HALOMETHYL—METAL COMPOUNDS

LXXIV*. ORGANOLEAD COMPOUNDS AS PRECURSORS FOR HALO-CARBENES

DIETMAR SEYFERTH*, GERALD J. MURPHY**, ROBERT L. LAMBERT, Jr.***
and ROBERT E. MAMMARELLA☆

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

The following organolead compounds were prepared and investigated as potential divalent carbon transfer agents: Ph_3PbCCl_3, Ph_3PbCBr_3, Ph_3PbCCl_2Ph, $Ph_3PbCHCl_2$ and $Ph_3PbCHClF$. Of these the CCl_3, CBr_3 and $CHCl_2$ compounds were found to be useful carbene sources at higher (120-150°) temperature. The reaction of triphenylleadlithium with 3,3,3-trichloropropene gave hexaphenyl-dilead and $Ph_3PbCH_2CH=CCl_2$, rather than the expected $Ph_3PbCCl_2CH=CH_2$.

Introduction

In our previous work we have studied in some detail the use of halomethyl-mercury compounds as divalent carbon transfer agents [2]. Three main procedures served in the preparation of such mercury reagents, the reaction of a mercury halide with a polyhalocarbon containing an acidic hydrogen (e.g., a halo-form) in the presence of an alkali metal alkoxide, the reaction of a mercury halide with the appropriate polyhaloalkyllithium reagent and the decarboxylation of an alkali metal salt of a halogenated acetic acid in the presence of a mercury halide. A number of halomethylmercury reagents which we felt might be of potential interest were not accessible by such anion-based routes. Furthermore, some organomercurials which we could prepare had properties which limited their usefulness, e.g., $PhHgCCl_2Ph$, which was very unstable toward hydrolysis [3].

We had investigated some halomethyltin compounds as potential divalent carbon transfer reagents, but these turned out to be too thermally stable to be usefully applicable in synthesis [4].

Willemsens and Van der Kerk [5-7] had prepared triphenyl(trichloromethyl)-lead by reaction of triphenyllead-lithium or -sodium with an excess of carbon tetrachloride (eqn. 1). This compound also was prepared by others by alternate pro-

$$Pb_6Pb_2 + 2M \xrightarrow{\text{THF, 25°}} 2\,Ph_3PbM \xrightarrow{\text{CCl}_4,\,\text{THF, }-60°} Ph_3PbCCl_3 \tag{1}$$

cedures, the reaction of triphenyllead methoxide with hexachloroacetone [8] and of trichloromethyltrifluorosilane with triphenyllead fluoride [9]. Triphenyl-(trichloromethyl)lead was shown by Willemsens to be a dichlorocarbene source, its reaction with cyclohexene (sealed tube at 115° for 7 h) giving 7,7-dichloro-norcarane in 70% yield [10]. This encouraging finding, as well as the novel synthetic approach of Willemsens and Van der Kerk to Ph_3PbCCl_3 (which had no counterpart in organomercury chemistry), prompted us to examine halomethyl-lead compounds in our continuing investigations of organometallic divalent carbon transfer chemistry.

Results and discussion

To obtain a better feeling for the relative merits of halomethyllead compounds as divalent carbon transfer agents, we first examined the dichlorocarbene transfer reactions of Ph_3PbCCl_3 in some detail. A comparison with analogous reactions of $PhHgCCl_3$ [2] would be informative from the point of view of the potential utility of the organolead approach.

The large-scale application of the Willemsens—Van der Kerk synthesis of triphenyl(trichloromethyl)lead proved difficult, but an alternate synthesis was found to be very satisfactory (eqn. 2). This reaction, adapted from an analo-

$$Ph_3PbCl + CCl_3CO_2^- Na^+ \xrightarrow{\text{DME, 85°}} Ph_3PbCCl_3 + NaCl + CO_2 \tag{2}$$

gous synthesis of $PhHgCCl_3$ [11], gave triphenyl(trichloromethyl)lead in 75% yield.
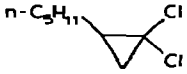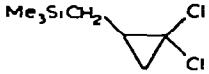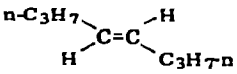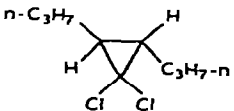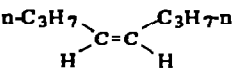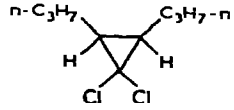
A comparison of the reactivity of Ph_3PbCCl_3 and $PhHgCCl_3$ toward cyclooctene in n-octane solution at 84° demonstrated the superiority of the organomercury reagent (Table 1). At higher temperatures the organolead reagent was much more reactive. Thus the 14% product yield (Table 1) was increased to 100% when the reaction mixture was heated for another 5 h at 132°. In a

