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HALOMETHYL—METAL COMPOUNDS

LXXVIII*. CYCLOHEXYL- AND β-PHENYLETHYL-(TRIHALOMETHYL)-MERCURY COMPOUNDS AS DIHALOCARBENE PRECURSORS AT ROOM TEMPERATURE

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Summary

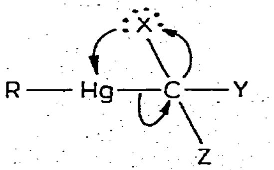
Alkyl(trihalomethyl)mercury compounds, RHgCXYBr (R = cyclohexyl and $PhCH_2CH_2$; X, Y = Cl, Cl; Cl, Br; Br, Br) as well as the corresponding $RHgCCl_3$ compounds have been prepared and evaluated as divalent carbon transfer reagents. All were found to be much more reactive than the corresponding phenyl(trihalomethyl)mercurials. The cyclo-C_6H_{11}HgCXYBr (X, Y = Cl, Cl; Cl, Br) compounds were found to be quite effective carbene transfer reagents at room temperature.

Introduction

Our previous research on the chemistry of trihalomethylmercury compounds has shown that their thermolysis proceeds by way of reversible extrusion of a dihalocarbene (eqn. 1) [2]. If suitable carbenophiles are present, they

$$RHgCX_3 \rightleftharpoons RHgX + CX_2 \qquad (1)$$

can intercept the carbene thus generated. The available evidence suggests that an intramolecular, concerted carbene extrusion reaction is involved [3]:



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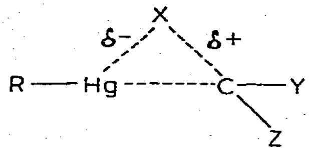
[*] Part LXXVII: ref. 1.

[**] Sloan Research Trainee, 1973-1974.

The transition state for this process would be:



(I)

We examined the effect of changing X, the leaving halogen substituent, on the rate of the extrusion process and have found this to be: I > Br > Cl ‖ F [4]. Thus $PhHgCCl_2I$ decomposition (to give PhHgI and CCl_2) in benzene/cyclohexene was complete within 24 h at room temperature [5], while similar CCl_2 extrusion from $PhHgCCl_2Br$ required 18 days [6]. Phenyl(trichloromethyl)mercury was still less reactive, and the decomposition of phenyl(fluorodichloromethyl)-mercury gave exclusively chlorofluorocarbene and phenylmercuric chloride [7]. We have also studied the effects of changing the substituents, Y and Z, of the incipient carbene in various functional phenyl(dihalomethyl)mercurials of type $PhHgCX_2Z$. The observations that when Z = Ph and F, carbene extrusion is accelerated [8,9] and when Z = H or a group which usually stabilizes an adjacent carbanionic center, the divalent carbon transfer is much slower [10], spoke in favor of transition state I.

The effect of the remaining variable on I, the other organic substituent on mercury, is the subject of the present report. We had carried out almost all of our studies with phenylmercury derivatives for several practical reasons. First, the phenylmercuric halides used in the phenyl(trihalomethyl)mercury preparations are easily prepared from commercially available starting materials. Second, the phenyl(trihalomethyl)mercurials in general are crystalline, readily purified materials which are stable to the moisture and oxygen in the air. Finally, the phenylmercuric halides formed in the carbene extrusion reaction are very poorly soluble in most organic solvents at room temperature, so that in most divalent carbon transfer reactions effected with phenyl(trihalomethyl)mercury reagents product work-up is quite simple. Any change of the organic group on mercury from the phenyl group usually used would have to be a major one; we had found that simply adding electron-releasing or electron-withdrawing substituents to the phenyl group had essentially no effect on the rate of carbene extrusion [3]. It was the interesting report on n-propyl(trihalomethyl)mercury compounds by Shcherbakov [11] which prompted us to investigate various alkyl(trihalomethyl)mercury systems in the hope of developing new and useful carbene transfer systems. Shcherbakov found that n-propyl(bromodichloromethyl)mercury can be prepared and isolated as an unpurifiable liquid which decomposes within 2-3 days at room temperature. This compound reacted with cyclohexene at room temperature to give 7,7-dichloronorcarane in 70% yield after a reaction time of three days. At 40°C, this CCl_2 transfer reaction was complete within 5 h. n-Propyl(trichloromethyl)mercury also was prepared [11]. This compound, a liquid, reacted with cyclohexene at 80°C, giving 7,7-dichloronorcarane in 82% yield in 8 h; hence it is considerably more reactive than $PhHgCCl_3$ which requires 36-48 h to effect the same conversion.

The high reactivity of these alkyl(trihalomethyl)mercurials was interesting, but the high toxicity of all volatile alkylmercurials and their tendency to autoxidize under normal laboratory conditions makes the n-propyl derivatives rather unattractive. Alkyl(trihalomethyl)mercury compounds which are relatively nonvolatile, crystalline solids whose decomposition gives crystalline, relatively poorly soluble alkylmercuric halides were desired for synthetic applications.

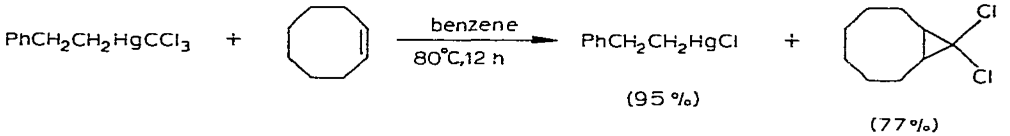
Results and discussion

Initial work focussed on the preparation of alkyl(trichloromethyl)mercury compounds. It was found that a modification of our standard procedure for phenyl(trihalomethyl)mercury preparation [12] was applicable (eqn. 2). Only one molar equivalent of potassium t-butoxide can be used; an excess resulted

$$\mathrm{RHgCl + Me_3COK \xrightarrow[\text{or } Me_2O/THF]{THF,\ -60^\circ} \xrightarrow{CHCl_3} RHgCCl_3 + Me_3COH + KCl} \qquad (2)$$

in loss of product. Low reaction temperatures were found to be essential, as were rapid work-up and product isolation. The $RHgCCl_3$ compounds are somewhat air-sensitive and are best stored under nitrogen or argon. Induced decomposition of the solid in the presence of small amounts of certain oxygen-containing solvents of the type encountered with phenyl(iododichloromethyl)mercury [5] also was observed with the alkyl(trihalomethyl)mercurials.

