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THIOCYANOGEN CLEAVAGE OF SOME SYMMETRICAL TETRAARYL- AND HEXAARYLDI-TIN AND -LEAD COMPOUNDS

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Summary

Ar_4M and Ar_3MMAr_3 compounds (Ar = phenyl and *p*-tolyl, M = Sn, and Pb) were treated with freshly prepared thiocyanogen $(SCN)_2$ in anhydrous carbon tetrachloride under various conditions. Unlike the tetraarylleads, the corresponding tin compounds reacted only to a small extent. The hexaaryldimetals were quite reactive. The metal-containing reaction products have an iso-Ar_3M—NCS structure.

Introduction

Bullpitt and Kitching [1] recently reported the cleavage of carbon—tin bonds by thiocyanogen $(SCN)_2$ in some tetraorganotin compounds of the type Me_3SnR, where R is an allenic group, and demonstrated by NMR that the reactions were quantitative. It was pointed out that when R is less reactive (e.g., Me or $PhCH_2$) towards electrophilic reagents the reactions were slow and polymerisation of $(SCN)_2$ preceded cleavage. Other metal alkyls and aryls have also been reported to form organometallic thiocyanates (B, Cd and Bi) and to yield isothiocyanates (As and Sb) [2]. Cleavages of Pb—C, Pb—Pb and Sn—Sn bonds with $(SCN)_2$ have not so far been reported.

In this paper we describe the thiocyanogen cleavage of symmetrical tetraaryltin and tetraaryllead compounds containing moderately active groups, viz. Ar = phenyl or *p*-tolyl, and the metal—metal bond cleavage in the corresponding hexaaryldi-tins and -leads (Ar_3MMAr_3).

Apart from the interest in the relative reactivity of the Ar—Sn or Ar—Pb bonds, these reactions also provide a potentially useful route to aryl thiocyanates and to triaryltin and triaryllead isothiocyanates:

$$Ar_4M + (SCN)_2 \rightarrow Ar_3MNCS + ArSCN$$

$$Ar_3MMAr_3 + (SCN)_2 \rightarrow 2\ R_3MNCS$$

Results and discussion

The pseudo-halogen $(SCN)_2$ is a much weaker electrophile than normal halogens, e.g., chlorine or bromine. Thus $(SCN)_2$ did not react with symmetrical tetraaryltin compounds (in 1/1 ratio or in excess) at 0° and reaction was sluggish even at room temperature. After about 6 h stirring in the dark at room temperature only 10-15 % of Ar_3SnNCS compound was formed together with a corresponding amount of aryl thiocyanate, further stirring or warming favoured rapid polymerisation of $(SCN)_2$ precluding cleavage, and most of the tetraaryltin was recovered unchanged.

Electrophilic reagents normally cleave Ar—Pb bonds much more readily than Ar—Sn bonds [3]. Accordingly, tetraaryllead compounds were found to react smoothly at room temperature, even in the absence of a catalyst, with $(SCN)_2$ in carbon tetrachloride to give Ar_3PbNCS compound together with the corresponding ArSCN compound. Cleavage of a second aryl group was not observed even when the tetraarylleads were treated with an excess of $(SCN)_2$ or when Ar_3PbNCS compounds were treated with a further quantity of $(SCN)_2$.

By contrast, cleavages of tetraarylleads with chlorine and bromine are exothermic and must be conducted carefully to prevent uncontrolled decomposition, indeed this system is not recommended for the preparation of Ar_3PbX or Ar_2PbX_2 species [4]. However, this procedure has been applied to the exclusive preparation of the diphenyllead diiodide by the iodination of tetraphenyllead.

The ready cleavage of Sn—Sn or Pb—Pb bonds which are more prone to attack by electrophilic reagents than Sn—Ar [5] or Pb—Ar [6] bonds was demonstrated by the formation of Ar_3MNCS in high yields when the hexaaryldimetals, R_3MMR_3 were treated with $(SCN)_2$ in carbon tetrachloride.

Halogenation of hexaaryldilead compounds is not suitable for the preparation of Ar_3PbX due to simultaneous attack of the halogen on the Pb—Pb bond and the Pb—C bonds. However, in the reaction of $(SCN)_2$ with hexaaryldi-tin and -lead compounds the sole product is Ar_3MNCS. The cleavage of the M—Ar bond does not take place even in the presence of a large excess of $(SCN)_2$. Unlike common halogens, less active chlorinating agents, e.g. hypochlorous acid, yield triaryllead chloride in chloroform with hexaaryldilead [7]. Parallel reactions of selenium diselenocyanate $Se(SeCN)_2$ with tetra and hexaorgano-lead and -tin compounds have been reported to yield triorganolead and -tin selenocyanates but tetraaryltin reacted to a lesser extent [8].

