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OXYGENATION OF 4-NITROPHENYLHYDRAZONES OF α,β-ENONES WITH Co(SALPR)

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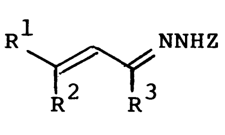
Oxygenation of 4-nitrophenylhydrazones of α,β-enones with Co(Salpr), a five coordinate cobalt(II) Schiff base complex, results in the oxidative cleavage of the double bond in the substrate. A proposed mechanism involves the decomposition of peroxidic intermediate *via* a dioxetane, which is promoted by the nitro group.

Chemical behaviors of metal complexes interacting reversibly with molecular oxygen are widely interested in connection with selective oxidation of organic compounds and biological oxidations.[1,2] We have reported that cobalt(II) Schiff base complexes promote the oxygenation of hindered phenols, indoles, flavonols, and hydrazones, which are unsusceptible to autoxidation without the catalysts.[3-5] Among these reactions, enamines and enols undergo oxidative cleavage of the C=C bond in analogy with the corresponding dioxygenase reactions.[3] However, little has been reported on the oxidative cleavage of simple olefins or enones caused by metal complex promoted oxygenations.

We now find that Co(Salpr), a five coordinate cobalt(II) Schiff base complex, promotes the oxygenation of 4-nitrophenylhydrazones of α,β-enones resulting in the oxidative cleavage of the C=C bond in the substrats. The oxygenation was carried out by bubbling of oxygen through a solution of hydrazone **1** (1 mmol) and Co(Salpr) (1.2 mmol) in dichloromethane (30 cm^3) at room temperature. The substrate was consumed normally in a few hours. The resulting mixture was separated on a silica gel plate being developed with dichloromethane, and compound **4**, the product resulting from oxidative cleavage of the C=C bond in **1**, was isolated together with hydroperoxides **2** and **3** (Table 1). The structures of **3** and **4** were determined by their analytical and spectral data (Table 2 and Table 3). Although purification of



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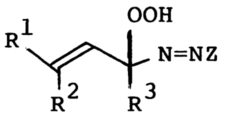

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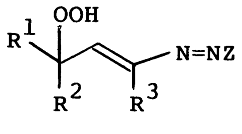


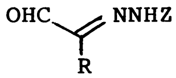
3

a: $R^1 = CH_3$; $R^2,R^3 = -CH_2C(CH_3)_2CH_2-$ b: $R^1 = CH_3$; $R^2,R^3 = -(CH_2)_3-$
c: $R^1 = CH_3$; $R^2,R^3 = -(CH_2)_2-$ d: $R^1 = R^2 = R^3 = CH_3$
e: $R^1 = R^2 = CH_3$; $R^3 = H$ $Z = 4\text{-}NO_2C_6H_4$

Table 1. Co(Salpr) Promoted Oxygenation of 4-Nitrophenylhydrazones of α,β-Enones (1).[a]

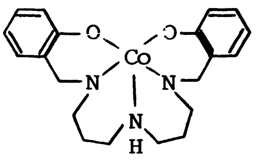
1	Reaction[b] time / h	Product yield / % [c]			
		2	3	4	Others
1a	1.5	27	26	48	
1a	24	-	-	67	
1b	0.8	18	15	44	
1c	2	trace	19	28	-[d]
1d	1	trace	trace	70	
1e	1	28	17	37	-[e]

a) Reaction conditions: 1 (1 mmol), Co (1.2 mmol), CH_2Cl_2 (30 cm^3) at room temperature. b) Time required for complete conversion of 1. c) Isolation yield.
d) Appreciable amounts of 3-methyl-2-cyclopentenone and 4-nitrophenol were obtained. e) $Me_2C=CHCON=NZ$ (8%).



4

a; R = $-CH_2C(CH_3)_2CH_2COCH_3$
b; R = $-(CH_2)_3COCH_3$
c; R = $-(CH_2)_2COCH_3$
d; R = CH_3
e; R = H



Co(Salpr)

Table 2. Physical Data of Hydroperoxides 3.

