Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

HALOMETHYL–METAL COMPOUNDS
XLI. PHENYL(α,α-DICHLOROBENZYL)MERCURY: A PHENYLCHLOROCARBENE PRECURSOR*

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(Received July 15th, 1970)

SUMMARY

Phenyl(α,α-dichlorobenzyl)mercury has been prepared via α,α-dichlorobenzyllithium. It was found to be unstable to heat and to moisture, its hydrolysis giving benzene, benzoic acid and elemental mercury. Thermolysis of this mercurial in the presence of olefins (*cis*-2-butene, trimethylethylene, tetramethylethylene, allyltrimethylsilane) gave the expected phenylchlorocyclopropanes in yields ranging from 28–67%, and in the presence of triethylsilane an 83% yield of triethyl(α-chlorobenzyl)silane was obtained.

INTRODUCTION

During the past eight years we have studied in some detail the application of halomethyl–mercury compounds as divalent carbon transfer agents. Compounds of type $PhHgCX_3$ (X = halogen, Cl, Br or F)[2–4], $PhHgCX_2H$[5,6] and $Hg(CH_2X)_2$[7] received major attention, and more recently we have investigated the generation of carbenes, RCX, via mercurials of type $PhHgCX_2R$. Reagents where R = Me_3Si[8], CO_2Me[9], CF_3[9], and  (R′ = H, Me, Ph)[10] were prepared and studied. Also of interest would be those reagents where R is a simple organic group, and we report here our studies concerning the case where R = Ph.

The organomercurial chosen for study was phenyl(α,α-dichlorobenzyl)mercury, $PhHgCCl_2Ph$, whose thermolysis would be expected to give phenylchlorocarbene. This carbene (or carbenoid) had been generated previously by other procedures: via $PhCHCl_2 + Me_3COM$ (M = Na[11] or K[12]), $PhCCl_3$ or $PhCHCl_2$ + n-BuLi (in THF at low temperature, a route involving $PhCCl_2Li$ as an intermediate)[13], and photolysis of phenylchlorodiazirine[14,15]. We have found organometallic routes to phenylchlorocarbene based on organotin and organoboron compounds (eqn. 1[16] and 2[17]) to have only marginal value. Trimethyl(α,α-dichlorobenzyl)tin was too

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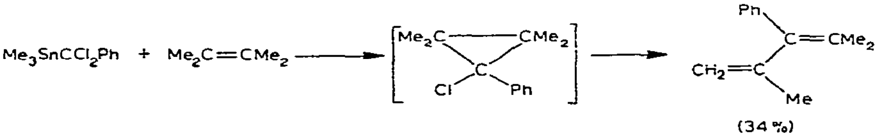
* For Part XL, see ref. 1.
** National Science Foundation Predoctoral Fellow, 1967–1970.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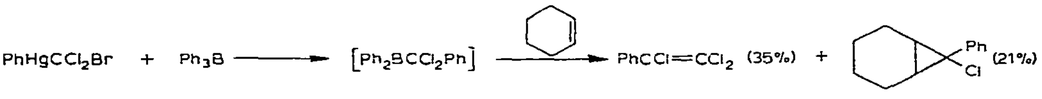
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stable (to 140–160°) to be a useful PhCCl transfer reagent, and the formation of the dichlorobenzylborane was complicated by a major side reaction in which α,β,β-trichlorostyrene was formed.

RESULTS AND DISCUSSION

Our initial experiments established that the standard procedures for phenyl(trihalomethyl)mercurial preparation[18,19] were not applicable to the preparation of phenyl(α,α-dichlorobenzyl)mercury[20]. The reported hydrolytic instability of diphenylchloromethylmercuric chloride[21,22] (in marked contrast to the stability toward hydrolysis of all the halomethylmercurials we had studied previously) led to the suspicion that hydrolytic instability of $PhHgCCl_2Ph$ might be the cause of our previous failures to prepare this compound by the usual method (which involved a hydrolytic work-up). With this possibility in mind, we investigated the possible synthesis of this mercurial via Hoeg's $PhCCl_2Li$ reagent[13].

