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NICKEL-CATALYZED SYNTHESIS OF PHOSPHONIUM SALTS

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Summary

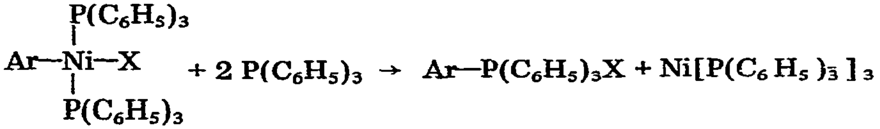
The nickel-catalyzed synthesis of phosphonium salts from aryl halides and triphenylphosphine is reported.

The formation of phosphonium salts occurs by the oxidative addition reaction of $Ni[P(C_6H_5)_3]_3$ on the aryl halides and reaction of the coordinated aryl groups with triphenylphosphine.

The influence of substituents on the aromatic nucleus is studied.

The reaction of coordinated allyl groups with triphenylphosphine to give allylphosphonium salts has been widely studied [1].

Now we wish to report that arylnickel complexes I react with triphenylphosphine to give phosphonium salts II and tris(triphenylphosphine)nickel III (eqn. 1) [2].



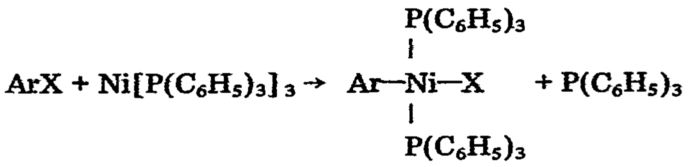
$$Ar-\underset{P(C_6H_5)_3}{\overset{P(C_6H_5)_3}{Ni}}-X + 2\,P(C_6H_5)_3 \rightarrow Ar-P(C_6H_5)_3X + Ni[P(C_6H_5)_3]_3 \qquad (1)$$

(I) (II) (III)

(X = Cl, Br, I)

Recently the formation of biaryls has been reported to occur by the thermal decomposition of complexes I [3]. We have observed that when an excess of triphenylphosphine is present in solution the formation of biaryls is strongly inhibited.

In the presence of an aryl halide the nickel complex III, formed in reaction 1, undergoes the oxidative addition and the arylnickel complexes I are readily formed [4,5] (eqn. 2).



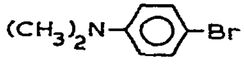
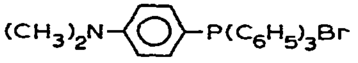
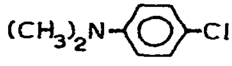
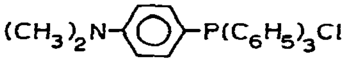
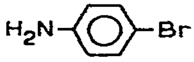
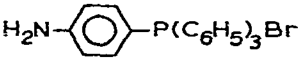
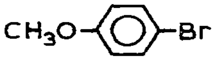
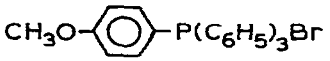
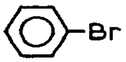
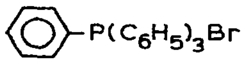
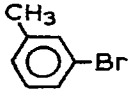
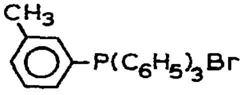
$$ArX + Ni[P(C_6H_5)_3]_3 \rightarrow Ar{-}\overset{P(C_6H_5)_3}{\underset{P(C_6H_5)_3}{Ni}}{-}X + P(C_6H_5)_3 \qquad (2)$$

(III) (I)

Thus a catalytic process results and arylphosphonium* salts are produced by treating aryl halides with triphenylphosphine in the presence of tris(triphenyl-

TABLE 1[a]

REACTIONS OF $Ni[P(C_6H_5)_3]_3$ WITH ARYL HALIDES

ArX	$ArP(C_6H_5)_3X$ (m.p. °C)	Yield[b] (%)	ArX/Ni complex[c]
		86	10
	(278–281)	87	50[e]
		58	10
	(325–327)[d]		
		77	10
	(323–326)[d]		
		85	10
	(229–231)[d]	93	10[f]
		35	10
	(294–296)		
		90	10
	(196–198)		

[a] Reactions in boiling ethanol; aryl halide and triphenylphosphine concentrations are 0.1 *M*/l, unless otherwise stated. [b] Yields are based upon the aromatic halide taken and are of isolated compounds. [c] $Ni[P(C_6H_5)_3]_3$ was used as catalyst unless otherwise indicated. [d] Melting point are of the compounds crystallized from $CHCl_3$/diethyl ether, which contain 1/2 mole of $CHCl_3$ per mole of phosphonium salt. [e] The concentration of aryl halide and triphenylphosphine is 0.46 *M*/l. [f] p-$CH_3OC_6H_4Ni[P(C_6H_5)_3]_2Cl$ was used as catalyst.

