# The Attack of Dichlorocarbene on Dialkylmercurials. Studies of the Stereochemistry and Mechanism of Insertion into the β-Carbon-Hydrogen Bond

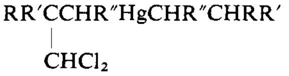
**John A. Landgrebe and Duane E. Thurman**[1]

*Contribution from the Department of Chemistry of the University of Kansas, Lawrence, Kansas 66044.* *Received September 16, 1968*

**Abstract:** The attack of dichlorocarbene on dialkylmercurials in which the alkyl function was ethyl, isopropyl, *n*-propyl, *sec*-butyl, *n*-butyl, isobutyl, 2-methylbutyl, *n*-amyl, isoamyl, cyclohexylmethyl, and cyclopropyl was carried out with the result that the ratio of β-C–H to C–Hg insertion increased from 0 to 9 as the β-C–H bond went from primary to tertiary. In two individual cases small amounts of products were isolated which corresponded to bis-β-C–H insertion and a combination of β-C–H plus C–Hg insertion, respectively. A very small amount of C–Hg insertion was noted for bis(cyclopropyl)mercury and no C–Hg insertion was found for diphenylmercury or dianisylmercury. Dichlorocarbene insertion into the β-C–H bond of bis((*S*)-methylbutyl)mercury was followed by degradation to (*R*)-α-ethylsuccinic acid, with over-all retention of configuration to the estimated extent of ~23%.

It is now well established that the attack of dichlorocarbene on a dialkylmercury compound produces, in addition to the expected insertion into the weak C–Hg bond,[2] a highly specific attack at the β-C–H bond[2b,3] which has also been noted in the case of certain derivatives of silicon and tin.[4] As has been previously stated,[2b] the known inertness of simple dialkylmercurials to strong bases and nucleophiles provides confidence that the observed products can be attributed to dichlorocarbene attack.

$$\underset{\mathbf{1}}{(RR'CHCH'')_2Hg} \xrightarrow{:CCl_2} \underset{\mathbf{2}}{RR'CHCHR''CCl_2HgCHR''CHRR'} +$$



3

$$\underset{\substack{| \\ CHCl_2}}{RR'C}HR''HgCHR''CHRR'$$

In view of the general difficulty with which dichlorocarbene (generated by the method of Parham[5]) inserts into ordinary aliphatic C–H bonds,[6] a thorough mechanistic study of the β-C–H insertion reaction in organometallic systems is of extreme interest.

In the following study, unless otherwise specified, dichlorocarbene was generated from an excess of ethyl trichloroacetate and sodium methoxide[5] in the presence of the dialkylmercurial in alkene-free pentane at 0° under a nitrogen atmosphere.[2b]

## Product Distribution Data

In general, the crude product mixtures, after being checked by thin layer chromatography and an nmr spectrum, were either subjected to C–Hg cleavage by bromine in carbon tetrachloride with subsequent isolation and identification of the bromides and/or were heated in order to decompose the C–Hg insertion product **2** to a vinyl chloride **4** and an alkylmercuric halide **5**[7] under conditions where the β-C–H insertion product was stable. Insertion product yields obtained in several cases from the bromine cleavage products were in the range of 30–67%.

$$\mathbf{2} \xrightarrow[100-150°]{} \underset{\mathbf{4}}{RR'CHCR''{=}CHCl} + \underset{\mathbf{5}}{RR'CHCHR''HgCl}$$

$$\mathbf{3} \xrightarrow[100-150°]{\not\ \ } $$

The nmr spectra of the β-C–H insertion products **3** were characterized by an absorption (singlet or doublet) in the range τ 3.90–4.40 which showed no $^{199}$Hg satellite peaks. In general the over-all nmr spectrum of either **2** or **3** was sufficiently complex[2b] that the chemical methods of structure identification outlined above and described in detail in the Experimental Section were essential. The halogenated insertion products were stable to methoxide

**Table I.** Relative Distribution of C–Hg and β-C–H Insertion Products by Dichlorocarbene Attack on $R_2Hg$[a]

| R group | β-C–H[b] | % C–Hg insert. | % β-C–H insert. |
|---|---|---|---|
| Ethyl | 1 | 100 | 0 |
| Isopropyl | 1 | 100 | 0 |
| *sec*-Butyl | 1, 2 | 100 | 0 |
| *n*-Propyl | 2 | 53 | 47 |
| *n*-Butyl | 2 | 67 | 33 |
| *n*-Amyl | 2 | 67 | 33 |
| Isoamyl | 2 | 65 | 35 |
| Isobutyl | 3 | 9 | 91 |
| 2-Methylbutyl | 3 | 6 | 94 |
| Cyclohexylmethyl | 3 | 13 | 87 |

[a] Product distribution data are from vpc analysis of the brominated reaction mixture. Absolute yields are not precisely measured but were in the range 30–60% as previously reported.[2] [b] 1 = primary, 2 = secondary, 3 = tertiary.

---

(1) Taken from the Ph.D. Dissertation of D. E. Thurman. Grateful acknowledgment of support by National Science Foundation Grant GP-6636 is given.

(2) (a) J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, **86**, 524 (1964); (b) *ibid.*, **88**, 3545 (1966).

(3) (a) J. A. Landgrebe and D. E. Thurman, *ibid.*, **89**, 4542 (1967); (b) *ibid.*, **90**, 6256 (1968).

(4) D. Seyferth and S. S. Washburne, *J. Organometal. Chem.*, **5**, 389 (1966).

(5) W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961).

(6) E. K. Fields, *ibid.*, **84**, 1744 (1962).

(7) J. A. Landgrebe and R. D. Mathis, *ibid.*, **88**, 3552 (1966).

ion under the conditions employed for generating the carbene.

Those reactions in which definitive values for the relative amount of C–Hg to β-C–H insertion were determined are summarized in Table I.

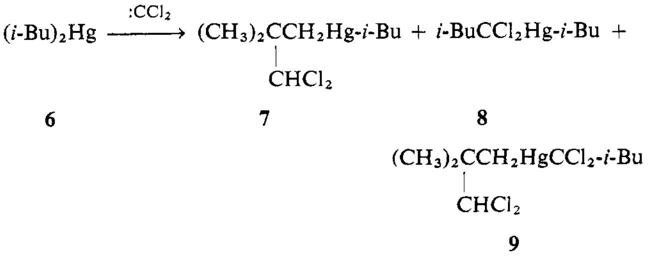
With the exception of di-*sec*-butylmercury (see Mechanistic Implications), there is a sharp increase in the ratio of β-C–H insertion to C–Hg insertion from 0 to 9 as one proceeds from a primary to a tertiary β-hydrogen atom. One example of special importance is diisoamylmercury in which, although the γ-hydrogen is tertiary, C–H insertion still takes place exclusively at the β position.

In an effort to determine qualitatively how the C–Hg and β-C–H insertion processes compete with the well-documented addition of dichlorocarbene to double bonds, the reactive intermediate was generated in the presence of di-*n*-butylmercury and cyclohexene to give an appreciable mixture of all three expected products.[8]

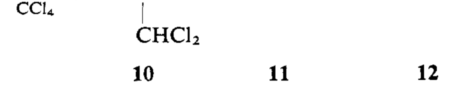
The results of the attack of dichlorocarbene on several mercurials, were not included in Table I. Dicyclopropylmercury was substantially recovered (*ca.* 90%) after an attempted insertion reaction, but a small amount of cyclopropylmercuric chloride was isolated which implied that some C–Hg insertion had taken place followed by the known thermal decomposition reaction.[7] No other products were identified.

Attempted reactions between dichlorocarbene and either diphenylmercury (in benzene or methylene chloride) or dianisylmercury (in methylene chloride or tetrahydrofuran) did not result in any isolable insertion products. The starting mercurials were recovered in approximately 66 and 77% yields, respectively, from the dark-colored reaction mixtures. Specific efforts to detect phenylmercuric chloride failed to indicate its presence.

