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Photoaccelerated Synthesis of 2-Vinylpyridines from Unsaturated Nitriles and Ethyne*

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The heterocyclization of unsaturated nitriles and ethyne catalyzed by cyclopentadienyl-1,5-*cis,cis*-cyclooctadiene-cobalt(I) and promoted by light has been studied in toluene as solvent. Acrylonitrile and substituted acrylonitriles gave results of interest in the preparation of 2-vinylpyridines. No reaction could be observed using fumaronitrile, maleonitrile or allyl cyanide.

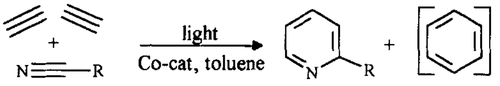
The (*E*)/(Z)-ratio of educts and products seems to be not influenced by conditions in the reaction

Keywords: acetylene; unsaturated nitriles; 2-vinylpyridines; cobalt(I) complexes; heterocyclotrimerization; photochemical activation

INTRODUCTION

The direct synthesis of 2-substituted pyridine derivatives by co-trimerization of ethyne and nitriles, catalyzed by cobalt(I) complexes, is a subject of active research. One particular target is 2-vinylpyridine, owing to its role as a monomer for special polymers and copolymers. Co-trimerizations of alkynes with acrylonitrile were studied by Bönnemann *et al.*[1] and Wakatsuki and Yamazaki.[2] Both groups used rather forcing conditions, i.e. elevated pressures and temperatures; however, yields and selectivities remained low owing to the formation of polymeric side-products and vinylation products.

Some years ago we found that co-trimerizations of simple nitriles with ethyne were largely facilitated using irradiation with light of appropriate wavelength[3] (Scheme 1). The reactions were conducted at ambient pressure and temperature and gave clean products in satisfactory to high yields. A broad spectrum of pyridine derivatives, substituted in the α-position, has thus become available.[4]



Scheme 1

Our first attempts to co-trimerize ethyne with acrylonitrile (to 2-vinylpyridine) by using photolytic conditions gave unsatisfactory results, probably due to otherwise inappropriate experimental conditions (acrylonitrile was used as liquid phase without a solvent). We initially tried to circumvent this difficulty by co-trimerizing instead 3-methoxypropionitrile with ethyne to 2-(2-methoxyethyl)pyridine, which by subsequent elimination of methanol, might be converted to 2-vinylpyridine itself.[5]

However, we later turned back to the acrylonitrile reaction itself and attacked the problems experienced, with a new series of experiments,[4] which finally led to some success. This paper reports the preliminary results of these investigations. The advantages of the syntheses used here are very mild conditions with respect to pressure and temperature and only one side-product, benzene.

RESULTS AND DISCUSSION

η^5-Cyclopentadienyl-1,5-cyclooctadiene-cobalt(I), CpCo(COD), was used as catalyst throughout the work. The experiments were run (under exclusion of oxygen and moisture) in thermostated (25 °C) reaction vessels, loaded with the nitrile, toluene as solvent, and the catalyst. The vessels were connected with a computer-linked automatic gasburet, providing the ethyne at a constant pressure of 1 atm.[6] Ethyne consumption during the reactions was measured on-line. Furthermore, the experimental arrangement, including the computing unit, made it possible to monitor simul-

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* Dedicated to Professor H.-D. Scharf on the occasion of his 65th birthday.

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taneously the concentrations of pyridine products and benzene.[7] Figure 1 shows the formation of some selected pyridine derivatives as a function of time.

Balancing of the ethyne consumption against production of pyridine and benzene respectively, revealed the absence of further products arising from the ethyne reactions. This was confirmed by GC MS analytical work. Acrylonitrile polymerization, observed as a side-reaction by Wakatsuki and Yamazaki[2] and Bönnemann and Brijoux,[8] took place to some extent only in the absence of solvents.

The catalyst/nitrile ratio of 1:100 resulted in a conversion of about 50% of nitrile and a turnover number (TON) of 50. Lower catalyst concentrations caused the TON to increase; for example, a catalyst/nitrile ratio of 1:3333 resulted in a TON of about 1500; however the reaction times in such cases were prolonged beyond practical use. This slowing down of the reaction is not caused by an inhibitory effect of the product, vinylpyridine, as checked by control experiments but, rather, by catalyst deactivation. Experimental results are listed in Tables 1 and 2. Pyridines listed in Table 1 were isolated and purified by distillation, but pyridines in Table 2 were determined only by GC and GC MS. The pyridine products in Table 1 were identified by microanalysis, ^{1}H and ^{13}C NMR, FTIR and mass spectroscopy and the data were compared with those of authentic samples and literature data. ^{1}H NMR data are given here only for estimation of (*E*)/(*Z*) ratios.

