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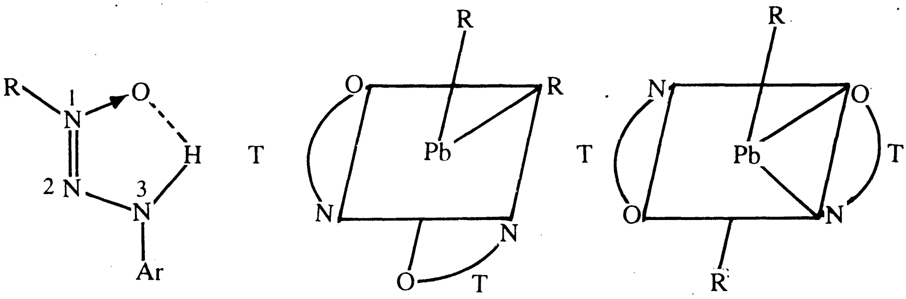
Organolead(IV) Complexes with O- and N-Donor Ligands

R. SHARMA*, GAJENDRA NATH PANDEY, S.N. SHARMA,
RAJEEV RANJAN AND PRAVEEN KUMAR
P.G. Department of Chemistry
R.D. & D.J. College, Munger-811 201, India

Organolead(IV) complexes of monobasic triazene-1-oxides have been synthesized and characterised by various physico-chemical techniques. The results have been found invariably to conform to R_2PbT_2. The disposition of two alkyl groups whether *cis*-or *trans*-were ascertained through the infra-red spectral bands of lead-carbon bond of the alkyl groups. It has been found that whereas the methyl group occupy *cis*-position while the bulkier alkyl groups occupy *trans*-positions.

INTRODUCTION

Tetravalent lead has been found to behave as oxidising agent. It is because of this that tetravalent lead complexes are dificult to synthesise. It is also believed that lead-carbon covalent bonds are stronger than lead-oxygen and lead-nitrogen bonds. But the smaller ionic radius of lead (IV), its greater polarisibility and steady decrease in M—C among group IV A elements make organo (IV) compounds susceptible to form Pb—O and Pb—N bonds with O— & N— donor groups by replacing two lead-carbon bonds.[1] Keeping these facts in view the present study reports the results of organolead(IV) derivatives with monobasic bidentate triazene-1-oxides (TH). The organolead(IV) derivatives were obtained after a long reflux of about 2 h, filteration, cooling and concentration pale yellow crystals of organolead(IV) derivatives of monobasic bidentate triazene-1-oxide formed. It has also been found that *para* substituted[3] N—C (Ar) triazene-1-oxides give diorganolead(IV) derivatives more readily than *ortho* and *meta* substituted



R = alkyl, aryl or substituted aryl
Ar = aryl or substituted aryl

N—C (Ar) triazene-1-oxides. The dialkyl group occupy *cis*- as well as *trans*-positions under different situations. (Fig 1–3).

Attempts were made to examine the increase in coordination of tetravalent lead beyond six with neutral monodentate ligands such as pyridine, pyridine-N-oxide, DMSO, amines etc. but in vain.

EXPERIMENTAL

All chemicals used were AnalaR grade unless otherwise specified. The triazene-1-oxides have been synthesises by following the published procedures, *i.e.* by coupling the benzene diazonium chloride or substituted benzene diazonium chloride with substituted methyl or phenyl hydroxyl amines at 0–5°C. Sodium acetate was used to control the pH. The crude products of triazene-1-oxides were recrystalised from aqueous ethanol or ethanol. The derivatives of lead alkyls with triazene-1-oxides are obtained by reacting with triazene-1-oxides in ethanolic medium on a water bath by refluxing between 110°–200°C for about 2 h. The crude products of dialkyl lead (IV) derivatives of triazene-1-oxides were recrystallised from acetone.