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* Other authors have reported the synthesis of phosphonium salts from aryl halides and tertiary phosphine in the presence of nickel(II) salts [6a] or several inorganic salts [6b] at 150—250°.

phosphine)nickel (eqn. 3). *trans*-Chloro(aryl)bis(triphenylphosphine)nickel(I) complexes can also be used as catalysts.

$$\mathrm{ArX} + \mathrm{P(C_6H_5)_3} \xrightarrow{\mathrm{Ni[P(C_6H_5)_3]_3}} \mathrm{ArP(C_6H_5)_3X} \qquad (3)$$

Some examples of this reaction are shown in Table 1. The reaction is general for *meta* and *para*-substituted aryl halides. Electron releasing substituents facilitate the formation of the phosphonium salts and in the case of *p*-amino- and *p*-dimethylaminobromobenzene the phosphonium salts are formed at room temperature (eqn. 3); in this case the intermediate arylnickel complex I is not easily isolable. When *para* and *meta*-electron withdrawing groups are present on the aromatic nucleus, the reaction (eqn. 3) is strongly inhibited and phosphonium salts are obtained only in low yields.

With *ortho*-substituted aryl halides the formation of phosphonium salts occurs only to a very limited extent even if electron releasing groups are present on the aromatic nucleus*. In this latter case the arylnickel complexes I can be isolated from the reaction mixture.

These observations on the substituent effect seem to indicate that both steric and electronic effects play an important role in the formation of phosphonium salts. The inhibiting action of *ortho* substituents can be attributed to their stabilizing effect on the aryl—nickel bond [8]. The strong effect of electron releasing groups suggests that the reaction involves electrophilic attack of the aryl group on the phosphorus atom. Carbonium ion character must be generated in the aryl group during the reduction of $\mathrm{Ni^{II}}$ to $\mathrm{Ni^0}$. Electron releasing substituents on the aryl group will facilitate the reduction by transferring charge to the nickel.

Experimental

All the reagents were commercially available, and were used without further purification.

$\mathrm{Ni[P(C_6H_5)_3]_3}$ [2] was prepared by treating $\mathrm{Ni[P(C_6H_5)_3]_2C_2H_4}$ with excess phosphine [9] in diethyl ether. The *trans*-chloro(*p*-anisyl)bis(triphenylphosphine)nickel was prepared from $\mathrm{Ni[P(C_6H_5)_3]_3}$ and *p*-chloroanisole [5].

All reactions were carried out under nitrogen. The products were identified by IR and NMR spectroscopy and elemental analysis. Some were also identified by comparison with known samples. Melting points were determined on a Kofler hot-stage apparatus and are not corrected.

General procedure for the synthesis of phosphonium salts

A 100 ml round bottomed flask was equipped with a magnetic stirrer, a thermometer and a water cooled condenser. The apparatus was swept out with nitrogen and $\mathrm{Ni[P(C_6H_5)_3]_3}$ (0.296 g, 0.35 mmol), ethanol (35 ml), $\mathrm{P(C_6H_5)_3}$ (0.914 g, 3.5 mmol) and *p*-bromoaniline (0.700 g, 3.5 mmol) were introduced. The boiling mixture was stirred for 24 h. The solvent was evaporated under

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* A similar substituent effect has been observed in the cyanation of arylnickel(II) complexes [7].

reduced pressure and the residue agitated with diethyl ether. The crude phosphonium salts (1.4 g, 3.0 mmol; 86%) was crystallized from $CHCl_3$ /diethyl ether.

References

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Note added in proof. A similar synthesis of phosphonium salts has been reported recently: O. Behrens, Dissertation, Mulheim a.d. Ruhr, 1973 (by courtesy of Prof. G. Wilke).