Oxygenation of Phenylacetylene catalysed by Co(salen) [H_2salen = 1,6-bis-(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene]

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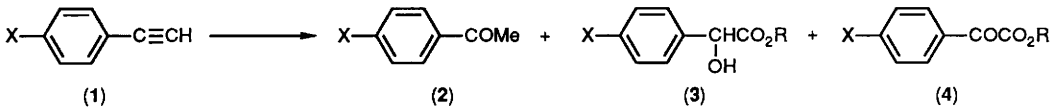
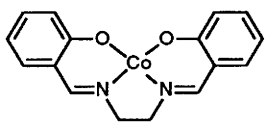
Co(salen) catalysed oxygenation of 4-substituted phenylacetylenes in alcohols results in highly selective incorporation of oxygen into the triple bond to give the corresponding acetophenones, and mandelic and phenylglyoxylic esters.

Cobalt(II) Schiff's base complexes are interesting because their catalytic activity resembles the functions of oxidoreductases including dioxygenases, mono-oxygenases, and peroxidases.[1] Mechanistic studies on the oxygenation of 1-alkenes in alcohols catalysed by Co(salen) giving the corresponding alkan-2-ones and alkan-2-ols[2] are of particular interest, because of the possibility of the asymmetric oxygenation of styrene.[3] Oxygenation of other unsaturated molecules should provide interesting results. We now find that the oxygenation of 4-substituted phenylacetylenes in alcohols results unex-



(1) (2) (3) (4)



Co(salen)

a; X = H
b; X = Me
c; X = Cl
d; X = NO_2

Scheme 1. *Conditions*: O_2, Co(salen), ROH, 60 °C.

Table 1. Oxygenation of phenylacetylenes (**1**) catalysed by Co(salen).[a]

(1)	ROH	(1)/Co	Reaction time/h	Conversion /%	Proportions/%[b] (2)	(3)	(4)
(**1a**)	MeOH	10	350	75	12	32	56
(**1a**)	MeOH	5	240	98	32	22	46
(**1a**)	EtOH	10	160	97	51	21	28
(**1a**)	EtOH	5	24	100	64	20	16
(**1a**)	Pr^{i}OH	10	75	62	61	32	7
(**1a**)	Pr^{i}OH	5	72	98	67	24	8
(**1b**)	Pr^{i}OH	5	54	99	75	18	7
(**1c**)	Pr^{i}OH	5	72	91	75	16	9
(**1d**)	Pr^{i}OH	5	72	28	40	40	20

[a] Reaction conditions: (**1**), 5 mmol in MeOH (100 ml), EtOH (100 ml), or Pr^{i}OH (160 ml) containing CH_2ClCH_2Cl (80 ml); 1 atm O_2; 60 °C. [b] Determined by the ^1H NMR spectrum of the reaction mixture.

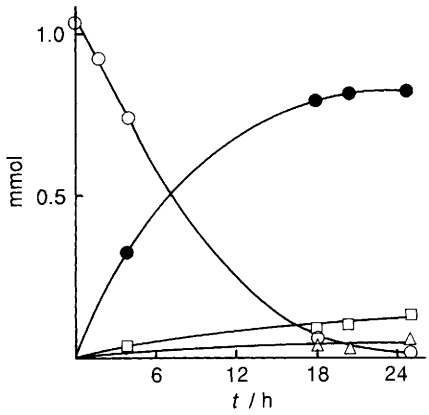
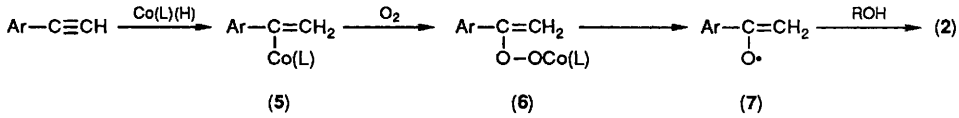


Figure 1. Time dependence of the oxygenation of (**1a**) (1 mmol) catalysed by Co(salen) (0.2 mmol) in EtOH (20 ml) (60.0 ± 0.1 °C; 1 atm O_2). ○ (**1a**); ● (**2a**); □ (**3a**; R = Et); △ (**4a**; R = Et).



