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(Pyridine)bis(8-quinolinato)oxovanadium(IV): A Free-Radical-like Metal Center in Reactions with Dioxygen, *p*-Benzoquinone, and Aromatic Nitroso Compounds

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A novel synthesis of bis(8-quinolinato)oxovanadium(IV), VOQ_2 (Q = 8-quinolinato anion), and the corresponding pyridine adduct, $pyVOQ_2$, is reported. Although both have been found to be reactive in one-electron redox processes, $pyVOQ_2$, which is soluble in organic solvents, was used as a model compound. $pyVOQ_2$ reacts very easily at room temperature and atmospheric pressure with O_2 producing the diamagnetic dinuclear μ-oxo complex $[Q_2OV{-}O{-}VOQ_2]$. When O_2 is replaced by *p*-benzoquinone in the same reaction, the dinuclear diamagnetic vanadium(V) complex $[Q_2OVO{-}C_6H_4{-}OVOQ_2]$ is obtained. The high affinity for oxygen along with the tendency to achieve both the +5 oxidation state and hexacoordination by vanadium in these complexes could be the driving force for the observed vanadium-promoted deoxygenation of aromatic nitroso compounds. $pyVOQ_2$ reacts with nitrosobenzene and 2-nitrosobiphenyl (ArNO) in a tetrahydrofuran (THF) solution giving $[Q_2OV{-}O{-}VOQ_2]$ and the corresponding azoxy derivatives (ArN(O)=NAr). The deoxygenation of 2-nitrosobiphenyl with $P(OR)_3$ produces only carbazole, which is supposed to be originated by a singlet nitrene, while the deoxygenation by $pyVOQ_2$ gives azoxybiphenyl without traces of carbazole.

Introduction

One of the most outstanding aspects of recent coordination chemistry is the investigation on model compounds which, for their electronic configuration and coordination geometry, exhibit reactivity patterns related to those of very well-known organic intermediates, carbenes and free radicals.[1]

In spite of their usual very low reactivity,[2] oxovanadium chelate complexes could be assumed as models for reactivity studies on the V=O ketone-like unit,[3-5] as well as free-radical-like activators of organic and inorganic molecules. A useful formalism based on the electronic configuration (d^1) of vanadium(IV) and on its coordination number, which is usually 5 in square-pyramidal geometry for oxovanadium complexes, may indicate a free-radical-like behavior. This is highly reminiscent of the very well-known reactivity pathways displayed by the d^7 low-spin five-coordinate cobalt(II) complexes $[Co(CN)_5]^{3-}$ [6] and (pyridine)[*N*,*N*′-ethylenebis(salicylideniminato)]cobalt(II), pyCo(salen).[7] In both classes of complexes, the metal undergoes a one-electron oxidative addition.[6] This chemical behavior is highly dependent on the ability of polydentate unsaturated ligands to stabilize a wide range of oxidation states of a coordinated metal ion.[8] It was found that this role is played in oxovanadium chemistry by the 8-quinolinol ligand, Q, in VOQ_2 and $LVOQ_2$ [L = solvent]. The redox chemistry of VOQ_2 was recently electrochemically explored, and the III, IV, and V oxidation states have been found easily accessible for vanadium when coordinated to this ligand.[9] An improved synthesis of VOQ_2 and VOQ_2py is reported, along with their transformation into hexacoordinate vanadium(V) complexes under very mild conditions by the action of dioxygen, *p*-benzoquinone, and aromatic nitroso compounds. An interesting relationship between this chemistry and the properties of bis(3,5-di-*tert*-butylcatecholato)vanadium(IV), which shows reversible binding of NO and O_2, could be found.[10]

Experimental Section

Unless otherwise stated, all the reactions described here were carried out under an atmosphere of purified nitrogen; solvents were purified by standard methods. Infrared spectra of the solid complexes in KBr disks were recorded with a Perkin-Elmer Model 282 spectrophotometer. Magnetic susceptibility measurements were made by the Faraday method with diamagnetic corrections through use of Pascal's constants. The O_2 absorption was measured by using a gas volumetric apparatus. Bis(pentane-2,4-dionato)oxovanadium(IV) was prepared as described previously.[11]

