

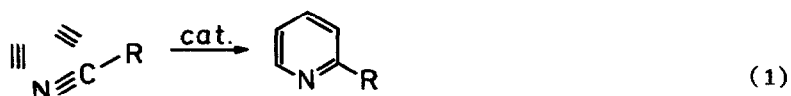
PHOTOASSISTED COCYCLIZATION OF ACETYLENE AND NITRILES CATALYZED BY COBALT  
COMPLEXES AT AMBIENT TEMPERATURE AND NORMAL PRESSURE

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**Abstract:** In 2-position substituted pyridines have been synthesized in good yields by cocyclization of acetylene and nitriles in the presence of cobalt complexes as catalysts and by promotion of light.

Pyridines are important starting products in chemical and pharmaceutical research and industry. The demand is increasing and especially 2-substituted pyridines are of growing interest /1/. The first cobalt complex catalyzed cocyclization of acetylene and nitrile was reported by Yamazaki and Wakatsuki in 1973 /2/. Bönnemann et al. /3/ developed this method into a well-established process with many variations in the catalyst, the nitrile and the ethyne component, respectively. A technical application seems to be limited owing to the relatively high pressure and temperature. In our laboratory we have some experience in the highly effective homocyclization of acetylene derivatives /4/ and we wish to report a catalytic cocyclization under very mild conditions.



cat.: R-cpCo(olefin)<sub>2</sub>, R-cp = substituted cyclopentadienyl (see table 1)  
olefin: ethylene,  $\frac{1}{2}$  (cis,cis-cycloocta-1.5-diene) (cod)

According to equation (1) cocyclization could be achieved with highly purified acetylene and nitrile. Some representative experiments are summarized in table 1. Entries 1 to 4 show, that the turnover number is significantly dependent on the influence of light. Actually, in comparison to the dark reaction, the yield of  $\alpha$ -picoline increased by about one order of magnitude by irradiation with a mercury high pressure lamp. No reaction in the dark

Table 1 Catalytic cocyclization of acetylene and nitriles

Entry	catalyst <sup>a)</sup> (mole%)	nitrile <sup>b)</sup> (%conversion)	reaction time in h	reaction temperature, °C	pyridine (% selectivity) <sup>c)</sup>	turnover <sup>d)</sup> number	remarks <sup>e)</sup>
1	A (2.95 · 10 <sup>-4</sup> )	AN (0.47)	3	40 °C	2-Me- (98.1)	1590	in the dark
2	A (1.3 · 10 <sup>-4</sup> )	AN (0.88)	3	40 °C	2-Me- (97.7)	6550	diffuse daylight
3	A (1.1 · 10 <sup>-4</sup> )	AN (1.17)	3	40 °C	2-Me- (97.9)	10490	sunlight
4	A (1.1 · 10 <sup>-4</sup> )	AN (2.41)	1	25 °C	2-Me- (98.8)	16640	Hg-lamp (125 W)
5	B (4.1 · 10 <sup>-4</sup> )	AN (1.57)	2	40 °C	2-Me- (98.3)	3860	254-580 nm
6	B (3.8 · 10 <sup>-4</sup> )	AN (2.22)	2	40 °C	2-Me- (99.0)	5930	320-370 nm
7	B (3.6 · 10 <sup>-4</sup> )	AN (4.35)	2	40 °C	2-Me- (99.3)	11584	> 400 nm
8	B (1.8 · 10 <sup>-3</sup> )	PN (12.73)	2	50 °C	2-Et- (99.6)	7240	
9	B (1.8 · 10 <sup>-3</sup> )	PN (12.9)	2	25 °C	2-Et- (99.6)	7370	Hg-lamp (125 W), internal,
10	B (1.8 · 10 <sup>-3</sup> )	PN (12.5)	2	-60 °C	2-Et- (94.5)	7170	
11	C (2.1 · 10 <sup>-3</sup> )	PN (19.3)	2	15 °C	2-Et- (99.7)	9340	filtered by
12	D (1.9 · 10 <sup>-3</sup> )	PN (13.73)	2	15 °C	2-Et- (99.6)	7430	Rasotherm
13	E (1.7 · 10 <sup>-3</sup> )	PN (12.46)	2	15 °C	2-Et- (99.6)	7220	glass
14	F (1.7 · 10 <sup>-3</sup> )	PN (10.7)	2	15 °C	2-Et- (99.6)	6510	
15	B (1.5 · 10 <sup>-3</sup> )	PN (20.25)	0.5	15 °C	2-Et- (98.8)	13400	Hg-lamps, external
16	B (1.3 · 10 <sup>-4</sup> )	PN (8.85)	0.5	15 °C	2-Et- (98.5)	66200	500 W, internal 125 W
17	B (8.4 · 10 <sup>-3</sup> )	PN (28.3)	5 min	15 °C	2-Et- (99.6)	3350	halogen lamps,
18	B (8.4 · 10 <sup>-3</sup> )	PN (43.34)	0.5	15 °C	2-Et- (99.1)	5100	external 800 W

a) A = (C<sub>5</sub>H<sub>5</sub>)Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, B = (C<sub>5</sub>H<sub>5</sub>)Co(cod), C = (Ph<sub>4</sub>C<sub>5</sub>H)Co(cod), D = (CH<sub>3</sub>OCOC<sub>5</sub>H<sub>4</sub>)Co(cod)

