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HALOMETHYL-METAL COMPOUNDS
XXVIII*. PHENYL(DIBROMOCHLOROMETHYL)MERCURY AS A BROMOCHLOROCARBENE SOURCE

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SUMMARY

A number of *gem*-bromochlorocyclopropanes has been prepared by the reaction of $PhHgCClBr_2$-derived bromochlorocarbene with olefins (cyclohexene, cyclooctene, 1-heptene, tetramethylethylene, *cis*- and *trans*-2-butene, styrene, acrylonitrile, vinyl acetate, allyltrimethylsilane, vinyltrimethylsilane, *cis*- and *trans*-1,2-dichloroethylene). Reaction of phenyl(dibromochloromethyl)mercury with 2,5-dihydrofuran gave an equimolar amount of the expected C=C addition product and the C–H insertion product, 2-(bromochloromethyl)-2,5-dihydrofuran. Similar C–H insertion was observed with tetrahydrofuran. With cumene CClBr insertion occurred exclusively into the benzylic position.

INTRODUCTION

The reaction chemistry of dichlorocarbene and dibromocarbene has been developed very extensively, but this is not true for bromochlorocarbene. Skell and Sandler[2] reported in a preliminary communication the isolation of both isomers of 6-bromo-6-chlorobicyclo[3.1.0]hexane and 7-bromo-7-chlorobicyclo[4.1.0]heptane from reactions of the $HCClBr_2/Me_3COK$ reagent with the appropriate olefins, but the details of this work have not been published in the intervening 10 years. Parham and Twelves[3], using the same procedure to generate bromochlorocarbene, studied its reaction with indene. The initially formed bromochlorocyclopropane derivative was not isolated; instead its decomposition products, α-bromo- and α-chloronaphthalene, were obtained.

During our earlier studies of the dihalocarbene transfer chemistry of phenyl(trihalomethyl)mercury compounds, we carried out only a few reactions with phenyl(dibromochloromethyl)mercury. It was found that when this mercurial was heated in benzene at reflux in the presence of cyclohexene, 7-bromo-7-chloronorcarane was produced in 85% yield [eqn. (1)][4]. *Only* this product was obtained; none of the 7,7-

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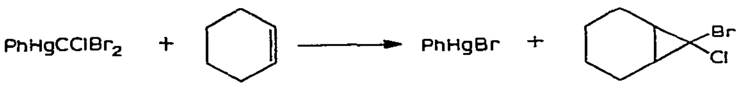
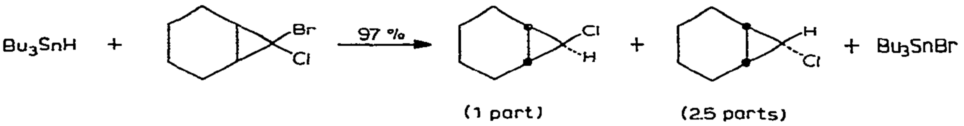


(1)

dibromonorcarane which would have resulted had phenylmercuric chloride been eliminated was detected. Further examples of the application of this organomercury reagent in CClBr transfer chemistry include its use in the preparation of bromopentachlorocyclopropane from tetrachloroethylene in 48% yield[4] and of 9-bromo-9-chlorobicyclo[6.1.0]nonane (98%) from cyclooctene[5].

While these few examples serve adequately to indicate the synthetic utility of phenyl(dibromochloromethyl)mercury as a CClBr transfer agent, we felt that further examples of such applications were required to emphasize the usefulness of this mercurial. Also, we wish to stress the utility of this reagent if *monochlorocyclopropanes* are sought.

None of the reagents which serve in the addition of CHCl to olefins—RLi/CH_2Cl_2[6], $PhHgCCl_2H$[7] or PhHgCClBrH[8], $Zn(CCl_2H)_2$[9] and $ClCHN_2$[10]—are very satisfactory from the standpoints of mild, convenient reaction conditions, good product yields, minimal side reactions and/or ease of reagent preparation. Thus the *direct* preparation of chlorocyclopropanes finds little practice. However, *gem*-bromochlorocyclopropanes are very easily reduced, selectively and in high yield, by tri-n-butyltin hydride to the corresponding chlorocyclopropanes[11] [eqn. (2)],



(2)

and for this reason, routes for their preparation are of special interest. It was this consideration which prompted the present study of the chemistry of phenyl(dibromochloromethyl)mercury in greater breadth. It should be noted that the utility of this mercurial has been greatly enhanced by the recent development of a much more easily effected procedure for its preparation in good yield[12].