3	Mp/°C	IR(Nujol) ν/cm^{-1}	^{1}H NMR ($CDCl_3$) δ/ppm R^1	R^2	R^3	C=CH	Ar	OOH
3a	100-101[c]	3450	1.54[d]	1.05[d],1.10[d],1.56[e],2.06[e],2.25[f]		7.00[g]	7.86[h],8.30[h]	7.83
3b	86-89[c]	3510	1.51[d]	1.56-2.53 (m, 6H)		6.97[g]	7.81[h],8.25[h]	8.17
3c[a]	-	-	1.54[d]	1.92-2.83 (m, 4H)		6.97[g]	7.87[h],8.30[h]	
3d[b]	-	3420	1.61[d]	1.61[d]	2.15[i]	6.97[j]	7.79[h],8.23[h]	8.28
3e	91-93[c]	3490	1.53[d]	1.53[d]	7.33[e]	7.10[e]	7.70[h],8.15[h]	8.33

a) Purification of **3c** was unsuccessful. b) Obtained by the autoxidation of **1d** as a 1 : 1 mixture of E- and Z-forms. The E-form (**3d**); oil. The Z-form (mp 104-105 °C); IR(Nujol), 3470 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 1.63(s, 6H), 2.02(d, 3H, J = 1 Hz), 6.53(q, 1H, J = 1 Hz), 7.86(d, 2H, J = 9 Hz), 8.30 (d, 2H, J = 9 Hz), 9.20(s, 1H, OOH). c) Satisfactory analytical data were obtained. d) Me group. e) d, 1H, J = 14 Hz. f) d, 2H, J = 1 Hz. g) t, 1H, J = 1 Hz. h) d, 2H, J = 9 Hz. i) d, 3H, J = 1 Hz. j) q, 1H, J = 1 Hz.

2 was not successful, the structure of 2 was easily deducible by a hydroperoxide test and ^{1}H NMR (olefinic H; δ, about 5.3 ppm).

The reaction of Co(Salpr)(OH) with hydroperoxide 3a in dichloromethane gave

Table 3. Physical Data of Compounds **4**.

4	Mp/°C$^{a)}$	IR(Nujol) ν/cm^{-1}	^{1}H NMR (CDCl$_3$)$^{b)}$ δ/ppm			
			R	Ar	CHO	NH
4a	134-136	3200, 1695, 1680	1.07$^{c)}$, 2.38$^{c)}$, 2.43$^{d)}$, 2.66$^{d)}$	7.38$^{e)}$, 8.17$^{e)}$	9.53	11.40
4b	167-170	3250, 1705, 1675	1.33-1.86(m)$^{d)}$, 2.17-2.83(m)$^{d)}$, 2.30$^{c)}$	7.50$^{e)}$, 8.17$^{e)}$	9.42	10.86
4c	166-167	3315, 1705, 1678	2.23$^{c)}$, 2.79(m)$^{d)}$	7.36$^{e)}$, 8.20$^{e)}$	9.43	10.83
4d	250	3220, 1678	2.02$^{c)}$	7.50$^{e)}$, 8.18$^{e)}$	9.38	10.93
4e	185(dec)	3195, 1673	7.45$^{f)}$	7.30$^{e)}$, 8.15$^{e)}$	9.51$^{f)}$	12.00

a) Satisfactory analytical data were obtained. b) Compounds **4d** and **4e** were measured in a mixture of DMSO-d_6 and CDCl$_3$. c) CH$_3$ group. d) CH$_2$ group. e) d, 2H, J = 9 Hz. f) d, 1H, J = 8 Hz.

