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A NEW SIMPLE APPROACH TO THE [6](2,5)PYRIDINOPHANE RING SYSTEM

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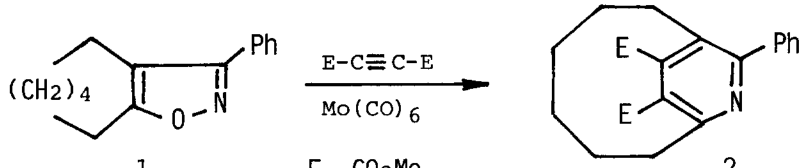
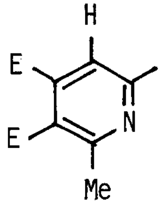
Abstract: Upon treatment with [Mo(CO)$_6$], 3-phenyl-4,5-hexamethyleneisoxazole undergoes an inclusion of acetylenic ester across the C_4-C_5 bond and elimination of an oxygen atom leading to [6](2,5)pyridinophane derivative.

The [n]paracyclophane ring system is known for most values of n from 16 to 6, of which ring system has been first reported in 1974.[1] However, it is only recently that the new efficient routes to [6]paracyclophane derivatives having substituents on the benzene ring have been developed. Their X-ray structure determinations have clarified that the benzene rings of them are highly deformed from planarity (ca. 20°).[2,3] In contrast, few examples of the heterocyclic analogue, such as [n](2,5)pyridinophane, have appeared.[4,5,6] The smallest [n](2,5)pyridinophane thus far obtained has, to our knowledge, been [8] isomer.[4]

It has previously been shown that [Mo(CO)$_6$] effects a reaction of substituted isoxazoles to undergo a novel inclusion of dimethyl acetylenedicarboxylate (DMAD) across the C_4-C_5 bond and elimination of an oxygen atom to lead to pyridine derivatives.[7] On the basis of this study, we report hereon a new simple preparation of [6](2,5)pyridinophane derivative by the [Mo(CO)$_6$]-induced reaction of 3-phenyl-4,5-hexamethyleneisoxazole (1) with DMAD. The former ring system is the first example of pyridine analogue of [6]paracyclophane, and could contain a highly deformed pyridine ring.



1 E = CO2Me 2



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A solution of 1[8,9] (1 mmol), DMAD (2 mmol), and [Mo(CO)$_6$] (1 mmol) in anhydrous benzene was refluxed for 8 h under a dry nitrogen atomosphere. The reaction mixture was then filtered through Celite and the filtrate was purified by TLC on silica gel using benzene as the eluent to give 8.2% yield of [6](2,5)pyridinophane derivative 2 [bp 120-130 °C (bath temp)/0.5 Torr]. No other organic product was obtained.

The structural assignment of 2[9] is based on the spectral data, which are listed in Table 1, along with those of the model compound 3.[7] The ultraviolet spectra of [n](2,5)pyridinophane are very characteristic. It has been known for some time[4] that as n decreases from 12 down to

Table 1. Spectroscopic Data of [6](2,5)Pyridinophane 2 and its Model Compound 3.

2: IR (CCl_4), 1721 cm^{-1}; UV (EtOH, log ε), 249 (4.12), 285 (3.90), 342 (3.80); ^1H NMR ($CDCl_3$), δ 0.45-0.98 (4H, m), 1.00-1.75 (4H, m), 2.50-3.05 (3H, m), 3.30 (1H, J=12.0, 6.0 Hz), 3.87 (3H, s), 3.93 (3H, s), 7.38-7.60 (3H, m), 7.90-8.10 (2H, m); ^{13}C NMR ($CDCl_3$), δ 24.8, 25.3, 31.5, 33.0, 33.8, 37.4 (side-chain), 52.2, 52.8 (methoxyl group), 127.6, 128.7, 130.1, 130.4, 136.3, 136.7, 142.5, 158.1, 164.4, 166.3, 168.2 (aromatic ring).

3: IR (CCl_4), 1743 cm^{-1}; UV (EtOH, log ε), 262 (4.28), 297 (4.33); ^1H NMR ($CDCl_3$), δ 2.70 (3H, s), 3.97 (3H, s), 3.98 (3H, s), 7.30-7.60 (3H, m), 7.85-8.20 (2H, m), 8.05 (1H, s); ^{13}C NMR ($CDCl_3$), δ 29.8 (methyl group), 52.4, 54.1 (methoxyl group), 104.2, 104.3, 105.9, 106.9, 114.0, 115.1, 133.5, 135.3, 142.5, 145.7 (aromatic ring).

8 in the series of [n](2,5)pyridinophanes, there is a red shift in the absorption of the pyridine chromophore. This could be attributed to the deviation from planarity of the pyridine ring.[10] The observed spectra of phenyl-substituted pyridine moiety for 2 and its model compound 3 are in good agreement with that anticipated for [6](2,5)pyridinophane ring system. The ^1H and ^{13}C NMR spectra are also fully consistent with the structure. The spectra of 2 show typical signals for protons and carbons of aromatic groups, methoxyl groups, and side chain. The signals of carbonyl carbon were not recorded. Considering the ^1H NMR spectrum, signals at δ 0.45-0.98 (4H) are substantially shielded. This shielding is attributed to the ring current of the pyridine ring. The unique aliphatic proton at δ 3.30 (1H) seems to be one which is pushed into deshielding region of the phenyl group of 2. Thus the structure of the present [6](2,5)pyridinophane 2 seems to be assessed.

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8. The isoxazole 1 was prepared by the cycloaddition of 1-pyrrolidinylcyclooctene with benzonitrile oxide and the subsequent elimination of pyrrolidine.
9. Elemental analyses and mass spectral data are satisfactory for all new compounds.
10. The ultraviolet spectra of a series of [n]paracyclophane as a function of bending of the benzene ring have been studied theoretically (Ref. 11), and the observed spectra were in good agreement with the predictions (Ref. 12).
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