The Insertion of Dichlorocarbene into the Carbon–Mercury Bond. Products and Stereochemistry[1,2]

John A. Landgrebe and Ronald D. Mathis

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

Abstract: Symmetrical dialkylmercury compound **1** ($R = R' = H$; $R = R' = CH_3$; $R = C_2H_5, R' = H$; $R = n\text{-}C_3H_7, R' = H$; $R = CH_3, R' = C_2H_5$) subjected to treatment with ethyl trichloroacetate and excess sodium methoxide in pentane at 0° produced organomercurial **2** (35–60% yield) characteristic of dichlorocarbene insertion into the carbon–mercury bond. Dichlorocarbene attack on di-*n*-propylmercury was shown to produce an equal amount of insertion in the carbon–mercury bond and the β-carbon–hydrogen bond. Structure determinations were based upon nmr spectral data and chemical degradation studies. The insertion of dichlorocarbene into active di-*sec*-butylmercury, $[\alpha]_D$ +6.29°, produced **11** which was degraded to α-methylbutyric acid with $[\alpha]_D$ +2.96°, a result which corresponds to 101 ± 6% retention of configuration. Mechanistic implications are discussed.

In spite of the large amount of data published on the mechanistic and synthetic aspects of reactions of dichlorocarbene[3] little is known about its insertion into single bonds. Fields[4] observed that the thermal decomposition of sodium trichloroacetate in the presence of cumene resulted in the formation of β,β-dichloro-*t*-butylbenzene in 35% yield. Similar benzylic carbon–hydrogen bond insertions were noted with ethylbenzene, *p*-diisopropylbenzene, tetralin, and diphenylmethane, but in general, yields dropped severely if the dichlorocarbene was produced from sodium methoxide and ethyl trichloroacetate at 0°. The thermal decomposition of phenyl(bromodichloromethyl)mercury in cumene[5] and the pyrolysis of chloroform in the presence of cyclohexene[6] have also been observed to produce carbon–hydrogen insertion products.

Several other instances of carbon–hydrogen bond and carbon–sulfur bond insertion by dichlorocarbene have been studied in systems in which an oxygen or sulfur atom is located either adjacent to or conjugated with the position of insertion.[7,8] Some of these reactions as well as several examples of nitrogen–hydrogen and carbon–nitrogen insertion which have been noted[9] have been rationalized in terms of an initial attack on the heteroatom to form an intermediate ylid which can decompose to the observed reaction products by any of several paths.[7d,10]

$$RSCH_2CH{=}CH_2 \xrightarrow{:CCl_2} \underset{\text{(major product)}}{RSCCl{=}CHCH{=}CH_2}$$

Although several reports have appeared in which dichlorocarbene insertion into the mercury–halogen bond has been claimed,[11] careful reinvestigation clearly showed that the products had resulted from nucleophilic displacement of the halide by the trichloromethyl anion.[12,13] An insertion of dichlorocarbene into the carbon–aluminum bond has been postulated to explain the products which result from the treatment of triisobutylaluminum with carbon tetrachloride.[14] Insertion into the silicon–hydrogen or germanium–hydrogen bond has been observed when various silanes or germanes are present during the thermal decomposition of phenyl(bromodichloromethyl)mercury.[5]

$$RHgX + {}^{-}CCl_3 \longrightarrow RHgCCl_3 + X^{-}$$

In addition to a general scarcity of data on dichlorocarbene insertions, there are only a few reported studies of the stereochemistry of any type of carbene insertion. The work of Cope[15] and of Friedman and Schechter[16] indicates that various transannular carbon–hydrogen insertions by cycloalkylidenes generated from diazo compounds such as diazocyclodecane proceed stereo-

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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] For a preliminary account see J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **86**, 524 (1964).

[3] (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (c) W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963); (d) T. Ambrus, *Rev. Chim.* (Bucharest), **15**, 739 (1964); (e) W. Kirmse, *Angew. Chem.*, **77**, 1 (1965).

[4] E. K. Fields, *J. Am. Chem. Soc.*, **84**, 1744 (1962).

[5] D. Seyferth and J. M. Burlitch, *ibid.*, **85**, 2667 (1963).

[6] F. E. Kung and W. E. Bissinger, *J. Org. Chem.*, **29**, 2739 (1964).

[7] (a) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961); (b) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964); (c) W. E. Parham and S. H. Groen, *ibid.*, **29**, 2214 (1964); (d) W. E. Parham and S. H. Groen, *ibid.*, **30**, 3181 (1965).

[8] (a) J. C. Anderson and C. B. Reese, *Chem. Ind.* (London), 575 (1963); (b) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 4874 (1964).

[9] (a) A. W. Hofmann, *Ann.*, **144**, 114 (1867); **146**, 107 (1868); (b) J. U. Nef, *ibid.*, **298**, 368 (1897); (c) P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.*, **23**, 1599 (1958); (d) M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959); **11**, 1 (1960); (e) M. B. Frankel, H. Feuer, and J. Bank, *Tetrahedron Letters*, **7**, 5 (1959).

[10] J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

[11] (a) O. A. Reutov and A. N. Lovtsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1716 (1960); *Chem. Abstr.*, **55**, 9319 (1961); (b) O. A. Reutov and A. N. Lovtsova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (English Transl.), 1599 (1960); (c) O. A. Reutov and L. N. Lovtsova, *Dokl. Akad. Nauk. SSSR*, **139**, 622 (1961); *Chem. Abstr.*, **56**, 1469 (1962); (d) G. A. Razuvaev, N. S. Vasileiskaya, and L. A. Nikitina, *Tr. po Khim. i Khim. Tekhnol.*, **3**, 638 (1960); *Chem. Abstr.*, **56**, 15116 (196).

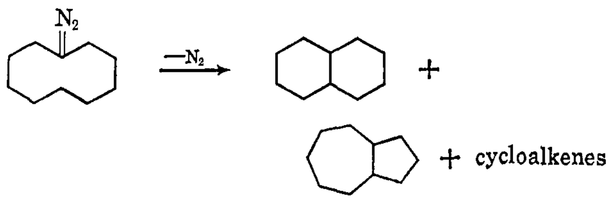
[12] (a) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962). (b) More recent evidence indicates that mercury–halogen insertion does occur under certain conditions: M. E. Gordon, K. V. Darragh, and D. Seyferth, *ibid.*, **88**, 1831 (1966).

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

[14] J. W. Collette, *ibid.*, **28**, 2489 (1963).

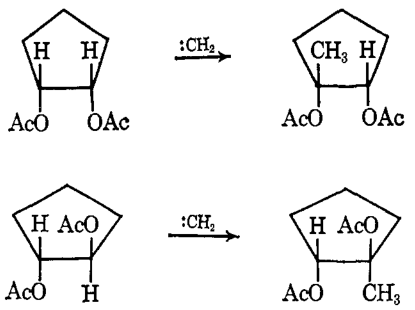
[15] A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6370 (1960).

[16] L. Friedman and H. Shechter, *ibid.*, **83**, 3159 (1961).