Synthesis of organo lead complexes

The general formula of lead (IV) compounds is R_{4-n} Pb X_n ($n = 0$ to 3), where R is alkyl or aryl and x is any of wide variety of atoms or groups (H, halogen, OR^1, NR^1_2, SR^1, $Mn(CO)_5$ etc). The elements may also form a heterocyclic ring, *e.g.*, $(R_2MO)^2_3$. The bonds to carbon are usually made via interaction of lithium, mercury or aluminium alkyls or RMgX and the group (IV) halides. The major commercial synthesis is by the interaction of a sodium lead alloy with CH_3Cl or C_2H_5Cl in a autoclave at 80°–100°C without solvent, for C_2H_5Cl but in toluene at higher temperature for CH_3Cl. The reaction is complicated and not fully understood, and only a quater of the lead appears in the desired product.

$$4\,NaPb + 4\,RCl \longrightarrow R_4Pb + 3\,Pb + 4\,NaCl$$

The required recycling of the lead is disadvantageous and electrolytic procedures have been developed. One process involves electrolytes of

$$4\,NaAlEt_4 + Pb \longrightarrow 4\,Na + PbEt_4 + 4\,AlEt_3$$

$$4\,Na + 2\,H_2 \longrightarrow 4\,NaH$$

$$4\,NaH + 4\,AlEt_4 + 2\,C_2H_4 \longrightarrow 4\,NaAlEt_4 + 2C_2H_6.$$

The alkyls are nonpolar, highly toxic liquids. The tetramethyl begins to decompose around 200°C and the tetraethyl around 130°C by free radical mechanism.

RESULTS AND DISCUSSION

The derivatives of organolead(IV) with variedly substituted triazene-1-oxides are placed in Table 1. The organolead(IV) complexes are all crystalline monomer and non-electrolytes. The derivatives are moisture sensitive and have to be stored either under vaccum or over silica gel. They have been also found to suffer dissociation on storage. The organo lead complexes were examined by several recrystallisation or simply loose adducts. It has been observed that the derivatives give consistent analytical data even after several recrystallisations from acetone.

TABLE-1

CHARACTERISATION TABLE OF ORGANOLEAD(IV) COMPLEXES OF TRIAZENE-1-OXIDES

Compounds	Substituents		% Analysis, Found (Calcd.)			
	R	Ar	Pb	N	C	H
$(CH_3)_2PbT_2$	CH_3	C_6H_5	38.13 (38.54)	15.61 (15.64)	35.38 (35.75)	3.89 (4.09)
$(CH_3)_2PbT_2$	C_6H_5	C_6H_5	31.01 (31.31)	12.32 (12.70)	47.09 (47.20)	4.01 (3.93)
$(CH_3)_2PbT_2$	CH_3	$C_6H_4CH_3(p)$	36.42 (36.63)	14.69 (14.86)	38.02 (38.23)	4.32 (4.60)
$(CH_3)_2PbT_2$	C_6H_5	$C_6H_4CH_3(p)$	30.10 (30.04)	12.06 (12.19)	45.13 (48.28)	4.02 (4.35)
$(C_2H_5)_2PbT_2$	CH_3	C_6H_5	36.39 (36.63)	14.73 (14.86)	38.10 (38.23)	4.35 (4.60)
$(C_2H_5)_2PbT_2$	C_6H_5	C_6H_5	30.12 (30.04)	12.08 (12.19)	45.09 (45.28)	4.02 (4.35)
$(C_2H_5)_2PbT_2$	CH_3	$C_6H_4CH_3(p)$	34.78 (34.90)	14.09 (14.16)	40.13 (40.47)	5.12 (5.05)
$(C_2H_5)_2PbT_2$	C_6H_5	$C_6H_4CH_3(p)$	28.62 (28.87)	11.43 (11.71)	50.14 (50.20)	4.35 (4.74)
$(CH_3)_2PbT_2$	CH_3	$C_6H_4NO_2(p)$	33.10 (33.03)	17.79 (17.86)	30.46 (30.62)	3.06 (3.18)
$(C_2H_5)_2PbT_2$	CH_3	$C_6H_4NO_2(p)$	31.52 (31.60)	17.12 (17.09)	32.87 (32.97)	3.49 (3.66)
$(CH_3)_2PbT_2$	CH_3	$C_6H_4CH_3(m)$	36.52 (36.63)	14.78 (14.86)	38.19 (38.23)	4.42 (4.60)
$(C_2H_5)_2PbT_2$	CH_3	$C_6H_4NO_2(m)$	31.58 (31.60)	17.10 (17.09)	32.89 (32.97)	3.51 (3.66)