Preparations. Bis(8-quinolinato)oxovanadium(IV), VOQ_2. Solid oxobis(pentane-2,4-dionato)oxovanadium(IV) (1.96 g, 7.4 mmol) was added to a solution of 8-quinolinol (2.15 g, 14.8 mmol) dissolved in 100 mL of dried benzene. A dark brown solution resulted from which VOQ_2 precipitated upon standing as brown microcrystalline solid in good yield (2.10 g, 80%). Anal. Calcd for $VC_{18}H_{12}N_2O_3$: C, 60.84; H, 3.38; N, 7.89. Found: C, 60.50; H, 3.45; N, 7.90. $\nu_{V=O}$(Nujol) = 963 cm^{-1}. μ(293 K) = 1.75 μ_B.

(Pyridine)bis(8-quinolinato)oxovanadium(IV). Method A. To 2.28 g of 8-quinolinol (15.17 mmol) dissolved in 50 mL of benzene and 30 mL of dried pyridine was added 2.0 g (7.5 mmol) of bis(pentane-2,4-dionato)oxovanadium(IV). A dark brown solution resulted. After 4 h the solvent was completely removed by heating in vacuo and the resulting dark brown solid was dissolved in 50 mL of benzene. The benzene solution gave, upon standing, $pyVOQ_2{\cdot}C_6H_6$ as a green microcrystalline solid (3.1 g, yield 80%). The solid is reasonably soluble in benzene and readily soluble in tetrahydrofuran (THF) and pyridine (py). Anal. Calcd for $VC_{29}H_{23}N_3O_3$: C, 67.97; H, 4.49; N, 8.20. Found: C, 67.85; H, 4.63; N, 8.05. $\nu_{V=O}$(Nujol) = 945 cm^{-1}. μ(295 K) = 1.64 μ_B. The presence of C_6H_6 and pyridine was confirmed by mass spectrum and GLC analysis. A THF solution of $VOQ_2py{\cdot}C_6H_6$ treated with dioxygen (vide infra) showed the presence of pyridine and C_6H_6 in 1/1 ratio determined by GLC. Molecular weight was determined by cryoscopy in benzene: calcd for $VC_{23}H_{17}N_3O_3$, 434; found, 442.

Method B. VOQ_2 (I) (0.7 g, 1.97 mmol) was suspended in 20 mL of pyridine, and the mixture was refluxed for 5 h. A brown solution was obtained from which $pyVOQ_2{\cdot}C_6H_6$ was obtained by addition of benzene (0.51 g, 50% yield). Anal. Calcd for $VC_{29}H_{23}N_3O_3$: C, 67.96; H, 4.49; N, 8.20. Found: C, 67.97; H, 4.64; N, 8.10.

Bis(2-methyl-8-quinolinato)oxovanadium(IV). To a toluene (150 mL) solution of 2-methyl-8-quinolinol, 2-Me-QH (6.02 g, 37.86 mmol) was added $VO(acac)_2$ (5 g, 18.8 mmol). The suspension was stirred overnight and the starting blue $VO(acac)_2$ was converted into a maroon-green microcrystalline solid (6.8 g, 95.6% yield). Anal. Calcd for $VO(2\text{-}Me\text{-}Q)_2$, $C_{20}H_{16}N_2O_3V$: C, 62.66; H, 4.18; N, 7.31. Found: C, 62.31; H, 4.07; N, 7.26. The reaction, when carried out in the presence of benzene (100 mL) and pyridine (50 mL), gave the unsolvated $VO(2\text{-}Me\text{-}Q)_2$. When $VO(2\text{-}Me\text{-}Q)_2$ was refluxed for 12 h in dry pyridine, the starting material was recovered unchanged. No absorption of O_2 was observed when 1.0 g of $VO(2\text{-}Me\text{-}Q)_2$ was suspended in 20 mL of DMF in a gas-volumetric apparatus.