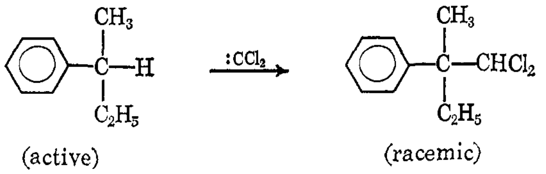


specifically with over-all retention (transfer of axial hydrogen) consistent with Doering's observations that bridgehead hydrogens of certain bicyclic hydrocarbons undergo insertion by methylene at a normal rate although attack from the rear is prohibited.[16,17]

Franzen[18] has reported that in both *cis*- and *trans*-1,2-diacetoxycyclopentane, methylene insertion into the carbon–hydrogen bonds of the atoms bearing acetoxy groups occurred with at least 95% retention of



configuration. However, he has observed that dichlorocarbene inserted into the benzylic carbon–hydrogen bond of active *sec*-butylbenzene with complete racemization.[19]



In the present study dichlorocarbene generated by the method of Parham[7a] at 0° has been allowed to attack simple symmetrical dialkylmercury compounds with subsequent insertion primarily in the carbon–mercury bond. Systems of the organomercury type offer a number of distinct advantages. (1) Dialkylmercury compounds are well known to be susceptible to electrophilic attack on the carbon–mercury bond.[20–22] (2) The alkyl carbon–mercury bond is sufficiently weak[23,24] that extensive insertion might be expected from attack by dichlorocarbene generated under mild conditions from ethyl trichloroacetate and sodium methoxide. (3) Active di-*sec*-butylmercury of known configuration and optical purity is available (see Discussion) for a complete stereochemical study of the reaction.

Product Identification

A series of symmetrical dialkylmercury compounds **1a–e** when subjected to treatment with ethyl trichloro-

$$\underset{\mathbf{1}}{RR'CHHgCHRR'} + Cl_3CCO_2Et + NaOMe \xrightarrow[0^\circ]{\text{pentane}} \underset{\mathbf{2}}{RR'CHCCl_2HgCHRR'}$$

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

acetate and excess sodium methoxide in pentane produced simple carbon–mercury insertion product (**2**) isolated in several cases to the extent of 35–60% yield based on **1**. For compounds **1c**, **1d**, and **1e** additional insertion was noted in the β-carbon–hydrogen bond, *vide infra*.[25] The simple dialkylmercury compound **1** is not affected by either ethyl trichloroacetate or sodium methoxide alone. That the reaction involves an attack by dichlorocarbene rather than the trichloromethyl anion is strongly suggested by the observation that dialkylmercury compounds are inert to attack by strongly nucleophilic iodide or thiosulfate ions as well as to strong bases.[26]

Although insertion product **2** was found to undergo appreciable thermal decomposition above 100° to give an equimolar mixture of an alkylmercuric chloride and a vinyl chloride,[27] it was stable enough at room temperature to be identified by spectral and chemical properties, *vide infra*. This is in sharp contrast to various reports of carbon–aluminum, -lithium, and -magnesium bond insertion by dichlorocarbene,[14] difluorocarbene,[28] fluorobromocarbene,[28] chlorocarbene,[29] and alkylchlorocarbene,[14,30,31] in which the proposed intermediates had only fleeting existence.

Diisopropylmercury (0.03 mole), bp 33–35° (0.3–0.4 mm), after treatment with ethyl trichloroacetate (0.06 mole) and excess sodium methoxide in pentane at 0°, produced an oily residue which was carefully distilled to give a 57% yield of isopropyl-α,α-dichloroisobutylmercury (**2b**), bp 94° (0.3–0.4 mm), a clear, viscous liquid with a hydrocarbon-like infrared spectrum nearly identical with that of the starting material with the exception of a prominent absorption at 692 cm^{-1} characteristic of the carbon–chlorine stretching mode.[32] Structural confirmation was based primarily upon nmr spectral data (Figure 1) and was consistent with the observed products of thermal decomposition.[27] Unlike the spectrum of diisopropylmercury[33] in which the methyl protons are observed as a singlet,[34] the spectrum

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(17) (a) W. von E. Doering, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21–30, 1961; see ref 16; (b) W. von E. Doering, unpublished results, in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 24.

(18) V. Franzen, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 26–29, 1962, p 23-O.

(19) V. Franzen, unpublished work, in ref 17b, p 162.

(20) F. R. Jensen, *J. Am. Chem. Soc.*, **82**, 2469 (1960).

(21) R. E. Dessy, G. F. Reynolds, and J. Y. Kim, *ibid.*, **81**, 2683 (1959).

(22) L. H. Gale, F. R. Jensen, and J. A. Landgrebe, *Chem. Ind.* (London), 118 (1960)

(23) In diethylmercury the bond dissociation energy has been determined as 41.5 ± 2 kcal/mole.[24]

(24) B. G. Gowenlock, J. C. Polanyi, and E. Warburst, *Proc. Roy Soc.* (London), **A218**, 269 (1953).

(25) A more detailed discussion of dichlorocarbene insertion β to a mercury atom will be deferred to a later publication.

(26) Experimental observations of the authors.

(27) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **88**, 3552 (1966).

(28) V. Franzen and L. Fikentscher, *Chem. Ber.*, **95**, 1958 (1962).

(29) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); **83**, 1003 (1961); **84**, 809 (1962); **85**, 99 (1963).

(30) W. Kirmse, *Angew. Chem.*, **72**, 716 (1960).

(31) W. Kirmse and B. v. Burlöw, *Chem. Ber.*, **96**, 3316, 3323 (1963).

(32) L. J. Bellamy, "The Infrared Spectra of Complex Molecules, 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 331.

(33) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

(34) The diamagnetic shielding effect of the mercury atom makes the

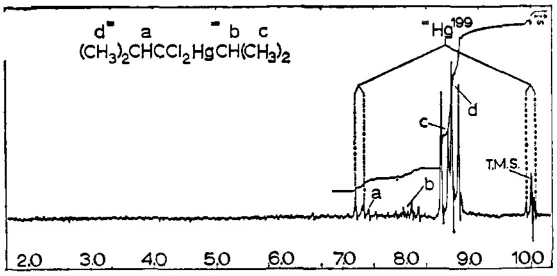

Figure 1. 60-Mc/sec nmr spectrum (carbon tetrachloride) of isopropyl-α,α-dichloroisobutylmercury (**2b**).

