sure with a rotary film evaporator to yield 48.0 g (0.142 mole) of crude D-(+)-*sec*-butylmercuric bromide (**9**). This was dissolved in 300 ml of absolute ethanol preheated to 50°, treated with 5.5 ml of water, stirred, and cooled slowly. When the temperature reached 40°, the mixture was seeded. D-(+)-*sec*-Butylmercuric bromide, mp 42–44° (lit.[67] (racemic) mp 39°, lit.[41] (optically pure) mp 44.0–44.8°), was recovered in a yield of 44.4 g (0.132 mole) and had $[\alpha]^{22}D$ +9.12 ± 0.40° (*c* 5, ethanol).

D-(+)-*sec*-Butyl-(+)-*sec*-butylmercury (10). An ether solution of *sec*-butylmagnesium bromide, prepared from magnesium turnings (3.78 g, 0.156 g-atom), *sec*-butyl bromide (21.3 g, 0.156 mole), and 125 ml of anhydrous ether, was filtered and added (1 hr, nitrogen atmosphere) to D-(+)-*sec*-butyl mercuric bromide (21.0 g, 0.0622 mole, $[\alpha]^{22}D$ +9.12 ± 0.40°) dissolved in 150 ml of anhydrous ether. The product was worked-up in the usual manner to yield a residue which was vacuum distilled to give D-(+)-*sec*-butyl-(±)-*sec*-butylmercury (**10**, 18.1 g, 0.0575 mole, 92% yield) with $[\alpha]^{22}D$ +6.29 ± 0.35° (*c* ~5, ethanol).

Generation of Dichlorocarbene in the Presence of D-(±)-*sec*-Butyl-(±)-*sec*-butylmercury (10). Ethyl trichloroacetate (19.1 g, 0.10 mole) in 15 ml of pentane was added to the previously prepared D-(+)-*sec*-butyl-(±)-*sec*-butylmercury (15.7 g, 0.0499 mole), sodium methoxide (10.8 g, 0.20 mole), and 40 ml of pentane. The usual work-up and removal of low-boiling material *in vacuo* gave 15.9 g of crude active *sec*-butyl-α,α-dichloro-β-methylbutylmercury (**11**).

Bromine Cleavage of Active *sec*-Butyl-α,α-dichloro-β-methylbutylmercury (11). The crude insertion product was dissolved in 45 ml of carbon tetrachloride and was treated with bromine (16.0 g, 0.10 mole) dissolved in 8 ml of carbon tetrachloride as described previously. Work-up gave a light yellow liquid which upon vacuum distillation (43° (2 mm)) yielded 6.10 g (0.0278 mole) of L-(−)-1-bromo-1,1-dichloro-2-methylbutane (**12**) with $[\alpha]^{27}D$ −2.92 ± 0.08° (*c* 25, ethanol). The yield was 56% of the theoretical amount based on **10**.

Hydrolysis of L-(−)-1-Bromo-1,1-dichloro-2-methylbutane (12) with Silver Nitrate in Aqueous Acetone. Silver nitrate (9.7 g, 0.057 mole) dissolved in 14 ml of water was added to L-(−)-1-bromo-1,1-dichloro-2-methylbutane (5.0 g, 0.023 mole) dissolved in 28 ml of acetone plus 4 ml of water and the mixture was stirred at room temperature for 2 hr. The silver halide was removed by filtration and washed with ether, and the ether was combined with the filtrate. This mixture was stirred at reflux for 3 hr, allowed to cool, and treated with 6 *N* hydrochloric acid until the excess silver ion was precipitated as the halide; the mixture had pH 2. The organic solvents were removed with a rotary film evaporator and the residue was made basic (pH 10) with 5% sodium hydroxide, extracted with ether (discarded), and reacidified to pH 2 with 6 *N* hydrochloric acid. The product isolated from an ether extract in the usual manner was distilled to yield L-(+)-α-methylbutyric acid (0.76 g, 0.0075 mole, 33% yield), bp 172–173° (lit.[68] bp 173–174°), with $[\alpha]^{25}D$ +2.96 ± 0.06° (*c* 34, ethanol). The nmr spectrum is consistent with the structure.

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[67] C. S. Marvel and H. O. Calvery, *J. Am. Chem. Soc.*, **45**, 821 (1923).

[68] O. Schütz and W. Marckwald, *Chem. Ber.*, **29**, 52 (1896).

