

PREPARATION AND CHARACTERIZATION OF SOME PLUMBACYCLOPENTANES

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Cyclic organolead compounds such as cyclopropyl¹ and cyclohexyl² plumbanes have been prepared. Work on the preparation of compounds with lead in the ring system has been very limited. An example of such a plumbacycloalkane is diethylplumbacyclohexane which was prepared in 1916 by Grüttner and Krause³ by reaction between diethyllead dichloride and pentamethylene 1,5-dimagnesium-bromide. Analogous methods were used with considerable success to prepare diethylplumbacyclopentane and diphenylplumbacyclopentane in these laboratories. In studying the preparation and derivatization of the plumbacyclopentanes, it was discovered that the cleavage reactions of these compounds do not always follow the course observed previously for the plumbacyclohexanes. Grüttner and Krause³ reported that in selective cleavage of diethylplumbacyclohexane with bromine at low temperatures, ring fission occurred to give diethyl(5-bromopentyl)lead bromide. We have found that treatment of diethylplumbacyclopentane with acetic acid or chloroacetic acid at room temperature results exclusively in the cleavage of one ethyl group instead of cleavage of the strained five-membered ring. Such selective cleavage of different alkyl groups from mixed lead alkyls has been observed before, wherein hydrogen chloride and propanoic acid cleaved different alkyl groups⁴.

Studying ethyl group *versus* ring cleavage in diethylplumbacyclopentane under varying conditions of acid strength (Table 1), the following results were obtained. One mole of gas was liberated from a mole of the plumbane by one mole or even a large excess of acetic acid. The stronger the acid, the faster was the reaction (trichloroacetic acid undergoing a violently exothermic reaction) and the less selective was the cleavage. Selectivity also decreased with increasing temperature.

In the acetic and chloroacetic acid reactions, the products which precipitated were identical with those obtained from reactions run in dilute ether solutions and these products were shown to be pure ethyltetramethylenelead acetate and chloroacetate.

Results of reactions of the five- and six-membered plumbacycloalkanes (Figure 1) show that complete degradation to inorganic salts occurs sometimes, that the five- and six-membered ring compounds under identical reaction conditions react differently with carboxylic acids and that these compounds show similar selective reactivity with bromine with important temperature effects established in the case of the plumbacyclopentane. The reactions of diethylplumbacyclohexane with acetic acid and with chloroacetic acid yielded lead (II) acetate and lead (II) chloroacetate, respectively. Titration of the plumbacyclopentane with a solution of bromine in carbon

TABLE I

CLEAVAGE STUDIES OF DIETHYLPLUMBACYCLOPENTANE BY GAS EVOLUTION

Mole compd.	Acid used	Mole acid	Gas vol. theoret. (ml)	Gas vol. actual (ml)	% of theory	Temp. (°C)
2.00	acetic	2.00	44.8	41.2	92	24
2.00	acetic	excess	44.8	39.0	87	24
2.00	chloroacetic	2.00	44.8	40.5	90.5	24
2.03	chloroacetic	2.00	44.8	33.1	74	above 35
2.00	dichloroacetic	2.00	44.8	31.0	69	exothermic
1.99	trichloroacetic	2.00	44.4	28.6	64	violently exothermic

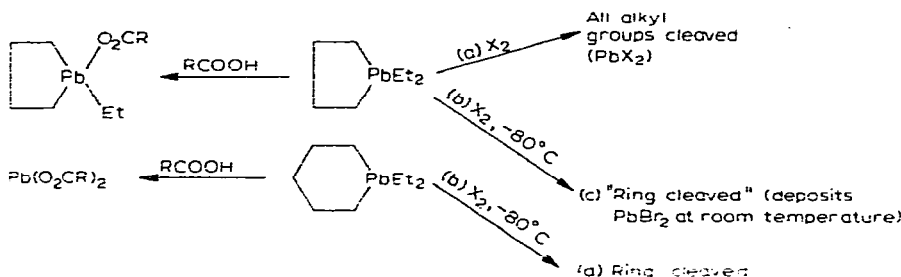


Fig. 1. R = CH₃ or ClCH₂. (a) Bromine in carbon tetrachloride or iodine in ether. (b) Bromine in ether. (c) IR indicates ring cleavage, product deposits PbBr₂ on warming to room temperature. (d) Grüttner and Krause³.

