We repeat our earlier[1,5,26,38] statement that these simple Z values cannot be equated to simple rates of formation, because the ions retain the substituent and decompose further. An approximation to rates of formation may sometimes be gained from low-voltage studies where intensities are no longer altered by further decomposition of the daughter ion of interest. This is not possible in the nitrobenzenes,[3,4] and the low-voltage data presented serve only to suggest a rough order of stability with respect both to formation and decomposition.

Kinetic energy release was calculated from the usual formula,[20] using data obtained at several accelerating voltages. The quoted error reflects not only the deviation of these different data, but also the error in estimating the width of the flat top of the metastable because of interference by the finite width of the normal peaks in some cases and difficulty in assigning the correct slope to the sides of the peak. The resolution of 450 used was a compromise between a low value, which would spread the normal peaks over the metastable to an unacceptable extent, and a high value, which would reduce the intensity of the metastable so much that analysis of its shape would have been very difficult.

The low-voltage data were obtained 3.0 V above the vanishing-current ionization potentials of each compound, *i.e.*, at nominal voltages of 12.22 V for II, 11.80 V for III, 12.44 V for IV, and 11.40 V for V. The reproducibility of the nominal ionization potential in a single set of three experiments was ±0.04. We emphasize that the vanishing-current method is not an elegant method for determining ionization potentials for future reference, and deliberately omit nominal ionization potentials obtained lest they be quoted. The merit of the vanishing-current method for this study is in the ability to arrive at a number representing a voltage 3.0 V higher than the potential of vanishing current without reference to an arbitrary fractional intensity at some point; practically all other methods of determining ionization potentials which are available to us demand this arbitrary assignment explicitly or implicitly, and render the final voltage used significant within only a narrow interpretation. We have commented on this before.[38]

The Z values for the low-voltage experiments described above, not corrected for further decomposition of the $(M - NO)^+$ ion,[39] were 0.06 for II, 0.03 for III, 0.045 for IV, and 0.04 for V. The fraction of the ion current carried by the molecular ion in these cases was 92% for II, 96% for III, 93% for IV, and 93% for V. The spectra were measured at high amplification with source conditions as for ionization-potential determinations (trap current, *ca.* 3 μA; other parameters adjusted to minimize fields in the source). A digital voltmeter (United Systems Corporation, Dayton, Ohio) was used for the assignment of precise potentials.

Acknowledgments. Partial support is gratefully acknowledged from the University Research Council of the University of North Carolina, from the Advanced Research Projects Agency through Contract SD-100 with the University of North Carolina, and from the National Science Foundation through a Science Development Award to the University of North Carolina (GV-2059).

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[38] M. M. Bursey, *Org. Mass Spectrom.*, 1, 31 (1968).

[39] Peaks indicating further decomposition of the $(M - NO)^+$ ions were those corresponding to a loss of CO, that is, the $(M - NO - CO)^+$ ions. They ranged in intensity from 2 to 8% of the $(M - NO)^+$ ions, and thus any correction of the Z values for them would be so slight that the interpretation would not change.

Halomethyl–Metal Compounds. XXX. CH_2 Transfer to Olefins Using Monohalomethylmercury Compounds[1]

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received April 10, 1969*

Abstract: The reaction of bis(bromomethyl)mercury with olefins at temperatures of 80° or above in inert solvents results in the formation of cyclopropanes *via* CH_2 transfer from the mercurial to the olefin. Bromomethylmercuric bromide is inert under these reaction conditions, but it can be brought into reaction by admixture of 1 molar equiv of diphenylmercury. The latter reacts with $BrCH_2HgBr$ to give the reactive bis(bromomethyl)mercury and possibly $PhHgCH_2Br$. Iodomethylmercuric iodide also transfers CH_2 to olefins and it also is "activated" by added diphenylmercury. The yields of cyclopropanes and their rates of production are variable, depending on the structure of the olefin. Olefins with electron-attracting substituents and hindered olefins react more slowly than simple alkyl-substituted olefins. The available evidence is against a free carbene mechanism and in favor of a direct reaction between the organomercury reagent and the olefin. Relative reactivity determinations show that electrophilic attack at the C=C bond is taking place and that steric factors are less important than electronic factors.

The preparation of cyclopropanes by divalent carbon transfer from an organometallic reagent, iodomethylzinc iodide, was first reported in 1958,[4] and in 1961, bis(iodomethyl)zinc was shown to react with olefins in similar fashion.[5] Extension of this organometallic cyclopropane synthesis to other halomethyl-metal compounds was of interest, but according to reports by Wittig and Schwarzenbach[5] and Simmons and his coworkers,[6] halomethylmercurials of type $Hg(CH_2X)_2$ and $XHgCH_2X$ were unreactive as reagents for cyclopropane synthesis.[7] It was difficult to assess the work of either group on these mercury compounds since experimental details were not provided.

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[1] (a) Part XXIX: D. Seyferth, R. Damrauer, R. M. Turkel, and L. J. Todd, *J. Organometal. Chem.* (Amsterdam), in press; (b) preliminary communication: D. Seyferth, M. A. Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, 86, 121 (1964).

[2] Postdoctoral Research Associate, 1962–1963.

[3] Postdoctoral Research Associate, 1963–1964.

[4] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, 80, 5323 (1958); 81, 4256 (1959).

[5] G. Wittig and K. Schwarzenbach, *Ann. Chem.*, 650, 1 (1961).

[6] H. E. Simmons, E. P. Blanchard, Jr., and R. D. Smith, *J. Am. Chem. Soc.*, 86, 1347 (1964).

[7] Monohalomethyl derivatives of various other metals, *e.g.*, lithium, sodium, magnesium, cadmium, aluminum, indium, iron, and iridium, were found to be active as CH_2 transfer agents. For leading references see ref 6 and 8.

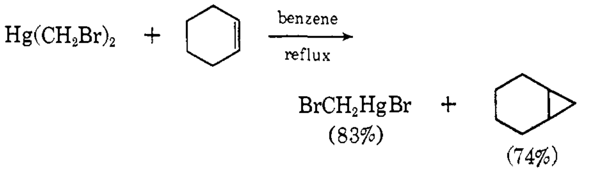
[8] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, 89, 4953 (1967).

