P_2S_5 method, 4-methyl-2-pyrone (2.0 g) afforded 2.4 g of pasty yellow crystals which were chromatographed on silica gel with a mixture of pentane and methylene chloride. The heart cut of the yellow band gave 1.75 g of yellow solid which afforded 1.0 g of 4-methylpyran-2-thione, mp 70–71°, after recrystallization from cyclohexane–benzene.

Preparation of Methyl 4-Formylpentanoate. The enamine from pyrrolidine and propionaldehyde[22] (230 g) was added to freshly distilled, neat methyl acrylate (195 g). A yellow color and an exothermic reaction ensued. The temperature was kept below 40° by cooling, and, after 1 hr, the colorless mixture was heated on a steam bath for several hours.

A portion of the reaction mixture (27 g), while chilled in ice, was treated with 11.5 ml of concentrated hydrochloric acid. After 2 hr, this mixture was extracted twice with ether and the combined extracts were washed with water and saturated sodium chloride solution, dried over Drierite, and concentrated under vacuum to leave methyl 4-formylpentanoate (84%) as a colorless oil: ^{1}H NMR (CCl_4) δ 9.21 (1 H, d, J = 1.5 Hz, CHO), 3.64 (3 H, s, OCH_3), 1.5–2.6 (5 H, m, aliphatic), 1.12 (3 H, d, J = 7 Hz, CH_3); dinitrophenylhydrazine mp 90.5–91.5° (ethanol).

Preparation of 4-Formylpentanoic Acid. The preceding methyl ester (257 g) was hydrolyzed by treatment at 25° with a solution of 232 g of K_2CO_3 in 1 l. of water with subsequent addition of 500 ml of methanol. It is necessary to make the ester basic before methanol is added, to avoid formation of the dimethyl acetal. After 12 hr at 25°, the desired acid was isolated by removal of the methanol under vacuum and ether extraction of the acidified hydrolysis mixture. Evaporation of the ether afforded 195 g of crude acid (84%). A portion of this acid was purified by distillation [110° (3 Torr)]: ^{1}H NMR (CCl_4) δ 10.45 [1 H, s, COOH), 8.96 (1 H, s, CHO), 1.4–2.8 (5 H, m, aliphatic), 1.16 (3 H, d, J = 7 Hz, CH_3); dinitrophenylhydrazone mp 167.5–169° (ethanol). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.12; H, 7.65.

Preparation of 5-Methyl-3,4-dihydro-2-pyrone. The procedure of Pettit et al.[23] was followed, using 15.7 g of 4-formylpentanoic acid. The crude 5-methyl-3,4-dihydro-2-pyrone was obtained as a colorless oil (64%) and was purified by distillation [75° (5 Torr)]: ^{1}H NMR (220 MHz, CCl_4) δ 6.3 (1 H, dt, J = 1.5, 1.5 Hz, vinyl), 2.55 (2 H, br t, J = 7.5 Hz, CH_2CO), 2.30 (2 H, br t, J = 7.5 Hz, allylic CH_2), 1.68 (3 H, dt, J = 1.5, 0.9 Hz, CH_3). Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.23; H, 7.16.

Preparation of 5-Methyl-2-pyrone.[19] The dihydropyrone (2.25 g) was brominated with N-bromosuccinimide as described by Pettit et al.[23] and dehydrobrominated with 1,5-diazabicyclo[4.3.0]non-5-ene. On distillation, 5-methyl-2-pyrone was obtained in 40% yield.

Registry No.—P_2S_5, 1314-80-3; acetyl chloride, 75-36-5; trifluoroacetic anhydride, 407-25-0; 2-ethoxy-5-methylpyrylium fluoroborate, 54657-91-9; triethyloxonium fluoroborate 368-39-8; 3-methylglutaconic anhydride, 54657-92-0; 4-methyl-2-pyrone, 22682-12-8; methyl 4-formylpentanoate, 40630-06-6; methyl 4-formylpentanoate 2,4-DNP, 54657-93-1; pyrrolidine and propionaldehyde enamine, 13937-88-7; 4-formylpentanoic acid, 3619-43-0; 4-formylpentanoic acid 2,4-DNP, 3770-62-5; 5-methyl-3,4-dihydro-2-pyrone, 54657-94-2.

References and Notes

(1) W. H. Pirkle, H. Seto, and W. V. Turner, *J. Am. Chem. Soc.*, **92**, 6984 (1970).

(2) W. H. Pirkle and M. Dines, *J. Am. Chem. Soc.*, **90**, 2318 (1968), have described these labeled 2-pyrones.

(3) W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1644 (1975).

(4) W. H. Pirkle and L. H. McKendry, *J. Am. Chem. Soc.*, **91**, 1179 (1969).

(5) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973).

(6) R. G. S. Pong and J. S. Shirk, *J. Am. Chem. Soc.*, **95**, 248 (1973).

