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Convenient Preparation of Tetraarylphosphonium Halides

Toshihiko MIGITA,* Tohru NAGAI, Kazuhiko KIUCHI, and Masanori KOSUGI
Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376

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Synopsis. Tetraarylphosphonium halides, particularly iodides, can be conveniently prepared by the Pd-catalyzed reaction of aryl halides and triarylphosphines in good yields.

There have been known a few reactions which can be used for preparation of tetraarylphosphonium salts:

$$\mathrm{PhI + PPh_3 \xrightarrow[65\,^{\circ}C,\ 46\,h]{h\nu} Ph_4P^{+}I^{-}} \qquad 23\%^{1)}$$

$$\mathrm{PhN(NO)COCH_3 + PPh_3 \xrightarrow[PhH]{aq.\ HBr} Ph_4P^{+}Br^{-}} \qquad 32\%^{2)}$$

$$\mathrm{PhMgBr + PhBr + PPh_3 \xrightarrow{CoCl_2} Ph_4P^{+}Br^{-}} \qquad 55\%^{2)}$$

These reactions, which belong to a reaction of aryl radical with triarylphosphine, give relatively low yields, and the experimental procedures are not simple.

Previously aryl iodide and bromide activated by zero-valent palladium were shown to undergo nucleophilic substitution with soft nucleophiles such as thiolate and triphenylphosphine.[3] Here we wish to note utility of the Pd-catalyzed reaction of aryl halide with triarylphosphine for the preparation of tetraarylphosphonium halides.

$$\mathrm{Ar'X + PAr_3 \xrightarrow{[Pd]} Ar'P^{+}Ar_3X^{-}}$$

The reaction takes place by heating a mixture of equimolar reactants, 1 mol% of $Pd(PPh_3)_4$ or more conveniently $Pd(OAc)_2$, and the solvent (aromatic hydrocarbon) at 120 °C for 25 h. The product, tetraarylphosphonium salt insoluble in the solvent, deposites as fine crystals, which can be easily collected and purified by recrystallization. Table shows a number of phosphonium salt obtained by using $Pd(OAc)_2$ as a catalyst.

The following tendencies about scope and limitation of the present method can be seen. Among halides, the best results were obtained by using aryl iodides as substrates. The reactions of aryl bromides gave only low yields and aryl chlorides hardly reacted with triarylphosphine under the conditions. Electron releasing substituents appear to enhance the reactivities of aryl halides. For example, *p*-methoxyiodobenzene reacts smoothly with triphenylphosphine even at lower temperature (100 °C), giving the corresponding quaternary salt in 96% yield. Reaction of negatively substituted iodobenzenes afforded poor yields such as given without the catalyst.

Perhaps due to steric hindrance, ortho substituents on aryl halide as well as triarylphosphine retard the reaction, giving quite low yields of phosphonium salts. Triarylphosphines bearing substituents which enhance the nucleophilicities of the phosphines gave better results.

TABLE 1. TETRAARYLPHOSPHOONIUM HALIDE, $YC_6H_4P^{+}(C_6H_4Z)_3X^{-}$ PREPARED FROM HALDE, YC_6H_4X AND TRIARYLPHOSPHINE, $P(C_6H_4Z)_3$

X	Y	Z	Yield %	Mp θ_m/°C	C (%) Calcd	C (%) Obsd	H (%) Calcd	H (%) Obsd
Cl	H	H	0					
Br	H	H	Trace	288	68.75	68.51	4.81	4.75
	p-CH₃	H	19	177	69.30	68.98	5.12	5.15
	p-NO₂	*p*-CH₃	16[b]	224d	64.04	64.57	4.98	5.10
I	H	H	98	346 (337)[a]	61.82	61.80	4.32	4.21
	H	*p*-CH₃	81	197	63.79	63.72	5.15	5.37
	H	*p*-Cl	32	298	50.60	50.73	3.01	3.09
	o-CH₃	H	Trace					
	m-CH₃	H	95	201 (199—201)[a]	62.52	62.88	4.62	4.49
	p-CH₃	H	100	214 (207—209)[a]	62.52	62.16	4.62	4.52
	p-CH₃	*p*-CH₃O	100	199	58.96	59.28	4.95	4.87
	o-CH₃O	H	27	168	60.50	60.86	4.47	4.67
	m-CH₃O	H	70	206	60.50	60.40	4.47	4.21
	m-CH₃O	*p*-CH₃	97	161	62.46	62.66	5.24	4.99
	p-CH₃O	H	99	219	60.50	60.22	4.47	4.50
	p-CH₃O	*p*-Cl	76	Very high	50.19	50.07	3.19	3.20
	p-Cl	H	28	212 (216—217)[a]	57.57	57.47	3.82	3.80

a) Known salts, in Ref. 2. b) N: calcd (%), 2.77; obsd (%), 3.03.

Experimental

Material. Triarylphosphines were prepared by the known method from the corresponding arylmagnesium bromides and trichlorophosphine.[4] Commercially available products of palladium acetates and aryl halides were used without purification.

Procedure. A mixture of aryl halide (2 mmol), triarylphosphine (2 mmol), palladium acetate (0.02 mmol), and 3 cm^3 of a solvent (benzene or toluene) was placed in a tube. The tube was evacuated and sealed, then immersed in a bath kept at 120 °C for 25 h. In the course of the period the catalyst was dissolved and phosphonium salt separated from the solution. The salts were filtered, washed with benzene, and recrystallized from chloroform–benzene. The yield and analytical data of the products obtained by this procedure are listed in Table 1.

In the above procedure, the mixture was heated in an evacuated sealed tube to avoid Pd-catalysed oxidation of the phosphine by air,[5] but refluxing a solution of the reactants and the catalyst in xylene gave similar results. Thus from iodobenzene and triphenylphosphine, tetraarylphosphonium iodide was obtained in 80% yield by the refluxing method.

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