Our own research during the period 1962–1964 demonstrated that phenyl(trihalomethyl)mercury compounds of type $PhHgCXYBr$ ($X = Y = Cl$; $X = Cl$, $Y = Br$; $X = Y = Br$) served excellently as dihalocarbene transfer agents and that they were particularly useful in the synthesis of *gem*-dihalocyclopropanes.[9–11] On the basis of this work, we felt that previous reports not withstanding, the halomethylmercury compounds should, under appropriate conditions, transfer CH_2 to olefins and to other substrates. Accordingly, we commenced a study of such mercury compounds.

Results and Discussion

The compounds chosen for this investigation were iodomethylmercuric iodide, ICH_2HgI,[12] and bis(bromomethyl)mercury, $Hg(CH_2Br)_2$,[1a,13] both of which could be prepared relatively easily and in good yield. A light-induced reaction of diiodomethane with metallic mercury served in the preparation of the former, while the latter was obtained by the reaction of diazomethane with mercuric bromide.

In the first orientational experiment, a benzene solution containing 30 mmol of bis(bromomethyl)mercury and 0.3 mol of cyclohexene was stirred at reflux under a nitrogen atmosphere. Gas–liquid partition chromatography (glpc) was used to examine the reaction mixture. After some hours of heating, a new component with glpc retention time identical with that of the expected product, norcarane, was detected. The reaction was continued until no further growth of the peak due to this component was noticeable in the gas chromatogram of the reaction mixture; this required a total reaction time of 8 days. During the progress of this reaction an insoluble, crystalline solid, identified as bromomethylmercuric bromide, also was formed. The identity of the organic product subsequently was confirmed as norcarane. Equation 1 summarizes the results of this experiment. A separate experiment confirmed the lack of reactivity of bromomethylmercuric bromide; no norcarane was formed when a suspension of this mercurial in cyclohexene–benzene was heated at reflux for 8 days.



(1)

The utilization of only one of the two bromomethyl groups of bis(bromomethyl)mercury in this new cyclopropane synthesis was an undesirable feature, especially since the starting material could not be made on a large scale. (In view of the potential hazards associated with large-scale reactions with diazomethane, only 0.125 mol of bis(bromomethyl)mercury was prepared at a time.) The known, very facile substituent exchange reactions in organic and inorganic mercury chemistry and the high insolubility of phenylmercuric bromide provided the basis for a modified procedure which allowed the synthetic utilization of the second bromomethyl group of bis(bromomethyl)mercury. When an equimolar mixture of bromomethylmercuric bromide *and diphenylmercury* in benzene solution containing an excess of cyclohexene was heated at reflux for 8 days, phenylmercuric bromide was formed in 74% yield (based on $Ph_2Hg \rightarrow 2PhHgBr$), and norcarane was produced in 40% yield. In similar fashion, a reaction of 10 mmol each of $Hg(CH_2Br)_2$ and diphenylmercury with 0.1 mol of 3-ethyl-2-pentene in benzene for 10 days gave 1,1-diethyl-2-methylcyclopropane in 73% yield, phenylmercuric bromide in 90% yield. In these experiments, it is the function of the added diphenylmercury to convert the unreactive bromomethylmercuric bromide to a reactive CH_2 transfer mercurial, either $PhHgCH_2Br$ or $Hg(CH_2Br)_2$ (eq 2, 3, and 4).

$$Ph_2Hg + BrCH_2HgBr \longrightarrow PhHgBr + PhHgCH_2Br \qquad (2)$$

$$PhHgCH_2Br \longrightarrow 0.5Ph_2Hg + 0.5Hg(CH_2Br)_2 \qquad (3)$$

or

$$PhHgCH_2Br + BrCH_2HgBr \longrightarrow PhHgBr + Hg(CH_2Br)_2 \qquad (4)$$

Although such substituent exchange reactions were postulated originally[1b] without experimental support, subsequent work showed that diphenylmercury and bromomethylmercuric bromide do indeed react to give phenylmercuric bromide and bis(bromomethyl)mercury as ultimate products. Thin layer chromatography of such a Ph_2Hg–$BrCH_2HgBr$ reaction mixture before work-up showed the presence of an organomercurial which could not be isolated and which appeared to decompose on further manipulation of the reaction mixture. It is quite possible that this compound was $PhHgCH_2Br$. In this connection, it is to be noted that $PhHgCH_2Cl$ is a rather unstable oil which deposits crystals of diphenylmercury on standing at room temperature.[14]

Iodomethylmercuric iodide was more reactive as a CH_2 transfer agent than was bromomethylmercuric bromide. It reacted with cyclohexene in benzene in the absence of diphenylmercury (8 days at reflux) to give norcarane in 24% yield. An identical experiment carried out in the presence of 1 molar equiv of diphenylmercury showed the expected increase in product yield; norcarane was formed in 64% yield. In this case also evidence for the intermediacy of the symmetrical mercurial ($Hg(CH_2I)_2$) was obtained. During an unsuccessful attempt to add CH_2 to phenylacetylene with the ICH_2HgI–Ph_2Hg reagent, work-up of the reaction mixture gave some bis(iodomethyl)mercury in addition to phenylmercuric iodide.

Our preliminary results thus showed that the appropriate halomethylmercury compounds can serve as CH_2 transfer agents and that they are potentially useful reagents for the synthesis of cyclopropanes from olefins. Their reactions with cyclohexene were very slow, but the reaction conditions were mild and the product yields reasonable. Therefore we felt that further investigation of these reagents was justified.

To date we have accumulated data concerning the general applicability of this reaction in cyclopropane synthesis as well as some information concerning the

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(9) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, 27, 1491 (1962).

(10) D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid.*, 28, 1163 (1963).

(11) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(12) E. P. Blanchard, Jr., D. C. Blomstrom, and H. E. Simmons, *J. Organometal. Chem.* (Amsterdam), 3, 97 (1965).

