CHEMISTRY LETTERS, pp. 1037-1040, 1975. Published by the Chemical Society of Japan

THE PREPARATION OF TRIPHENYLLEAD AROMATIC DITHIOCARBOXYLATES, AND THEIR REACTIONS WITH METAL ALKOXIDES.

NEW SYNTHESIS OF THION ESTERS

Tomonori KATADA, Shinzi KATO, and Masateru MIZUTA
Department of Chemistry, Faculty of Engineering, Gifu University,
Kagamihara, Gifu 504

Some crystalline triphenyllead aromatic dithiocarboxylates [$ArCS_2PbPh_3$] have been prepared in good yields. Treatment of these esters with metal alkoxides gave thion esters in fair to good yields.

In the previous papers,[1),2)] we reported the preparation and reactions of some triphenylstannyl dithioates. The present paper describes the preparation of triphenyllead aromatic dithioates and new synthetic method of thion esters starting from these metal esters.

When an equimolar amount of piperidinium salt of aromatic dithioic acid (1) was treated with triphenyllead chloride, substituted triphenyllead dithiobenzoate (2) was obtained in good yields as shown in Table 1.

(1)

1 2

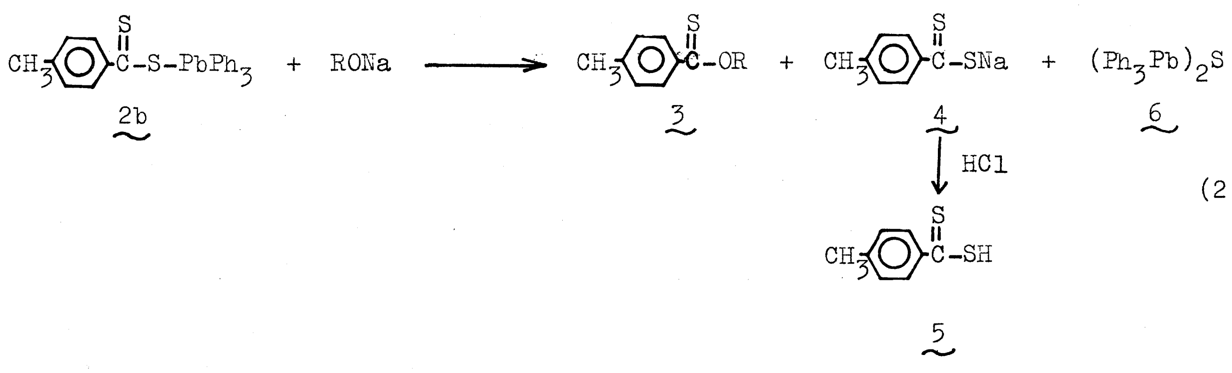
A typical experiment was carried out as follows. An equimolar mixture of piperidinium p-dithiotoluate (1.01 g, 4.0 mmol) and triphenyllead chloride (1.90 g, 4.0 mmol) in dry ether (40 ml) was stirred at room temperature for 1 hr. After removal of the precipitate by filtration, evaporation of the filtrate and recrystallization of the resulting residue from petroleum ether (bp $<40°C$) gave reddish pink microfine crystals of triphenyllead p-dithiotoluate (2b), mp 108-109°C, (2.09 g, 86 %). The structure of (2b) was established on the basis of the following spectral data as well as elemental analysis. Calcd. for $C_{26}H_{22}S_2Pb$: C, 51.57; H, 3.64; S, 10.58; Pb, 34.21 %. Found: C, 51.51; H, 3.64; S, 10.37; Pb, 34.37 %. UV(cyclohexane) λmax (ε) 318 nm(24,100), 520 nm(170). NMR($CDCl_3$): δ(ppm) 3.38(s,3H,CH_3-), 7.38(m,19H, aromatic). IR(KBr): νc=s 1218 cm^{-1}.