It is of interest to note that in the previous work on C–Hg and β-C–H insertion,[2b] no observations were ever made of multiple insertion products. In the present study two such products have been found. The reaction of diisobutylmercury and dichlorocarbene, in addition to forming the expected β-C–H and C–Hg insertion products, 7 and 8, also produced a small amount of product 9 in which both C–Hg and β-C–H insertion had apparently taken place. Bromine cleavage of the crude product mixture produced 10, 11, and 12, none of which provides evidence for the existence of 9. Dibromide 12 presumably arises from a free-radical bromination process (see Experimental Section). The first hint of the existence of

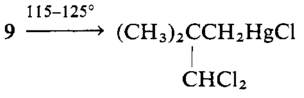


$$\underset{\mathbf{6}}{(i\text{-Bu})_2\text{Hg}} \xrightarrow{:\text{CCl}_2} \underset{\mathbf{7}}{(\text{CH}_3)_2\underset{\text{CHCl}_2}{\text{C}}\text{CH}_2\text{Hg-}i\text{-Bu}} + \underset{\mathbf{8}}{i\text{-BuCCl}_2\text{Hg-}i\text{-Bu}} + \underset{\mathbf{9}}{(\text{CH}_3)_2\underset{\text{CHCl}_2}{\text{C}}\text{CH}_2\text{HgCCl}_2\text{-}i\text{-Bu}}$$



$$\mathbf{6}+\mathbf{7}+\mathbf{8}+\mathbf{9} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \underset{\mathbf{10}}{(\text{CH}_3)_2\underset{\text{CHCl}_2}{\text{C}}\text{CH}_2\text{Br}} + \underset{\mathbf{11}}{i\text{-BuBr}} + \underset{\mathbf{12}}{(\text{CH}_3)_2\text{CBrCH}_2\text{Br}}$$

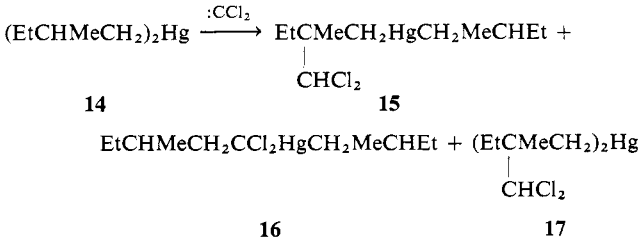
bis insertion product 9 was an nmr spectrum of the crude reaction mixture which showed a shoulder on the singlet at $\tau$ 4.40 normally attributed to the dichloromethyl group of a β-C–H insertion product. Pyrolysis of the crude product mixture at 115–125° followed by fractional crystallization of the alkylmercuric halides resulted in the isolation of a solid, mp 97.5–98.5°, which gave the correct analysis for $C_5H_9Cl_3Hg$ and on the basis of its nmr spectrum was unequivocally assigned structure **13**, a compound which we suggest was formed by thermal decomposition of **9**.[9] The nmr spectrum ($CCl_4$) of **13** exhibited a singlet at $\tau$ 4.30 (1 H, $CHCl_2$), a singlet at 7.90 (2 H, $J_{^{199}\text{Hg}-^{1}\text{H}_\alpha}$ = 198 Hz, $CH_2$), and a singlet at 8.70 (3 H, $J_{^{199}\text{Hg}-^{1}\text{H}_\gamma}$ = 16 Hz, $CH_3$).[10]



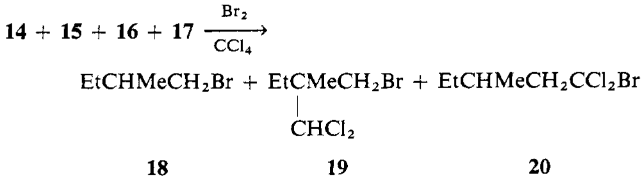
$$\mathbf{9} \xrightarrow{115\text{–}125°} \underset{\mathbf{13}}{(\text{CH}_3)_2\underset{\text{CHCl}_2}{\text{C}}\text{CH}_2\text{HgCl}}$$

Although an alternative possibility for the origin of **9** is a thermal redistribution reaction involving **7** and **8**, measurements by Reynolds and Daniel[12] have indicated that such equilibrations with simple alkyl and perfluoroalkyl groups require several days even at 100°. Because the insertion was carried out at 0° over a period of several hours, this explanation for the formation of **9** seems very unlikely.

The attack of dichlorocarbene on bis(2-methylbutyl)-mercury (**14**) in addition to producing expected products **15** and **16** formed a small amount of bis-β-C–H insertion product **17**. Careful bromine cleavage of the crude reaction mixture produced only bromides **18**, **19**, and **20** with the ratio of **19** and **20** to **18** being 2.27:1.0 instead of ⩽1:1 if only **14**, **15**, and **16** had been present in the starting material. Pyrolysis of the mixture of **14–17** resulted in 2-methylbutylmercuric chloride and a liquid mixture of



$$\underset{\mathbf{14}}{(\text{EtCHMeCH}_2)_2\text{Hg}} \xrightarrow{:\text{CCl}_2} \underset{\mathbf{15}}{\text{Et}\underset{\text{CHCl}_2}{\text{C}}\text{MeCH}_2\text{HgCH}_2\text{MeCHEt}} + \underset{\mathbf{16}}{\text{EtCHMeCH}_2\text{CCl}_2\text{HgCH}_2\text{MeCHEt}} + \underset{\mathbf{17}}{(\text{Et}\underset{\text{CHCl}_2}{\text{C}}\text{MeCH}_2)_2\text{Hg}}$$



$$\mathbf{14}+\mathbf{15}+\mathbf{16}+\mathbf{17} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \underset{\mathbf{18}}{\text{EtCHMeCH}_2\text{Br}} + \underset{\mathbf{19}}{\text{Et}\underset{\text{CHCl}_2}{\text{C}}\text{MeCH}_2\text{Br}} + \underset{\mathbf{20}}{\text{EtCHMeCH}_2\text{CCl}_2\text{Br}}$$

---

[8] Addition of dichlorocarbene to cyclohexene occurs much faster than β-C–H insertion in organotin and organosilicon derivatives.[4]

[9] Although it was suggested by a referee that **13** could also arise from the thermal decomposition of a bis-C–Hg insertion product, our unsuccessful attempts to detect such a product in the nmr spectra of

$$\text{RCCl}_2\text{HgCCl}_2\text{R} \xrightarrow[\Delta]{} 2\text{R}{=}\text{CHCl} + \text{HgCl}_2$$

$$\text{HgCl}_2 + \mathbf{7} \rightarrow \mathbf{13}$$

crude reaction mixtures from attack of dichlorocarbene on very simple dialkylmercurials[2b] would make this origin for **13** seem improbable.

[10] The field independence of the assigned $^{199}\text{Hg}-^{1}\text{H}_\gamma$ coupling was checked by running the spectrum at 100 MHz. The reported value for $J_{^{199}\text{Hg}-^{1}\text{H}_\gamma}$ for neopenylmercuric chloride in deuteriochloroform is 13.2 Hz.[11]

[11] G. Singh, *J. Organometal. Chem.*, **5**, 577 (1966).

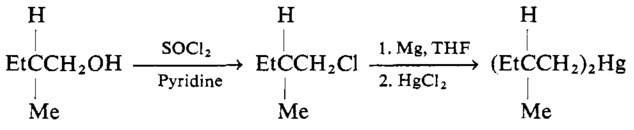
**14**, **15**, and **17** from which **17** was isolated. The material gave the correct analysis for $C_{11}H_{22}Cl_4Hg$ and showed a sharp singlet in the nmr at τ 4.25 with complex multiplets upfield.

For convenience a summary of $^{199}$Hg–H$_\alpha$ and $^{199}$Hg–H$_\beta$ coupling constants observed for the mercurials prepared in this study has been included as Table III of the Experimental Section. It should be noted that the value for $J_{^{199}\mathrm{Hg}-^{1}\mathrm{H}_\gamma}$ of 16.0 ± 0.5 Hz reported for structure **13** in carbon tetrachloride changes to 17.0 ± 0.5 Hz in chloroform-*d* and 14.0 ± 0.5 Hz in dimethyl-$d_6$ sulfoxide, a trend which is different from that observed by Singh[11] for neopentylmercuric halide.

## Stereochemistry

Because of the unique specificity of dichlorocarbene attack at the β position of simple dialkylmercurials, a study of the stereochemistry of this process was undertaken in order to clarify the mechanistic features of the reaction.

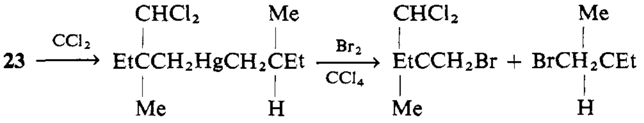
Bis((*S*)-2-methylbutyl)mercury (**23**) was a relatively ideal starting material because 94% of the dichlorocarbene attack took place at the β position (Table I) and because the absolute configuration of the optically active material has been established by simple chemical transformations which allow a direct correlation with (−)-isoleucine.[13] However, it should be emphasized that the maximum rotation for optically pure **23** is not known with certainty, *vide infra*.



$$\mathrm{Et}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2OH} \xrightarrow[\text{Pyridine}]{\mathrm{SOCl_2}} \mathrm{Et}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2Cl} \xrightarrow[\text{2. HgCl}_2]{\text{1. Mg, THF}} (\mathrm{Et}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2})_2\mathrm{Hg}$$