(13) R. Kh. Freidlina, A. N. Nesmeyanov, and F. A. Tokareva, *Ber.*, **69**, 2019 (1936).

(14) L. Hellerman and M. D. Newman, *J. Am. Chem. Soc.*, **54**, 2859 (1932).

mechanism of these reactions. The experiments carried out are summarized in Table I.

The data in Table I show the following. (1) The reaction is stereospecific: a *cis*-1,2-dialkylethylene gave the *cis*-1,2-dialkylcyclopropane and the *trans* isomer gave the *trans*-1,2-dialkylcyclopropane.

(2) The nature of the olefin has a large effect on the rate of the reaction. Electronegative substituents retard the rate of CH_2 transfer, as the examples of vinyl acetate, 2,5-dihydrofuran, and tetrachloroethylene show. Very hindered olefins such as *t*-amylethylene react especially slowly. To obtain more information concerning the effect of electronic and steric factors associated with the olefin on the rate of the CH_2 transfer reaction, a series of competition experiments was carried out in which mixtures of 5 molar equiv each of cyclohexene and a second olefin were allowed to compete for 1 molar equiv of bis(bromomethyl)mercury in refluxing benzene solution. The product yields were determined by gas–liquid partition chromatography and the values of the relative rate constants for each olefin then were calculated by the method of Doering and Henderson.[15] The results are given in Table II. It is clear that the olefins reactivities are affected principally by electronic factors, the more nucleophilic olefin being the more reactive. Steric factors appear to be of considerably lesser importance. Thus the active reagent involved in the CH_2 transfer from bis(bromomethyl)mercury is an electrophilic species.

Other experiments in addition to those in Table I indicated that the nature of the olefin directly affected the rate of product formation, *i.e.*, that the product-forming reaction was the rate-determining step. In a set of experiments summarized in Table III, three different olefins were allowed to react with bis(bromomethyl)mercury, all under identical conditions of temperature and concentration, until a *ca.* 50% product yield had been achieved. It is quite clear from the results obtained that the rate of product formation parallels the olefin relative reactivities listed in Table II.

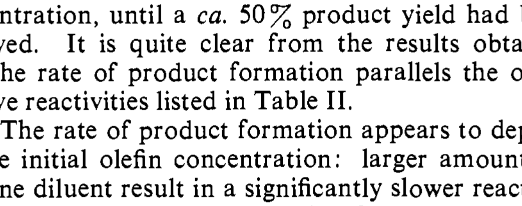
(3) The rate of product formation appears to depend on the initial olefin concentration: larger amounts of benzene diluent result in a significantly slower reaction.

(4) Higher temperatures result in a faster CH_2 transfer, as the case of cyclooctene shows. However, a reaction temperature of 140° is perhaps too high for general application in cyclopropane synthesis.

Thus this new CH_2 transfer reaction is somewhat limited in scope. Best results (good yields of product in a reasonably rapid reaction) are obtained at higher temperatures in the absence of diluent.

The question of mechanism is an interesting one. Our previous work with $PhHgCCl_2Br$-based CCl_2 transfer to olefins indicated that a free dichlorocarbene intermediate was operative:[8] eq 5 and 6. On the other hand, Blanchard and Simmons[16] showed that CH transfer to olefins from iodomethylzinc iodide did not involve free methylene as an intermediate, rather that it proceeded *via* a bimolecular reaction between the olefin and the organometallic reagent. In the case of bis(bromomethyl)mercury and iodomethylmercuric iodide it therefore was of interest to establish which factor was more important in determining the nature of the transfer process: the metal or the divalent carbon species transferred.

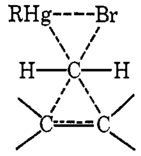
$$PhHgCCl_2Br \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{slow})}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (5)$$



(6)

All of our observations can be rationalized in terms of a direct reaction between the organomercury reagent and the olefin. They do not speak in support of a free CH_2 mechanism.

First, in all of these reactions addition of CH_2 to the C=C bonds was the only process observed; no evidence of CH_2 insertion into C—H bonds was obtained.[17] If a methylene intermediate were to be involved, this would argue in favor of CH_2 in the triplet state.[19] On the other hand, the reactions of bis(bromomethyl)mercury with *cis*- and *trans*-3-heptene were stereospecific and this would be evidence in favor of CH_2 in the singlet state.[19] The other observations resolve this contradiction by providing evidence against a free CH_2 mechanism. Most notable is the fact that bis(bromomethyl)mercury is stable in refluxing benzene; heating times of up to 20 days were examined. Only in the presence of a CH_2 acceptor does CH_2 extrusion from the mercurial take place. The initial concentration of the olefin appears to affect the rate of this transfer process. Very striking is the great dependence of the rate of CH_2 transfer on the nature of the olefin. These observations are very different from those made with CCl_2 transfer from phenyl(bromodichloromethyl)mercury.[8,11] A direct reaction between the mercury reagent and the olefin is strongly indicated. A kinetic study is required to define the exact nature of this transfer reaction. On the basis of the present results and in the absence of further information, it would be tempting to write this transfer process as an analog of the suggested ICH_2ZnI–olefin reaction transition state (I). However, a comparison of the relative rate constants for bis(bromomethyl)mercury–olefin reactions in Table II with relative rate constants for iodomethylzinc iodide–olefin reactions ($Me_2C{=}CMe_2$, 1.29; $Me_2C{=}CHMe$, 2.18; $MeEtC{=}CH_2$, 2.53; cyclohexene, 1.00; n-$C_5H_{11}CH{=}CH_2$, 0.39; ref 16)



I

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[15] W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **78**, 5430 (1956).

[16] E. P. Blanchard, Jr., and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

[17] G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964), have reported that uv irradiation of bis(iodomethyl)mercury in cyclohexene for 2 days gives norcarane (0.5%), 1-methylcyclohexene (0.3%), and 3- and 4-methylcyclohexenes (0.7%), all identified by glpc retention time only. In view of the difference in reaction conditions, we hesitate to relate this result to our experiments. This photolysis experiment produced a black solid (mercury?) and this suggests to us that it is perhaps more closely related to the generation of carbenes *via* photolysis of halomethanes[18] than to our thermal experiments.

