

## HALOMETHYL-METAL COMPOUNDS XLVIII\*. CHCl TRANSFER TO OLEFINS VIA PHENYL(DICHLORO- METHYL)- AND PHENYL(BROMOCHLOROMETHYL)MERCURY

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### SUMMARY

Phenyl(dichloromethyl)mercury and phenyl(bromochloromethyl)mercury were found to transfer CHCl to olefins when these reagents were heated together at temperatures ranging from 84–140°. Phenyl(dichloromethyl)mercury was the less reactive of the two mercurials. Product yields were variable and the application of these reagents in chlorocyclopropane synthesis seems limited. The evidence obtained suggests that free monochlorocarbene is not an intermediate in this CHCl transfer reaction, rather that a direct reaction between the organomercury reagent and the olefin is involved.

### INTRODUCTION

Transfer of CCl<sub>2</sub>, CClBr and CBr<sub>2</sub> from a variety of reagents to olefins to give *gem*-dihalocyclopropanes can be accomplished easily and in excellent yield<sup>2-5</sup>, but this is not true for CHCl and CHBr transfer. The action of organolithium reagents on methylene chloride in the presence of olefins serves in the preparation of monochlorocyclopropanes<sup>6</sup>, but yields in general are only fair. A disadvantage of this reagent system is that it utilizes a strong base and strong nucleophile to generate the carbenoid and thus it is incompatible with many organic and organometallic functional groups. Less practical than this procedure are methods based on chlorodiazomethane<sup>7</sup>, 1,1-dichloroacetophenone<sup>8</sup> and bis(dichloromethyl)zinc<sup>9</sup>. When we began this work, it was clear that a more generally applicable CHCl transfer agent was needed.

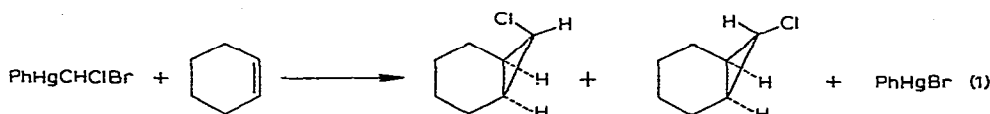
The very successful application of phenyl(trihalomethyl)mercury compounds as dihalocarbene sources<sup>10</sup> prompted us to examine the easily prepared phenyl(dichloromethyl)- and phenyl(bromochloromethyl)mercury<sup>11,12</sup> as potential CHCl transfer agents in the direct synthesis of monochlorocyclopropanes from olefins.

\* Part XLVII, see ref. 1.

\*\* National Science Foundation Predoctoral Fellow, 1962–1964; National Institutes of Health Predoctoral Fellow, 1964–1965.

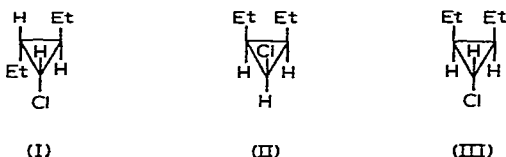
## RESULTS AND DISCUSSION

In the phenyl(trihalomethyl)mercury series it was found that phenylmercuric bromide elimination was highly favored over phenylmercuric chloride elimination;  $\text{PhHgCCl}_2\text{Br}$  was a much more reactive  $\text{CCl}_2$  transfer agent than was  $\text{PhHgCCl}_3$ <sup>10</sup>. Thus it was not surprising that  $\text{PhHgCHCl}_2$  was the less reactive of the two phenyl-(dihalomethyl)mercurials examined. When this compound was heated at reflux in cyclohexene solution for 7 days, phenylmercuric chloride was formed in only 19% yield, and a nearly equimolar mixture of the two 7-chloronorcarane isomers (16% yield) was formed in the reaction. However, a reaction of the mercurial and this olefin carried out in a sealed tube at about 140° for 60 h gave 7-chloronorcarane in 57% yield, while a 95% yield of phenylmercuric chloride was isolated. In contrast, when a cyclohexene solution of  $\text{PhHgCHClBr}$  was heated at reflux for 6 days, a 63% yield of 7-chloronorcarane (*cis/trans* ratio of 1.3) was obtained and phenylmercuric bromide was present in 81% yield (eqn. (1)). In a 3 day reaction time under comparable conditions, the 7-chloronorcarane and phenylmercuric bromide yields were only 29% and 42%, respectively.