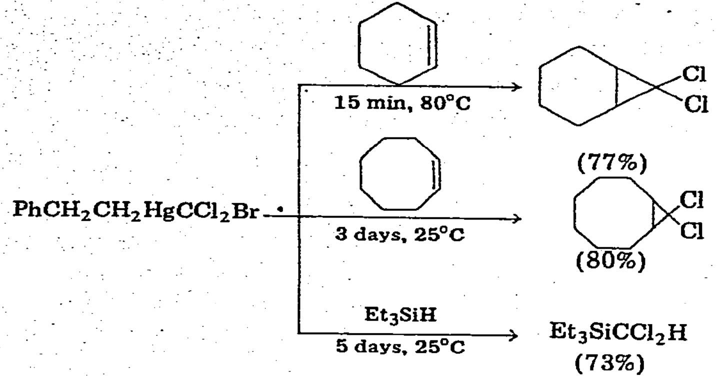
Benzyl(trichloromethyl)mercury, m.p. 65°C, a known compound [13], was prepared and tested first as a CCl_2 source. This mercurial, however, decomposed to give elemental mercury, not benzylmercuric chloride, presumably by way of a homolytic process, when heated at 80°C in the presence of cyclooctene. This observation was confirmed subsequently by Reutov and his coworkers [14]. β-Phenylethyl(trichloromethyl)mercury, obtained as a low-melting solid, m.p. 43-45°C with decomposition, on the other hand, was an effective CCl_2 reagent (eqn. 3). A similar reaction with cyclohexene in benzene medium at 80°C gave



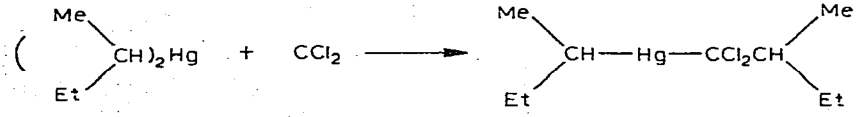
(3)

7,7-dichloronorcarane in 65% yield after 14 h. In view of the higher reactivity of $PhCH_2CH_2HgCCl_3$, as compared with $PhHgCCl_3$, we prepared $PhCH_2CH_2HgCCl_2Br$, which would then be expected to react more rapidly than $PhHgCCl_2Br$ with carbenophiles. This proved to be the case, as shown in Scheme 1.

Our further attention focussed on cyclohexyl(trihalomethyl)mercury compounds, all of which are crystalline solids. Cyclohexyl(trichloromethyl)mercury, m.p. 50-52°C, had been prepared previously but not examined as a CCl_2 source [13], and we also prepared cyclo-$C_6H_{11}HgCCl_2Br$, m.p. 53-56°C, cyclo-$C_6H_{11}HgCClBr_2$, m.p. 60-63°C (dec), and cyclo-$C_6H_{11}HgCBr_3$, m.p. 53-56°C (dec). With the exception of the latter, these were found to be very effective dihalocarbene transfer reagents, at 80°C and at room temperature. Table 1 summarizes their reactions with carbenophiles which were studied. With reactive carbenophiles, SCHEME 1



the product yields were high, but fair to poor product yields were obtained with poor carbenophiles in spite of high yields of RHgX solids which indicated complete CX_2 extrusion from the mercurial. In view of the fact that no more than traces of the tetrahaloethylenes were formed in these low yield transfer reactions, some alternate consumption of the dihalocarbene, perhaps reactions with the cyclohexylmercury starting material or with the cyclohexylmercuric halide product, must have been taking place. (Reaction of di-s-butylmercury with dichlorocarbene has been reported (eqn. 4)) [15]. However, this point was not

 (4)

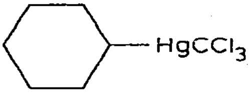
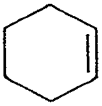
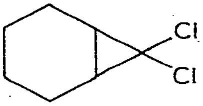
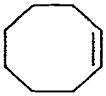
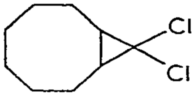
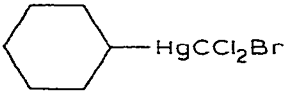
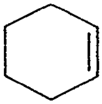
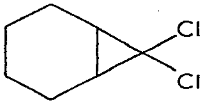
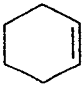
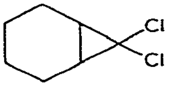
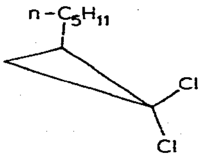
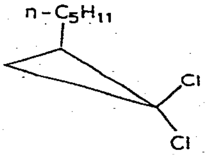
examined further. The dibromocyclopropane yields obtained in reactions of cyclohexyl(tribromomethyl)mercury were unaccountably low, even with reactive carbenophiles, although the cyclohexylmercuric bromide yields were high. β-Phenylethyl(tribromomethyl)mercury was even less satisfactory as a CBr_2 transfer reagent.

