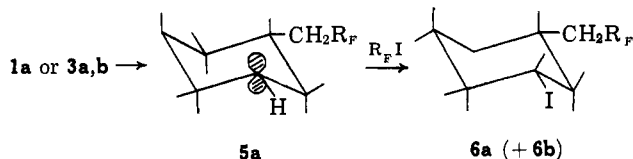
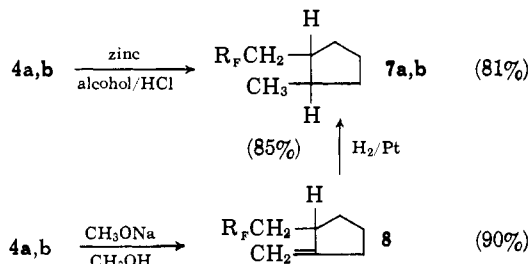


Not observed



way will seek further evidence relating to this problem and its obvious implications for cyclic polymerization and other radical rearrangements.

Evidence for *cis*- and *trans*-1-heptafluorobutyl-2-iodomethylcyclopentane structures for **4a,b** is as follows:⁶ (1) zinc reduction of a 20:80 mixture of **4a,b** gave a 20:80 mixture of isomeric heptafluorobutyl-2-methylcyclopentanes⁷ (**7a,b**); (2) dehydrohalogenation of **4a,b** gave a single olefin⁸ **8**, which added hydrogen at 45 p.s.i. over a platinum catalyst, giving a 45:55 mixture of **7a,b**.



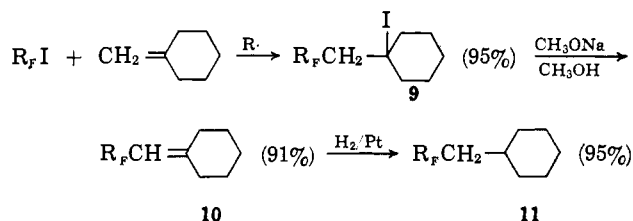
(6) The cyclic isomer mixture (**4a,b**), b.p. 92–93° (5.5 mm.), $n_D^{25} 1.4295$ –1.4309, was analyzed by g.l.c., but could not be separated by distillation. G.l.c. analyses were done with a Perkin-Elmer vapor fractometer using a polypropylene glycol column (Perkin-Elmer "R" column) at 150°. *Anal.* Calcd. for $C_{10}H_{12}F_7I$: C, 30.63; H, 3.09; F, 33.9; I, 32.4. Found: C, 30.9; H, 3.1; F, 34.0; I, 32.0. Olefinic monoadduct **1** (b.p. 65° (4.2 mm.), $n_D^{25} 1.4160$), had an infrared absorption (C=C) band at 6.00 and at 10.10 μ , and the same analysis.

(7) **7a,b**, b.p. 97° (138 mm.), $n_D^{25} 1.3562$. *Anal.* Calcd. for $C_{10}H_{12}F_7$: C, 45.12; H, 4.92; F, 50.0. Found: C, 45.6; H, 5.0; F, 50.0. A fraction containing 90% of isomer with retention time of 16.7 min. at 80° was arbitrarily called **7b**; **7a** was separated by gas chromatography, with retention time of 13.4 min.

(8) **8**, b.p. 97° (144 mm.), $n_D^{25} 1.3638$. *Anal.* Calcd. for $C_{10}H_{11}F_7$: C, 45.46; H, 4.20; F, 50.34. Found: C, 45.6; H, 4.2; F, 50.2. Infrared absorption bands at 6.00 and at 11.30 μ with an overtone band at 5.62 μ strongly indicates $CH_2=CR_1R_2$; rather than $RCH=CHR$ for **8**.

Infrared and n.m.r. spectra⁹ were consistent with structures **4a,b**, **7a,b**, and **8**. There was no proton resonance at -4.50 p.p.m. (relative to tetramethylsilane at 60 Mc.) in **4a,b**, characteristic for $-CHI$ as in iodocyclohexane,¹⁰ but a resonance pattern at -3.25 p.p.m. (*two*-proton area) was obtained as found for 1-iodobutane.¹¹ A methyl proton resonance split into a doublet ($J = 7$ c.p.s.) at -0.85 p.p.m. appeared only in **7b**; in **7a** the methyl peak was at -1.10 p.p.m. Mass spectra of **7a** and **7b** were identical; the principal peak had mass of 56, and next in abundance was 41, consistent with reported spectra for methyl- or dimethylcyclopentanes.¹² Zinc reduction of **6a,b** should have given only one product; dehydrohalogenation ought to have given two olefins, which on hydrogenation could give only one product.