The Thermal Decomposition of α,α-Dihalodialkylmercury Compounds[1]

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Contribution from the Department of Chemistry of the University of Kansas, Lawrence, Kansas. *Received November 27, 1965*

Abstract: When thermally decomposed, compounds of the α,α-dichlorodialkylmercury type **1** produce a 1:1 molar ratio of a 1-chloro-1-alkene **2** and the alkylmercuric chloride **3**. Both the *cis* and *trans* isomers of **2** are formed in approximately the thermodynamic ratio. Evidence for the intermediacy of a carbene during the decomposition is presented. Iodine-catalyzed equilibrations of 1-chloro-1-butene and 1-chloro-2-methyl-1-butene are reported.

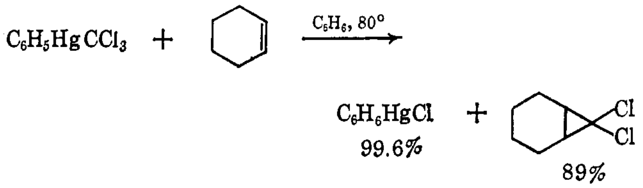
In view of the finding that the thermal decomposition of certain organosilicon compounds results in olefins from an α-elimination process[2] and that the decomposition of trichloromethyltrichlorosilane

$$CHFClCF_2SiCl_3 \xrightarrow[\Delta]{} CHF{=}CFCl + SiFCl_3$$

$$CFCl_2CF_2SiCl_3 \xrightarrow[\Delta]{} CFCl{=}CFCl + SiFCl_3$$

in the presence of cyclohexene gave a 60% yield of 7,7-dichloronorcarane, Haszeldine has suggested that α elimination from α-haloalkylmetallo compounds may be a general reaction.[3] Difluorocarbene had previously been postulated as an intermediate to explain the quantitative formation of perfluorocyclopropane during the pyrolysis of trimethyltrifluoromethyltin in the presence of tetrafluoroethylene.[4] Various other reported decompositions of organometallic derivatives to olefinic[5–7] and cyclopropyl[8] products can be readily interpreted in terms of the intervention of a carbene intermediate.[9]

More recently Seyferth and co-workers[10] have shown that phenyltrihalomethylmercury decomposes readily at temperatures as low as 80° by an apparent α elimina-



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[1] Taken from the Ph.D. dissertation of R. D. Mathis, University of Kansas, 1965. Support of this work by a grant from the National Science Foundation (GB 3519) is gratefully acknowledged.

[2] R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 394 (1959).

[3] W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.* (London), 789 (1961).

[4] H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

[5] R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952).

[6] W. T. Miller, Jr., A. H. Fainberg, and E. Bergman, *J. Am. Chem. Soc.*, **79**, 4159 (1957).

[7] P. B. Ayscough and H. J. Emeléus, *J. Chem. Soc.*, 3381 (1954).

[8] H. Hoberg, *Ann.*, **656**, 1 (1962).

[9] This interpretation of these reactions is not unique and in several instances[5–7] did not represent the preferred interpretation of the authors.

[10] 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. Am. Chem. Soc.*, **87**, 4259 (1965), and references cited therein.

tion to the dihalocarbene. Similar results have been obtained for trichloromethylmercuric chloride and bis(trichloromethyl)mercury.[11]

Thermal Decompositions

In the present study, α,α-dichloroorganomercurial (**1**), which had been obtained by the insertion of dichlorocarbene into the carbon–mercury bond of the corresponding dialkylmercury compound,[12] was thermally

$$\underset{\mathbf{1}}{RR'CHCCl_2HgCHRR'} \xrightarrow[\Delta]{} \underset{\mathbf{2}}{RR'C{=}CHCl} + \underset{\mathbf{3}}{RR'CHHgCl}$$

a, $R = R' = CH_3$
b, $R = C_2H_5; R' = H$
c, $R = n\text{-}C_3H_7; R' = H$
d, $R = C_2H_5; R' = CH_3$

decomposed to a mixture of vinyl chloride **2** and alkylmercuric chloride **3**. Although very slow decomposition did occur at room temperature, the rate of decomposition was appreciable only at temperatures above 90°. As a general procedure the insertion product **1** was pyrolyzed neat and the volatile vinyl chloride was collected in an iced receiver. The alkylmercuric chloride was obtained pure by extraction of the distillation residue and crystallization from ethanol.