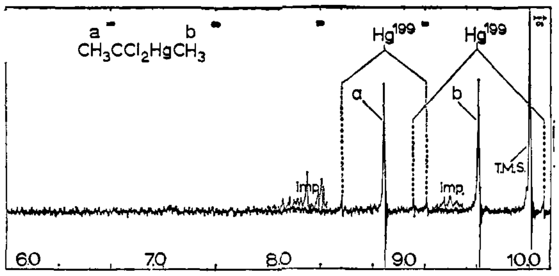

Figure 2. 60-Mc/sec nmr spectrum (carbon tetrachloride) of methyl-α,α-dichloroethylmercury (**2a**).

of **2b** clearly shows two nonequivalent sets of methyl protons as doublets (J = 7 cps) at 8.63 and 8.79.[35] The small complex multiplets centered at *ca.* 7.3 and 8.1 were assigned to the tertiary proton of the α,α-dichloroisobutyl and isopropyl group, respectively. Two small Hg^{199} satellite[36] doublets (J = 7 cps) are symmetrically oriented about the isopropyl doublet at 8.63 with $J_{Hg^{199}H^1}$ = 163 cps, consistent only with the assignment of the 8.63 doublet to the methyl groups β to the mercury atom.[37,38] The Hg^{199}-β-H coupling constant of 163 cps for **2b** is intermediate between that for a simple dialkylmercury compound and an alkylmercuric halide (Table I), a result which might have been expected in view of the observation that both vicinal[39a-e] and geminal[39d,f] proton–proton coupling is affected (but only to a small extent) by the electronegativity of substituents on or adjacent to the carbon atoms in question.

Table I. Hg^{199}–H^1 Spin–Spin Coupling Constants (cps)

Compound	α-C–H	β-C–H
Dimethylmercury	102[a]	. . .
Diethylmercury	91[a]	120[a]
Di-*n*-propylmercury	90[a]	108[a]
Diisopropylmercury	78[a]	126[a]
Di-*n*-butylmercury	96	105
Di-*sec*-butylmercury	*b*	119
Methylmercuric chloride	209–212[c]	. . .
n-Propylmercuric chloride	201	289
Isopropylmercuric chloride	*b*	284
sec-Butylmercuric chloride	*b*	293
Methyl-α,α-dichloroethylmercury (**2a**)	126	81[d]
Isopropyl-α,α-dichloroisobutylmercury (**2b**)	*b*	163[e]
sec-Butyl-α,α-dichloro-β-methylbutylmercury (**2e**)	*b*	164[e]

[a] See ref 33. [b] Definite assignment not made. [c] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964). [d] Methyl group adjacent to *gem*-dichloro group. [e] β-Methyl group.

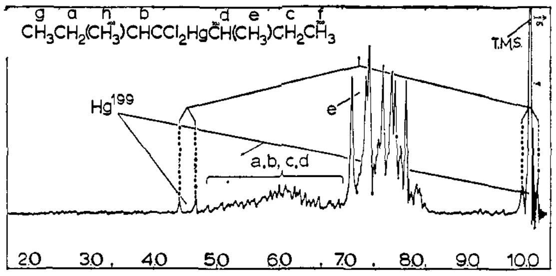

Figure 3. 60-Mc/sec nmr spectrum (carbon tetrachloride) of *sec*-butyl-α,α-dichloro-β-methylbutylmercury (**2e**).

Vacuum distillation of the reaction mixture in which dichlorocarbene was generated in the presence of dimethylmercury (**1a**) gave a very small amount of slightly impure methyl-α,α-dichloroethylmercury (**2a**) which was identified by its characteristic nmr spectrum (Figure 2). If the low-field singlet at 7.68 is assigned to the α,α-dichloro group on the basis of the large deshielding effect expected from the *gem*-chloro group, the values of $J_{Hg^{199}-H_\alpha{}^1}$ = 126 cps and $J_{Hg^{199}-H_\beta{}^1}$ = 81 cps are obtained from the two sets of Hg^{199} satellite peaks. Comparison of the observed Hg^{199} coupling constants with those of other compounds in Table I reveals that the presence of the *gem*-dichloro group markedly increases the Hg^{199} coupling to the α-protons and decreases coupling to the β protons (adjacent to the *gem*-dichloro group) relative to similar coupling constants in simple dialkylmercury compounds.

Generation of dichlorocarbene in the presence of di-*sec*-butylmercury (**1e**) produced *sec*-butyl-α,α-dichloro-β-methylbutylmercury (**2e**) isolated by column chromatography on Florisil in 59% yield. Attempted distillation resulted in thermal decomposition.[27] The infrared spectrum of **2e** like that of **2b** exhibits a strong absorption of 688 cm^{-1} tentatively assigned to the carbon–chlorine stretching vibration of the *gem*-dichloro group.[32] Although the nmr spectrum (Figure 3) is rather complex, the satellite doublets (J = 7.5 cps) at 7.27 and 10.0 centered about the doublet (J = 7.5 cps) at 8.63 allow the assignment of the latter absorption to the β-methyl group and correspond to $J_{Hg^{199}-H_\beta{}^1}$ = 164 cps in good agreement with the value of 163 cps found for the similar coupling constant in **2b**. In order to verify the structure, **2e** was cleaved with excess bromine in carbon tetrachloride to give a mixture of mercuric bromide, *sec*-butyl bromide, and a material (isolated in 56% yield) which gave the correct analysis for $C_5H_9BrCl_2$ and was assigned the structure 1-bromo-1,1-dichloro-2-methylbutane (**3**) on the basis of its infrared and nmr spectra. Treatment of **3** with potas-

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methyl and methine protons magnetically equivalent thereby removing any visible coupling.

(35) Given in τ values throughout.

(36) The Hg^{199} isotope (spin of 1/2) has a natural abundance of 16.9%.

(37) No Hg^{199} coupling to γ protons in dialkylmercury compounds has been observed.[33]

(38) The reason that the methyl doublet of the α,α-dichloroisobutyl group is at slightly higher field than that of the isopropyl group is not clear but may be associated with an unusual anisotropic shielding effect by the mercury atom.

(39) (a) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963); (c) A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *ibid.*, **85**, 2185 (1963); (d) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, 34, 115 (1962); (e) P. Laszlo and P. von R. Schleyer, *Bull. Soc. Chim. France*, 87 (1964); (f) K. L. Williams, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

$$\underset{\mathbf{2e}}{CH_3CH_2C(CH_3)HCCl_2HgCH(CH_3)CH_2CH_3} \xrightarrow[CCl_4]{2Br_2} HgBr_2 +$$

$$CH_3CH_2(CH_3)CHBr + \underset{\mathbf{3}}{CH_3CH_2(CH_3)CHCCl_2Br} \xrightarrow[HOCH_2CH_2OH]{KOH}$$

$$\underset{\mathbf{4}}{CH_3CH_2(CH_3)C{=}CCl}$$

sium hydroxide produced a single major product (78% yield), bp 130–131°, which was identified from its elemental analysis and infrared and nmr spectra as 1,1-dichloro-2-methyl-1-butene (**4**).