E = (CH<sub>3</sub>COC<sub>5</sub>H<sub>4</sub>)Co(cod), F = (PhCOC<sub>5</sub>H<sub>4</sub>)Co(cod)

b) AN = acetonitrile, PN = propionitrile

c) selectivity in relation to benzene

d) number of catalytic cycles until catalyst deactivation

e) entries 1-16: 1.5 to 5.3 moles nitrile; entries 17-18: 0.028 mole nitrile as substrate

could be observed with catalyst B containing cod as olefinic ligand, but entries 5 to 7 display an activation of this catalyst by irradiation. We found that uv-irradiation  $< 360$  nm gave only low yield owing to a decomposition of the catalyst. According to the absorption maxima of the uv spectra of reaction mixture (see fig. 1) irradiation with light between 360 and 500 nm acts highly effective.

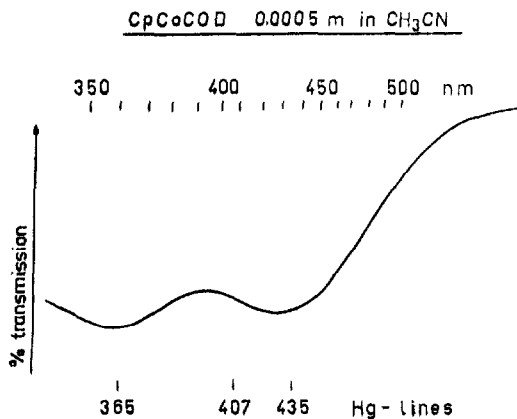


Fig. 1

Preliminary experiments with a high intensity of radiation gave turnover numbers up to 66 000 moles per mole catalyst (entry 16). A premise for high turnover numbers is a low concentration of catalyst and a high intensity of light. However, it is possible to get high conversions owing to increased catalyst concentrations and very high light intensities. In the case of entries 17 and 18 the amount of substrate was reduced significantly. Interruption of light stopped the reaction immediately with catalyst B and decreased the conversion significantly with catalyst A, that means, that the reaction is photoassisted. Effectiveness and selectivity observed are much better than in the pressure process /5/. Bönemann et al. /3/ used relatively high reaction temperatures (80 - 160 °C), whereas we found an independence of the catalyst effectivity in a wide temperature range (entries 9 to 10). These results are rather unexpected because at -60 °C the concentration of acetylene has to be about ten times higher than at 50 °C. The selectivity - decreases a little with the increase of acetylene concentration (entry 10).

A short discussion about structure modifications of the catalyst shall follow. A necessary step to get free coordination sites is the dissociation of the olefin. In the thermally induced reaction this step is influenced by the structure of the cyclopentadienyl ligand: electron withdrawing substituents promote the leaving of olefin /3/. On the contrary in the photoassisted reaction we found no important differences between our standard catalyst

(entry 9) and modified catalysts C, D, E, F (entries 11 - 14). We conclude a photoinduced ring-slippage from  $\eta^5$ -cp to  $\eta^3$ -cp, which facilitates the olefin dissociation. However, we cannot exclude a photoactivation of the removal of the pyridine formed. Probably both mechanisms are acting simultaneously.

No reaction could be found between acetylene and acrylonitrile, leading to 2-vinylpyridine, but we got excellent yields in the reaction of  $\beta$ -methoxypropionitrile or, alternatively,  $\beta$ -ethoxypropionitrile and acetylene. The 2-(2-alkoxy)pyridines formed could be cleaved into 2-vinylpyridine by acid catalysts, this reaction, however, will be presented in a subsequent paper.

The procedure of cocyclization is very simple. In a photoreactor containing 160 - 260 ml of nitrile and  $2.5$  to  $4.0 \times 10^{-4}$  mole % of catalyst with a water-cooled lamp in the center highly pure acetylene was bubbled from the bottom through a thin layer (4 - 7 mm) of reaction mixture. Surplus acetylene was cooled in a condenser to return the containing nitrile. At the end of the reaction the mixture turned black. All experiments were analyzed by glc and distillation.

In experiments 17 and 18 we used a new type of reactor with a small volume of substrate in a layer of ca. 4 mm. It was radiated with a high intensity of light by external sources. Attempts to use a flow reactor are in progress.

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