TABLE 1

DICHLOROCARBENE TRANSFER TO CYCLOOCTENE (at 84° in n-octane, 3/1 olefin/CCl₃ reagent ratio)

CCl_3 compound	Yield(%) of 9,9-dichlorobicyclo[6.1.0]nonane after		
	20 h	44 h	68 h
$PhHgCCl_3$	60	88	100
Ph_3PbCCl_3	3	9	14

TABLE 2

CCl$_2$ TRANSFER FROM Ph$_3$PbCCl$_3$ (5 h at 125° in n-octane solution)

Carbenophile	mmol	mmol Ph$_3$PbCCl$_3$	Product	Yield (%)	Yield(%) of Ph$_3$PbCl
	21[a]	6.85		100	95
	21.3	6.85		98	98
n-C$_5$H$_{11}$CH=CH$_2$	28	9.35		88	98
Me$_3$SiCH$_2$CH=CH$_2$	27	9.1		100	99
PhCH=CH$_2$	20[b]	6.42		93	94
n-C$_3$H$_7$ C=C H / H C$_3$H$_7$-n	28	9.2		92	99
n-C$_3$H$_7$ C=C H / C$_3$H$_7$-n H	26	8.8		97	99
Et$_3$SiH	22	7.35	Et$_3$SiCCl$_2$H	87	97

[a] Neat olefin, 2 h at 125°. [b] 10 h at 125°.

separate experiment, a reaction time of 3 h at 132° was found sufficient to prepare 9,9-dichlorobicyclo[6.1.0]nonane in 97% yield by reaction of Ph$_3$PbCCl$_3$ with cyclooctene. Consequently, the further preparative Ph$_3$PbCCl$_3$/ olefin reactions studied were carried out for 5 h at 125° in n-octane solution. These are summarized in Table 2. Included is an example in which the lead reagent was used to insert CCl$_2$ into the Si—H bond of triethylsilane. n-Octane is preferred as solvent over an aromatic hydrocarbon since the triphenyllead chloride produced in the transfer reaction is much less soluble in paraffins.

A useful alternative to thermal CCl$_2$ extrusion from phenyl(trichloromethyl)mercury is the sodium iodide-induced generation of this species from the mercury reagent [12]. This procedure also can be applied successfully to the preparation of gem-dichlorocyclopropanes from the lead compound, permitting the application of this reagent at a lower temperature (eqn. 3).

Similar studies were carried out with triphenyl(tribromomethyl)lead which was prepared by reaction of triphenyllead methoxide with bromoform [8]. This compound also was much less reactive than its mercury analog, as

$$Ph_3PbCCl_3 \quad + \quad NaI \quad + \quad \text{(cyclohexene)} \quad \xrightarrow[\text{85°, 15 h}]{\text{1,2-dimethoxyethane}} \tag{3}$$

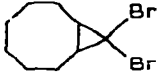$$Ph_3PbI \quad + \quad NaCl \quad + \quad \text{(7,7-dichlorobicyclo[4.1.0]heptane)}$$

(98%) (81%)
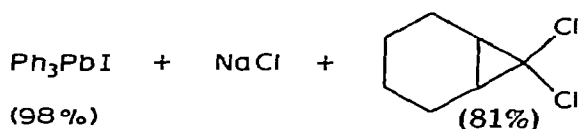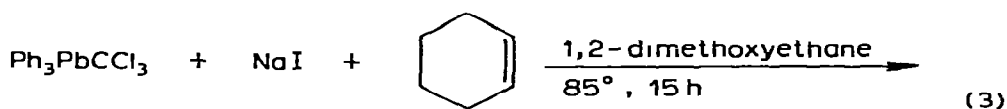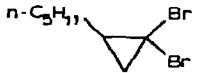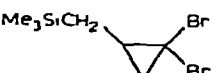
eqns. 4 and 5 demonstrate. Much faster CBr_2 transfer rates were observed at higher temperature and several synthetic reactions were carried out in refluxing n-octane at ca. 132° (Table 3).

$$PhHgCBr_3 \quad + \quad \text{(cyclohexene)} \quad \xrightarrow[\text{2 h}]{\text{reflux (∼ 86°)}} \quad PhHgBr \quad + \quad \text{(dibromobicycloheptane)} \tag{4}$$

(83%)

$$Ph_3PbCBr_3 \quad + \quad \text{(cyclohexene)} \quad \xrightarrow[\text{2 h}]{\text{reflux (∼86°)}} \quad Ph_3PbBr \quad + \quad \text{(dibromobicycloheptane)} \tag{5}$$

