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SYNTHESES OF ORGANOLEAD COMPOUNDS

VI. REACTION OF DINITROGEN TETROXIDE WITH ORGANOLEAD COMPOUNDS

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SUMMARY

The reactions of dinitrogen tetroxide with tetraethyllead and tetramethyllead have been studied in detail. Dinitrogen tetroxide reacts with the organolead compounds to give organolead nitrates and nitrosoalkanes. Spectral data for trialkyllead nitrates, dialkyllead nitrates, and complexes between dialkyllead dinitrates and the *cis* dimers of the corresponding nitrosoalkanes are reported.

The organometallic chemistry of several elements of the fourth main group has been of considerable interest in the last few years[1]. The interest in lead has included synthesis[2], reactions of the organometallic compounds, coordination chemistry of the organometallic cations and spectral properties of the organometallic compounds and cations. Reactions of Group IV organometallics with organic and inorganic acids, halogens, and gaseous inorganic oxides have been reported[1,3]. The coordination chemistry of the organometallic cations has been studied and considerable emphasis has been placed on the correlation of the proton magnetic resonance and infrared spectra with the geometry of the complexes[4,5].

In 1963 Hetnarski and Urbański[6] reported that dinitrogen tetroxide reacts with tetraethyllead or tetra-n-propyllead in ether to form tetraalkyldinitrosyllead dinitrate $\{[PbR_4(NO)_2]^{2+}[NO_3]_2^-\}$. Recently, Potts and Walker[7] reported that they could not reproduce the work of Hetnarski and Urbański. These authors stated that dinitrogen tetroxide reacts with tetraethyllead in both nitromethane and diethyl ether as solvents to give exclusively diethyllead dinitrate.

The reaction of dinitrogen tetroxide with tetraethyllead and tetramethyllead has now been studied in detail. We have found that some of the earlier conclusions are in error[6,7]. We have also obtained some interesting and unusual results which were not observed by the previous workers. The infrared and proton magnetic resonance spectra for several organolead nitrates synthesized in this work are presented.

DISCUSSION

As reported previously[6,7], tetraalkyllead compounds react readily with dinitrogen tetroxide in solution; and in fact, the reactions proceed in the expected manner to give organolead nitrates. The confusion which arose between the previous investigators was due to the by-product which is formed along with the organolead nitrates. We have isolated and identified two compounds from the reaction of dinitrogen tetroxide with tetramethyllead in chloroform or tetraethyllead in ether or chloroform solvent at low temperature. In each case, we isolated both the dialkyllead dinitrate and a compound which we have identified as a 1/1 complex between the dialkyllead dinitrate and the *cis* dimer of the corresponding nitrosoalkane. Formation of the isolated products is depicted by the following equations:

$$R_4Pb + 2\,N_2O_4 \rightarrow R_2Pb(NO_3)_2 + 2\,RNO \qquad (1)$$

$$2\,RNO \rightarrow (RNO)_2 \qquad (2)$$

$$R_2Pb(NO_3)_2 + (RNO)_2 \rightarrow [R_2Pb(RNO)_2][NO_3]_2 \qquad (3)$$

The reaction of dinitrogen tetroxide with tetramethyllead or tetraethyllead in chloroform solvent proceeded in a similar manner. When pentane is used as solvent, dinitrogen tetroxide reacts with tetramethyllead or tetraethyllead to give essentially quantitative yields of the mononitrates (*i.e.*, trimethyllead nitrate or triethyllead nitrate). Nitrosoalkanes are formed along with the trialkyllead nitrates in the reaction

$$R_4Pb + N_2O_4 \rightarrow R_3PbNO_3 + RNO \qquad (4)$$

$$RNO \rightarrow \tfrac{1}{2}(RNO)_2 \qquad (5)$$

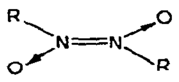
The trialkyllead cations, being relatively weak acids, do not enhance the formation of stable complexes between the nitrosoalkane dimers and the trialkyllead nitrates. In pentane the reaction stops after one alkyl group is cleaved by the dinitrogen tetroxide because the trialkyllead nitrates are insoluble and precipitate. The formation of nitrosoalkanes in the reaction of dinitrogen tetroxide with organolead compounds is certainly not unexpected since dinitrogen tetroxide reacts as if it exists in a dissociated form[8].