This investigation was continued with a more detailed study of the reactions of phenyl(bromochloromethyl)mercury with olefins. In view of the slow reaction which occurred with cyclohexene at 80°, all further experiments were carried out at higher temperatures (ca. 120–150°). The most favorable results were obtained with systems in which the reaction was carried out at atmospheric pressure without inert diluent. Thus a reaction of phenyl(bromochloromethyl)mercury with a large excess of cyclooctene at 140° was essentially complete within 5 h, giving 9-chlorobicyclo-[6.1.0]nonane (*cis/trans* ratio 2.1) (90%) and phenylmercuric bromide (94%). Fair (45–55%) chlorocyclopropane product yields were obtained in sealed tube reactions at 135–140° with *cis*- and *trans*-3-hexene and allyltrimethylsilane, but with 1-heptene the yield of 1-n-amyl-2-chlorocyclopropane was only 20%. Yields of product also were fair when a high boiling diluent (chlorobenzene, or better, *o*-xylene) was added to the system so that reasonably high (122–130°) reaction temperatures could be achieved at atmospheric pressure. Thus the reaction of cyclohexene with phenyl-(bromochloromethyl)mercury in chlorobenzene at about 123° for 70 h gave 7-chloronorcarane (*cis/trans* ratio 1.22) in 59% yield, while a similar reaction of allyltrimethylsilane in *o*-xylene at 130° (18.5 h) gave 1-chloro-2-(trimethylsilylmethyl)cyclopropane in 62% yield. However, the use of high-boiling solvents has disadvantages due to the fact that in some cases their volatility is similar to that of the product, making isolation of the latter difficult. The results of our experiments are summarized in Table 1.

The results obtained with *cis*- and *trans*-3-hexene indicate that  $\text{CHCl}$  transfer via  $\text{PhHgCHClBr}$  is stereospecific. Only one product (I) was obtained from the *trans* isomer, while two products, both different from (I), namely (II) and (III), were obtained in 3.9 ratio from the *cis* olefin.



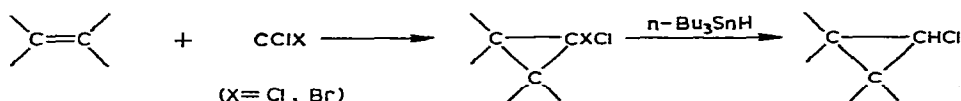
The assignment of the configuration of the geometrical isomers obtained in these reactions was accomplished by consideration of their NMR spectra. In general, the signal due to the halomethine proton of the *cis* isomer occurs at lower field (3.02–3.40 ppm) with a larger coupling constant ( $J_{cis}$  7.0–8.0 Hz) than that of the *trans* isomer (2.26–2.90 ppm;  $J_{trans}$  3.0–5.0 Hz)<sup>13,14</sup>.

The observed *cis/trans* isomer ratios of the various substituted chlorocyclopropanes prepared were quite variable. A preference for the *cis* isomer is to be noted, but from this fact alone we can draw no conclusions concerning mechanism.

Another experiment, however, gives strong indication that the PhHgCHClBr-olefin reaction does not proceed by way of free chlorocarbene. Two samples of phenyl(bromochloromethyl)mercury were heated in solution in the same oil bath for 7 days at about 82°. In one case benzene was the solvent; in the other, the solvent was cyclohexene. The mercurial sample which was heated in benzene solution was recovered unchanged in 85% yield; phenylmercuric bromide was formed in only 4% yield and no volatile products were formed. In cyclohexene solution, the mercurial was converted to phenylmercuric bromide in 61% yield and PhHgCHClBr was recovered in only 7.5% yield. The yield of 7-chloronorcarane (*cis/trans* ratio 1.2) was 33% in this experiment. Thus phenyl(bromochloromethyl)mercury appears to be stable in the absence of a divalent carbon trap and the  $\alpha$ -elimination of phenylmercuric bromide occurs only when a substrate capable of accepting the divalent carbon fragment is present. Such also was the case with bis(bromomethyl)mercury where other evidence also spoke against a free carbene mechanism<sup>15</sup>, and this kind of behavior is quite different from that observed in the case of phenyl(bromodichloromethyl)mercury, whose  $\text{CCl}_2$  transfer reactions to olefins were shown to proceed via free dichlorocarbene<sup>16</sup>.

Had the results of these few reactions been more encouraging, we would have extended the scope of our study of olefin cyclopropanation via PhHgCHClBr to include a variety of functional olefins as well. However, the high temperatures required to obtain useful reaction rates and the fact that product yields in the presence of inert diluents were only moderate made this reaction of only marginal preparative value and thus we did not extend these studies.


