of distillate was found by glpc analysis to contain tetramethyltin, *cis*-3-chloropiperylene, and the *trans* isomer in 3:3:1 area ratio. A small amount of dimethyltin dichloride sublimed into the glass connecting tube.

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(25) Varian NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 60.