The generation of dichlorocarbene in the presence of di-*n*-propylmercury (**1c**) produced the unexpected result that insertion occurred to an equal extent in the carbon–mercury bond and the β-carbon–hydrogen bond[25] to form a mixture of *n*-propyl-α,α-dichloro-*n*-butylmercury (**2c**) and *n*-propyl-γ,γ-dichloro-β-methylpropylmercury (**5**). Vacuum distillation (bp 103–104° (0.8–0.9 mm)) of the crude reaction mixture resulted in partial decomposition of the carbon–mercury insertion product **2c** to *n*-propylmercuric chloride and 1-chloro-1-butene.[27] The alkylmercuric halide was removed by extraction with sodium thiosulfate solution, and the products were chromatographed on Florisil. Although the nmr spectrum of the mixture of **2c** and **5** is rather complex, the presence of a small doublet at 4.28 (J = 3 cps) is quite indicative of a proton on a dichloromethyl group vicinal to a tertiary proton and suggests the presence of a product which resulted from dichlorocarbene insertion into a secondary carbon–hydrogen bond. The absence of Hg^{199} satellite peaks about the 4.28 absorption implies that the insertion has taken place at the β rather than the α position on the *n*-propyl group. Confirmation of the product structures was made by carrying out a bromine cleavage which resulted in the formation of mercuric bromide, *n*-propyl bromide, 1-bromo-1,1-dichlorobutane (**6**), and 3-bromo-1,1-dichloro-2-methylbutane (**7**). Halide **6**, the expected cleavage product from **2c**, had the correct analysis for $C_4H_7Cl_2Br$ and exhibited an infrared spectrum typical of a saturated hydrocarbon but with additional strong bands at 760, 755, 726, 698, and 670 cm^{-1} which were assumed to be associated with the trihalomethyl group.[32] The nmr spectrum of **6** shows a triplet at 8.92 (J = 7 cps, area 3) assigned to the methyl group and complicated multiplets at *ca.* 7.2 (area 2) and *ca.* 8.1 (area 2) which were assigned to the α- and β-methylene protons, respectively. The complexity of the latter absorptions was presumed to be due to a sufficiently high barrier to rotation about the trihalomethylmethylene bond to allow observation of separate nmr signals from the two *gauche* conformations **6a** and **6b**.[40]

$$\underset{\mathbf{1c}}{(CH_3CH_2CH_2)_2Hg} \xrightarrow{:CCl_2} \underset{\mathbf{2c}}{CH_3CH_2CH_2CCl_2HgCH_2CH_2CH_3} +$$

$$\underset{\mathbf{5}}{CH_3CH(CHCl_2)CH_2HgCH_2CH_2CH_3}$$

$$\mathbf{2c} + \mathbf{5} \xrightarrow[CCl_4]{Br_2} HgBr_2 + CH_3CH_2CH_2Br + \underset{\mathbf{6}}{CH_3CH_2CH_2CCl_2Br} +$$

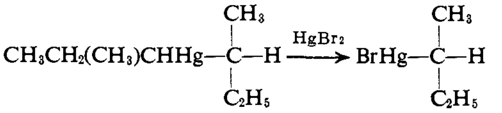
$$\underset{\mathbf{7}}{CH_3CH(CHCl_2)CH_2Br}$$

6a **6b**

Halide **7**, the expected bromine cleavage product of **5**, also had the correct analysis for $C_4H_7Cl_2Br$ and exhibited infrared absorptions typical of a simple hydrocarbon in addition to strong absorptions at 770, 747, 701, and 649 cm^{-1}. The nmr spectrum of **7** shows a doublet at 8.65 (J = 6.5 cps, area 3) assigned to the methyl protons, a complicated multiplet at *ca.* 7.4 (area 1) assigned to the tertiary proton, a doublet at 6.45 (J = 6.5 cps, area 2) assigned to the protons of the bromine-bearing carbon atom, and a doublet at 3.81 (J = 4 cps, area 1) assigned to the proton of the *gem*-dichloromethyl group.

Stereochemistry of Insertion

Although optically pure L-(−)-*sec*-butyl-(±)-*sec*-butylmercury has not been prepared, the absolute configuration of the compound has been established,[41] and its maximum rotation can be calculated from data on the completely stereospecific cleavage of dialkylmercury compounds by mercuric halide.[20,42–48] The value of $[\alpha]^{22}\text{D}$ −25.8° for optically pure L-(−)-*sec*-butylmercuric bromide[41] provided the basis for calculating the specific rotation of optically pure L-(−)-*sec*-butyl-(±)-*sec*-butylmercury (**8**). Cleavage of **8**, $[\alpha]^{22}\text{D}$ −5.52°, with mercuric bromide has been shown to give L-(−)-*sec*-butylmercuric bromide with $[\alpha]^{22}\text{D}$ −3.36°,[46] a value which corresponds to $[\alpha]^{22}\text{D}$ −21.2° for optically pure **8**. The cleavage of di-L-(−)-*sec*-butylmercury, $[\alpha]^{25}\text{D}$ −7.57°, with mercuric bromide has been shown to give L-(−)-*sec*-butylmercuric bromide with $[\alpha]^{25}\text{D}$ −4.60°, which indicated a value of $[\alpha]^{25}\text{D}$ −42.4° for optically pure di-L-(−)-*sec*-butylmercury.[48] Application of the rule of optical superposition[49] gives $[\alpha]^{25}\text{D}$ −21.2° for optically pure **8**, in complete agreement with the previously estimated value. Calculation of the specific rotation of pure **8** from data obtained from the conversion of L-(−)-*sec*-butylmercuric bromide to **8** by reaction with *sec*-butylmagnesium bromide gives a value slightly lower than −21.2°. This reaction, although reported to be



8, −5.52° −3.36°

$$CH_3CH_2(CH_3)CHHg{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}{-}H \xrightarrow{HgBr_2} BrHg{-}\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}{-}H$$

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[40] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1962, pp 99–103.

[41] F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 2466 (1960).

[42] A. N. Nesmeyanov, A. E. Borisov, and A. N. Guskova, *Bull. Acad. Sci. USSR, Classe Sci. Chim.*, 639 (1945); *Chem. Abstr.*, 40, 4659 (1946).

[43] G. F. Wright, *Can. J. Chem.*, 30, 268 (1952).

[44] O. A. Reutov, *Angew. Chem.*, **69**, 688 (1957).

[45] S. Winstein, T. G. Traylor, and C. S. Garner, *J. Am. Chem. Soc.*, 77, 3741 (1955).

[46] F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **81**, 1262 (1959).

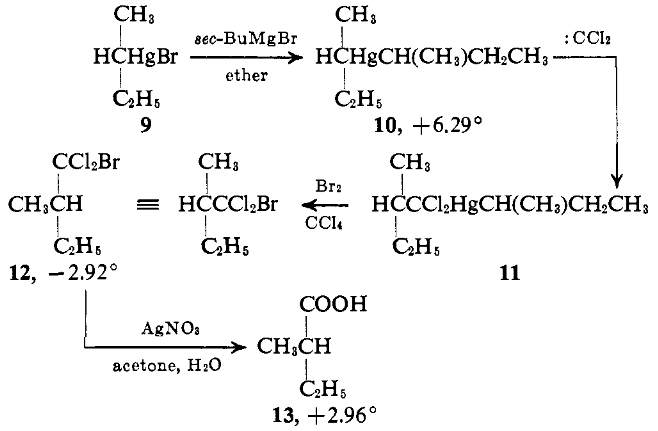
[47] H. B. Charman, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2530 (1959).

[48] F. R. Jensen and J. A. Landgrebe, *J. Am. Chem. Soc.*, **82**, 1004 (1960).

[49] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 110.