The results of this study indicate that the higher divalent carbon transfer reactivity of alkyl(trihalomethyl)mercurials in comparison to the analogous phenyl(trihalomethyl)mercurials is a general phenomenon. If this difference in reactivity is due to the difference in inductive effects of phenyl vs. alkyl, then perhaps a highly alkylated phenyl(trihalomethyl)mercury compound might be significantly more reactive than the simple phenyl compound. To test this idea, mesityl(trichloromethyl)mercury was prepared. An investigation of its CCl_2 transfer reactivity showed that the $+I$ effect of its three methyl substituents was insufficient to provide any significant enhancement of reactivity. When this mercury reagent was heated in cyclooctene at 80°C for 6 h, the yield of 9,9-dichlorobicyclo[6.1.0]nonane was only 44%; CCl_2 transfer was not complete at this temperature until more than 36 h had elapsed and even then the 9,9-dichlorobicyclo[6.1.0]nonane yield was only 75%. In contrast, in a similar experiment with phenyl(trichloromethyl)mercury, a 99% yield of this product was obtained after 27.5 h at 80°C.

(continued on p. 17)

TABLE 1

DIVALENT CARBON TRANSFER REACTIONS OF CYCLOHEXYL- AND β-PHENYLETHYL-(TRIHALOMETHYL)MERCURY COMPOUNDS

Carbenophile	Reaction conditions[a]		Product,	(% yield)	RHgX (% yield)
	Time	Temp. (°C)			
A. 					
	6.5 h	80		(92)	
	8 h	80		(90)	95
Et_3SiH	8h	80	Et_3SiCCl_2H	(88)	97
B 					
	6 min	80		(96)	95
	49h	25		(95)	85
n-$C_5H_{11}CH{=}CH_2$	8 min	80		(76)	91
n-$C_5H_{11}CH{=}CH_2$	41 h	25		(85)	94

continued

TABLE 1 (continued)

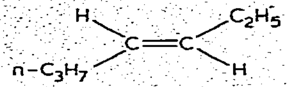
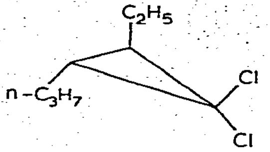
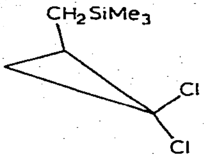
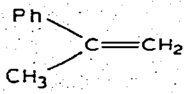
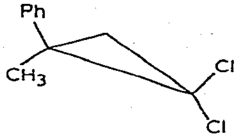
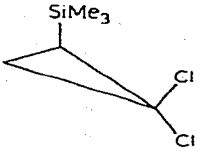
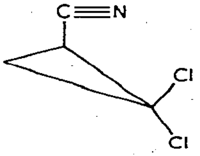
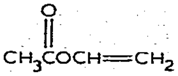
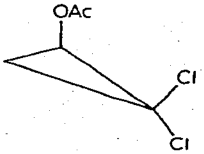
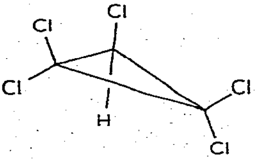
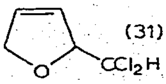
Carbenophile	Reaction conditions[a]		Product, (% yield)		RHgX (% yield)
	Time	Temp. (°C)			
	50 h	25		(88)	80
$Me_3SiCH_2CH{=}CH_2$	46 h	25		(88)	93
	46h	25		(84)	94
$Me_3SiCH{=}CH_2$	44h	25		(68)	79
$CH_2{=}CHCN$	46h	25		(45)	72
 $CH_3COCH{=}CH_2$	48h	25		(81)	97
$CHCl{=}CCl_2$	48h	25		(22)	92
	10min	80	 (24) + 	(31)	84

TABLE 1 (continued)

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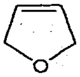
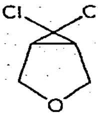
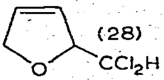
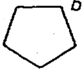
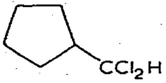
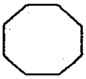
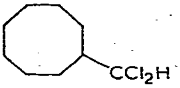
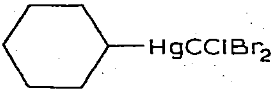
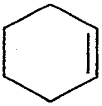
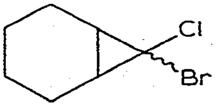
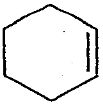
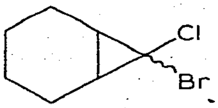
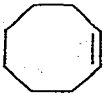
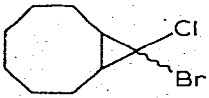
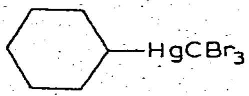
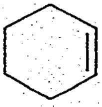
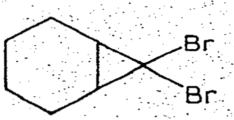
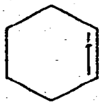
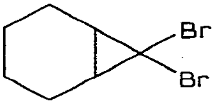
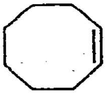
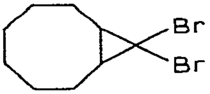
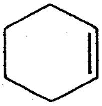
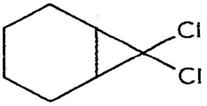
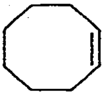
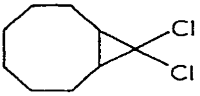
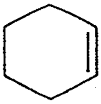
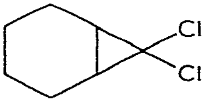
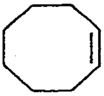
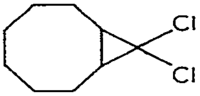
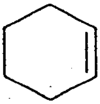
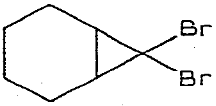
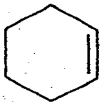
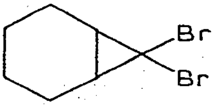
	72 h	25	 (34) +  (28)	88
 [b]	42 h	25	 (35)	71
 [b]	48 h	25	 (38)	90
Et_3SiH	50 h	25	Et_3SiCCl_2H (80)	89
C. 				
	7 min	80	 (85)	90
	72 h	25	 (87)	91
	72 h	25	 (83)	90
Et_3SiH	72 h	25	$Et_3SiCClBrH$ (70)	90
D. 				
	10 min	80	 (40)	90[c]

continued

TABLE 1 (continued)