[18] T. Marolewski and N. C. Yang, *Chem. Commun.*, 1225 (1967).

[19] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapters 2 and 12.

Table I. Reactions of Halomethylmercury Compounds with Olefins

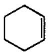
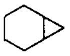
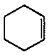
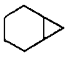
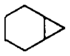
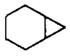
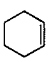
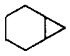
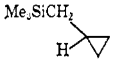
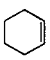
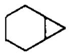
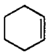
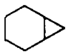
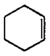
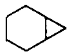
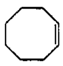
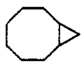
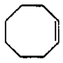
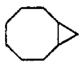
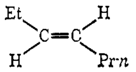
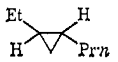
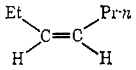
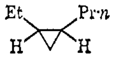
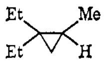
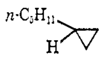
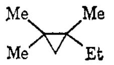
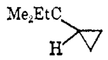
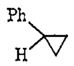
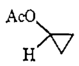
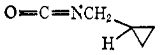
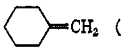
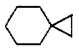
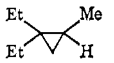
Halomethylmercury reagent (mmol)	Olefin (mmol)	Solvent (ml)	Reaction time, hr, at 80–85°	Product (% yield)	RHgX (% yield)	Starting mercurial, % recovery
$Hg(CH_2Br)_2$ (30)	 (300)	C_6H_6 (30)	8 days	 (74)	$BrCH_2HgBr$ (83)	
$BrCH_2HgBr$ (14)	 (500)	C_6H_6 (10)	8 days	No reaction	$BrCH_2HgBr$	
$BrCH_2HgBr$-Ph_2Hg (14 each)	 (500)	C_6H_6 (10)	8 days	 (39)	PhHgBr (74)	
ICH_2HgI (20)	 (365)	C_6H_6 (15)	8 days	 (24)		
ICH_2HgI-Ph_2Hg (20 each)	 (365)	C_6H_6 (15)	8 days	 (64)	PhHgI (91)	
$Hg(CH_2Br)_2$ (10)	 (200)	None	20	 (62)	$BrCH_2HgBr$ (73)	26
$Hg(CH_2Br)_2$ (3.94)	$Me_3SiCH_2CH{=}CH_2$ (13)	C_6H_6 (1.3)	72	 (77)	$BrCH_2HgBr$ (91)	8.6
$Hg(CH_2Br)_2$ (10)	 (100)	C_6H_6 (1) EtC_6H_5 (1)	47	 (65) (62 after 28 hr)	$BrCH_2HgBr$ (81)	19
$Hg(CH_2Br)_2$ (12.5)	 (100)	C_6H_6 (4) EtC_6H_5 (1)	115	 (73)	$BrCH_2HgBr$ (87)	13
$Hg(CH_2Br)_2$ (10)	 (20)	C_6H_6 (3) EtC_6H_5 (1)	115	 (72)	$BrCH_2HgBr$ (75)	24
$Hg(CH_2Br)_2$ (5)	 (50)	C_6H_6 (15)	96	 (82)	$BrCH_2HgBr$ (85)	
$Hg(CH_2Br)_2$ (5)	 (50)	C_6H_5Cl (15)	8 (reaction temp 140°)	 (65)	$BrCH_2HgBr$ (86)	8
ICH_2HgI-Ph_2Hg (10 each)	 (100)	C_6H_6 (30)	139	 (47)	PhHgI (69)	
ICH_2HgI-Ph_2Hg (10 each)	 (50)	C_6H_6 (30)	149	 (45)	PhHgI (72)	
$Hg(CH_2Br)_2$ (8.30)	$Et_2C{=}CHMe$ (50)	C_6H_6 (2.7) EtC_6H_5 (0.5)	15	 (68)	$BrCH_2HgBr$ (69)	27
$Hg(CH_2Br)_2$ (16.6)	n-$C_5H_{11}CH{=}CH_2$ (100)	C_6H_6 (5) EtC_6H_5 (1)	138	 (46)	$BrCH_2HgBr$ (76)	24
$Hg(CH_2Br)_2$ (10)	$Me_2C{=}CMeEt$ (100)	C_6H_6 (20)	120	 (72)	$BrCH_2HgBr$ (95)	
$Hg(CH_2Br)_2$ (5)	$Me_2EtCCH{=}CH_2$ (50)	C_6H_6 (15)	34 days	 (25)	$BrCH_2HgBr$ (31)	
$Hg(CH_2Br)_2$ (5)	$PhCH{=}CH_2$ (50)	C_6H_6 (15)	8 days	 (22)	$BrCH_2HgBr$ (24)	
$Hg(CH_2Br)_2$ (15.1)	$CH_2{=}CHOAc$ (100)	C_6H_6 (5.6)	23 days	 (36)	$BrCH_2HgBr$ (55)	45
$Hg(CH_2Br)_2$ (15.1)	 (100)	C_6H_6 (7.4)	20 days	 (~6)		91
$Hg(CH_2Br)_2$ (15.10)	$CH_2{=}CHCH_2N{=}C{=}O$ (100)	C_6H_6 (6,5)	20 days	 (16)	$BrCH_2HgBr$ (56)	43
$Hg(CH_2Br)_2$ (7.55)	 (50)	C_6H_6 (1) EtC_6H_5 (0.5)	18	 (76)	$BrCH_2HgBr$ (94)	4
$Hg(CH_2Br)_2$-Ph_2Hg (10 each)	$Et_2C{=}CHMe$ (100)	C_6H_6 (15)	10 days	 (73)	PhHgBr (90)	

Table I (*continued*)