(7) A. Krantz, *J. Am. Chem. Soc.*, **96**, 4992 (1974).

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, p 123.

(9) This result has been independently reported: C. R. Engel, A. F. de Krassny, A. Belanger, and G. Dionne, *Can. J. Chem.*, **51**, 3263 (1973).

(10) Isolation of 3-hydroxy-2-pyrone from this pyrolysis is somewhat puzzling, since 3-hydroxy-2-pyrone itself is completely converted under similar conditions to noncondensable products (−78°, 1 Torr). However, it is perhaps relevant to the latter fragmentation that hydrolysis of a mixture of 3- and 5-trifluoroacetoxy-2-pyrone affords a mixture containing 3-hydroxy-2-pyrone and a number of other components, none of which has a ^{1}H NMR spectrum judged to be appropriate for 5-hydroxy-2-pyrone.

(11) P. Beak, D. S. Mueller, and J. Lee, *J. Am. Chem. Soc.*, **96**, 3867 (1974).

(12) R. B. Woodward and R. Hoffmann (ref 8, p 123n) refer to only one dubious example.

(13) R. Mayer, W. Broy, and R. Zahradnik, *Adv. Heterocycl. Chem.*, **8**, 219 (1967).

(14) Although dithiopyrones may also be prepared from 2-pyrones by conversion to pyran-2-thiones followed by reaction with potassium sulfide, hydrolysis of dithiopyrones to thiapyran-2-ones typically proceeds in low yield.[13]

(15) J. W. Pavlik and E. L. Clennan, *J. Am. Chem. Soc.*, **95**, 1697 (1973).

(16) W. H. Pirkle and M. Dines, *J. Heterocycl. Chem.*, **6**, 1 (1969).

(17) Similar downfield shifts of H-3 of pyridthiones relative to those of H-3 of pyridones have been observed by W. E. Stewart and T. H. Siddall, *J. Phys. Chem.*, **74**, 2027 (1970), and attributed to increased magnetic anisotropy of thione over carbonyl. However, in the pyridthiones, consistent downfield shifts of H-5 and H-6 were also observed.

(18) W. H. Pirkle and M. Dines, *J. Org. Chem.*, **34**, 2239 (1969).

(19) Cmr data for this compound are found in W. V. Turner and W. H. Pirkle, *J. Org. Chem.*, **39**, 1935 (1974).

(20) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

(21) C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970).

(22) G. Opitz, H. Helmann, and H. W. Schubert, *Justus Liebigs Ann. Chem.*, **623**, 112 (1959).

(23) G. R. Pettit, D. C. Fessler, K. D. Paull, P. Hofer, and J. C. Knight, *J. Org. Chem.*, **35**, 1398 (1970).

Halomethyl Metal Compounds. 75. Organomercury Reagents for Room Temperature Dihalocarbene Generation[1]

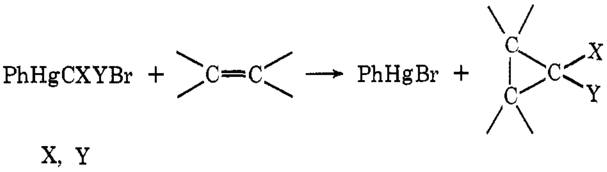
Dietmar Seyferth* and Carol K. Haas[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 22, 1974

The new organomercury reagents $PhHgCCl_2I$, PhHgCClBrI, and $PhHgCBr_2I$ were prepared and found to be effective divalent carbon transfer agents. They react with carbenophiles within 1–4 days at room temperature and within minutes at 80°. The reasons for their high reactivity are discussed.

Phenyl(bromodichloromethyl)mercury, phenyl(dibromochloromethyl)mercury, and phenyl(tribromomethyl)mercury react with a wide variety of carbenophiles (e.g., eq 1, which shows their reaction with an olefin).[3,4] At 80°, these reactions are rapid and go to completion within 2 hr. At lower temperatures, the rates are correspondingly slower. These reactions proceed even at room temperature, but 16–18 days are required in order to obtain high product yields.[5]

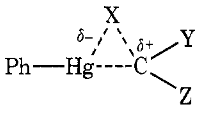


(1)

X, Y
Cl, Cl
Cl, Br
Br, Br

The advantages of these organomercury reagents are that they release dihalocarbenes under neutral conditions by a direct carbene extrusion mechanism, without intervention of other intermediates such as the trihalomethyl anion,[6] and that their divalent carbon transfer reactions proceed in high yield because carbene-diverting side reactions do not intrude with most carbenophiles.