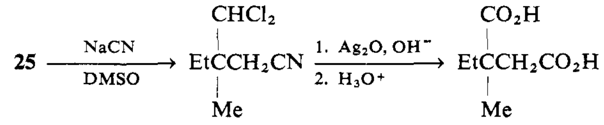
**21** **22** **23**

Treatment of 98% optically pure (*S*)-(−)-2-methylbutanol (Aldrich) with thionyl chloride and pyridine, according to the procedure of Brown and Groot,[14] resulted in chloride **22** with $[\alpha]^{25}\mathrm{D}$ +1.41° (neat, *l* 1, $d^{24}_{4}$ ~ 0.8836[15]) which corresponds to an optical purity of only 82.9% if we use the reported maximum rotation of $[\alpha]^{15}\mathrm{D}$ +1.70°.[16] Transformation of the chloride to a Grignard reagent[18] and subsequent treatment with mercuric chloride produced the desired active mercurial **23** with $[\alpha]^{27.5}\mathrm{D}$ +8.01° (neat, *l* 1, $d^{27.5}_{4}$ 1.657[20]), a value higher than any previous values reported for this compound.[21] The generation of dichlorocarbene in the presence of the active **23** followed by Florisil chromatography and bromine cleavage of mercurial **24** in carbon tetrachloride afforded (−)-1,1-dichloro-2-(bromomethyl)-2-methylbutane (**25**) $[\alpha]^{25}\mathrm{D}$ −0.67° (*c* 134, CHCl$_3$), and (+)-1-bromo-2-methylbutane (**26**), $[\alpha]^{25}\mathrm{D}$ +2.48° (*c* 6.2, CHCl$_3$). Although the optical purity of **26** can be calculated as approximately 61.3%,[23] this value is not useful for establishing the exact optical purity of mercurial **23** since bromide **26**, which was isolated by preparative vpc at 82°, has been reported to undergo partial racemization during atmospheric distillation.[23-25] In a second reaction sequence which started from **21**, trihalide **25** was formed with $[\alpha]^{25}\mathrm{D}$ −1.13 ± 0.3° (*c* 31, CHCl$_3$) and halide **26** was formed with $[\alpha]^{25}\mathrm{D}$ 2.89° (*c* 22.6, CHCl$_3$) or 71.4% optically pure.



$$\mathbf{23} \xrightarrow{\mathrm{CCl_2}} \mathrm{Et}\overset{\mathrm{CHCl_2}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2HgCH_2}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Et} \xrightarrow[\mathrm{CCl_4}]{\mathrm{Br_2}} \mathrm{Et}\overset{\mathrm{CHCl_2}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2Br} + \mathrm{BrCH_2}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Et}$$

**24** **25** **26**



$$\mathbf{25} \xrightarrow[\text{DMSO}]{\text{NaCN}} \mathrm{Et}\overset{\mathrm{CHCl_2}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2CN} \xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. Ag}_2\text{O, OH}^-} \mathrm{Et}\overset{\mathrm{CO_2H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2CO_2H}$$

**27** **28**

Optically active **25** with rotation −1.13° was then carefully converted to nitrile **27**, $[\alpha]^{25}\mathrm{D}$ −1.61° (*c* 5.27, CHCl$_3$), which upon oxidative hydrolysis produced (−)-α-methyl-α-ethylsuccinic acid with $[\alpha]^{25}\mathrm{D}$ −6.78 ± 0.3° (*c* 1.4, CHCl$_3$). In a second displacement reaction on the active trihalide with cyanide ion in dimethylformamide followed by oxidative hydrolysis, diacid **28** had $[\alpha]^{25}\mathrm{D}$ −6.04 ± 0.3° (*c* 0.99, CHCl$_3$).

The method of quasiracemates has been used to establish the relative configurations for a series of α-monosubstituted and α,α-disubstituted succinic acids,[26,27] including α-methylsuccinic acid, the absolute configuration of which has been determined by X-ray diffraction techniques.[28] Although it is now known that the sign and magnitude of rotation of diacid **28** are concentration dependent in chloroform,[29] use of recently published experimental data on this phenomenon[30] allows an unequivocal assignment of the configuration of active diacid **28** as *R*.[31] Therefore the insertion of dichlorocarbene has occurred with some retention of configuration. A plot of the concentration dependence of the rotation of

---

[12] G. F. Reynolds and S. R. Daniel, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburg, Pa., March 22–31, 1966, Abstract N-120.

[13] (a) W. S. Foues, *J. Amer. Chem. Soc.*, **76**, 1377 (1954); (b) E. J. Badin and E. Pacsu, *ibid.*, **67**, 1352 (1945); (c) J. Trommel and J. M. Bijvoet, *Acta Cryst.*, **7**, 703 (1954).

[14] H. C. Brown and C. Groot, *J. Amer. Chem. Soc.*, **64**, 2563 (1942).

[15] The density was estimated from the data of McKenzie and Clough[16] and Whitmore and Olewine.[17]

[16] A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 698 (1913).

[17] F. C. Whitmore and L. Olewine, *J. Amer. Chem. Soc.*, **60**, 2570 (1938).

[18] Lardicci and Conti[19] claim that less than 3% racemization occurs in this step.

[19] L. Lardicci and L. Conti, *Ann. Chim.* (Rome), **51**, 823 (1961).

[20] S. Murahashi, S. Nozakura, and S. Takeuchi, *Bull. Chem. Soc. Jap.*, **33**, 658 (1960).

[21] Values of $[\alpha]^{27.5}\mathrm{D}$ +7.65°[20] and $[\alpha]^{21}\mathrm{D}$ +7.82° (CHCl$_3$)[22] have been reported.

[22] G. Franckel and D. T. Dix, *J. Amer. Chem. Soc.*, **88**, 979 (1966).

[23] D. H. Brauns, *J. Res. Nat. Bur. Stand.*, *A*, **18**, 315 (1937).

[24] H. E. Heller, *J. Amer. Chem. Soc.*, **74**, 4858 (1952).

[25] G. Y. Brokaw and W. R. Brode, *J. Org. Chem.*, **13**, 194 (1948).

[26] J. Porath, *Arkiv Kemi*, **3**, 163 (1951).

[27] α-Substituted succinic acids of the same relative configuration were shown to have the same sign of rotation.

[28] A. T. McPhail, G. A. Sim, J. D. M. Asher, J. M. Robertson, and J. V. Silverton, *J. Chem. Soc.*, *B*, 18 (1966).

[29] See discussion in ref 3b.

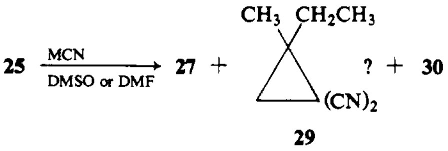
[30] See footnote 6 in G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

[31] It is useful to point out that in the original work on this diacid by Stallberg-Stenhagen[32] in which the rotations given in chloroform were not in exact agreement with those now reported by Krow and Hill,[30] and in which the rotation values were measured at a concentration close to that at which the change of sign occurs, the assigned configuration is fortuitously correct because the author converted his diacid sample to the dimethyl ester, the rotation sign of which is not concentration dependent.

[32] S. Stallberg-Stenhagen, *Arkiv Kemi*, **3**, 273 (1951).

diacid **28** suggests that at $c = 1.4$ g/100 ml the rotation of optically pure **28** should be *ca.* 30°. If we assume that the optical purity of mercurial **23** was 98%, insertion took place with approximately 23% retention and 79% racemization whereas if we assume the minimum possible optical purity for **23** of 71.4%, insertion took place with about 32% retention. While quantitative uncertainty remains, retention is clearly incomplete.[33]

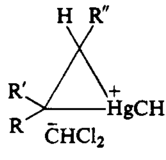
The reaction by which **25** was converted to **27** is worthy of some additional comments. In initial attempts to find the most ideal conditions for this simple displacement (Table II), an inactive sample of trihalide **25** produced, in addition to the desired nitrile **27**, two additional nitriles **29** and **30**, one of which has been tentatively identified as 1,1-dicyano-2-methyl-2-ethylcyclopropane (see Experimental Section).



## Mechanistic Considerations

Not only is the relative rate of β-C–H attack by dichlorocarbene highly favored over the rate of attack at any other C–H bond on the dialkylmercury compounds, but the ratio of β-C–H to C–Hg attack is unusually large in light of simple bond energy considerations. For example, although the reported bond dissociation energy for a secondary hydrogen in propane is 94 kcal/mol[34] and for the C–Hg bond of di-*n*-propylmercury is ~42 kcal/mol,[35] the ratio of insertion into the two bonds is approximately 1:1. This fact together with the observation that one obtains β attack even when the β-C–H bond is secondary and a *t*-C–H bond exists elsewhere along the alkyl chain would appear to rule out the possibility of a direct carbene insertion by any simple abstraction–recombination path either ionic or free radical.[37]

In order to account for the observations of extreme selectivity and lack of a high degree of stereospecificity, we suggest that a possible route to product **3** could involve the intervention of an intermediate mercurinium ion pair **35**[41] which might be expected to open to give both retained and inverted product as observed. No products have ever been found which would have resulted from methylene chloride anion attack at the least substituted ring carbon atom in structure **35** in analogy with the observed product distribution in oxymercuration reactions,[41d,42] and the observed direction of ring openings of protonated epoxides.[43]



**35**

$(RR'CHCHR'')_2\overset{\pm}{Hg}\overset{\mp}{C}Cl_2$

**36**

An ion pair such as **35** could arise from a direct attack of dichlorocarbene on the β-C–H bond with simultaneous mercury participation or perhaps *via* the rearrangement of an initially formed dialkylmercury–dichlorocarbene complex such as structure **36**.[44] Although the intermediacy of an ylide such as **36** seems reasonable in view of the implication of such species in a variety of carbene reactions with compounds containing sulfur,[45] nitrogen,[45,46] silicon,[4] and tin,[4] it is not essential in order to explain the currently available data.