The thermal decomposition of isopropyl-α,α-dichloroisobutylmercury (**1a**) at 100–120° gave isopropylmercuric chloride (**3a**) and 1-chloro-2-methyl-1-propene (**2a**) as the sole products and in a molar ratio of 1.00:1.09, respectively. Identification of **2a** was

$$\underset{\mathbf{1a}}{(CH_3)_2CHCCl_2HgCH(CH_3)_2} \xrightarrow{100\text{–}120°} \underset{\mathbf{2a}}{(CH_3)_2C{=}CHCl} + \underset{\mathbf{3a}}{(CH_3)_2CHHgCl}$$

(mole ratio 1.09:1.00)

confirmed by comparison of the nmr spectrum with that published for the authentic material.[13]

The decomposition (120–140°) of *n*-propyl-α,α-dichloro-*n*-butylmercury (**1b**), the product of dichlorocarbene insertion into the carbon–mercury bond of di-*n*-propylmercury,[14] gave *n*-propylmercuric chloride (**3b**) and a mixture of *cis*- and *trans*-1-chloro-1-butene (**2b**) in a ratio of 4.13 (Table I). Isomer identification was made by direct comparison with authentic samples prepared by dehydrohalogenation of 1,1-dichlorobutane to a mixture of *cis*-**2b** (lit.[15] bp 63.4–63.6°) and *trans*-**2b** (lit.[15] bp 68.0–68.2°) which was separated by a combination of fractional distillation and preparative vapor phase chromatography (see the Experimental Section). The original stereochemical assignments, based on the assumption that the rate of dehydrohalogenation from *cis*-**2b** should exceed that from *trans*-**2b** (observed $k_{cis\text{-}\mathbf{2b}}/k_{trans\text{-}\mathbf{2b}} = 2.9$[15]), was confirmed from the infrared spectra. Both spectra were very similar with the exception of a strong absorption at 893 cm^{-1} for *cis*-**2b** which shifted to 931 cm^{-1} in the *trans* isomer consistent with the observation by Kitson[16] that seven compounds of the *trans*-1-cyano- and *trans*-1-halo-1-alkene type had a strong absorption at 931 ± 30 cm^{-1} associated with an ethylenic, carbon–hydrogen, out-of-plane bending vibration. Further confirmation of the structures was made by means of the nmr spectra (*vide infra*).

Table I. Isomer Distribution for Vinyl Chlorides Resulting from the Thermal Decomposition of α,α-Dihalodialkymercury Compounds

	Thermal product		Thermodynamic	
Starting compd	% *cis*	% *trans*[a]	% *cis*	% *trans*[a–c]
1b	80.5	19.5 (120–140°)	71	29 (100°)
			65	35 (45°)
1c	77.2	22.8[d]	...	...
1d	39.2	60.8[d,e]	34	66 (100°)[e]

[a] Values were determined by direct comparison of integrated areas on a vapor phase chromatogram. [b] Equilibrations were done by ultraviolet irradiation of samples in sealed tubes together with an iodine catalyst. [c] Duplication of equilibrations from different starting mixtures gave an average deviation of ≤2 for the percentage values. [d] Decompositions were carried out on a small scale with an infrared heat source. The temperature can be estimated as 100–150°. [e] See ref 19.

The thermal decomposition of *n*-butyl-α,α-dichloro-*n*-amylmercury (**1c**)[17] produced *n*-butylmercuric chloride (**3c**) and a mixture of *cis*- and *trans*-1-chloro-1-pentene (**2c**) in a ratio of 3.39 (Table I). Stereochemical assignments were based on the assumption that the relative vpc retention times for *cis*- and *trans*-1-chloro-1-pentene would be the same under a given set of conditions as for *cis*- and *trans*-1-chloro-1-butene, for which it was established that the *cis* isomer had the shorter retention time (see the Experimental Section).

The decomposition of *sec*-butyl-α,α-dichloro-β-methylbutylmercury (**1d**), the product of dichlorocarbene insertion into the carbon–mercury bond of di-*sec*-butylmercury, gave *sec*-butylmercuric chloride (**3d**) and a mixture of *cis*- and *trans*-1-chloro-2-methyl-1-butene[19] in a ratio of 0.645 (Table I). Stereochemical assignments, unlike those for the previous vinyl chloride isomer mixtures, were made on the basis of the nmr spectra for the pure isomers, which were synthesized by dehydrohalogenation of 1,1-dichloro-2-methylbutane.[20] The isomer mixture was separated by a combination of fractional distillation and preparative vapor phase chromatography. Pertinent chemical shift values for the stereochemical assignments are listed in Table II. Note that for the isomers of vinyl chloride **2b**, the allylic methylene group *cis* to the chlorine is 0.19 ppm downfield compared with the same group in the *trans* orienta-

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[11] T. J. Logan, *J. Org. Chem.*, **28**, 1129 (1963).

[12] J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **88**, 3545 (1966).

[13] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 67.

[14] The starting material used for the thermal decomposition was a mixture of **1b** and *n*-propyl-γ,γ-dichloro-β-methylpropylmercury, the product resulting from a dichlorocarbene insertion into the β-carbon–hydrogen bond of di-*n*-propylmercury.[12] The observed decomposition products, **2b** and **3b**, were only structurally consistent with the decomposition of **1b** in agreement with the observations made for the thermal decomposition of compounds with structure **1** which were not contaminated with the corresponding β-carbon–hydrogen insertion products.