The transition state which is believed to be involved in the carbene extrusion step is I,[6] i.e., a concerted process in-



I

volving intramolecular nucleophilic attack by X at mercury and heterolytic Hg–C and C–X bond fission to give PhHgX and the carbene CYZ. Consequently, if all other factors are held constant in I, one might expect that the carbene extrusion reactivity would change as X was varied in the order I > Br > Cl, since this is the well-known order of halide ion nucleophilicity and since the C–X bond energies increase in the order C–I < C–Br < C–Cl. In earlier work we had found $PhHgCCl_3$ (PhHgCl eliminated) to be a much less reactive dichlorocarbene source than $PhHgCCl_2Br$ (PhHgBr eliminated),[3,4] so a phenyl(trihalomethyl)mercury compound whose decomposition would involve phenylmercuric iodide elimination would be expected to be rather more reactive than an analogous one in which the decomposition proceeded by way of phenylmercuric bromide elimination. Accordingly, we decided to investigate the synthesis, thermal stability, and preparative utility of mercurials of the type PhHgCXYI (X = Cl, Br).

Results and Discussion

Our general procedure for the preparation of $PhHgCCl_2Br$ (eq 2)[7] has been adapted, with minor varia-

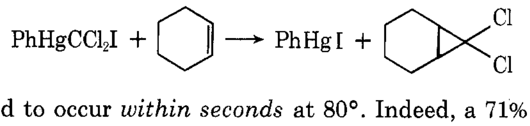
$$PhHgCl + Me_3COK + HCCl_2Br \xrightarrow{\text{THF, -25°}} PhHgCCl_2Br + Me_3COH + KCl \quad (2)$$

tions, to the synthesis of many other organomercurials.[4] This procedure also could be applied successfully to the preparation of $PhHgCCl_2I$, PhHgCClBrI, and $PhHgCBr_2I$, but some modifications were required in view of the very limited stability of these reagents.

Several attempts to prepare phenyl(iododichloromethyl)mercury from phenylmercuric chloride in THF according to the published[7] procedure failed; phenylmercuric iodide was the only organomercury product isolated. Its isolation, together with the observation of the yellow color of the CCl_2I^- anion during the addition of $CHCl_2I$ to the $PhHgCl–Me_3COK$ mixture and its apparent discharge on reaction with phenylmercuric chloride, suggested that the desired mercurial was being formed but that it was too reactive under the conditions of work-up to allow isolation. Consequently, in subsequent reactions, lower reaction temperatures were used, a minimum quantity of reaction solvent mixture was used, and all extraction solvents were chilled to 0° before use; in addition, all steps of the synthesis were carried out with maximum dispatch. In the successful preparation of $PhHgCCl_2I$, the iododichloromethane was added to the slurry of phenylmercuric chloride and potassium *tert*-butoxide in a minimum amount of 1:1 THF–diethyl ether at −70°. Immediately upon completion of the addition the work-up procedure was initiated and the desired organomercury reagent was obtained consistently in about 50% yield. An analytically pure sample could be obtained, but the extreme reactivity of phenyl(iododichloromethyl)mercury makes its complete purification extremely difficult and inefficient. The attempt to recrystallize this material slowly always results in some decomposition to phenylmercuric iodide. For practical purposes it is better to filter a solution of the crude product in dichloromethane into pentane which has been chilled to −78° and collect the solid which precipitates. The microcrystalline yellow solid thus obtained has a purity of 75–90%, as determined by its reaction with cyclohexene. In this synthesis it is essential that all operations, in particular the removal of solvents from the reaction mixture, be carried out *as quickly as possible.*

The application of this modified method to the synthesis of phenyl(iodobromochloromethyl)mercury and phenyl(iododibromomethyl)mercury also proved successful. Both mercury compounds also are yellow, microcrystalline, and very reactive solids. All three of the new reagents prepared were found to be stable for several weeks at 0° as the dry solid; they also are stable toward oxygen. However, care must be taken to avoid contamination of these materials with traces of oxygen-containing solvents such as THF, diethyl ether, acetone, methanol, or ethanol. When traces of any of these are present, the solid mercurials will invariably undergo exothermic and complete decomposition. Such a catalytic decomposition even occurred with a sample of $PhHgCCl_2I$ which was being stored at 0° in the refrigerator in a flask that had been rinsed with acetone but apparently still contained traces of the rinse liquid. The exact nature of this decomposition is not known; it is not effected by atmospheric oxygen or by light and is in accord with the observed lower stability of halomethylmercurials in ether solvents when compared to hydrocarbon solvents. Presumably an exothermic chemical reaction of the mercurial with the oxygen-containing solvent is involved which generates a "hot spot" in the solid sample and provides the activation energy for further (rapid) decomposition. Moistening of these mercurials with hexane, benzene, or dichloromethane did not result in such decomposition. A similar phenomenon has been observed with phenyl(fluorodibromomethyl)mercury, which is another reactive, "room temperature" dihalocarbene precursor.[8]

