

Reactions of Tetraorgano Derivatives of Ge(IV), Sn(IV) & Pb(IV) with Cyanogen Bromide & Iodide

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The Ar_4M compounds ($Ar = \text{phenyl and } p\text{-tolyl}$; $M = \text{Ge and Sn}$) and Bu_3PhSn were found to react with cyanogen bromide and iodide in the presence of $AlCl_3$ to produce the corresponding arylhalides. Ar_4Pb compounds did not react with either of the reagents in the absence of $AlCl_3$ under various conditions.

CLEAVAGE of metal-carbon bonds in tetraorgano derivatives of group IV metals ($M = \text{Si, Ge, Sn and Pb}$) by electrophilic reagents have been extensively studied both from synthetic and mechanistic point of view¹. In recent years, several reports have appeared regarding the cleavage of group IV metal-aryl bonds with inter- and pseudo-halides, e.g. ICl , IBr (ref. 2, 3), $(SCN)_2$ (ref. 4, 5) and $Se(SCN)_2$ (ref. 6). These reactions are useful for functionalization of aromatic rings at predetermined positions¹ and for synthesizing R_3MX or R_2MX_2 derivatives in one-step^{2,6}.

Though the reactions involving inter-pseudohalides such as cyanogen halides XCN ($X = \text{Cl, Br, I}$), cyanogen azide (CNN_3), iodine azide (IN_3) and iodine cyanate ($INCO$) have been extensively studied for stereospecific addition to olefins⁷, reports regarding their action on compounds containing metal-carbon bonds are rare. Challenger *et al.*^{8,9} studied the interaction of Ph_3E compounds ($E = \text{P, As, Sb and Bi}$) with cyanogen halides and found that while ICN adds oxidatively to yield Ph_3EICN ($E = \text{P, As and Sb}$), it yields PhI with Ph_3Bi . The corresponding reactions of $CNCl$ and $CNBr$ with Ph_3Bi produce $PhCN$. Recently, Eaborn *et al.*¹⁰ investigated the cleavage of aryl-silicon and aryl-tin bonds with $CNCl$ and $CNBr$ in the presence of $AlCl_3$ and observed that $CNCl$ yields aryl nitriles while $BrCN$ gives the corresponding aryl bromides. Grignard reagents have also been reported to behave differently with these cyanogen halides¹¹.

In view of such contrasting behaviour of cyanogen halides and of our interest in the group IV metal-aryl bond cleavages with electrophilic reagents^{3,5,12,13}, we report here the interaction of aryl-metal ($M = \text{Ge, Sn and Pb}$) bonds with $BrCN$ and ICN .

Materials and Methods

Phenyltributyltin¹⁴, tetraarylgermanium, -tin and -lead compounds^{3,5} and cyanogen bromide¹⁵ were prepared by previously reported methods. Cyanogen iodide (Eastman Organic Chemicals) was recrystallized before use. The solvents were purified and dried before use.

TABLE 1 — REACTIONS OF ICN AND $BrCN$ WITH TETRAARYL-GERMANIUM AND -TIN (Ar_4M) COMPOUNDS^(a)

Ar_4M Ar =	XCN (b) X =	ArX(c) (% yield)	b.p./lit. ¹⁸ b.p. °C
Ge(IV)			
Ph	I	50	184/184-86
<i>p</i> -Tolyl	I	52	208/211-12
Ph	Br	43	155/157
<i>p</i> -Tolyl	Br	47	180/182-84
Sn(IV)			
Ph	I	60	184/184-86
<i>p</i> -Tolyl	I	63	208/211-12
Ph	Br	54	155/157
<i>p</i> -Tolyl	Br	58	180/182-84

(a) One mole of cyanogen halides was employed in each case along with one mole of $AlCl_3$.

(b) Reactants were mixed at 0° and were then allowed to attain the room temperature over a period of 1 hr under constant stirring.

(c) Calculated on the basis of mono-cleavage.

Two representative experiments are described below. The data on other reactions are summarized in Table 1.

Reaction of Bu_3SnPh with XCN in the presence of $AlCl_3$ — Cyanogen bromide (1.70 g, 0.016 mol) was carefully added with stirring and exclusion of moisture to a solution of phenyltributyltin (5.50 g, 0.015 mol) and finely powdered anhydrous aluminium chloride (2.4 g, 0.018 mol) in dichloromethane kept at 0°C. On allowing the mixture to warm up to the room temperature, a moderately exothermic reaction set in. After stirring for 1 hr at room temperature, the mixture was poured over crushed ice. The organic layer was separated, washed with 0.1M NaOH solution to destroy residual $BrCN$ followed by water, dried over sodium sulphate and fractionally distilled to give bromobenzene, b.p. 155° (1.45 g, 62%), identical (IR) with an authentic specimen. To examine the residual part for the presence of Bu_3SnCN , it was refluxed with pet. ether (b.p. 60-80°), filtered, the

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filtrate concentrated and cooled; but the material obtained could neither be identified nor did it exhibit the characteristic IR band for nitrile function¹⁶.

Similarly, phenyltributyltin (5.50 g, 0.015 mol) in dichloromethane and cyanogen iodide (2.44 g, 0.016 mol) in the same solvent in the presence of AlCl_3 (2.4 g, 0.018 mol) produced iodobenzene, b.p. 184° (2.02 g, 66%).