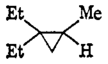
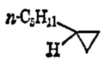
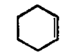
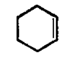
Halomethylmercury reagent (mmol)	Olefin (mmol)	Solvent (ml)	Reaction time, hr, at 80–85°	Product (% yield)	RHgX (% yield)	Starting mercurial, % recovery
$Hg(CH_2Br)_2$-Ph_2Hg (10 each)	$Et_2C{=}CHMe$ (100)	DME (15)	6 days	 (33)	PhHgBr (86)	
$Hg(CH_2Br)_2$-Ph_2Hg (40 each)	n-$C_5H_{11}CH{=}CH_2$ (100)	C_6H_6 (20)	11 days	 (47)	PhHgBr (90)	
ICH_2HgI-Ph_2Hg (20 each)	$Cl_2C{=}CCl_2$ (300)	None	24	No reaction		

Table II. Relative Rate Constants for the $Hg(CH_2Br)_2$–Olefin Reaction in Benzene Solution at 80°

Olefin	k_o/k_c (duplicate)[a]
$Me_2C{=}CMeEt$	26.9 (25.3)[b]
$Et_2C{=}CHMe$	4.22 (4.09)[c]
	1.00
n-$C_5H_{11}CH{=}CH_2$	0.221 (0.234)[d] (0.215)[e]

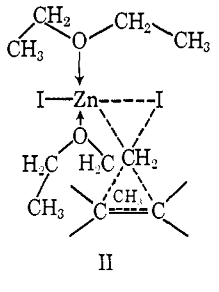
[a] o = second olefin; c = cyclohexene. [b] Reaction time, 48 hr. [c] Reaction time, 80 (70) hr. [d] Reaction time, 68 hr. [e] Olefins in tenfold excess.

Table III. The Effect of the Olefin Structure on the Rate of Product Formation in the $Hg(CH_2Br)_2$–Olefin Reaction

Olefin[a]	k_{rel} (Table II) toward $Hg(CH_2Br)_2$	Cyclopropane yield, %[b] 23 hr	69 hr	207 hr
$Et_2C{=}CHMe$	4.2	68 (after 15 hr)		
	1.0	16	55	
n-$C_5H_{11}CH{=}CH_2$	0.23	9	33	49

[a] Olefin concentration 4.97 *M;* mercurial concentration 0.825 *M;* benzene solvent. [b] Percentage yield based on mercurial after stated time.

suggests at first sight that such an analogy might not be appropriate. Steric effects are not very important in the case of the mercurial, but with the zinc reagent steric factors obviously play an important role. We suggest that this difference finds its most reasonable explanation in the nature of the two reagents under discussion. The $Hg(CH_2Br)_2$ reagent is used in benzene solution and most certainly is not strongly solvated. Thus even in a transition state such as I steric factors should not be very important. In contrast, the zinc reagent is prepared and used in ether solvents and undoubtedly solvation of the metal atom is very strong. An analogy to the Grignard reagent, which tightly binds two ether molecules, $RMgX \cdot 2Et_2O$, would not be out of place. Thus the zinc reagent with its associated ether molecules would be sterically more demanding in such a transition state, as shown in II.



II

Finally, the question arises as to why the $PhHgCCl_2Br$–olefin reactions proceed *via* a free carbene mechanism while the $Hg(CH_2Br)_2$–olefin reactions do not. We are dealing with bromine-substituted methylmercury compounds in both cases, but it would appear that it is not the metal, rather the potential divalent carbon fragment which is more important in determining the nature of the transfer process. Among the carbenes, dichlorocarbene is one of the more stable, very possibly because of stabilization *via* internal ($Cl \rightarrow C$) p_π–p_π bonding similar to the ($Cl \rightarrow B$) p_π–p_π bonding believed to occur in the isoelectronic BCl_3 molecule.[20] On the other hand, free CH_2, no matter what its multiplicity, is a species of much higher energy and one whose stability cannot be enhanced by internal π bonding. Thus it is not too surprising that CH_2 transfer from $HgCH_2X$ compounds to olefins proceeds by a direct process which does not involve free CH_2 as an intermediate.

In summary, bromo- and iodomethylmercury compounds do transfer CH_2 to olefin in a direct reaction, the nature of which is not yet well understood. With the more nucleophilic olefins this reaction can be a useful route to cyclopropanes, especially if carried out at temperatures above 80° and in the absence of an inert diluent. At present any application of this reaction to cyclopropane synthesis is hampered by the fact that the preparations of iodomethylmercuric iodide and bis(bromomethyl)mercury do not lend themselves to the rapid accumulation of larger amounts of these mercurials. For this reason, a current study is devoted to finding improved syntheses for these compounds.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen in flame-dried glassware. Infrared spectra were recorded with a Perkin-Elmer Infracord 337 infrared spectrophotometer, nmr spectra with a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in δ units, parts per million (ppm) downfield from internal TMS. Gas–liquid partition chromatography (glpc) of reaction mixtures (analysis and isolation of pure samples) was accomplished using an MIT isothermal unit with glass columns packed with 20% General Electric Co. SE-30 silicone rubber gum on 80–100 mesh Johns-Manville Chromosorb P. Helium at 15–20 psi was used as carrier gas. The internal standard method was used for quantitative analyses.

The olefins used were commercial materials and were distilled before use. The method of Blanchard, *et al.*,[6] was used to prepare iodomethylmercuric iodide. The preferred procedure for bis(bromomethyl)mercury was described in detail in the previous paper of this series.[1a] Diphenylmercury was prepared by the reaction of phenylmagnesium bromide in THF with mercuric chloride.

Preparation of Authentic Samples of Cyclopropanes by the Iodomethylzinc Procedure. The procedure of Simmons and Smith[4] was used to prepare authentic samples for characterization and deter-

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[20] (a) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956); (b) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

mination of glpc response factors of a number of the cyclopropanes expected from these halomethylmercurial–olefin reactions. In most cases yields were not determined; only sufficient sample for our purposes was isolated and purified. In the cases of previously prepared compounds, the infrared spectra of our samples were in good agreement with published infrared data.