(26%)
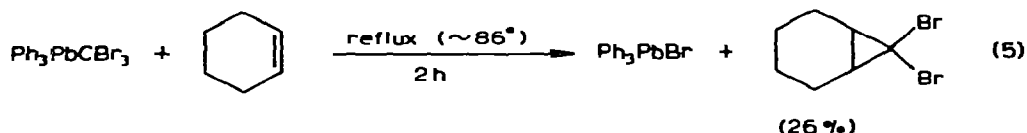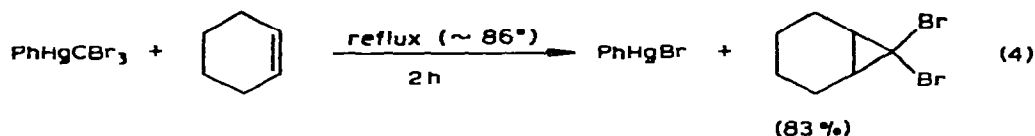
The finding that Ph_3PbCCl_3 and Ph_3PbCBr_3 are effective dihalocarbene transfer agents, albeit at higher temperature, led us to examine other halomethyllead compounds. Phenyl(α,α-dichlorobenzyl)mercury is a very reactive phenylchlorocarbene transfer agent, but its thermal and hydrolytic instability make its preparation most difficult [3]. In the hope that the organo-

TABLE 3

CBr_2 TRANSFER FROM Ph_3PbCBr_3 (5 h at 132° in n-octane solution)

Carbenophile	mmol	mmol Ph$_3$PbCBr$_3$	Product	Yield (%)	Yield(%) of Ph$_3$PbBr
(cyclooctene)	19.2	5.84	(dibromobicyclononane)	94	96 *
(cyclohexene)	18.7	5.73	(dibromobicycloheptane)	83	92
n-C$_5$H$_{11}$CH=CH$_2$	15.6	5.81	n-C$_5$H$_{11}$—(dibromocyclopropane)Br,Br	52	85
Me$_3$SiCH$_2$CH=CH$_2$	27	8.65	Me$_3$SiCH$_2$—(dibromocyclopropane)Br,Br	71	91
Et$_3$SiH	27.6	8.72	Et$_3$SiCBr$_2$H	44	85^a

^{a} Impure material.

lead analog, Ph_3PbCCl_2Ph, might have more attractive properties, we chose this compound as the next to study. Triphenyl(α,α-dichlorobenzyl)lead was prepared by reaction of triphenylleadlithium with benzotrichloride in THF at about $-80°$ in 57% yield. This compound proved to be much more thermally stable than its phenylmercury counterpart and was hydrolytically stable. It did transfer PhCCl to carbenophiles at about 115°, but product yields were very low, very likely in large part because of product instability at these temperatures. (The thermal instability of 7-chloro-7-phenylnorcarane has been noted specifically [13].) A somewhat more satisfactory reaction was that with triethylsilane (eqn. 6), but the product yield still was low. The known [6]

$$Ph_3PbCCl_2Ph + Et_3SiH \xrightarrow[\text{octane}]{115°, 40 h} Ph_3PbCl + Et_3SiCHClPh \qquad (6)$$

$$(77\%) \qquad (32\%)$$
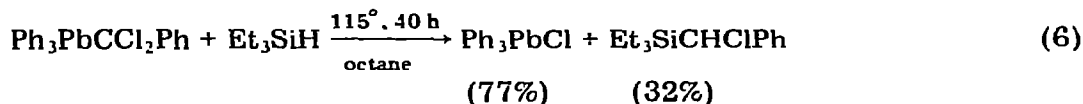
triphenyl(dichloromethyl)lead also was prepared and tested as a CHCl transfer agent. Like $PhHgCHCl_2$ [14], it did react slowly with an olefin at higher temperature to give a monochlorocyclopropane (eqn. 7), but offered no ad-

$$Ph_3PbCHCl_2 + \qquad \xrightarrow[80h]{145-148°} \qquad + \qquad + Ph_3PbCl \qquad (7)$$

