

CONDENSATION REACTIONS OF HALOGERMANES AND HALOSILANES WITH CYCLOHEXENE OXIDE

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SUMMARY

Condensation products of several halogermanes and halosilanes with cyclohexene oxide have been identified and characterized. The opening of the oxide linkage of cyclohexene oxide has been investigated through hydrolysis of the intermediate products (*cis/trans* cyclohexene halohydrin isomers) produced in these reactions. It is proposed that the subject condensation reactions proceed via a pentacovalent type intermediate.

INTRODUCTION

In recent publications preliminary accounts of the action of halogermanes on various cyclic ethers and supporting kinetic data were reported^{1,2}. Though second order kinetics were obtained, it was apparent upon investigation of the rates of reaction and direction of ring opening that information concerning the mechanism of the subject reaction sequence would have to be obtained by correlating rate studies with the stereochemical direction of ring opening. This information is essential since the mechanism of ring opening in many cases may not be necessarily the same. This paper reports an investigation concerned with the geometrical isomers obtained by the treatment of cyclohexene oxide with halogermanes and halosilanes.

RESULTS AND DISCUSSION

Cyclohexene oxide was chosen to initiate this study because its stereochemical behavior would lead to the formation of geometrical isomers and this fact would not be dependent on the oxide directly, but on the nature of the organometallic halide. Furthermore, cleavage of the intermediate cyclohexyloxysilanes or germanes would yield known halohydrin derivatives. Previous work with the silanes has shown that hydrolysis of a Si-O-C linkage in acid solution involves cleavage of the Si-O bond

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TABLE I
PERCENT *cis/trans*-CYCLOHEXENE HALOHYDRIN ISOMERS

Organometallic reagent	Product	Method of cleavage ^a	Yield of cleavage product (%)	Cyclohexene halohydrin (%)	
				Cis	Trans
Methyltrichlorosilane	Methyltris(2-chlorocyclohexyloxy)silane	A	89.0	57.0	43.0
Trimethylchlorosilane	Trimethyl(2-chlorocyclohexyloxy)silane	A	64.5	66.0	34.0
Trimethylbromosilane	Trimethyl(2-bromocyclohexyloxy)silane	A	91.6	2.7	97.3
Triethylbromosilane	Triethyl(2-bromocyclohexyloxy)silane	A	76.8	42.6	56.4
Tri- <i>n</i> -butylchlorosilane	Tri- <i>n</i> -butyl(2-chlorocyclohexyloxy)silane	A	^b		
Tri- <i>n</i> -butylbromosilane	Tri- <i>n</i> -butyl(2-bromocyclohexyloxy)silane	A	^b		
Tri- <i>n</i> -hexylchlorosilane	Triethyl(2-chlorocyclohexyloxy)germane	B	98.9	2.3	97.7
Triethylchlorogermane	Triethyl(2-bromocyclohexyloxy)germane	B	96.0		100
Tri- <i>n</i> -propylchlorogermane	Tri- <i>n</i> -propyl(2-chlorocyclohexyloxy)germane	B	100	61.0	39.0
Tri- <i>n</i> -propylbromogermane	Tri- <i>n</i> -propyl(2-bromocyclohexyloxy)germane	B	90.8	7.3	92.7
Triisobutylchlorogermane	Triisobutyl(2-bromocyclohexyloxy)germane	B	81.2	18.7	81.3
Triisobutylbromogermane					
Triphenylchlorogermane ^d	Triphenyl(2-bromocyclohexyloxy)germane ^e				
Triphenylbromogermane ^d					

^a See experimental section for methods of cleavage. ^b Not cleaved by methods employed. ^c No reaction. ^d The triphenyl derivatives were treated with cyclohexene oxide in "carbitor" solvent. ^e Obtained in trace amounts only.

