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A KINETIC TEMPLATE EFFECT IN THE METAL ION-CATALYSED FORMATION OF ARYLPHOSPHONIUM SALTS

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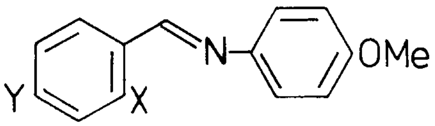
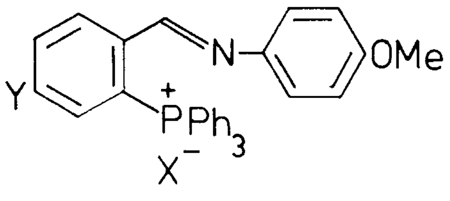
Abstract Tertiary phosphines react with o-halobenzaldimines and o-bromodiarylazo compounds, under mild conditions in the presence of a metal ion catalyst, with displacement of the halogen to form the related arylphosphonium salts. The corresponding p-haloaryl compounds do not undergo these reactions.*

While tertiary phosphines react readily with most alkyl halides to form phosphonium salts, the corresponding reactions with aryl halides only proceed at high temperatures (150-200°) in the presence of a metal salt catalyst e.g. Co(II)Br_2, Ni(II)Br_2 or Cu(II)Br_2, usually in the absence of a solvent, although these reactions have also been conducted in refluxing benzonitrile (b.p. 190°).[1-4] We wish to report preliminary details of reactions leading to the formation of arylphosphonium salts under mild conditions (refluxing ethanol), which appear to be examples of electron-transfer catalysis assisted by a kinetic template effect.

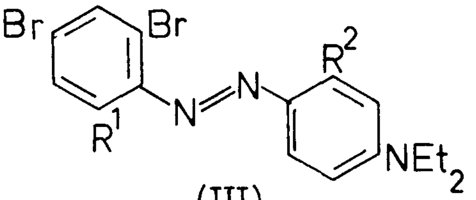


(I)

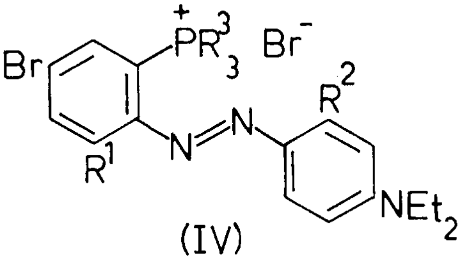


(II)

When the Schiff's base (I, X = Br, Y = H) is heated under reflux in ethanol with triphenylphosphine (2 mol.) in the presence of nickel (II) bromide (0.1 mol.), the salt (II, X = Br, Y = H) is formed over several hours. Similarly the related chlorocompound (I, X = Cl, Y = H) is also converted into the phosphonium salt (II, X = Cl, Y = H). Comparative rate studies show that the o-bromo Schiff's base undergoes the reaction at a faster rate than the o-chloro analogue. The isomeric p-halo compounds (I, X = H, Y = Cl or Br) do not react with triphenylphosphine under these conditions. The dichloro Schiff's base (I, X = Y = Cl) undergoes a regiospecific reaction in which only the o-halogen is replaced to give the salt (II, X = Y = Cl). These reactions do not take place in the absence of the nickel (II) catalyst, and also do not occur with other nucleophilic reagents, e.g. triphenylarsine. The reactions also fail to occur if the nickel (II) catalyst is replaced by cobalt (II) or copper (II) salts. The related oximes and semicarbazones derived from o-halobenzaldehydes also do not undergo these reactions, which clearly must involve some very specific co-ordination template effects in which the Schiff's base nitrogen ortho to the halogen replaced by phosphorus plays a key role.