As expected, phenyl(iododichloromethyl)mercury is a very reactive dichlorocarbene transfer reagent. When this mercurial was stirred with an excess of cyclohexene in benzene solution at room temperature, the yellow color of the mercury compound was discharged completely within 24 hr, while white phenylmercuric iodide precipitated. 7,7-Dichloronorcarane was formed in 89% yield during this time (eq 3). A similar transfer of CCl_2 to cyclohexene was



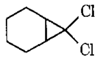
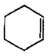
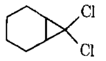
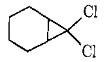
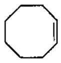
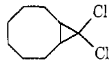
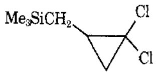
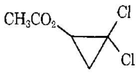
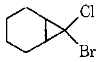
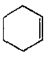
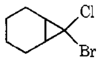
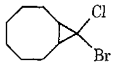
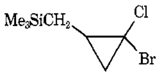
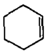
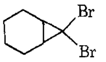
(3)

found to occur *within seconds* at 80°. Indeed, a 71% yield of 7,7-dichloronorcarane could be obtained by stirring a solution of $PhHgCCl_2I$ with cyclohexene at 0° for 8 days. A comparison of similar CCl_2 transfer to cyclohexene at 80° and at room temperature using $PhHgCCl_2Br$ (vide supra) shows the dramatic effect of changing the halogen atom X in $PhHgCCl_2X$ from Br to I.

The transfer of dichlorocarbene from $PhHgCCl_2I$ to other carbenophiles could be effected in high yield within 24 hr at room temperature; these results are included in Table I. Again, the progress of these reactions could be followed by noting the gradual disappearance of the yellow color of the reagent. In no cases were any organic iodine products observed.

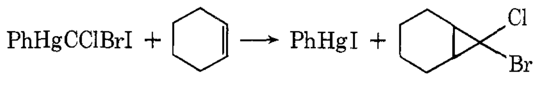
Phenyl(iodobromochloromethyl)mercury served as a

Table I
Divalent Carbon Transfer Reactions of Phenyl(iododihalomethyl)mercury Compounds

Mercury reagent[a] (mmol)	Carbenophile (mmol)		Ml of benzene	Reaction time	Reaction temp, °C	Product (% yield)		PhHgI, % yield
$PhHgCCl_2I$ (10.5)[c]		(30)[d]	15	24 hr	25		(89)	92
$PhHgCCl_2I$ (10)		(30)	25	<1 min	80		(85)	94
$PhHgCCl_2I$ (7.5)		(30)	15	8 days	0		(71)	80
$PhHgCCl_2I$ (7.3)		(30)[e]	15	24 hr	25		(93)	93
$PhHgCCl_2I$ (9.8)	$Me_3SiCH_2CH{=}CH_2$	(30)[f]	15	24 hr	25		(95)	88
$PhHgCCl_2I$ (10)	$CH_3CO_2CH{=}CH_2$	(30)[g]	15	24 hr	25		(38)	72
$PhHgCCl_2I$ (7.1)	Et_3SiH	(30)	15	24 hr	25	Et_3SiCCl_2H	(83)	82
PhHgCClBrI (10)[h]		(30)	20	4 days	25		(75)[b]	80
PhHgCClBrI (10)		(30)	50	<10 min	80		(81)[b]	82
PhHgCClBrI (10)		(30)	20	4 days	25		(83)[b]	87
PhHgCClBrI (10)	$Me_3SiCH_2CH{=}CH_2$	(30)	20	4 days	25		(78)[b]	80
PhHgCClBrI (10)	Et_3SiH	(30)[i]	20	4 days	25	$Et_3SiCHBrCl$	(60)	84
$PhHgCBr_2I$ (10.4)[j]		(30)	20	7 days	25		(65)	70

[a] Number of millimoles of active reagent in sample used (usually 70–90% purity). [b] Mixture of isomers. [c] Registry no., 33441-85-9. [d] Registry no., 110-83-8. [e] Registry no., 931-88-4. [f] Registry no., 762-72-1. [g] Registry no., 108-05-4. [h] Registry no., 35349-96-3. [i] Registry no., 617-86-7. [j] Registry no., 54724-58-2.

source of chlorobromocarbene at room temperature. However, a reaction time of 4 days was required with cyclohexene in benzene solution before the yellow color of the mercury reagent had disappeared and thin layer chromatography[3] indicated that the starting material had been consumed. Again, exclusive elimination of phenylmercuric iodide appeared to be occurring, since only chlorobromocarbene-derived products were obtained (eq 4). Transfer of



(4)

CClBr from this mercurial was complete within minutes at 80°.

The divalent carbon transfer reactivity of phenyl(iododibromomethyl)mercury, which could not be obtained analytically pure, was investigated only briefly. A solution of this compound and cyclohexene in benzene required stirring for 7 days at room temperature before TLC indicated that the starting material had been consumed. Thus $PhHgCBr_2I$ is only about two times more reactive than $PhHgCBr_3$. Furthermore, the product yields obtained with $PhHgCBr_2I$ unaccountably were not high (60–65%), so no advantage can be gained by using this reagent.