It is to be expected that the presence of a small amount of $AlCl_3$ as catalyst in these reactions may increase the extent of cleavage, especially of aryltin compounds, and hence improve the yields of ArSCN as has been reported by Eaborn et al., for reactions involving several $ArMMe_3$ (M = Si,Sn) compounds with CNCl and CNBr [9], NOCl [10], ICl [11], $ArSO_2Cl$ [12] etc. However, as our current aim was (i) to compare the action of $(SCN)_2$ on Sn—Ar and Pb—Ar bonds (ii) to isolate and characterize the aryltin and aryllead moieties and, (iii) to study the number of M—Ar bonds cleaved, such $AlCl_3$-catalysed reactions were not carried out as this would have contaminated Ar_3MNCS products with arylmetal chlorides during hydrolysis of $AlCl_3$. Furthermore, the Ar_3SnNCS

species could hardly be expected to survive such drastic conditions.

In each of the above reactions, triarylmetal isothiocyanates (Ar_3M-NCS) were identified by comparison of their IR spectra and melting points with those previously reported, or with authentic samples. The formation of Ar_3MNCS in the present studies may be explained on the lines proposed by Bullpitt and Kitching [1] for Me_3SnNCS. We also note that organo-tin or -lead thiocyanates ($M-SCN$) have not hitherto been reported.

Experimental

Materials

Tetraphenyltin and tetra-*p*-tolyltin were synthesised by the Wurtz reaction of aryl chlorides and stannic chloride in the presence of sodium in benzene by previously reported methods [13]. Tetraphenyllead was a gift from the International Lead Zinc Research Organization.

Tetra-*p*-tolyllead was prepared from *p*-tolylmagnesium bromide and lead(II) chloride.

The hexaarylditins were prepared from the coupling of triaryltinlithiums with triaryltin chlorides, while the hexaaryldileads were synthesised from appropriate Grignard reagents and lead dichloride.

Fresh thiocyanogen, in approximately known concentrations, was generated in carbon tetrachloride in the reported manner [14] from $Pb(SCN)_2$ and bromine.

All the cleavages were carried out in the dark and generally at room temperature in order to retard the polymerisation of $(SCN)_2$.

Anhydrous CCl_4 was the solvent used throughout, and moisture was excluded wherever necessary.

Reactions of tetraaryltins and tetraarylleads with $(SCN)_2$

Two typical experiments are described. Further details are given in Table 1.

(i). A freshly prepared solution of thiocyanogen (0.58 g, 0.005 mol) in

TABLE 1

REACTIONS OF THIOCYANOGEN WITH TETRAARYL- AND HEXAARYLDI-TIN AND -LEAD COMPOUNDS

Ar	M	Reaction time (h)[a]	Ar_3MNCS	
			Yield(%)	M.p (°C)
Reactions of Ar_4M				
Ph	Sn	6(0°)	No reaction	
p-Tolyl	Sn	6	14	126[b]
p-Tolyl	Pb	4	65	215[c,d]
Reactions of Ar_3MMAr_3				
p-Tolyl	Sn	3	70	126
Ph	Pb	3	75	230
p-Tolyl	Pb	3	78	215

[a] Reaction at room temperature, except where noted otherwise. [b] Lit. m.p. 128° [15]. [c] Found: C, 50.3; H, 4 3; N, 2 4. $C_{22}H_{21}NPbS$ calcd.: C, 49.5; H, 3.9; N, 2.6%. [d] Also obtained *p*-tolyl isocyanate (70%), b.p. 238° (lit. [19] 240-245°).

CCl_4 (30 ml) was added with stirring to tetraphenyltin (2.13 g, 0.005 mol) in CCl_4 (50 ml) at room temperature. The reaction mixture was subsequently stirred for 6 h, and the yellowish-white solid, containing a little polymerised $(SCN)_2$, which separated was filtered, washed with CCl_4 and dried. After recrystallization from petroleum ether (b.p. 60-80°) the white solid was characterized as triphenyltin isothiocyanate (0.2 g, 9.4 %); [ν_{asym} (NCS) 2075 cm^{-1}, lit. [15] 2080 cm^{-1}]; m.p. 170° (lit. [16] 172-173°). The filtrate was refluxed (4h) in order to completely polymerise unreacted $(SCN)_2$ and then the CCl_4 solvent was replaced by benzene (20 ml) and the solution was again refluxed (1 h). The yellow solid (polymeric thiocyanogen) was filtered off and unreacted tetraphenyltin (1.65 g, 77 %) was crystallized from the filtrate by cooling. Removal of the solvent from the filtrate (after filtering Ph_4Sn) yielded a small amount of viscous material whose IR spectrum was identical to that of an authentic sample of PhSCN: ν_{asym} (SCN) 2160 cm^{-1} [15].