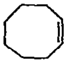
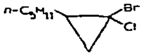
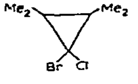
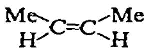
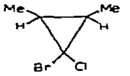
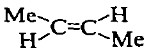
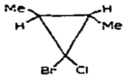
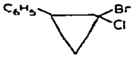
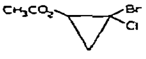
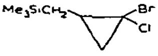
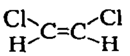
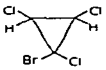
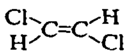
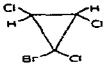
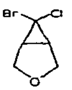
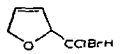
RESULTS AND DISCUSSION

Reactions of phenyl(dibromochloromethyl)mercury in refluxing benzene with a broad spectrum of olefins proceeded readily and gave the expected *gem*-bromochlorocyclopropanes in generally good yield (Table 1). Olefins whose conversion to *gem*-dichlorocyclopropanes is difficult or impossible to effect via the $CHCl_3/Me_3COK$ or CCl_3CO_2Na reagents were found in our previous studies[4] to add dichlorocarbene readily and in high yield when phenyl(bromodichloromethyl)mercury was used as the CCl_2 source. These included base-sensitive olefins such as acrylonitrile and vinyl acetate, electronically deactivated olefins such as tetrachloroethylene and hindered olefins such as vinyltrimethylsilane. Similar behavior was found in the case of $PhHgCClBr_2$, as Table 1 shows. The *gem*-bromochlorocyclopropane yields are in general quite good, and in some cases where they are not, this can be attributed to the instability of the products (*e.g.*, the case of the 1,2-dichloroethylene isomers).

With many of the olefins in Table 1 one might expect to observe two isomeric products. For example, in the case of *cis*-2-butene these would be (I) and (II). However,

TABLE 1

REACTIONS OF $PhHgCClBr_2$ WITH OLEFINS

Olefin	Product (% yield)	n_D^{25}	Analysis found (calcd.) (%) C	H
	 (84)	1.5290[a]		
	 (98)	1.5272[b]		
$n\text{-}C_5H_{11}CH{=}CH_2$	 (83)	1.4740	42.85 (42.59)	6.23 (6.26)
$Me_2C{=}CMe_2$	 (98)	g	39.77 (39.74)	5.92 (5.72)
 $\mathrm{MeHC{=}CHMe}$	 (99)[c]	1.4858	33.18 (32.73)	4.77 (4.39)
 $\mathrm{MeHC{=}CHMe}$	 (84)[d]	1.4835	32.70 (32.73)	4.38 (4.39)
$C_6H_5CH{=}CH_2$	 (78)	1.5746	46.69 (46.69)	3.40 (3.48)
$CH_2{=}CHC{\equiv}N$	 (61)	1.5142	26.80 (26.62)	1.70 (1.68)
$CH_3CO_2CH{=}CH_2$	 (74)	1.4789	28.09 (28.13)	2.89 (2.83)
$Me_3SiCH_2CH{=}CH_2$	 (84)	1.4759	34.91 (34.79)	5.73 (5.84)
$Me_3SiCH{=}CH_2$	 (53)	1.4800	31.82 (31.66)	5.25 (5.32)
 $\mathrm{ClHC{=}CHCl}$	 (50)[e]	1.5425	16.05 (16.06)	1.01 (0.90)
 $\mathrm{ClHC{=}CHCl}$	 (39)[f]	1.5380	15.41 (16.06)	0.75 (0.90)
	 (45)	1.5219	30.53 (30.41)	3.23 (3.06)
	 (45)	1.5290	30.33 (30.41)	3.05 (3.06)

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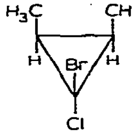
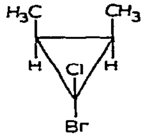
[a] Lit.[4] n_D^{25} 1.5293. [b] Lit.[5] n_D^{25} 1.5263. [c] GLPC retention time 2.88 min (MIT isothermal unit, 20% General Electric Co. XF1150 on Chromosorb W, 8 ft. glass column, 150°, 15 psi helium). [d] GLPC retention time 3.62 min (same conditions as in *c*). [e] GLPC retention time 4.70 min (20% General Electric Co. SE-30 on Chromosorb W, 8-1/2 ft. glass column, 170°). NMR: 3.65 s, 3.80 s (∴ mixture of both possible isomers). [f] GLPC retention time 3.54 min (same conditions as in *e*). NMR: 3.94 (1H) d (*J* 6 Hz), 4.14 (1H) d (*J* 6 Hz). [g] M.p. 63.5–65°.

in none of these cases shown in Table 1 could gas-liquid partition chromatographic (GLPC) separation of isomers be achieved. The available spectroscopic evidence suggests that in most cases both of the possible isomers were formed. The product

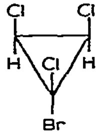


I

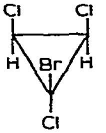


II

obtained when CClBr was added to *cis*-1,2-dichloroethylene was a mixture of the two possible isomers, (III) and (IV). The NMR spectrum (in CCl_4) of the 1-bromo-1,2,3-trichlorocyclopropane formed in this reaction showed singlets at δ 3.65 and 3.80 ppm.



