Journal of Organometallic Chemistry, 105 (1976) 45—49
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CLEAVAGE OF METAL—ARYL (M = Ge, Sn, Pb) BONDS WITH IODINE MONOCHLORIDE AND MONOBROMIDE

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(Received June 6th, 1975; in revised form July 30th, 1975)

Summary

Tetraaryl-germanium, -tin and -lead compounds (aryl(Ar) = phenyl, *p*-tolyl) were treated with IX (X = Cl, Br) in dry carbon tetrachloride under various conditions. Iodine monochloride cleaved one M—Ar bond in case of Ge and two bonds in case of Sn and Pb to give triarylgermanium chloride and diaryl-tin and -lead dichlorides respectively. In contrast iodine monobromide reacted only to a small extent (~5%) with Ph_4Ge in boiling ethylene bromide; with Ar_4Pb the corresponding dibromides were formed, while Ar_4Sn gave both mono- and dibromides.

The Sn—Ar bond is cleaved in preference to Sn—alkyl bonds in Bu_nSnPh_{4-n} ($n = 2, 3$). Reaction of Ph_3SnCl with IBr or Br_2 produced a mixed halogeno-derivative, $Ph_2SnClBr$, and the corresponding phenyl halide.

Introduction

Cleavage of Group IVB metal—carbon bonds by halogens has been extensively studied. Reactions of chlorine with Sn—C [1] and Pb—C [2] and of bromine with Pb—C [2] bonds are difficult to control and are rarely used for the preparation of R_3MX and R_2MX_2 compounds. However, iodine cleavage has been carried out to give satisfactorily yields of R_2MI_2 (M = Sn [1], Pb [3]) and R_3MI (M = Ge [4], Sn [1]).

There are few references to the use of an interhalogen, ICl, for one step preparation of organo-germanium [5] and -tin chlorides [6]. ICl has been used to produce trimethylchlorosilane and phenyl iodide from trimethylphenylsilane [7] in absence of catalyst. A kinetic study of reactions of IBr with tetramethyl-

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and tetrapropyl-tin has also been reported [8]. Related reactions of Ph_4Sn and Ph_4Pb with ICl_3 give the corresponding dichlorides (the lead compound being contaminated with some monochloride as well) [9]. Reactions of ICl with Me_3M—$M'Me_3$ (M, M' = C, Si, Ge, Sn) have also been reported [10]. While this work was in progress, reactions of Bu_4Sn and Ph_4Sn with IX (X = Cl, Br) were reported [11].

In continuation of our work on electrophilic cleavage of tin— and lead—aryl bonds with thiocyanogen [12] and iodine [13] we report the interaction of ICl and IBr now with symmetrical tetraaryl-germanium, -tin and -lead, Ar_4M (Ar = phenyl, *p*-tolyl), and di- and tri-butylphenyltin Bu_nSnPh_{4-n} ($n = 2, 3$) compounds. Our object was (i) to study the extent and relative ease of cleavage in Ar_4M compounds, (ii) to develop a one-step synthesis of Ar_3MX or Ar_2MX_2 and $Ar_2SnBrCl$ and (iii) the preferential cleavage of Bu—Sn or Ph—Sn bond(s).

Results and discussion

Contrary to the bromination of tetraphenyllead which results in the formation of lead dibromide among other products [2], suggesting excessive cleavage of lead—carbon bonds, both iodine monochloride and iodine monobromide cleave only two Pb—C bonds at —5°C irrespective of the ratio of the interhalogen to the tetraorganolead. Attempts to prepare the monohalides, Ar_3PbX, by slowly adding only one mole of IX to Ar_4Pb at —5°C failed.

With tetraphenyltin 1 mol ICl gave a mixture containing mostly diphenyltin dichloride along with ~10% of triphenyltin chloride and some unchanged Ph_4Sn* (formation of traces of Ph_3SnCl has been reported for this same reaction [11]). Tetra-*p*-tolyltin, with 1 mol of ICl gave only the dichloride and no monochloride. By variation of the reaction conditions iodine monobromide can be used, however, to produce either Ar_3SnBr or Ar_2SnBr_2.