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (6)$$

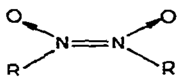
The reaction is believed to proceed by an electrophilic attack of the nitrosonium cation (NO^+) on the lead–carbon bond. The monomeric nitrosoalkanes which are formed in the reaction combine to give the dimeric products which are observed in the reaction mixture.

Hetnarski and Urbański[6] suggested an octahedral structure for their proposed tetraalkyldinitrosyllead dinitrate compounds. However, we now know that the compounds are actually 1/1 complexes between the dialkyllead dinitrates and the *cis* dimers of nitrosoalkanes. Thus, the structures of the complexes may be octahedral with the nitrate ions occupying sites, but tetra-coordinate complexes are also a possibility[4].

The above conclusions are consistent with the following data. In all the reactions between tetraorganolead compounds and dinitrogen tetroxide a blue-green colored solution was always produced. This color is characteristic of the nitrosomonomers which contain an unpaired electron[9]. In the reaction between tetramethyllead and dinitrogen tetroxide a solid was isolated whose mass, infrared, and ultraviolet spectra were identical to those reported for the *trans* dimer of nitrosomethane[9-12].



trans



cis

The dimer of nitrosomethane was isolated and identified as the *trans* structure by comparison of its infrared[11] (see Experimental) and ultraviolet spectra[12] with those reported in the literature. Recently the ultraviolet spectrum alone was used to identify the *cis* dimer of nitrosomethane[13]. In the complexes between the dialkyllead dinitrates and the nitrosoalkane dimers the infrared, ultraviolet and proton magnetic resonance spectra as well as elemental analysis were used for their characterization.

Infrared spectra

The infrared spectra of the methyllead nitrates and ethyllead nitrates are tabulated in Tables 1 and 2, respectively. Our spectra for triethyllead nitrate and diethyllead dinitrate (KBr disc) do not agree at all with those reported for these compounds by Potts and Walker[7] (Nujol and hydrocarbon mulls). With each of the organolead nitrates absorption bands are observed in the 468 to 500 cm^{-1} region which are associated with carbon–lead vibrations[3]; the two bands at 1382 (very strong) and 832 cm^{-1} are present in all the compounds and are due to the nitrate anion (the band at 1382 cm^{-1} also shields the deformation vibrations of the methyl and methylene groups). We found the spectra of the trialkyllead nitrates were identical regardless of whether the compounds were prepared by reaction of the tetraalkylead compounds with dinitrogen tetroxide or alcoholic silver nitrate.

TABLE 1

TABULATION OF INFRARED DATA FOR THE METHYLLEAD NITRATES
s = strong, m = medium, w = weak, vw = very weak, (sh) = shoulder, sp = sharp, dbl = doublet.

$(CH_3)_3PbNO_3$	$(CH_3)_2Pb(NO_3)_2$	$[(CH_3)_2Pb(CH_3NO)_2](NO_3)_2$
3022 vw	3030 w	3022 w, dbl
2925 w	2925 w	2926 w
2848 vw	2846 vw	2848 vw
2770 vw	2760 vw	2760 vw
2422 2400 } w, dbl	2422 2400 } w, dbl	2422 w (sh) 2400 w
2290 w		
1765 m, sp	1765 m, sp	1765 m, sp
1431 w (sh)	1431 w (sh)	1431 w (sh)
1382 vs	1380 vs	1382 vs
1160 vw, sp	1162 w	
1152 w, sp		
		1032 s
832 m, sp (sh)	832 m, sp	832 m, sp
825 m, sp (sh)	820 m (sh)	825 m, sp
780 796 } s, dbl		790 m
		740 m
		622 m
500 s, sp	498 w	500 m

The infrared spectrum obtained for the 1/1 complex of the *cis* dimer of nitrosoethane with diethyllead dinitrate is identical with that reported by Hetnarski and Urbański for their proposed tetraethyldinitrosyllead dinitrate. The bands near 2375, 1762, and 1134 cm^{-1} are not due to the nitrosyl group as proposed by the authors. The absorptions near 2375 and 1762 cm^{-1} are present in all the organolead nitrates reported in Tables 1 and 2, and the band near 1134 cm^{-1} is present in diethyllead dinitrate and triethyllead nitrate as well as the complex between diethyllead dinitrate and the dimeric *cis*-nitrosoethane.