α,α-Dichlorobenzyllithium, prepared in the tetrahydrofuran/dimethyl ether solvent system[23] below −100°, was treated with phenylmercuric chloride and this reaction gave the desired $PhHgCCl_2Ph$. In confirmation of the suspicion mentioned above, this compound indeed was *very* unstable to moisture, and, furthermore, its thermal stability was quite limited. Moreover, thermal decomposition seemed to be accelerated when it was in solution, making a rapid work-up imperative. The preparation of phenyl(α,α-dichlorobenzyl)mercury reported here represents the best yield of purified product obtained in several variations of the work-up procedure.

Phenyl(α,α-dichlorobenzyl)mercury, a white, crystalline solid, m.p. 84–86° (dec.), is stable when stored at −15° for periods of several months. However, at room temperature the mercurial became dark in a matter of hours and when exposed to atmospheric moisture at room temperature, it decomposed spontaneously and exothermally after several minutes.

Because phenyl(α,α-dichlorobenzyl)mercury did not appear to be a stable "shelf reagent", an attempt was made to prepare α,α-dichlorobenzylmercuric chloride (eqn. 3) which might be less labile. However, although benzene was obtained in 94%

$$PhHgCCl_2Ph + HCl \xrightarrow{PhCl} C_6H_6 + PhCCl_2HgCl \qquad (3)$$

yield, the expected organomercury compound could not be isolated in pure form.

The results obtained in the controlled hydrolysis of phenyl(α,α-dichlorobenzyl)mercury are shown in eqn. (4). The products of this reaction are analogous to

$$PhHgCCl_2Ph \xrightarrow{H_2O/THF} \underset{(69\%)}{PhCO_2H} + \underset{(80\%)}{C_6H_6} + \underset{(64\%)}{Hg^0} + HCl \qquad (4)$$

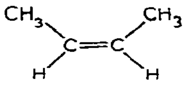
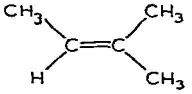
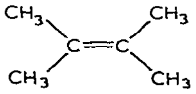
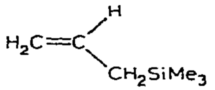
those of the hydrolysis of diphenylchloromethylmercuric chloride (eqn. 5), for which a carbonium ion mechanism was proposed[22] but not rigorously proven.

$$\mathrm{Ph_2CClHgCl} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_2C{=}O+Hg^0+HCl} \qquad (5)$$

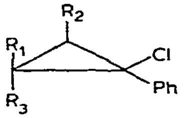
Phenyl(α,α-dichlorobenzyl)mercury was found to be a moderately good source of PhCCl. When this mercurial was heated in the presence of olefins under relatively mild conditions (60–80° in benzene solution), excellent yields of phenylmercuric chloride were obtained in every case (Table 1), indicating nearly quantitative decomposition of the mercury reagent. The cyclopropane yields, however, were rather lower, most likely because of secondary decomposition. Phenylchlorocyclopropanes have been noted[12,24] to be relatively unstable and some decomposition is not surprising. In our reactions phenylmercuric chloride and possibly traces of mercuric chloride are present and these could catalyze cyclopropane ring opening. In the reaction of $PhHgCCl_2Ph$ with allyltrimethylsilane to give 1-chloro-1-phenyl-2-(trimethylsilylmethyl)cyclopropane, γ-elimination of trimethylchlorosilane from the

TABLE 1

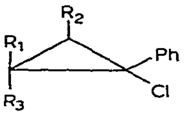
PHENYLCHLOROCYCLOPROPANATION REACTIONS

Olefin	Yield of cyclopropane (%)	Yield of PhHgCl (%)	Temp. (°C)	*syn*-Cl/*anti*-Cl ratios[a]
	28	92	75	2.4
	24	87	60	2.5
	67	95	50–55	3.2
	64	97	70–75	
	32	93	60–68	
	29	90	80–90	1.0

[a] *Syn*- and *anti*-isomers of unsymmetrical 1,1-disubstituted cyclopropanes are named with respect to one of the substituents and the greater number of alkyl groups at C_{2-3}. Following Moss and Przblya (*Tetrahedron*, 25 (1969) 647) isomers of phenylhalocyclopropanes will be named with respect to the halogen substituent.



syn-Cl



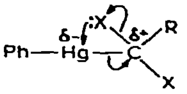
anti-Cl

product also is a potential mode of decomposition[25]. The *syn/anti* ratios listed for the products obtained with *cis*-2-butene, trimethylethylene and allyltrimethylsilane should not be considered significant in view of the possible preferential decomposition of one of the isomers under our reaction and isolation conditions, and a comparison with *syn/anti* ratios of PhCCl adducts of *cis*-2-butene and trimethylethylene obtained via other routes[12,14] is not meaningful.