In an attempt to prepare diaryltin dihalides containing two different halogen atoms (Ar_2SnXX') iodine was treated with triphenyltin chloride. Iodine remained unconsumed even after prolonged stirring in boiling carbon tetrachloride. Triphenyltin chloride however, yielded diphenyltin dichloride with ICl and the mixed halogeno derivative, $Ph_2SnClBr$, with IBr or Br_2. These reactions are of interest as they should provide an easy route to (i) diaryltin dichloride from the monochlorides and (ii) diaryltin dihalides containing two different halogens. Reactions of the latter type are currently being investigated in detail.

Halogenation of Sn—aryl bonds is known to be faster than Sn—alkyl bonds [14]. Thus, not surprisingly the reactions of tributylphenyltin and dibutyldiphenyltin with IX (Cl, Br) proceeded with the preferential cleavage of phenyl group(s). Controlled cleavage of one or two Sn—Ph bonds in Bu_2SnPh_2 with 1 or 2 mol of IBr produced $Bu_2SnPhBr$ or Bu_2SnBr_2, but with 1 mol of ICl only Bu_2SnCl_2 was obtained at room temperature.

Tetraarylgermanium reacted with ICl in boiling CCl_4 to give the monochloride, Ar_3GeCl, and no cleavage of a second Ar—Ge bond was observed even with an excess of ICl. The yield of the chlorides was increased and the reaction time

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* We found it almost impossible to separate diphenyltin dichloride by the petroleum ether extraction method, and could only separate the dihalide after distilling off the phenyl iodide.

decreased by using a higher boiling solvent such as chlorobenzene. This method is very useful as a one step preparation of Ar_3GeCl and should be preferred over the reaction involving heating of Ar_4Ge with $GeCl_4$ in presence of $AlCl_3$ [15]. IBr on the other hand did not react under similar conditions, and on prolonged refluxing in ethylene bromide only ~5% of Ph_3GeBr was obtained. Tetrabutylgermanium also failed to react with ICl of IBr.

The presence of $AlCl_3$ as catalyst in the R_4Ge/IX reactions may increase the extent of cleavage as has been reported for several reactions of Group IV compounds with electrophiles [16]. We did not use such catalysed reactions since the organogermanium halides are likely to get hydrolysed and/or contaminated during the work-up.

Experimental

Materials

Tetraaryl-germanium [15], -tin [12], and -lead [12] were synthesized by published methods. Phenyltributyltin and diphenyldibutyltin were prepared from phenylmagnesium bromide and the appropriate organotin chloride, and had boiling points agreeing with those of the literature. Iodine monochloride (Fluka) was distilled before use. Iodine monobromide was prepared by dissolving iodine in an excess of bromine and then removing the excess bromine under reduced pressure. It was purified by the published method [11].

Carbon tetrachloride and petroleum ether (40-60°) were distilled from $CaCl_2$ and sodium, respectively. Moisture was excluded where necessary.

Reactions of tetraaryl-germanium, -tin, and -lead compounds with ICl and IBr

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

Reaction of Ph_4Ge with ICl (1:1)

A solution of ICl (0.81 g, 0.005 mol) in CCl_4 (50 ml) was slowly added with vigorous stirring to a refluxing suspension of tetraphenylgermanium (1.9 g, 0.005 mol) in CCl_4 (200 ml). The blood-red colour of ICl solution slowly changed to light pinkish-brown. After the addition (2 h) the mixture was further refluxed for 4 h. The solvent was distilled off and the residue was washed with petroleum ether (15 ml) to give unreacted tetraphenylgermanium (0.25 g, 13%); m.p. 228°C (Lit. [17] m.p. 230-231°C). The washings were concentrated and then distilled to give a colourless liquid (0.65 g, 63%), b.p. 63-65°C/10 mmHg (Lit. [18] b.p. 184-186°C) whose IR spectrum was identical to that of an authentic sample of PhI. The residue (after distilling off PhI) was recrystallized from cold petroleum ether and identified as triphenylgermanium chloride (1.25 g, 74%, based on Ph_4Ge) m.p. 115-116°C (Lit. [17] m.p. 117°) (authentic IR spectra).

A similar experiment with chlorobenzene instead of CCl_4 gave triphenylgermanium chloride in 80% yield.

No trace of diphenylgermanium dichloride was observed even in presence of excess (1.3 mol) ICl in the above reactions.