Carbenophile	Reaction conditions[a]		Product, (% yield)		RHgX (% yield)
	Time	Temp. (°C)			
	48 h	25		(50)	80[c]
	48 h	25		(34)	80[c]
E. $PhCH_2CH_2HgCCl_3$					
	14h	80		(65)	89
	12h	80		(77)	95
F. $PhCH_2CH_2HgCCl_2Br$					
	15 min	80		(77)	91
	72 h	25		(80)	85
Et_3SiH	120h	25	Et_3SiCCl_2H	(73)	72
G $PhCH_2CH_2HgCBr_3$					
	96h	25		(10)	
	20 min	80		(24)	42[c]

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[a] Three molar equivalents of carbenophile per equivalent of mercury reagent in benzene solution unless otherwise noted. [b] Cycloalkane used as solvent. [c] Impure material; grey in color.

Since the availability of crystalline alkyl(trihalomethyl)mercury compounds appeared limited and since the stability on storage of these compounds was much poorer than that of the corresponding aryl compounds, possible in situ generation of alkyl(trihalomethyl)mercury compounds was explored:

$$RHgCl + PhHgCCl_3 \rightarrow RHgCCl_3 + PhHgCl \quad (5)$$

or

$$R_2Hg + CCl_3HgCl \rightarrow RHgCCl_3 + RHgCl \quad (6)$$

Both systems where R = cyclohexyl were examined. In the case of the first reaction, an experiment was carried out in which cyclooctene in benzene was heated with $PhHgCCl_3$ and one molar equivalent of cyclohexylmercuric chloride. A modest increase in the initial rate of formation of 9,9-dichlorobicyclo[6.1.0]-nonane was observed, but the rate of CCl_2 transfer in no way approached that observed in a similar reaction of cyclohexyl(trichloromethyl)mercury. The reaction of the system dicyclohexylmercury/trichloromethylmercuric chloride/cyclooctene in benzene at reflux gave only traces of 9,9-dichlorobicyclo[6.1.0]-nonane within 6 h.

Concluding remarks

This study has confirmed Shcherbakov's observations that alkyl(trihalomethyl)mercury compounds are more reactive divalent carbon transfer reagents than the corresponding aryl(trihalomethyl)mercurials (Table 2). The cyclohexyl(trihalomethyl)mercury system seems particularly good for CCl_2 and CClBr transfer at 80°C and at room temperature and these reagents could well find useful application at room temperature when the more conventional dihalocarbene generating reactions cannot be applied. In particular, cyclohexyl(dibromochloromethyl)mercury is the most useful organomercury reagent for generation of CClBr at room temperature under mild, neutral conditions. On the debit side, one must recognize that because they are so reactive, the cyclohexyl(trihalomethyl)mercury reagents are more difficult to isolate than their phenylmercury analogs. Furthermore, they appear to be subject to autoxidation, induced decomposition in the presence of various oxygen-containing solvents, and, in general, they exhibit poor stability on storage. The search for a practical alkyl(trihalomethyl)mercury reagent can by no means be considered to be completed. We have tried to prepare crystalline $RHgCX_3$ compounds with R = Me_3CCH_2, Me_3SiCH_2, $PhMe_2CCH_2$ and $PhMe_2SiCH_2$, but in these cases obtained only oils. Other R groups might be tried (norbornyl, adamantyl, etc.), but further work in this area is beyond the scope of our present interests.

Experimental

Preparation of organomercury reagents

(1) Cyclohexylmercuric chloride. Cyclohexylmagnesium bromide was prepared from 300 g (1.85 mol) of cyclohexyl bromide and 43 g (1.8 mol) of magnesium turnings in 1200 ml of THF. To this solution was added 272 g (1.0 mol) of mercuric chloride in 500 ml of THF during 1.5 h. The reaction

TABLE 2

APPROXIMATE REACTION TIMES FOR CX_2 TRANSFER FROM $RHgCX_3$

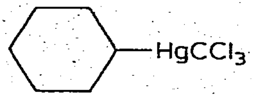
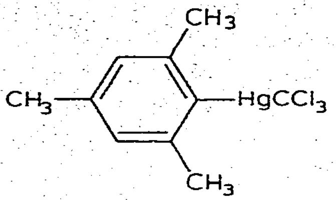
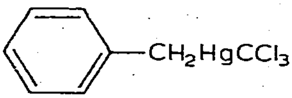
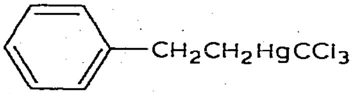
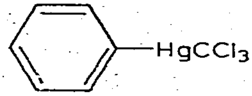
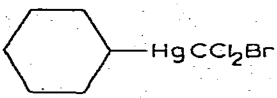
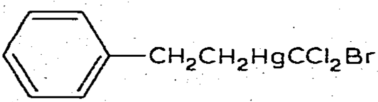
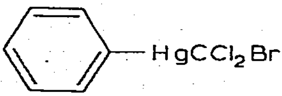
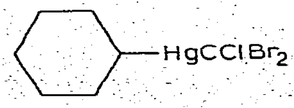
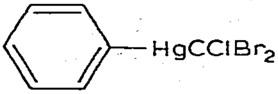
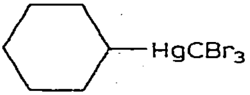
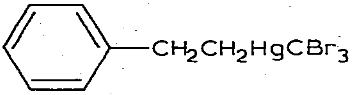
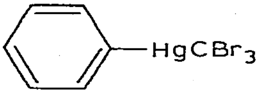
Mercurial	Time	
	Room temp.	80°C
		8 h[c]
		30 h[c]
		rapid formation of Hg^0; no CCl_2
		12 h[c]
		30-48 h[a]
	2 d[d]	<10 min[e]
	3 d[d]	<15 min[e]
	18 d[b]	2 h[a]
	3 d[d]	<10 min[e]