Phenyl(α,α-dichlorobenzyl)mercury also inserts phenylchlorocarbene into the silicon–hydrogen bond, and a study of this reaction has provided a measure of the reactivity of this mercurial as a divalent carbon transfer agent (eqn. 6). When identical solutions of $PhHgCCl_2Ph$ and triethylsilane in benzene were heated at 76–79°, the

$$\underset{}{PhHgCCl_2Ph + Et_3SiH} \xrightarrow{\text{benzene } 80^\circ} \underset{(83\%)}{Et_3SiCHClPh} + \underset{(97\%)}{PhHgCl} \qquad (6)$$

yields of phenylmercuric chloride obtained after 30 min and 60 min were 90% and 97%, respectively. Complete work-up for both products of a similar reaction mixture after 12 h gave the product yields shown in eqn. (6). Thus phenyl(α,α-dichlorobenzyl)-mercury is the most labile and the most reactive mercurial of type $PhHgCCl_2R$ ($R =$ Cl, F, H, Ph, CF_3, CH_3[26], CO_2Me, $SiMe_3$, $R'C\langle{}^{O}_{O}\rangle$) that we have examined to date. (A comparison with those mercurials in whose decompositions and/or reactions phenylmercuric *bromide* is eliminated is not meaningful.) We shall defer detailed discussion of this point at this time, but note that this, together with other evidence derived from not yet completed studies suggests that the transition state for carbene extrusion from halomethylmercurials is one in which a partial positive charge develops at the incipient carbene carbon atom (I). In the present case, the phenyl sub-



(I)

stituent on this carbon atom serves to stabilize this partial positive charge and thus to facilitate the carbene extrusion process.

Thermal decomposition of $PhHgCCl_2Ph$ in the absence of a carbene trapping reagent gave phenylmercuric chloride (95%), *trans*-dichlorostilbene (37%) and other unidentified solid products. A similarity to tetrachloroethylene formation in the thermolysis of $PhHgCCl_2Br$ in the absence of a carbene trap[2] is apparent.

In summary, phenyl(α,α-dichlorobenzyl)mercury can be prepared and isolated, provided exceptional precautions are taken, and it can be used as a phenylchlorocarbene source. However, the difficulty with which it is prepared and isolated, in large part due to its hydrolytic instability, do not make it the reagent of choice for preparative chemistry with this carbene.

EXPERIMENTAL

General comments

All reactions using organolithium or organomercury reagents were carried out under an atmosphere of dry nitrogen or argon unless otherwise specified in flame-dried glassware.

Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Associates A-60 or T-60 high resolution spectrometer. Chemical shifts are reported in δ units using either tetramethylsilane (δ 0.00) or chloroform (δ 7.27) as internal standards.

Infrared spectra were recorded using a Perkin–Elmer 237B, 337, or 257 grating infrared spectrometer. Intensities are reported as very strong (vs), strong (s), medium (m), weak (w), or shoulder (sh) with reference to the strongest band.

Gas–liquid partition chromatography (GLC) was used routinely for yield determinations and for collection of analytical samples. Commercial stainless steel columns were employed with either an F&M Model 700, 720, or 5754 gas chromatograph. Several different columns were used: (A) 6 ft × 0.25 in 10% DC-200 silicone oil (5754); (B) 4 ft × 0.25 in 10% UC-W98 silicone rubber (5754); (C) 6 ft × 0.25 in 10% Carbowax 20M (5754); (D) 6 ft × 0.25 in 20% DC-200 silicone oil (700 or 720); (E) 6 ft × 0.25 in 20% UC-W98 silicone rubber (700); (F) 6 ft × 0.25 in 20% XE-60 silicone gum nitrile (700 or 720); (G) 12 ft × 0.25 in 20% Carbowax 20M (700); (H) 6 ft × 0.25 in 20% polyphenyl ether (700); (I) 6 ft × 0.25 in 20% Carbowax 20M (700); (J) 6 ft × 0.25 in 10% Apiezon L (5754); (K) 6 ft × 0.25 in 20% Apiezon L (720); and (L) 4 ft × 0.25 in 20% LAC 728 (700). All columns were packed on acid-washed, dimethylchlorosilane-treated Chromosorb W; a helium carrier gas flow rate of 40–60 ml/min was commonly employed. Internal standards were used in all yield analyses. Empirical response factors (*RF*) were determined separately using standard solutions according to the formula:

$$RF = \frac{\text{Area (standard)}}{\text{mmole (standard)}} \times \frac{\text{mmole (product)}}{\text{Area (product)}}$$

Peak areas were measured using an Ott planimeter.