Additional evidence was obtained by synthesis of the anticipated heptafluorobutylcyclohexane (**11**).



The infrared spectrum of **11** was completely different from that of **7a,b** and consistent with a cyclohexane ring. There was no CH_3C- band at 7.24 μ and no methyl proton resonance in the n.m.r. spectrum. The mass spectrum of **11** gave a base peak of mass 83, as found for other alkylcyclohexanes.¹²

Reaction of $R_F I$ with biallyl ether gave a product mixture analogous to 1,6-heptadiene; biallyl cyanamide and diethyl 1,6-heptadiene-4,4-dicarboxylate gave apparently only cyclic monoadducts. An investigation into the scope of this unusual cyclization reaction is underway, and a complete description of these reactions will be published shortly.

(9) The author is indebted to Dr. R. K. Miller for infrared spectra and to T. E. Beukelman for n.m.r. spectra reported herein.

(10) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963).

(11) Varian Associates, "NMR Spectra Catalog," spectrum No. 71. Compare with spectrum No. 72 (2-iodobutane).

(12) The author is indebted to Dr. F. Kitson, who obtained time-of-flight mass spectra of compounds separated by g.l.c. and aided in interpretation of the results.

CONTRIBUTION NO. 361

NEAL O. BRACE

THE PIONEERING RESEARCH SECTION
JACKSON LABORATORY
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE

RECEIVED NOVEMBER 16, 1963

Carbene Insertion into the Carbon-Mercury Bond. Formation of Stable Dichlorocarbene Insertion Products which Undergo an Unusual Thermal Breakdown

Sir:

Although Reutov¹ has reported an insertion of dichlorocarbene into a mercury-chlorine bond, the product has been shown more recently to have resulted from a simple nucleophilic displacement of chloride by the trichloromethyl anion.²

We wish to report the first observation of dichlorocarbene (ground electronic state³) insertion into one carbon-mercury bond of several simple *sym*-dialkyl-

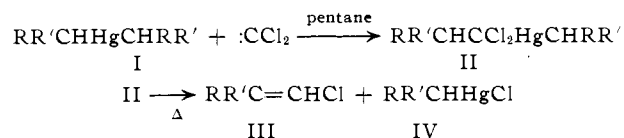
(1) O. A. Reutov and A. N. Lovtsova, *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961), and references cited therein.

(2) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

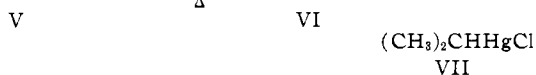
(3) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

mercury compounds. To our knowledge this is the first example in which the product of attack of a carbene on any carbon-metal bond has been isolated as a stable compound.⁴

Although the insertion product II is stable at room temperature, it was found to decompose at higher temperatures to form nearly equimolar amounts of vinyl chloride III and alkylmercuric chloride IV. The reaction has been carried out with R = R' = H; R = R' = CH₃; R = *n*-C₃H₇, R' = H; and R = CH₃, R' = C₂H₅.



For example, diisopropylmercury (0.03 mole), b.p. 33–35° (0.3–0.4 mm.), in pentane was treated with dichlorocarbene generated from ethyl trichloroacetate (0.06 mole) by the method of Parham and Schweizer.⁶ The pentane solution was washed, dried, and evaporated in the usual manner to an oily residue. At no time during the reaction or work-up was any free mercury observed. Upon careful distillation, the crude product yielded a small amount of recovered diisopropylmercury and 57% of the theoretical amount of insertion product V, b.p. 94–95° (0.3–0.4 mm.); a clear viscous liquid structure was confirmed by its chemical and spectral properties. The infrared spectrum was nearly identical with that of diisopropylmercury. The 60 Mc./sec. n.m.r. spectrum showed two doublets (CH₃)₂CHCCl₂HgCH(CH₃)₂ $\xrightarrow{\Delta}$ (CH₃)₂C=CHCl +



at τ 8.63 and 8.79, respectively ($J = 7$ c.p.s.), which were assigned to the two sets of isopropyl methyl groups. The two tertiary proton multiplets were visible at *ca.* τ 7.3 and 8.1, but were complicated because of noise and the presence of Hg¹⁹⁹ satellite peaks.⁷

That mercury compound V did not arise because of a nucleophilic attack of the trichloromethyl anion on the mercury atom is suggested by the fact that simple dialkylmercury compounds are completely inert to attack by strongly nucleophilic iodide or thiosulfate ions as well as by strong bases such as sodium methoxide.⁹

The thermal decomposition of pure V at 100–120° resulted in a 1.00:1.09 mole ratio of isopropylmercuric chloride (VI) to 2-methyl-1-chloro-1-propene (VII), each of which was unequivocally identified by melting or boiling point, infrared spectrum, and n.m.r. spectrum. No other products were observed.