The ratio of pyridine/benzene products was found to be >1 as a rule; however, as mentioned above, the selectivity of pyridine formation from nitrile consumption is practically 100%. Methacrylonitrile gave somewhat lower, and 3-methylcrotonitrile higher pyridine yields than acrylonitrile. An additional finding is that (*E*)–(*Z*) isomerization appeared not to happen to a significant extent. Crotonitrile was used as a mixture of 69% (*E*) and 31% (*Z*) isomers and gave a mixture of 64% (*E*) and 36% (*Z*) isomers of 2-(prop-2-enyl)pyridine. Pure (*Z*)-pent-2-enenitrile gave rise to only one GC signal; however, we do not know whether this is the (*E*) or (*Z*) isomer of the product pyridine. The same results were obtained with pure (*E*)-cinnamonitrile, (*Z*)-*α*-phenylcinnamonitrile, (*E*) and (*Z*) mixtures of *p*-methylcinnamonitrile and (2-furyl)-3-acrylonitrile.

Fumaronitrile and maleonitrile failed to co-trimerize under the applied conditions. This may be due to stable *π*-complex formation with the electron-poor double bond, exerted by that nitrile group which remains uneffected by the initial steps of the co-trimerization reaction. Likewise, but probably for other reasons, allyl cyanide and derivatives, e.g. (*E*)-pent-3-enenitrile and 2-acetoxybut-3-enenitrile, are unreactive. We suspect that destruction (or inhibition) of the catalyst

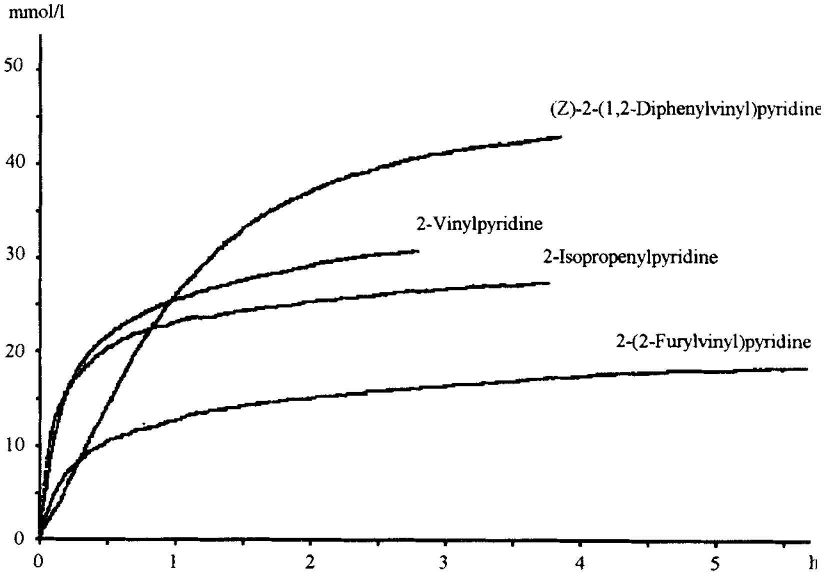
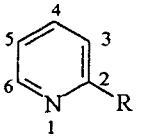
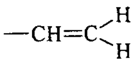
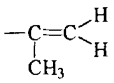
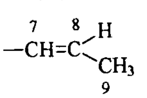
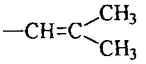
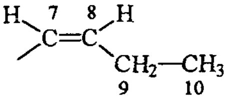
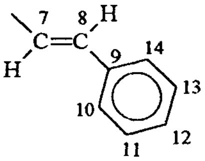


Figure 1 Formation of selected pyridines and dependence on time.