Ph_3SnCl with IBr and Br_2 (1:1)

A solution of IBr (1.03 g, 0.005 mol) in CCl_4 (20 ml) was dropwise added

TABLE 1

REACTIONS OF ICl AND IBr WITH Ar_4M (Ge, Sn, Pb) AND OTHER ORGANOTIN COMPOUNDS

Reactants				Reaction conditions[a] (h)	Products[b]	Yield (%)[c]	M.p. (°C) (Lit. m.p. (°C))
Ar_4M		IX					
Ar	M	X	mol				
Ph	Pb	Cl	1	1	Ph_2PbCl_2	70[d]	280-282 (dec.) (284-286 dec. [19])
Ph	Pb	Cl	2.2	1	Ph_2PbCl_2	83	281-283 (dec.)
p-Tol	Pb	Cl	2	1	$(p\text{-Tol})_2PbCl_2$	80[e]	272-275 (dec.)
p-Tol	Pb	Br	2	1	$(p\text{-Tol})_2PbBr_2$	78[f]	270 (dec.)
Ph	Pb	Br	2	1	Ph_2PbBr_2	75	248-249 (dec.) (250 dec. [19])
Ph	Sn	Cl	1	1[g]	Ph_2SnCl_2	70[h]	41-42(42-44 [20])
Ph	Sn	Cl	2	1	Ph_2SnCl_2	88	41-42
p-Tol	Sn	Cl	2	1	$(p\text{-Tol})_2SnCl_2$	92	47-49 (48-49 [20])
Ph	Sn	Br	1	2	Ph_3SnBr	80	120 (122 [20])
Ph	Sn	Br	2	6[i]	Ph_2SnBr_2	84	37-38 (38 [20])
p-Tol	Sn	Br	1	1	$(p\text{-Tol})_3SnBr$	80	97-98 (98.5 [20])
p-Tol	Sn	Br	2	3[i]	$(p\text{-Tol})_2SnBr_2$	90	73-74 (74 [20])
Ph	Ge	Cl	1.3	4	Ph_3GeCl	76	115-116 (116-117 [17])
p-Tol	Ge	Cl	1.3	4	$(p\text{-Tol})_3GeCl$	80	118-120 (120-121 [17])
Ph	Ge	Br	1	10	No reaction		
Ph	Ge	Br	2	8[j]	Ph_3GeBr	5	137-138 (138 [17])
Ph_nSnY_{4-n}							B.p. (°C/mmHg) or m.p. (°C)
n	Y						
1	Bu	Cl	1	2	Bu_3SnCl	81[k]	
1	Bu	Br	1	2	Bu_3SnBr	93[k]	
2	Bu	Cl	1	1	Bu_2SnCl_2	79[l]	115/3 (134-136/10 [20])
2	Bu	Cl	2	2	Bu_2SnCl_2	90[m]	
2	Bu	Br	2	2[i]	Bu_2SnBr_2	90[m]	
2	Bu	Br	1	1	$Bu_2PhSnBr$	80[n]	
3	Cl	Cl	1	1	Ph_2SnCl_2	80	40-42 (42-44 [20])

[a] Reactions with lead compounds at −5°C, with tin compounds at 25°C and with germanium compounds at reflux temperature of CCl_4. [b] Corresponding amounts of ArI were also obtained. [c] Based on reacted organometallic derivative. [d] Unreacted Ph_4Pb (0.5 mol) was also isolated. [e] Found: C, 36.1; H, 3.1. $C_{14}H_{14}Cl_2Pb$ calcd.: C, 36.4; H, 3.0%. [f] Found: C, 30.2; H, 2.3. $C_{14}H_{14}Br_2Pb$ calcd.: C, 30.5; H, 2.5%. [g] At 0°C. [h] Ph_3SnCl (~10%), was also isolated along with unreacted Ph_4Sn. [i] Refluxing CCl_4. [j] Refluxing ethylene bromide. [k] Isolated as Bu_3SnF, m.p. 242-243°C (Found: C, 46.3; H, 8.1. $C_{12}H_{27}FSn$ calcd.: C, 46.6; H, 8.7%). [l] Unreacted Bu_2SnPh_2 (~0.5 mol) was also obtained. [m] Based on Bu_2SnF_2; Found: C, 34.8; H, 6.8 $C_8H_{18}F_2Sn$ calcd.: C, 35.4; H, 6.6%; m.p. >300°C. [n] Found: C, 42.6; H, 5.7; $C_{14}H_{23}SnBr$ calcd.: C, 43.1; H, 5.9%. The ^1H NMR spectra showed two multiplets centered at τ 8.62 (Bu) and τ 2.63 (Ph) in a ratio of 18/5.