Mass spectra were recorded using a Consolidated Electrodynamics Company 130 or a Hitachi–Perkin–Elmer RMU6D mass spectrometer.

Preparation of phenyl(α,α-dichlorobenzyl)mercury

A 1000-ml Morton (creased) flask equipped with a high-speed stirring unit (Labline Catalog No. 1280), a pressure-equalizing addition funnel, and a Claisen head fitted with a pentane thermometer and a nitrogen inlet was used to prepare a solution of α,α-dichlorobenzyllithium[13] at −100 to −110° from 15.73 g (80.6 mmoles) of α,α,α-trichlorotoluene (Eastman White Label, washed with aqueous sodium bicarbonate and distilled, b.p. 95°/17 mm) in 50 ml of dimethyl ether and 150 ml of tetrahydrofuran by adding 50 ml of 1.60 *N* n-butyllithium in hexane (80 mmoles) dropwise over a 20 min period. The resulting deep purple slurry was stirred for 40 min to insure complete formation of the organolithium intermediate. Phenylmercuric chloride, 25.2 g (80.5 mmoles), then was added as the solid over a five-minute period, causing the reaction mixture to become yellow-orange in color. After an additional 2 h of stirring at low temperature, the reaction mixture was allowed to warm slowly to −40°. The clear orange solution was transferred under nitrogen to a 2000-ml round-bottomed flask and evaporated at water pump pressure using a Dry Ice-trapped rotary evaporator. During this and all other parts of the work-up procedure the product solutions were kept as cold as possible. The remaining brown oil was taken up in 800 ml of benzene and suction filtered using a Buchner funnel under a stream of nitrogen to remove grey solid material. The volume of the benzene solution was then reduced to ca. 100 ml and 600 ml of pentane was added. The solution which resulted was again filtered, and then cooled rapidly using powdered Dry Ice to precipitate a yellow solid. The solid was quickly filtered and dried under vacuum. A second crop was recovered from the concentrated mother liquor to give a total of 21.3 g (61 % crude yield) of the title mercurial, m.p. 78–82°. Recrystallization was accomplished by dissolving the mercurial in 60 ml of benzene and adding 240 ml of pentane to give a clear solution at room temperature. Refrigeration at −15° led to the formation of white prisms, m.p. 84–86° (slow decomposition giving yellow liquid, then slow formation of a white solid); the total yield from two crops was 19.1 g (54 %). (Found: C, 35.41; H, 2.28. $C_{13}H_{10}Cl_2Hg$ calcd.: C, 35.67; H, 2.30%.) Infrared spectrum (CH_2Cl_2): 3055 sh, 3005 m, 1970 sh, 1895 w, 1875 w, 1820 w, 1636 w, 1591 m, 1574 m, 1490 vs, 1476 vs, 1440 m, 1427 sh, 1190 m, 1172 sh, 1074 m, 1061 m, 1030 sh, 1020 s, 996 s and 846 m cm^{-1}.

The procedure for handling this mercurial consisted of allowing its sealed container to warm to 0–5° (frozen condensate on outside melted and was wiped away) and then weighing and transferring it to the reaction solution under nitrogen. Yields of PhCCl transfer products as high as 83 % and nearly quantitative phenylmercuric chloride returns were obtained using this handling method.

Reaction of phenyl(α,α-dichlorobenzyl)mercury with anhydrous hydrogen chloride

In a 100-ml three-necked flask equipped with a magnetic stirring unit, a gas bubbler tube, and a nitrogen inlet system for gas exit was placed a solution of 6.55 g (15.0 mmoles) of phenyl(α,α-dichlorobenzyl)mercury in 60 ml of chlorobenzene. Anhydrous hydrogen chloride (Matheson) was bubbled vigorously into the mixture for 25 min causing the precipitation of a white solid. Stirring was continued for 20 min after which time the reaction mixture was frozen and the volatiles were trap-to-trap distilled into a receiver at −78° (60°/0.1 mm, open system). The distillate was analyzed by GLC (Column C, 112–170°, toluene standard) and was found to contain a 94 % yield of benzene, identified by its GLC retention time and by the NMR spectrum of a distilled sample with b.p. 80–81°. No benzal chloride was detected. Crystallization of the solid material which remained after the trap-to-trap distillation was attempted using 2/1 benzene/hexane. However, the product turned dark and appeared to decompose rapidly (no attempt to exclude air or atmospheric moisture) during this procedure and work-up was discontinued.