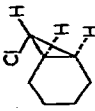
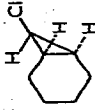

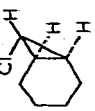
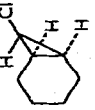

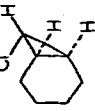
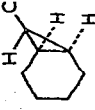

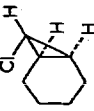
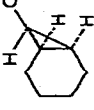

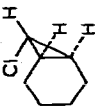
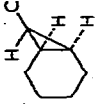
In view of the limited applicability of phenyl(bromochloromethyl)mercury in CHCl transfer chemistry, there still is lacking a generally applicable reagent for the direct preparation of monochlorocyclopropanes from olefins. The most useful route to such compounds remains the two-step procedure involving synthesis of a *gem*-dichloro-, or better, of a *gem*-bromochlorocyclopropane and reduction of the latter to the monochlorocyclopropane<sup>14,17</sup>:


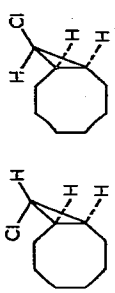
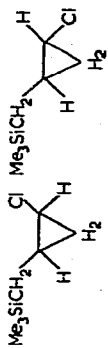
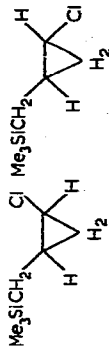
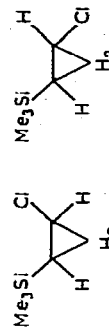
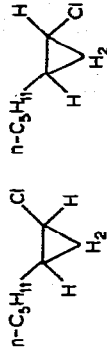


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TABLE I

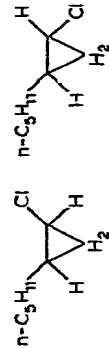
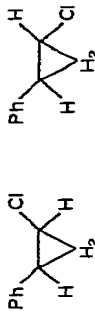
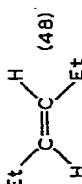
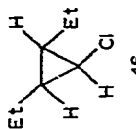
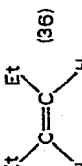
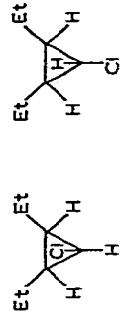
REACTIONS OF  $\text{PhHgCHClBr}$  AND  $\text{PhHgCHCl}_2$  WITH OLEFINS

Olefin (mmoles)	Mercurial (mmoles)	Solvent (ml)	Reaction temperature ( $^{\circ}\text{C}$ )	Reaction time	Yield of $\text{PhHgBr}$ (%)	Cyclopropane products (% Yield; isomer ratio <sup>a</sup> )
(A) With $\text{PhHgCHClBr}$						
 (200)	20	None	~ 84	6 days	81	  (63; 1.3/1)
 (200)	20	None	~ 84	3 days	42	  (29; 1.3/1)
 (60)	20	$\text{C}_6\text{H}_6$ (10)	~ 84	3 days	18	  (10; 1.3/1)
 (60)	20	$\text{C}_6\text{H}_6$ (5)	~ 84	6 days	46	  (37; 1.3/1)
 (23)	5.6	$\text{PhCl}$ (20)	~ 123	70 h	88	  (59; 1.22/1)


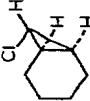
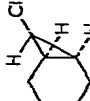

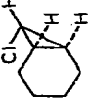
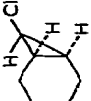

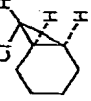
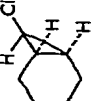
	(169)	5.6	None	~140	5 h	94		(90; 2.1/1)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (26)	4.9	<i>o</i> -Xylene (20)	~130	18 h	80		(62; 1.60)	
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (35)	4.9	None	~140 <sup>b</sup>	4 h	74		(55; 2.30)	
$\text{Me}_3\text{SiCH}=\text{CH}_2$ (18)	4.9	$\text{C}_6\text{H}_6$ (3)	~130 <sup>b</sup>	30 h	35		(10; 0.6/1)	
$n\text{-C}_3\text{H}_7\text{CH}=\text{CH}_2$ (36)	7.4	PhCl (20)	~123	45 h	42		(23; 1.66/1)	

(Continued)

TABLE 1 (continued)

