SYNTHESIS AND PROPERTIES OF CYCLOPHANE CONTAINING HETERO AROMATIC.

II . 13-SUBSTITUTED [2.2]METACYCLO(3,5)PYRIDINOPHANES

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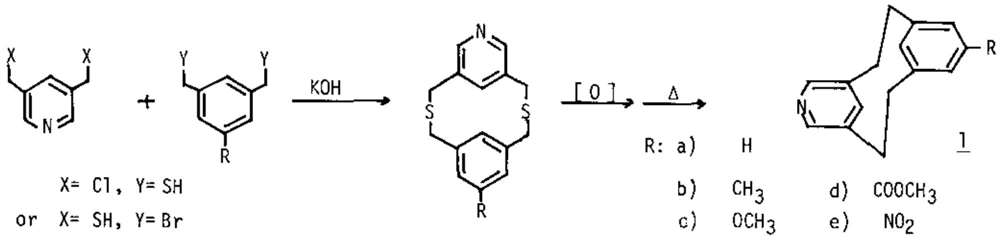
[2.2]Metacyclo(3,5)pyridinophane 1a and its some derivatives 1b-1e were synthesized by pyrolysis of the corresponding cyclic bissulfone as follows.



The structure of 1 was assigned on the basis of the spectral evidences. For example, ^{1}H-NMR spectrum shows the upfield shifts of the aromatic inner protons (H-8 and H-16) due to magnetic anisotropy of the faced another ring. The NMR spectral data of 1 are summarized in the following table.

NMR DATA OF 1 (δ value in $CDCl_3$)

1	H-4 & 6	H-8	H-16	C-4 & 6	C-8	C-16
a)	8.30	4.37	4.42	146.63	138.44	138.25
b)	8.29	4.39	4.25	146.58	138.54	135.93
c)	8.29	4.38	4.09	146.43	139.85	131.97
d)	8.36	4.44	4.53	146.87	138.49	143.70
e)	8.40	4.54	4.59	147.11	139.56	143.60

The chemical shifts of H-4 and 6 vary from 8.29 to 8.40 according to the substituent on C-13. Those of C-4 and 6 show same tendency and the linear correlation obtained of C-4 chemical shifts vs. σ^+ is reasonably good, correlation coefficient, r= 0.977 . It suggests that the substituent on C-13 influences the faced pyridine ring due to π-transannular interaction.