All of the dihalocarbene transfer reactions effected with these new reagents are summarized in Table I.

A comparison of the periods of time required for complete decomposition at room temperature of various phenyl(trihalomethyl)mercury reagents in the presence of the same carbene trap, cyclohexene, is given in Table II. In all

Table II
Times Required for Decomposition in Benzene Solution in the Presence of Cyclohexene at Room Temperature

Compd	Registry no. (X = Br)	X = Br[5]	X = I
$PhHgCCl_2X$	3294-58-4	18 days	24 hr
PhHgCClBrX	3294-59-5	16 days	4 days
$PhHgCBr_2X$	3294-60-8	15 days	7 days

cases substitution of an iodine for a bromine as the eliminated halide results in increased thermal lability. This is entirely in accord with the ideas discussed in the introduction.

The variation of decomposition rate among the various iodine-containing mercurials possibly can be rationalized in terms of the ability of the other halogen substituents to stabilize the carbene center. Thus chlorine provides better p_π–p_π stabilization at the incipient carbene center than does bromine. Our other studies[9] have provided evidence that the stability of the extruded carbene is an important factor in determining the effectiveness of a halomethylmercury compound; the more stable the carbene formed, the faster its rate of extrusion.

The lack of practical utility of $PhHgCBr_2I$ already has been noted. Another factor which is of some importance as far as the application of these new reagents in synthesis is concerned is the availability of the required haloforms. The preparation of dibromoiodomethane and chlorobromoiodomethane is cumbersome and this immediately detracts from any potential attractiveness of $PhHgCBr_2I$ and PhHgCClBrI. On the other hand, the preparation of dichloroiodomethane is not difficult. However, in spite of this fact and in spite of the attractive synthetic applicability of $PhHgCCl_2I$ as described above, this reagent cannot be recommended as a "routine" CCl_2 source. Its handling requires the greatest care in view of its thermal lability and its ready catalytic decomposition by various common solvents. Prudence dictates that its synthesis and storage be carried out on a relatively modest scale—no more than about 0.25 mol. As a result, for room-temperature applications the less reactive but equally reliable[5] and much more easily prepared and handled $PhHgCCl_2Br$ will be preferable.[10]

Experimental Section

General Comments. All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF), benzene, and hexane (all reagent grade) were distilled from sodium benzophenone ketyl before use.

Infrared spectra were recorded using a Perkin-Elmer 257 or 457A grating infrared spectrophotometer, NMR spectra using a Varian Associates T60 or a Perkin-Elmer Hitachi R-20B spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Chloroform (δ 7.27 ppm) and dichloromethane (δ 5.30 ppm) also were used as internal standards.

Gas chromatography (GLC) was used routinely for isolation of pure samples, for determination of purity, and for yield determinations using an appropriate internal standard. All columns were packed with acid-washed dimethyldichlorosilane-treated Chromosorb W.

Preparation of Haloforms. Iododichloromethane was prepared by a modification of the procedure of Soroos and Hinkamp[11] for the preparation of iodoform. In this case a large excess (1200 ml) of chloroform was treated with iodomethane (400 g) and a catalytic amount of aluminum chloride (30 g) at reflux until evolution of chloromethane ceased. In this manner, $CHCl_2I$ could be prepared in 54% yield on up to a 7-mol scale with no difficulty. Iodobromochloromethane and iododibromomethane were prepared by treatment of dibromochloromethane and bromoform, respectively, with sodium methoxide in the presence of sodium iodide by the method of Hine and Prossner.[12] In both cases, the yields were low and careful fractional distillation was required to separate product and starting material. All three haloforms are very sensitive toward light.

An alternate procedure for the preparation of iododibromomethane was developed which involves the iodination of $CHBr_2MgCl$. This has the advantage of making the isolation of the product easier, since no bromoform remains in the reaction mixture.

Into a 2-l. flask equipped with mechanical stirrer, addition funnel, pentane thermometer, and nitrogen inlet were placed 69 ml (0.8 mol) of bromoform and 500 ml of THF. The solution was cooled to −80° and 0.8 mol of isopropylmagnesium bromide was added over a 1-hr period, while the temperature was kept below −70°. In portions, 200 g (0.8 mol) of iodine was added over a 10-min period via a transfer tube. The reaction mixture at −70° was stirred for 6 hr and subsequently was hydrolyzed with ca. 100 ml of saturated ammonium chloride solution and filtered to remove the precipitated magnesium salts. The organic layer was reduced in volume to 400 ml by rotary evaporation and the remaining brown liquid was washed with several portions of 1 *M* sodium thiosulfate solution totaling 400 ml in volume. The residue was trap-to-trap distilled (50°, 0.2 mm); the distillate was washed with 100 ml of 1 *M* thiosulfate solution, which removed all the remaining brown color. Redistillation (10-cm Vigreux column) yielded 50 g (25%) of iododibromomethane, bp 62° (2.8 mm), $n^{25}D$ 1.6807.