***trans*-1-Ethyl-2-*n*-propylcyclopropane**, from *trans*-3-heptene (the iodomethylzinc iodide–olefin reaction is known to be stereospecific[4]), bp 99° (760 mm), n^{25}D 1.4028.

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.60; H, 14.52.

***cis*-1-Ethyl-2-*n*-propylcyclopropane**, from *cis*-3-heptene, n^{25}D 1.4039.

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.43; H, 14.74.

1,1-Diethyl-2-methylcyclopropane, from 3-ethyl-2-pentene, n^{25}D 1.4127; n^{20}D 1.4159.

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.19; H, 14.74.

1-Ethyl-1-*n*-propylcyclopropane, from 2-ethyl-1-pentene, n^{25}D 1.4079.

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.60; H, 14.32.

***n*-Amylcyclopropane**, from 1-heptene, n^{25}D 1.4112 (lit.[21] n^{25}D 1.4105).

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.81; H, 14.35.

1-Ethyl-1,2,2-trimethylcyclopropane, from 2,3-dimethyl-2-pentene, n^{25}D 1.4134 (lit.[22] n^{20}D 1.4160).

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.65; H, 14.34.

Norcarane, from cyclohexene, n^{25}D 1.4543 (lit.[4] n^{25}D 1.4546); bp 115–118° (760 mm) (lit.[4] bp 116.5°).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.41; H, 12.53.

Cyclopropyl acetate, from vinyl acetate, bp 110–112° (760 mm), n^{25}D 1.4091 (lit.[4] bp 112°, n^{25}D 1.4099).

Anal. Calcd for C_5H_8O: C, 59.98; H, 8.06. Found: C, 59.71; H, 7.98.

Phenylcyclopropane, from styrene, n^{25}D 1.5302, bp 66–67° (20 mm) (lit.[4] n^{25}D 1.5309, bp 69° (22 mm)).

1-Methylnorcarane, from 1-methylcyclohexene, bp 124–126° (760 mm), n^{20}D 1.4480, n^{25}D 1.4463 (lit.[23] bp 124.5° (762 mm), n^{20}D 1.4480).

Stability of Bis(bromomethyl)mercury in Refluxing Benzene Solution. A solution of 3.88 g (10 mmol) of the mercury compound in 10 ml of dry benzene was heated at reflux under nitrogen for 20 days. The solution was trap-to-trap distilled at 0.2 mm (room temperature). The solid residue, mp 36–41°, was impure bis(bromomethyl)mercury; 3.85 g (99%). Recrystallization from pentane gave 3.74 g (96.4% recovery) of pure material, mp 42–43.5° (lit.[1a] mp 43–44.5°).

Reaction of Bis(bromomethyl)mercury with Cyclohexene. A mixture of 3.88 g (10 mmol) of the mercurial and 16.40 g (0.2 mol) of cyclohexene in a one-necked, 50-ml flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was immersed in a 95° oil bath and stirred at reflux for 20 hr. The reaction mixture was cooled and filtered. The residue was washed with cold cyclohexene and dried to give 2.72 g (73%) of bromomethylmercuric bromide, mp 125.5–127° (lit.[13] mp 124.5–125.5°). Ethylbenzene (0.5305 g, 5.0 mmol) was added to the filtrate as internal standard. Glpc analysis showed that norcarane had been formed in 62% yield. Trap-to-trap distillation of the filtrate at 0.3 mm (pot temperature to 50°) left 1.01 g of solid residue, mp 38–41°. This is impure starting mercurial, a 26% recovery.

This general procedure was followed in all $Hg(CH_2Br)_2$–olefin reactions. In most cases gas chromatography was used to monitor the progress of the reaction and refluxing was continued until the glpc peak due to the product ceased to grow in area. As an example, in the case of a reaction of 12.5 mmol of $Hg(CH_2Br)_2$ and 0.10 mol of cyclohexene in a solvent mixture of 4 ml of benzene and 1.0 ml of ethylbenzene at 80.0 ± 0.1° the norcarane yield increased as follows: after 23 hr, 34%; 46 hr, 55%; 69 hr, 64%; 92 hr, 68%; 115 hr, 73%; 138 hr, 74%. In this reaction bromomethylmercuric bromide was recovered in 87% yield.

Reactions of Bis(bromomethyl)mercury with Other Olefins. The same general procedure as described above was used. In all the examples described in Table I the reaction mixture was stirred at reflux until the product peak in the gas chromatogram ceased to grow any further.

In the $Hg(CH_2Br)_2$–3-ethyl-2-pentene reaction (8.3 mmol of mercurial, 50 mmol of olefin, 3 ml of solvent at 80°), the 1,1-diethyl-2-methylcyclopropane yield was 31% after 5 hr, 60% after 10 hr, and 68% after 15 hr. The product had n^{25}D 1.4128. In the case of the reaction of 1-heptene (0.10 mol) with this mercurial (16.6 mmol) in 6 ml of solvent at 80°, the reaction was much slower: a 9% yield of *n*-amylcyclopropane after 23 hr, 22% after 46 hr, 33% after 69 hr, 40% after 92 hr, 45% after 115 hr, and 46% after 138 hr. The product had n^{25}D 1.4114.

In those cases where authentic samples of the product cyclopropanes had been prepared by the Simmons–Smith procedure, direct comparison of spectral properties and refractive indices was possible and in all these cases excellent agreement was observed. In other reactions the product cyclopropanes were fully characterized if they were new compounds or their spectral properties and refractive indices were compared with literature data if they had been reported previously.

***t*-Amylcyclopropane**, from 3,3-dimethyl-1-pentene (*t*-amylethylene), n^{25}D 1.4152.

Anal. Calcd for C_8H_{16}: C, 85.62; H, 14.38. Found: C, 85.49; H, 14.29.

(Triethylsilylmethyl)cyclopropane, from allyltriethylsilane, n^{25}D 1.4460.

Anal. Calcd for $C_{10}H_{22}Si$: C, 70.49; H, 13.02. Found: C, 70.66; H, 13.18.