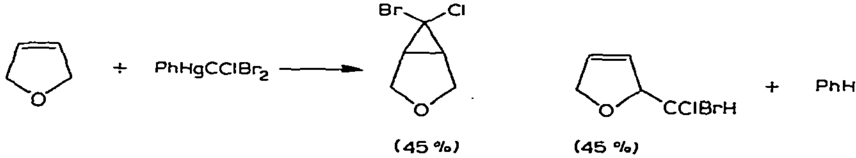
III



IV

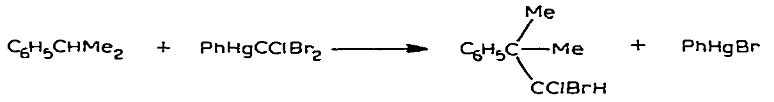
These resonances had an integrated ratio of 1/1.5. However, olefinic products most likely derived from decomposition of the cyclopropanes also were present. Since it is not known whether or not these represent preferential decomposition of one of the 1-bromo-1,2,3-trichlorocyclopropane isomers, no significance can be attached to this observed isomer ratio. The product from the CClBr/vinyltrimethylsilane reaction had an NMR spectrum which was more complicated than that of 1,1-dichloro-2-(trimethylsilyl)cyclopropane, and this may indicate that a mixture of both isomers of 1-bromo-1-chloro-2-(trimethylsilyl)cyclopropane had been formed. The products obtained from CClBr addition to *cis*-2-butene and *trans*-2-butene and to *cis*- and *trans*-1,2-dichloroethylene in each case were different (NMR and IR spectra, n_D^{25}, GLPC retention times), a strong indication that the addition of CClBr, like that of CCl_2 and CBr_2[4], to the C=C bond occurs without change in the configuration of olefin substituents.

When 2,5-dihydrofuran was allowed to react with $PhHgCCl_2Br$-derived dichlorocarbene, a mixture of the expected C=C addition product, 3-oxa-6,6-dichlorobicyclo[3.1.0]hexane (44%), and the C–H insertion product, 2-(dichloromethyl)-2,5-dihydrofuran (52%), resulted[4]. A very similar result was observed when $PhHgCClBr_2$ and 2,5-dihydrofuran were allowed to react [eqn. (3)]. In contrast, CFCl (from $PhHgCCl_2F$)[13] and CF_2 (from Me_3SnCF_3/NaI)[14] are much more selective, favoring C=C addition by a large margin. The reaction of CClBr with tetrahydrofuran gave 2-(bromochloromethyl)tetrahydrofuran in 39% yield.



(3)

The reaction of phenyl(dibromochloromethyl)mercury-derived CClBr with cumene is very similar to the previously described[15] CCl_2/cumene reaction, giving exclusively CClBr insertion into the benzylic C–H bond [eqn. (4)]. The product, 1-bromo-1-chloro-2-methyl-2-phenylpropane, was rather unstable and was obtained in only 21% yield upon the usual work-up by distillation and even then not in analytical purity. For this reason the $PhHgCClBr_2$/cumene reaction was repeated and the insertion product was reduced to the stable 1-chloro-2-methyl-2-phenylpropane with tri-n-butyltin hydride without prior isolation [eqn. (5)]. The yield of the reduc-



$$C_6H_5CHMe_2 + PhHgCClBr_2 \longrightarrow C_6H_5\underset{CClBrH}{\overset{Me}{C}}{-}Me + PhHgBr \qquad (4)$$

$$C_6H_5\underset{CClBrH}{\overset{Me}{C}}{-}Me + n\text{-}Bu_3SnH \longrightarrow C_6H_5\underset{CH_2Cl}{\overset{Me}{C}}{-}Me + n\text{-}Bu_3SnBr \qquad (5)$$