$$(66\%) \qquad (18\%) \qquad (98\%)$$
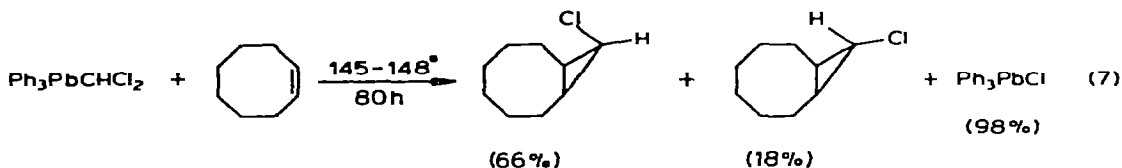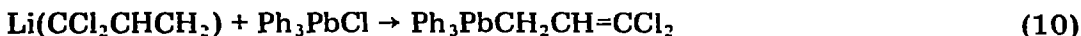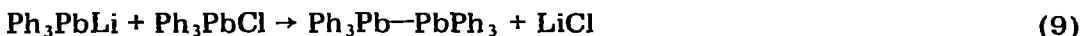
vantage over the mercury reagent. An organomercury reagent for CHF generation was not available, hence triphenyl(chlorofluoromethyl)lead was prepared by reaction of triphenylleadlithium with dichlorofluoromethane in THF at $-55°$ in 87% yield. However, in two attempted CHF transfer reactions, with cyclooctene and allyltrimethylsilane, a 24 h heating period at 155° gave lead metal but apparently no triphenyllead chloride.

Finally, other studies in these laboratories required a source of vinylchlorocarbene, $CH_2=CHCCl$. An organomercurial of type $RHgCCl_2CH=CH_2$ could not be prepared, and the possibility of a triphenyllead reagent was investigated. 3,3,3-Trichloropropene is easily prepared from commercially avilable $CCl_3CH_2CH_2Cl$ and its reaction with triphenylleadlithium should, in principle, give the desired $Ph_3PbCCl_2CH=CH_2$, in analogy with the other Ph_3PbLi—polyhalide reactions. However, such was not the case. The products of this reaction, carried out by adding a solution of Ph_3PbLi in THF to $CCl_3CH=CH_2$ at $-60°$, were the isomeric $Ph_3PbCH_2CH=CCl_2$ (28%) and hexaphenyldilead (60%). This suggests the reaction course as shown by eqns. 8-10. It may be noted that gem-dichloroallyllithium, the product of reaction

$$Ph_3PbLi + CCl_3CH=CH_2 \rightarrow Ph_3PbCl + Li(CCl_2CHCH_2) \qquad (8)$$

$$Ph_3PbLi + Ph_3PbCl \rightarrow Ph_3Pb—PbPh_3 + LiCl \qquad (9)$$

$$Li(CCl_2CHCH_2) + Ph_3PbCl \rightarrow Ph_3PbCH_2CH=CCl_2 \qquad (10)$$

8, reacts with heavy metal halides in this manner [15]. The organolead product, while not a $CH_2=CHCCl$ source (its pyrolysis gave radical-derived $CCl_2=CHCH_2-$

$CH_2CH=CCl_2$ as major product), was found to be an excellent precursor for the preparation of *gem*-dichloroallyllithium [15-16] and its practical utility was decisively enhanced by the development of a much better synthesis based on the reaction of triphenylleadmagnesium chloride with 1,1,3-trichloropropene [15].

The formation of $Ph_3PbCH_2CH=CCl_2$ rather than $Ph_3PbCCl_2CH=CH_2$ in the $Ph_3PbLi/CCl_3CH=CH_2$ reaction may be of broader significance. A direct coupling mechanism has been assumed to be operative in other Ph_3PbM (M = Li and Na)/ polyhalomethane reactions, i.e., nucleophilic attack by the triphenyllead anion at carbon [5-7]. In view of the reluctance of polyhalomethanes, especially the carbon tetrahalides, to undergo nucleophilic attack at carbon, more likely alternate possibilities may be discussed. One involves a sequence of the type shown in eqns. 8 and 10. In the case of carbon tetrachloride, this would involve initial formation of $LiCCl_3$ and Ph_3PbCl followed by subsequent rapid reaction of these before they can diffuse apart and before triphenyllead chloride can react with triphenylleadlithium to any great extent as in eqn. 9, i.e., a solvent cage process. The other possibility involves an electron transfer mechanism (eqn. 11) of a type which is not unknown in organolithium chemistry. Again, an efficient cage reaction would be required*.

