

Novel coupling reaction of pentaarylantimony with carbon electrophiles

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Abstract

The cross-coupling reactions of pentaarylantimony with organic halides and allyl acetate were studied under various conditions of acetonitrile solvent, palladium catalysts and copper iodide. Acetonitrile solvent enabled a nucleophilic coupling reaction with allylic halides, although a radical reaction and an intramolecular ligand coupling have been regarded as general under other conditions. Palladium catalysts were effective for the coupling reaction with allyl acetate. Copper iodide promoted the reaction of organic halides, such as methyl iodide and ethyl bromoacetate. In the latter two cases, the formation of diaryls is a significant side reaction.

Keywords: Alkyl halide; Antimony; Solvent; Acetate; Palladium

1. Introduction

Organoantimony compounds have recently been noticed as a novel synthesis tool [1–3]. The reactivity of pentavalent organoantimony compounds is generally superior to that of trivalent ones ¹ [2]. Although alkylantimony compounds are very versatile reagents [2], their low stability prevents the study of the detailed reaction behaviour ² [4]. Therefore, the utilization of pentaarylantimony is advantageous because of its high stability and isolable character [5].

McEwen and Lin claimed there were three types of behaviour in the reaction of pentaphenylantimony with carbon tetrachloride [6]. The first type of behaviour is the intramolecular reductive elimination (ligand coupling) to form diaryl where no free aromatic species, such as aryl radical or aryl anion, is involved (Eq. (1)) [7]. The second type of behaviour is the homolytic fission of antimony–carbon bond in pentaarylantimony (Eq. (2)). The two radical species thus formed (Ar₄Sb· and Ar·) cause complicated radical chain reactions [6].

The third type of behaviour is the ionic fission of the antimony–carbon bond, forming aryl anion species (Eq. (3)). Although benzotrichloride (PhCCl₃) can be formed by the nucleophilic substitution of a phenyl anion of pentaphenylantimony with carbon tetrachloride (Eq. (4)), only trace amounts of the compound are obtained [6]. Furthermore, Razuvaev et al. reported that the reaction of pentaphenylantimony with methyl iodide resulted in the formation of triphenylantimony and iodobenzene [8]. Therefore, the nucleophilic substitution of an aryl anion of pentaarylantimony has not been effected. However, we recently found that pentaarylantimony reacted with acid halide (Eq. (5)), aldehyde and ketone (Eq. (6)), producing the corresponding coupling products in good yields [9]. An aryl group of pentaarylantimony acted as a nucleophile in this case. Although some palladium-catalysed reactions of organoantimony compounds ³ [3,10,11], including ours [9], have been reported, no coupling reaction of pentaarylantimony with common organic halides and their analogues has been studied.

In this report, we wish to describe some novel reactions of pentaarylantimony. Nucleophilic reaction of pentaarylantimony occurred in acetonitrile solution. Furthermore, palladium catalysts and a copper salt pro-

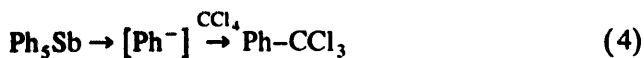
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¹ Huang et al. reported that the transformation of tributylantimony (Bu₃Sb) into pentaorganoantimony (Bu₃SbR₂) improved the nucleophilicity of substituents in organoantimony compounds.

² Pentaalkylantimony was characterized by only mass spectrometry.

³ A palladium-catalysed cross-coupling reaction of dipropynyltrimethylantimony with acid chlorides has been reported.

moted the coupling with carbon electrophiles, including halides and allyl acetate.



2. Results and discussion

2.1. Direct reaction of pentaarylantimony with organic halides

We first examined the reaction of pentaarylantimony with common organic halides, such as allyl halides; the results are shown in Table 1. Both allyl chloride and allyl bromide readily reacted with pentaphenylantimony in acetonitrile to give allylbenzene in good yields (runs 1,2). Acetonitrile was an essential solvent for the coupling, and a trace amount of allylbenzene was obtained in benzene or THF solution (runs 3,4). Triphenylantimony and tetraphenylstibonium bromide were ineffective and these compounds were completely recovered after treatment (runs 5,6). Penta-*p*-tolylantimony and penta-*p*-chlorophenylantimony also gave the corresponding coupling products in good yields (runs 7,8). Cinnamyl bromide reacted with pentaphenylantimony in

almost quantitative yield to give 1,3-diphenylpropylene ($\text{PhCH}=\text{CHCH}_2\text{Ph}$) and 3,3-diphenylpropylene ($\text{Ph}_2\text{CHCH}=\text{CH}_2$) in a ratio of 35:65 (run 9). The $\text{S}_{\text{N}}2'$ reaction is predominant over $\text{S}_{\text{N}}2$ reaction. Other bromides, such as *n*-pentyl bromide, benzyl bromide, and ethyl bromoacetate, gave no coupling adducts (runs 10–12).