TABLE 2 (continued)

Mercurial	Time	
	Room temp.	80°C
	16 d[b]	2 h[a]
	2 d[d]	<10 min[e]
	4 d[d]	<20 min[e]
	15 d[b]	2 h[a]

[a] Ref. 16. [b] Ref. 6. [c] Obtained by GLC monitoring of product formation in a reaction with cyclooctene in benzene solution. [d] Estimated by noting when precipitation of alkylmercuric halide ceased. GLC monitoring is not applicable because further reaction occurs during GLC analysis. [e] A maximum value; no starting material remained when a reaction with cyclohexene was carried out for this length of time.

mixture was heated at reflux and stirred for 90 min and then was hydrolyzed with saturated ammonium chloride solution. The organic layer was filtered and added to a solution of 218 g of mercuric chloride in 400 ml of THF. The mixture was stirred and cooled, then was filtered to give a 71% yield of cyclohexylmercuric chloride, m.p. 160°C, in two crops; lit. [17] m.p. 164°C.

(2) Cyclohexyl(bromodichloromethyl)mercury. Into a 500 ml, three-necked flask equipped with a mechanical stirrer, a Dry-Ice—acetone condenser, pentane thermometer and nitrogen inlet tube was condensed 100-130 ml of dry dimethyl ether. The condenser was removed and 16 g (50 mmol) of cyclohexylmercuric chloride was added to the stirred solvent at —60°C. To the resulting white suspension was added a solution of 5.6 g (50 mmol) of unsolvated potassium t-butoxide (MSA Corp.) in 65 ml of cold, dry THF. After the mixture had been stirred for 5 min at —60°C, 8 ml (excess) of bromodichloromethane was added over a 5 min period, causing the reaction mixture to become transluscent and homogeneous. The reaction solution was immediately decanted into a one-liter flask and the solvent was removed rapidly using a rotary evaporator (bath at <40°C, solvent trap at —78°C). The residual green oil was extracted with 300 ml of cold benzene and 70 ml of cold water. The aqueous layer was back-extracted with 50 ml of cold benzene. The combined organic layers were filtered and evaporated at reduced pressure to leave a colorless oil which was dissolved in

70 ml of cool hexane. The solution was filtered and the filtrate immediately placed in the freezer at —19°C. Two crops, 18.0 g total (83%), of white, crystalline product, m.p. 53-56°C*, were collected. (Found: C, 19.05; H, 2.12; Br, 17.63; Hg, 45.37. $C_7H_{11}BrCl_2Hg$ calcd.: C, 18.82; H, 2.48; Br, 17.90; Hg, 44.92%.) IR (in Nujol, cm^{-1}): 1441s, 1347w, 1333m, 1282w, 1262w, 1243s, 1157s, 1064m, 995m, 928w, 861m, 847m, 746m, 690s and 620s. The NMR spectrum (in CCl_4) showed broad multiplets centered at about δ 1.60, 1.95 and 2.70 ppm.

(3) Cyclohexyl(trichloromethyl)mercury. A 3-necked 500-ml flask was equipped with a pentane thermometer, addition funnel, mechanical stirrer and nitrogen inlet and was charged with a suspension of 24 g (75 mmol) of cyclohexylmercuric chloride in 80 ml of THF which then was chilled to —60°C. Subsequently, 8.4 g (75 mmol) of potassium t-butoxide in 80 ml of THF was added over a 5 min period. After a 10 min period of stirring, 10 ml (125 mmol) of chloroform was added over a 5 min period, while the temperature was maintained below —55°C. After 10 min of stirring, the solvent was removed from the slightly grey solution by evaporation at reduced pressure. The solid residue was extracted with 300 ml of benzene and 100 ml of water. The water layer was washed twice with 50 ml portions of benzene and the combined benzene layers filtered. After evaporation of the benzene, the oily residue was crystallized from 40 ml of hot hexane. Filtration afforded 12 g (40%) of cyclohexyl(trichloromethyl)mercury, m.p. 50-52°C (lit. [13] m.p. 52-55°C). Evaporation to half volume of the mother liquor and further chilling gave a second crop weighing 6.0 g (20%), m.p. 51-52°C.

(4) Cyclohexyl(dibromochloromethyl)mercury. To 16.0 g (50 mmol) of cyclohexylmercuric chloride stirred in 50 ml of THF at —60°C was added over a 5 min period, 5.6 g (50 mmol) of potassium t-butoxide in 80 ml of THF. A 10 min period of stirring was followed by the addition of 8 ml (56 mmol) of dibromochloromethane over a 5 min period during which time a light yellow color developed. After a 10 min period of additional stirring at —60°C, the solvent was removed by rotary evaporation. The remaining solid was extracted with 300 ml of benzene and 100 ml of water. The aqueous layer was extracted with two 50 ml portions of benzene and the combined light yellow organic layers were filtered through a paper towel. The solvents were removed by evaporation and the remaining oil was dissolved in 100 ml of hexane at room temperature. After filtering, the hexane solution was immediately placed in the freezer. After several hours, 30 mmol (60%) of dense white needles were collected. A twice recrystallized sample, m.p. 60-63°C (dec.), was analyzed. (Found: C, 17.07; H, 2.32; Br, 31.98. $C_7H_{11}Br_2ClHg$ calcd.: C, 17.12; H, 2.27; Br, 32.55%.) IR (in CCl_4, cm^{-1}): 2920vs, 2840s, 1460(sh), 1440s, 1350w, 1335m, 1260w, 1242s, 1170m, 1158m, 1080w, 1060w, 990w, 840w, 657s and 600s.