Preparation of Phenyl(iododichloromethyl)mercury. Into a 1-l. flask equipped with mechanical stirrer, pressure-equalizing dropping funnel, pentane thermometer, and nitrogen inlet were placed 50.0 g (0.16 mol) of phenylmercuric chloride and 150 ml of diethyl ether. To this slurry, chilled to −55°, was added, over a 5-min period, 25 g (0.22 mol) of potassium *tert*-butoxide (M. S. A.) in 120 ml of THF. The resulting mixture was stirred at −55° for a 15-min period, during which time most of the mercuric halide dissolved. To this was added, over a 10-min period, keeping the temperature below −55°, 40.0 g (0.18 mol) of iododichloromethane. After 3 min of additional stirring, the solvents were removed rapidly in vacuo from the dark yellow-green reaction mixture. To the colored solids were added 75 ml of water and 600 ml of chilled (ca. 0°) methylene chloride. The methylene chloride layer was decanted through a paper towel into a chilled flask (ca. −70°). The water layer was extracted with two 100-ml portions of methylene chloride. The filtered organic layers were combined and the solvent was removed rapidly on a rotary evaporator. The yellow solid was dissolved in 200 ml of chilled methylene chloride and the solution was filtered into 600 ml of pentane chilled in a Dry Ice–acetone bath. After 3 min, 40 g (52%) of the mercurial was collected by filtration as a yellow, microcrystalline solid. Evaporation of the mother liquor to 150 ml produced another 5 g (6%) of the desired material. The solid was identified as phenyl(iododichloromethyl)mercury on the basis of the following: mp 72° (instant decomposition); ir (CCl_4) 3030 m, 3025 m, 1805 w, 1630 m, 1573 w, 1480 m, 1433 s, 1330 w, 1300 w, 1065 w, 1030 m, 1003 m, 915 w, 850 w, 735 m, 700 s, 633 cm^{-1} m; NMR ($CDCl_3$) δ 7.30 (s, 5, C_6H_5).

Anal. Calcd for $C_7H_5Cl_2IHg$: C, 17.24; H, 1.03; I, 26.04. Found: C, 17.09; H, 1.08; I, 25.72. (Calcd for C_6H_5HgI: C, 17.80; H, 1.25; I, 31.37.)

Thermal Analysis of Phenyl(iododichloromethyl)mercury. Into a tared 50-ml flask with magnetic stir bar were placed 1.498 g of the crude title mercurial and 2 ml of cyclohexene. The mercurial solution was stirred at 40° for 12 hr, during which time PhHgI was precipitated. All volatile materials (cyclohexene and 7,7-dichloronorcarane by GLC) were removed by evacuation (40°, 0.07 mm) for 5 hr and the flask was reweighed. A 0.2170-g weight loss was noted. Calculations as follows indicated a sample purity of 86%: 0.2170 g of dichlorocarbene formed/0.0829 g/mol of dichlorocarbene = 2.62 mmol of carbene in sample; 2.62 mmol × 487.5 mg of $PhHgCCl_2I$/mmol = 1280 mg of $PhHgCCl_2I$ in sample; 1.280 g of $PhHgCCl_2I$/1.498 g of sample = 86% pure by weight.

Catalytic Solvent-Induced Decomposition of Phenyl(iododichloromethyl)mercury. Into a 10-ml erlenmeyer flask was placed ca. 0.2 g of the title mercurial. Two drops of the appropriate solvent was placed directly onto the solid. When acetone, THF, methanol, ethanol, or ether was used, after 10 sec had elapsed, decomposition accompanied by emission of white fumes abruptly commenced. When hexane, benzene, methylene chloride, chloroform, or water was employed, no such decomposition ensued; the mercurial remained unchanged. Similar results were obtained in flasks flushed with argon or air, or in flasks exposed to or shielded from the light.

Preparation of Phenyl(iodobromochloromethyl)mercury. Into a 1-l. flask equipped with mechanical stirrer, addition funnel, pentane thermometer, and nitrogen inlet were placed 50 g (0.16 mol) of phenylmercuric chloride and 150 ml of anhydrous diethyl ether. To this slurry, chilled to −65°, was added over a 3-min period 25 g (0.22 mol) of potassium *tert*-butoxide (M. S. A.) in 120 ml of THF. This mixture was stirred at −65° for 15 min. To this was added over a 10-min period, while the temperature was kept below −60°, 44 g (0.18 mol) of freshly distilled iodobromochloromethane. After the solvents had been removed from the deep orange solution at reduced pressure, 800 ml of chilled methylene chloride and 75 ml of cold water were added to the remaining solids. The yellow organic layer was rapidly filtered into a flask chilled to −70°. After removal of the methylene chloride, the solid residue was dissolved in 150 ml of methylene chloride and the solution was filtered into 600 ml of hexane chilled to −70°. After 5 min of chilling, 61 g of yellow, microcrystalline phenyl(iodobromochloromethyl)mercury was filtered with suction. The mother liquor was reduced in volume to 200 ml and an additional 4 g of solid was collected to give a total yield of 76%. The dry mercurial was stored in the freezer. A twice recrystallized sample melted at 78° with decomposition: ir (Nujol mull) 1500 w, 1435 m, 1370 m, 1025 w, 1000 w, 735 s, 720 s, 695 m, 660 w, 635 cm^{-1} m; NMR ($CDCl_3$) δ 7.32 (s, 5, C_6H_5).