Absorption of Dioxygen by $pyVOQ_2$. (a) $pyVOQ_2{\cdot}C_6H_6$ (2.91 g, 5.69 mmol) was dissolved in 80 mL of THF under nitrogen. The reaction flask was evacuated and then filled with O_2 dried over P_2O_5. A few minutes later, $[VOQ_2]_2O$ precipitated out as microcrystalline black solid, which was very well washed with THF (2.0 g, 97%). Anal. Calcd for $V_2C_{36}H_{24}N_4O_7$: C, 59.60; H, 3.31; N, 7.71. Found: C, 58.86; H, 3.42; N, 7.38. χ_M^{cor}(293 K) = +195 × 10^{-6} cgsu; $\nu_{V=O}$(Nujol) = 950 cm^{-1}; $\nu_{V=O}$(Nujol) = 715 cm^{-1}.

(b) A 1.183-g sample of $pyVOQ_2{\cdot}C_6H_6$ in 20 mL of DMF absorbed 13.5 mL of O_2 in 30 min at 15.8 °C, corresponding to O_2/V = 0.249.

(c) A 1.081-g sample of $pyVOQ_2{\cdot}C_6H_6$ in 20 mL of py absorbed 12.0 mL of O_2 in 24 h at 15 °C, corresponding to O_2/V = 0.242.

Dioxygen Absorption by VOQ_2. VOQ_2 (0.5 g) gives, in boiling DMF (50 mL), a deep green solution which reacts rapidly at room tem-

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perature with O_2 and in 2 h $[VOQ_2]_2O$ separates.

The dioxygen absorption by VOQ_2 suspended in different solvents at 16 °C has been followed gas volumetrically: (a) 0.831 g (2.38 mmol) in DMF (20 mL) absorbs 0.58 mmol of O_2 in 2 days [$O_2/V = 0.243$]; (b) 0.489 g (1.40 mmol) in dry acetone (20 mL) absorbs 0.33 mmol of O_2 in 3 h [$O_2/V = 0.235$]; (c) 0.782 g (2.24 mmol) in dry toluene (20 mL) absorbs 0.113 mmol of O_2 in 2 days [$O_2/V = 0.050$].

Reaction of $pyVOQ_2$ with *p*-Benzoquinone. $pyVOQ_2 \cdot C_6H_6$ (1.40 g, 2.73 mmol) was dissolved in THF (50 mL) and to the resulting solution was added *p*-benzoquinone (0.143 g, 1.30 mmol). Black solid starts immediately to precipitate (0.90 g, 80% yield). Anal. Calcd for $V_2C_{42}H_{28}N_4O_8$: C, 61.41; H, 3.42; N, 6.48. Found: C, 61.47; H, 4.26; N, 6.54. $\nu_{V=O}$(Nujol) = 960 cm^{-1}; χ_M^{cor}(293 K) = 278 × 10^{-6} cgsu. The mass spectrum did not show the presence of the parent peak.

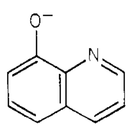
Deoxygenation of Nitrosobenzene and 2-Nitrosobiphenyl by $pyVOQ_2$. Nitrosobenzene (0.33 g, 3.1 mmol) was added to 50 mL of THF containing 1.06 g of $pyVOQ_2 \cdot C_6H_6$ (2.07 mmol). The color of the solution changed from brown to black in 2 h. Black microcrystalline solid started to separate after 1 day (0.52 g, 70% yield). Anal. Calcd for $V_2C_{36}H_{24}N_4O_7$: C, 59.50; H, 3.31; N, 7.71. Found: C, 58.74; H, 3.35; N, 7.78. The solid, identified by the IR spectrum, was filtered out, and the solution evaporated to dryness gave a residue soluble in benzene. The benzene solution was shown by thin-layer chromatography to contain nitrosobenzene and azoxybenzene only, which have been separated by chromatography on silica gel. By elution with benzene (30%) and hexane (70%), azoxybenzene has been recovered (mp 36 °C).