tion product was 53%. Since CClBr appears to be equivalent to CCl_2 in reactivity as far as C–H insertion is concerned, the CClBr insertion–CBr reduction sequence as typified by eqns. (4) and (5) may prove to be a useful route to monochloro derivatives that are difficult to prepare by other methods.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen in flame-dried glassware. Analyses were performed by Dr. S. M. Nagy (M.I.T.), the Galbraith Laboratories and the Scandinavian Microanalytical Laboratories. IR spectra were recorded using a Perkin–Elmer Model 237B Infracord spectrometer, NMR spectra using a Varian Associates A60 or T60 NMR spectrometer. Chemical shifts are recorded in δ units (ppm downfield from tetramethylsilane). Gas–liquid partition chromatography (GLPC) was used for product separation, isolation and yield analysis. M.I.T. isothermal units and F&M Model 700 and 720 gas chromatographs were used. Mostly columns were filled with 20% General Electric Co. SE-30 silicone rubber gum on Chromosorb W, but in some cases a more polar liquid phase, General Electric Co. XE-60 or XF-1150 on Chromosorb W, was used. The progress of the mercurial/olefin reactions usually was monitored by thin layer chromatography[16]. Product yields were determined by GLPC using the internal standard procedure.

Reaction of phenyl(dibromochloromethyl)mercury with olefins

The reaction of this mercurial with 1-heptene is described as an example of the procedure used throughout this study.

A 100 ml, three-necked flask equipped with reflux condenser, magnetic stirring assembly, nitrogen inlet tube and a thermometer was charged with 9.88 g (20.4 mmoles) of $PhHgCClBr_2$[12], 4.46 g (45.5 mmoles) of 1-heptene (99% purity, from Chemical Samples Co.) and 50 ml of dry benzene (distilled from Na benzophenone ketyl). The reaction mixture was stirred at the reflux temperature for 3 h. Filtration gave phenylmercuric bromide, m.p. 280–283°, in 97% yield. The filtrate was distilled at 0.03 mm (pot temperature to 80°) into a receiver at −78°. GLPC analysis of the distillate showed that 1-bromo-1-chloro-2-n-amylcyclopropane had been formed in 83% yield. The M.I.T. isothermal unit was employed, using an 8 ft glass column filled with 20% SE-30 on Chromosorb P, to collect samples for analysis and spectroscopic characterization.

All other reactions were carried out in much the same manner (with olefin/mercurial ratios of 3/1–2/1). The yields obtained and analytical data are given in Table 1. IR and NMR spectra were recorded for all products. The similarity of the spectra of these *gem*-bromochlorocyclopropanes and those of the analogous *gem*-dibromo- and *gem*-dichlorocyclopropanes, all of which had been prepared previously in these Laboratories[4] was of great assistance in confirming the structure of the products of the present study. Some of the *gem*-bromochlorocyclopropanes prepared were of only limited stability, notably those derived from vinyl acetate and 2,5-dihydrofuran. All products were liquids except that derived from tetramethylethylene. The latter, 1-bromo-1-chloro-2,2,3,3-tetramethylcyclopropane was purified by sublimation at 0.05 mm.

The reactions with the two 2-butene isomers were carried out by bubbling the gaseous olefin slowly into a stirred solution of the mercurial in benzene at 80° until the mercury reagent had been consumed. The reaction of $PhHgCClBr_2$ with *cis*-1,2-dichloroethylene was carried out in the absence of solvent [4.53 g (9.35 mmoles) of mercurial and 11.30 g (130 mmoles) of olefin] in a bomb tube heated at 85° for 2.5 h. The cyclopropanes obtained from *cis*- and *trans*-1,2-dichloroethylene appeared to be somewhat unstable. In both cases olefinic by-products were formed in *ca.* 20–30% yield; these may have been formed in electrophilic ring opening of the cyclopropanes, and they were not investigated further. The reaction of $PhHgCClBr_2$ with vinyltrimethylsilane was carried out at *ca.* 58° because of the low b.p. (54°) of the olefin; a reaction time of 24 h gave phenylmercuric bromide in 80% yield.

The reaction of phenyl(dibromochloromethyl)mercury with 2,5-dihydrofuran (1/3 ratio) gave two products. The first to be eluted on GLPC separation using an XE-60 on Chromosorb W column at 110° was the C–H insertion product, 2-(bromochloromethyl)-2,5-dihydrofuran, the second, the C=C addition product, 3-oxa-6-bromo-6-chlorobicyclo[3.1.0]hexane. The IR and NMR spectra of these products were quite similar to those of the CCl_2 insertion and addition products of 2,5-dihydrofuran[17]. In particular, the C=C stretching frequency observed in the IR spectrum of the CClBr insertion product at 1620 cm^{-1} was absent in the spectrum of the C=C addition product.