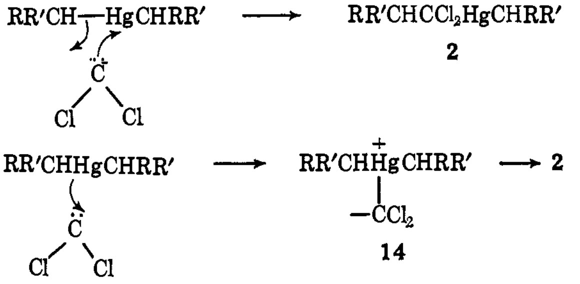
completely stereospecific,[47] must proceed with only partial stereospecificity under certain conditions. For example, a range of 90–98% retention of configuration has been reported for the conversion of L-(−)-*sec*-butylmercuric bromide to **8** *via* the Grignard reaction and subsequent cleavage of **8** back to L-(−)-*sec*-butylmercuric bromide with mercuric bromide.[20] The slight loss of configuration during the cycle must have occurred during the preparation of **8** if we consider that the cleavage by mercuric bromide has been shown to be completely stereospecific.[42–48]

sec-Butylmercuric bromide was partially resolved and the resulting D-(+)-*sec*-butylmercuric bromide (**9**), $[\alpha]^{22}\mathrm{D}$ +9.12 ± 0.40°, was treated with *sec*-butylmagnesium bromide to give D-(+)-*sec*-butyl-(±)-*sec*-butylmercury (**10**), $[\alpha]^{22}\mathrm{D}$ +6.29 ± 0.35°. Dichlorocarbene was generated in the usual manner in the presence of the optically active organomercurial **10**, and the insertion product **11** which resulted was cleaved with bromine in carbon tetrachloride to give L-(−)-1-bromo-1,1-dichloro-2-methylbutane (**12**) with $[\alpha]^{27}\mathrm{D}$ −2.92 ± 0.08° in a yield of 56% based on **10**. Treatment of **12** with silver nitrate in aqueous acetone gave L-(+)-α-methylbutyric acid (**13**), $[\alpha]^{25}\mathrm{D}$ +2.96 ± 0.06°.



Only the dichlorocarbene insertion step involves breaking a bond to the optical center and at the same time gives an optical dilution of one-half since the probability of insertion into either carbon–mercury bond is the same. Consideration of the optical dilution and the use of $[\alpha]^{25}\mathrm{D}$ −19.8° for the specific rotation of optically pure D-(−)-α-methylbutyric acid as reported by Freudenberg and Lwowski[50] allows one to calculate that dichlorocarbene insertion into the carbon–mercury bond proceeded with 101 ± 6% retention of configuration.[51,52]

One might visualize at least two general mechanistic paths which are consistent with the observed stereochemistry: (1) direct electrophilic attack of dichlorocarbene on the carbon–mercury bond in a concerted manner; (2) formation of an intermediate ylid **14** and



subsequent stereospecific alkyl migration. Although there is reason to believe that ylids ae involved in insertion reactions of dichlorocarbene with various sulfur-[7a–c] and nitrogen-containing[9b,10] compounds and although stable ylids can be prepared upon generation of halocarbenes in the presence of phosphine derivatives,[54] the present results do not allow one to distinguish between the two postulated paths. A more detailed account of the insertion mechanism including further consideration of the products arising from the formal insertion of dichlorocarbene into the β-carbon–hydrogen bond will be deferred to a future publication.[55]

Experimental Section[57]

Materials. Diisopropylmercury, bp 33–35° (0.3–0.4 mm) (lit.[58] bp 60° (8 mm)), di-*n*-propylmercury, bp 37° (0.6 mm) (lit.[59] bp 189–191° (760 mm)), di-*n*-butylmercury, bp 90° (5 mm) (lit.[60] bp 105° (10 mm)), and di-*sec*-butylmercury, bp 45–47° (0.4–0.5 mm) (lit.[61] bp 46° (0.3 mm)) were prepared by the method of Reynolds, Dessy, and Jaffé.[62] Dimethylmercury was purchased from Eastman Kodak and was purified by distillation immediately prior to use.

n-Pentane, used as the solvent for all carbene reactions, was purified by treatment with concentrated sulfuric acid for 24 hr. The pentane was separated, washed with aqueous sodium bicarbonate, dried with magnesium sulfate, distilled, and stored over sodium wire.

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(50) K. Freudenberg and W. Lwowski, *Ann.*, **594**, 76 (1955).

(51) Because some loss of configuration apparently occurred during the conversion of 9 to 10, the experimental rotation of 11 was used as a starting point for the determination of the over-all stereospecificity in the reaction. Use of the rotation for 9 gives a result somewhat greater than 100% retention.

(52) Curtin[53] reported a value of $[\alpha]\mathrm{D}$ −48.8° for optically pure di-L-(−)-*sec*-butylmercury. Although he arrived at this number by calculation of numerical data reported by Jensen and co-workers[46] for the conversion of L-(−)-*sec*-butylmercuric bromide to L-(−)-*sec*-butyl-(±)-*sec*-butylmercury and reconversion to L-(−)-*sec*-butylmercuric bromide, we have been unable to duplicate this calculation from Jensen's values. The specific rotation of the α-methylbutyric acid obtained by degradation of the carbon–mercury insertion product clearly indicates that the value $[\alpha]\mathrm{D}$ −48.8° from optically pure di-L-(−)-*sec*-butylmercury as reported by Curtin is too high since it would indicate *ca.* 115% retention of configuration for our reaction.

(53) D. Y. Curtin and W. J. Koehl, Jr., *Chem. Ind.* (London), 262 (1960).

(54) (a) A. J. Speziale, G. J. Marco, and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960); (b) A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962); (c) D. Seyferth, S. O. Grim, and T. O. Read, *ibid.*, **82**, 1510 (1960).

(55) The generation of dichlorocarbene in the presence of di-*n*-butylmercury results in *ca.* 50% of the insertion occurring in the β-carbon–hydrogen bond while for diisobutylmercury most of the insertion takes place in the β-carbon–hydrogen bond.[56]

(56) Unpublished results of J. A. Landgrebe and D. E. Thurman.

(57) 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). Vapor phase chromatographic analyses were effected on either a Wilkens Aerograph Hy-Fi Model 600 chromatograph equipped with a flame ionization detector, or on a F and M Model 700 chromatograph with a thermal conductivity detector and a power proportioning temperature programmer. Chromatograms were drawn by a Barber-Coleman 10-in. recorder equipped with a disk integrator. Optical rotations were determined with a Carl Zeiss polarimeter equipped with a sodium spectral bulb and a double-band interference filter for wavelengths 589.0 and 589.6 mμ. Microanalyses were carried out by Weiler and Strauss, Oxford, England, or by Huffman Laboratories, Wheatridge, Colo.

(58) C. T. Mortimer, H. O. Pritchard, and H. A. Skinner, *Trans. Faraday Soc.*, **48**, 220 (1952).

(59) H. C. Kaufman, "Handbook of Organometallic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p 50.

(60) W. J. Jones, D. P. Evans, T. Gulwell, and D. C. Griffiths, *J. Chem. Soc.*, 45 (1935).

(61) J. Tafel, *Chem. Ber.*, **39**, 3628 (1906).