Spiro[2.5]octane, from methylenecyclohexane, n^{25}D 1.4455 (lit.[24] n^{20}D 1.4476); nmr (in CCl_4) δ 0.19 (4 H) s, 1.0–1.8 ppm (10 H) m; ir (in CCl_4) 3060 m, 2980 m, 2950 sh, 2925 s, 2850 s, 2780 w, 1455 sh, 1445 m, 1425 m, 1370 w, 1315 w, 1288 w, 1249 s, 1114 w, 1040 w, 1029 w, 1009 m, 957 w, 926 m, 896 w, 840 w, 692 m, and 680 sh cm^{-1}.

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.16; H, 12.87.

Bicyclo[6.1.0]nonane, from cyclooctene, n^{25}D 1.4669 (lit.[11] n^{25}D 1.4662).

3-Oxabicyclo[3.1.0]hexane, from 2,5-dihydrofuran, n^{25}D 1.4352 (lit.[25] 1.4351); ir (liquid film) 3060 m, 3040 m, 2985 m, 2950 m, 2915 m, 2845 s, 2760 sh, 2710 w, 2675 w, 2640 w, 1475 w, 1440 m, 1390 w, 1370 w, 1334 m, 1302 w, 1240 w, 1198 m, 1090 s, 1055 w, 1039 w, 990 s, 945 s, 915 s, 900 s, 858 m, 815 m, 758 m, and 705 m cm^{-1}.

Cyclopropylcarbinyl isocyanate, from allyl isocyanate, n^{25}D 1.4285; nmr δ 0.1–1.0 (*ca.* 4 H) m, 1.0–1.6 (*ca.* 1 H) m, 3.29 ppm (*ca.* 2 H), d (J = 6.6 Hz); ir (liquid film) 3130 sh, 3090 m, 3015 m, 2950 m, 2885 m, 2270 s (N=C=O), 2080 w, 1470 m, 1460 sh, 1435 m, 1400 m, 1390 sh, 1380 sh, 1355 w, 1335 s, 1270 w, 1203 w, 1166 w, 1110 w, 1055 m, 1028 s, 1000 s, 985 sh, 945 s, 904 w, 865 s, 832 w, 800 m, 772 w, and 685 w cm^{-1}.

Anal. Calcd for C_5H_7NO: C, 61.83; H, 7.27. Found: C, 62.45; H, 7.36.

Olefin polymerization was a problem in the case of the reactions of bis(bromomethyl)mercury with styrene, α-methylstyrene, and methyl acrylate. However, a 22% yield of phenylcyclopropane was obtained when undistilled styrene which was inhibited with *t*-butylcatechol was used. With the other two olefins polymerization occurred even when an inhibitor was present at the start of the attempted mercurial reaction.

Reactions of the Bis(bromomethyl)mercury–Diphenylmercury Reagent with Olefins. The reaction of this reagent system with 3-ethyl-2-pentene is described as an example.

In a one-necked, 50-ml flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was prepared a solution of 3.87 g (10 mmol) of bis(bromomethyl)mercury, 3.55 g (10 mmol) of diphenylmercury, and the olefin (9.82 g, 0.1 mol) in 15 ml of benzene. The reaction mixture was stirred at reflux until no further growth was noticeable in the product peak

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(21) H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, 20, 1613 (1964).

(22) R. Ya. Levina, *Vestnik Moskov. Univ.*, 3, 123 (1948); *Chem. Abstr.*, 44, 7784 (1950).

(23) O. M. Nefedov, N. N. Novitskaya, and V. I. Shiryaev, *Dokl. Akad. Nauk SSSR*, 161, 1089 (1965).

(24) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, 70, 946 (1948).

(25) W. R. Moore and J. A. De Feo, unpublished work.

in the gas chromatogram of the reaction mixture. This required a 10-day reaction period. The volatiles were removed by trap-to-trap distillation at 0.3 mm (pot temperature to 50°). The solid residue was washed with benzene and dried under vacuum to give 6.44 g (90%) of phenylmercuric bromide, mp 270–273°. Glpc analysis (ethylbenzene internal standard) of the distillate showed that 1,1-diethyl-2-methylcyclopropane had been formed in 73% yield.

A similar procedure was followed in the reaction of bromomethylmercuric bromide and diphenylmercury (14 mmol each) with 500 mmol of cyclohexene in benzene.

Reaction of the Iodomethylmercuric Iodide–Diphenylmercury Reagent with Cyclohexene. A mixture of 9.36 g (20 mmol) of ICH_2HgI (mp 115–118°), 7.09 g (20 mmol) of diphenylmercury, 37 ml (0.365 mol) of cyclohexene, and 15 ml of dry benzene was stirred at reflux for 8 days. Filtration gave 14.7 g (91%) of phenylmercuric iodide, mp 271–274°. A recrystallized sample had mp 274–275° and did not depress the melting point of an authentic sample of phenylmercuric iodide. Glpc analysis of the trap-to-trap distilled filtrate showed that norcarane had been formed in 64% yield. An isolated sample had $n^{25}D$ 1.4548. At least five other components were observed, but they were present only in trace amounts. During the course of another such reaction, samples were withdrawn and the product yield was determined by glpc: 28% after 42 hr, 44% after 90 hr, 54% after 139 hr, 56% after 163 hr, 64% after 195 hr, and 64% after 216 hr.

A similar reaction of 20 mmol of ICH_2HgI with 37 ml of cyclohexene in 15 ml of benzene at reflux for 8 days gave norcarane in 24% yield. The reaction solids were red (HgI_2) and yellow in color.

The reactions of the $ICH_2HgI–Ph_2Hg$ reagent system with *cis*- and *trans*-3-heptenes were carried out in similar fashion.