Reaction of phenyl(dibromochloromethyl)mercury with tetrahydrofuran

A mixture of 4.70 g (9.7 mmoles) of the mercury compound and 2.05 g (20.8 mmoles) of tetrahydrofuran in 50 ml of benzene was stirred at reflux for 3 h. Filtration gave phenylmercuric bromide in 87% yield. Trap-to-trap distillation of the filtrate at 0.05 mm (pot temperature to 90°) was followed by GLPC analysis of the distillate (silicone oil column at 140°). The presence of 2-(bromochloromethyl)tetrahydrofuran in 39% yield was indicated. Samples of this rather unstable product were isolated by preparative GLPC. It was necessary to handle them in acid-washed equipment with strict exclusion of air and moisture. (Found: C, 30.58; H, 3.85. C_5H_8BrClO calcd.: C, 30.10; H, 4.04%.) NMR (in CCl_4): δ 0.71–1.32 (4H) m; 1.65–2.24 (3H) m; 5.87 ppm (1H, –CClBrH) d (J 8 Hz).

Reaction of phenyl(dibromochloromethyl)mercury with cumene

A mixture of 5.83 g (48.3 mmoles) of cumene and 9.69 g (20.0 mmoles) of the mercurial in 50 ml of dry benzene was stirred at reflux under nitrogen for 3 h. Phenylmercuric bromide (85%) was filtered and the filtrate trap-to-trap distilled at 0.05 mm (room temperature). The remaining liquid was distilled using a short path distillation unit to give 1.06 g of liquid, b.p. 45–50° (0.03 mm). GLPC analysis showed the distillate to be *ca.* 95% pure, the impurities being benzene and cumene. Purification by GLPC was not possible, and a satisfactory combustion analysis could not be obtained. The crude yield of the insertion product was 21%. It had n_D^{25} 1.5670 and its IR spectrum (liq. film) showed the following absorptions: 3080 m, 3050 m, 3020 m, 2980 s, 2920 m, 2870 m, 1900 w, 1880 w, 1860 w, 1800 w, 1600 m, 1590 w, 1580 w, 1495 s, 1470 (sh), 1460 s, 1450 m, 1440 m, 1385 s, 1365 s, 1290 w, 1275 w, 1260 w, 1220 w, 1190 (sh), 1180 s, 1155 w, 1125 w, 1100 m, 1090 m, 1075 m, 1050 m, 1030 m, 1000 w, 950 m, 935 m, 895 m, 855 s, 820 w, 800 w, 770 s, 750 s, 730 s, 710 m, 700 s, 665 s, cm^{-1}. NMR (in CCl_4): 1.48 (6H, CH_3) s; 5.94 (1H, $-CBrClH$) s; 7.26 (5H, C_6H_5) s.

This reaction was repeated using 9.79 g (20.2 mmoles) of $PhHgCClBr_2$ and 35 ml of cumene (no benzene). The reaction mixture was stirred while being heated in an oil bath maintained at 90° for 1.75 h. Filtration gave phenylmercuric bromide in 91% yield. The filtrate containing the $C_6H_5CMe_2CClBrH$ was charged into a 50 ml, three-necked flask equipped with a magnetic stirring assembly, a nitrogen inlet tube and an addition funnel, and 5.80 g (20 mmoles) of tri-n-butyltin hydride was added dropwise over a 60 min period. The temperature of the reaction mixture was maintained between 10–20° during the addition of the hydride and for 30 min after the addition had been completed. The grayish reaction mixture was trap-to-trap distilled at 0.05 mm (pot temperature to 80°) to remove the more volatile components and the residue was then distilled using a 3" Vigreux column to give a major fraction at 86–87° (6 mm), 1.66 g (53%). The latter was found to be *ca.* 95% pure by GLPC (20% LAC-728 at 100°). A pure sample was obtained via preparative GLPC, n_D^{25} 1.5240 (lit.[18] n_D^{25} 1.5250 for 1-chloro-2-methyl-2-phenylpropane). NMR (in CCl_4): δ 1.44 (6H, CH_3) s; 3.56 (2H, $-CH_2Cl$) s; 7.30 ppm (5H, C_6H_5) s. Further distillation gave 6.13 g (85%) of tri-n-butyltin bromide, b.p. 85° (0.1 mm), n_D^{25} 1.5050; lit.[19] b.p. 120° (1.8 mm) and n_D^{25} 1.5022.

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