with vigorous stirring to a solution of triphenyltin chloride (1.92 g, 0.005 mol) at 25°C. After refluxing (1 h) the reaction mixture it was freed from solvent. Phenyl iodide (0.71 g, 70%) was then distilled off at 63-65°C/10 mmHg and the residue on recrystallisation from cold petroleum ether (40-60°) afforded bromochlorodiphenyltin (1.3 g, 67%), m.p. 37-38°C (Lit. [20] m.p. 39°C).

Similarly, triphenyltin chloride (1.92 g, 0.005 mol) and bromine (0.80 g, 0.005 mol) at −5°C gave phenyl bromide (0.57 g, 73%), b.p. 155°C (Lit. [21]

157°C), and bromochlorodiphenyltin (1.4 g, 72%), m.p. 38-39°C (Lit. [20] m.p. 39°C) after recrystallization from cold petroleum ether (40-60°).

Unsuccessful reactions

In the following reactions the colour of IX was not discharged and the organo-germanium, -tin and -lead compounds were recovered quantitatively under the given conditions: (a) Bu_4Ge with ICl and IBr in refluxing (6 h) CCl_4, (b) Ph_2PbCl_2 with ICl in refluxing CCl_4 and (c) Ph_3SnCl with I_2 in refluxing (4 h) CCl_4.

Acknowledgement

We are thankful to U.G.C., New Delhi for the award of a Junior Research Fellowship to P.R. and to the International Lead Zinc Research Organization for a gift of tetraphenyllead; to Nitto Kasei Kogyo Co., Osaka for tributyltin chloride; to Cincinnati Milacron Chemicals, New Jersey, U.S.A.; for dibutyltin dichloride and to Dr. T.N. Srivastava of this department for germanium tetrachloride and helpful discussions.

References

1 A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 2, Part II, Marcel Dekker, New York, 1972, p. 74.
2 Ref. 1, p. 153.
3 L.C. Willemsens and G.J.M. van der Kerk, Investigation in the Field of Organolead Chemistry, Intern. Lead Zinc Res. Organ., New York, 1965, p. 112.
4 Ref. 1, p. 11.
5 P. Mazerolles, J. Dubac and M. Lesbre, J. Organometal. Chem., 5 (1966) 35.
6 C. Eaborn, A.A. Najam and D.R.M. Walton, J. Chem. Soc. Perkin Trans., (1972) 2481.
7 L.M. Stock and A.R. Spector, J. Org. Chem., 28 (1963) 3272.
8 G. Redl, B. Altner, D. Anker and M. Minot, Inorg. Nucl. Chem. Lett., 5 (1969) 861.
9 Z.M. Manulkin, Uzbek. Khem. Zhur., 1960-No. 2, 66-68; Chem. Abstr., 55 (1961) 12330d.
10 C.F. Shaw and A.L. Allred, Inorg. Chem., 10 (1971) 1340.
11 A. Folaranmi, R.A.N. McLean and N. Wadibia, J. Organometal. Chem., 73 (1974) 59.
12 S.N. Bhattacharya, Prem Raj and R.C. Srivastava, J. Organometal. Chem., 87 (1975) 279.
13 T.N. Srivastava and S.N. Bhattacharya, Z. Anorg. Allgem. Chem., 102 (1966) 344.
14 R.W. Bott, C. Eaborn and J.A. Waters, J. Chem. Soc., (1963) 681.
15 F. Rijkens and G.J.M. van der Kerk, Investigations in the field of Organogermanium Chemistry, Germanium Research Committee, 1964, p. 123.
16 E.H. Bartlett, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 46 (1972) 267 and refs. therein.
17 Otto H. Johnson, Chem. Rev., 48 (1951) 259.
18 A.I. Vogel, Practical Organic Chemistry, Longmans, London, 1971, p. 538.
19 R.J.H. Clark, A.G. Davies and R.J. Puddephatt, Inorg. Chem., 8 (1969) 457.
20 R.K. Ingham, S.K. Rosenburg and H. Gilman, Chem. Rev., 60 (1960) 459.
21 Ref. 18, p. 536.