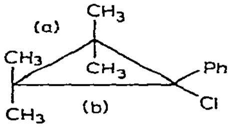
Hydrolysis of phenyl(α,α-dichlorobenzyl)mercury

Into a dried 50-ml three-necked flask equipped with a nitrogen inlet, a vacuum adapter, and a magnetic stirring unit was placed 15 ml of freshly distilled tetrahydrofuran. The solvent was frozen and degassed to insure the complete absence of oxygen, and once again was blanketed with nitrogen. Phenyl(α,α-dichlorobenzyl)mercury (3.94 g, 9.0 mmoles) and distilled water (3.0 g, ca. 170 mmoles) were then added and the resulting clear, yellow solution was stirred at room temperature. A pool of metallic mercury which formed during the first 15–30 min of the reaction period was separated after 2 h by transferring the solution (unchanged in appearance) by syringe into another three-necked flask. The weight of mercury isolated (1.15 g) represented a 64 % yield based on starting mercurial. The reaction solution was stirred for an additional 17 h, and then trap-to-trap distilled into a receiver at −78° (25°/0.5 mm, closed system). Examination of this distillate by GLC (Column C, 70°, toluene standard) revealed the presence of benzene in 80% yield, identified in a separate experiment (*vide infra*). Extraction of the distillation residue with 50 ml of benzene gave a clear solution which was filtered from a small amount of yellow solid and evaporated. The resulting yellow solid was crystallized from 100 ml of water to obtain 0.753 g (69%) of a white, flaky solid, which was identified as benzoic acid by means of its melting point (m.p. 121–122°, lit.[27] 122.4°) and infrared spectrum.

In a separate experiment, the mercurial (4.38 g, 10.0 mmoles) was stirred with a heterogenous mixture of chlorobenzene (20 ml) and water (1.0 ml). The mercury formed was suspended in a white solid (2.05 g total weight) which was partially characterized as mercurous chloride (positive test [black color] when treated with concentrated ammonia).Benzoic acid and benzene were detected in 70 and 84% yields, respectively. The latter isolated by fractional distillation, b.p. 80–81°, and was identified by comparison of its infrared spectrum and GLC retention time with those of an authentic sample.

*Reaction of phenyl(α,α-dichlorobenzyl)mercury with olefins**

(*a*). 2,3-*Dimethyl-2-butene*. Into a 50-ml, three-necked flask equipped with a magnetic stirring unit and a condenser with a nitrogen inlet atop were placed 1.078 g (2.47 mmoles) of the mercurial and 3.5 g (42 mmoles) of 2,3-dimethyl-2-butene (distilled from $LiAlH_4$, b.p. 73°) in 3.0 ml of benzene. The reaction mixture was heated at reflux for 48 h. On cooling 0.75 g (97%) of phenylmercuric chloride, m.p. 251–253°, was filtered and the reaction solution then was evaporated under reduced pressure leaving 0.60 g of white solid residue. Crystallization from hexane at −78° afforded 0.21 g of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane: m.p. 66–67° (lit.[12] 65.5–66.5°). A second crop, 0.12 g, m.p. 63–65°, was isolated from the evaporated mother liquor by sublimation at 75°/0.1 mm. The combined yield of the two portions was 64%. NMR ($CDCl_3$): δ 1.03 (s, 6 H_a), 1.37 (s, 6 H_b) and 7.23 ppm (m, 5 H, Ph) (lit.[12], δ 1.03, 1.37, and 7.23 ppm).



