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Preliminary communication

UNEXPECTED CYCLOCOTRIMERIZATION OF α,ω-DIALKYNES AND NITRILES TO ALKYNYLPYRIDINES CATALYZED BY ARENE-SOLVATED COBALT ATOMS

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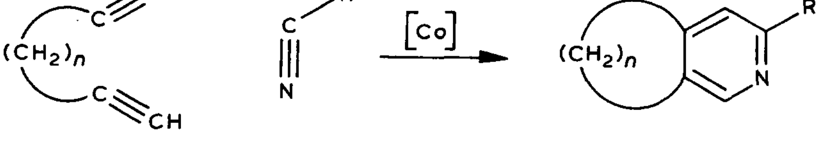
Summary

Arene solvated cobalt atoms have been found to promote an unusual conversion of α,ω-dialkynes and nitriles to alkynyl-substituted pyridines.

The synthesis of the pyridine nucleus from condensation of two alkynes and one nitrile catalyzed by Co compounds has received a great deal of attention in recent years [1]. A wide variety of alkynes has been used, including α,ω-dialkynes, which have been found to react with nitriles in ratio 1/1 to make annelated pyridines as the only cyclocooligomerization product in the presence of conventional cobalt-containing catalysts [2] or Co atoms directly generated in the presence of the reagent [3] (Scheme 1). We report here that when arene-solvated cobalt atoms, obtained by reaction of Co vapour and arenes [4], are used as catalysts a different cyclization occurs, with stoichiometry involving reaction of two α,ω-diyne and one nitrile molecule to give an alkynyl-substituted pyridine (Scheme 2). In both cases diyne oligomers are also formed as by-products.

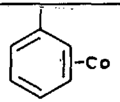
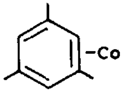
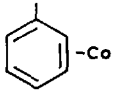
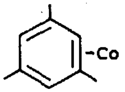
In a typical experiment cobalt metal (0.5 g; 0.8 mgatom) was evaporated during 40 min and cocondensed with mesitylene (30 ml) at liquid nitrogen temperature in a glass metal atom reactor [5]. The red-brown matrix obtained was warmed to ca.



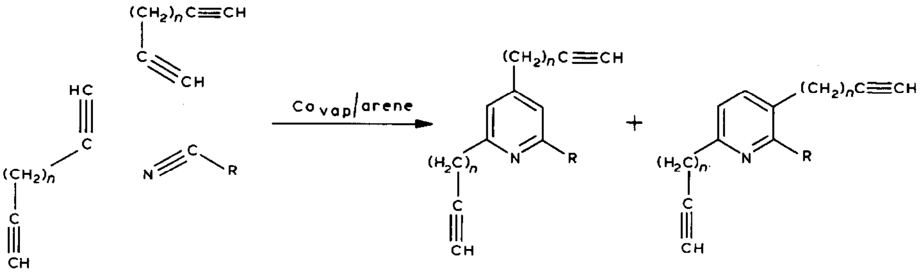
SCHEME 1.

TABLE 1

PYRIDINES OBTAINED FROM α,ω-DIALKYNES AND CH_3CN WITH ARENE-SOLVATED Co ATOMS AS CATALYSTS [a].

Dialkyne	Arene/Co catalyst	Temperature (°C)	Conversion of dialkyne (%)	Products (%) [b]		Distribution of pyridines(%) [c]		
				pyridine derivatives	diyne oligomers [d]	I	IIa	IIb
1,7-Octadiyne		25	40	73	27	86	12	2
		50	67	62	38	93	5	2
		25	36	66	34	45	44	11
		50	63	72	28	78	16	6
1,8-Nonadiyne		25	34	64	36	5	79	16
		50	56	66	34	16	59	25
		25	37	79	21	traces	78	22
		50	59	83	17	traces	67	33

[a] Dialkyne 15 mmol; CH_3CN/dialkyne (mol/mol) 5; Co 0.8 mgatom; reaction time 48 h; work-up by acid–base separation. [b] Molar composition determined on isolated products. [c] As indicated by GLC. [d] As mixture of dimers and trimers.



SCHEME 2.

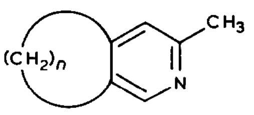
$-40\,°C$ and the resulting brown solution filtered under nitrogen in a Schlenk tube and subsequently handled only at low temperature. Dialkynes and nitriles (1/5) were added to this solution, and the mixture gently warmed to the reaction temperatures, 25 or 50 °C.

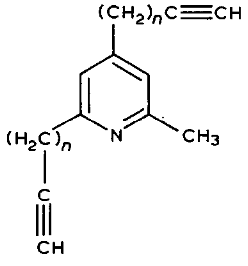
The results obtained by reaction of 1,7-octadiyne or 1,8-nonadiyne with acetonitrile are reported in Table 1. 1,7-Octadiyne reacts with CH_3CN, at 25 °C in the presence of toluene-cobalt cocondensates as catalyst, with conversion of ca. 40% of the dialkyne into a mixture of pyridines and diyne oligomers with high chemoselectivity for the pyridine derivatives (73%). The annelated pyridine, I, is the largest component (86%) of the cyclocooligomerization products, while the alkynyl pyridines IIa and IIb, (which were previously unreported [6]), are formed in yields of 12 and 2%, respectively. After 48 h, at 50 °C, the dialkyne conversion is 67%; I is still the main pyridine product while the total amount of IIa and IIb is lowered to 7%.

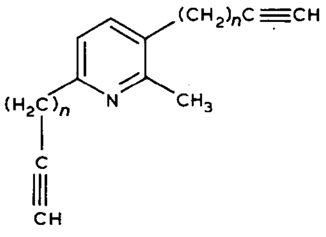
When mesitylene-solvated Co atoms are used, after 48 h at 25 °C the yields of IIa and IIb are markedly increased to 55% of the pyridines. At 50 °C the annelated pyridine I is again the major cyclocooligomerization product (78%).

With 1,8-nonadiyne and the toluene/Co catalyst, the pyridine products are mainly IIa and IIb (95% at 25 °C, and 84% at 50 °C). With the mesitylene/Co catalyst, IIa and IIb are the only pyridines formed, the amount of annelated pyridine I being below the detection limit.

Several results are particularly noteworthy: (1) The arenecobalt cocondensates are more active than conventional Co-containing catalysts, requiring lower tempera-


(I)


(II a)


(II b)

tures and shorter reaction times. (2) In contrast to previous work, annelated pyridines, I, are not the only cyclocooligomerization product: alkynyl-substituted pyridines, IIa and IIb, are also formed. The relative amounts of cyclocotrimerization to II and cyclocodimerization to I depend on various factors such as the reaction temperature, the nature of the arene cocondensed with the Co vapour, and the type of α,ω-dialkyne employed (see Table 1). (3) The alkynyl-substituted pyridines, which were hitherto unknown, can be conveniently prepared by use of Co atoms-derived catalysts.

It has been suggested that catalysts which give rise to annelation are characterized by binding of the diyne functions to the same Co atom, making both functions readily accessible for building the pyridine nucleus [1,2]. This unique ability of Co/arene cocondensates to give alkynyl pyridines rather than annelation may indicate that in this case only one end of the diyne molecule is available for the synthesis of pyridines, the diyne acting as a monoacetylene ligand.

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