The Reaction of Olefines with Lead Tetracarboxylates

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(Received April 18, 1963)

Recently decarboxylative syntheses using lead tetraacetate have been reported by Corey and Casanova[1]. We wish to report on the reaction of olefines with lead tetracarboxylates. Lead tetra-monocarboxylates (I), as well as lead di-dicarboxylates (II), can be prepared by warming the corresponding acid with lead tetraacetate (Table I). Bachman and Wittmann[2] reported recently a similar procedure for the synthesis of lead tetra-monocarboxylates.

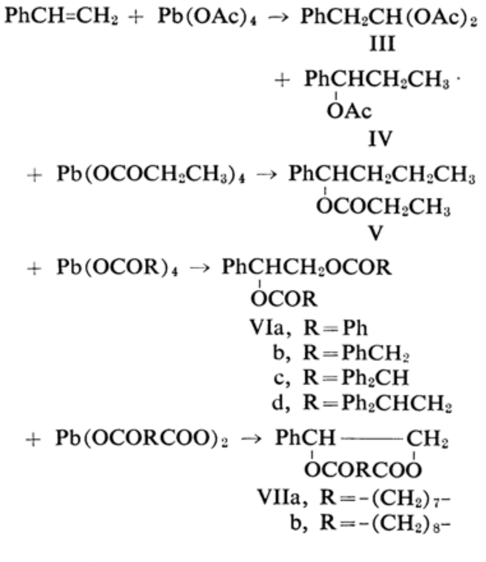
$$\underset{\text{I}}{Pb(OCOR)_4} \qquad \underset{\substack{\text{IIa, } R=-(CH_2)_7- \\ \text{b, } R=-(CH_2)_8-}}{Pb(OCORCOO)_2}$$

Lead diazelate (IIa) and lead disebacate (IIb) are colorless stable solids and have high melting points (m. p., 260°C and 233~236°C respectively).

It is well-known that the reaction of styrene with lead tetraacetate gives phenylacetaldehyde diacetate (a rearrangement product) (III) or 1-phenylpropanol acetate (an addition product of the methyl radical) (IV). The reaction of styrene with lead tetrapropionate gave 1-phenylbutanol propionate (an addition product of the ethyl radical) (V). On the other hand, styrene glycol dicarboxylates (VI) were obtained in the reactions with lead tetra-monocarboxylates prepared from higher carboxylic acids than propionic acid. In the case of lead di-dicarboxylates, the reaction proceeds slowly at 70°C in benzene and gives a macrocyclic compound (VII) in a 50% yield. Because the reaction of styrene is accompanied by some polymerization of styrene, the high yield of macrocyclic compound is striking in such a concentrated solution.

TABLE I. LEAD TETRA-MONOCARBOXYLATES (I)

R-	M. p., °C
CH_3CH_2-	133.0~133.5
$CH_3(CH_2)_{10}$-	95~97
$CH_3(CH_2)_{12}$-	104~105
$CH_3(CH_2)_{14}$-	104
$CH_3(CH_2)_{16}$-	103~104
Ph-	180
$PhCH_2$-	170
Ph_2CH-	175~180
Ph_2CHCH_2-	109~113



$$PhCH{=}CH_2 + Pb(OAc)_4 \rightarrow \underset{\text{III}}{PhCH_2CH(OAc)_2} + \underset{\text{IV}}{\underset{OAc}{PhCHCH_2CH_3}}$$

$$+ Pb(OCOCH_2CH_3)_4 \rightarrow \underset{\text{V}}{\underset{OCOCH_2CH_3}{PhCHCH_2CH_2CH_3}}$$

$$+ Pb(OCOR)_4 \rightarrow \underset{OCOR}{PhCHCH_2OCOR} \quad \begin{array}{l}\text{VIa, } R=Ph \\ \text{b, } R=PhCH_2 \\ \text{c, } R=Ph_2CH \\ \text{d, } R=Ph_2CHCH_2\end{array}$$

$$+ Pb(OCORCOO)_2 \rightarrow \underset{OCORCOO}{PhCH\text{———}CH_2} \quad \begin{array}{l}\text{VIIa, } R=-(CH_2)_7- \\ \text{b, } R=-(CH_2)_8-\end{array}$$