Olefin (mmoles)	Mercurial (mmoles)	Solvent (ml)	Reaction temperature (°C)	Reaction time	Yield of PhHgBr (%)	Cyclopropane products (% Yield; isomer ratio <sup>a</sup> )
$n\text{-C}_5\text{H}_{11}\text{CH}=\text{CH}_2$ (28)	4.9	None	$\sim 135^b$	20 h	50 <sup>c</sup>	 $n\text{-C}_5\text{H}_{11}$ $n\text{-C}_5\text{H}_{11}$ (26; 1.75/1)
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ (26)	4.9	$\text{PhCl}$ (15)	$\sim 135$	24 h	69	 $\text{Ph}$ $\text{Ph}$ (28; 1.46/1)
 (48)	4.9	None	$\sim 135^b$	18 h	92	 46
 (36)	4.9	None	$\sim 140^b$	2 h	88	 (49; 3.9/1)


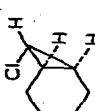
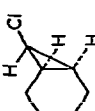
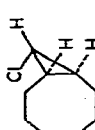
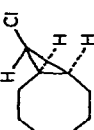
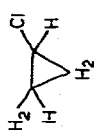
(B) With  $\text{PhHgCHCl}_2$ 

 (200)	20	None	~84	7 days	19 <sup>d</sup>	  (16:11) <sup>f</sup>
 (100)	21	None	~140 <sup>b</sup>	60 h	95 <sup>d</sup>	  (57:11) <sup>f</sup>
 (200)	15 <sup>c</sup>	None	~84	8 days		  (8 <sup>f</sup> :11 <sup>f</sup> :12)

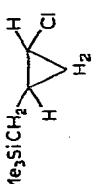
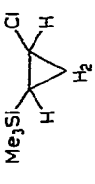
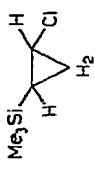
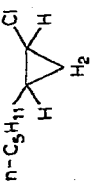
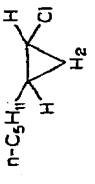
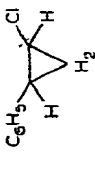
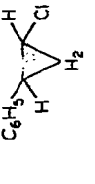
<sup>a</sup> Ratio of isomers = first isomer listed/second. <sup>b</sup> Sealed tube reaction. <sup>c</sup>  $\text{PhHgCHClBr}$  recovered in 25% yield. <sup>d</sup>  $\text{PhHgCl}$ . <sup>e</sup>  $\text{Hg}(\text{CHCl})_2$  was the mercurial used. <sup>f</sup> Yield based on utilization of  $\text{CHCl}_2$  groups of the reagent.

TABLE 2

## MONOCHLOROCYCLOPROPANES PREPARED


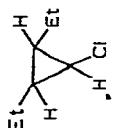
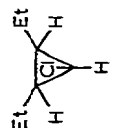
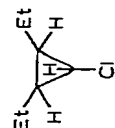
Compound	$n_D^{25}$	Analysis found (calcd.) (%) <sup>a</sup>		NMR $\delta$ (ppm) 	IR (cm <sup>-1</sup> ) (neat liquid)
		C	H		
	1.4803 <sup>b</sup>	Known compound <sup>14</sup>		(Ref. 14)	
	1.4879 <sup>c</sup>	Known compound <sup>14</sup>		(Ref. 14)	
	1.4889	Known compound <sup>18</sup>		(Ref. 18)	(Ref. 18)
	1.4931	Known compound <sup>18</sup>		(Ref. 18)	(Ref. 18)
	1.4440	51.48 (51.66)	9.28 (9.29)	3.02 m 1 <sup>f</sup>	3080 w, 3050 w, 3000 w, 2958 w, 2920 (sh), 2890 m, 2800 w, 1432 m, 1360 m, 1272 s, 1248 vs, 1196 m, 1181 m, 1035 m, 990 w, 860 vs, 840 vs, 782 w, 750 w, 698 s, 650 s