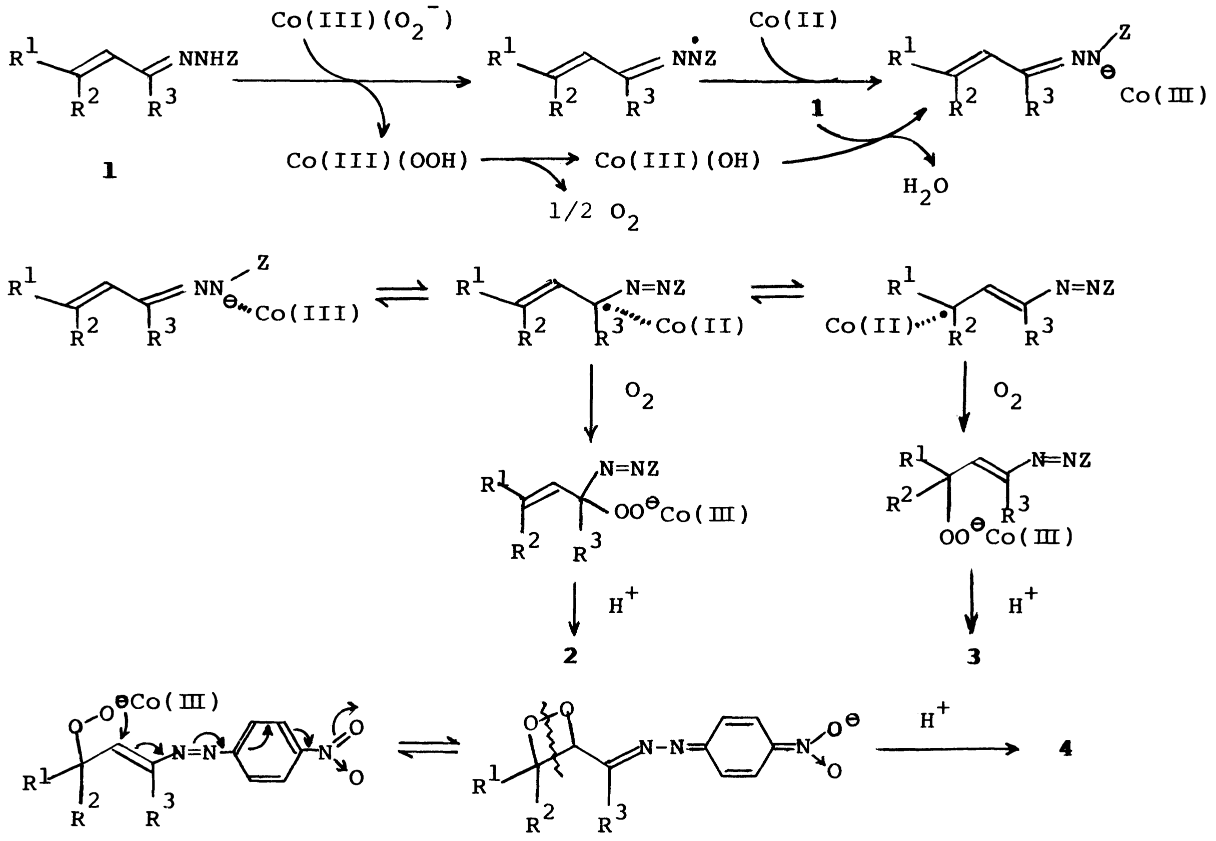
4a, whereas the oxygenation of isophorone phenylhydrazone (**1a**; Z = Ph) with Co(Salpr) gave only hydroperoxide **3a** (Z = Ph) but not **4a** (Z = Ph). It is therefore rationalized that a peroxy cobalt(III) complex formed as the primary oxygenated product$^{5)}$ undergoes decomposition induced by the electron-withdrawing nitro group, and the decomposition should involve a dioxetane intermediate. A Baeyer-Villiger type decomposition mechanism can not explain this substituent effect on the decomposition.

The substrate **1** is not oxidized by oxygen under strong basic conditions (t-BuOK in DMF at room temperature). This indicates that Co(Salpr)(O$_2^-$), an active species in the Co(Salpr) promoted oxygenations,$^{5)}$ does not act as a base but abstracts hydrogen from **1** for the initiation in the present oxygenation.

Interestingly, hydrazones **1** undergo normal autoxidation in dichloromethane to give hydroperoxides **3** exclusively, in contrast to the case of 4-nitrophenylhydrazones of aromatic ketones, where no autoxidation takes place.$^{5)}$ The results in the autoxidation of **1** suggest that dioxygen incorporation into **1** by radical process occurs specifically at the γ-position. Therefore, the formation of **3** in the oxygenation with Co(Salpr) should be considered to result from the radical process.

On the other hand, the oxygenation of **1a** with Co(Salpr)(OH) gave the same results as those obtained with Co(Salpr). Since Co(Salpr)(OH) functions as a base,$^{6)}$ the formation of **3a** in the oxygenation of **1a** with Co(Salpr)(OH) strongly suggests that the cobalt(III) complex of the substrate anion formed in the initial step undergoes homolysis. However, when a solution of **1a** and Co(Salpr)(OH) in dichloromethane was allowed to stand at room temperature for 24 h under a nitrogen atmosphere, no radical dimer of **1a** was obtained but a major part of the starting material was recovered. The results are rationalized by assuming a strong interaction between the substrate radical and Co(Salpr).

Thus, from all the findings the reaction paths of the present oxygenation may be depicted as the following scheme. It is noted that Co(Salpr) accelerates



the oxygenation of 1 but decreases the regioselectivity of the oxygen incorporation, in contrast to the Co(Salpr) promoted oxygenation of hindered phenols where the high regioselective oxygen incorporation is observed.[6] The decrease in the regioselectivity is also understood in terms of a strong interaction between the Co(III) species and the substrate anion leading to electron transfer.

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