[15] L. Navez, *Bull. Soc. Chim. Belges*, **39**, 435 (1930).

[16] R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

[17] The starting material is known to be a mixture of **1c** and *n*-butyl-β-(dichloromethyl)butylmercury,[18] the product of β-carbon–hydrogen insertion by dichlorocarbene into di-*n*-butylmercury, but the thermal decomposition products are only consistent with the decomposition of **1c**. See ref 14.

[18] Unpublished results of J. A. Landgrebe and D. Thurman.

[19] The terms *cis* and *trans* used in reference to vinyl chloride **2d** refer to the chlorine atom being *cis* or *trans* to the ethyl group.

[20] Product vinyl chlorides **2d** were compared with the synthesized isomers by means of vpc retention times (see the Experimental Section).

tion.[21] A similar shift of 0.12 ppm for the allylic methylene groups of the **2d** isomers allowed the assignment of the *cis* and *trans* stereochemistry. For the two cases in which the chemical shift difference for an allylic methyl group *cis* or *trans* to the chlorine was measured (**2a** and **2d**) the differences were only 0.00 and 0.04 ppm (*cis*-methyl deshielded), respectively. The close correspondence of the observed product distribution for the isomers of **2d** with the thermodynamically equilibrated isomers (Table I) provided further confirmation for the stereochemical assignments (*vide infra*).

Table II. 60-Mc/sec Chemical Shift Values for the Allylic Methylene or Methyl Groups of 1-Chloro-1-alkenes

Compd	Chemical shift, τ		Orientation to Cl
	Methyl	Methylene	
2a	8.23	...	*cis* and *trans*
2b	...	7.76	*cis*
	...	7.95	*trans*
2d	8.19	7.70	*cis*
	8.23	7.82	*trans*

Thermodynamic Equilibrations

The observation that the *cis* isomer was the predominant vinyl chloride formed upon thermal decomposition of **1b** and **1c** is in accord with the known thermodynamic stability of simple 1-halo-1-alkenes. Harwell and Hatch[24] reported the equilibrium mixture for 1-bromopropene to be 68% *cis* and 32% *trans*. Predominance of the *cis* isomer at equilibrium has also been reported qualitatively for 1-iodopropene,[25] and Crump[26] has found that equilibration of 1-chloropropene with bromine in sunlight gave 76% of the *cis* isomer and 24% of the *trans* isomer.

Although the greater stability of *cis*-1-chloropropene (relative to the *trans* isomer) has been rationalized in terms of the electronic interaction of permanent dipoles,[26] the observation by Harwell and Hatch[24] that the equilibrium value for 1-bromopropene remained unchanged from 40 to 100°, and our finding that the equilibrium ratio for 1-chloro-1-butene shifted in favor of the *cis* isomer as the temperature was increased, together with the fact that for 1-chloro-2-methyl-1-butene the *trans* isomer[19] is favored (100°) (*vide infra*), clearly indicates the inadequacy of a simple dipole-interaction theory.[27]

In order to verify that vinyl chloride (**2**) resulting from the thermal decomposition was actually being produced in a thermodynamically controlled isomer distribution, equilibrations of both 1-chloro-1-butene (**2b**) and 1-chloro-2-methyl-1-butene (**2d**) were carried out. The equilibration of three different mixtures of *cis*- and *trans*-1-chloro-1-butene with iodine[28] at 45° under the influence of ultraviolet light[31] gave a mixture which contained 65% of the *cis* isomer and 35% of the *trans* isomer. At 100° the equilibrium was 71% *cis* and 29% *trans*, values which are approaching the observed 80.5% *cis*- and 19.5% *trans*-1-chloro-1-butene obtained from the thermal decomposition of **1b** at 120–140° (Table I). Similar thermodynamic equilibration of 1-chloro-2-methyl-1-butene (**2d**) at 100° gave a mixture which contained 34% of the *cis* isomer and 66% of the *trans* isomer, values which compare favorably with the 39.2% *cis*-**2d** and 60.8% *trans*-**2d** obtained from the thermal decomposition of **1d**.