Table 1. Yields and Some Physical Properties of Triphenyllead Aromatic Dithiocarboxylates (2)

No	Compound (2)	Yield (%)*	Mp (°C)	νc=s (cm^{-1})
a	$C_6H_5CS_2PbPh_3$	80	98.5-100	1215 (s)
b	p-$CH_3C_6H_4CS_2PbPh_3$	86	108 -109	1218 (m)
c	o-$CH_3C_6H_4CS_2PbPh_3$	83	127 -128	1240 (w)
d	p-$CH_3OC_6H_4CS_2PbPh_3$	78	109 -110	1230 (m)
e	p-$ClC_6H_4CS_2PbPh_3$	73	123 -124	1208 (m)
f	m-$ClC_6H_4CS_2PbPh_3$	72	92.0-94.0	1200 (s)

* Isolated yield

The lead esters (2) obtained were quite stable at room temperature, and unreactive toward methanol even when refluxed for 24 hrs. However, when (2b) was stirred with sodium alkoxides in dry ether for 1 hr at room temperature, the corresponding thion esters were obtained in good yields, which were readily isolated by decantation from the reaction mixture containing sodium dithioate (4) (isolated as dithioic acid (5)) and bis(triphenyllead) sulfide (6).



(2)

The yields of these reaction products are summarized in Table 2. The products were identified by comparison of their spectral data with those of the authentic samples.

Table 2. Reactions of Lead Esters (2) with Metal Alkoxides*

Lead Ester	Alkoxide (ROM) R	M	Mol Ratio ROM/2	Temp	Time hr	Products (%)** 3	5	6
2b	CH_3	Na	1.2	rt	1	51	39	44
2b	CH_3	Na	3.0	reflux***	3	83	11	40
2b	C_2H_5	Na	1.2	rt	2	46	32	42
2e	CH_3	Na	1.2	rt	1	65	21	39
2e	C_2H_5	Na	1.2	rt	2	55	30	45
2e	n-C_3H_7	K	2.0	rt	5	30	60	35
2e	i-C_3H_7	K	2.0	rt	10	15	63	35
2e	$C_6H_5CH_2$	Na	1.2	rt	3	42	52	39

* Solvent, Et_2O

** Isolated yield (based on the lead ester 2 following formula (2))

3 (R=CH_3) Bp 90-91°C/1.5 mmHg (lit.[3] 170-173°C/150 mmHg). IR νc=s 1125 cm^{-1}. NMR($CDCl_3$) δ(ppm) 2.33(s,3H,CH_3-), 4.24(s,3H,CH_3O-), 7.14(d,2H), 8.10 8.10(d,2H).

6 Mp 139-140°C (lit.[4] 139-141°C)

*** Stirred for 1 hr at room temperature, then, refluxed for 3 hrs.

While thion esters have been prepared by a number of methods,[3],[5] this method is convenient to prepare the corresponding thion esters by a variety of metal alkoxides.

The mechanism of the reaction mentioned above is now under investigation. The fact that the thion esters were isolated over 50 % yield, except propyl group, suggests that the direct attack of the alkoxide ion on the thiocarbonyl carbon of lead ester (2) takes place in main.

REFERENCES

1) S.Kato, M.Mizuta, and Y.Ishii, J. Organometal. Chem., 55, 121 (1973).

2) S.Kato, T.Kato, T.Yamauchi, Y.Shibahashi, E.Kakuda, M.Mizuta, and Y.Ishii, J. Organometal. Chem., 76, 215 (1974).

3) Y.Sakurada, Mem. Coll. Sci. Eng. Kyoto, 9, 237 (1926).

4) W.T.Reichle, Inorg. Chem., 1, 650 (1962).

5) a) H.Eilingsfeld, M.Seefelder, and H.Weidinger, Chem. Ber., 96, 2671 (1963).

b) A.Ohno, T.Koizumi, and G.Tsuchihashi, Tetrahedron Lett., 2083 (1968).

c) M.Mori, Y.Ban, and T.Oishi, Int. J. Sulfur Chem., A, Volume 2, 79 (1972).

(Received July 17, 1975)