(5) Cyclohexyl(tribromomethyl)mercury. In the standard apparatus were placed 16.0 g (50 mmol) of cyclohexylmercuric chloride and 80 ml THF. To this slurry, chilled to —60°C, was added over a 5 min period, 5.6 g (50 mmol)

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* The melting point of this compound is highly dependent on the manner in which it is obtained. The same crop of crystals gave the following results: Bath at ambient temp., 2°/min heating rate: 40-42°C (dec.). Bath at ambient temp., 5°/min heating rate: 48-50°C (dec.). Bath at 43°, 5°/min heating rate: 56-58°C (dec.). Bath at 55°, 5°/min heating rate: 57-59°C (dec.).

of potassium t-butoxide in 80 ml of THF. The mixture was stirred at —60°C for an additional 5 min period. To this was added over a 5 min period, 13.7 g (50 mmol) of bromoform which produced a yellow color. After 10 min of additional stirring, the solvents were removed in vacuo. To the remaining solid were added 300 ml of benzene and 100 ml of water. The aqueous layer was washed with two 50 ml portions of benzene and the combined yellow organic layers filtered. After removal of the benzene, the remaining solid was dissolved in 100 ml of hexane at room temperature, filtered and the filtrate immediately placed in the freezer. After 2 h, 30 mmol (60%) of light yellow cyclohexyl(tribromomethyl)mercury was collected. A twice recrystallized sample, m.p. 53-56°C (dec.), was analyzed. (Found: C, 14.51; H, 2.14. $C_7H_{11}Br_3Hg$ calcd.: C, 15.70; H, 2.07%.) IR (in CCl_4, cm^{-1}): 2920s, 2850m, 1455(sh), 1440m, 1348w, 1335w, 1240m, 1170w, 1155w, 1080w, 1060w, 990w and 600m.

(6) β-Phenylethyl(trichloromethyl)mercury. Bis(β-phenylethyl)mercury was prepared by the Grignard procedure. Treatment of this compound with an equimolar quantity of mercuric chloride in methanol or THF gave β-phenylethylmercuric chloride, m.p. 164-166°C; lit. [18] m.p. 165.5-166°C).

To 34 g (0.10 mol) of β-phenylethylmercuric chloride in 250 ml of THF chilled to —50°C was added 11.2 g (0.10 mol) of potassium t-butoxide in 150 ml of THF. After a period of 20 min of additional stirring at —40°C, 20 ml (250 mmol) of chloroform was added over a 5 min period. After 15 additional min of stirring at —45°C, the solvents were removed in vacuo and the solids extracted with 800 ml of benzene and 200 ml of water. The organic layer was filtered, the solvent removed and the remaining solid recrystallized from 600 ml of hot 5/1 hexane/chloroform. A 74% yield of β-phenylethyl(trichloromethyl)mercury was obtained in two crops. A twice recrystallized sample had m.p. 43-45°C (dec.). (Found: C, 25.93; H, 2.24; Cl, 22.66. $C_9H_9Cl_3Hg$ calcd.: C, 25.48; H, 2.14; Cl, 25.08%.) IR (in CCl_4, cm^{-1}): 3085w, 3065w, 3025m, 2950m, 2920m, 2850m, 1940w, 1860w, 1800w, 1602m, 1490s, 1450s, 1415w, 1311w, 1290w, 1230m, 1200w, 1180w, 1140w, 1113w, 1060w, 1025w, 905w and 700vs. NMR (in $CDCl_3$): δ 2.15 (t, 2H, CH_2Hg), 2.99 (t, 2H, CH_2Ph) and 7.28 ppm (m, 5H).

(7) β-Phenylethyl(bromodichloromethyl)mercury. To 25.5 g (75 mmol) of β-phenylethylmercuric chloride in 200 ml of THF cooled to —50°C was added 8.4 g (75 mmol) of potassium t-butoxide in 100 ml of THF. After an additional 20 min of stirring, 12 ml (144 mmol) of bromodichloromethane was added dropwise keeping the temperature below —45°C. A 15 min period of further stirring was followed by evaporation in vacuo of the solvents and extraction of the solids with 500 ml of benzene and 100 ml of water. The solvents were removed from the filtered organic layer and the remaining solid recrystallized from 500 ml of 6/1 pentane/chloroform. A 53% yield of β-phenylethyl(bromodichloromethyl)mercury was obtained in 3 crops. A twice recrystallized sample, m.p. 50-52°C (dec.), was analyzed. (Found: C, 23.15; H, 1.96; Br, 17.45. $C_9H_9Cl_2BrHg$ calcd.: C, 23.07; H, 1.94; Br, 17.05%.) NMR (in $CDCl_3$): triplets at δ 2.19 and 2.97, a broad singlet at 7.33 ppm.

