Catalytic Nitrosation of Styrene by Nitric Oxide in the Presence of Cobalt Complex and BH_4^-

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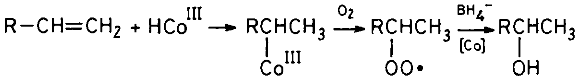
$Co(DMGH)_2(py)Cl$ (DMGH = mono anion of dimethylglyoxime, py = pyridine) catalyses the regioselective hydronitrosation of styrene to yield acetophenone oxime.

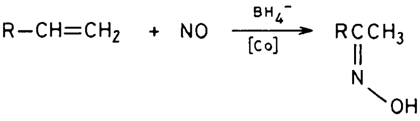
Although nitrogen oxide (NO) is known as versatile ligand existing as bent and linear nitrosyl groups in soft and hard transition metal complexes, respectively, its use for carbon–nitrogen bond formation in synthesis is not widespread. Some stoicheiometric reactions have been reported *e.g.* the reaction of Grignard reagents or dialkylzinc to give a ligand of formula ON(R)NO,[1] and the transformation of η^3-allyl transition metal complexes into complexes of acrolein oxime.[2] However, the catalytic formation of a C–N bond with NO has not been reported in the literature.[3] One reason for this may be the reluctance of the co-ordinated NO and carbon–metal bond to undergo a migratory insertion reaction.[4]

Since NO has the characteristics of a free radical, nitrosation must be achieved by radical reactions if a free radical or its equivalent is generated from the substrate. During the course of our study on the oxygenation of an olefin with molecular oxygen, we suggested the mechanism given in equation (1) for the cobalt catalysed oxygenation.[5] In this mechanism, the reaction of an intermediate alkyl–cobalt complex with dioxygen produces a peroxyalkyl compound, which further reacts under the reaction conditions to yield an alcohol as the final product. If the suggested mechanism is correct,† other radical species similar to dioxygen might also be effective as the reagent which attacks the intermediate alkyl–cobalt complex so that the addition of a radical and a hydrogen atom to olefins might take place under mild reaction conditions.

On the basis of the discussion presented above, the nitrosation of styrene with NO was examined in the presence of $Co(DMGH)_2(py)Cl$ (DMGH = mono anion of dimethylglyoxime, py = pyridine) and BH_4^- [equation (2)].



$$R{-}CH{=}CH_2 + HCo^{III} \rightarrow \underset{Co^{III}}{RCHCH_3} \xrightarrow{O_2} \underset{OO\bullet}{RCHCH_3} \xrightarrow[{[Co]}]{BH_4^-} \underset{OH}{RCHCH_3} \quad (1)$$



$$R{-}CH{=}CH_2 + NO \xrightarrow[{[Co]}]{BH_4^-} RC(=N{-}OH)CH_3 \quad (2)$$

The reaction took place at room temperature with atmospheric pressure of NO giving acetophenone oxime as the sole isolated product in 83% yield‡ in 35 h. No reaction took place when the catalyst was not present or when lithium aluminium hydride was used in the place of BH_4^-. Hexamethylphosphoramide, dimethylformamide, and dimethoxyethane–propan-2-ol were suitable solvents but acetonitrile and benzene did not give good results. The addition to styrene was regioselective yielding acetophenone oxime exclusively without the formation of the other isomer (2-phenyl-1-nitrosoethane or its derivative). 1-Phenylbuta-1,3-diene gave 1-phenyl-3-hydroxyiminobut-1-ene as the sole product (21%).

Since the rearrangement of a nitroso compound to an oxime is a ready process when there is a hydrogen atom at the α-carbon, the primary product of the reaction with styrene was expected to be 1-phenyl-1-nitrosoethane. Although 1-phenyl-1-nitrosoethane was not isolated in this reaction, the slow reaction with 2-phenylpropene gave blue 2-phenyl-2-nitrosopropane as the main isolated product (10%), which confirms the primary formation of a nitroso compound during the oximation process. Although the overall turnover of catalyst is 4—5 at present, this reaction is, to our knowledge, the first example of the catalytic formation of a C–N bond by the use of NO.

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† HCo^{III} might be Co^I and H^+ which are in equilibrium.

‡ Yields are based on the amount of olefin used.

The regioselectivity of addition in the nitrosation bears a close resemblance to the oxygenation of an olefin by the same catalyst,[5] indicating a similarity in the mechanism of both reactions. The catalytic reaction proceeded more smoothly for oxygenation than nitrosation. Nitrosation was very slow when the catalyst was a Co^{II} complex such as $Co(DMGH)_2(H_2O)_2$. Addition of pyridine to this mixture increased the reactivity which reached a maximum at py:Co 1:1 and decreased at higher concentrations of pyridine. As the substitution of co-ordinated water by pyridine takes place easily, the result suggests that one co-ordination site is required for the catalysis. A complex with two open co-ordination sites showed a decreased reactivity compared with a complex with one, which suggests that the co-ordination of NO decreases the catalytic reactivity of the complex. In the oxygenation of styrene, the effect was not significant because oxygen is not so strongly co-ordinating as NO.

These results represent not only the use of NO in catalytic nitrosation but also support the homolytic mechanism for oxygenation in the cobalt-catalysed conversion of an aryl olefin into a benzylic alcohol.

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