$$Ph_3\overset{-}{Pb}\overset{+}{Li} \;+\; CCl_4 \;\longrightarrow\; Ph_3Pb\cdot \;+\; Li^+\left[CCl_4\right]^{\overset{-}{\cdot}}$$

$$\longrightarrow \cdot CCl_3 \;+\; LiCl$$
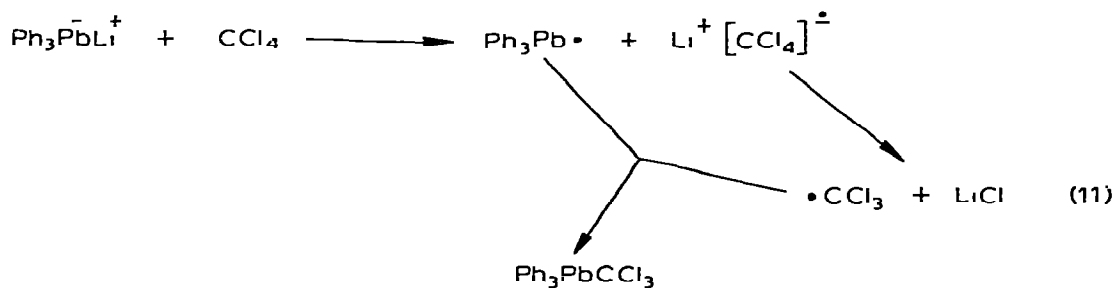
$$Ph_3PbCCl_3 \tag{11}$$

In conclusion, we note that Warner and Noltes [10] considered bis(triphenyllead)dichloromethane as a possible reagent for the generation of a lead-substituted carbene, Ph_3PbCCl, but found no evidence for extrusion of this species when the organolead compound was heated in refluxing xylene solution.

From the results of this work we must conclude that triphenyl(polyhalomethyl)lead compounds are not particularly useful carbene sources, their divalent carbon transfer reactions requiring conditions far more extreme than those which suffice for carbene extrusion from analogous phenyl(polyhalomethyl)mercury compounds. Two factors may be considered to be responsible for this finding: (1) the greater stability of a lead—carbon bond, compared with the analogous mercury—carbon bond (about 7 kcal/mol difference in the C(alkyl)—metal bonds [17]), and (2) the greater steric hindrance toward intramolecular nucleophilic attack by halogen at lead due to the presence of three bulky phenyl substituents on lead (cf. I), compared with the analogous process with a phenyl(polyhalomethyl)mercury compound.

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* A similar multiplicity of possible mechanisms of R_3SnNa reactions with organic halides has been noted [23].
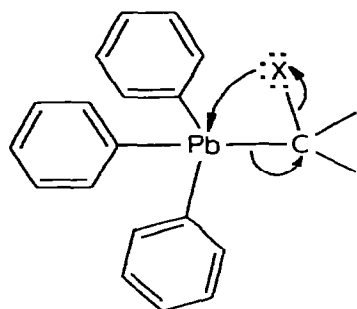
(I)

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All solvents were rigorously dried. Infrared spectra were recorded using a Perkin—Elmer 457A grating infrared spectrophotometer, ¹H NMR spectra using a Varian Associates T60 spectrometer. Proton chemical shifts are reported in δ units using tetramethylsilane as internal standard. Gas chromatography was employed to analyze product mixtures, to determine product yields and to isolate samples of products. The internal standard method was used in yield determinations.

Preparation of triphenyllead chloride

The following procedure was used to prepare the large amounts of pure triphenyllead chloride required in this work.

(a) Preparation of allyltriphenyllead. The Grignard reagent prepared from 1.7 mol of magnesium turnings and 1.8 mol of bromobenzene in 2.5 pints of dry THF in a Morton flask was cooled to about 0° and 139 g (0.5 mol) of powdered PbCl₂ was added within 30 sec with vigorous stirring. The solution became bright yellow and later yellow-green. The mixture was stirred at room temperature overnight under nitrogen. During this time the lead(II) chloride dissolved completely and an olive green solution of Ph₃PbMgBr was formed Subsequently 72.5 g (0.6 mol) of allyl bromide (freshly distilled, b.p. 70.5-71°) was added at 0-10° over 20 min. The olive green color was discharged. The cold reaction mixture was hydrolyzed with saturated NH₄Cl solution to the "lump point", 400 ml of THF was added and the organic layer was decanted. The salts were washed with THF and the washings added to the organic layer. The organic phase was evaporated and the residue was dissolved in 1000 ml of dichloromethane. This solution was dried over MgSO₄ and evaporated to give 197 g of crude product. This solid was recrystallized (3 crops) from 1000 ml of hexane, removing a small amount of hexaphenyldilead contaminant and giving 173 g (72%) of allyltriphenyllead, m.p. 74.5-75° (lit. [18] m.p. 76-77°).
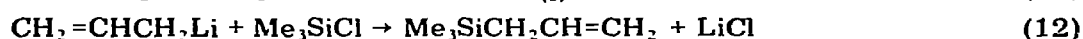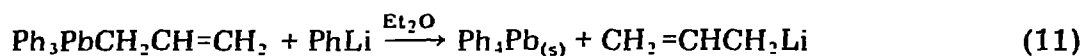
(b) HCl cleavage of allyltriphenyllead. A 5 liter three-necked flask equipped