(8) β-Phenylethyl(tribromomethyl)mercury. To 17 g (50 mmol) of β-phenylethylmercuric chloride in 100 ml of THF stirred at —60°C was added over a 5 min period 5.6 g (50 mmol) of potassium t-butoxide in 100 ml of THF. After an additional 10 min of stirring, 10 ml (120 mmol) of bromoform

was added dropwise over a 5 min period. Five more minutes of stirring was followed by removal of solvents in vacuo and extraction with 400 ml of benzene and 50 ml of water. The organic layer was filtered, the solvent removed and the residue recrystallized from 150 ml of 2/1 hexane/methylene chloride. β-Phenylethyl(tribromomethyl)mercury was obtained in two crops, 18 g (65%). A twice recrystallized sample, m.p. 71-73°C (dec.), was analyzed. (Found: C, 19.53; H, 1.69; Br, 42.73. $C_9H_9Br_3Hg$ calcd.: C, 19.39; H, 1.63; Br, 43.00%.) NMR (in $CDCl_3$): triplets at δ 2.22 and 2.88 and a broad singlet at 7.34 ppm.

(9) Benzyl(trichloromethyl)mercury. Into a 500 ml flask equipped with an addition funnel, mechanical stirrer and pentane thermometer were placed 24 g (74 mmol) of benzylmercuric chloride, 8 ml (100 mmol) of chloroform and 100 ml of THF. To this mixture, chilled to —50°C, was added, over a 10 min period, a slurry of 11 g (100 mmol) of potassium t-butoxide and 10 ml (100 mmol) of t-butanol in 100 ml of THF. After an additional 15 min of stirring, the solvents were removed by rotary evaporation from the dark brown solution. The remaining solid was extracted with 200 ml of benzene and 100 ml of water, the solvents were removed from the filtered organic layer and the remaining red oil recrystallized from 200 ml of hot 3/1 hexane/chloroform. A 35% yield of benzyl(trichloromethyl)mercury, m.p. 65°C (lit. [13] m.p. 55-56°C) was obtained in two crops, off-white needles.

(10) Mesityl(trichloromethyl)mercury. In a 1-l flask equipped with a mechanical stirrer, pentane thermometer and addition funnel was placed 35.5 g (0.10 mol) of mesitylmercuric chloride (prepared by the mercuration of mesitylene [19]) in 150 ml of THF. After cooling to 0°C, 17.0 g (0.14 mol) of potassium t-butoxide in 150 ml of THF was added over 15 min. After 10 additional min of stirring at 0°C, 12 ml (0.15 mol) of chloroform was added over a 10 min period. A 5 min period of additional stirring was followed by the removal of solvents in vacuo and extraction of the solids with 600 ml of benzene and 100 ml of water. After washing the aqueous layer with two 100 ml portions of benzene, the combined organic layers were filtered and the solvents evaporated. The remaining solid was twice recrystallized from carbon tetrachloride to give a 42% yield of mesityl(trichloromethyl)mercury, m.p. 111-113°C. Further heating resulted in decomposition at 170°C. (Found: C, 27.01; H, 2.63; Cl, 23.42 $C_{10}H_{11}Cl_3Hg$ calcd.: C, 27.41; H, 2.53; Cl, 24.28%.) NMR (in $CDCl_3$) δ 2.33 (s, p-CH_3, 3H), 2.47 (s, o-CH_3, 6H) and 6.87 ppm (broad s, 2H). IR (in CCl_4, cm^{-1}): 3030w, 3000m, 2958m, 2918s, 2855m, 1590m, 1555w, 1460(sh), 1443s, 1418(sh), 1324s, 1292s and 850s.

GLC-monitored reaction of cyclohexyl(trichloromethyl)mercury with cyclohexene at 80°C.

Into a 50 ml, 3-necked flask equipped with thermometer, rubber septum, reflux condenser and nitrogen inlet were placed 4.69 g (11.7 mmol) of cyclohexyl(trichloromethyl)mercury, 3.0 ml (30 mmol) of cyclohexene, 1.70 g (10 mmol) dodecane and 10 ml of benzene. The reaction mixture was heated to 78°C for 10 h while at various time intervals, 0.3 ml aliquots were withdrawn via syringe and analyzed immediately by GLC (20% SE-30, 140°C). The reaction mixture remained completely homogeneous during the entire heating period; cyclohexylmercuric chloride precipitated only upon cooling. Filtration of the remaining cooled reaction mixture yielded 3.75 g (67%) of cyclohexylmercuric chloride, m.p. 146°C. The filtrate was trap-to-trap distilled (r.t./ 0.03 mm). GLC analysis (10% UC-W98, 130°C) of the distillate showed the presence of 11.5 mmol (98%) of 7,7-dichloronorcarane. Listed below are the results of the monitoring. A sample taken before heating was begun showed no measurable amount of dichloronorcarane.

Time (h)	% yield of product
1.5	33
5.0	79
6.5	92
10.0	102

Reaction of β-phenylethyl(trichloromethylmercury) with cyclooctene at 80°C

Into a 50 ml flask equipped with a reflux condenser, rubber septum and nitrogen inlet were placed 4.24 g (10.0 mmol) of the title mercurial, 3.9 ml (30 mmol) of cyclooctene, 1.00 ml (4.4 mmol) of dodecane and 15 ml of benzene and heated to 80°C for 24 h. At periodic intervals, 0.1 ml aliquots were withdrawn and analyzed by GLC (20% SE-30, 140°C). The yields of 9,9-dichlorobicyclo[6.1.0]nonane observed for two separate runs are listed below:

Time (h)	Yield run A (%)	Yield run B (%)
0.0	2	2
1.5	32	
3.5	46	
4.0		49
6.0		56
6.5	58	
8.0		59
10.0		61
12.0		64
14.0		65
16.0	77	65
22.5	76	

From reaction A, 2.6 g (78%) of β-phenylethylmercuric chloride, m.p. 168°C (lit. [18] m.p. 165.5-166°C) was removed by filtration after the mixture had been cooled to room temperature.