TABLE 2

TABULATION OF INFRARED DATA FOR THE ETHYLLEAD NITRATES

Et_3PbNO_3	$Et_2Pb(NO_3)_2$	$[Et_2Pb(EtNO)_2](NO_3)_2$
2978 m	2980 m	2980 m
2945 m	2945 m	2945 m
2925 m	2920 m	2920 m
2865 m	2860 m	2850 m
2423 w }	2422 m }	2425 w }
2398 w } dbl	2395 m } dbl	2395 w } dbl
1761 m, sp	1765 m, sp	1765 m, sp
1453 w (sh)		
1430 w (sh)	1432 w (sh)	1432 w (sh)
1385 vs	1382 vs	1382 vs
		1300 w (sh)
1222 m		
1147 s	1147 s }	
	1135 s } dbl	1134 s
		1080 m
		1049 s
1020 m	1022 m	
		992 w
960 m	957 m	959 m
942 m	942 m (sh)	
	832 s, sp	834 s, sp }
824		825 s, sp } dbl
	711 m, sp	710 s
680 s	682 m	620 w
		500 m
648 m	472 w	467 w

The spectrum of the complex formed from dimethyllead dinitrate and the *cis* dimer of nitrosomethane contains a strong absorption at 1032 cm^{-1} which is not present in dimethyllead dinitrate. We propose that this band is associated with nitrogen–oxygen stretching in the complexed dimer. We believe that the strong absorption which occurs at 1387 cm^{-1} in the *cis* dimer of nitrosomethane[11] is shifted on complexation to a lower frequency. Similarly we propose that the bands at 1049 and 1080 cm^{-1} in the complex from diethyllead dinitrate and the *cis* dimer of nitrosoethane are due to nitrogen–oxygen stretching and have shifted from 1426 and 1370 cm^{-1} in the uncomplexed *cis* dimer of nitrosoethane[11].

TABLE 3

TABULATION OF PROTON MAGNETIC RESONANCE DATA FOR ALKYLLEAD NITRATES IN D_2O SOLUTION

Compound	*δ (ppm)*[a]						*J(^{207}Pb-H)(Hz)*		
	CH_3Pb	CH_3CPb	CH_2Pb	CH_3N	CH_3CN	CH_2N	CH_3Pb	CH_3CPb	CH_2Pb
$(CH_3)_3PbNO_3$	+2.18						77		
$(CH_3)_2Pb(NO_3)_2$	+1.17						136		
$[(CH_3)_2Pb(CH_3NO)_2][NO_3]_2$	+1.17			−0.50			136		
$(C_2H_5)_3PbNO_3$		+1.97[b]	+1.55[c]					180	40±5
$(C_2H_5)_2Pb(NO_3)_2$		+1.83	+0.46					318	72
$[(C_2H_5)_2Pb(C_2H_5NO)_2][NO_3]_2$		+1.87	+0.48		+2.23	−0.83		316	73

[a] Chemical shifts are relative to dioxane. [b] Center of a non-first order distorted triplet. [c] Approximate center of a non-first order distorted quartet.

Ultraviolet spectra

The spectrum of an aqueous solution of dimethyllead dinitrate shows a weak absorption at 300 nm which is characteristic of the nitrate anion. The spectrum of an aqueous solution of the complex between diethyllead dinitrate and the *cis* dimer of nitrosomethane shows an intense band at 265 nm (log ε 4.02) which is characteristic of the presence of the *cis* dimer of nitrosomethane[12]. In the complexes the nitrate band at 300 nm is obscured by the intense ligand absorption. Similarly the spectrum of an aqueous solution of diethyllead dinitrate shows a weak absorption at 300 nm and the complex exhibits an intense absorption at 266 nm (log ε 4.00). The band at 266 nm is characteristic of the *cis* dimer of nitrosoethane[12].

It is now apparent that the samples of diethyllead dinitrate used by Potts and Walker[7] in recording their spectra were contaminated with some of the complexed *cis* dimer of nitrosoethane. We found that spectrophotometric measurements at 266 and 265 nm offered a convenient quantitative method to check the purity of the complexes (ethyl and methyl respectively).

