# Deoxygenation of 2-Nitrosophenols and of their Metal Complexes with Triphenylphosphine. Synthesis of Phenazines, Dihydrophenazines, Triphenyl(*o*-hydroxyphenylimino)phosphoranes and their Metal Complexes

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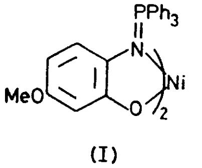
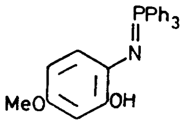
*Summary* Deoxygenation of 2-nitrosophenols with $Ph_3P$ affords dihydrophenazines, whereas deoxygenation of their $Ni^{II}$, $Cu^{II}$, $Zn^{II}$, and $Fe^{III}$ complexes yields phenazines or complexes of triphenyl(*o*-hydroxyphenylimino)-phosphoranes depending on the metal; these reactions are interpreted in terms of nitrene intermediates.

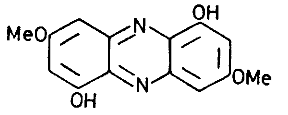
NITRENES are of considerable interest and figure prominently as reactive intermediates.[1] In some cases these species have been trapped as metal complexes.[2] In attempting to obtain nitrene complexes by deoxygenation of metal complexes of 2-nitrosophenols with triphenylphosphine we have discovered several reactions of interest and potential synthetic utility. Here we report on reactions which yield 1,6-dihydroxyphenazines or metal complexes of triphenyl(*o*-hydroxyphenylimino)phosphoranes and which may involve intermediate nitrene species. Analogous reactions of free 2-nitrosophenols leading to 1,6-dihydroxy-5,10-dihydrophenazines are also described.



(I)

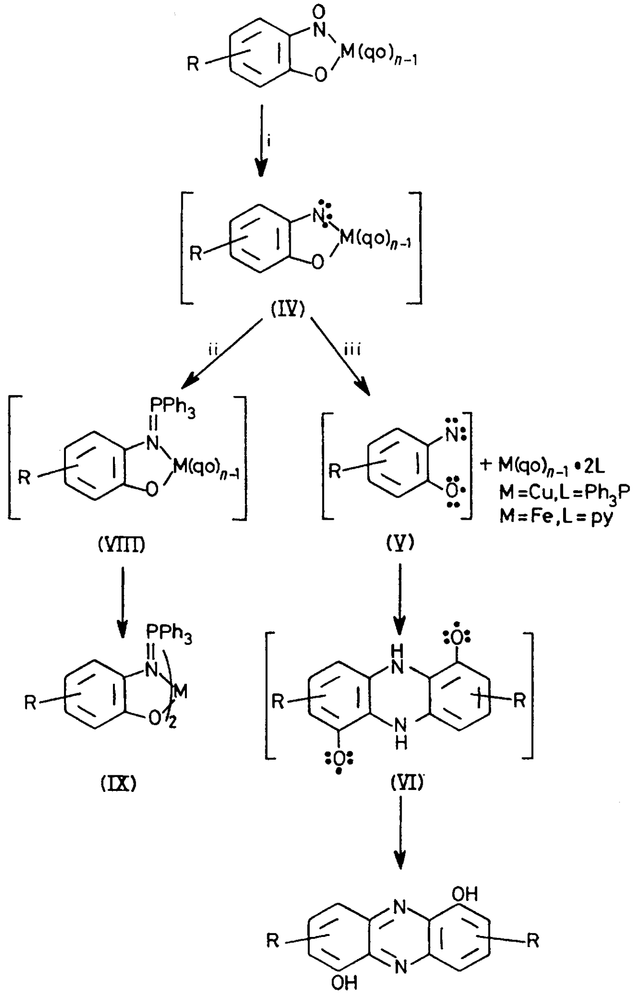


(II)



(III)