(62) G. F. Reynolds, R. E. Dessy, and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

Isopropyl-α,α-dichloroisobutylmercury (2b). Diisopropylmercury (8.24 g, 0.0286 mole), sodium methoxide (6.5 g, 0.12 mole, Matheson Coleman and Bell), and 40 ml of alkene-free pentane were stirred at 0° in a nitrogen atmosphere while a solution of ethyl trichloroacetate (11.5 g, 0.060 mole, Eastman Kodak) in 15 ml of pentane was slowly added (20 min). The mixture was maintained at 0° for 6 hr, warmed to room temperature overnight, and hydrolyzed with 50 ml of water while the flask was immersed in an ice bath. The pentane extract of the reaction mixture was washed with water, dried over anhydrous magnesium sulfate, and distilled *in vacuo* (0.5 mm). Low-boiling constituents were collected in a Dry Ice–isopropyl alcohol cooled trap. A small portion of the remaining high-boiling fraction was withdrawn and extracted with 1 *M* sodium thiosulfate. Upon addition of 1 *M* potassium iodide no precipitate was formed, which indicated the absence of alkylmercuric chloride. Upon careful distillation, the crude brown product yielded a small amount of unchanged diisopropylmercury and a light yellow liquid, bp 94° (0.5 mm). The liquid was extracted four times with 1 *M* sodium thiosulfate to give 6.02 g (0.0163 mole) of isopropyl-α,α-dichloroisobutylmercury (**2b**) or 57% yield based on diisopropylmercury.

A second experiment produced a 37% yield of **2b** which was shown by thin layer chromatography (cyclohexane, silica gel) to be free from diisopropylmercury and isopropylmercuric chloride. The infrared spectrum is nearly identical with that of diisopropylmercury with the exception of a strong absorption at 692 cm^{-1} which is absent in the spectrum of the latter. The nmr spectrum is shown in Figure 1.

Anal. Calcd for $C_7H_{14}Cl_3Hg$: C, 22.74; H, 3.82. Found: C, 22.84; H, 3.87.

Methyl-α,α-dichloroethylmercury (2a). Ethyl trichloroacetate (15.3 g, 0.080 mole) in 25 ml of alkene-free pentane was added to dimethylmercury (8.76 g, 0.0376 mole), sodium methoxide (8.64 g, 0.16 mole), and 60 ml of pentane as previously described. After work-up and removal of all low-boiling material, the remaining liquid was vacuum distilled to yield a small amount of crude methyl-α,α-dichloroethylmercury (**2a**). The nmr spectrum is shown in Figure 2.

***sec*-Butyl-α,α-dichloro-β-methylbutylmercury (2e).** Ethyl trichloroacetate (11.5 g, 0.060 mole) in 10 ml of alkene-free pentane was added to di-*sec*-butylmercury (9.45 g, 0.030 mole), sodium methoxide (6.5 g, 0.12 mole), and 20 ml of pentane as previously described. The high-boiling, brown liquid obtained after the usual work-up was shown by tlc (cyclohexane, silica gel) to consist of unchanged di-*sec*-butylmercury, residue, and a major component thought to be **2e**. Attempted isolation of **2e** by vacuum distillation (bath temperature 85–150°) resulted in decomposition to form a low-boiling liquid (3.2 g obtained in a cold trap), a portion of which was subsequently identified as 1-chloro-2-methyl-1-butene[27] (2.1 g, 0.020 mole). Three minor components of the liquid were not identified. Extraction of the distillation residue with 1 *M* sodium thiosulfate and subsequent treatment with 1 *M* potassium iodide produced a precipitate of *sec*-butylmercuric iodide, indicative of the presence of the chloride in the distillation residue. Slightly impure *sec*-butylmercuric chloride was isolated by ethanol extraction of the distillation residue from a second reaction. Both 1-chloro-2-methyl-1-butene and *sec*-butylmercuric chloride were shown to be thermal decomposition products of **2e**. The amount of chloroalkene formed in the first reaction corresponded to a 67% yield of **2e** based on di-*sec*-butylmercury.

As another approach to isolate the insertion product, column chromatography techniques were employed. Attempted separation of the components of the crude, brown, high-boiling liquid on Woelm acid, neutral (activity I and II), and basic alumina and on powdered silicic acid columns resulted in decomposition of the insertion product. Although 100–200 mesh Florisil did not effect a separation of the insertion product from the unchanged di-*sec*-butylmercury, it did remove the brown residue and did not cause decomposition, provided the contact time between the insertion product and the Florisil was short. The observation that di-*sec*-butylmercury decomposed quite readily when left in natural light at room temperature, while the insertion product showed only slight decomposition under the same conditions, provided an efficient means for removal of the unchanged di-*sec*-butylmercury. The mixture was allowed to sit in an open flask at room temperature for 8 days. Finely divided mercury was observed at the end of this time. The crude mixture was passed through three columns of 100–200 mesh Florisil (20 g/column) and eluted with petroleum ether (bp 60–110°) to give, after evaporation of the petroleum ether, a clear liquid. This was extracted five times with 1 *M* sodium thiosulfate, dried over calcium hydride, and filtered through glass wool to give 7.04 g (0.0177 mole) of *sec*-butyl-α,α-dichloro-β-methylbutylmercury (**2e**) or 59% of the theoretical yield based on di-*sec*-butylmercury. Thin layer chromatography (cyclohexane, silica gel) showed only one component present. Addition of 1.21% (1 *M*) di-*sec*-butylmercury to **2e** gave a mixture which was clearly shown by thin layer chromatography to contain 2 components. The infrared spectrum of **2e** (carbon tetrachloride, carbon disulfide) is nearly identical with that of di-*sec*-butylmercury (carbon tetrachloride) with the exception of a very strong absorption at 688 cm^{-1} which is absent in the latter. The nmr spectrum of **2e** (Figure 3) is similar in general appearance although much more complex than the spectrum of di-*sec*-butylmercury. The analysis is slightly high in carbon content because of the presence of minute amounts of di-*sec*-butylmercury which could not be completely removed even after extensive chromatography.

Anal. Calcd for $C_9H_{18}Cl_2Hg$: C, 27.18; H, 4.56; Cl, 17.83. Found: C, 29.29; H, 4.27; Cl, 17.31.

The nmr spectrum of a neat sample of **2e** shows a very small doublet ($J = 3$ cps) at 4.0. This doublet, obscured by noise if the sample is diluted, was tentatively assigned to the presence of a very small amount of a compound which resulted from dichlorocarbene insertion into the carbon–hydrogen bond of the β-methylene group.