One interesting reaction requires further comment. Although there is a β-methylene group in di-*sec*-butylmercury, no β-C–H insertion was observed for this compound. It is not clear whether this unique result is caused by an unusually reactive C–Hg bond or an unusually unreactive β-methylene group. One might infer from the increase in thermal stability on going from di-*t*-butylmercury[47] to the bridgehead system, di-4-camphylmercury,[48] that there could be a buttressing interaction between α-alkyl groups and the large mercury atom, which would weaken the C–Hg bond. This problem is now under experimental investigation.

The complete lack of C–Hg insertion products noted for diphenylmercury and dianisylmercury is consistent with the higher C–Hg bond energy for these compounds compared with dialkylmercurials[49] but should be contrasted with results for the cleavage of the carbon–mercury bond by other electrophiles such as hydrogen chloride in

---

[33] Dr. John Jacobus, Department of Chemistry, Princeton University, has communicated to us that he has repeated our dichlorocarbene insertion on mercurial **23** and has obtained approximately 50% retention, 50% racemization in the product.

[34] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 127.

[35] The value used is that measured for diethylmercury.[36]

[36] A. S. Carson, E. M. Carson, and B. Wilmhurst, *Nature*, **170**, 320 (1952).

[37] A free-radical process also seems less likely in view of the evidence that dichlorocarbene is a singlet in its ground state.[38,39] However, there appears to be evidence for free-radical abstraction processes by singlet divalent carbon species in certain circumstances.[40]

[38] L. D. Wescott and P. S. Skell, *J. Amer. Chem. Soc.*, **87**, 1721 (1965), and references cited therein.

[39] J. Hine, "Divalent Carbons," The Ronald Press Co., New York, N. Y., 1964, pp 44–46.

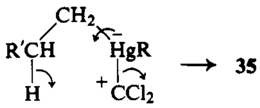
[40] D. W. Setzer, R. Littrell, and J. C. Hassler, *J. Amer. Chem. Soc.*, **85**, 2062 (1963).

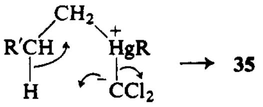
[41] (a) R. E. Dessy and W. Kitching, *Advan. Organometal. Chem.*, **4**, 268 (1966); (b) K. Ichikawa, K. Nishimura, and S. Takayama, *J. Org. Chem.*, **30**, 1593 (1965); (c) N. S. Zefirow, *Russ. Chem. Rev.*, **34**, 527 (1965); (d) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[42] F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, N. Y., 1921, p 115.

[43] E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc. New York, N. Y., 1956, p 107.

[44] One can envision either nucleophilic attack by dichlorocarbene to produce a trivalent negatively charged mercury salt or electrophilic attack by the divalent species which would imply electron donation from mercury to carbon. Either ylide could rearrange to **35** as shown.





[45] (a) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); (b) *ibid.*, **30**, 728 (1965); (c) *ibid.*, **30**, 3181 (1965); (d) W. E. Parham and E. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961); (e) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964); (f) W. E. Parham and S. H. Groen, *ibid.*, **31**, 1694 (1966); (g) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960); (h) S. Searles, Jr., and R. E. Mann, *Tetrahedron Letters*, 2899 (1965).

[46] (a) Reference 39, p 63; (b) P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.*, **23**, 1599 (1958); (c) M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959); (d) M. B. Frankel, H. Feuer, and J. Blank, *Tetrahedron Letters*, **7**, 5 (1959).

[47] C. S. Marvel and H. O. Calvery, *J. Amer. Chem. Soc.*, **45**, 822 (1923).

[48] S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956).

[49] The C–Hg bond dissociation energy for diphenylmercury is 60 kcal/mol[36] compared to 42 kcal/mol for diethylmercury.[34]

dimethyl sulfoxide in which diphenylmercury was more reactive than dialkylmercurials.[50] The mechanism of the hydrogen chloride cleavage of the carbon–mercury bond has been extensively discussed in terms of a four-center transition state.[51]

## Experimental Section[52]

**Materials.** Dialkyl and diarylmercurials were prepared and purified by standard procedures.[53-55] The preparation[53] of previously unreported bis(cyclohexylmethyl)mercury afforded a distillate, bp 133° (0.7 mm) which was further purified by passage through Florisil (44% yield based on mercuric bromide). The nmr spectrum showed a doublet at τ 8.97 ($J$ = 6.0 Hz) superimposed on a very broad multiplet from τ 7.7–9.1, and $J_{^{199}\mathrm{Hg}-\mathrm{H}_\alpha} = 92$ Hz. The product was treated with mercuric chloride in ether followed by the addition of ethanol and evaporation of the solvent to give crystals of cyclohexylmethylmercuric chloride. Recrystallization from ether–petroleum ether (bp 30–60°) gave long brittle needles, mp 72–73°. The nmr spectrum showed the partially resolved doublet at 7.90 superimposed on a broad multiplet from 7.7–9.2, and $J_{^{199}\mathrm{Hg}-\mathrm{H}_\alpha} = 200$ Hz.

*Anal.* Calcd for $C_7H_{13}ClHg$: C, 25.23; H, 3.93; Cl, 10.64. Found: C, 25.27; H, 3.87; Cl, 10.60.

**Generation of Dichlorocarbene in the Presence of Di-*n*-amylmercury.** Di-*n*-amylmercury (17.23 g, 0.05 mol), sodium methoxide (10.8 g, 0.20 mol, Matheson Coleman and Bell), and 40 ml of alkene-free pentane[2b] were stirred at 0° ($N_2$) while ethyl trichloroacetate (19.1 g, 0.10 mol, Eastman Kodak) in pentane (15 ml) was added (20–30 min). The mixture was stirred in an ice bath and allowed to come to room temperature overnight. The cold solution was hydrolyzed with 50 ml of water and the aqueous layer then extracted with pentane which was dried ($MgSO_4$) and evaporated. Methyl ethyl carbonate was removed from the brown product under vacuum. Tlc of the crude mixture indicated unreacted di-*n*-amylmercury and two partially superimposed spots of smaller $R_f$ values. The brown mixture was passed through a column of Florisil to give, after removal of the petroleum ether, a colorless liquid which displayed an nmr doublet at 4.12 ($J$ = 3.0 Hz) and three spots on tlc.

A small portion of the product heated at 140° for several hours was treated with pentane and filtered to give *n*-amylmercuric chloride, which was recrystallized from hot ethyl acetate, plates, mp 124° (lit.[56] mp 127°). The filtrate was passed through a column of Florisil and the solvent evaporated. Tlc indicated two spots. Molecular distillation (bath at 60–80° (0.15–3 mm)) produced a colorless heavy liquid shown by tlc to contain only a trace of di-*n*-amylmercury. An nmr spectrum showed a doublet at 4.12 ($J$ = 3.0 Hz) and complex multiplets at 7.3–9.2. The structure *n*-amyl-β-(dichloromethyl)amylmercury was tentatively assigned. Because the elemental analysis was high in both carbon and hydrogen due to the presence of small amounts of the starting dialkylmercury compound, further structural evidence was obtained by bromine cleavage of the original insertion mixture.

*Anal.* Calcd for $C_{11}H_{22}Cl_2Hg$: C, 31.03; H, 5.22. Found: C, 32.44; H, 5.40.

A portion of the insertion mixture was treated with bromine and carbon tetrachloride at 0°.[2b,57] After the mixture was filtered and treated with aqueous sodium bicarbonate solution, the organic layer was washed with water, dried ($NaSO_4$), and the low-boiling material distilled. An nmr spectrum indicated the presence of *n*-amyl bromide. Vpc (10 ft, QF-1, 110°) of the resulting higher boiling material showed in addition to *n*-amyl bromide, two peaks at longer retention times with relative areas of 67 and 33%, respectively, which were collected with an Autoprep chromatograph (10 ft, QF-1/XF-1150, 130°).

The 67% peak, identified as 1-bromo-1,1-dichlorohexane, showed an nmr spectrum which exhibited a multiplet at 7.18 (2 H), a triplet at 9.02 ($J$ = 7 Hz, 2 H), and multiplets from 8.0 to 8.9 (6 H).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74. Found: C, 30.97; H, 4.75.

Treatment of the trihalide with silver nitrate in aqueous acetone by the procedure of Mathis[2b] afforded *n*-caproic acid. An nmr spectrum was identical with that of an authentic sample.