Table 1 Selected data for isolated 2-vinylpyridines



Pyridine R	Yield of py (%) GC	 Isolated	Selectivity, [py]/[b]	B.p. (°C mbar^{-1})	Ref. py
1 2-Vinylpyridine  $-CH=C\genfrac{}{}{0pt}{}{H}{H}$	57	50 (a)	0.98	72/36	10
2 2-Isopropenylpyridine  $-\underset{CH_3}{C}=C\genfrac{}{}{0pt}{}{H}{H}$	47	39 (a)	1.49	54–55/12	11
3 (*E*)- and (*Z*)-2-Propenylpyridine[b]  $-\overset{7}{CH}=\overset{8}{C}\genfrac{}{}{0pt}{}{H}{\underset{9}{CH_3}}$ (*E*) (*Z*) ni 69% 31% py 64% 36%	54.5	49.0 (b)	1.73	68–69/19	12
4 2-(2-Methylpropenyl)pyridine  $-CH=C\genfrac{}{}{0pt}{}{CH_3}{CH_3}$	61	55 (b)	1.06	51/8	13
5 (*Z*)-2-Butenylpyridine[c]  $\overset{7}{C}H=\overset{8}{C}H-\underset{9}{CH_2}-\underset{10}{CH_3}$	38	32 (b)	1.39	124/93	14
6 (*E*)-2-Styrylpyridine[d] 	45	40 (a)	1.77	152/8	15

Abbreviations: py, pyridine; b, benzene; ni, nitrile.

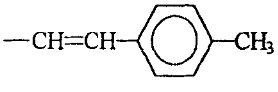
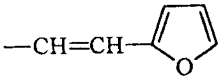
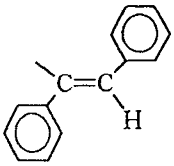
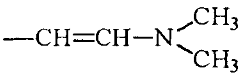
[a] (a) and (b) refer to GC conditions (see Experimental section).

[b] ^{1}H NMR: (*E*): dd: 2.05, —CH$_3$ (3H); dq: 5.97, =CH—(1H) J = 12 Hz; dq: 6.46, —CH=(1H), J = 12 Hz; m: 7.05, H$_5$ (1H); m: 7.2, H$_3$ (1H); td: 7.60, H$_4$(1H); d: 8.58, H$_6$ (1H).
(*Z*): dd: 1.9, —CH$_3$ (3H); dq: 6.47, —CH= (1H), J = 17 Hz; dq: 6.7, =CH— (1H), J = 17Hz; m: 7.05, H$_5$ (1H); m, 7.2, H$_3$ (1H); td: 7.55, H$_4$ (1H); d: 8.49, H$_6$ (1H).

[c] ^{1}H: t: 1.06, —CH$_3$ (3H); m: 2.5–2.63, —CH$_2$ (2H); dt: 5.7, =CH— (1H); d: 6.4, —CH= (1H), J = 12 Hz; dd: 7.05, H$_5$ (1H); d: 7.2, H$_3$ (1H); td: 7.6, H$_4$ (1H); d: 8.55, H$_6$ (1H).

[d] ^{1}H: ddd: 7.04–7.06, H$_5$ (1H); d: 7.07–7.11, =CH—(1H), J = 16 Hz; m: 7.18–7.23, H$_{12}$ (1H); m: 7.27–7.31, H$_{11\text{-}13}$ (2H); m: 7.29–7.34, H$_3$ (1H); m: 7.49–7.51, H$_{10\text{-}14}$ (2H); d: 7.54–7.58, —CH= (1H), J = 16 Hz; ddd: 7.54–7.59, H$_4$ (1H); d: 8.52–8.53, H$_6$ (1H).

Table 2 Selected data for substituted 2-vinylpyridines[a] investigated by GC and characterized by GC MS

Pyridine R	Yield of py (%) GC[b]	Selectivity [py]/[b]	Time (h)	Ref.	
				py	ni
7 (*E*)- and (*Z*)-2-(4-Methylstyryl)pyridine	30 (a)	1.625	2	16	17
					
(*E*) (*Z*) ni 24% 76% py[c] 25% 75%					
8 (*E*)- and (*Z*)-2-(2-Furylvinyl)pyridine	34 (a)	2.19	5.5	18	17
					
(*E*) (*Z*) ni 40% 60% py[c] 47% 53%					
9 (*Z*)-2-(1,2-Diphenylvinyl)pyridine	68 (a)	1.77	3	19	20
					
10 (*E*)- and (*Z*)-2-(2-Methoxyvinyl)pyridine	24 (b)	2.27	3.5	—	—
$-\mathrm{CH{=}CH{-}OCH_3}$					
(*E*) (*Z*) ni 72% 28% py[d]					
11 (*E*)- and (*Z*)-2-2-*N*,*N*-Dimethylamino-vinylpyridine	19 (a)	1.62	4	21	22
 $-\mathrm{CH{=}CH{-}N(CH_3)_2}$					
(*E*) (*Z*) ni 83% 17% py[d]					

Abbreviations: py, pyridine; b, benzene; ni, nitrile.

[a] Formula as in Table 1.

[b] (a) and (b) refer to GC conditions (see Experimental section).