Generation of Dichlorocarbene in the Presence of Di-*n*-propylmercury. Ethyl trichloroacetate (19.1 g, 0.10 mole) in 15 ml of pentane was added to di-*n*-propylmercury (14.3 g, 0.0499 mole), sodium methoxide (10.8 g, 0.20 mole), and 40 ml of pentane as previously described. The usual work-up gave a brown liquid which was shown by tlc (cyclohexane, silica gel) to contain unchanged di-*n*-propylmercury, residue, and two partially superimposed spots in the relative region occupied by the insertion product in the other systems investigated. The crude material was passed through two columns of 100–200 mesh Florisil (20 g/column) and was eluted with 30–60° petroleum ether, to give, after evaporation of the petroleum ether, a light yellow liquid. Vacuum distillation gave 2.4 g (0.0084 mole) of unchanged di-*n*-propylmercury and a yellow liquid (bp 103–104° (0.8–0.9 mm)), some of which solidified in the condenser during the distillation. After completion of the distillation, this solid was washed from the condenser and extracted with 1 *M* sodium thiosulfate. Addition of 1 *M* potassium iodide precipitated *n*-propylmercuric iodide. This indicated the presence of *n*-propylmercuric chloride which was later shown to be a thermal decomposition product of *n*-propyl-α,α-dichloro-*n*-butylmercury (**2e**). The yellow liquid obtained in the receiving flask was extracted with 1 *M* sodium thiosulfate and dried over anhydrous calcium chloride to give 3.1 g of a light yellow liquid. This was passed through a column of 100–200 mesh Florisil (20 g/column) and was eluted with petroleum ether (bp 30–60°) to give, after evaporation of the petroleum ether, 2.9 g of clear liquid. Thin layer chromatography (cyclohexane, silica gel) showed only the two original partially superimposed components to be present. A nmr spectrum showed, in addition to the expected high-field peaks, a doublet at 4.28 ($J = 3$ cps).

Anal. Calcd for $C_7H_{14}Cl_2Hg$: C, 22.74; H, 3.82; Cl, 19.18; Hg, 54.26. Found: C, 22.27; H, 3.54; Cl, 18.84; Hg, 51.2.

Generation of Dichlorocarbene in the Presence of Di-*n*-butylmercury. Ethyl trichloroacetate (23.0 g, 0.12 mole) in 20 ml of pentane was added to di-*n*-butylmercury (18.9 g, 0.060 mole), sodium methoxide (13.0 g, 0.24 mole), and 40 ml of pentane as previously described. The reaction mixture was worked-up in the usual manner and the residue, which was shown by the previously mentioned extraction test with sodium thiosulfate not to contain any *n*-butylmercuric chloride, was subjected to vacuum distillation at an oil bath temperature which did not exceed 125°. The solid material which formed in the condenser and fractionation column was extracted with ethanol and recrystallized from cold ethanol to give *n*-butylmercuric chloride, mp 124–126° (lit.[63] mp 125.5°). A liquid obtained from the cold trap of the vacuum pump was shown by vpc (8-ft Carbowax 20M, column, 170°) to consist of a major and a very minor component, the latter being a shoulder of slightly longer retention time. The material, capillary bp 100–102°, gave a positive test for unsaturation (potassium permanganate in acetone) and a positive Beilstein test for halide. The nmr spectrum[64] shows a complex multiplet at *ca.* 4.2 which corresponds to the vinyl protons, a complex multiplet at *ca.* 7.8

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(63) J. Tiffeneau, *Chem. Zentr.*, **92**, III, 26 (1921).

(64) D. Thurman and J. A. Landgrebe, work in progress.

which corresponds to the allylic methylene group, and a very complex set of multiplets from 8.2 to 9.2 for the remaining protons. With the exception of the absorptions above 8.2, the spectrum was very similar to that of a mixture of *cis*- and *trans*-1-chloro-1-butene.[27] The material was identified as a mixture of *cis*- and *trans*-1-chloro-1-pentene (lit.[65] bp 102–106°). Both the vinyl chlorides and the alkylmercuric halide were shown to be thermal decomposition products of *n*-butyl-α,α-dichloro-*n*-amylmercury.[27] A sample of the original crude insertion products was heated in order to decompose the *n*-butyl-α,α-dichloro-*n*-amylmercury. *n*-Butylmercuric chloride was removed by extraction with sodium thiosulfate solution and the residue was heated at 60° under vacuum for several hours in order to remove any volatile vinyl chlorides. The remaining material was tentatively identified as *n*-butyl-β-(dichloromethyl)butylmercury by analogy with the β-carbon–hydrogen insertion product found for dichlorocarbene attack on di-*n*-propylmercury.[25]

Anal. Calcd for $C_9H_{18}Cl_2Hg$: C, 27.18; H, 4.56. Found: C, 27.23; H, 4.61 (average of two analyses).

Cleavage of *sec*-Butyl-α,α-dichloro-β-methylbutylmercury (2e) with Bromine. Crude *sec*-butyl-α,α-dichloro-β-methylbutylmercury was cleaved with bromine by a modification of the procedure of Jensen and Gale.[66] The insertion product **2e** derived from a reaction between ethyl trichloroacetate (19.1 g, 0.10 mole), di-*sec*-butylmercury (15.7 g, 0.0499 mole), and sodium methoxide (10.8 g, 0.20 mole) in the usual manner was dissolved in 45 ml of carbon tetrachloride and treated at 0° with a solution of bromine (16.0 g, 0.10 mole) in 8 ml of carbon tetrachloride. The color persisted after slow addition of half of the bromine solution. The ice bath was removed and the remaining bromine solution was added. The mixture was heated and stirred at 60° for 3 hr, cooled, and filtered to remove mercuric bromide. The latter was washed with carbon tetrachloride and the combined carbon tetrachloride fractions were treated with aqueous sodium bisulfite, dried over anhydrous sodium sulfate and magnesium sulfate, and evaporated *in vacuo* to give 10.2 g of a brown, liquid residue. Vacuum distillation (44° (2 mm)) yielded 6.10 g (0.0278 mole) of 1-bromo-1,1-dichloro-2-methylbutane (**3**), capillary bp 176° (56% yield based on di-*sec*-butylmercury).

An infrared spectrum of **3** (carbon tetrachloride, carbon disulfide) shows the normal saturated hydrocarbon bands in addition to very strong absorptions at 784, 765, and 730 cm^{-1}. The nmr spectrum of **3** shows a triplet at 8.98 and a doublet at 8.69 in addition to complex multiplets which extend from 7.4 to 8.1.

Anal. Calcd for $C_5H_9BrCl_2$: C, 27.30; H, 4.12; Br, 36.33; Cl, 32.24. Found: C, 27.41; H, 4.42; Br, 36.65; Cl, 31.60.

Identification was based on the above evidence together with a study of the dehydrohalogenation products, *vide infra.*

Dehydrohalogenation of 1-Bromo-1,1-dichloro-2-methylbutane (3). 1-Bromo-1,1-dichloro-2-methylbutane (6.10 g, 0.0278 mole) and potassium hydroxide (4.30 g, 0.0766 mole) dissolved in 30 ml of ethylene glycol were heated and stirred at 150° for several hours. Organic distillate collected in an ice-cooled receiver was dried with anhydrous calcium chloride to give 3.34 g of material which was shown by vpc (8 ft, Carbowax 20M column, 125°) to contain two components in the area ratio 9:1. The major component (shorter retention time) was collected and an infrared spectrum (carbon tetrachloride, carbon disulfide) indicated an absorption at 1628 cm^{-1} and a very strong absorption at 893 cm^{-1}. The nmr spectrum shows a triplet at 8.93 (J = 7.5 cps, area 3), a singlet at 8.11 (area 3), and a quartet at 7.67 (J = 7.5 cps, area 2). On the basis of these data and the microanalysis the structure 1,1-dichloro-2-methyl-1-butene (**4**) was assigned.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.19; H, 5.80; Cl, 51.01. Found: C, 43.14; H, 5.99; Cl, 50.85.

