Copper(II) Ethanoate-assisted Phosphonation of Aryl Halides

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Summary A mixed valence trinuclear copper complex $[\mathrm{Cu_3(OAc)_5\{P(OR)_3\}_2}]$ is formed in the reaction between a 2-halogenoaryl azo compound and a trialkyl phosphite in the presence of copper(II) ethanoate which gives the corresponding 2-(dialkylphosphonato)aryl azo compound.

The nature of the copper-containing species which participate in the Ullmann[1] reaction is poorly defined, in spite of various investigations.[2,3] The recent report[4] that copper(II) salts promote the reaction between various 2-bromodiarylazo compounds and trialkyl phosphites to give the corresponding 2-(dialkylphosphonato)diaryl azo compounds in the manner of a Delfs reaction,[5] has led to this study which has concentrated upon the role of the metal.

Copper(II) ethanoate reacts with trialkyl phosphites $\mathrm{P(OR)_3}$ (R = Me, Et, or $\mathrm{Pr^i}$) in dry alcohol, ROH, under anaerobic conditions to form green, air sensitive crystalline complexes† $[\mathrm{Cu_3(OAc)_5\{P(OR)_3\}_2}]$, (**1**). The complex (**1a**) (R = Et) has been shown by *X*-ray diffraction[6] to have the unusual 1-dimensional polymeric structure (A), in which a conventional copper(II) ethanoate unit provides an ethanoate ligand as a bridge to a $[\mathrm{Cu^I(OAc)\{P(OEt)_3\}_2}]$ unit which, in turn, provides the axial ethanoate ligand linking the copper(II) chain. The $(\mathrm{Cu^{II}O_2Cu^I})$ ring is not planar.

Reaction of complex (**1a**) with pyridine in ethanol results in cleavage of the $(\mathrm{Cu^{II}O_2Cu^I})$ bridge and formation of $[\mathrm{Cu_2(OAc)_4py_2}]$, together with the air sensitive *liquid* (m.p. 285 K) complex† $[\mathrm{Cu(OAc)\{P(OEt)_3\}_2}]$, (**2**) which is probably dimeric. Compound (**2**) is also formed together with triethyl phosphate when (**1a**) reacts with an excess of triethyl phosphite. The copper(I) complex, (**2**), reacts with bidentate ligands, L, such as 2,2′-bipyridyl, 1,2-diaminoethane, and 1,2-bis(diphenylphosphino)ethane to form mononuclear four co-ordinate complexes† $[\mathrm{Cu(OAc)\{P(OEt)_3\}L}]$, (**3**). It is noteworthy that monodentate ligands such as pyridine do not form complexes analogous to (**3**) under similar conditions. Complexes (**3**) undergo reversible release of the phosphite ligand in solution. There is no evidence that this happens in the case of (**1a**) or (**2**)

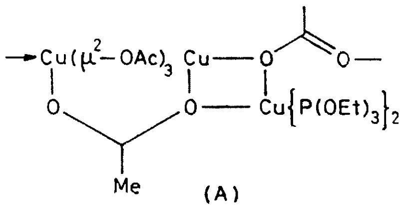
The azo compound (**4a**) reacts with triethyl phosphite in the presence of copper(II) ethanoate in boiling ethanol [conditions which, in the absence of (**4a**), give (**1a**) and (**2**)] to produce the phosphonate (**4b**) in high yield.[4] We find that the copper complexes (**1a**), (**2**), and (**3**) (L = bipy), when mixed with (**4a**) in ethanol at ambient temperature in the absence of added triethyl phosphite, also give (**4b**) together with minor quantities of the products of reductive replacement, (**4c**) and biaryl coupling. The relative rate of the second order reaction which is first order in (**4a**) and first order in copper-triethyl phosphite complex, decreases in the order (**1a**) (30) > (**2**) (10) > (**3**) (1). The yield of biaryl coupling increases in the order (**1a**) (4%) < (**2**) (12%) < (**3**) (25%).

$[\mathrm{Cu_3(OAc)_5\{P(OR)_3\}_2}]$
(1)
a, R = Et

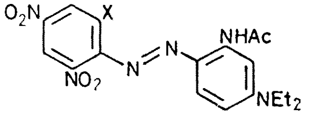
$[\mathrm{Cu^I(OAc)\{P(OEt)_3\}_2}]$
(2)

$[\mathrm{Cu(OAc)\{P(OEt)_3\}L}]$
(3)

L = 2,2′-bipyridyl, 1,2-diaminoethane, or 1,2 bis-(diphenylphosphino)ethane, etc



(A)



(4)
a, X = Br
b, X = P(O)(OEt)2
c, X = H

Detailed analysis of the products of these reactions showed that, in each case, the ethyl group lost from triethyl phosphite is isolated as ethyl ethanoate. This is consistent with nucleophilic attack by ethanoate upon the co-ordinated phosphite to give phosphonate, for which precedent exists.[7] The bromide ion lost from (**4a**) is isolated as $[\mathrm{CuBr\{P(OEt)_3\}}]$. These observations indicate that the reaction is not of the Michaelis Arbusov type.

There is no evidence for the formation of a stable chelate complex between (**4a**) and any of the copper compounds (**1a**), (**2**), (**3**), although it is well known that, for example, 2-hydroxydiaryl azo compounds readily form complexes with copper.[8] However, we find that any halides lacking

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† Satisfactory analytical (C,H,Cu,N,P) and spectroscopic characterisation was obtained for all new complexes.

the additional donor sites are unreactive under these conditions. This suggests that the aryl cation radical produced following inner sphere electron transfer[9] needs to be stabilised transiently within the copper co-ordination sphere while undergoing nucleophilic attack by the phosphonate ligand.

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