Oxidations of a Quadridentate Iron(II) Schiff Base Complex by Organic Molecules

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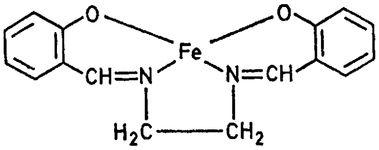
Summary The reactions of *NN′*-ethylenebis(salicylideneiminato)iron(II) with $ArNO_2$, RNO_2, ArNO, and RHal (R = benzyl or allyl) led to deoxygenation and dehalogenation.

A KNOWLEDGE of the type of molecules capable of undergoing redox reactions with iron(II) chelates may contribute to the understanding of 'electron transport' in biological systems.[1]

We have already reported on some aspects of the reducing properties of *NN′*-ethylenebis(salicylideneiminato)iron(II) Fe(salen), (I), toward oxygen[2] and a series of *o*- and *p*-quinones.[3] We now report some substantially quantitative oxidations of (I) to give iron(III) derivatives promoted by benzylic or allylic halides, and nitro- and nitroso-compounds at room temperature.

The organic compounds studied caused (i) deoxygenation of the nitro- and nitroso-compounds, (ii) dehalogenation of the benzylic or allylic halides.



Fe(salen),(I)

The reactions of (I) with aromatic ($PhNO_2$) and aliphatic ($MeNO_2$, $EtNO_2$) nitro-compounds were carried out with the nitro-compound by itself or in CH_2Cl_2 or dilute THF solution at room temperature, in each case $Fe(salen)_2O$ being formed.[4] Both reactions (1) and (2) may lead to an

$$\mathrm{Fe(salen)} \xrightarrow{PhNO_2} \mathrm{Fe(salen)_2O} + \mathrm{PhN(O){=}NPh} \qquad (1)$$

$$\mathrm{Fe(salen)} \xrightarrow[\mathrm{(R{=}Me,Et)}]{RNO_2} \mathrm{Fe(salen)_2O} + \text{organic products} \qquad (2)$$

intermediate nitroso-derivative. The explanation for the almost quantitative yield of azoxybenzene in reaction (1) may be the rapid further reduction of nitrosobenzene (*vide infra*). The consumption of Fe(salen) for reaction (2), which is always approximately in the ratio 2 : 1 to the nitro-derivative, shows that in the case of aliphatic nitro-derivatives the reaction stops when one oxygen atom has been lost. The deoxygenating ability of (I) is reminiscent of the reduction of nitro- and nitroso-compounds by tervalent phosphorus reagents.[5]

Nitroso aromatic compounds, RNO, (R = Ph, 2-biphenyl 4-dimethylaminophenyl), react with (I) according to

$$\mathrm{Fe(salen)} \xrightarrow{RNO} \mathrm{Fe(salen)_2O} + \mathrm{RN{=}NR} + \mathrm{RN(O){=}NR} \qquad (3)$$

reaction (3). Reactions (3) were carried out in THF at room temperature, the reaction time being 1—6 h, depending on R. With R = Ph, we obtained only azoxybenzene almost quantitatively, irrespective of the RNO : Fe(salen) ratio. We verified that no deoxygenation of azoxybenzene by Fe(salen) takes place. When R = 2-biphenyl we obtained the azo- and azoxy-compounds in different ratios depending on the RNO : Fe(salen) ratio, but no carbazole in detectable amounts. Carbazole might be expected from an intermediate nitrene, as was postulated in the deoxygenation of 2-nitrosobiphenyl by $(EtO)_3P$.[6] Reaction (3) with R = 4-dimethylaminophenyl, yielded almost quantitatively the corresponding azo- and azoxy-compounds in a 4 : 1 to 6 : 1 ratio depending on the reactant ratio. Relevant to these results is the close relationship between the deoxygenation of nitro- and nitroso-compounds by Fe(salen) and the reported[7] reactions of $Co(CN)_5^{3-}$ with the same organic compounds. In this case the reactions yielded aryl cobalt nitroxides.

Other recent results related to reactions (1)—(3) of this paper are the observed[8,9] catalytic reduction of nitro- and nitroso-compounds by BH_4^- in the presence of cobalt chelates.

A suspension of (I) in THF can be slowly oxidised at room temperature by benzyl chloride, benzyl bromide, and

$$2\,\mathrm{Fe(salen)} + 2\,\mathrm{RHal} \longrightarrow 2\,\mathrm{Fe(salen)Hal} + \mathrm{R{-}R} \qquad (4)$$

allyl chloride, reaction (4). By this reaction, *NN'*-ethylenebis(salicylideneiminato)halogenoiron(III) derivatives[10] were obtained almost quantitatively. Reaction (4) is reminiscent of the oxidation of cobalt(II) chelates[11] and iron(II) porphyrins[12] by organic halides.

Iron(II) chelates, such as (I), may be regarded as simple inorganic imitators for naturally-occurring reactions, in particular for redox reactions. Moreover, low-valent iron(II) chelates, such as (I), by virtue of their unique co-ordination, should be highly efficient reagents for organic syntheses.

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