The deoxygenation of 2-nitrosobiphenyl (0.71 g, 3.89 mmol) by $pyVOQ_2 \cdot C_6H_6$ (1.99 g, 3.89 mmol) was carried out in THF (60 mL) under the same conditions. The reaction is much slower. The solid μ-oxo compound separated in 3 days. Thin-layer chromatography of the solution showed the presence of azoxybiphenyl, which was isolated (mp 158 °C).

Results and Discussion

The synthesis of bis(8-quinolinato)oxovanadium(IV), VOQ_2 [Q = 8-quinolinato anion], is performed by having a benzene solution of 8-quinolinol react with bis(pentane-2,4-dionato)oxovanadium(IV), $VO(acac)_2$ (eq 1). II is obtained as a

$$\underset{\text{I}}{VO(acac)_2} + 2QH \longrightarrow \underset{\text{II}}{VOQ_2} + 2acacH \qquad (1)$$



Q = 8-quinolinol anion (oxine)

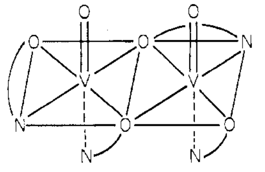
yellow-brown microcrystalline solid [$\nu_{V=O}$(Nujol) = 963 cm^{-1}; μ_{eff} = 1.75 μ_B at 293 K].[8] When reaction 1 is carried out in the presence of pyridine (py), $pyVOQ_2$, III,[12] is obtained as a green microcrystalline solid [$\nu_{V=O}$(Nujol) = 945 cm^{-1}; μ_{eff} = 1.64 μ_B at 295 K] containing benzene of crystallization. While II is very poorly soluble in all solvents, III·C_6H_6 is soluble in THF, acetone, and benzene, in which it is monomeric. We note that, contrary to an earlier report, II was converted to III in boiling pyridine, from which III·C_6H_6 is recovered by addition of benzene. When a THF solution of $pyVOQ_2 \cdot C_6H_6$ is kept standing for a long time, it loses pyridine and gives back the much less soluble VOQ_2.

On the basis of the results outlined above, equilibrium 2 is

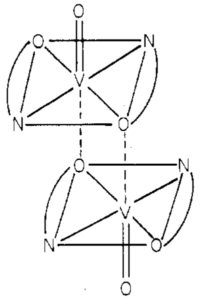
$$\underset{\text{II}}{VOQ_2} + py \rightleftarrows \underset{\text{III}}{pyVOQ_2} \qquad (2)$$

suggested. While the monomeric nature of III is proved by a molecular weight determination in benzene, the molecular complexity of II will be discussed later. The color of the oxovanadium complex may be diagnostic for the presence of a formally five-coordinate (yellow-maroon) or six-coordinate monomeric (green) vanadium complex. The earlier synthesis of II is carried out in aqueous solution by using oxovanadium sulfate and 8-quinolinol.[9,12-14] This synthesis, however, generally affords a mixture of two complexes, VOQ_2 and $(H_2O)VOQ_2$. The mixture of these two species has been so far employed as a single well-defined complex.[9] At this point, it would be interesting to compare the properties of bis(2-methyl-8-quinolinato)oxovanadium(IV), $(2\text{-Me-Q})_2VO$, for which the solid-state structure is known,[15] with those of II. Although the synthesis of $(2\text{-Me-Q})_2VO$, IV, was carried out in aqueous solution by the same procedure cited above, complex IV is obtained without a coordinated water molecule.[15] When 8-quinolinol is replaced with 2-methyl-8-quinolinol in reaction 1, IV is obtained as a maroon-yellow microcrystalline solid [$\nu_{V=O}$(Nujol) = 970 cm^{-1}]. Its conversion to the pyridinato derivative does not occur either by carrying out the synthesis in the presence of pyridine or by boiling IV in dry pyridine. The failure to obtain a solvated species of IV can be explained by its trigonal-bipyramidal structure, which is rather unaccessible to potential donor ligands. It should be noticed that the tendency to achieve hexacoordination is probably parallel to the tendency to participate in redox processes with electron-acceptor molecules, such as O_2 and quinones, which remain in the coordination sphere of the metal.