Ethyl vinyl ether, when reacted with lead tetra-monocarboxylate in benzene at room temperature, afforded 1-ethoxyethyleneglycol dicarboxylate (VIII) in a good yield. The hydrolysis of VIII gave glycolaldehyde (2, 4-dinitrophenylhydrazone; m. p., 159°C). No macrocyclic addition products were obtained in the reaction with lead di-dicarboxylate, in contrast to the case of styrene. The major product was IX namely, 1-ethoxyethyleneglycol dicaprylate, obtained from the reaction with lead diazelate. This means the occurrence of

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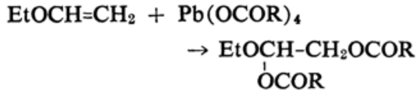
[1] E. J. Corey and J. Casanova, *J. Am. Chem. Soc.*, **85**, 165 (1963).

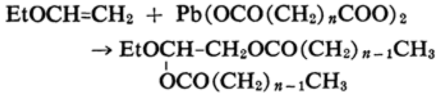
[2] G. B. Bachman and J. W. Wittmann, *J. Org. Chem.*, **28**, 65 (1963).

the decarboxylation of a dicarboxylic residue to give a monocarboxylic residue.



$$EtOCH{=}CH_2 + Pb(OCOR)_4 \rightarrow \underset{\displaystyle OCOR}{EtOCH}{-}CH_2OCOR$$

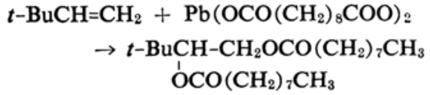
VIII



$$EtOCH{=}CH_2 + Pb(OCO(CH_2)_nCOO)_2 \rightarrow \underset{\displaystyle OCO(CH_2)_{n-1}CH_3}{EtOCH}{-}CH_2OCO(CH_2)_{n-1}CH_3$$

IX

When *t*-butylethylene was treated with two equivalents of lead di-sebacate in benzene at room temperature, a similar decarboxylated addition product, 3, 3-dimethylbutane-1, 2-diol dipelargonate (b. p., 100∼103°C/0.9 mmHg, m. p. 6∼8°C) was obtained in a 65% yield.



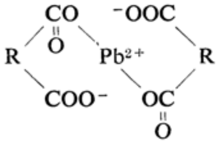
$$t\text{-}BuCH{=}CH_2 + Pb(OCO(CH_2)_8COO)_2 \rightarrow t\text{-}\underset{\displaystyle OCO(CH_2)_7CH_3}{BuCH}{-}CH_2OCO(CH_2)_7CH_3$$

The infrared spectra of lead tetracarboxylates show that lead tetra-monocarboxylates (I) absorb at 1417 and 1510 cm^{-1}, indicating the presence of a carboxylate anion group, but lead di-dicarboxylates (II) absorb at 1405, 1505 and 1710 cm^{-1}, the last band being assignable to the carbonyl in the carboxyl group.

It is of interest that II has a band of the carbonyl group in addition to those due to the carboxylate anion group. This suggests that there are two types of bonds between the lead and carbonyl groups in II. The one has mainly an ionic character, while the other has mainly a covalent character X.

TABLE II. INFRARED SPECTRA (1400∼1800 cm^{-1} REGION) OF I AND II IN KBr

		C=O group	COO$^-$ group	
	R=$CH_3(CH_2)_{12}$-	—	1417	1511
I	R=$CH_3(CH_2)_{14}$-	—	1417	1510
	R=$CH_3(CH_2)_{16}$-	—	1416	1508
	IIa	1718	1403	1500
	IIb	1703	1406	1510



X

The macrocyclic addition to styrene and the decarboxylated addition to ethyl vinyl ether or *t*-butylethylene can be understood from the above structure X of II. The details and mechanism of the reaction will be published elsewhere.

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