Proton magnetic resonance spectra

The chemical shifts and lead–proton coupling constants for aqueous (D_2O) solutions of the organolead nitrates and complexes are assembled in Table 3. It is interesting to observe that the chemical shifts and lead–proton coupling constants for the pure dialkyllead dinitrates and the complexes of the dialkyllead dinitrates with the nitrosoalkane dimers are the same (within experimental error). The coupling constant $J(^{207}Pb\text{–}CH_3)$ of 136 Hz in the dimethyllead derivatives indicates[14] the species in solution is $(CH_3)_2Pb^{2+}$. Thus, the *cis* dimer of nitrosomethane is probably replaced by water in aqueous solution. The same probably holds true for the diethyllead compounds.

$$[(CH_3)_2Pb(CH_3NO)_2][NO_3]_2 \xrightarrow{H_2O} [(CH_3)_2Pb]^{2+} + 2NO_3^- + (CH_3NO)_2 \qquad (7)$$

Table 4 contains the proton magnetic resonance data for diethyllead dinitrate and the complex between diethyllead dinitrate and the *cis* dimer of nitrosoethane in hexadeuterioacetone. The chemical shifts of the methyl and methylene protons are different for the complexed and uncomplexed diethyllead dinitrate. In the two compounds the lead coupling with the methylene protons differ by 10 Hz which lends further support to eqn. (7). With both of the complexes formed from the dialkyllead dinitrates and the corresponding nitrosoalkane dimers an integration of the PMR spectrum indicated a 1/1 ratio of the two materials.

TABLE 4

TABULATION OF NUCLEAR MAGNETIC RESONANCE DATA FOR ALKYLLEAD NITRATES IN HEXADEUTERIOACETONE SOLUTION

Compound	*δ (ppm)*[a]				*J(²⁰⁷Pb–H) (Hz)*	
	CH₃CPb	*CH₂Pb*	*CH₃CN*	*CH₂N*	*CH₂CPb*	*CH₂Pb*
$(C_2H_5)_2Pb(NO_3)_2$	−1.96	−3.43			316	80
$[(C_2H_5)_2Pb(C_2H_5NO)_2](NO_3)_2$	−1.85	−3.23	−4.85	−1.52	318	90

[a] Chemical shifts are relative to TMS.

EXPERIMENTAL

The reactions were carried out in the vacuum trap apparatus in which the dip leg was used as an inlet for the dinitrogen tetroxide. Dinitrogen tetroxide was obtained in lecture bottles from the Matheson Company and the organolead compounds were commercial grade (Ethyl Corporation) from our own plant sources.

The proton magnetic resonance spectra were recorded using a Varian Associates A-60 spectrometer. Infrared spectra were determined in KBr discs on a Perkin-Elmer Model 621 spectrophotometer; the ultraviolet spectra were recorded using a Perkin-Elmer Coleman EPS-3T spectrophotometer.

Note: We have found that all of the organolead nitrates and complexes prepared in these experiments are shock sensitive. Care should be used when handling these compounds.

A. Reaction of dinitrogen tetroxide with tetramethyllead

1. *Pentane as solvent.* Dinitrogen tetroxide was slowly bubbled into a stirred solution of 4 g of tetramethyllead in 50 ml of pentane. A white precipitate was formed immediately and the solution became blue-green in color. The addition of dinitrogen tetroxide was continued until brown vapors began escaping from the solution. Excess dinitrogen tetroxide was purged from the reaction vessel by flushing with purified nitrogen. The precipitate was collected by filtration and washed several times in the minimum amount of chloroform (approximately 30 ml) and filtered. Pentane was added to the chloroform solution to precipitate trimethyllead nitrate in almost quantitative yield. The material was identical with a sample prepared by reacting silver nitrate with tetramethyllead in ethanol[15] and had the following analysis. (Found: C, 11.25; H, 2.93; Pb, 65.30. $C_3H_9NO_3Pb$ calcd.: C, 11.46; H, 2.89; Pb, 65.89%.)