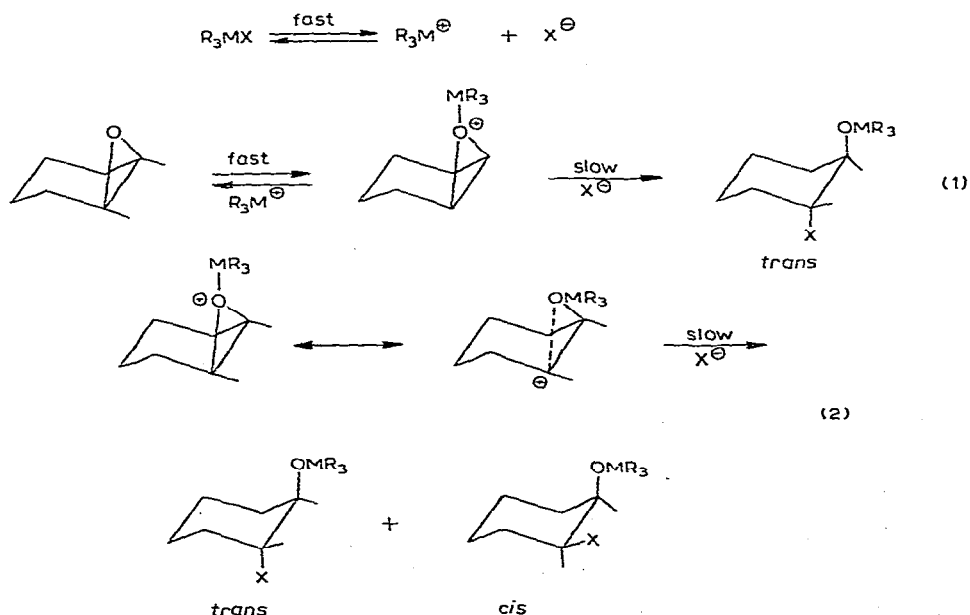
and not the O-C bond. Khaskin³ demonstrated this by the exchange of oxygen which accompanies hydrolysis of tetraethoxysilane in water containing H_2O^{18} .

A similar cleavage is most likely in the case of the Ge-O-C linkage, but this has not been demonstrated by experimentation to our knowledge. However, in the present work, this was circumvented by the use of dry hydrogen chloride⁴.

The *cis*- and *trans*-chlorohydrins derived from the hydrolysis of the silanes and germanes have been fully characterized and a method developed to determine the amount of each isomer in a mixture of the two⁵. The ratio of *cis*- and *trans*-cyclohexene halohydrins obtained by the intermediate alkoxysilanes and germanes are summarized in Table 1.

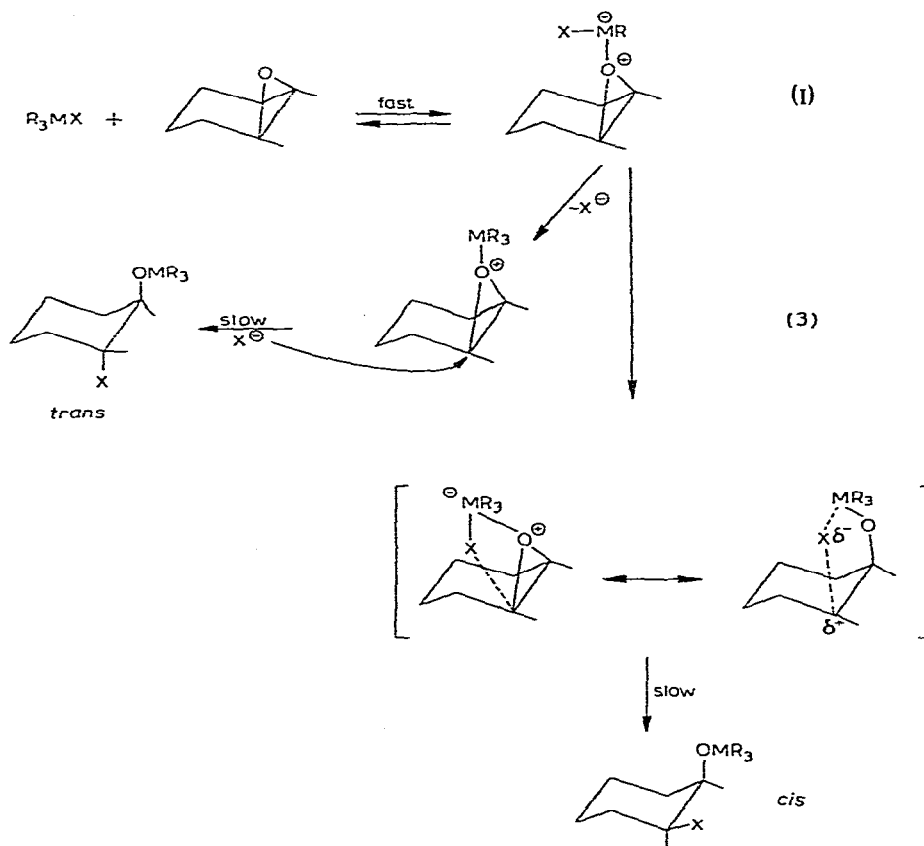
In the original considerations of a proposed reaction sequence, from a mechanistic point of view, the authors had contemplated two general types. The first of these was an assisted four-centered reaction⁶ by which the validity of the proposed reaction sequence could be proposed judged on the basis of stereo-chemical results. The mechanism would assume that the epoxide ring be opened with retention of configuration. The other major possibility appeared to be a more normal $\text{S}_{\text{N}}2$ -displacement sequence which may or may not involve a pentacovalent intermediate. Kinetic results alone cannot distinguish between these possibilities and the fact that the reaction is catalyzed by acids^{1,2} is also consistent with either of the mechanistic sequences. In both cases the separation of the halide ion would be assisted by an electrophilic species.