The small differences in the *cis*:*trans* ratios which were observed between the decomposition mixtures and the equilibrated mixtures[31] might be the result of a small degree of stereospecificity in the thermal decomposition step, or might be due to a difference in the equilibrium constants for the interconversion of the vinyl–iodine complexes (if such are formed[28]) and the vinyl compounds alone.[32]

Mechanistic Considerations

Because of the several reports that α-haloorganometallic compounds break down thermally to form intermediates which exhibit the behavior of carbenes,[3,10] it is reasonable to consider a carbene as a possible intermediate during the thermal cleavage of organomercurial **1**. Consistent with this view is the fact that

$$\mathbf{1} \xrightarrow[\Delta]{} \mathbf{3} + \underset{\mathbf{4}}{\mathrm{RR'CH\ddot{C}Cl}} \xrightarrow{\mathrm{H}\sim} \mathbf{2}$$

the product vinyl chlorides are formed in an isomer distribution which lies close to the thermodynamic ratio in general agreement with the observations by Kirmse[33] that the reactions of 1,1-dichloropropane with methyllithium and of chloroform with ethyllithium gave 1-chloro-1-propene in a *cis*:*trans* ratio of *ca.* 9:1.[34] It was postulated that the vinyl halide was the result of a hydrogen migration in an intermediate ethylchlorocarbene. If carbene **4** were an intermediate, hydrogen migration, a reaction for which there is ample precedent,[36] should be preferred.

In an effort to obtain further evidence for the intermediacy of a carbene, isopropyl-α,α-dichloroisobutyl-

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[21] Spatial deshielding effects by chlorine (and other halogens) have been previously reported.[22,23]

[22] E. R. Malinowski, M. S. Manhas, G. H. Muller, and A. K. Bose, *Tetrahedron Letters*, 1161 (1963).

[23] E. W. Warnoff, *J. Org. Chem.*, **28**, 887 (1963).

[24] K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).

[25] H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

[26] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963).

[27] An adequate explanation for the increasing *cis* to *trans* ratio for **2b** with increasing temperature must include an important entropy factor.

[28] Iodine has been used as a catalyst for the *cis–trans* isomerization of cinnamic acid,[29a–c] stilbene,[29d] diiodoethylene,[29e] and dichloroethylene,[29f] among others. Muizebelt and Nivard[30] investigated iodine-catalyzed isomerizations in an attempt to determine whether an ethylene–iodine complex or a covalently bonded radical was the intermediate. The structure of the intermediate remains controversial.

[29] (a) C. Liebermann, *Chem. Ber.*, **23**, 512 (1890); (b) A. Berthoud and Ch. Urech, *J. Chim. Phys.*, **27**, 291 (1930); (c) R. G. Dickinson and H. Lotzkar, *J. Am. Chem. Soc.*, **59**, 472 (1937); (d) S. Yamashita, *Bull. Chem. Soc. Japan*, **34**, 487 (1961); (e) R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Am. Chem. Soc.*, 67, 1319 (1945); (f) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

[30] W. J. Muizebelt and R. J. F. Nivard. *Chem. Commun.*, 148 (1965).

[31] The possibility exists that the use of ultraviolet could result in a photostationary state rather than an equilibrium.

[32] Although isomer ratios are not necessarily being compared at identical temperatures, the data from Table I seem to indicate that the isomer mixtures do not change more than *ca.* 6% over a range of 55°.

[33] W. Kirmse and V. Bulöw, *Chem. Ber.*, **96**, 3316 (1963).

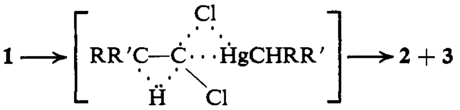
[34] In view of the possible complexation effects between lithium salts and carbenes,[35] one might not expect exact agreement between the 9:1 (*cis*/*trans*) value of Kirmse[33] and the *ca.* 4:1 (*cis*/*trans*) value obtained for the product mixture from decomposition of **1b** and **1c** in the present work.

[35] G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965), and references cited therein.

[36] L. Friedman and H. Schechter, *ibid.*, **83**, 3159 (1961).

mercury (**1a**) was thermally decomposed in the presence of cyclohexene and 2,3-dimethyl-2-butene, but in neither case could the presence of a cyclopropyl derivative be detected, a result which was not unexpected in view of the well-known tendency of alkylcarbenes to undergo predominantly intramolecular reactions;[37] for this reason alkylcarbene additions to double bonds are rarely found.[38,39]

In view of the doubt which exists concerning the nature of the intermediate in the decomposition of organomercurial **1**, a concerted formation of the observed products cannot be completely eliminated.



Experimental Section[40]

Thermal Decomposition of Isopropyl-α,α-dichloroisobutylmercury (1a). Isopropyl-α,α-dichloroisobutylmercury (**1a**) (1.36 g, 0.00368 mole), prepared and isolated as previously described,[12] was heated for 1 hr at 100–120° in a small distillation apparatus equipped with a Dry Ice–isopropyl alcohol cooled trap. The distillate, which showed only one component by vpc analysis (8-ft, diisodecyl phthalate column, 45°), gave a positive Beilstein test for halogen, a positive test for unsaturation (potassium permanganate in acetone), a negative test with sodium iodide in acetone, and a negative test with alcoholic silver nitrate. The structure, 1-chloro-2-methyl-1-propene, was assigned on the basis of the above evidence, the capillary boiling point of 64.5° (lit.[41] bp 65–68°), and the identity of the nmr spectrum to that published for an authentic sample.

