

COBALT-CATALYZED SYNTHESIS OF PYRIDINES FROM ACETYLENES AND NITRILES

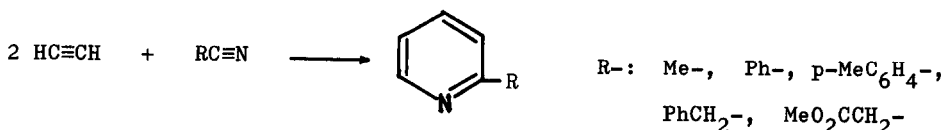
Yasuo Wakatsuki and Hiroshi Yamazaki

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

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Although many synthetic methods of pyridines have been known, few reports have appeared concerning the reaction between acetylenes and nitriles. Only example known to date seems to be the use of alkali metal catalyst though the pyridine formation has been limited to some special cases, the main product being pyrimidines¹.

It has now been found that substituted pyridines can be prepared by the reaction of 2 moles of acetylene and 1 mole of nitrile in the presence of a catalytic amount of π -cyclopentadienyl(triphenylphosphine)cobaltatetraphenylcyclopentadiene $\text{I}(\text{R}=\text{Ph})$ as shown by the equation.

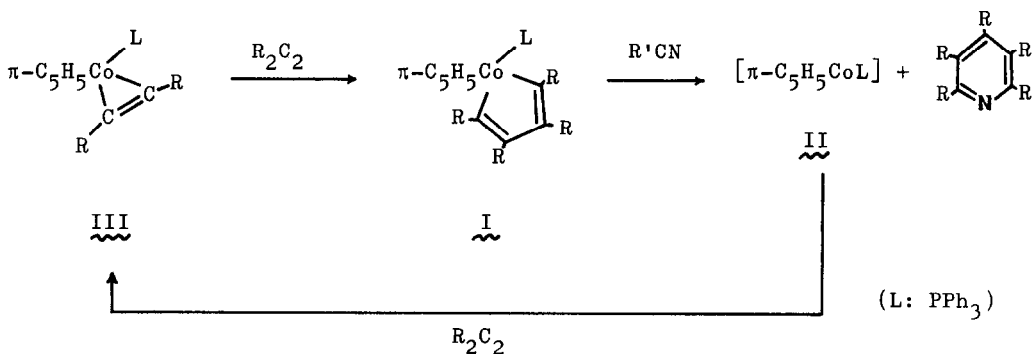


Thus on treatment of acetonitrile (2.3 g) and $\text{I}(\text{R}=\text{Ph})$ (50 mg) with acetylene (initial pressure at room temp.: 11 Kg/cm² in a 200 ml autoclave) in benzene (10 ml) at 70° for 7 hours, 1.20 g of 2-picoline was obtained. Benzonitrile, p-tolunitrile, benzylnitrile and methyl cyanoacetate react similarly to give corresponding 2-substituted pyridines in comparable yield.

Substituted acetylenes also react with nitriles to give poly-substituted pyridines. For example, diphenylacetylene (200 mg) or 1,4-dimethoxy-2-butyne

(880 mg) reacts with acetonitrile (10 ml) in benzene (10 ml) in the presence of $\underline{\text{I}}(\text{R}=\text{Ph})$ (50 mg) at 70° for 48 hours to give 2-methyl-3,4,5,6-tetraphenylpyridine (170 mg) and 2-methyl-3,4,5,6-tetra(methoxymethyl)pyridine (220 mg), respectively. Mono-substituted acetylene ($n\text{-BuC}\equiv\text{CH}$ or $\text{PhC}\equiv\text{CH}$) gives a mixture of two or four isomers in a yield similar to that of di-substituted acetylenes.

These catalytic reactions can best be explained by means of cobalt-cyclopentadiene mechanism shown below.



The formation of cobaltacyclopentadiene complexes $\underline{\text{I}}$ by the reaction of cobalt-acetylene complex $\underline{\text{III}}$ with acetylenes^{2,3}, and the stoichiometric reaction of complex $\underline{\text{I}}$ with nitriles affording pyridines have been reported previously³.

In the reactions of $\text{HC}\equiv\text{CH}$, the reaction temperature can be lowered by the use of cobalt-diphenylacetylene complex $\underline{\text{III}}(\text{R}=\text{Ph})$ ^{2,3} instead of $\underline{\text{I}}(\text{R}=\text{Ph})$. Thus by shaking 3.5 g of acetonitrile, acetylene (initial pressure 11 Kg/cm² in a 200 ml autoclave) and 75 mg of $\underline{\text{III}}(\text{R}=\text{Ph})$ in benzene (15 ml) at room temperature, 1.25 g of 2-picoline was obtained.

More extensive study on these catalytic reactions is in progress.

References

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3. Y. Wakatsuki and H. Yamazaki, J. C. S. Chem. Comm., 280 (1973).