tetrachloride, until the decoloration of the bromine solution ceased, consumed 2.9 moles of bromine, close to the 3.0 moles needed for complete conversion to lead bromide. Treatment of diethylplumbacyclopentane with iodine in ether at 0° gave a clear solution from which lead iodide precipitated when it was warmed to room temperature. Similar treatment with equimolar amounts of freshly distilled bromine in ether at -80° yielded a pale yellow solution in which the presence of a trialkyllead salt was shown by the dithizone test⁵ and from which lead bromide precipitated when it was left to stand at room temperature. Lead bromide precipitated spontaneously from the yellow oil obtained on removal of the solvent. This oil showed a very strong peak for ethyl-to-lead structure at 1163 cm⁻¹ and absence of peaks at 1081, 909 and 725-735 cm⁻¹ in the IR indicating initial ring cleavage (see Table 2).

Diphenylplumbacyclopentane was found to require a slow molecular distillation for isolation and seemed to be less selective in its cleavage reactions, giving intractable, sticky solids on reactions with acetic and chloroacetic acids. Diphenylplumbacyclohexane has been synthesized by Bajér and Post, but this compound has been described as unstable and analysis or derivatization has not been reported⁶. Both diethyl- and diphenylplumbacyclopentane decolorize bromine in carbon tetrachloride with formation of precipitates and reduce alcoholic silver nitrate. With the latter reagent, the diphenyl compound gives transient yellow or green colors, perhaps

TABLE 2

TABULATION OF INFRARED DATA (PERKIN-ELMER MODEL 137 SPECTROPHOTOMETER)

Et_4Pb	$Et_2Pb(CH_2)_4$	$Et_2Pb(CH_2)_5$	$Ph_2Pb(CH_2)_4$	Ph_4Pb
3030 s	3030 s	3030 s	3030 s	3030 s
2941 s	2941 s	2941 s	2941 s	2941 s
			1600 m	1626 m
			1493 m	1563 m
1471 m	1471 m	1471 m	1471 m	1471 m
1429 w	1429 w	1429 w	1449 s	1429 s
1383 m	1383 m	1383 m		
		1361 m		
		1282 w		1316 w
		1227 w		1299 m
1227 w	1227 w	1227 w	1227 w	1250 w
	1191 w	1191 m	1191 m	1177 w
1163 s	1163 s	1163 s		
		1136 w		
	1081 w	1075 w	1087 m	1149 w
			1058 m	1058 m
1020 s	1020 s	1020 m	1020 m	1020 m
			1000 m	1000 m
962 m	962 m	971 m		971 w
			952 w	
939 w	939 w	935 w		
	909 w	909 m	909 w	909 w
	862 w	862 w	862 w	855 w
			735 m	
	727 s	725 s	725 s	725 s
		676 s	694 s	694 s

due to complex formation⁷ or intermediate formation of a phenyllead-silver compound⁸.

Much interest has developed over the past few years in the assignment of bands due to heterocyclic ring systems containing group IV A elements other than carbon. Oshesky and Bentley⁹ have reported tentative band assignments for the silacyclohexane ring vibrations at 909–920 and 475–495 cm^{-1} . A series of a weak and two strong bands occurring at 2650, 990–965 cm^{-1} and 910 cm^{-1} have been reported in a study of diphenylmetalacyclohexane compounds of the group IVA elements⁶. Although diethylplumbacyclohexane showed no appreciable peak at 2650 cm^{-1} , peaks were found at 971 cm^{-1} and 909 cm^{-1} consistent with the reports above^{6,9}. Both the five- and six-membered heterocyclic rings show peaks at 962–1000 cm^{-1} . These peaks may be characteristic of five-membered plumbacycloalkanes also. Unfortunately, simple alkyl and aryl lead compounds (see Table 2) sometimes also show peaks at these frequencies.

In the region 690–740 cm^{-1} , these plumbaheterocyclics all show an absorption band at 725–735 cm^{-1} . It is interesting that this absorption occurs in the region of the open chain vibration of the type $-(\text{CH}_2)_n-$ ($n=4$ or more), and that this absorption, does not occur in cyclohexane and cyclopentane. Diphenylplumbacyclopentane also shows two peaks for monosubstituted phenyl in the 690–740 cm^{-1} region.