Anal. Calcd for $C_7H_5BrClIHg$: C, 15.80; H, 0.95; I, 23.86; Hg, 37.70. Found: C, 15.62; H, 0.87; I, 23.74; Hg, 38.06.

Preparation of Phenyl(iododibromomethyl)mercury. To a slurry of 50 g (0.16 mol) of phenylmercuric chloride in 120 ml of diethyl ether chilled to −70° was added a solution of 25 g (0.22 mol) of potassium *tert*-butoxide (M. S. A.) in 100 ml of THF over a period of 5 min. This slurry was stirred for 1 hr, and then 60 g (0.20 mol) of iododibromomethane was added over a 7-min period while the temperature was maintained below −60°. The solvents were removed at reduced pressure from the yellow-orange solution, and the remaining solid was treated with 600 ml of chilled methylene chloride and 50 ml of water. The solvents were removed quickly from the filtered, orange organic layer. The remaining solid was dissolved in 150 ml of methylene chloride and filtered into 600 ml of hexane chilled to −70°. After the filtrate had been chilled for 5 min, 45 g (49%) of a yellow, microcrystalline solid was removed by filtration. Satisfactory elemental analysis on a twice recrystallized sample of mp 85° dec was not obtained but the spectral data support the assignment of structure as phenyl(iododibromomethyl)-mercury. Similar features to those for $PhHgCCl_2I$ and PhHgCClBrI are seen in the infrared spectrum. TLC indicates that only one compound is present: ir (Nujol mull) 3060 w, 2857 m, 1523 w, 1475 m, 1460 m, 1258 w, 1058 w, 1021 w, 1012 w, 992 w, 908 w, 798 w, 728 s, 693 cm^{-1} s; NMR ($CDCl_3$) δ 7.38 (s, 5, C_6H_5).

Anal. Calcd for $C_7H_5Br_2IHg$: C, 14.58; H, 0.88. Found: C, 11.91; H, 0.98.

Several attempts were made to recrystallize this mercurial more slowly. While this was occasionally successful, several times a dark red color appeared as phenylmercuric halide was rapidly deposited. Once this decomposition commenced, none of the desired mercurial could be recovered.

Reaction of Phenyl(iododichloromethyl)mercury with Cyclohexene at Room Temperature. Into a 50-ml flask equipped with thermometer and nitrogen inlet were placed 2.46 g (30 mmol) of cyclohexene (distilled from $LiAlH_4$), 6.0 g of 86% pure (10.5 mmol of active reagent) title mercurial, and 15 ml of benzene. The solution was stirred for 24 hr, during which time the yellow color of the mercurial was discharged and white phenylmercuric iodide precipitated. TLC monitoring confirmed that the starting material had been consumed by the end of this period. The mixture was filtered to give 4.72 g (92%, corrected for starting mercurial purity) of phenylmercuric iodide, mp 264° (lit.[13] mp 269°). The clear filtrate was trap-to-trap distilled (40°, 0.05 mm) into a liquid nitrogen chilled receiver. GLC analysis (10% UC-W98, 120°) using dodecane as the internal standard indicated an 89% yield of 7,7-dichloronorcarane. The product was identified by comparison of its GLC retention time and the infrared spectrum of a GLC-collected sample (20% UC-W98, 140°) with those of authentic material.

Reaction of Phenyl(iododichloromethyl)mercury with Cyclohexene at 0°. Into a 50-ml flask were placed 2.46 g (30 mmol) of cyclohexene, 4.88 g of 75% pure (7.5 mmol) phenyl(iododichloromethyl)mercury, and 15 ml of benzene. The yellow solution was stirred for 8 days at 0°, during which time the yellow color of the mercurial gradually disappeared. Filtration yielded 80% of phenylmercuric iodide, mp 260°. Trap-to-trap distillation and GLC yield analysis as above showed the presence of a 71% yield of 7,7-dichloronorcarane.