The complexes $M(qo)_n$ (qoH = 5-methoxy-2-nitrosophenol; $n$ = 2, M = Ni, Cu, or Zn; $n$ = 3, M = Fe) react readily at 20 °C with $Ph_3P$ to give $Ph_3PO$ and other products whose nature depends on the metal. Thus, $Ni(qo)_2$ (1 mol. equiv.) and $Ph_3P$ (5 mol. equiv.) in chloroform or pyridine give the iminophosphorane complex $Ni(qoPPh_3)_2$ (I) (40%)† which, on treatment with aqueous HCl, affords the protonated ligand (II) (65%). Analogous behaviour is shown by $Zn(qo)_2$. In contrast reaction of $Cu(qo)_2$ (1 mol. equiv.) with $Ph_3P$ (5 mol. equiv.) in chloroform or pyridine results in reduction of the metal and formation of the complex $Cu(qo)(PPh_3)_2$ (40%) and of the phenazine (III) (50%). Similarly, reaction of $Fe(qo)_3$ (1 mol. equiv.) with $Ph_3P$ (3 mol. equiv.) in pyridine (py) results in the formation of the phenazine (III) (30%) and of the diamagnetic iron(II) complex $Fe(qo)_2.2py$.



SCHEME. i, $+Ph_3P$, $-Ph_3PO$; ii, $+Ph_3P$, M = Ni or Zn, $n$ = 2; iii, M = Cu, $n$ = 2; M = Fe, $n$ = 3. qoH = 2-Nitrosophenol. py = Pyridine.

Corresponding results have been obtained with several other $M(qo)_n$ (qoH = a 2-nitrosophenol; $n$ = 2, M = Cu or Ni; $n$ = 3, M = Fe) complexes. Since such complexes are readily available,[3] by the nitrosation of phenols in the presence of metal salts, the present investigations provide

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† Yields quoted in the text refer to pure, recrystallised products.

convenient, widely applicable, routes to 1,6-dihydroxyphenazines and iron(II) 2-nitrosophenol complexes of the type $Fe(qo)_2$. Iminophosphorane complexes of type (I) have not been previously reported but recently the synthesis of several triphenyl(*o*-hydroxyphenylimino)phosphoranes has been described.[4]

The reaction of 5-methoxy-2-nitrosophenol (1 mol. equiv.) with $Ph_3P$ (1 or 5 mol. equiv.) in chloroform or pyridine at 20 °C gives 3,8-dimethoxy-1,6-dihydroxy-5,10-dihydrophenazine (50%) and traces of triphenyl (*o*-hydroxy-4-methoxyphenylimino)phosphorane. Although other 2-nitrosophenols behave similarly, the utility of the system 2-nitrosophenol–$Ph_3P$ for the synthesis of dihydrophenazines is limited because only a few 2-nitrosophenols are known.

The formation of dihydrophenazines, phenazines, and iminophosphorane complexes in the reactions outlined above may be envisaged as proceeding *via* the intermediate formation of nitrenes or nitrene metal complexes (Scheme). Formation of the $\geqslant$P=N– linkage in deoxygenation reactions of nitroso-compounds with tervalent phosphorus compounds is indicative of nitrene intermediacy.[15] Furthermore nitrenes have been postulated as intermediates in reactions involving deoxygenation of complexed nitroso-compounds[6] and in the formation of phenazines by the thermolysis of azides.[7] In the latter, reaction is accompanied by amine formation and has been ascribed to the dimerisation of anilino-radicals derived from triplet nitrenes by hydrogen abstraction. Although the differing behaviour of the metal complexes of 2-nitrosophenols towards $Ph_3P$ is not clearly understood, it parallels the readiness of the metal to undergo reduction and can be rationalised in these terms. As shown in the Scheme, it is assumed that deoxygenation of one of the ligands of the complex $M(qo)_n$ occurs initially to give the intermediate nitrene complex (IV). When M = Cu or Fe, reduction of the metal in (IV) leads to the nitrene species (V) and an adduct of the complex $M(qo)_{n-1}$. Subsequent dimerisation of (V) or interaction of (V) with $M(qo)_n$ or (IV) leads to (VI) which, on rearrangement, gives the phenazine (VII). When M = Ni or Zn, reduction of the metal is not easy and thus (IV) couples with $Ph_3P$ to give (VIII) and finally the iminophosphorane complex (IX).

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