with a mechanical stirrer, a reflux condenser topped with a nitrogen inlet and an addition funnel was charged with 290 g (0.61 mol) of allyltriphenyllead and 3 liters of denatured alcohol. This mixture was warmed to reflux and 55.5 ml of concentrated hydrochloric acid in 100 ml of ethanol was added during 30 min. The reaction mixture was heated for 1 h at reflux upon completion of the addition, then was cooled to room temperature and filtered to give 250.4 g (88%) of triphenyllead chloride, m.p. 207-208°. Recrystallization from hot ethanol gave long white needles, m.p. 207-208°.

In our hands, this procedure gave much better results than HCl cleavage of tetraphenyllead.

The cleavage of allyltriphenyllead in alcohol solution with 48% hydrobromic acid, at reflux for 20 min, using essentially the same procedure gave triphenyllead bromide, m.p. 165-166°, in 94% yield.

Preparation of allyltrimethylsilane. The allyltrimethylsilane used in this study was prepared by the route shown in eqns. 11 and 12. A procedure identical to that reported for generation of allyllithium from allyltriphenyltin [19]

$$Ph_3PbCH_2CH=CH_2 + PhLi \xrightarrow{Et_2O} Ph_4Pb_{(s)} + CH_2=CHCH_2Li \qquad (11)$$

$$CH_2=CHCH_2Li + Me_3SiCl \rightarrow Me_3SiCH_2CH=CH_2 + LiCl \qquad (12)$$

was used and gave allyltrimethylsilane in 96% yield.

Preparation of triphenyl(polyhalomethyl)lead compounds

(a) Triphenyl(trichloromethyl)lead. A one-liter, flame-dried and nitrogen-flushed single-necked flask, fitted with a Claisen adapter, no-air stopper and reflux condenser topped with a nitrogen inlet, and equipped with a magnetic stirring unit, was charged with 47.0 g (99.3 mmol) of Ph_3PbCl, 37.0 g (200 mmol) of sodium trichloroacetate (prepared from trichloroacetic acid and sodium methoxide in methanol) and 400 ml of 1,2-dimethoxyethane (DME) which had been distilled from sodium benzophenone ketyl. The reaction mixture was stirred and warmed to reflux, initiating a gentle evolution of carbon dioxide. After 2 h of heating, the reaction mixture was cooled to room temperature, poured into 600 ml of water and extracted with 900 ml of chloroform. The organic layer was washed with two 1000 ml portions of water, dried and evaporated at reduced pressure to leave 56.5 g of crude yellow solid contaminated with Ph_3PbCl. This material was dissolved in 1000 ml of hot 3/1 hexane/chloroform, treated with decolorizing charcoal and filtered through a 2″ bed of silicic acid. A second such filtration produced a filtrate which was free of triphenyllead chloride (by TLC). Concentration of the filtrate gave, in 3 crops, 41.4 g (75%) of pure Ph_3PbCCl_3, dense, colorless prisms, m.p. 176-177°, with violent decomposition at 185° (lit. [5] m.p. 172-173°). (Found: C, 40.93; H, 2.76; Cl, 18.86. C_{19}H_{15}Cl_3Pb calcd.: C, 40.98; H, 2.71; Cl, 19.10%.)

(b) Triphenyl(α,α-dichlorobenzyl)lead. A 500 ml three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube was charged with 72.0 g (82 mmol) of hexaphenyldilead and 250 ml of dry THF and cooled to 0°. Finely chopped lithium wire (1.23 g, 0.176 mol) was added and the mixture was stirred for 2 days, until all of the lithium had reacted. Another one-liter, three-necked flask was charged with 34.0 g (0.174 mol) of PhCCl_3 and

300 ml of dry THF and cooled to $-90°$. The Ph_3PbLi solution was added to this solution by syringe during a 10 min period while the internal temperature was maintained between -85 and $-70°$. After the reaction mixture had been stirred at $-80°$ for 90 min, it was allowed to warm to room temperature and then evaporated at reduced pressure. The residue was caused to solidify by adding hexane (100 ml) and evaporating again. The residue was extracted with 500 and 100 ml portions of benzene. The extracts were evaporated and the solid which remained was dissolved in hot 4/1 hexane/benzene, treated with charcoal and the solution was filtered and crystallized in the freezer. The crystalline solid obtained, 55.5 g (57%), had m.p. 92-94° (dec). Two more recrystallizations from hexane did not raise the melting point. (Found: C, 50.48; H, 3.48. $C_{25}H_{20}Cl_2Pb$ calcd.: C, 50.17; H, 3.37%.) IR (KBr): 3050m, 3030(sh), 3000w, 2975w, 2570w, 1960w, 1940w, 1885w, 1865w, 1810w, 1625w, 1560s, 1465m, 1425s, 1330m, 1302m, 1262w, 1188m, 1160w, 1062s, 1015vs, 995vs, 908w, 850w, 722vs, 694vs, 436s cm^{-1}.