Reaction of Phenyl(iododichloromethyl)mercury with Cyclohexene at 80°. Into a 50-ml flask equipped with thermometer, reflux condenser, pressure-equalizing dropping funnel, and nitrogen inlet were placed 2.56 g (30 mmol) of cyclohexene and 3 ml of benzene. The olefin solution was heated to reflux, and then a solution of 5.7 g (10 mmol) of 86% pure title mercurial in 20 ml of benzene was added over a period of 3 min. The yellow color of the mercurial was completely discharged within 10 sec of its addition. After the reaction mixture was cooled, 4.63 g (94%) of phenylmercuric iodide, mp 260°, was collected by filtration. Trap-to-trap distillation and yield analysis, as above, showed an 85% yield of 7,7-dichloronorcarane.

Reaction of Phenyl(iodobromochloromethyl)mercury with Cyclohexene at 80°. Into a 50-ml flask equipped with thermometer, reflux condenser, pressure-equalizing dropping funnel, and nitrogen inlet were placed 2.46 g (30 mmol) of cyclohexene and 3 ml of benzene. To the refluxing olefin was added 5.3 g (10 mmol) of the title mercurial in 20 ml of benzene over a period of 4 min. The yellow color of the mercurial was completely discharged within 3 min of its addition. After the reaction mixture had been cooled, 3.3 g (82%) of phenylmercuric iodide, mp 255°, was collected by filtration. GLC analysis of the distilled filtrate (as above) showed an 81% yield of 7-bromo-7-chloronorcarane.

Reaction of Phenyl(iododibromomethyl)mercury with Cyclohexene at Room Temperature. In a 50-ml flask 2.86 g (30 mmol) of cyclohexene (distilled from $LiAlH_4$), 6.0 g (10.4 mmol) of the title mercurial, and 20 ml of benzene were stirred for 7 days at room temperature, during which time the dark yellow-orange color of the mercurial became less intense. TLC monitoring of the reaction indicated that the starting mercurial had been consumed by the end of this period. Filtration yielded 2.5 g (70%) of white phenylmercuric iodide, mp 255°. GLC analysis (column A, 140°, dodecane) of the trap-to-trap distillate (60°, 0.05 mm) indicated a 65% yield of 7,7-dibromonorcarane. Spectral data on a GLC-collected sample agreed with those for authentic material.

All other reactions listed in Table I were carried out using these general procedures at the temperatures indicated. In all reactions carried out, samples of the dihalocyclopropane or the triethyl(dihalomethyl)silane produced were isolated by GLC and their identities were confirmed by comparison of their GLC retention times and ir spectra with those of authentic samples from our previous studies with $PhHgCCl_2Br$, $PhHgCClBr_2$, and $PhHgCBr_3$.[3,14-16]

Acknowledgments. The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-72-2204) for generous support of this research and to M & T Chemicals, Inc., for gifts of chemicals.

Registry No.—Iododichloromethane, 594-04-7; iodobromochloromethane, 34970-00-8; iododibromomethane, 593-94-2; $CHBr_2MgCl$, 17609-20-0; phenylmercuric chloride, 100-51-6.

References and Notes

(1) Part 74: D. Seyferth, G. J. Murphy, R. L. Lambert, Jr., and R. E. Mammarella, *J. Organomet. Chem.*, **90**, 173 (1975).
(2) National Science Foundation Graduate Fellow, 1970–1973; Sloan Research Trainee, 1973–1974.
(3) 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).
(4) D. Seyferth, *Acc. Chem. Res.*, **5**, 65 (1972).
(5) D. Seyferth and H. Shih, *Organomet. Chem. Synth.*, **1**, 415 (1972).
(6) (a) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 4953 (1967); (b) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *ibid.*, **90**, 6182 (1968).
(7) D. Seyferth and R. L. Lambert, Jr., *J. Organomet. Chem.*, **16**, 21 (1969).
(8) D. Seyferth and S. P. Hopper, *J. Organomet. Chem.*, **51**, 77 (1973).
(9) Discussed in summary form in ref 8 and in D. Seyferth and R. A. Woodruff, *J. Organomet. Chem.*, **71**, 335 (1974).
(10) If the olefinic carbenophile contains no functional groups that are very base sensitive or if it is not one which can intercept a trihalomethyl anion, then the phase transfer catalysis procedure can, of course, be applied to dihalocyclopropane preparation at around room temperature. For a review see E. V. Dehmlow, *Angew. Chem.*, **86**, 187 (1974).
(11) H. Soroos and J. B. Hinkamp, *J. Am. Chem. Soc.*, **67**, 1642 (1945).
(12) J. Hine and F. P. Prosser, *J. Am. Chem. Soc.*, **80**, 4282 (1958).
(13) A. N. Nesmejanow, *Ber.*, **62**, 1013 (1929).
(14) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organomet. Chem.*, **7**, 405 (1967).
(15) D. Seyferth, S. P. Hopper, and T. F. Jula, *J. Organomet. Chem.*, **17**, 193 (1969).
(16) D. Seyferth and S. P. Hopper, *J. Organomet. Chem.*, **23**, 99 (1970).