The residue in the distillation flask was extracted with 1 *M* sodium thiosulfate solution which was then treated with 1 *M* potassium iodide to give isopropylmercuric iodide (0.857 g, 0.00231 mole). Residue from a second reaction was extracted with ethanol and the resulting isopropylmercuric chloride after two recrystallizations from ethanol gave mp 94–95° (lit.[42] mp 97°) and an nmr spectrum consistent with the assumed structure.

Thermal Decomposition of *n*-Propyl-α,α-dichloro-*n*-butylmercury (1b). A mixture of *n*-propyl-α,α-dichloro-*n*-butylmercury (**1b**) and *n*-propyl-γ,γ-dichloro-β-methylpropylmercury (total 1.90 g, 0.0050 mole), obtained from the generation of dichlorocarbene in the presence of di-*n*-propylmercury as previously described,[12] was heated to 120–140° in a distillation apparatus equipped with a receiver immersed in an ice bath. The distillate gave a positive test for unsaturation (potassium permanganate in acetone) and a positive Beilstein test for halogen. The nmr spectrum shows a triplet at 8.98 (J = 7.5 cps, area 3), a complicated multiplet at *ca.* 7.8 (area 2), and a complicated multiplet at *ca.* 4.2 (area 2). Careful vpc analysis (8-ft, Carbowax 20-M column, 64°) showed two components in the relative amounts 80.5 and 19.5% (area per cent in order of increasing retention times) which were assigned as *cis*- and *trans*-1-chloro-1-butene (**2b**), respectively. The structures were confirmed by a direct vpc comparison with the authentic isomers (*vide infra*).

Extraction of the distillation residue with ethanol and recrystallization from cold ethanol yielded *n*-propylmercuric chloride, mp 136° (lit.[43] mp 140°).

Apparently the *n*-propyl-γ,γ-dichloro-β-methylpropylmercury is stable at 140°, for no other decomposition products were observed.

***cis*- and *trans*-1-Chloro-1-butene (2b).** The procedure of Henne, Renoll, and Leicester[44] was modified for the preparation of 1,1-dichlorobutane. *n*-Butyraldehyde (200.0 g, 2.77 moles, Eastman Kodak) was added dropwise with stirring to phosphorus pentachloride (416.5 g, 2.0 moles, Baker) at 0°. The mixture was stirred for 12 hr at room temperature, hydrolyzed with 500 ml of water, maintained at reflux for several hours, and cooled. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and distilled on a 10-in. Vigreux column to give 1,1-dichlorobutane (104.7 g, 0.823 mole, 30% yield), bp 112° (lit.[45] bp 113.8–113.9°).

The product of the above reaction together with potassium hydroxide (53.2 g, 0.95 mole) in 400 ml of *n*-butyl alcohol was heated at *ca.* 100° and the 1-chloro-1-butene mixture which formed was collected in a receiver cooled to 0°. The crude distillate was dried and distilled on a 3-ft wire spiral column at a reflux ratio of 7:1 to give four fractions analyzed by vpc (8-ft, Carbowax 20-M column, 60°) as indicated in Table III. The assignment of *cis* and *trans* isomers was based on nmr and infrared data (see Discussion) in addition to a comparison with reported boiling points: *cis*-1-chloro-1-butene (lit.[15] bp 63.4–63.6°), *trans*-1-chloro-1-butene (lit.[15] bp 68.0–68.2°).

Table III

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Bp, °C	60–63	63–64	64–67	67–68
cis-**2b**, %	85	72	58	28
trans-**2b**, %	12	28	42	72
Unknown compd, %	3			

Samples of pure *cis*-**2b** and *trans*-**2b** were collected with an Autoprep (20-ft, Carbowax 20-M column, 105°). A strong infrared absorption at 931 cm^{-1} (carbon tetrachloride) was found for the *trans* isomer, but was absent in the spectrum of the *cis* isomer.[16] The nmr spectrum of the *cis* isomer shows a triplet at 8.98 (J = 7.5 cps, area 3), a quintet at 7.76 (J = 7.5 cps, area 2) which shows fine splitting on each of the peaks, and a multiplet of six to nine peaks at *ca.* 4.2 (area 2). The nmr spectrum of the *trans* isomer shows a triplet at 8.98 (J = 7.5 cps, area 3), a very complicated multiplet centered at 7.95 (area 2), and a multiplet at 4.13 (area 2) which appears to be a large singlet superimposed on a small multiplet.