In IR spectra of compounds containing ethyl groups, a peak occurred at 1383 cm^{-1} , ascribed to symmetrical vibration of the $\text{CH}_3\text{-C}$ group, and at 1163 cm^{-1} characteristic of ethyl-to-lead compounds¹⁰. The 1058 cm^{-1} peak assigned to the metal-to-phenyl absorption¹¹ was observed in the spectrum of diphenylplumbacyclopentane.

The 1471 cm^{-1} absorption assigned to C-H deformation was present along with incompletely resolved shoulders in all of the lead compounds studied. A peak at $1429\text{-}1449\text{ cm}^{-1}$ was observed to vary in intensity, appearing strong in the phenyl-substituted compounds.

Chromatograms (Table 3) on silica gel activated by heating at 100° for about $\frac{1}{2}$ hour were developed with hexane and spotted with 1% iodine in methanol followed by 0.2% 2',7'-dichlorofluorescein. This is, to the authors' knowledge, the first data obtained on thin-layer chromatography of plumbanes of varied structure, including tetraethyl-, tetravinyl-, tetracyclopropyl- and cyclic plumbanes.

TABLE 3

THIN-LAYER SEPARATION OF PLUMBANES

<i>Pb alkyl</i>	<i>Solvent front (cm)</i>	<i>Spot (cm)</i>	<i>R_f</i>
Et_4Pb	13.5	9.5	0.70
(cyclo- C_3H_5) ₄	13.5	6.4	0.475
Vi_4Pb	13.5	6.2	0.46
$\text{Et}_2\text{Pb}(\text{CH}_2)_4$	13.5	2.0	0.15
$\text{Ph}_2\text{Pb}(\text{CH}_2)_4$	13.5	2.5	0.185
<i>Silica Gel-Eastman Chromagram Kit (k301 R)</i>			
Et_4Pb	17.7	16.6	0.94
$\text{Et}_2\text{Pb}(\text{CH}_2)_4$	17.1	6.3	0.36
$\text{Et}_2\text{Pb}(\text{CH}_2)_5$	17.0	6.1	0.36

EXPERIMENTAL

Preparation of diethylplumbacyclopentane

Tetramethylenedimagnesium dibromide was prepared from 140 g (0.65 mole) of 1,4-dibromobutane and 34 g (1.4 g-atom) of magnesium metal in 500–600 ml of dry ether. The ether solution of the dihalide was added dropwise to the magnesium in a 3 liter flask equipped with dropping funnel, stirrer, and an efficient reflux condenser. After the reaction started, external cooling was applied, and the ether solution of the halide was added at a rate sufficient to maintain reflux. After addition of the halide was completed, the reaction mixture was stirred and refluxed for three hours to complete the reaction. At this point in the reaction two phases were present, a clear upper layer and a dark lower layer. Some additional ether (200–300 ml) was added before continuing. Diethyllead dichloride (168 g, 0.50 mole) was then added in small portions with vigorous stirring. The addition gave rise to an exothermic reaction, causing the ether to reflux. After completion of the addition (2–3 h), the mixture was refluxed with stirring for an additional hour. In one run, the addition of the diethyllead dichloride was made

at 0–5°, but no appreciable improvement of yield resulted. At a temperature of 0–5°, 500 ml of water was added dropwise with stirring. After completion of the hydrolysis, the ether layer was separated and the ether was distilled off through a two foot Vigreux column at atmospheric pressure. The ether distillate gave a white precipitate with alcoholic silver nitrate, indicating presence of a small amount of codistilled, unreacted halide and the absence of organolead compounds. The residue was transferred to a 250 ml flask, immersed up to its neck in boiling water, and flash distilled under vacuum (0.5–1 mm). The crude product (134 g, 0.418 mole) was collected in a flask cooled to –78°. This material was redistilled through a 3-foot Vigreux column with a reflux ratio of about ten to one. After removal of a small forerun, consisting mostly of tetraethyllead, 112 g (70%) of diethylplumbacyclopentane was collected in three constant boiling fractions, b.p. 31–32°/0.18 mm. The analyses of these fractions are reported below. Some decomposition occurred during the distillation. The middle fraction gave a refractive index of n_D^{29} 1.5452. (Found: C, 29.99, 30.09, 30.20; H, 5.37, 5.59, 5.53; mol. wt., 325. $C_8H_{18}Pb$ calcd.: C, 29.89; H, 5.64%; mol. wt., 321.) GLC indicated that this product contains up to 5–10% tetraethyllead. Separation by GLC was effected on a 5 ft., $\frac{3}{8}$ in. Carbowax 20 M on 60–80 mesh Chromosorb P as well as a 3 ft., $\frac{1}{4}$ in. Apiezon M on 45–60 mesh Chromosorb P column. This isolated product also gave analysis for carbon and hydrogen which agreed with theory.

