

## Novel Synthesis of Heterocyclic Compounds from Acetylenes

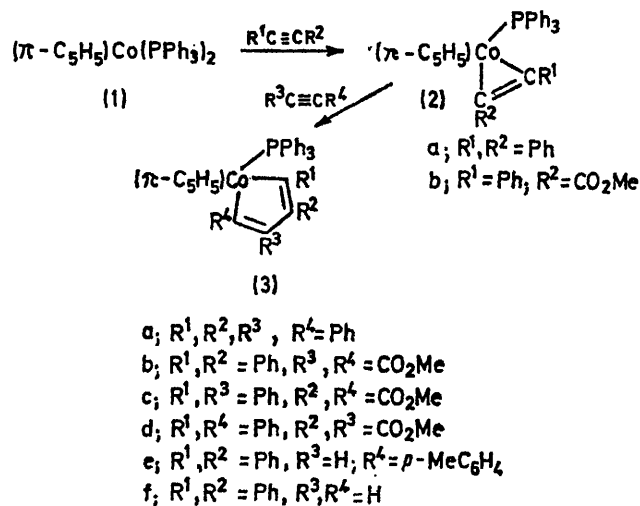
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**Summary** Pyridines, 1,2-dithiopyrones, and *N*-methyl-tetraphenyl-2-thiopyridone are synthesized by the reaction of cobaltacyclopentadiene complexes with nitriles, carbon disulphide, and methyl isothiocyanate respectively.

THE preparation of a five-membered heterocyclic compound by replacing the iron atom of the ferracyclopentadiene complex,  $\text{Fe}_2(\text{CO})_8(\text{Ph}_2\text{C}_2)_2$ , by a phosphorous atom has been reported.<sup>1</sup> The same method has been applied to the synthesis of thiophens, selenophens, and pyrroles.<sup>2</sup>

We now report the formation of six-membered heterocyclic compounds by the reaction of (3a),<sup>3</sup> with nitriles, carbon disulphide, or methyl isothiocyanate. Acetonitrile reacts with (3a) in benzene at 70° to give white crystals of 2-methyl-3,4,5,6-tetraphenylpyridine, isolated by chromatography on alumina. Similar reactions of benzonitrile and acrylonitrile with (3a) give 2,3,4,5,6-pentaphenylpyridine and 2-vinyl-3,4,5,6-tetraphenylpyridine, respectively.



Reactants	Product	Yield, %
(3a), MeCN	2-methyl-3,4,5,6-tetraphenylpyridine	(33)
(3a), PhCN	2,3,4,5,6-pentaphenylpyridine	(30)
(3a), $\text{CH}_2=\text{CHCN}$	2-vinyl-3,4,5,6-tetraphenylpyridine	(72)
(3b), MeCN	2-methyl-3,4-dimethoxycarbonyl-5,6-diphenylpyridine	(33)
(3c), MeCN	2-methyl-3,5-dimethoxycarbonyl-4,6-diphenylpyridine	(61)
(3d), MeCN	2-methyl-3,6-diphenyl-4,5-dimethoxycarbonylpyridine	(33)
(3e), MeCN	mixture of 2-methyl-3- <i>p</i> -tolyl-5,6-diphenylpyridine and 2-methyl-3,4-diphenyl-6- <i>p</i> -tolylpyridine	(39)
(3a), $\text{CS}_2$	3,4,5,6-tetraphenyl-1,2-dithiopyrone	(50)
(3f), $\text{CS}_2$	mixture of 3,4-diphenyl-1,2-dithiopyrone and 5,6-diphenyl-1,2-dithiopyrone	(13)
(3a), MeNCS	<i>N</i> -methyltetraphenyl-2-thiopyridone	(10)

The reaction of carbon disulphide with (3a) in benzene at 70° gives dark-red crystalline 3,4,5,6-tetraphenyl-1,2-dithiopyrone. Treatment of (3a) with methyl isothiocyanate under similar conditions affords pale-yellow crystalline *N*-methyltetraphenyl-2-thiopyridone.

These reactions have been applied to other cobaltacyclopentadiene complexes which have been prepared

stepwise from (1) and acetylenes (equation 1). The Table summarizes the heterocyclic compounds thus obtained.

We also found that 2-methyl-3,4,5,6-tetraphenylpyridine could be obtained catalytically from  $\text{C}_2\text{Ph}_2$  and acetonitrile in the presence of (3a). Further study on this catalytic reaction is in progress.

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<sup>3</sup> H. Yamazaki and N. Hagihara, *J. Organometallic Chem.*, 1970, **21**, 431. H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, 1971, **44**, 2260.