Thermal Decomposition of *n*-Butyl-α,α-dichloro-*n*-amylmercury (1c). A portion of crude di-*n*-butylmercury insertion product, prepared as previously described,[12] was placed in a small distillation apparatus and heated with an infrared bulb. A low-boiling liquid, previously identified as 1-chloro-1-pentene (see the Experimental Section in ref 12), was collected in the cooled receiver and was shown by vpc analysis (8-ft, Carbowax 20-M column, 85°) to be a mixture of the *cis* and *trans* isomers in the relative amounts 77.2 and 22.8%, respectively (order of increasing retention time; see Discussion).

The distillation residue was extracted with ethanol and the crude solid obtained was recrystallized from cold ethanol to give *n*-butylmercuric chloride, mp 124° (lit.[46] mp 125.5°).

Thermal Decomposition of *sec*-Butyl-α,α-dichloro-β-methylbutylmercury (1d). *sec*-Butyl-α,α-dichloro-β-methylbutylmercury (1.67 g, 0.00419 mole) was thermally decomposed with an infrared lamp in the same manner as was **1c**. The liquid distillate (0.253 g) gave a positive test for unsaturation (potassium permanganate in acetone) and was identified as 1-chloro-2-methyl-1-butene, capillary bp 97° (lit.[47] bp 96–97°). Both *cis* and *trans*[19] isomers were present in the relative amounts 39.2 and 60.8%, respectively (order of increasing retention time), as determined by vpc analysis (8-ft, Carbowax 20-M column, 70°). The structural assignment was confirmed by spectral and vpc comparisons with authentic samples

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[40] All capillary melting and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-8 double-grating spectrophotometer. All nmr spectra were measured on a Varian A-60 spectrometer and chemical shifts are expressed in parts per million relative to an internal tetramethylsilane standard (τ scale). Microanalyses were carried out by Weiler and Strauss, Oxford, England, or by Huffman Laboratories, Wheatridge, Colo. A description of vapor phase chromatographic apparatus and columns can be found in ref 12.

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of the isomers, *vide infra*. Confirmation of the stereochemical assignment was based on the nmr spectra (see Discussion).

The distillation residue was extracted with ethanol and the resulting material was crystallized from cold ethanol to give *sec*-butylmercuric chloride, mp 28.5–29.0° (lit.[48] mp 30.5°).

cis- **and** *trans*-**1-Chloro-2-methyl-1-butene (2d).** The procedure of Henne, Renoll, and Leicester[44] was modified for the preparation of 1,1-dichloro-2-methylbutane. The modification was that previously described for the preparation of 1,1-dichlorobutane, the intermediate used in the synthesis of vinyl chlorides *cis*-**2b** and *trans*-**2b** (*vide supra*).

1,1-Dichloro-2-methylbutane (55.3 g, 0.392 mole) and potassium hydroxide (30.0 g, 0.536 mole) dissolved in 200 ml of cyclohexanol, 100 ml of ethylene glycol, and 5 ml of water were maintained at 140°, and the distillate from the reaction mixture was collected in a receiver at 0° and dried over anhydrous magnesium sulfate to give 1-chloro-2-methyl-1-butene (31.8 g, 0.304 mole, 78% yield). A vpc analysis of the product (8-ft, Carbowax 20-M column, 70°) indicated the presence of the *cis* and *trans* isomers in the relative amounts of 38.7 and 61.3%, respectively (see Discussion).

Fractional distillation of the above isomer mixture on a 3-ft wire spiral column at 100:1 reflux ratio followed by vpc analysis gave the results tabulated in Table IV. Pure samples of the isomers were collected on an Autoprep (20-ft, Carbowax 20-M column, 110°) for infrared and nmr analysis.

Table IV

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Bp, °C	93–94	94–95	95–96	96–97
cis-**2d**, %	50	43	31	18
trans-**2d**, %	50	57	69	82

The infrared spectra of the two isomers are quite similar and show the expected bands at 3095 and 1639 cm^{-1}. The major difference is the shift in frequency of a strong absorption in the 800–850-cm^{-1} region. In the *cis* isomer (carbon tetrachloride) this absorption is at 842 cm^{-1}, whereas in the *trans* isomer it appears at 829 cm^{-1}, and there is an additional small unresolved band on the high wavelength side of this major absorption.

The nmr spectra of the two isomers are similar with the exception of the chemical shift observed for the methylene group. In the spectrum of the *cis* isomer, the methylene group appears as a quartet at 7.70 (J = 7.5 cps), whereas in the *trans* isomer the methylene quartet appears at 7.82 (J = 7.5 cps). This distinction was used to make the stereochemical assignments (see Discussion).

