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SYNTHESIS OF CERTAIN [8](2,5)HETEROPHANES

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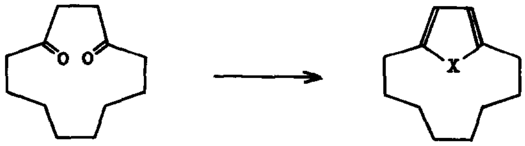
We wish to record a synthesis of novel [8](2,5)heterophanes starting from 1,4-cyclododecanedione (I) which is readily accessible from cyclododecanone (1).

Dehydration of the diketone I by treating with a mixture of phosphorus pentoxide and ethanol (2) at 80° for 1 hr gave [8](2,5)furanophane (II), b.p. 104-106°/11 mm, in an 81% yield. IR spectrum (neat) showed characteristic bands at 3095 (=CH-), 1570 (C=C), 1020 (COC) and 780 cm^{-1} (2,5-disubstituted furan), while UV maximum (n-hexane) occurred at 225 mμ (log ε 3.91). Treatment of I with ammonium carbonate at 100-120° for 2 hr yielded crystalline [8](2,5)pyrrolophane (III), m.p. 154-154.5° (from n-hexane), in an 83% yield. IR (KBr): 3375 (NH), 3120 (=CH-), 1585 and 1505 (C=C), and 760 cm^{-1} (2,5-disubstituted pyrrole). UV (n-hexane): 223 mμ (log ε 3.86). Finally, heating of I with phosphorus pentasulphide at 80° for 1 hr afforded [8](2,5)thiophenophane (IV), b.p. 80-81°/1.5 mm, in a 51% yield. IR (neat): 3075 (=CH-) and 790 cm^{-1} (2,5-disubstituted thiophene). UV (n-hexane): 199 and 250 mμ (log ε 3.90 and 3.79, respectively). Elemental analyses and NMR spectra were consistent with the structures assigned (3).

Inspection of Dreiding models of II-IV indicates the existence of considerable strain, which may bring about distortion of the heteroaromatic rings from normal planar shape. Bathochromic shifts of the UV bands as compared with the corresponding nonbridged models (4) are in accord with the expectation (5). As shown in Fig. 1, NMR signals of several methylene protons were observed at anomalously high field. This would be associated with the transannular shielding effect of the heteroaromatic rings or alternatively with the anisotropy of the heteroatoms. The NMR spectrum of IV at room temperature showed certain



I

II, X = O

III, X = NH

IV, X = S

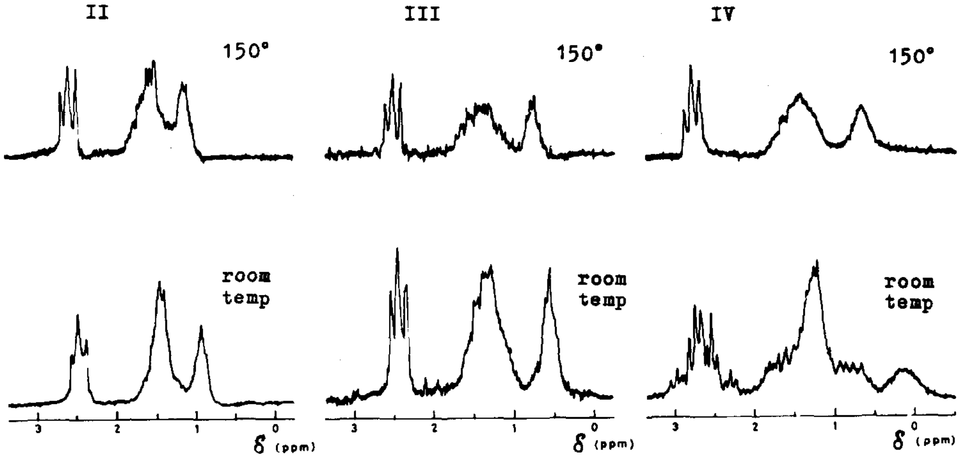


FIG. 1

NMR Spectra of [8](2,5)Heterophanes (60Mc, o-$C_6H_4Cl_2$ soln, TMS standard) (6)

points of dissimilarity to those of II and III, which disappeared at elevated temperature. This might imply that conformational change of thiophenophane IV occurs more slowly than those of furan and pyrrole analogues (II and III).

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2. The procedure was carried out according to the method of T. Mukaiyama and T. Hata, Bull. Chem. Soc. Japan 34, 99 (1961).

3. The smallest 2,5-bridged pyrrole recorded is [4](2,5)pyrrolophane (J. M. Patterson, J. Brasch and P. Drenchko, J. Org. Chem. 27, 1652 (1962)). To our best knowledge, II is the first example of [n](2,5)furanophane and lower homologue of IV seems to have not been reported.

4. UV maximum of 2,5-dimethylfuran (n-hexane): 218.5 mμ (log ε 3.88). 2,5-Dimethylpyrrole: 216 mμ (3.76). 2,5-Dimethylthiophene: 194, 196 and 237 mμ (3.92, 3.93 and 3.86).

5. D. J. Cram, C. S. Montgomery and G. R. Knox, J. Am. Chem. Soc. 88, 515 (1966). See also B. H. Smith, Bridged Aromatic Compounds p. 359, Academic Press, New York (1964).

6. Measurement in $CDCl_3$ solution at room temperature gave practically the same spectra.

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