Upon investigation of the data in Table 1, the assisted four-centered type reaction sequence was eliminated since this would produce essentially *cis*-product. In considering the classical $\text{S}_{\text{N}}2$ type displacement, the following probable reaction sequences were considered.



In sequence (1), one would expect essentially *trans*-product which is inconsis-

tent with the data obtained. In sequence (2), which proceeds via a "carbonium ion" type intermediate, both *cis*- and *trans*-products are possible, the ratios of which would also be dependent on steric factors. However, in both reaction sequences (1) and (2), ionization of the organometallic halide is first presumed; although such a possibility is not discounted, the authors feel that such a premise is difficult to envision, based upon the reaction conditions employed, *i.e.*, weak nucleophile, non-polar solvent, etc.



Therefore, the reaction sequence (3), proceeding via a pentacovalent type intermediate, is proposed. The amount of *cis/trans*-products obtained will depend on when bond formation occurs *vs.* bond breaking. The governing factors will be the nature of the M-X linkage as well as the nature and size of the R groups. However, there is in addition the possibility that the intermediate (I) may give rise momentarily to a "carbonium ion" type intermediate which can also yield *cis/trans*-isomers. This would be similar to (2) above. Work is presently being done in our laboratories to determine whether or not such a "carbonium ion" type intermediate is possible.

The fact that the monobromo-derivatives yield a higher percentage of *trans*-product than the monochloro-derivatives is not inconsistent with the proposed mechanism. There are several indications in the literature that the Ge-Br and the Si-Br linkages ionize more readily than the Ge-Cl and the Si-Cl linkages⁷⁻¹⁰.

It is also noted that as the size of the R groups increases, this increases the percentage of *cis*-product directly. This can be explained from the point of view of steric hindrance in orientation of the pentacovalent intermediate. It is seemingly apparent that the actual instant of bond formation of the carbon-halogen linkage *vs.* bond breaking of the metal-halogen linkage is critical. When the R groups are small in comparison to the halogen the preferred conformation would be with the halogen away from the cyclohexene oxide ring. However, as we increase the size of the R groups the more likely orientation would be with the halogen towards the ring. This would therefore increase the possibility of a frontal attack of the halide ion upon breaking of the metal-halogen linkage.

In addition, as is observed in the case of the tri-*n*-hexylchlorosilane and triisobutylchlorogermanes, there appears to be a distinct steric limitation to the subject condensation reactions under similar conditions. It is interesting to note that the tri-*n*-butyl(2-halocyclohexyloxy)silanes can be prepared, but did not cleave under the conditions used in the present work. These observations indicate that a steric limitation is imposed not only on cleavage of the ring but also on cleavage of the metal-O-C bond of the product.

Evidence that the reaction sequence may be assisted by a coordination step which does not involve true coordination in the sense of replacement of ligand by ligand can be seen from IR data. The epoxide linkage exhibits a strong bond at 1260 cm^{-1} . A room temperature mixture of the systems studied (under which conditions reaction does not take place^{1,2}) did not shift the absorption band of the epoxide linkage. If strong coordination existed in the absolute sense, a shift in the absorption band would be expected.