As the radical reaction of pentaarylantimony was often claimed [6,8], the effect of a radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN), or a radical quencher, Galvinoxyl, were investigated. The addition of AIBN clearly depressed the coupling (run 13). If the coupling products were formed by the radical mechanism, it is thought that AIBN increases and Galvinoxyl reduces the yield of the products. However, the results showed that the radical reaction initiated by AIBN caused other types of reaction, probably such as the radical chain reactions proposed by McEwen and Lin [6]. Furthermore, the lack of influence of Galvinoxyl on the yield of the coupling products (run 14) also strongly suggested that the cross-coupling product was not formed by the radical mechanism [6], and was thus not responsible for the coupling.

The polarity of the solution is an important factor in determining the reactivity of pentaarylantimony. As mentioned above, acetonitrile was a particularly effective solvent. The antimony-carbon bond of pentaarylantimony was polarized in acetonitrile solution to promote the nucleophilic reaction of an aryl group of pentaarylantimony with allyl halides. In benzene or THF, the polarization of the antimony-carbon bond was not enough, and radical chain reactions took place similar to the reaction with carbon tetrachloride. The reactivity of

Table 1
Cross-coupling reaction of pentaarylantimony with organic halides^a

Run	Antimony	R-X	Temperature (°C)	Yield (%) ^b	
				R-Ar	Ph-Ph
1	Ph ₅ Sb	CH ₂ =CHCH ₂ Cl	40	85	13
2	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	60	91	tr
3 ^c	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	80	tr	5
4 ^d	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	65	tr	tr
5	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	60	0	0
6	Ph ₄ SbBr	CH ₂ =CHCH ₂ Br	60	0	0
7	<i>p</i> -Tol ₅ Sb	CH ₂ =CHCH ₂ Br	60	66	tr
8	(<i>p</i> -ClC ₆ H ₄) ₅ Sb	CH ₂ =CHCH ₂ Br	60	67	tr
9	Ph ₅ Sb	PhCH=CHCH ₂ Br	80	95 ^e	tr
10	Ph ₅ Sb	<i>n</i> -C ₅ H ₁₁ Br	80	0	12
11	Ph ₅ Sb	PhCH ₂ Br	80	tr	68
12	Ph ₅ Sb	EtOCOCH ₂ Br	80	~0	58
13 ^f	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	80	17	6
14 ^g	Ph ₅ Sb	CH ₂ =CHCH ₂ Br	80	85	tr
15	Ph ₅ Sb	—	80	—	23

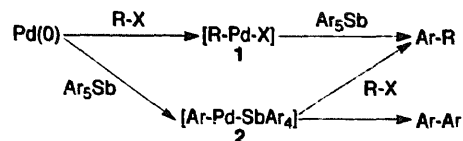
^a Antimony/R-X = 1/3 mmol, solvent MeCN 1 ml, 24 h. ^b Determined by GLC based on antimony compounds. ^c Solvent PhH. ^d Solvent THF. ^e Yields of PhCH=CHCH₂Ph and Ph₂CHCH=CH₂ were 33% and 62% respectively. ^f AIBN (0.1 mmol) was added. ^g Galvinoxyl (0.1 mmol) was added.

n-pentyl bromide was very poor for the nucleophilic reaction. In the case of benzyl bromide and ethyl bromoacetate, it seems that the radical reaction prevented the nucleophilic reaction. It was confirmed that the effective activation of antimony–carbon bonds in pentaarylantimony could promote nucleophilic reactions.

2.2. Transition-metal-promoted reaction of pentaarylantimony

To extend the coupling reaction to electrophiles other than allyl halides, we examined two novel reactions of pentaarylantimony using transition metals. Palladium complexes were employed as summarized in Table 2. The cross-coupling reaction with allyl acetate and allyl phenyl ether were apparently promoted, because only a small amount of allylbenzene was obtained without catalyst (runs 1 and 10). Tetrakis(triphenylphosphine)palladium was the most effective catalyst in our case (run 2). Other palladium catalysts, such as bis(triphenylphosphine)palladium dichloride, benzylbis(triphenylphosphine)palladium chloride and palladium acetate (runs 5–7), were less active. Benzyl bromide gave diphenylmethane, although in a low yield (run 12). An aromatic halide, *p*-iodotoluene, also afforded the corresponding coupling product in 27% yield (run 14).