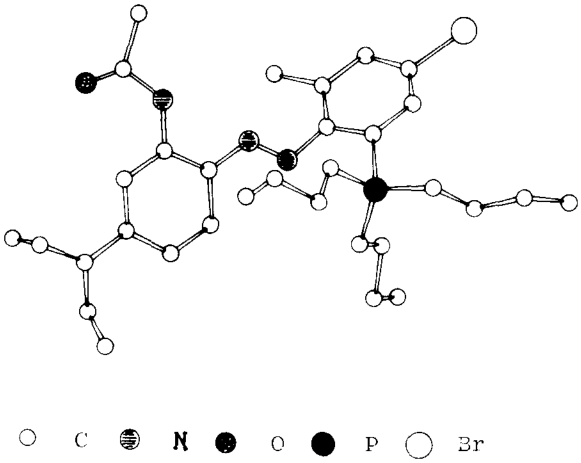


(III)



(IV)

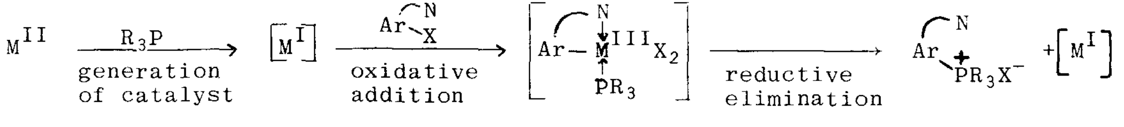
We have also found that an azo group in the ortho position to the halogen is able to function as a co-ordination template in the metal-catalysed replacement of the halogen by a tertiary phosphine. Thus the dyestuffs (III, R^1 = H or Me, R^2 = H or NHCOMe) react readily with tributyl- or triphenylphosphine (2 mol.) in refluxing ethanol in the presence of either nickel (II) bromide (0.1 mol.) or copper (II) acetate (0.1 mol.) to form the salts (IV, R^3 = Bu or Ph). The reactions all occur with complete regiospecificity with replacement of the halogen ortho to the azo group. The para-halogen is not affected. The reactions do not occur in the absence of the metal salt. Proof of structure of the phosphonium salts rests on (i) elemental analysis, (ii) ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy and (iii) the results of an X-ray crystallographic study of the salt (IV, R^1 = Me, R^2 = NHCOMe, R^3 = Bu) (Figure).



Crystal Data: *Crystals suitable for X-ray study were obtained from chloroform-ether. Monoclinic,*
$\underline{a}$ = 25.696, $\underline{b}$ = 10.910,
$\underline{c}$ = 25.363Å; β = 90.63°.
Space group C2/c, Z = 8.
R = 0.069 for 710 reflections classified as observed,
$I/\sigma(I) \geq 3.0$

(Figure) Structure of the cation of phosphonium salt (IV, R^1 = Me, R^2 = NHCOMe, R^3 = Bu)

The formation of the above o-phosphoniodiarylazo compounds (IV) has much in common with related reactions of o-bromodiarylazo compounds with triethylphosphite (and diethylphosphite) in ethanol, catalysed by copper (II)[5-7] acetate, which lead to the formation of o-diethylphosphonatodiarylazo compounds. There are, nevertheless, some significant points of difference. Price et al have shown that in the reactions with phosphites, only those dyestuffs in which $R^1 \neq H$ undergo the reaction readily, and also that those in which R^2 = NHCOMe (or some other potential co-ordinating group) react faster than those in which R^2 = H. These reactions are also only catalysed by copper (II). In the above reactions with phosphines, however, it is not necessary to have a group R^1 other than hydrogen at C6 and both nickel (II) and copper (II) salts function as catalysts. Indeed, these reactions also take place in the presence of cobalt (II) salts, but at a considerably slower rate. Furthermore, whereas dyestuffs in which R^2 = NHCOMe react faster with phosphines in the presence of a copper (II) catalyst than those in which R^2 = H, the reverse is the case for the related reactions catalysed by nickel (II) salts. Again the involvement of some very specific co-ordination effects is implied.



Scheme

It is likely that these reactions involve electron-transfer catalysis (ETC)[8], in which the metal salt is initially reduced to a lower oxidation state e.g. Ni^{I} (the active catalytic species), which then undergoes a co-ordination template-assisted oxidative-addition step, followed by formation of the P-C bond and a reductive-elimination of the product, with regeneration of the catalyst, as in the Scheme. Reduction of copper (II) to copper (I) by phosphorus (III) compounds is well-known[9,10]. The related reduction of nickel (II) to nickel (I) is less well-documented, but it has been shown that the zerovalent nickel complex $[(EtO)_3P]_4Ni$ is formed when nickel (II) chloride is heated in triethylphosphite.[11] Oxidative-addition of aryl halides to nickel (O) and nickel (I) species is now well-established[12-14] and so too is the formation of arylphosphonium salts from arylnickel (II) and arylnickel (III) intermediates.[14,15]

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