Preparative reactions

(a) Reaction of cyclohexyl(trichloromethyl)mercury with triethylsilane at 80°C. A 50 ml, three-necked flask equipped with a reflux condenser, a magnetic stirring unit and a nitrogen inlet tube was charged with 4.02 g (10 mmol) of the mercury reagent, 3.45 g (30 mmol) of triethylsilane and 10 ml of dry benzene. The mixture was stirred and heated at reflux (83°C) under nitrogen for 8 h. The solution was homogeneous throughout the heating period. Cyclohexylmercuric chloride (3.10 g, 97%, m.p. 160°C) precipitated after the mixture had been cooled and 5 ml of hexane had been added. Filtration was followed

by trap-to-trap distillation of the filtrate at 35°C and 0.01 mmHg. GLC analysis of the distillate (10% UC-W98 at 120°C) showed the presence of triethyl(dichloromethyl)silane in 88% yield. A sample of the product was collected by GLC. Its GLC retention time and IR and NMR spectra agreed with those of an authentic sample [19].

(b) Reaction of cyclohexyl(bromodichloromethyl)mercury with cyclohexene at room temperature. The standard apparatus was charged with 4.46 g (10 mmol) of the mercurial, 3.0 ml (30 mmol) of cyclohexene and 5 ml of dry benzene. Precipitation of cyclohexylmercuric bromide began after the initially homogeneous reaction mixture had been stirred at room temperature for about 30 min. The reaction mixture was filtered after 24 h to give 2.61 g (72%) of cyclohexylmercuric bromide, m.p. 148-150°C, lit. [17] m.p. 153°C. The filtrate was stirred for another 24 h and then was filtered to remove 0.30 g (8%) of cyclohexylmercuric bromide. The filtrate was stirred at room temperature after the second filtration, but no significant amount of precipitate formed.

In another reaction, 11.4 mmol of the mercury compound, 3.0 ml (30 mmol) of cyclohexene and 5 ml of benzene were mixed and stirred at room temperature for 49 h. Filtration of the chilled reaction mixture after 5 ml of hexane had been added gave 3.55 g (85%) of cyclohexylmercuric bromide. The clear filtrate was trap-to-trap distilled at 35°C and 0.05 mmHg. GLC analysis of the distillate (10% UC-W98 at 130°C) showed the presence of 7,7-dichloronorcarane in 95% yield. A sample of this product was collected by GLC and identified by means of its IR and NMR spectra.

(c) Reaction of cyclohexyl(bromodichloromethyl)mercury with 1-heptene at 80°C. A solution of 3.0 ml (30 mmol) of 1-heptene in 5 ml of dry benzene was heated to reflux in the standard apparatus which also was equipped with an addition funnel containing 2.30 g (5.15 mmol) of the mercury reagent in 7 ml of benzene. The latter solution was added to the stirred and refluxing olefin solution over a period of 3 min and the reaction mixture was heated at reflux for another 5 min. It then was cooled to room temperature and filtered to remove 1.7 g (91%) of cyclohexylmercuric bromide, m.p. 150-152°C. GLC analysis of the filtrate showed the presence of 1,1-dichloro-2-n-amylcyclopropane in 76% yield. A sample was collected by GLC and identified spectroscopically.

(d) Reaction of cyclohexyl(dibromochloromethyl)mercury with cyclohexene at room temperature. A mixture of 37.0 g (7.53 mmol) of the mercurial, 30 mmol of cyclohexene and 7 ml of dry benzene was stirred under nitrogen at room temperature for 24 h. After this time, 1.1 g (40%) of cyclohexylmercuric bromide was filtered. Stirring of the filtrate was continued for another 24 h and then 0.45 g (17%) of cyclohexylmercuric bromide was filtered. The reaction solution was stirred at room temperature for a third 24 h period, during which 0.23 g (8%) of cyclohexylmercuric bromide precipitated. No significant amount of solid formed on further stirring of the filtrate at room temperature

In another experiment, 10.1 mmol of the mercury reagent and 30 mmol of cyclohexene in 7 ml of benzene was stirred at room temperature of 3 days. The mixture was cooled after 5 ml of hexane had been added and then was filtered to remove 3.2 g (91%) of cyclohexylmercuric bromide. Trap-to-trap distillation of the filtrate was followed by GLC analysis of the distillate. 7-Bromo-7-chloronorcarane [16] was present in 87% yield.

An 85% yield of this product was obtained in a similar reaction carried out at 80°C during 7 min using the general procedure described in (*c*).

(e) Other divalent carbon transfer reactions. The procedures described in (*a*) through (*d*) above were used in all other reactions listed in Scheme 1 and Table 1. All products were known compounds and have been described in previous papers of this series: *gem*-dichlorocyclopropanes [16]; *gem*-bromochlorocyclopropanes [16,21]; *gem*-dibromocyclopropanes [16]; triethyl(bromochloromethyl)silane [22]; (dichloromethyl)cycloalkanes [23].

Reaction of phenyl(trichloromethyl)mercury with cyclooctene in the presence of cyclohexylmercuric chloride

Two separate 50 ml flasks were equipped with a reflux condenser, rubber septum and thermometer. To each were added 2.75 ml (21 mmol) of cyclooctene, 2.80 g (7.0 mmol) of phenyl(trichloromethyl)mercury, 1.0 ml (4.4 mmol) of dodecane and 14 ml of benzene. To reaction A was added 2.2 g (7.0 mmol) of cyclohexylmercuric chloride. The flasks were heated to reflux for 48 h during which time samples were periodically withdrawn via syringe and analyzed by GLC (20% SE-30, 125°C). The yields of A and B are listed below as well as their ratio.

Time (h)	A (%)	B (%)	A/B
0	0	0	
2	19	11	1.74
4	33	35	0.93
6	55	44	1.26
8	67	68	0.98
10	71	63	1.13
13	77	76	1.02
16	91	86	1.05
23.5	97	95	1.03
27.5	97	99	0.98
48	97	99	0.98

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