Ethyltetramethylenelead acetate

To 3.21 g (0.01 mole) of diethylplumbacyclopentane dissolved in 50 ml anhydrous ether was added 0.61 g (0.01 mole) of glacial acetic acid. The flask was flushed with nitrogen, stoppered, and set aside for 48 h. The crystalline product was filtered off and washed several times with ether and hexane, yielding 3.1 g (88%) of material, m.p. 152–153° dec. (Found: C, 26.93; H, 4.89; mol. wt., 337. $C_8H_{16}O_2Pb$ calcd.: C, 27.34; H, 4.59%; mol. wt., 351.) Alternatively, equivalent amounts of diethylplumbacyclopentane and acetic acid were combined with a few crystals of silica gel as catalyst. After standing for two days, the entire mixture was converted to a crystalline mass. This product was washed with ether and found to be identical with that above. It sublimes completely at 110°/1 mm without change in melting point.

Ethyltetramethylenelead chloroacetate

To 1.60 g (0.005 mole) of diethylplumbacyclopentane dissolved in 20 ml of anhydrous ether was added 0.47 g (0.005 mole) of chloroacetic acid. The mixture was shaken until the acid dissolved. The flask was then flushed with nitrogen and set aside for 48 h. The crystalline mass which formed (1.3 g, 68%) was collected by filtration, washed with ether and hexane. The crude product (0.40 g) was suspended in 40 ml of ether and sufficient methanol was added to dissolve it. This solution was treated with 0.25 g of neutral Woelm, activated alumina, stirred for 30 min, filtered, evaporated to one-third its original volume, and cooled for one hour at –78°. The product which crystallized was dried at 80°/1 mm over P_2O_5 for 5 h. This procedure yielded 0.34 g of colorless needles, m.p. 132–133° dec. (Found: C, 24.90; H, 4.16; mol. wt., 353. $C_8H_{15}ClO_2Pb$ calcd.: C, 24.91; H, 3.92%; mol. wt., 385.)

Diphenylplumbacyclopentane

The product was prepared from 0.06 mole of tetramethylene dimagnesium-

bromide in 125 ml of dry tetrahydrofuran and 21.7 g (0.052 mole) of diphenyllead dichloride following the procedure used for diethylplumbacyclopentane, except that after hydrolysis the mixture was extracted 3 times with 70 ml portions of ether. This procedure yielded about 14 g of a yellow oil. Attempted distillation of this oil at 0.5 mm failed. No product distilled when the pot temperature was raised to 150°/0.5 mm, but decomposition was observed. The product was then transferred to a Hickman molecular still and slowly distilled at a temperature of 145–165°/0.5 mm. A colorless oil was obtained which solidified at 0° to yield 5.1 g (24.5%) of colorless crystals. (Found: C, 46.23; H, 4.47. $C_{16}H_{18}Pb$ calcd.: C, 46.03; H, 4.34%.)

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SUMMARY

Diethylplumbacyclopentane and diphenylplumbacyclopentane were prepared by the addition of tetramethylenedimagnesium dibromide to diethyllead dichloride and diphenyllead dichloride, respectively. Some cleavage and derivatization studies were carried out with diethylplumbacyclopentane. As distinguished from simple lead alkyls, diethylplumbacyclopentane and diethylplumbacyclohexane show a tendency in certain cleavage reactions to give complete degradation to inorganic lead salts. Infrared and thin-layer chromatographic work is presented.

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