Diaryls were obtained in considerable yields in almost all cases. Although palladium catalysts apparently effected the cross-coupling, undesirable ligand coupling was promoted as well. Some similar ligand coupling reactions of organoantimony compounds have already been reported [7]. In some cases, the sums of allylbenzene and diaryl were over 100%, probably because two or three aryl groups in pentaarylantimony reacted. The



Scheme 1. Plausible reaction path of cross-coupling reaction of pentaarylantimony.

antimony compounds with five antimony–carbon bonds were suitable for this palladium-catalysed reaction. Triphenylantimony was inert (run 3), and tetraphenylstibonium bromide had low activity for the cross-coupling reaction, affording diphenyl in high yield (run 4). This tendency was also observed in the reactions with acid halide, aldehyde [9] and allyl halide.

The addition of copper iodide was found to be effective for the coupling reaction of pentaarylantimony with ethyl bromoacetate, which had not been promoted even by palladium catalyst (run 15). Toluene was also obtained in 27% yield from pentaphenylantimony and methyl iodide (run 16). The radical route was obviously excluded in the toluene formation. It seems that a nucleophilic reaction promoted by copper iodide occurred, because the direct reaction was reported to give no toluene by a radical-type reaction [8].

A plausible reaction path of this palladium-catalysed coupling reaction is shown in Scheme 1. In the first step, two types of oxidative addition to palladium catalysts can be proposed. The oxidative addition of carbon electrophiles [12] or antimony compounds [10] forms the complexes 1 or 2 respectively. The conspicuous difference in the reaction mode between pentaarylantimony and other organometallics is found in the formation of diaryl by the reductive ligand coupling reaction.

Table 2
Transition-metal-promoted cross-coupling reaction of pentaarylantimony^a

Run	Antimony	R-X	Additive	Yield (%) ^b	
				R-Ar	Ar-Ar
1	Ph ₅ Sb	CH ₂ =CHCH ₂ OAc	—	5	22
2	Ph ₅ Sb	CH ₂ =CHCH ₂ OAc	Pd(Ph ₃ P) ₄	42	40
3	Ph ₃ Sb	CH ₂ =CHCH ₂ OAc	Pd(Ph ₃ P) ₄	0	tr
4	Ph ₄ SbBr	CH ₂ =CHCH ₂ OAc	Pd(Ph ₃ P) ₄	8	92
5	Ph ₅ Sb	CH ₂ =CHCH ₂ OAc	(Ph ₃ P) ₂ PdCl ₂	31	92
6	Ph ₅ Sb	CH ₂ =CHCH ₂ OAc	BzPd(Cl)(Ph ₃ P) ₂	28	90
7	Ph ₃ Sb	CH ₂ =CHCH ₂ OAc	Pd(OAc) ₂	13	72
8	<i>p</i> -Tol ₅ Sb	CH ₂ =CHCH ₂ OAc	Pd(Ph ₃ P) ₄	16	74
9	(<i>p</i> -ClC ₆ H ₄) ₅ Sb	CH ₂ =CHCH ₂ OAc	Pd(Ph ₃ P) ₄	16	76
10	Ph ₅ Sb	CH ₂ =CHCH ₂ OPh	—	0	25
11	Ph ₅ Sb	CH ₂ =CHCH ₂ OPh	Pd(Ph ₃ P) ₄	33	63
12	Ph ₅ Sb	PhCH ₂ Br	Pd(Ph ₃ P) ₄	14	85
13	Ph ₅ Sb	EtOCOCH ₂ Br	Pd(Ph ₃ P) ₄	0	98
14 ^c	Ph ₅ Sb	<i>p</i> -CH ₃ C ₆ H ₄ I	Pd(Ph ₃ P) ₄	27	66
15 ^d	Ph ₅ Sb	EtOCOCH ₂ Br	CuI	19	29
16 ^e	Ph ₅ Sb	CH ₃ I	CuI	27	47

^a Antimony/R-X/Pd = 1/3/0.05 mmol, solvent MeCN 1 ml, 80 °C, 24 h. ^b Determined by GLC based on antimony compounds. ^c Antimony/R-X/Pd = 1/10/0.05 mmol, solvent MeCN 1 ml, 25 °C, 24 h. ^d Ph₅Sb/EtOCOCH₂Br/CuI = 0.5/5/0.08 mmol, 80 °C, 4 h. ^e Ph₅Sb/CH₃I/CuI = 0.5/8/0.6 mmol, using autoclave (N₂; 20 kg/G).