The 33% peak, identified as 1,1-dichloro-2-(bromomethyl)-pentane, showed an nmr spectrum which exhibited a doublet at 3.94 ($J$ = 4 Hz, 1 H), a doublet at 6.45 ($J$ = 6 Hz, 2 H), a multiplet at 7.7 (1 H), a multiplet at 8.4 (4 H) and a multiplet at *ca.* 8.90 (3 H).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74; Cl, 30.31; Br, 34.15. Found: C, 30.92; H, 4.85; Cl, 30.28; Br, 34.00.

**Generation of Dichlorocarbene in the Presence of Di-*n*-butylmercury.** Ethyl trichloroacetate (19.1 g, 0.10 mol) in pentane (20 ml), di-*n*-butylmercury (15.7 g, 0.05 mol), and sodium methoxide (10.8 g, 0.20 mol) were treated as previously described and worked up in the usual manner. Tlc showed unreacted dialkylmercury compound and two partially superimposed components. An nmr spectrum exhibited a doublet at 4.12 ($J$ = 3 Hz).

A portion of the product mixture heated at 125–130° for 3 hr produced *n*-butylmercuric chloride, mp 125.5° (lit.[58] mp 125.5°). An nmr spectrum was identical with that of an authentic sample. Tlc of the residual liquid showed only one spot in addition to unreacted dialkylmercury compound. Molecular distillation (bath at 60–80° (0.15–0.5 mm)) afforded a heavy liquid distillate which contained only a small amount of the dialkylmercury compound. The nmr spectrum which showed a doublet at 4.12 ($J$ = 3 Hz) and complex upfield multiplets was assigned to *n*-butyl-β-(dichloromethyl)butylmercury. Because the elemental analysis was high in both C and H because of the presence of a small amount of the starting materials, the insertion compound was cleaved with bromine and the resulting bromine cleavage products carefully identified.

*Anal.* Calcd for $C_9H_{18}Cl_2Hg$: C, 27.41; H, 4.56. Found: C, 28.72; H, 4.73.

A vpc (10 ft, QF-1, 110°) of the crude bromine cleavage products obtained as previously described showed two peaks in addition to *n*-butyl bromide, each with a longer retention time and with relative areas of 67 and 33%, respectively. Samples of the peaks were collected with an Autoprep (10 ft, Carbowax 20 M, 130°).

The 67% peak, identified as 1-bromo-1,1-dichloropentane, showed an nmr spectrum which exhibited a multiplet at 7.25 (2 H), an unsymmetrical triplet at 8.99 ($J$ = 6 Hz, 3 H), and a multiplet at 8.36 (4 H).

The 33% peak, identified as 1,1-dichloro-2-(bromomethyl)butane, showed an nmr spectrum which exhibited a doublet at 3.98 ($J$ = 4 Hz, 1 H), a doublet at 6.45 ($J$ = 6 Hz, 2 H), an unsymmetrical triplet at 8.97 ($J$ = 6.5 Hz, 3 H), and a multiplet centered at 8.09 (3 H).

*Anal.* Calcd for $C_5H_9Cl_2Br$: C, 27.30; H, 4.12. Found: C, 26.75; H, 3.93.

Treatment of the β-insertion product isolated from the pyrolysis

---

(50) R. E. Dessy, G. F. Reynolds, and J. Y. Kim, *J. Amer. Chem. Soc.*, **81**, 2683 (1959).

(51) (a) R. E. Dessy and Y. K. Lee, *ibid.*, **82**, 689 (1960); (b) R. E. Dessy and J. Y. Kim, *ibid.*, **83**, 1167 (1961); (c) R. E. Dessy, W. L. Budde, and C. J. Woodruff, *ibid.*, **84**, 1172 (1962); (d) see critical discussion in F. R. Jensen, "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, p 51.

(52) All melting points (capillary) and boiling points are uncorrected. Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer at 60 MHz, unless otherwise specified, and with a Varian Model HA-100 spectrometer at 100 MHz. Chemical shifts are expressed in parts per million (ppm) relative to internal tetramethylsilane, which is given the arbitrary position of 10 (τ scale). All nmr and infrared spectra were determined in carbon tetrachloride unless otherwise specified. Optical rotations were determined with a Bodenseewerk/Perkin-Elmer Model 141 polarimeter equipped with a digital readout. Rotations were measured at the sodium D line, 589 mμ, in a water-jacketed microcell (*l* 1 dm). Concentrations are expressed in grams/100 ml. Chemical analyses were performed either by Huffman Laboratory Inc., Wheat Ridge, Colo. or on an F & M Model 185 carbon–hydrogen–nitrogen analyzer by the Department of Pharmacy, University of Kansas, Lawrence, Kan. Mass spectral data were obtained with a Nuclide mass spectrometer at 70 eV. Thin layer chromatography was effected with Brinkman silica gel G on microscope slides, cyclohexane development, and identification of spots with iodine. Column chromatography was effected with 100–200 mesh Florisil and petroleum ether (bp 30–60°) elution, unless otherwise specified.

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

(54) S. W. Winstein and T. G. Traylor, *J. Amer. Chem. Soc.*, **78**, 2599 (1956).

(55) F. Challenger, *J. Chem. Soc.*, 894 (1938).

(56) C. M. McCloskey and G. H. Coleman in "Organic Synthesis," Coll. Vol. III, E. C. Horning, Ed., John Wiley & Sons, Inc., New York, N. Y., 1955, p 221.

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

(58) C. S. Marvel and C. G. Gould, *ibid.*, **44**, 156 (1922).

reaction with excess bromine and carbon tetrachloride afforded only a mixture of *n*-butyl bromide and 1,1-dichloro-2(bromomethyl)-butane. The carbene insertion reaction was repeated and produced identical results.

**Generation of Dichlorocarbene in the Presence of Diisoamylmercury.** Ethyl trichloroacetate (19.1 g, 0.10 mol) diisoamylmercury (10.8 g, 0.03 mol), and sodium methoxide were treated as previously described. Tlc showed unreacted starting material in addition to two overlapping spots. An nmr spectrum exhibited a doublet at 3.90 ($J = 3$ Hz).

A portion of the insertion mixture heated at 140° for several hours produced isoamylmercuric chloride, mp 94.5°, which has an nmr spectrum identical with that of an authentic sample. Bromine cleavage in carbon tetrachloride produced isoamyl bromide and two peaks of longer vpc retention time with relative areas 65 and 35%, respectively. Samples were collected with an Autoprep (10 ft, QF-1/XF-1150, 135°).

The 65% peak, identified as 1-bromo-1,1-dichloro-4-methylpentane, showed an nmr spectrum which exhibited a multiplet at 7.25 (2 H), a doublet at 9.0 ($J = 5$ Hz, 6 H), and a multiplet at 8.31 (3 H).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74. Found: C, 31.11; H, 4.79.

Treatment of the trihalide with silver nitrate in aqueous acetone by the method described previously[2b] afforded isocaproic acid, which exhibited infrared absorptions at 1709 (C=O) and 1385 cm$^{-1}$ ($(CH_3)_2CH-$ doublet) (lit.[59] 1709 and 1380 cm$^{-1}$).

The 35% peak, identified as 1,1-dichloro-2-(bromomethyl)-3-methylbutane, showed an nmr spectrum which exhibited a doublet at 3.89 ($J = 3.5$ Hz, 1 H), a doublet at 8.90 ($J = 6$ Hz, 6 H), a multiplet at 6.42 (2 H), and a multiplet at 7.72 (2 H).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74; Cl, 30.31; Br, 34.15. Found: C, 30.92; H, 4.85; Cl, 30.28; Br, 34.00.

**Generation of Dichlorocarbene in the Presence of Diethylmercury.** Ethyl trichloroacetate (19.1 g, 0.10 mol), diethylmercury (12.3 g, 0.048 mol), and sodium methoxide (10.8 g, 0.20 mol) were treated as previously described. An nmr spectrum showed no absorption in the 3.8–4.5 region.

A portion of the insertion mixture was heated at 100–110° for several hours and worked up to give ethylmercuric chloride, mp 192° (lit.[60] mp 192.5°).

The insertion mixture was treated with excess bromine in carbon tetrachloride to give ethyl bromide and 1-bromo-1,1-dichloropropane. A preparative sample was collected (20 ft, SE-30/E-600, 100°). The nmr spectrum showed a quartet at 7.20 ($J = 7$ Hz, 2 H) and a triplet at 8.69 ($J = 7$ Hz, 3 H). A $^{199}$Hg satellite quartet corresponding to $J_{^{199}\mathrm{Hg}-\mathrm{H}_\beta} = 70$ Hz was observed.

*Anal.* Calcd for $C_3H_5Cl_2Br$: C, 18.78; H, 2.63; Cl, 36.95; Br, 41.64. Found: C, 19.01; H, 2.72; Cl, 36.73; Br, 41.80.

Vpc analysis of the bromine cleavage product showed a ratio of ethyl bromide to 1-bromo-1,1-dichloropropane which corresponded to 60% yield of the original carbon–mercury insertion product.