Similar dichlorocarbene insertion reactions were carried out on di-*sec*-butylmercury (I, R = CH₃, R' = C₂H₅) and di-*n*-butylmercury (I, R = H, R' = CH₃CH₂CH₂). In each instance thermal decomposition of the insertion product occurred before it was

(4) Evidence for the insertion of halo carbenes into carbon-alkali metal bonds has been published,⁵ but the intermediate products which are postulated apparently eliminate alkali metal halide to form a carbene that goes on to produce the observed products.

(5) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963), and references cited therein.

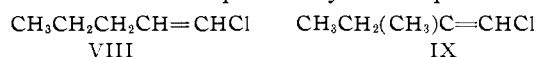
(6) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1773 (1959).

(7) Two Hg¹⁹⁹ satellite doublets were symmetrically oriented about the large doublet at 8.63 and correspond to $J_{\text{Hg}^{199}\text{-H}^1} = 165$ c.p.s., a value assigned to the coupling between Hg¹⁹⁹ and the protons on the β -carbon atom.⁸ Thus, the doublet at 8.63 is associated with the isopropyl group directly attached to the mercury atom of V.

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

(9) Experimental observations of the authors.

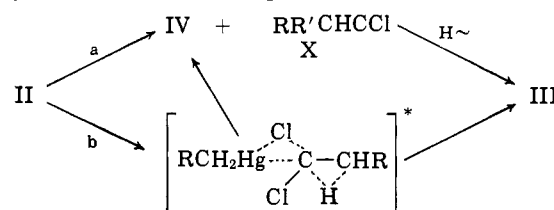
distilled. The product vinyl chlorides VIII and IX were obtained¹⁰ accompanied by the expected alkyl-



mercuric chlorides. A simple test for the alkylmercuric halide¹¹ revealed that it was present only *after* the thermal decomposition had taken place.

The attack of dichlorocarbene on the carbon-mercury bond is not surprising in view of the known susceptibility of dialkylmercury compounds to cleavage by a variety of electrophiles.^{12–14} Further work on the stereochemistry and relative reactivity of various types of carbon-mercury bonds is being carried out to elucidate the nature of the transition state in this reaction.

The thermally induced breakdown of insertion product II is particularly interesting in view of the formal similarity to the decomposition of phenyl(trichloromethyl)mercury to form dichlorocarbene.¹⁵ In analogy with the latter transformation, path a, in which a distinct intermediate carbene (X) is formed and undergoes a subsequent hydrogen migration, for which ample precedent exists,¹⁶ would appear more likely than the concerted path b. Direct evidence for



the intermediacy of carbene X is presently being sought.

(10) Preliminary vapor phase chromatographic data on VIII indicated a mixture of stereoisomers with one in predominance.

(11) Alkylmercuric chlorides form water-soluble thiosulfate salts which can be readily precipitated as the iodide.

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

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

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

(15) D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. A. Burlitch, and S. R. Dowd, *J. Org. Chem.*, **28**, 1163 (1963).

(16) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961), and references cited therein.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

JOHN A. LANDGREBE
RONALD D. MATHIS

RECEIVED NOVEMBER 21, 1963

Synthesis of a Benzocyclopropene Derivative

Sir:

Benzocyclopropene (I) should be intermediate in strain between benzocyclobutene, a stable entity,¹ and benzyne,² which has only been observed³ as a transient species. However, past efforts to obtain I or its derivatives⁴ have been unsuccessful. We now report the preparation of 1,1-dimethyl-3-carbomethoxybenzocyclopropene (II), a crystalline compound of moderate stability.

Methyl 3,3-dimethylindiazene-6-carboxylate⁵ (III,

(1) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); **80**, 2255 (1958).

(2) For a review, see R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(3) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); R. S. Berry, G. N. Spokes, and M. Stiles, *ibid.*, **84**, 3570 (1962).

(4) E. F. Ullman and E. Buncel, *ibid.*, **85**, 2106 (1963).

(5) Compound III was prepared (J. M. Muchowski, Ph.D. Thesis, University of Ottawa, 1962) from the N-nitroso derivative of methyl 3-benzamido-4-isopropylbenzoate by Huisgen's procedure for the synthesis of indazoles (R. Huisgen and H. Nakatani, *Ann.*, **573**, 181 (1951)). The longest wave-length absorption band in the ultraviolet spectrum of III occurred at 350 m μ (log ϵ 2.40).