 $\text{Me}_3\text{SiCH}_2$	1.4379			2.54 quintet, $1 J_{\text{cis}}$ $7.0 J_{\text{trans}}$ 3.5 and 3.5 Hz $^f$	3080 w, 3050 w, 3002 w, 2960 s, 2900 m, 2882 (sh), 2800 w, 1435 w, 1410 w, 1370 w, 1290 (sh), 1260 vs, 1250 vs, 1192 w, 1180 w, 1100 w, 1070 w, 1058 w, 1030 m, 945 m, 920 m, 890 m, 860 vs, 840 vs, 782 w, 750 w, 698 s, 650 s
 $\text{Me}_3\text{Si}$	48.90 (48.46)	8.80 (8.81)		3.23 octet 1 $J_{\text{cis}}$ 6.5 and 8.5 $J_{\text{trans}}$ 3.5 Hz $^f$	3039 w, 3026 w, 3002 w, 2960 s, 2900 w, 1468 w, 1410 w, 1292 s, 1280 (sh), 1250 s, 1040 m, 980 s, 945 s, 890 s, 760 s, 700 m, 683 w, 658 w, 642 w
 $\text{Me}_3\text{Si}$				2.78 octet 1 $J_{\text{cis}}$ 6.0 $J_{\text{trans}}$ 3.5 and 4.7 Hz $^f$	3079 w, 3040 w, 3000 w, 2960 s, 2900 w, 1405 w, 1318 m, 1298 m, 1250 s, 1200 w, 1100 m, 1080 w, 1040 w, 989 m, 930 s, 897 m, 890 vs, 755 m, 700 w, 615 m
 $n\text{-C}_5\text{H}_{11}$	65.71 (65.52)	10.30 (10.31)		3.03 sextet 1 $J_{\text{cis}}$ 7.5 and 7.5 $J_{\text{trans}}$ 4.0 Hz $^f$	3090 w, 3059 w, 3001 w, 2960 vs, 2932 vs, 2879 (sh), 2860 m, 1450 m, 1380 w, 1305 (sh), 1281 s, 1030 m, 900 w, 820 m, 730 w, 658 m
 $n\text{-C}_5\text{H}_{11}$	1.4344			2.60 m $1^f$	3080 w, 3052 w, 3002 w, 2960 m, 2930 vs, 2890 s, 2930 m, 1455 m, 1380 w, 1272 w, 1258 m, 1230 w, 1090 w, 1070 w, 920 w, 830 w, 680 m
 $\text{C}_6\text{H}_5$	70.82 (70.83)	6.03 (5.94)		3.13 sextet 1 (in $\text{CCl}_4$ ) $J_{\text{cis}}$ 7.5 and 7.5; $J_{\text{trans}}$ 5.0 Hz	3088 w, 3062 w, 3036 w, 3002 w, 1600 m, 1496 m, 1450 s, 1445 w, 1288 s, 1220 w, 1160 w, 1100 w, 1070 m, 1040 w, 1030 w, 1020 w, 930 w, 920 w, 816 m, 770 vs, 732 m, 702 vs, 662 m
 $\text{C}_6\text{H}_5$				2.96 m, 1 (in $\text{CCl}_4$ )	3090 (sh), 3062 m, 3032 m, 3004 (sh), 1600 m, 1580 w, 1500 s, 1445 m, 1430 w, 1380 w, 1300 w, 1278 w, 1260 s, 1220 w, 1170 w, 1160 w, 1100 m, 1070 m, 1040 m, 1030 m, 1010 w, 995 m, 940 m, 920 w, 890 m, 865 m, 816 w, 765 vs, 702 vs, 685 s

(Continued)

TABLE 2 (continued)

Compound	$n_D^{25}$	Analysis found (calcd.) (%) <sup>a</sup>		NMR $\delta$ (ppm) 	IR (cm <sup>-1</sup> ) (neat liquid)
		C	H		
	1.4275	63.43 (63.39)	9.80 (9.88)	2.68 m t <sup>f</sup>	3040 w, 2961 vs, 2950 s, 2868 s, 1460 s, 1378 m, 1350 m, 1298 w, 1271 s, 1238 w, 1198 w, 1170 w, 1125 w, 1100 w, 1060 w, 1010 w, 1000 w, 975 w, 918 (sh), 900 w, 860 w, 680 w, 672 w, 645 w, 620 (sh), 602 m
	1.4390	63.51 (63.39)	9.93 (9.88)	3.11 t t <sup>f</sup> $J_{cis}$ 7.0 Hz	3050 w, 2962 vs, 2828 s, 2878 m, 1460 s, 1455 s, 1378 m, 1370 (sh), 1321 w, 1300 w, 1272 s, 1255 w, 1170 w, 1110 w, 1092 w, 1078 w, 1010 w, 1000 w, 800 m, 760 w, 745 m, 687 s
				2.26 t t $J_{trans}$ 3.0 Hz <sup>f</sup>	3002 (sh), 2962 s, 2918 m, 2880 m, 1451 m, 1412 w, 1380 w, 1300 w, 1280 m, 1120 w, 1060 w, 982 m, 918 w, 870 w, 810 w, 789 m, 730 w.