**Generation of Dichlorocarbene in the Presence of Bis(cyclohexylmethyl)mercury.** Ethyl trichloroacetate (19.1 g, 0.10 mol), bis(cyclohexylmethyl)mercury (21.2 g, 0.0537 mol), and sodium methoxide (10.8 g, 0.20 mol) were treated in the usual manner. The nmr spectrum of the resulting viscous liquid showed a singlet at 4.21 and a singlet at 8.50 superimposed on a broad multiplet at 7.90–9.20.

The insertion mixture was treated with excess bromine in carbon tetrachloride. Vpc (10 ft, Carbowax 20M, 120°) showed two products with relative areas of 13.1 and 86.9%, respectively. A sample of the 86.9% peak collected on the chromatograph was identified as 1-(bromomethyl)-1-(dichloromethyl)cyclohexane. The nmr spectrum showed a singlet at 4.04 (1 H), a singlet at 6.29 (2 H), and a multiplet at 8.0–9.0 (10 H).

*Anal.* Calcd for $C_8H_{13}Cl_2Br$: C, 36.95; H, 5.04. Found: C, 37.36; H, 5.00.

The 13.1% component of the product mixture was not isolated but was tentatively identified as 1-bromo-1,1-dichloro-2-cyclohexylethane. An nmr spectrum of the mixture displayed a doublet at 7.29 ($J = 4.5$ Hz) among other absorptions.

**Generation of Dichlorocarbene in the Presence of Diisobutylmercury.** Ethyl trichloroacetate (19.1 g, 0.10 mol), diisobutylmercury (15.7 g, 0.05 mol), and sodium methoxide (10.8 g, 0.20 mol) were treated as previously described. An nmr spectrum of the crude product showed a singlet with a shoulder at 4.40 and complex multiplets upfield. Tlc showed unreacted dialkylmercury compound and at least two (possibly three) overlapping spots of smaller $R_f$ values. The mixture of insertion products was heated at 115–125° (6 hr) and worked up to give a white solid and a liquid which showed a sharp singlet in the nmr at 4.40. Tlc of the liquid showed what appeared to be two superimposed spots in addition to one for diisobutylmercury.

The solids recovered from the pyrolysis mixture had a mp 43–45° and an nmr spectrum which indicated isobutylmercuric chloride to be the major component. A minor component was present which displayed singlets at 4.25 and 8.65. Isobutylmercuric chloride prepared from diisobutylmercury and mercuric chloride had a mp 48°. The solid mixture obtained from a second reaction was fractionally crystallized from chloroform–ethanol and after six recrystallizations produced a small amount of fibrous needles, mp 96.5–97.5°. An nmr spectrum showed a trace of isobutylmercuric chloride. Recrystallization (ether–petroleum ether) gave needles, mp 97.5–98.5°. Nmr spectral assignments are given in the Discussion. The structure β-(dichloromethyl)isobutylmercuric chloride was assigned.

*Anal.* Calcd for $C_5H_9Cl_3Hg$: C, 15.97; H, 2.41; Cl, 28.28. Found: C, 15.84; H, 2.40; Cl, 28.05.

Bromine cleavage of the solid, mp 43°, from the pyrolysis reaction produced a small amount of 1,1-dichloro-2,2-dimethyl-3-bromopropane in addition to some of the other products described in subsequent paragraphs.

A portion of the insertion mixture was treated with excess bromine and carbon tetrachloride as described previously. Vpc (10 ft, SE-30, 125°) indicated three peaks in addition to one for isobutyl bromide. The two peaks with longest retention times had relative areas of 9 and 91%, respectively. The 91% peak, bp 49° (0.08 mm), was identified as 1,1-dichloro-3-bromo-2,2-dimethylpropane. The nmr spectrum showed singlets at 4.14 (1 H), 6.55 (2 H), and 8.77 (6 H).

*Anal.* Calcd for $C_5H_9Cl_2Br$: C, 27.30; H, 4.12. Found: C, 28.01; H, 3.78.

In addition to the previously mentioned peaks, the nmr spectrum of the mixture showed a doublet at 7.26 ($J = 5.5$ Hz, 2 H) and a doublet at 8.88 ($J = 6$ Hz, 6 H) attributed to the 9% product peak, 1-bromo-1,1-dichloro-3-methylpropane.

A collected sample (preparative vpc, 10 ft, SE-30, 125°) of the third product peak gave an nmr spectrum which showed two sharp singlets at 6.14 (1 H) and 8.13 (3 H) and was identified as 1,2-dibromo-2-methylpropane which has a published identical spectrum.[61]

**Cleavage of Diisobutylmercury with Bromine.** Diisobutylmercury (15.7 g, 0.05 mol) was treated with bromine (16 g, 0.10 mol) in carbon tetrachloride as previously described. The product mixture contained 92.3% isobutyl bromide and 7.7% 1,2-dibromo-2-methylpropane.

**Treatment of Isobutyl Bromide with Bromine.** Isobutyl bromide treated with bromine and carbon tetrachloride for 20 hr at 25° afforded a mixture of 20% isobutyl bromide and 80% 1,2-dibromo-2-methylpropane.

**Generation of Dichlorocarbene in the Presence of Bis(2-methylbutyl)mercury.** Ethyl trichloroacetate (38.2 g, 0.20 mol), bis(2-methylbutyl)mercury (31.46 g, 0.10 mol), and sodium methoxide (21.6 g, 0.40 mol) were treated as previously described and the crude product was purified by passage through a column of Florisil. An nmr spectrum of the products showed a singlet at 4.30 in addition to more complex multiplets upfield. Tlc showed unreacted dialkylmercury compound and several overlapping spots of smaller $R_f$ values.

A portion of the insertion mixture heated at 120° for several hours produced 2-methylbutylmercuric chloride, mp 48°, and a liquid mixture. 2-Methylbutylmercuric chloride prepared from bis(2-methylbutyl)mercury and mercuric chloride had mp 50° after several recrystallizations from chloroform–ethanol. Vacuum distillation of the liquid mixture produced a fraction at 60° (0.2 mm) which showed two overlapping spots by tlc. Another fraction at 120° (0.2 mm) gave a single spot on tlc which corresponded to one of the overlapping spots from a previous chromatogram. An nmr spectrum of the latter material showed a singlet at 4.25 and complex

---

(59) "Sadtler Standard Infrared Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum 2706.

(60) R. Crymble, *J. Chem. Soc.*, **105**, 668 (1914).

(61) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Varian NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, Spectrum 412.

multiplets upfield. The structure bis(β-dichloromethyl-β-methylbutyl)mercury was assigned.

*Anal.* Calcd for $C_{11}H_{22}Cl_4Hg$: C, 26.60; H, 4.46. Found: C, 26.69; H, 4.55.

A portion of the insertion mixture was treated with excess bromine in carbon tetrachloride as previously described. Vpc (15 ft, QF-1, 130°) showed, in addition to 1-bromo-2-methylbutane, three peaks at longer retention times, the last two with relative areas of 6 and 94%, respectively. Samples of the three peaks were collected with an Autoprep chromatograph (10 ft, QF-1, XF-1150, 105°).

The peak with longest retention time, identified as 1,1-dichloro-2-(bromomethyl)-2-methylbutane, gave an nmr spectrum which showed a singlet at 4.10 (1 H), a singlet at 6.52 (2 H), a singlet at 8.82 (3 H), a multiplet at 8.28 (2 H), and a triplet at 9.08 ($J$ = 7 Hz, 3 H). Fractional distillation of the insertion mixture afforded pure material, bp 49° (0.4 mm).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74. Found: C, 30.85; H, 4.77.

The 6% product, identified as 1-bromo-1,1-dichloro-3-methylpentane, showed an nmr spectrum which exhibited a multiplet at 7.25 (2 H), a multiplet at 8.40 (3 H), a doublet at 8.85 ($J$ = 6.5 Hz, 3 H), and a symmetrical triplet at 9.05 ($J$ = 5.5 Hz, 3 H).

*Anal.* Calcd for $C_6H_{11}Cl_2Br$: C, 30.80; H, 4.74; Cl, 30.31; Br, 34.15. Found: C, 30.64; H, 4.52; Cl, 30.03; Br, 33.98.

The third peak, identified as 1,2-dibromo-2-methylbutane,[62] gave an nmr spectrum which showed a singlet at 6.17 (2 H), a singlet at 8.18 superimposed on a quartet (total 5 H), and a triplet at 8.93 ($J$ = 6.5 Hz, 3 H).

In a second insertion reaction in which the bromine cleavage process was kept at 0°, no free-radical bromination product, 1,2-dibromo-2-methylbutane, was observed. Vpc (15 ft, QF-1, 130°) of the halide mixture showed a 2.27:1 ratio of 1-bromo-1,1-dichloro-3-methylpentane and 1,1-dichloro-2-(bromomethyl)-2-methylbutane to 1-bromo-2-methylbutane.