Competition Experiments. a. Competition of 3-Ethyl-2-pentene and Cyclohexene for Bis(bromomethyl)mercury. A solution of the mercurial (10.0 mmol) and 50 mmol each of the olefins in 25 ml of benzene was immersed in an oil bath at 85° and stirred for 80 hr under nitrogen. Volatiles were removed by trap-to-trap distillation at 0.5 mm (pot temperature to 50°) and the solid residue was extracted with pentane. Bromomethylmercuric bromide, 1.59 g (42%), mp 120–123°, remained. Ethylbenzene (20 mmol) was added to the distillate as an internal standard and subsequent glpc analysis showed the yields of 1,1-diethyl-2-methylcyclopropane and norcarane to be 33.4 and 7.9%, respectively. From these data a k_{rel} ($k_{3-ethyl-2-pentene}/k_{cyclohexane}$) of 4.22 could be calculated by the method of Doering and Henderson.[15] A duplicate experiment (70-hr reaction time) gave 36.9% 1,1-diethyl-2-methylcyclopropane and 9.0% norcarane for $k_{rel} = 4.09$.

b. Competition of 1-Heptene and Cyclohexene for Bis(bromomethyl)mercury. A similar experiment was carried out using 10.0 mmol of the mercury compound and 10.0 mmol each of the olefins in 25 ml of benzene, 68 hr at reflux. The yields of *n*-amylcyclopropane and norcarane were 6.1 and 27.5% respectively; in a duplicate experiment, 5.96% and 25.4%. The k_{rel} values calculated were 0.221 and 0.234, respectively.

c. Competition of 2,3-Dimethyl-2-pentene and Cyclohexene for Bis(bromomethyl)mercury. A similar competition reaction was carried out using 10.0 mmol of the mercurial and 50 mmol of each olefin in 25 ml of benzene; reaction time, 48 hr. The bromomethylmercuric bromide yield was 48%. Preliminary examination of the trap-to-trap distillate disclosed that the peaks corresponding to 2,3-dimethyl-2-pentene and its derived cyclopropane were too close together for an accurate yield determination at the column temperature required by the other components of the reaction mixture. It therefore was decided to remove the unconverted olefins from the mixture by a hydroboration procedure.

A solution of $BF_3 \cdot OEt_2$ (32.7 g, 230 mmol) in dry diglyme (25 ml) was placed in a flask which was fitted with a nitrogen inlet tube, a pressure-equalizing addition funnel, a magnetic stirrer, and a diborane outlet tube. The dropping funnel was charged with a solution of sodium borohydride (3.79 g, 100 mmol) in 75 ml of diglyme. Dry tetrahydrofuran, 25 ml, was added to the distillate from the competition reaction and this solution was placed in a flask equipped with a sintered-glass gas dispersion tube which was connected to the outlet of the B_2H_6 generator. The entire system was flushed with nitrogen and then the $NaBH_4$ solution was added to the boron fluoride, slowly over a 1-hr period. Upon completion of the hydroboration reaction, ethylbenzene (4.00 mmol) was added to the flask containing the hydroborated reaction mixture. Subsequent glpc analysis showed that 1-ethyl-1,2,2-trimethylcyclopropane and norcarane had been produced in yields of 43.5 and 1.62%, respectively, giving a k_{rel} value of 26.9. A duplicate experiment gave $k_{rel} = 25.3$.

A separate experiment in which a mixture of 88 mmol of cyclohexene and 44 mmol of norcarane was hydroborated in similar fashion showed that such a procedure converts all of the olefin present but does not affect the cyclopropane present.

Reaction of Bromomethylmercuric Bromide with Diphenylmercury. A mixture of 1.87 g (5.0 mmol) of bromomethylmercuric bromide and 0.88 g (2.5 mmol) of diphenylmercury in 20 ml of benzene was stirred at high speed in a Morton flask for 5 hr at room temperature. The reaction mixture then was examined by thin layer chromatography (tlc) using Eastman silica gel chromatography sheet with methylene chloride–cyclohexane (25:75) eluent. Development was achieved by iodine vapor treatment followed by sodium sulfide solution spraying. Comparison of the chromatogram of the reaction mixture with tlc data for bromomethylmercuric bromide (R_f 0.15), diphenylmercury (R_f 0.65) and bis(bromomethyl)mercury (R_f 0.56) indicated the presence of bromomethylmercuric bromide and also of a new mercury compound, R_1 0.49.

The reaction mixture was filtered, and the white, crystalline solid was dried *in vacuo* to give 1.14 g of phenylmercuric bromide, mp 278–283° (3.19 mmol, 63.8% yield based on eq 7). The solvent

$$2BrCH_2HgBr + Ph_2Hg \longrightarrow (BrCH_2)_2Hg + 2PhHgBr \qquad (7)$$

was removed from the filtrate, leaving a mixture of an oil and a solid. This was extracted with chloroform. Filtration gave 0.55 g of $BrCH_2HgBr$, mp 120–123°, a recovery of 29.4%.

Heptane was added dropwise to the chloroform extract until precipitation of solid was complete. Most of the solvent was removed at reduced pressure and the remaining liquid was decanted from the solid present. The latter, 0.63 g, was identified as bis(bromomethyl)mercury, mp 41–43°. A yield of 64.8% was realized. The product showed no melting point depression when mixed with authentic material.

It would seem that the new compound detected by tlc decomposed during work-up to form bis(bromomethyl)mercury, and it is possible that this compound was $PhHgCH_2Br$.

Isolation of Bis(iodomethyl)mercury from an Attempted Reaction of $ICH_2HgI–Ph_2Hg$ with Phenylacetylene. A mixture of 12.25 g (120 mmol) of phenylacetylene, 40 mmol each of the mercury compounds, and 75 ml of dry benzene was heated under nitrogen at reflux for 4 hr. A bright yellow reaction mixture resulted. Filtration gave phenylmercuric iodide, mp 272–275°. The filtrate was evaporated to near dryness in the presence of 20 g of silica gel. This then was placed on top of a silica gel column and eluted with cyclohexane containing increasing percentages of benzene. A white, crystalline solid, mp 78–79°, was eluted with a 4:1 mixture of cyclohexane–benzene. The melting point reported for $Hg(CH_2I)_2$ is 81–82°.[6]

Anal. Calcd for $C_2H_4I_2Hg$: C, 4.95; H, 0.83; I, 52.55. Found: C, 4.98; H, 0.61; I, 52.70, 52.40.

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