(*b*). 2-*Methyl-2-butene*. Using the procedure outlined in the preceding experiment 3.28 g (7.50 mmoles) of the mercurial and 5.95 g (85 mmoles) of 2-methyl-2-butene (Phillips, freshly distilled from $LiAlH_4$, b.p. 39–40°) in 10 ml of benzene was stirred at 50–55° for 24 h. Phenylmercuric chloride, m.p. 251–254°, was separated in 95% yield from the cooled reaction mixture. The clear, yellow filtrate then was concentrated at reduced pressure and distilled using a short path apparatus to give 0.98 g (67%) of 1-chloro-1-phenyl-2,2,3-trimethylcyclopropane (mixed isomers): b.p. 46–

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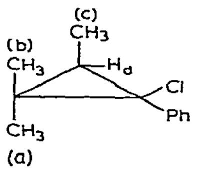
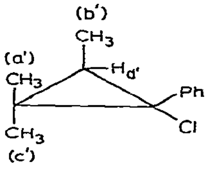
* Reaction times longer than necessary were used in these orientational experiments and thus these do not represent optimum conditions. From the results of the triethylsilane experiment (*vide infra*), a reaction time of no longer than 2 h seems indicated.

48°/0.06 mm, n_D^{25} 1.5210 (lit.[12] b.p. 42–50°/0.15 mm). The product was identified by comparison of its NMR spectrum with that reported in the literature[12]. The major isomer was that assigned the *syn*-Cl structure. NMR (CCl_4, mixed isomers) *syn*-Cl: δ 0.76 (s, 3 H_a), 1.23 (m, 7 H_{b-d}), and 7.20 ppm (m, 5 H, Ph); *anti*-Cl: δ 0.90 (s, 3 $H_{a'}$), 1.03 (m, 3 $H_{b'}$), 1.53 (s, 3 $H_{c'}$) and 7.20 ppm (m, 5 H, Ph); (lit.[12] *syn*-Cl: δ 0.81, 1.26, and 7.25 ppm; *anti*-Cl: δ 0.93, 1.0, 1.50, and 7.20 ppm). The integrated NMR spectrum



syn-Cl

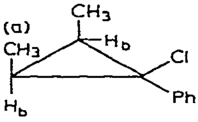


anti-Cl

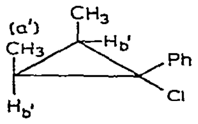
was used to determine the isomer ratio. Comparison of several sets of resonances gave a *syn*-Cl/*anti*-Cl ratio of 3.2±0.3.

(c). *cis-Butene.* A 35-ml sealed tube was charged with a solution of 6.56 g (15.0 mmoles) of the mercurial and ca. 6 g (110 mmoles) of *cis*-butene (Matheson, passed through a drying tower containing calcium chloride and magnesium sulfate) in 10 ml of benzene. The tube was sealed and shaken for 15 h at 75°. At the end of this time the reaction vessel was cooled and opened and the olefin was allowed to evaporate under a nitrogen atmosphere. The reaction mixture was washed with hexane through a filter which separated 4.35 g (92%) of phenylmercuric chloride, m.p. 249–251°, and then concentrated at reduced pressure. Short-path distillation of the concentrate using an oil bath heat source (85° max.) afforded 0.77 g (28%) of the expected 1-chloro-1-phenyl-*cis*-2,3-dimethylcyclopropane (mixed isomers): b.p. 51–56°/0.2 mm, n_D^{25} 1.5299 (lit.[12] b.p. 51–55°/0.3 mm). The product was identified by comparison of its NMR spectrum with that reported in the literature[12]. The more abundant isomer was that assigned the *syn*-Cl structure. NMR ($CDCl_3$, mixed isomers) *syn*-Cl: δ 1.18 (unresolved m, 8 H_{a-b}), and 7.23 ppm (m, 5 H, Ph); *anti*-Cl: δ 0.88 (unresolved m, 6 $H_{a'}$), 1.18 (m, 2 $H_{b'}$), and 7.23 ppm (m, 5 H, Ph) (lit.[12], *syn*-Cl: δ 1.22 and 7.37 ppm; *anti*-Cl: δ0.92 and 7.37 ppm). The $H_{b'}$ resonance at 1.18 ppm was unassigned in the literature, but it may be assigned by analogy to the NMR spectrum of the mixed 1-bromo-1-phenyl-2,3-dimethylcyclopropanes[28]. The integrated NMR spectrum was used to determine the isomer ratio according to the method of Closs[12]. Comparison of the δ 0.88 and 1.18 resonances gave a *syn*-Cl/*anti*-Cl ratio of 2.4.