(c) Triphenyl(chlorofluoromethyl)lead. Triphenylleadlithium was prepared from 63.5 g (0.134 mol) of triphenyllead chloride and 2.1 g (0.303 mol) of lithium in 450 ml of dry THF [20]. A two-liter three-necked Morton (creased) flask equipped with a mechanical stirrer, a pentane thermometer, an addition funnel and a nitrogen inlet was charged with 100 ml of $CHFCl_2$ (Matheson) and 1000 ml of dry THF and cooled to $-55°$. The triphenyllead-lithium solution then was added over a period of 1 h while the temperature was maintained around $-55°$. The reaction mixture was stirred at $-50°$ for another hour, warmed to room temperature and hydrolyzed with saturated NH_4Cl solution. The organic layer was evaporated and the residue extracted with chloroform. The dried extracts were evaporated to give 63.1 g of white, crystalline solid. This was dissolved in 800 ml of 4/1 hexane/dichloromethane, filtered through a pad of silicic acid and the filtrate was concentrated to give 58.9 g (81%) of $Ph_3PbCHClF$, m.p. 107-109°. (Found: C, 45.11; H, 3.38. $C_{19}H_{16}ClFPb$ calcd.: C, 45.10; H, 3.19%.) ^{19}F NMR (at 56.446 MHz, in $CDCl_3$): doublet 15.2 ppm downfield from C_6F_6, $J(^1H-^{19}F)$ 44.5 Hz, $J(^{207}Pb-^{19}F)$ 407Hz. The ^1H NMR spectrum (at 60 MHz in $CDCl_3$) showed one line of the expected doublet for the CHFCl proton at δ 6.93 ppm. The other line was obscured by the $(C_6H_5)_3Pb$ multiplet centered at δ 7.5 ppm. The expected ^{207}Pb satellites were observed upfield of the 6.93 ppm signal with a separation of 45 Hz.

Reaction of triphenylleadlithium with 3,3,3-trichloropropene

Triphenylleadlithium was prepared as above by reaction of 0.13 mol of lithium wire with 44 mmol of triphenyllead chloride in THF. The reaction mixture was centrifuged and the supernatant solution was decanted for further use (all operations under nitrogen). This Ph_3PbLi solution was added dropwise with stirring to a solution of 8.50 g (58.5 mmol) of 3,3,3-trichloropropene [21] in 300 ml of THF at $-60°$ and the reaction mixture was stirred at $-60°$ for 30 min. Subsequently, it was warmed to 0°, evaporated at reduced pressure and extracted with chloroform. The dried chloroform extracts were evaporated, the residue was taken up in 1000 ml of 7/3 hexane/chloroform and this solution was filtered through a 2″ pad of silicic acid. The filtrate was

evaporated. Crystallization of the residue from hexane gave 11.5 g (60%) of hexaphenyldilead, m.p. 158-160° dec. Evaporation of the mother liquor and crystallization of the residue from ethanol yielded 6.8 g (28%) of Ph_3PbCH_2-$CH=CCl_2$, m.p. 83-84.5°. (Found: C, 46.25; H, 3.05. $C_{21}H_{18}Cl_2Pb$ calcd.: C, 45.98; H, 3.31%.) NMR (in CCl_4): δ 2.75 (d, J(H—H) 9.0 Hz, $J(^{207}Pb—H)$ 79.0 Hz, $PbCH_2$), 6.20 (t, vinyl H) and 7.10-7.70 ppm (m, Ph).

Dichlorocarbene transfer reactions of triphenyl(trichloromethyl)lead

The reaction of Ph_3PbCCl_3 with cyclohexene is described to illustrate the procedure which was used.

A 50 ml, flame-dried, nitrogen-flushed three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube was charged with 3.81 g (6.85 mmol) of the lead compound, 2.2 ml (21 mmol) of cyclohexene, 20 ml of n-octane (Aldrich, puriss) and 0.787 g of n-dodecane as internal standard. The reaction mixture was heated with stirring and became homogenous just before reflux (125°). Triphenyllead chloride began to precipitate after 30 min at reflux. After 2 h at reflux a GLC yield determination showed the presence of 7,7-dichloronorcarane in 81% yield. After 5 h the reaction mixture was cooled to room temperature and filtered to give 3.16 of triphenyllead chloride (98%), m.p. 208-210°. GLC analysis of the filtrate (25% SE-30 at 105°) showed that 7,7-dichloronorcarane had been formed in 98% yield. The product was identified by comparison of its IR spectrum and GLC retention time with that of an authentic sample.