It had been originally reported^{1,2} that condensation products between the triphenylhalogermanes and cyclic ethers did not take place in a solvent system such as ether, benzene, or toluene even in the presence of various Lewis acids and bases. Though unsuccessful with triphenylchlorogermane, trace amounts of the condensation product of triphenylbromogermane with cyclohexene oxide was obtained when a protic type solvent such as "carbitol" was employed. Further investigation of these general systems is underway in our laboratories.

EXPERIMENTAL

Preparation of the alkyl- and aryl(2-halocyclohexyloxy)silanes and -germanes

Methyltris(2-chlorocyclohexyloxy)silane. Cyclohexene oxide (19.6 g, 0.2 mole) and freshly distilled methyltrichlorosilane (7.5 g, 0.05 mole) were placed in a 100 ml flask attached to a reflux condenser under an atmosphere of nitrogen. With stirring, this solution was heated at 57° for 72 h. The resulting material was concentrated under reduced pressure (20 mm) at 40° to remove unreacted cyclohexene oxide and methyltrichlorosilane. Fractionation of the high boiling liquid residue gave a forerun (2.2 g) having b.p. $165\text{--}208^\circ$ (2.2 mm), n_D^{27} 1.4831. The desired material, methyltris(2-chlorocyclohexyloxy)silane (16.2 g) distilled having b.p. $214\text{--}218^\circ$ (2.1 mm), n_D^{26} 1.4939 [Lit. value¹¹: b.p. $211\text{--}214^\circ$ (2.5 mm), n_D^{20} 1.4971]. (Found: Si, 6.32. $\text{C}_{19}\text{H}_{33}\text{Cl}_3\text{O}_3\text{Si}$ calcd.: Si, 6.16 %.)

The following is an example of the reactions of cyclohexene oxide with the trialkylmonohalosilanes and the trialkylmonohalogermanes. The products of these

TABLE 2
ALKYL- AND ARYL(2-HALOXYCLOHEXYLOXY)SILANES AND -GERMANES

Product ^a	Mol.wt.	B.p. [°C(mm)]	Index of refraction	Metal analysis (%)	
				Found	Calcd.
Trimethyl(2-chlorocyclohexyloxy)silane	206.83	63-64° (2.8)	n_D^{25} 1.4484	Si, 13.12	Si, 13.57
Trimethyl(2-bromocyclohexyloxy)silane	251.22	71-72.5° (1.5)	n_D^{28} 1.4665	Si, 11.19	Si, 11.86
Triethyl(2-bromocyclohexyloxy)silane	293.30	119-123° (2.8)	n_D^{26} 1.4769	Si, 9.55	Si, 9.57
Tri-n-butyl(2-chlorocyclohexyloxy)silane	333.00	94-98° (2.8)	n_D^{26} 1.4452	Si, 8.39	Si, 8.44
Tri-n-butyl(2-bromocyclohexyloxy)silane	377.46	164-168° (3.5)	n_D^{23} 1.4707	Si, 7.65	Si, 7.49
Triethyl(2-chlorocyclohexyloxy)germane	293.37	121-125° (2.5)	n_D^{25} 1.4765	Ge, 25.63	Ge, 24.74
Triethyl(2-bromocyclohexyloxy)germane	337.83	134-136° (2.5)	n_D^{25} 1.4890	Ge, 20.89	Ge, 21.49
Tri-n-propyl(2-chlorocyclohexyloxy)germane	335.46	135-138° (2.2)	n_D^{27} 1.4742	Ge, 21.61	Ge, 22.00
Tri-n-propyl(2-bromocyclohexyloxy)germane	379.92	150-155° (2.8)	n_D^{25} 1.4880	Ge, 19.21	Ge, 19.11
Tri-n-isobutyl(2-bromocyclohexyloxy)germane	422.00	105-110° (1.0)	n_D^{26} 1.4854	Ge, 17.29	Ge, 17.20

^a Reaction time of reactants to produce products varied from 8 to 72 h, and reflux temperature from 57° to 95°.

reactions including pertinent data are summarized in Table 2.