The capillary boiling point was 130–131°. The yield based on vpc information was 3.01 g (0.0216 mole) or 78%. The minor component was not definitely identified but was assumed to be 1-bromo-1-chloro-2-methyl-1-butene, the product from elimination of hydrogen chloride rather than hydrogen bromide.

Cleavage of the Di-*n*-propylmercury Insertion Products with Bromine. Dichlorocarbene was generated in the normal manner in the presence of 14.3 g (0.0499 mole) of di-*n*-propylmercury. Work-up gave a dark brown residue which was passed through two columns of 100–200 mesh Florisil (20 g/column) and was eluted with petroleum ether (bp 30–60°), to give, after removal of the petroleum ether, 10.9 g of the crude insertion products. This material was dissolved in 40 ml of carbon tetrachloride and was treated with 11.0 g (0.069 mole) of bromine in 10 ml of carbon tetrachloride as described previously. After the usual work-up, the low-boiling material was distilled. This distillate was shown by nmr to contain *n*-propyl bromide in addition to carbon tetrachloride. Vapor phase chromatography (4-ft, SE-30 column, 80°) information on the remaining higher boiling material is tabulated in Table II in order of increasing retention times. Peak number 1 was not identified.

Table II

Peak no.	Ret time, min	Rel area, %
1	3.25	2.6
2	5.00	51.7
3	7.00	45.7

Samples of the two major peaks were collected with the Autoprep (20-ft SE-30 column, 110°) for nmr, infrared, and chemical analyses.

The 51.7% peak had a capillary boiling point of 154–155°. An infrared spectrum (carbon tetrachloride, carbon disulfide) shows, in addition to the bands expected for a saturated hydrocarbon, strong absorptions at 775, 760, 726, 698, and 670 cm^{-1}. The nmr spectrum shows a triplet at 8.92 (J = 7 cps, area 3), a complicated multiplet at *ca.* 8.1 (area 2), and a complicated multiplet at *ca.* 7.2 (area 2). The structure 1-bromo-1,1-dichlorobutane was assigned.

Anal. Calcd for $C_4H_7BrCl_2$: C, 23.33; H, 3.43; Br, 38.81; Cl, 34.44. Found: C, 23.52; H, 3.38; Br, 40.38; Cl, 32.20.

The 45.7% peak had a capillary boiling point of 181°. An infrared spectrum (carbon tetrachloride, carbon disulfide) shows, in addition to the bands expected for a saturated hydrocarbon, strong absorptions at 770, 747, 701, and 649 cm^{-1}. The nmr spectrum shows a doublet at 8.65 (J = 6.5 cps, area 3), a complicated multiplet at *ca.* 7.4 (area 1), a doublet at 6.45 (J = 6.5 cps, area 2), and a doublet at 3.81 (J = 4 cps, area 2). The structure 3-bromo-1,1-dichloro-2-methylpropane was assigned.

Anal. Calcd for $C_4H_7BrCl_2$: C, 23.33; H, 3.43; Br, 38.81; Cl, 34.44. Found: C, 23.47; H, 3.53; Br, 36.43; Cl, 36.12.

D-(+)-*sec*-Butylmercuric Bromide. (±)-*sec*-Butylmercuric bromide was resolved according to the procedure of Jensen, Whipple, Wedegaertner, and Landgrebe[41] with the following major changes: D-(+)-mandelic acid was used instead of L-(−)-mandelic acid; *sec*-butylmercuric bromide was used instead of *sec*-butylmercuric chloride.

Alcoholic potassium hydroxide (452 ml of 0.5 *M*, 0.226 mole) was added to (±)-*sec*-butylmercuric bromide (76.3 g, 0.226 mole) dissolved in 90 ml of warm, absolute ethanol. The potassium bromide was removed by suction filtration and was washed with absolute ethanol which was combined with the filtrate. D-(+)-Mandelic acid, $[\alpha]^{22}D$ +155° (24.2 g, 0.159 mole, Aldrich), was added to the filtered solution and the crude (+)-*sec*-butylmercuric (+)-mandelate which was formed was isolated by removal of the ethanol under reduced pressure with a rotary film evaporator. This crude material was dissolved in 28 ml of 1:1 glyme–dioxane mixture at 70°, allowed to cool to room temperature, and then cooled at 5° for *ca.* 48 hr to yield 58.2 g (0.142 mole) of the (+,+)-diastereomer. This was dissolved in 25 ml of 1:1 glyme–dioxane mixture at 70° and allowed to cool at 5° overnight to yield 49.3 g (0.121 mole) of the (+,+)-diastereomer, which was dissolved in 23 ml of 1:1 glyme–dioxane mixture at 70° and allowed to recrystallize at room temperature for 8 hr to give 36.7 g (0.0898 mole) of the (+,+)-diastereomer.

In like manner, 63.0 g (0.187 mole) of (±)-*sec*-butylmercuric bromide and 20 g (0.131 mole) of D-(+)-mandelic acid yielded, after three recrystallization, 32.6 g (0.0797 mole) of the (+,+)-diastereomer.

The combined (+)-*sec*-butylmercuric (+)-mandelate (69.3 g, 0.169 mole) was dissolved in 400 ml of methylene chloride, aqueous sodium bromide (340 ml of 1 *M*, 0.340 mole) was added, and the mixture was shaken vigorously. The layers were separated and the methylene chloride layer was treated with a similar sodium bromide solution. The aqueous layers were washed with methylene chloride, the combined organic layers dried over anhydrous magnesium sulfate, and the methylene chloride removed under reduced pres-

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(65) A. Lemke and D. Tischtschenko, *Chem. Zentr.*, **110**, 2397 (1939).

(66) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960).

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 $[\alpha]^{22}\mathrm{D}$ +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, $[\alpha]^{22}\mathrm{D}$ +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 $[\alpha]^{22}\mathrm{D}$ +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 $[\alpha]^{27}\mathrm{D}$ −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 $[\alpha]^{25}\mathrm{D}$ +2.96 ± 0.06° (*c* 34, ethanol). The nmr spectrum is consistent with the structure.

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

John A. Landgrebe and Ronald D. Mathis

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.

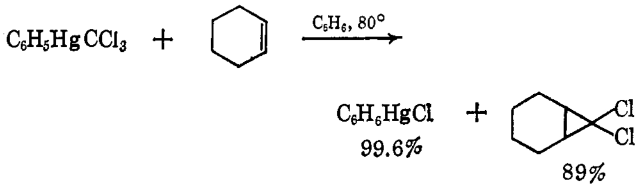
In view of the finding that the thermal decomposition of certain organosilicon compounds results in olefins from an α-elimination process[2] and that the decomposition of trichloromethyltrichlorosilane

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

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

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.

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

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