**Generation of Dichlorocarbene in the Presence of Dicyclopropylmercury.** Ethyl trichloroacetate (19.1 g, 0.01 mol), dicyclopropylmercury (9.6 g, 0.034 mol), and sodium methoxide (10.8 g, 0.20 mol) were treated as previously described. A portion of the insertion mixture was passed through a column of Florisil to give a colorless liquid which showed complex multiplets at 8.3–10.2 in the nmr. The eluent from the column (methylene chloride) gave after evaporation a small amount of yellow white residue, mp 175–180°, which was recrystallized from ethanol to give plates, mp 185–186°, identified as cyclopropylmercuric chloride (lit.[63] mp 186–187°).

In a separate reaction 90% of the starting dicyclopropylmercury was recovered in a vacuum distillation of the crude product mixture. A small amount of cyclopropylmercuric chloride was also noted.

Cleavage of the crude product mixture with bromine and carbon tetrachloride as previously described failed to yield any material which exhibited the properties expected from simple carbon-mercury insertion in the original dicyclopropylmercury compound by dichlorocarbene.

**Generation of Dichlorocarbene in the Presence of Diarylmercury.** Ethyl trichloroacetate (15.32 g, 0.08 mol), diphenylmercury (14.18 g, 0.04 mol), and sodium methoxide (8.64 g, 0.61 mol) were treated as previously described in benzene. Removal of benzene from the product followed by recrystallization from chloroform–ethanol gave diphenylmercury, mp 124–125° (lit.[64] mp 125°) in 66% of the original amount. Phenylmercuric chloride was shown to be absent by testing a benzene solution of the brown solid with 1 $M$ sodium thiosulfate solution followed by the addition of aqueous potassium iodide.[2b] Spectral data on the recovered diphenylmercury were identical with those of the starting material. In a second reaction carried out in methylene chloride parallel results were obtained.

A similar reaction on dianisylmercury carried out in methylene chloride and in tetrahydrofuran gave exactly the same results; 77% of the starting dianisylmercury was recovered.

**Generation of Dichlorocarbene in the Presence of Diethylmercury and Cyclohexene.** Ethyl trichloroacetate (4.78 g, 0.025 mol), diethylmercury (10.0 g, 0.0386 mol), cyclohexene (3.10 g, 0.0386 mol), and sodium methoxide (2.70 g, 0.05 mol) were treated in pentane as previously described. After removal of the pentane the resulting liquid was vacuum distilled to give methyl ethyl carbonate and a mixture of diethylmercury and 7,7-dichloronorcarane (by nmr). Solid ethylmercuric chloride collected in the distillation head. Parallel results were obtained from the generation of dichlorocarbene in the presence of di-*n*-butylmercury and cyclohexene.

**Attempted Identification of Methylene Chloride in the Reaction of Dichlorocarbene with Diisobutylmercury.** Dichlorocarbene was generated in the usual manner in the presence of diisobutylmercury (7.1 g, 0.0226 mol) in pentane. After the reaction mixture had been stirred several hours at 0° and quenched with water, the pentane solution was distilled and all low-boiling material collected up to a temperature of 100° and subjected to vpc analysis (20 ft, SE-30/E-600, 40°). No methylene chloride could be detected.

**(*S*)-(+)-1-Chloro-2-methylbutane.** (*S*)-(−)-2-Methylbutanol (30 g, 0.34 mol, 98% optically pure, Aldrich Chemical Company) in pyridine (26.9 g, 0.34 mol) at −10° was treated with thionyl chloride (58.6 g, 0.51 mol) according to the procedure of Brown and Groot.[14] Work-up and distillation afforded (*S*)-(+)-1-chloro-2-methylbutane (30,0 g, 0.28 mol, 82.8%), bp 96–98° (lit.[14] bp 99.5°). The product had $[\alpha]^{25}\mathrm{D}$ +1.41° (neat, $l$ 1 dm, $d^{25}{}_4$ 0.8836 estimated[16,17]), corresponding to 82.9% optical purity.[16] The nmr spectrum was consistent with the structure and indicated no impurity.

**(+)-Bis((*S*)-2-methylbutyl)mercury.** (*S*)-(+)-1-Chloro-2-methylbutane (16.8 g, 0.157 mol) and magnesium turnings (9.73 g, 0.4 g-atom) in tetrahydrofuran (150 ml) were treated with ethylene dibromide (3.76 g, 0.20 mol) in tetrahydrofuran (50 ml). Treatment of the filtered Grignard reagent with mercuric chloride (17.6 g, 0.065 mol) in tetrahydrofuran (80 ml), work-up, and vacuum distillation afforded (+)-bis((*S*)-2-methylbutyl)mercury (8.9 g, 0.0258 mol), bp 68° (0.35 mm) (lit.[22] 94.0–96.0° (1 mm)), or 40% yield based on mercuric chloride. The product had $[\alpha]^{27.5}\mathrm{D}$ +8.01° (neat, $l$ 1 dm, $d^{27.5}{}_4$ 1.657[20]). In a second reaction the mercurial product had $[\alpha]^{27.5}\mathrm{D}$ +8.02° (neat, $l$ 1 dm, $d^{27.5}{}_4$ 1.657[20]). The compound did not lose activity on standing for long periods of time or when distilled.

**Generation of Dichlorocarbene in the Presence of (+)-Bis((*S*)-2-methylbutyl)mercury.** Ethyl trichloroacetate (9.55 g, 0.05 mol) in pentane (20 ml), (+)-mercurial (8.9 g, 0.0258 mol, $[\alpha]^{27.5}\mathrm{D}$ +8.01°), and sodium methoxide (5.4 g, 0.10 mol) in pentane (50 ml) were treated as previously described. The crude product mixture after being purified on a column of Florisil was cleaved with bromine and carbon tetrachloride.

In a second reaction ethyl trichloroacetate (19.1 g, 0.10 mol), (+)-mercurial (1.40 g, 0.040 mol, $[\alpha]^{27.5}\mathrm{D}$ +8.02°), and sodium methoxide (10.8 g, 0.20 mol) were allowed to react in an identical manner and the crude product mixture was cleaved with bromine in carbon tetrachloride.

The bromine cleavage products of the first reaction were distilled to give (−)-1,1-dichloro-2-(bromomethyl)-2-methylbutane (3.1 g, 0.0258 mol), bp 55° (0.6 mm), $[\alpha]^{25}\mathrm{D}$ −0.67° ($c$ 134, $CHCl_3$). A preparative sample of the corresponding (+)-1-bromo-2-methylbutane formed in the bromine cleavage reaction (F & M chromatograph, 15 ft, QF-1, 82°) had $[\alpha]^{25}\mathrm{D}$ +2.48° ($c$ 6.2, $CHCl_3$) which corresponds to 61.3% optical purity.[23]

The (−)-1,1-dichloro-2-(bromomethyl)-2-methylbutane from the second reaction collected on an Autoprep chromatograph (10 ft, QF-1/XF-1150, 125°) had $[\alpha]^{25}\mathrm{D}$ −1.13 ± 0.3° ($c$ 31, $CHCl_3$). A collected sample of the corresponding (+)-1-bromo-2-methylbutane had $[\alpha]^{25}\mathrm{D}$ +2.89° ($c$ 22.6, $CHCl_3$) which corresponds to 71.4% optical purity.[23]

**2-(Dichloromethyl)-2-methylpentanenitrile.** Dimethyl sulfoxide was purified by the method of Cason.[65] 1,1-Dichloro-2-(bromomethyl)-2-methylbutane (10.2 g, 0.43 mol) in dimethyl sulfoxide (3 ml) was added to a stirred suspension of potassium cyanide (3.91 g, 0.06 mol) in dimethyl sulfoxide (40 ml) at 110°, and was heated for 22 hr, cooled, and hydrolyzed. Ether (20 ml) was added and the aqueous layer was ether extracted. The ether was washed, dried, and evaporated to give a yellow oil the nmr spectrum of which indicated a 1:1 ratio of starting bromide to nitrile product. Distillation afforded four fractions the last of which was identified as 2-(dichloromethyl)-2-methylpentanenitrile (4.5 g, 0.02 mol) bp 65° (0.3 mm). The nmr spectrum showed singlets at 4.19 (1 H), 7.44 (2 H), 8.78 (3 H), a triplet at 9.04 ($J$ = 7 Hz, 3 H), and a quartet at 8.21 (2 H). The infrared spectrum exhibited among other absorptions a band at 2250 cm$^{-1}$ (C≡N).

*Anal.* Calcd for $C_7H_{11}Cl_2N$: C, 46.68; H, 6.15. Found: C, 46.60; H, 6.27.

---

[62] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2849 (1963).

[63] E. Tobler and D. J. Foster, *Z. Naturforsch.*, **176**, 135 (1962).

[64] W. E. Bachman, *J. Amer. Chem. Soc.*, **55**, 2830 (1933).