Scheme 2. L = salen.

pectedly in selective incorporation of oxygen and of the alcohol into the triple bond without cleavage of the carbon–carbon bond to give the corresponding acetophenones, and mandelic and phenylglyoxylic esters. Little has been reported about the metal catalysed oxidation of alkynes.[4]

A solution of phenylacetylene (**1**) (1 mmol) and Co(salen) (0.2 mmol) in an appropriate alcohol (20 ml) was warmed at 60 °C under 1 atm of oxygen. TLC then gave acetophenone (**2**), the mandelic ester (**3**), and the phenylglyoxylic ester (**4**). The products were identical with authentic samples (IR, ^1H NMR).

As seen from Table 1, the reaction rate depends on the solvent and the aromatic substituent (Pr^{i}OH > EtOH > MeOH; X = Me > H > Cl > NO_2). No reaction takes place in Bu^{t}OH. The same solvent effect was observed in the Co(salen) catalysed oxygenation of styrene;[2] no substituent effect was observed with 4-substituted styrenes, however.[2] The solvent also affects the product distribution; the oxygenation of (**1a**) in EtOH or Pr^{i}OH gives acetophenone (**2a**) predominantly, whereas in MeOH the esters (**3**) and (**4**) predominate.

$R^1C{\equiv}CR^2$

(**1e**) R^1 = $PhCH_2CH_2$, R^2 = H
(**1f**) R^1 = $Me[CH_2]_5$, R^2 = H
(**1g**) R^1 = cyclo-C_6H_{11}, R^2 = H
(**1h**) R^1 = Me, R^2 = Ph
(**1i**) R^1 = R^2 = Ph

Aliphatic terminal alkynes may also be oxygenated similarly. For example, in Pr^{i}OH 4-phenylbut-1-yne (**1e**) gives 4-phenylbutan-2-one (75%), isopropyl 2-hydroxy-4-phenylbutanoate (19%), and isopropyl 2-oxo-4-phenylbutanoate (6%); from oct-1-yne (**1f**) and cyclohexylacetylene (**1g**) octan-2-one (73%) and 1-cyclohexylethanone (77%) are obtained, respectively. Internal alkynes such as 1-phenylpropyne (**1h**) and diphenylacetylene (**1i**) also undergo the oxygenation in Pr^{i}OH to give 1-phenylpropane-1,2-dione and benzil, respectively. However, these reactions are quite slow: % conversions (*t*/h): (**1e**), 30(120); (**1f**), 33(96); (**1g**), 25(144); (**1h**), 20(168); (**1i**), 9(120). A study of the time dependence of the oxygenation of phenylacetylene (**1a**) in ethanol at 60 °C shows that the products are formed competitively at the expense of an equimolar amount of the substrate (Figure 1).

The formation of the ketone (**2**) may be rationalised by a mechanism involving the addition of Co(salen)(H), produced *in situ* by the decomposition of Co^{III}(salen) (OR), to (**1**), followed by dioxygen incorporation and homolysis of the O–O bond in the resulting peroxo complex (**6**), eventually giving rise to the enoxyl radical (**7**), which abstracts hydrogen from the alcohol solvent (Scheme 2), analogous to the mechanism proposed for the Co(salen) catalysed oxygenation of styrene.[2] In fact, the oxygenation of (**5**), synthesized separately by the reaction of Co(salen) with $NaBH_4$ followed by phenylacetylene[5] and isolated by silica gel chromatography with ethyl acetate as eluant, gives (**2**) quantitatively. The substituent effect on the reaction rate suggests that the rate-controlling step is the formation of (**5**). Although the mechanism for the formation of (**3**) and (**4**) is not yet clear, R–CH=CH–Co(salen), a possible addition product of Co(salen)(H) to the alkyne substrate,[5] or the acetylide complex R–C≡C–Co^{III}(salen) may be intermediates.

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