In a separate experiment 4.38 g (10.0 mmoles) of the mercurial and ca. 6 g (110 mmoles) of *cis*-butene in 10 ml of benzene were shaken at 60° for 57 h. Work up as before afforded 2.74 g (87%) of phenylmercuric chloride, m.p. 254–256°, and 0.427 g (24%) of the 1-chloro-1-phenyl-*cis*-2,3-dimethylcyclopropanes: b.p. 50–55°/0.2 mm, n_D^{25} 1.5297, *syn*-Cl/*anti*-Cl ratio 2.5.

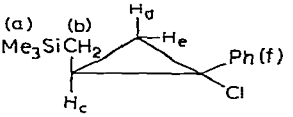


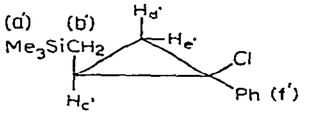
syn-Cl



anti-Cl

(*d*). *Allyltrimethylsilane*. Using the procedure outlined for the reaction of phenyl(α,α-dichlorobenzyl)mercury with 2,3-dimethyl-2-butene, 8.756 g (20.0 mmoles) of the mercurial and 5.55 g (53 mmoles) of allyltrimethylsilane in 25 ml of benzene were heated at 80–90° for 6 h. Phenylmercuric chloride, m.p. 256–257°, was filtered from the cooled reaction mixture in 90% yield. The filtrate then was concentrated and distilled using a short path apparatus to give 1.39 g (29%) of 1-chloro-1-phenyl-2-(trimethylsilylmethyl)cyclopropane (mixed isomers): b.p. 81–86°/0.07 mm. A moderate amount (1.70 g) of black tarry residue remained in the distillation pot. A redistilled sample, b.p. 60–61°/0.02 mm had n_D^{25} 1.5140. (Found: C, 65.05; H, 7.85; Cl, 14.94. $C_{13}H_{19}ClSi$ calcd.: C, 65.37; H, 8.02; Cl, 14.85%.) NMR (CCl_4, cyclohexane standard): δ 0.00 and 0.10 (s (2), 9 H_a+9 $H_{a'}$), 0.50–1.73 (m, H_{b-e}+$H_{b'-e'}$), and 7.31 ppm (m, 5 H_f+5 $H_{f'}$). Infrared spectrum (film): 3080 sh, 3055 w, 3022 w, 2994 w, 2948 vs, 2889 w, 2870 w, 2790 sh, 1944 w, 1690 w, 1598 w, 1580 sh, 1493 m, 1444 s, 1409 m, 1324 w, 1286 w, 1258 sh, 1248 vs, 1183 m, 1111 m, 1075 w, 1058 w, 1037 w, 1004 w, 931 w, 900 sh, 860 vs, 840 vs, 781 w, 749 s, 697 vs, and 642 w cm⁻¹.





In a second experiment 4.376 g (10.0 mmoles) of the mercurial and 1.552 g (13.6 mmoles) of allyltrimethylsilane in 10 ml of benzene were heated at 60–68° for 20 h. Work-up as before afforded 2.91 g (93%) of phenylmercuric chloride, m.p. 252–253°, and 0.76 g (32%) of the 1-chloro-1-phenyl-2-(trimethylsilylmethyl)cyclopropanes, b.p. 77–81°/0.05 mm, n_D^{25} 1.5148.