R and Ar are substituents to $\overset{1}{N}$ and $\overset{3}{N}$ atoms of the triazene-1-oxides

The stoichiometrics of the organo lead derivatives of monobasic variedly substituted triazene-1-oxides were further confirmed by study of infra-red spectral studies[3–8]. The $\overset{3}{N}$—H stretch at 3200 cm^{-1} in the free ligand disappears on complexation and the $\overset{1}{N} \rightarrow O$ bond at 1310–1295 cm^{-1} is lowered considerably (Table 2) by about 60 cm^{-1}. The identification of entirely new ν(Pb—O) at 450–440 cm^{-1} and ν(Pb—N) at 525–510 cm^{-1} absent in free ligands further support that the ligands behave as bidentate ones and both the donor groups $\overset{3}{N}$ and $\overset{1}{N} \rightarrow O$ oxygen participated in bonding.[9] The position of the two alkyl groups whether *cis-* or *trans-* have also been ascertained by noting the Pb—C stretch in the range 725–715 cm^{-1}. In case of lead(IV) triazene-1-oxide derivatives the Pb—C stretch splits up into *asym* Pb—C band and *sym* Pb—C bands[10, 11] whereas in case of bulkier alkyl derivatives a single *asym* Pb—C stretch is observed[12]. On the basis of these above observations a *cis* configuration has been assigned to dimethyllead(IV) triazene-1-oxide derivatives while a *trans* configuration has been suggested for bulkier organolead(IV) derivatives of triazene-1-oxides.

TABLE-2

MAJOR IR BANDS (cm^{-1}) OF TH AND ITS DERIVATIVES WITH ORGANOLEAD COMPOUNDS

S. No.	Compounds	Substituents		^{3}N—H	^{1}N—O	Pb—O	Pb—N
		R	Ar				
1.	TH	CH_3	C_6H_5	3200	1290	—	—
2.	TH	C_6H_5	C_6H_5	3190	1285	—	—
3.	TH	CH_3	$C_6H_4NO_2(p)$	3190	1290	—	—
4.	TH	CH_3	$C_6H_4NO_2(p)$	3190	1295	—	—
5.	TH	CH_3	$C_6H_4NO_2(m)$	3200	1290	—	—
6.	TH	CH_3	$C_6H_4CH_2(m)$	3200	1295	—	—
7.		CH_3	C_6H_5	—	1215	440	505
8.		C_6H_5	C_6H_5	—	1210	445	500
9.		CH_3	C_6H_5	—	1210	440	495
10.		C_6H_5	C_6H_5	—	1210	440	500
11.	$(CH_3)_2PbT_2$	CH_3	$C_6H_4CH_3(p)$	—	1215	445	495
12.	$(C_2H_5)_2PbT_2$	C_6H_5	$C_6H_5CH_3(p)$	—	1215	440	500
13.	$(CH_3)Pb$	CH_3	$C_6H_4NO_2(p)$	—	1210	440	495
14.	$(CH_3)_2PbT_2$	CH_3	$C_6H_4CH_3(m)$	—	1215	445	500
15.	$(CH_3)_2PbT_2$	CH_3	$C_6H_4NO_2(m)$	—	1215	440	495

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