The reaction of tetraphenylstibonium bromide with *trans*-bis(triphenylphosphine)palladium in the absence of a carbon electrophile produced diphenyl in 82% yield in acetonitrile at 80°C for 24 h, although no diphenyl was detected without the palladium catalyst. In the former reaction, an intermediate, Ph–Pd–SbPh₃Br, analogous to the complex **2** seems to be formed. The poor yield of allylbenzene from tetraphenylstibonium bromide (run 4 in Table 2) indicated that this intermediate did not play a significant role in the cross-coupling reaction with a carbon electrophile. Furthermore, the cross-coupling reaction of an aromatic halide, where the Ar–Pd–X species is known to be formed, was observed. Therefore, it is thought that the complex **1** from palladium and a carbon electrophile is the key-intermediate of the cross-coupling. In the case of the palladium-catalysed reaction of pentavalent organoantimony compounds, the cross-coupling and the reductive ligand coupling proceeded competitively.

In conclusion, pentaarylantimony reacted with allylic halides to give the corresponding coupling products. Acetonitrile was an essential solvent for the direct coupling reaction, because the nucleophilic reaction of pentaarylantimony was promoted. Palladium catalyst and copper iodide were effective for the coupling reaction of pentaarylantimony with allylic compounds and organic halides which were inactive for the direct reaction. In all cases, the significance of five organic substituents in antimony was confirmed to achieve the cross-coupling reaction. Furthermore, the results obtained here suggest that the efficient activation of antimony–carbon bonds promotes the nucleophilic reaction of pentaarylantimony and probably other pentavalent antimony compounds, presenting some novel and useful synthesis reactions.

3. Experimental section

3.1. Materials

All reagents except antimony compounds are commercially available and were used without further purification. All solvents were employed after distillation. Triphenylantimony was purchased and was used after recrystallization using ethanol. Preparation techniques of other antimony compounds have been described elsewhere [9].

3.2. Reaction procedure

3.2.1. Typical procedure of the reaction of pentaarylantimony with organic electrophiles

Under a nitrogen atmosphere, the mixture of pentaarylantimony (1 mmol), an organic electrophile (3 mmol) and an additive (when used) in a solvent (1 ml) was stirred at the described temperature for 24 h to complete the reaction. After volatiles were removed

under reduced pressure, the residual solid was subjected to silica gel column chromatography. The products obtained were identified by ¹H NMR (JEOL α-500; 500 MHz) and GLC and compared with the data of commercially available ones in almost all cases. The yields of products were determined by GLC.

1,3-Diphenylpropylene and 3,3-diphenylpropylene were obtained as mixture, and were determined by ¹H NMR.

1,3-Diphenylpropylene: ¹H NMR (CDCl₃): δ 3.5 (d, 2H, C₆H₅CH=CHCH₂C₆H₅); 6.3–6.4 (m, 1H, C₆H₅CH=C HCH₂C₆H₅); 6.4–6.5 (m, 1H, C₆H₅CH=CHCH₂C₆H₅); 7.1–7.4 (m, 10H, C₆H₅CH=CHCH₂C₆H₅) ppm.

3,3-Diphenylpropylene: ¹H NMR (CDCl₃): δ 4.7 (d, 1H, (C₆H₅)₂CHCH=CH₂); 5.0 (d, 1H, (C₆H₅)₂CHCH=C H₂); 5.2 (d, 1H, (C₆H₅)₂CHCH=C H₂); 6.2–6.3 (m, 1H, (C₆H₅)₂CHCH=C H₂); 7.1–7.3 (m, 10H, (C₆H₅)₂CHCH=CH₂) ppm.

3.2.2. The reaction of pentaphenylantimony and methyl iodide with copper iodide

The mixture of pentaphenylantimony (0.5 mmol), methyl iodide (8 mmol) and copper iodide (0.6 mmol) in acetonitrile (1 ml) was stirred in an autoclave.

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