(ii). To a stirred solution of tetraphenyllead (4.00 g, 0.0077 mol) in CCl_4 (60 ml) was slowly added a freshly prepared solution of thiocyanogen (0.89 g, 0.0077 mol) in CCl_4 (40 ml) at room temperature over 1 h. The reaction was stirred for 3 h more and the solid which separated was filtered, washed with CCl_4 (3 X 5 ml) and dried. After recrystallization from ethanol it was characterized as triphenyllead isothiocyanate (2.4 g, 62%); m.p. 228° (lit. [17] 230°); [ν_{asym} (NCS) 2100 cm^{-1}, lit. [17] 2103 cm^{-1}]. The filtrate was freed from unreacted thiocyanogen (if any) as before and then distilled to yield phenyl thiocyanate (0.65 g, 62%); b.p. 226° (lit. [18] 232°); [ν_{asym}(SCN) 2162 cm^{-1}, lit. [1] 2165 cm^{-1}]; PMR: δ 7.50 ppm.

Reactions of hexaarylditins and hexaaryldileads with $(SCN)_2$

A freshly prepared solution of thiocyanogen (0.29 g, 0.0025 mol) in CCl_4 (20 ml) was slowly added to a solution of hexaphenylditin (1.80 g, 0.0025 mol) in CCl_4 (40 ml) at room temperature. The reaction mixture was stirred for 3 h and then worked up as above to give triphenyltin isothiocyanate (1.17 g, 65 %). Details of other preparations are given in Table 1.

Attempted reaction of Ar_3PbNCS with $(SCN)_2$

A freshly prepared solution of $(SCN)_2$ (0.29 g, 0.0025 mol) in CCl_4 (20 ml) was slowly added to Ph_3PbNCS (1.25 g, 0.0025 mol) in CCl_4 (30 ml) at room temperature. The reaction mixture was stirred for 3 h and then worked up as before. Ph_3PbNCS, m.p. 228°, was quantitatively recovered.

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References

1 M.L. Bullpitt and W. Kitching, J. Organometal Chem., 34 (1972) 321.
2 T. Wizemann, H. Muller, D. Seybold and K. Dehnicke, J. Organometal. Chem., 20 (1969) 211.
3 R.O.C. Norman and R. Taylor, Electrophilic Substitution in Benzenoid Compounds, Elsevier, Amsterdam, 1965, p. 235-237.
4 H. Shapiro and F.W. Frey, The Organic Compounds of Lead, Wiley, London 1968, p. 267-268.
5 R.C. Poller, The Chemistry of Organotin Compounds, Logos Press, London, 1970, p.145.
6 Ref. 4, p. 166-167
7 A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 2, Part II, Marcel Dekker, New York, 1972, p. 156.
8 E.E. Aynsley, N.N. Greenwood, G. Hunter and M.J. Sprague, J Chem. Soc. A, (1966) 1344.
9 E.H. Bartlett, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 46 (1972) 267.
10 E.H. Bartlett, C. Eaborn and D.R.M. Walton, J. Chem. Soc. C, (1970) 1717.
11 C. Eaborn, A.A. Najam and D.R.M. Walton, J. Chem. Soc. Perkin Trans. I, (1972) 2481.
12 S.N. Bhattacharya, C. Eaborn and D R.M Walton, J. Chem. Soc. C, (1969) 1367.
13 R.K. Ingham, S.D. Rosenberg and H. Gilman, Chem. Rev., 60 (1960) 465.
14 R. Adams (Ed.), Org. React., 3 (1947) 255
15 T.N Srivastava and S.N. Bhattacharya, J. Inorg. Nucl. Chem., 28 (1966) 2445.
16 T.N. Srivastava and S.K. Tandon, Ind. J. Appl. Chem., 26 (1963) 171.
17 H.J. Emeleus and P.R. Evans, J. Chem. Soc., (1964) 510.
18 E D. Hodgman, Handbook of Physics and Chemistry, Chemical Rubber Co., Cleveland, Ohio, 41st ed , 1960.
19 Beilsteins Handbuch der Organischen Chemie, Vol. VI, 1923, p. 422.