Reaction of Ph_4Pb and XCN in the absence of AlCl_3 —To a stirring suspension of Ph_4Pb (1.43 g, 0.0027 mol) in chloroform (150 ml), cyanogen iodide (0.43 g, 0.0028 mol) in the same solvent (30 ml) was added dropwise during 30 min at ice temperature. The reaction mixture was stirred for a further period of 2 hr. Chloroform was distilled off and the residual white solid washed with a mixture of dichloromethane and ether (3×10 ml) to remove unreacted cyanogen iodide. The solid residue was characterized as Ph_4Pb , m.p. 228° (lit.¹⁷ m.p. 229°C) and unreacted ICN from filtrate was recovered quantitatively.

The above reaction was also attempted unsuccessfully (i) at room temperature over a week with constant stirring, (ii) at reflux temperature of CH_2Cl_2 (35°), CHCl_3 ($58-60^\circ$) and CCl_4 ($76-79^\circ$) for about 3 hr and (iii) by heating the reactants in CCl_4 solution at 100° in a sealed tube for 72 hr.

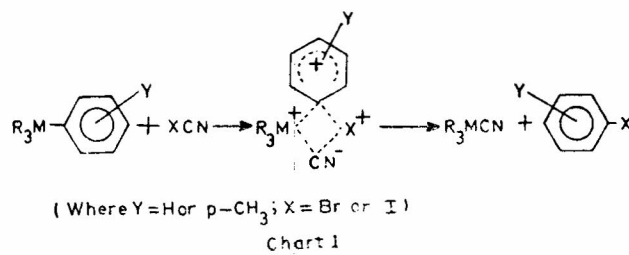
Similar results were obtained when the reactions were attempted with cyanogen bromide under conditions described above.

Results and Discussion

Reactions of tetraorgano-germanium and -tin compounds were carried out with BrCN and ICN in CH_2Cl_2 in the presence of AlCl_3 . Both the cyanogen halides were found to yield the corresponding isomerically pure aryl halides confirmed by GLC which show in each case the presence of a single constituent in yields ranging from 43 to 52% for Ar_4Ge and 54 to 66% for the tin compounds. Thus, reactions with tetra-*p*-tolylmetallic derivatives yielded pure *p*-tolyl halides (Table 1). No traces of aryl nitriles were detected in any of these reactions as evidenced by the absence of absorption for the $\text{C}\equiv\text{N}$ group¹⁰. Since the aryl halides were obtained through hydrolysis of the reaction products the organometallic species could not be isolated as they were not expected to survive during work-up. Furthermore, Ar_3SnCN are known to be very susceptible to moisture¹⁶.

As the tetraorganolead compounds undergo vigorous reaction with AlCl_3 even under mild conditions yielding a mixture of organolead chlorides¹⁹, the reactions of BrCN and ICN with tetraarylleads were conducted under various conditions in different solvents in the absence of a catalyst. The aryl-lead bonds remained unaffected with either of the reagents and the reactants were recovered quantitatively in each case.

The cleavage of aryl- MR_3 bonds (demetallations) by electrophilic reagents are closely analogous to familiar aromatic substitutions¹; in the latter, the aryl-H bond is broken in the direction $\text{C}-\text{H}^+$, and in the demetallation the aryl- MR_3 bond is broken in the direction $\text{C}-\text{MR}_3^+$. The ease of electro-



philic cleavage of such bonds increases with the increase in the polarity of the bond.

The mechanism of such reactions may possibly involve a four-centred transition state (Chart 1) in which nucleophilic attack on the metal atom (facilitated by the availability of vacant *d*-orbitals) by the incipient cyanide ion is synchronous with electrophilic attack by incipient halonium ion on carbon atom of the aromatic ring. An argument in favour of such a transition state has been based on the observation that a similar reagent iodine monochloride reacts with phenyltrimethylsilane (to give iodobenzene) about 8-times as fast as does chlorine²⁰. The presence of AlCl_3 in the above reactions induces some degree of polarization in cyanogen halides, $\text{X}^+(\text{AlCl}_3\text{CN})^-$ and thereby increasing their electrophilic character towards $\text{C}-\text{M}^+$ bond(s).

It appears that both ICN and BrCN are much weaker electrophiles as compared to halogens^{2,3,12}, interhalogens^{2,3}, or pseudohalides⁴⁻⁶ which are all reported to react with these metal-aryl bonds in the absence of a catalyst.

Being relatively weak electrophiles and in view of an earlier reported work¹⁰ where considerable amounts of aryltrimethyltins were obtained unchanged it is reasonable to assume that the cleavage in the present reactions is confined to only one metal-aryl bond in tetraaryl-germanium and -tin compounds. No appreciable increase in the yields of the aryl halides was observed when an excess (>1 mole) of cyanogen halides was employed. Furthermore, the CN group once introduced in R_3MCN compounds will have a strong deactivating effect on the three remaining M-aryl bonds due to its electron withdrawing nature decreasing the polarity of M-aryl bonds, and thus will discourage substitution by further cyanogen halide molecules²¹.

From the facts that (i) under identical conditions the percentage yields of aryl halides (Table 1) are always higher with ICN than BrCN , (ii) ICN reacts under milder conditions with Ph_3Bi than BrCN ^{8,9} and (iii) ClCN does not react with the Si-Ar bond while BrCN does¹⁰, it is reasonable to arrange these cyanogen halides in the following decreasing order of reactivity: $\text{ICN} > \text{BrCN} > \text{ClCN}$, which is also the decreasing order of their bond polarity²² and thus lends support to the mechanism proposed above where electrophiles with greater bond polarity are expected to be more reactive.

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