[65] J. Cason, *J. Org. Chem.*, **26**, 3648 (1961).

**Table II.** Results of Various Cyanide Displacement Attempts on 1,1-Dichloro-2-(bromomethyl)-2-methylbutane

| Solvent | Cation | Temp, C° | Time, hr | % conversion **27** | **29** | **30** |
|---|---|---|---|---|---|---|
| Ethanol | $Na^+$ | 78 | 63 | 0 | 0 | 0 |
| Ethylene glycol | $Na^+$ | 100 | 10 | 0 | 0 | 0 |
| Diethyl Carbitol | $Na^+$ | 120 | 3 | 0 | 0 | 0 |
| DMSO | $K^+$ | 100–125 | 22 | 50 | 0 | 0 |
| DMSO | $K^+$ | 110 | 84 | Trace | High | Low |
| DMSO | $Na^+$ | 55–90 | 7 | 14.3 | 0 | 0 |
| DMSO | $Na^+$ | 75–85 | 75 | Low | —High— | |
| DMF | $Na^+$ | 120–155 | 1.5 | 57.8 | 21.1 | 26.1 |

**Table III.** $^{199}Hg$–$^{1}H$ Spin–Spin Coupling Constants

| R group | Solvent | $J_{Hg-H_\alpha}$ Hz | $J_{Hg-H_\beta}$ Hz |
|---|---|---|---|
| RHgR | | | |
| Methyl | $CCl_4$ | $102^{a,b}$ | . . . |
| Ethyl | $CCl_4$ | 92, $96.6^{c}$ | 127, $126.7^{c}$ |
| Isopropyl | $CCl_4$ | $78^{a}$ | $117,^{a}$ $126^{b}$ |
| *n*-Propyl | $CCl_4$ | $95,^{a}$ $90^{b}$ | $108^{a,b}$ |
| *n*-Butyl | $CCl_4$ | 96 | 105 |
| *sec*-Butyl | $CCl_4$ | . . . | $119^{a}$ |
| Isobutyl | $CCl_4$ | 94 | 116 |
| *n*-Amyl | $CCl_4$ | . . . | 107 |
| Isoamyl | $CCl_4$ | 98 | 104 |
| 2-Methylbutyl | $CCl_4$ | 96 | 124 |
| Cyclohexylmethyl | $CCl_4$ | 92 | . . . |
| Benzyl | $CDCl_3$ | 132, $133^{d}$ | . . . |
| RHgCl | | | |
| Methyl | Dioxane | $209^{d}$ | . . . |
| | $CH_2Cl_2$ | $202.5^{e}$ | . . . |
| Ethyl | $CDCl_3$ | 204 | . . . |
| | Pyridine | $216^{c}$ | 296 |
| *n*-Propyl | $CDCl_3$ | $201^{a}$ | 289 |
| Isopropyl | $CDCl_3$ | . . . | $284^{a}$ |
| *n*-Butyl | $CDCl_3$ | 204 | . . . |
| *sec*-Butyl | $CCl_4$ | . . . | $293^{a}$ |
| Isobutyl | $CDCl_3$ | 207 | . . . |
| *n*-Amyl | $CDCl_3$ | 204 | . . . |
| Isoamyl | $CDCl_3$ | 207 | . . . |
| Cyclohexylmethyl | $CDCl_3$ | 201 | . . . |
| Benzyl | $CDCl_3$ | 270 | . . . |

[a] Reference 2b. [b] R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959). [c] J. V. Hatton, W. G. Schneider, and W. Siebrand, *ibid.*, **39**, 1330 (1963). [d] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964). [e] J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 5125 (1962).

In a second cyanide displacement reaction, in which the starting bromide (4.3 g, 0.018 mol) and sodium cyanide (1.5 g, 0.03 mol) were heated at 75–85° for 75 hr in dimethyl sulfoxide (30 ml), a mixture of three nitriles was obtained as indicated by vpc (20 ft, SE-30/E-600, 165°) one of which corresponded to the nitrile obtained in the previous reaction.

A collected sample (15 ft, XF-1150) of the nitrile with longest retention time yielded a solid, mp 53° (recrystallized from ethanol) tentatively identified as 1,1-dicyano-2-methyl-2-ethylcyclopropane (**29**). The nmr spectrum showed singlets at 8.62 (3 H) and 8.18 (2 H), a triplet with secondary splitting at 8.87 (3 H), and a multiplet at 8.41 (2 H).[66] The infrared spectrum exhibited characteristic absorptions at 3050 and 2240 $cm^{-1}$. Although the parent ion in the mass spectrum was almost undetectable, there were significant peaks at *m/e* 28 for $H_2CN$, 27 for HCN, and 106 for $M^+ - H_2CN$.[67]

*Anal.* Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 70.74; H, 7.54; N, 20.01.

The other two nitrile products were first collected together by vpc on a 15-ft XF-1150 column (retention time 63 min) and then separated and collected on a SE-30/E-600 column at 165° (retention time 2 hr). One of the nitriles corresponded to 2-(dichloromethyl)-2-methylpentanenitrile. The other, nitrile **30**, was an oil which gave a positive Beilstein test and exhibited an infrared absorption at 2240 $cm^{-1}$. The nmr spectrum showed a doublet at 6.78 ($J = 7.5$ Hz), a multiplet at 8.34, an unsymmetrical triplet at 8.98, a singlet at 8.65, and a singlet at 8.80. No positive structural assignment was made. Samples of **29** and **30** from optically active **25** were optically active, *vide infra.*

*Anal.* Calcd for $C_7H_{10}ClN$: C, 58.54; H, 7.02; Cl, 24.60; N, 9.75. Found: C, 59.34; H, 7.16; Cl, 23.12; N, 9.41.

**Cyanide Displacement on (−)-1,1-Dichloro-2-(bromomethyl)-2-methylbutane.** The (−)-bromide (3.1 g, 0.0258 mol, $[\alpha]^{25}\mathrm{D}$ −0.67°), and potassium cyanide (3.91 g, 0.06 mol) in dimethyl sulfoxide (40 ml) were stirred at 110° for 84 hr and worked up in the manner previously described. Vpc (20 ft, SE-30/E-600, 145°) produced only a trace of the desired product together with much larger amounts of unidentified nitrile and 1,1-dicyano-2-methyl-2-ethylcyclopropane. A collected sample of the cyclopropyl nitrile, mp 51–51.5°, had $[\alpha]^{25}\mathrm{D}$ +4.20° (*c* 5.8, $CHCl_3$). A preparative sample of the unidentified nitrile had $[\alpha]^{25}\mathrm{D}$ −0.074° (*c* 2.7, $CHCl_3$).

Sodium cyanide (0.49 g, 0.01 mol) and the starting bromide (1.23 g, 0.0053 mol, $[\alpha]^{25}\mathrm{D}$ −1.13 ± 0.3°) in dimethyl sulfoxide (25 ml) were stirred at 55–90° for 6 hr and worked up to give a 6:1 mixture of unchanged starting bromide to product nitrile 2-(dichloromethyl)-2-methylpentanenitrile. A sample of the desired nitrile was collected (15 ft, XF-1150, 165°) and had $[\alpha]^{25}\mathrm{D}$ −1.61° (*c* 5.27, $CHCl_3$).

In a second displacement carried out with sodium cyanide in dimethylformamide (distilled from barium oxide) at 120–155° for 1.5 hr, a sample of the desired (−)-nitrile was collected. Vpc of the mixture showed a ratio of 52.8:26.1:21.1 of 2-(dichloromethyl)-2-methylpentanenitrile to unidentified nitrile to 1,1-dicyano-2-methyl-2-ethylcyclopropane with an over-all yield of 74.5%.

**(−)-α-Methyl-α-ethylsuccinic Acid.** (−)-2-(Dichloromethyl)-2-methylpentanenitrile (0.0627 g, 0.33 mol, $[\alpha]^{25}\mathrm{D}$ −1.61°) was maintained at reflux with aqueous sodium hydroxide and silver oxide for 43 hr and produced (−)-α-methyl-α-ethylsuccinic acid (0.0180 g, 0.112 mol, 33.8%), mp 62–63° (lit.[32] mp 64.5°). The nmr spectrum ($CDCl_3$, 100 MHz) was identical with that of the racemic acid. The product acid had $[\alpha]^{25}\mathrm{D}$ −6.78 ± 0.3° (*c* 1.4, $CHCl_3$)

The nitrile collected from the cyanide displacement in dimethylformamide was maintained at reflux for 21 hr under conditions similar to those described above. Work-up afforded the (−)-acid (0.0118 g, 0.074 mol), mp 62°, which had $[\alpha]^{25}\mathrm{D}$ −6.04 ± 0.3° (*c* 0.99, $CHCl_3$).

---

(66) The nmr spectrum of 1,1-dicyano-2,2-dimethylcyclopropane, mp 39–40°, exhibits singlets at τ 8.34 (2 H) and 8.54 (6 H).[67]

(67) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).