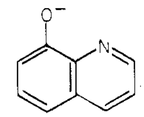
On the basis of the very low solubility, the tendency to produce highly soluble solvated species, and the equilibrium depicted in reaction 2, the dimeric structures A and B can be proposed for II. Vanadium achieves hexacoordination in the solid state in both cases sharing one oxygen donor of the oxine ligand between two metal atoms.[16] The V=O stretching frequency (963 cm^{-1}) excludes that the vanadyl oxygen, as found for other complexes, might be involved in the dimerization process.[17] Such dimerization is very well-known in salen derivatives of many transition metals.[18] The reaction of II with coordinating solvents would cleave the dimeric structure with a molecule of solvent occupying the sixth position around vanadium.[19] Recent work seems to suggest a cis arrangement of the vanadyl oxygen with the coordinating solvent.[9]

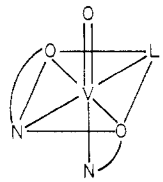


A



B

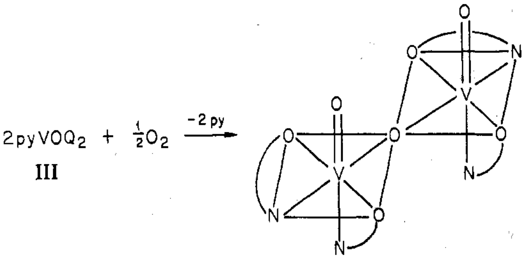
ON =  , oxine



L = H_2O, py,...

This would induce one to prefer A instead of B for the proposed dimeric structure of II. While both II and III are transformed under mild conditions into hexacoordinate vanadium(V) derivatives by the action of dioxygen, *p*-benzoquinone, and nitroso compounds, $(2\text{-Me-Q})_2VO$ is completely unreactive toward dioxygen. On the basis of the considerations outlined above, it seems reasonable to suppose that the access to the hexacoordination by vanadium(IV) may be the step controlling its conversion into vanadium(V) derivatives by oxidative addition reactions.

Reaction with Dioxygen. Solutions of $pyVOQ_2$ in THF, *N,N*-dimethylformamide, DMF, and pyridine, py, react with dioxygen at room temperature, producing the known dinuclear μ-oxo complex V, for which the proposed structure is sketched[9,14,20,21] (eq 3). The amount of dioxygen absorbed was followed gas volumetrically. While the absorption of O_2 is fairly fast in DMF (30 min) and THF, an equimolar solution in pyridine absorbs O_2 in 24 h. Complex V is formed by a very slow absorption of O_2 by a suspension of II in DMF, acetone, and THF, the slowest absorption being observed for a toluene suspension, while a rather dilute solution of II in DMF (see Experimental Section) absorbs O_2 very rapidly. No absorption of O_2 was observed by using $(2\text{-Me-Q})_2VO$ in the same solvents.

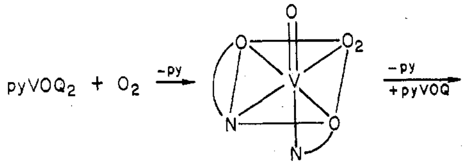


III

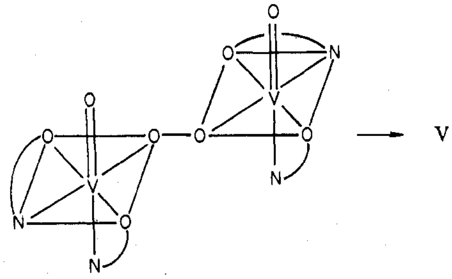
V

(3)

In the most likely first step of reaction 3, O_2 would produce the substitution of the pyridine ligand, generating a superoxovanadium(V) complex:



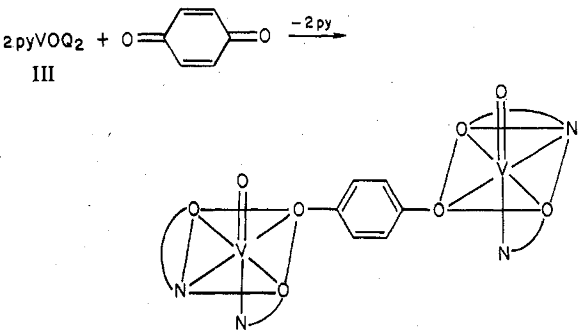
VI



V (4)

The same result can be achieved with O_2 causing the cleavage of the dimeric structure of II. It was previously suggested that superoxo complexes like VI produce μ-oxo dinuclear complexes, as exemplified in (4).[22]

The slowing of the O_2 absorption rate observed in a pyridine solution of III vs. solutions in less coordinating solvents, such as DMF and THF, is due to the competition of pyridine with oxygen in filling the sixth coordination site around vanadium. The apparently higher reactivity of III compared with II might depend on the fact that the very low solubility of II prevents one from having finite concentration of II in solution. Henceforth III will be used as a model compound in redox reactions, by virtue of its good solubility. It should be pointed out that, while the nature of V is well established in the literature,[9,20,21] its synthesis is described as formation from a dehydration process on the hydroxo complex $OVQ_2(OH)$ under drastic conditions or more quantitatively by use of ester derivatives $VO(OR)Q_2$.[9,20] Some insight into the reaction between III and O_2 would come from replacing it with *p*-benzoquinone, which can be used as a model molecule imitating the dioxygen molecule in many aspects, i.e., the formation of superoxo- and peroxo-like species.[23,24] A THF solution of $pyVOQ_2$ reacts with *p*-benzoquinone producing a black microcrystalline solid, VII (eq 5). VII is diamagnetic and its mass spectrum shows a *m*/*e* peak corresponding to the dinuclear unit $V_2O_4C_6H_4$. Although molecular weight determination in solution is prevented by the very low solubility of VII, its formulation as a dinuclear peroxo-like complex[23,24] seems the natural consequence of the diamagnetism and its stoichiometry. Moreover, the IR spectrum (Nujol) does not show any band at 1700–1600 cm^{-1}. This is an indication that *p*-benzoquinone has undergone a significant reduction to either a semiquinone of a hydroquinone.[23,24] Reaction 5 is supposed to produce, in a first step, a semiquinone complex which undergoes a further attack by a free-radical vanadyl complex producing the final peroxo-like complex.[23,25] VII can be assumed as a structural model for the supposed peroxo complex. The relative arrangement of the groups in VII is based on the proposed structures of similar μ-oxo complexes,[20,21] while an X-ray analysis carried out on $VOQ_2(O\text{-}i\text{-Pr})$ confirms the main feature of this structure: the cis configuration of the terminal oxygen and the isopropoxo ligand.[26]



III

VII

(5)

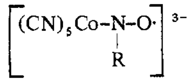
Deoxygenation of Aromatic Nitroso Compounds. Deoxygenation reactions received wide attention in synthetic organic chemistry, where the reagent *par excellence* is $P(OEt)_3$.[27] This reaction occurs catalytically by means of transition-metal carbonyls, which reduce nitro and nitroso compounds by the action of CO which is converted into CO_2.[28] Very recently stoichiometric oxygen transfers from nitro and nitroso compounds to transition metal complexes have been found to involve the metal center.[29,30] Nitrosobenzene and 2-nitrosobiphenyl are deoxygenated in THF solution by $pyVOQ_2$, giving the corresponding azoxy derivatives; $pyVOQ_2$ is oxidized to the μ-oxo derivative V, which crystallizes out from the solution:

$$\underset{\text{III}}{2pyVOQ_2} + 2ArNO \xrightarrow{-2py} ArN(O){=}NAr + Q_2OV{-}\underset{\text{V}}{O}{-}VOQ_2 \quad (6)$$

The yield of a azoxy derivative is practically quantitative, and in both cases it is the only detectable product. Azoxybenzene is not further deoxygenated by $pyVOQ_2$, as it was found with [*N,N'*-ethylenebis(salicylideniminato)]iron(II), Fe(salen),[29] and uranocenes.[30]