<sup>a</sup> Where two isomers were isolated, the analysis given is for a mixture of both isomers. <sup>b</sup> Lit.<sup>14</sup>:  $n_D^{25}$  1.4807. <sup>c</sup> Lit.<sup>14</sup>:  $n_D^{25}$  1.4890. <sup>f</sup> Neat.

## EXPERIMENTAL

*General comments*

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen using rigorously dried solvents. The standard apparatus consisted of a three-necked flask of appropriate size equipped with a reflux condenser topped with a nitrogen inlet tube, a thermometer and a magnetic stirring assembly.

Infrared spectra were recorded using a Perkin-Elmer Model 337, 237B or 257 grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 spectrometer. Chemical shifts are expressed in  $\delta$  units, ppm downfield from internal tetramethylsilane. Gas-liquid partition chromatography (GLC) was used routinely for yield determinations and for analysis of reaction mixtures and collection of samples. The MIT isothermal and F&M Model 700, 720 or 5754 gas chromatographs were used. Thin layer chromatography (TLC) was used to follow the course of the reactions (except those carried out in sealed tubes). Eastman silica gel TLC sheet, type K301-R was used; it was developed using 20% benzene in cyclohexane. After it has been dried, the sheet was visualized in an iodine chamber followed by spraying with 10%  $\text{Na}_2\text{S}$  in 50% aq. ethanol.

Phenyl(bromochloromethyl)mercury was prepared as described in an earlier paper of this series<sup>1,2</sup>.

*Reaction of phenyl(bromochloromethyl)mercury with olefins at atmospheric pressure (cf. Tables 1 and 2)*

The mercurial and the olefin (the latter in fivefold or greater excess) in the appropriate solvent (generally 20 ml when 6–8 mmol of mercurial was used) were stirred and heated under nitrogen at the specified temperature for the specified length of time (Table 1). The reaction mixture then was filtered to remove phenylmercuric bromide and the filtrate was trap-to-trap distilled at low pressure (0.05–0.5 mm) into a trap maintained at  $-78^\circ$ . The distillate then was analyzed by GLC, in some cases after preliminary concentration by disillation to remove a part of the solvent. Samples of the products were isolated by GLC for analytical and spectroscopic characterization and product yields were determined by GLC, usually using the internal standard method. The GLC columns used included 10 and 20% Dow Corning DC-200 silicone fluid, 20% General Electric Co. SE-30 silicone rubber gum, 20% Carbowax 20M and 20% polyphenyl ether, all on Chromosorb W.

*Reactions of phenyl(bromochloromethyl)mercury with olefins in sealed tubes (cf. Tables 1 and 2)*

The mercurial and an excess of the olefin and the solvent when one was used were charged into a thick-walled Pyrex combustion tube which had been flushed well with nitrogen and argon (a typical tube size was 18 cm by 2.5 cm o.d.). The tube was sealed, a thermocouple lead was attached to the outside wall, and the tube was placed in an insulated, wire-heated cylindrical steel tube mounted on a Burrell shaker. In some other experiments, a magnetic stirring bar was sealed into the tube with the reaction mixture and the tube was immersed and heated in an oil bath with magnetic stirring. After the tube had been opened, the work-up of the reaction mixture followed the procedure described above.

*Comparative stability of phenyl(bromochloromethyl)mercury in benzene and cyclohexene at reflux*

Two standard reaction apparatuses were used. One was charged with 10 mmol of  $\text{PhHgCHClBr}$  and 25 ml of dry cyclohexene, the other with 10 mmol of the mercurial and 25 ml of dry benzene. Both flasks were placed in the same oil bath and stirred and heated at reflux ( $83 \pm 2^\circ$ ) for 7 days. A white solid started to precipitate in the cyclohexene reaction after 2 days, but the benzene solution remained clear throughout the heating period.

From the cyclohexene reaction mixture 2.2 g (61%) of phenylmercuric bromide was filtered (m.p.  $278\text{--}283^\circ$ ). Trap-to-trap distillation of the filtrate at  $40^\circ$  (0.05 mm) left 0.3 g of solid residue (7.5%), identified as unconverted starting mercurial by TLC. GLC analysis of the distillate showed the presence of 7-chloronorcarane (*cis/trans* ratio 1.2) in 33% yield.

The cooled benzene solution was filtered from 0.15 g of solid, identified as phenylmercuric bromide, m.p.  $280\text{--}285^\circ$  (4% yield). Trap-to-trap distillation of the filtrate left behind 3.5 g (85%) of starting mercurial, m.p.  $62\text{--}65^\circ$ . GLC analysis of the distillate showed benzene to be the only volatile compound present.

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