The chloroform/pentane solution from above was evaporated to dryness and a small amount of white solid material was obtained. The material was identified as the *trans* dimer of nitrosomethane from its characteristic mass[10], infrared[11] and ultraviolet spectra[12]. The infrared spectrum of the dimer showed the following absorptions: 3047 w, 1675 w, 1432 w, 1394 w (sh), 1384 m, 1283 s, 1133 s, 934 s, 535 s, 352 w (sh), and 332 m cm^{-1}. The mass spectrum showed mass numbers of 90, 75, 60, 45, 30 and 15. In deuterochloroform the proton magnetic resonance spectrum showed one absorption at δ -3.96 ppm (TMS as standard).

2. *Chloroform as solvent.* Dinitrogen tetroxide was bubbled into a stirred solution of 2 g of tetramethyllead in 50 ml of chloroform. The solution became blue-green in color and slowly warmed to reflux because of the exothermic reaction. Dinitrogen tetroxide was added until brown vapors began escaping from the solution. The white precipitate which was formed was collected by filtering and washing with chloroform. The precipitate was extracted twice with 25 ml and 15 ml of acetone. The acetone-insoluble material was dried under a vacuum and weighed (1.1 g of material). This material was identified as a 1/1 complex of the *cis* dimer of nitrosomethane and dimethyllead dinitrate. (Found: C, 10.45; H, 2.78; Pb, 46.0. $C_4H_{12}N_4O_8Pb$ calcd.: C, 10.65; H, 2.68; Pb, 45.9%.)

The acetone extracts from the above preparation were evaporated to yield 1.3 g of dimethyllead dinitrate. (Found: Pb, 56.9. $C_2H_6N_2O_6Pb$ calcd.: Pb, 57.3%.)

B. Reaction of dinitrogen tetroxide with tetraethyllead

1. *Pentane as solvent.* Dinitrogen tetroxide was slowly bubbled into a stirred solution of 3.3 g of tetraethyllead in 50 ml of pentane. A yellow oil was formed which collected on the bottom of the reaction vessel. The addition of nitrogen tetroxide was continued until brown vapors began escaping from the solution. Stirring was continued for 30 min and the oil slowly crystallized and a white precipitate was formed. The white solid was collected by filtration. This material was dissolved in the minimum amount of chloroform and filtered. The chloroform solution was then evaporated under reduced pressure and a viscous oil was obtained. The oil slowly crystallized while heating under vacuum with a water bath at 50–60°. The white crystalline solid was identified as triethyllead nitrate by comparison of its spectral properties with a sample of triethyllead nitrate prepared from reaction of tetraethyllead and silver nitrate. Its purity was checked by PMR and lead analysis. (Found: Pb, 57.6. $C_6H_{15}NO_3Pb$ calcd.: Pb, 58.1%.)

2. *Chloroform as solvent.* Dinitrogen tetroxide was bubbled into a solution of 3.3 g of tetraethyllead in 50 ml of chloroform. The solution turned blue-green in color and a white precipitate was formed. Dinitrogen tetroxide was added until the brown vapors no longer were absorbed. The white solids were collected by filtering and washed with chloroform. An almost quantitative yield of diethyllead dinitrate was obtained. The material was purified by recrystallization from acetone. (Found: C, 12.27; H, 2.65; Pb, 53.17. $C_4H_{10}N_2O_4Pb$ calcd.: C, 12.34; H, 2.59; Pb, 53.2%.)

A PMR spectrum of the crude material showed also that the product contained a small amount of a 1/1 complex of the *cis* dimer of nitrosoethane and diethyllead dinitrate. (See next reaction for proof of identity.)

3. *Diethyl ether as solvent.* Dinitrogen tetroxide was bubbled into a solution of 5 g of tetraethyllead in 50 ml of ether. The solution became blue-green at the beginning of the addition but the color slowly disappeared as the reaction progressed. When the solution became yellow because of dissolved dinitrogen tetroxide, the addition of the gas was stopped. The white precipitate which formed was washed with chloroform and ether. The precipitate was dissolved in acetone, filtered and concentrated and cooled by evaporation at reduced pressure. Several crops of crystals were obtained. The most soluble fraction was identified as diethyllead dinitrate and the least soluble fraction was identified as a pure sample of the 1/1 complex formed from diethyllead dinitrate and the *cis* dimer of nitrosoethane. (Found: C, 19.00; H, 3.97; Pb, 40.80. $C_8H_{20}N_4O_8Pb$ calcd.: C, 18.94; H, 3.97; Pb, 40.82%.)

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