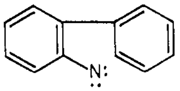
It was suggested that azo and azoxy derivatives are formed either by the deoxygenation of the nitroso dimer or by a coupling of the nitroso functional group with an intermediate nitrene.[27] The most likely first step of this reaction is the displacement of the pyridine molecule by the nitroso group oxygen[31] at the vanadium atom with concurrent electron transfer from the metal to the nitroso group, which may be attacked by a second metal[32] generating V and a nitrene species. A model reaction exemplifying this first step could be found in the interaction of the free-radical-like $[Co(CN)_5]^{3-}$

adding to nitro and nitroso compounds producing a nitroxide radical:[33]

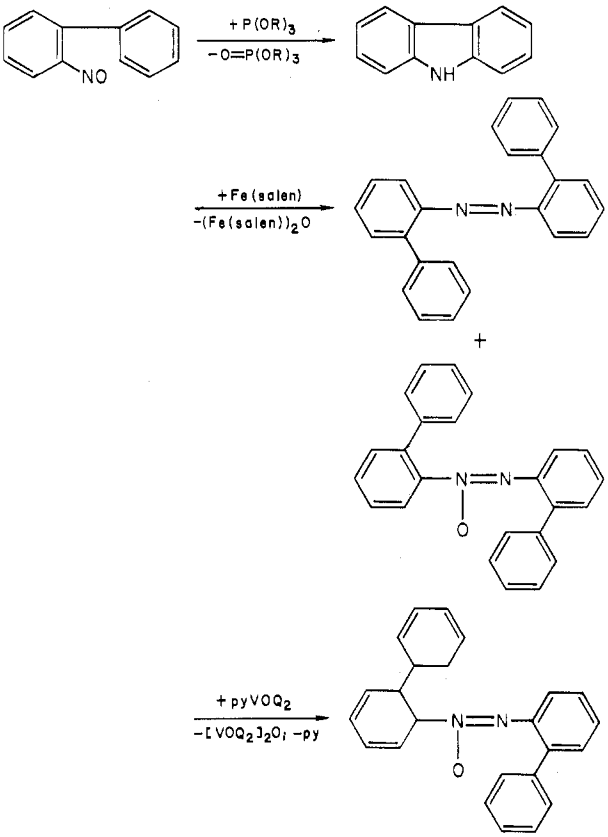


$$\left[(CN)_5Co\text{-}\underset{R}{\underset{|}{N}}\text{-}O\cdot\right]^{3-}$$

Nitrene intermediates have been suggested in many nitro and nitroso deoxygenations.[27,34] As a test for these intermediates, 2-nitrosobiphenyl was reacted with $pyVOQ_2$ (III) and was found not to produce carbazole. Carbazole is the only significant product of the deoxygenation of 2-nitrosobiphenyl with $P(OR)_3$[35] and the pyrolysis of 2-biphenyl azide.[36] Both of these reactions apparently involve a nitrene intermediate:



It was recently suggested that the nature of the deoxygenation products is directly related to electronic properties of the intermediate nitrene.[37] While a singlet nitrene gives mainly insertion reactions, i.e., into the C–H bond, the triplet nitrenes would be mainly responsible for coupling products, azo and azoxy. When transition-metal complexes are employed, the presence of carbazole has never been observed, only 2,2′-azobiphenyl and 2,2′-azoxybiphenyl being produced in reaction 7.[29,30]



(7)

The very mild conditions along with the selective pathway suggest a special utilization of transition metal complexes in stoichiometric deoxygenations of organic substrates.

Acknowledgment. We thank the CNR (Rome) for financial support.

Registry No. I, 3153-26-2; II, 70659-25-5; III, 70701-75-6; IV, 31323-29-2; V, 70748-61-7; VII, 70702-61-3; nitrosobenzene, 586-96-9; 2-nitrosobiphenyl, 21711-71-7; azoxybenzene, 495-48-7; azoxybiphenyl, 7334-10-3.

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