Thermal Decomposition of Isopropyl-α,α-dichloroisobutylmercury (1a) in the Presence of Cyclohexene. A mixture of crude isopropyl-α,α-dichloroisobutylmercury (18.7 g) and cyclohexene (62.3 g) was maintained at reflux for 4 days, cooled, and extracted with 1 *M* sodium thiosulfate solution. Addition of 1 *M* potassium iodide to the extract precipitated isopropylmercuric iodide (12.9 g, 0.0344 mole).

The remaining organic material was distilled to give, in addition to cyclohexene and 1-chloro-2-methyl-1-propene, a small amount of diisopropylmercury as the only high-boiling material. The latter obviously resulted from an incomplete separation of the insertion product from unchanged starting material in the work-up of the carbene insertion reaction. Nuclear magnetic resonance spectrometry gave no evidence for the presence of 7-chloro-7-isopropylnorcarane, the expected cyclohexene–chloroisopropylcarbene adduct.

Thermal Decomposition of Isopropyl-α,α-dichloroisobutylmercury (1a) in the Presence of 2,3-Dimethyl-2-butene. Isopropyl-α,α-dichloroisobutylmercury (2.25 g, 0.00610 mole) and 2,3-dimethyl-2-butene (5.13 g, 0.0610 mole) were sealed in a 20-cm × 13 mm i.d. Pyrex combustion tube and maintained at 90–100° for 1 week in an oil bath. The tube and contents were allowed to cool to room temperature, the tube was opened, and the mixture was filtered to give 1.42 g (0.00510 mole) of isopropylmercuric chloride, which was found to be only slightly soluble in 2,3-dimethyl-2-butene. The remaining organic filtrate was concentrated to 3–4 ml by evaporation at room temperature of the low-boiling 1-chloro-2-methyl-1-propene and 2,3-dimethyl-2-butene, extracted with 1 *M* sodium thiosulfate, and then allowed to evaporate nearly to dryness. The small amount of yellow oil which remained was dissolved in carbon tetrachloride and an nmr spectrum was taken. No evidence for the presence of 1,1,2,2-tetramethyl-3-chloro-3-isopropylcyclopropane was obtained.

Thermodynamic Equilibration of *cis*- **and** *trans*-**1-Chloro-1-butene (2b).** A mixture of 72% *cis*- and 28% *trans*-1-chloro-1-butene (0.150 g, 0.00166 mole), alkene-free pentane (0.472 g, 0.00640 mole), and one crystal of iodine was sealed in a 10-cm × 8 mm i.d. Pyrex tube and illuminated at 45° for 10 days with a G.E. 275-w sunlamp. At the end of this time vpc analysis (10-ft, Carbowax 20-M column, 60°) indicated the mixture to be 65% *cis*- and 35% *trans*-1-chloro-1-butene.

Similarly, a mixture of 58% *cis*- and 42% *trans*-1-chloro-1-butene (0.150 g, 0.00166 mole), alkene-free pentane (0.472 g, 0.00654 mole), and one crystal of iodine after illumination at 45° for 10 days contained 65% *cis*- and 35% *trans*-1-chloro-1-butene.

In like manner, a mixture of 28% *cis*- and 72% *trans*-1-chloro-1-butene (0.166 g, 0.00183 mole), alkene-free pentane (0.453 g, 0.00628 mole), and one crystal of iodine after illumination at 45° for 10 days contained 65% *cis*- and 35% *trans*-1-chloro-1-butene.

A mixture of 72% *cis*- and 28% *trans*-1-chloro-1-butene (0.183 g, 0.00202 mole), alkene-free pentane (0.375 g, 0.00520 mole), and one crystal of iodine after illumination at 100° for 10 days contained 69% *cis*- and 31% *trans*-1-chloro-1-butene.

A mixture of 28% *cis*- and 72% *trans*-1-chloro-1-butene (0.180 g, 0.00199 mole), alkene-free pentane (0.385 g, 0.00534 mole), and one crystal of iodine after illumination at 100° for 10 days contained 73% *cis*- and 27% *trans*-1-chloro-1-butene.

Thermodynamic Equilibration of *cis*- **and** *trans*-**1-Chloro-2-methyl-1-butene (2d).** A mixture of 31% *cis*- and 69% *trans*-1-chloro-2-methyl-1-butene (0.183 g, 0.00175 mole), alkene-free pentane (0.374 g, 0.00520 mole), and one crystal of iodine was sealed in a 10 cm × 8 mm i.d. Pyrex tube and illuminated at 100° for 10 days with a G.E. 275-w sunlamp. At the end of this time vpc analysis (10-ft, Carbowax 20-M column, 70°) indicated the mixture to be 34% *cis*- and 66% *trans*-1-chloro-2-methyl-1-butene.

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