9,9-Dichlorobicyclo[6.1.0]nonane, 1,1-dichloro-2-phenylcyclopropane, 1,1-dichloro-2-n-amylcyclopropane and triethyl(dichloromethyl)silane had been prepared in previous studies in these laboratories and authentic samples for comparison were available. Parham and Yong [22] have prepared the 1,1-dich-loro-2,3-di-n-propylcyclopropane isomers: *cis* isomer, n_D^{25} 1.4568, vs. our n_D^{25} 1.4561; *trans* isomer: n_D^{25} 1.4520 vs. our n_D^{25} 1.4518.

7,7-Dichloronorcarane also was prepared by the sodium iodide procedure. A 100 ml flask equipped as described above was charged with 6.73 g (12.1 mmol) of Ph_3PbCCl_3, 5.0 ml (50 mmol) of cyclohexene and 20 ml of dry DME. This solution was heated with stirring to reflux and then a solution of 2.27 g (15.1 mmol) of dry (24 h at 150° and 0.02 mm Hg) sodium iodide in 20 ml of DME added slowly with stirring. As the sodium iodide was added, a bright yellow color developed which soon was discharged and sodium chloride began precipitating immediately. The reaction mixture was heated and stirred at reflux for 15 h, cooled and filtered. The filtrate was trap-to-trap distilled (100°, 0.02 mm Hg) and the distillate analyzed by GLC (10% UC-W98, 120°). 7,7-Dichloro-norcarane was found to be present in 81% yield. The trap-to-trap distillation residue was dissolved in hot hexane and filtered through a 2" bed of silicic acid. Removal of solvent under reduced pressure gave 6.70 g (98%) of TLC-pure triphenyllead iodide, m.p. 142-143°; lit. [5] m.p. 143°.

Dibromocarbene transfer reactions of triphenyl(tribromomethyl)lead

Essentially the same procedure was used in carrying out reactions of Ph_3PbCBr_3 [8] with olefins and with triethylsilane (1/3 lead compound / substrate ratio) in n-octane (15 ml for 4 mmol of Ph_3PbCBr_3) at reflux for

5 h. Tetradecane was used as internal standard. All products were known compounds with the exception of 1,1-dibromo-2-n-amylcyclopropane, which was characterized: n_D^{25} 1.4972 (Found: C, 35.76; H, 5.25; Br, 58.93. C_8H_{14}-Br_2 calcd.: C, 35.58; H, 5.23; Br, 59.19%.) Triphenyllead bromide, m.p. 163-165°, was the other product of these reactions.

Reaction of triphenyl(α,α-dichlorobenzyl)lead with triethylsilane

The standard apparatus was charged with 5.59 g (9.34 mmol) of Ph_3-$PbCCl_2Ph$, 15 ml of triethylsilane (PCR Inc.) and 10 ml of dry n-octane. The reaction mixture was stirred and heated at reflux (115-116°) for 40 h. At this time TLC showed that all of the starting lead compound had been consumed. The cooled reaction mixture was filtered to remove triphenyllead chloride (3.42 g, 77%, m.p. 198-201°) and the filtrate was distilled to give 0.72 g (32%) of $Et_3SiCHClPh$, b.p. 62-65° (0.005 mmHg), the comparison of whose IR and NMR spectra with those of authentic material [3] proved its identity. Some impurities were present but were not removed.

Reaction of triphenyl(dichloromethyl)lead with cyclooctene

The standard apparatus was charged with 4.96 g (9.5 mmol) of Ph_3Pb-$CHCl_2$ and 20 ml of cyclooctene. The resulting mixture was stirred and heated under nitrogen for 80 h, until TLC showed that the starting lead reagent had been consumed. Hexane (15 ml) was added to ensure complete precipitation of triphenyllead chloride and the reaction mixture was filtered to give a 72.3% yield of this material. Trap-to-trap distillation of the filtrate in vacuo was followed by GLC analysis of the distillate. 9-Chlorobicyclo[6.1.0]nonane was obtained in 84% yield with an *anti/syn* ratio of 3.66. Authentic samples of both isomers were available [14] for spectral and GLC comparison. Work-up of the distillation pot residue gave another 1.14 g of triphenyllead chloride, for a total yield of 97.5%.

Acknowledgments

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