[c] Assignment for (*E*) and (*Z*) is not reliable.

[d] No GC separation of (*E*) and (*Z*).

by the allylic species is the cause. There is a color shift of the reaction mixture to deep red within a short time of irradiation which is not observed when acrylonitrile is used (Fig. 2).[9]

Only the spectrum with fumaronitrile was taken without irradiation; the spectra with acrylonitrile and with allyl cyanide were measured after 10 min of irradiation time. With irradiation the

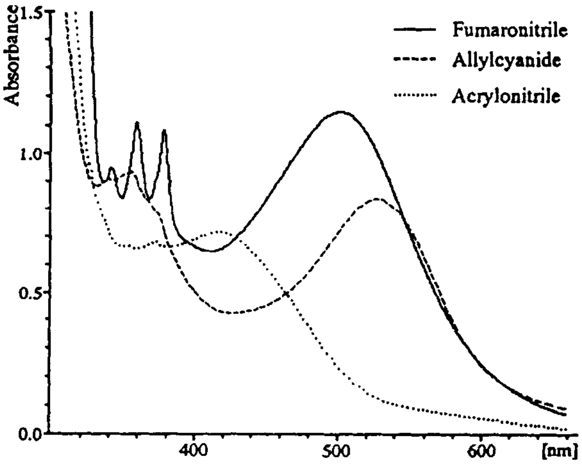


Figure 2 Selected UV/VIS spectra of the 'catalyst' system in heptane (0.0021 mmol CpCoCOD + 6.4 mmol fumaronitrile and 6.19 mmol allyl cyanide and 7.6 mmol acrylonitrile, respectively, in 5 cm^3 heptane; $d = 1$ cm; for irradiation conditions, see text).

fine structure of the bands at 360 nm disappears, although the acrylonitrile system works well in catalysis. To estimate the reactivity of unsaturated nitriles we did some competition experiments. *N*,*N*-Dimethylaminoacetonitrile, an excellent reagent for cotrimerization with ethyne, and equivalent amounts of acrylonitrile were cotrimerized as a mixture, leading to 45% 2-vinylpyridine and 55% dimethylaminomethylpyridine. Thus the reactivity of both nitriles is comparable. A mixture of allyl cyanide and *N*,*N*-dimethylaminoacetonitrile, failed completely to react under the same conditions, however. Our tentative conclusion is that a π-allyl complex of cobalt is formed by ligand substitution, and is inactive.

EXPERIMENTAL

The reactor consisted of a water-jacketed reaction vessel connected with a gas buret for automatic ethyne feed. Reaction mixtures were stirred magnetically at high speed. Two 460 W irradiation lamps were positioned around the reactor. All operations were performed under an atmosphere of prepurified argon. Ethyne of 99.5% purity (Linde) was passed through a −78 °C trap before use. Solvents were purified by standard methods and distilled. CpCo(COD) was prepared according to literature procedures.[23] Nitriles were purchased commercially (Merck, Aldrich) or prepared as indicated in Table 1 and distilled under argon before use.

NMR spectra were recorded using Bruker AC 250 and ARX 300 MHz spectrometers. GC analysis was done on an HP 5890 II chromatograph (also in combination with the mass spectrometer, HP 5989 A) with (a) OV 101 coated fused silica capillaries of length 12.5 m (temperature program: 10 min at 30 °C isothermally, then 10 °C min^{-1} up to 220 °C; argon as carrier gas, 1 cm^3 min^{-1}; split 1:60) and (b) FFAP 50m (temperature program: 10 min at 50 °C isothermally, then 10 °C min^{-1} up to 220 °C; argon as carrier gas, 1 cm^3 min^{-1}; split 1:100).

Example of the experimental procedure: 2-isopropenylpyridine

A water-jacketed reaction vessel, volume 25 cm^3, was charged with a solution of 3-methacrylonitrile (5 g; 74.6 mmol) in 14 cm^3 of toluene under an atmosphere of ethyne and kept at 25 °C. After saturation with ethyne, a solution of CpCoCOD (25 mg; 0.11 mmol) in 5 cm^3 of toluene was added.

After connecting the vessel with a gas buret delivering ethyne at constant normal pressure, the stirred mixture was irradiated for 5 h by a device comprising two Philips HPM 12 (460 W) lamps, placed at a short distance (2 cm). The reaction was quenched by opening the vessel to air. The product was isolated by vacuum distillation (b.p. 54–55 °C/12 mbar); yield 3.5 g (39%). The purity of the product (99.5%) was checked by GC.

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