Trimethyl(2-chlorocyclohexyloxy)silane. Using the procedure described for the previous system, cyclohexene oxide (9.8 g, 0.1 mole) was treated with trimethylchlorosilane (21.10 g, 0.2 mole). Fractionation of the liquid residue yielded 11.8 g of the desired silane having b.p. 63–64° (2.8 mm), n_D^{25} 1.4485 [Lit. value¹¹: b.p. 60–61.5° (3.0 mm), n_D^{20} 1.4565]. (Found: Si, 13.12. $C_9H_{19}ClOSi$ calcd.: Si, 13.57%.)

Cleavage of the alkyl(2-halocyclohexyloxy)silanes and -germanes

Two general procedures were used to cleave the subject compounds to obtain the halohydrin mixtures. These are illustrated using the stated compounds. Table 1 summarizes the method employed for each reactant.

Method A. Trimethyl(2-chlorocyclohexyloxy)silane (7.5 g, 0.036 mole) was dissolved in a mixture of 25 ml of 95% ethanol, 10 ml of water, and 1.5 ml of concentrated hydrochloric acid. This mixture was stirred at room temperature for a period of 12 h. Water (50 ml) was then added and the non-aqueous layer separated by extraction with three 25 ml-portions of ether. The ethereal extracts were combined and dried over sodium sulfate. The ether and the lower boiling material were removed by distillation at atmospheric pressure leaving a liquid residue which was then fractionated through a semi-micro column. There was obtained 3.1 g of the cyclohexene chlorohydrin having b.p. 72° (8.0 mm), n_D^{25} 1.4878. [Lit. value⁵: b.p. 93° (26 mm)]. (Found: Cl, 26.20. $C_6H_{11}ClO$ calcd.: Cl, 26.40%.)

Method B. Tri-*n*-propyl(2-chlorocyclohexyloxy)germane (3.6 g) was dissolved in 25 ml of benzene and hydrogen chloride gas passed through the solution for one h at room temperature and for two h at 50°. The flow of gas was then stopped and the solution heated at reflux temperature for two additional h. After concentration of the benzene solution under reduced pressure (40°, 10 mm) the liquid residue was dissolved in 20 ml of petroleum ether. Elution chromatography on silica gel (10 inch column) was used to separate the tri-*n*-propylchlorogermane product from the desired cyclohexene chlorohydrin. Petroleum ether and diethyl ether were used as elution solvents. The germanium derivative was eluted from the column using petroleum ether (75 ml), the cyclohexene chlorohydrin with the diethyl ether (75 ml). Concentration of the combined petroleum ether fractions followed by fractionation of the liquid residue gave 2.6 g of tri-*n*-propylchlorogermane having a b.p. 73–76° (3.0 mm), n_D^{27} 1.4598 [Lit. value¹²: b.p. 227° (760 mm), n_D^{20} 1.4641].

Concentration of the diethyl ether fractions gave a liquid residue which on distillation gave 1.5 g of cyclohexene chlorohydrin having b.p. 63–64° (4.5 mm), n_D^{26} 1.4891. (Found: Cl, 26.81. $C_6H_{11}ClO$ calcd.: Cl, 26.40%.)

Determination of the cis-trans ratio

The *cis/trans* ratio for the cyclohexene chlorohydrins was determined by titration with standard alkali according to the method developed by Bartlett⁵.

The *cis/trans* ratio for the cyclohexene bromohydrins was determined by titration with standard alkali and by vapor phase chromatography using a silica gel column. The areas under the curves were cut out and the ratio determined by weighing. The peak for the *trans*-isomer was established using the pure material prepared by the method of Dalton¹³. The results are summarized in Table 1.

Preparation of triphenyl(2-bromocyclohexyloxy)germane

In a 100 ml round bottom flask 2.1 g (0.0068 moles) of triphenylgermanium bromide allowed to react with an equimolar amount of cyclohexene oxide in 50 ml of "carbitol" in the presence of 0.2 g of magnesium bromide. The mixture was refluxed for 48 h under a nitrogen atmosphere. The resulting material was then concentrated under reduced pressure (20 mm) at 80°. The liquid residue yielded a small amount of white (0.2 g) crystals which were recrystallized from petroleum ether having m.p. 179–180°. (Found: Ge, 15.49. C₂₄H₂₅BrGeO calcd.: Ge, 15.06 %)

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