Reaction of phenyl(α,α-dichlorobenzyl)mercury with triethylsilane

A solution of 6.55 g (15.0 mmoles) of the mercurial and 6.15 g (52.8 mmoles) of triethylsilane (Peninsular ChemResearch, distilled from $LiAlH_4$) in 20 ml of benzene was prepared in a 100-ml flask equipped with a magnetic stirring device and a condenser topped with a nitrogen inlet. The clear mixture was heated in an 80–85° oil bath for 12 h. At the end of the reaction period 4.56 g (97%) of phenylmercuric chloride, m.p. 252–254°, was filtered from the cooled solution. The clear yellow filtrate was concentrated and then distilled using a short path apparatus to give 3.00 g (83%) of α-chlorobenzyltriethylsilane: b.p. 82–87°/0.10 mm. A redistilled sample, b.p. 77–82°/0.08 mm, had n_D^{25} 1.5220. (Found: C, 64.63; H, 8.81; Cl, 14.83. $C_{13}H_{21}ClSi$ calcd.: C, 64.83; H, 8.79; Cl, 14.72%.) NMR ($CDCl_3$): δ 0.30–1.13 (m, 15 H, Et_3Si), 4.40 (s, 1 H, SiCHClPh), and 7.05 ppm (m, 5 H, Ph). Infrared spectrum (film) 3070 w, 3050 w, 3012 w, 2942 vs, 2925 sh, 2901 s, 2865 vs, 2712 w, 1597 w, 1579 w, 1490 s, 1460 sh, 1447 s, 1412 m, 1377 w, 1327 w, 1312 sh, 1288 w, 1237 w, 1177 w, 1151 w, 1120 m, 1070 m, 1007 s, 972 sh, 907 w, 829 m, 787 s, 740 vs, and 697 vs cm⁻¹. Mass spectrum: *m/e* (rel. int.) 242, 240 (1.7, 5.3; M^+), 145 (22.5), 115 (100; Et_3Si^+), 91 (14.1), 87 (90; Et_2SiH^+), and 59 (28.1; $EtSiH_2^+$).

As further proof of the product structure, a 1.09 g (4.53 mmole) sample in 25 ml of cyclohexane was shaken with 2.1 g of sodium bicarbonate and 0.18 g of 10% Pd/C catalyst under ca. 3 atm of hydrogen in a Parr apparatus for 18 h. The mixture was then filtered, concentrated, and short path distilled to give 0.80 g (86%) of benzyltriethylsilane. b.p.53–55°/0.04 mm, n_D^{25} 1.5007 (lit.[29] b.p. 250–252°/atm. pr., n_D^{20} 1.5030), which was greater than 99% pure by GLC (Column D, 190°). NMR spectrum: δ 0.22–1.13 (m, 15 H, Et_3Si), 2.03 (s, 2 H, $SiCH_2Ph$), and 6.96 ppm (m, 5 H, Ph). A GLC purified sample (Column D, 190°) was analyzed. (Found: C, 75.63; H, 10.71. $C_{13}H_{22}Si$ calcd.: C, 75.65; H, 10.74%.)

In a separate experiment, duplicate reaction mixtures containing 0.876 g (2.00 mmoles) of the mercurial and 8.0 ml of a standard solution of triethylsilane in benzene (7.4 mmoles triethylsilane) were heated simultaneously in a 76–79° oil bath. Heating was discontinued for one of the mixtures after 30 min, and for the second, after 60 min. The mixtures were diluted with 10 ml of hexane and filtered to isolate phenylmercuric chloride. A 90% yield was obtained from the 30-min reaction mixture and a 97% yield, from the 60-min reaction mixture.

Thermal decomposition of phenyl(α,α-dichlorobenzyl)mercury without substrate

A solution of 4.08 g (9.32 mmoles) of the mercurial in 15 ml of benzene was prepared in a 50-ml flask equipped with a magnetic stirring unit and a condenser with a nitrogen inlet atop, and was heated in an 80–90° oil bath for 12 h. At the end of this period the cooled reaction mixture was filtered from 2.71 g (93%) of phenylmercuric chloride, m.p. 254–255°. The volatiles were evaporated from the filtrate at reduced pressure leaving 1.46 g of yellow, semisolid residue. Attempted crystallization from 25 ml of ethanol at −5° gave 0.05 g (2%) of crude phenylmercuric chloride, m.p. 246–249°. When the ethanol mother liquor was cooled to ca. −40°, 0.171 g of yellow crystals, m.p. 126–129°, were obtained. The infrared spectrum of this material was identical to that of *trans*-dichlorostilbene[30]. A second crop (0.271 g, m.p. 120–135°) was isolated from ethanol/water at −5°, giving a total crude yield of 0.442 g (37%). A small sample was recrystallized from ethanol, m.p. 139–140° (lit.[31] 139°). Repeated attempts to isolate additional pure products from the evaporated ethanol/water residue were unsuccessful.

In a separate experiment, resolution of the filtered reaction mixture was attempted using column chromatography with Woelm alumina. However, no material corresponding to the expected *cis*-dichlorostilbene was isolated.

ACKNOWLEDGEMENTS

The authors are grateful to the Air Force Office of Scientific Research (SRC)-OAR (USAF Grant AFOSR-68-1350) for generous support of this work.

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