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SYNTHESIS OF [6](2,4)HETEROPHANES

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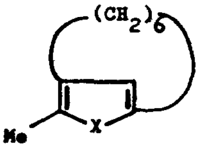
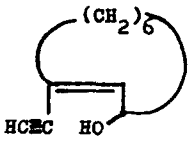
The title compounds (I) have the shortest polymethylene bridges ever reported[1,2] and the route of preparation is given below.

3-Ethynyl-2-cyclononenol (II)[3] was prepared from 2-cyclononenone. Hydration of II afforded 3-acetyl-2-cyclononenol (III) (IR 3437, 1670 cm^{-1}. m/e 182 (M^+)).[4] This is in sharp contrast to the behaviour of the 12-membered homologue, which gave 11-methyl-[9](2,4)-furanophane as the result of intramolecular hydration of ethynyl group.[1] Oxidation of III with activated manganese dioxide or chromic acid afforded 3-acetyl-2-cyclononenone (IV) (IR 1680, 1658 cm^{-1}. m/e 180 (M^+)),[4] which in turn yielded 3-acetylcyclononanone (V) (IR 1707, 1700 cm^{-1}. m/e 182 (M^+))[4] on Zn-AcOH reduction.

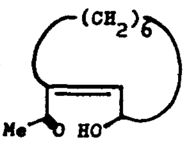
Attempted dehydration of V to furanophane proved unsuccessful, but treatment of V with phosphorus pentasulphide gave 8-methyl[6](2,4)thiophenophane (Ia) in a 67% yield. The thiophenophane Ia was a labile but distillable liquid and exhibited IR bands characteristic of the thiophene ring. Heating of V with aromatic amines in the presence of hydrochloric acid resulted in ring closure to give the corresponding N-aryl-8-methyl-[6](2,4)pyrrolophanes: N-phenyl (Ib, 36%), N-o-tolyl (Ic, 56%) and N-p-tolyl derivative (Id, 37%).[4,5] The properties and spectral data of Ia-Id are collected in Table 1. The benzenoid absorption band of Ia (λ_{max} 243.5 nm, log ϵ 3.76) appeared at longer wavelength than that of 2,3,5-trimethylthiophene (λ_{max} 237 nm, log ϵ 3.83).[6] This bathochromic shift may be ascribed to the nonplanarity of the thiophene ring introduced by the



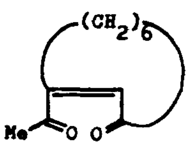
Ia: X = S
Ib: X = N-Ph
Ic: X = N-C_6H_4-Me(o), Id: X = N-C_6H_4-Me(p)



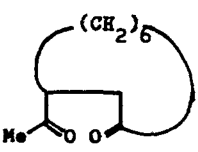
II



III



IV



V

short hexamethylene chain.[7] The NMR signals of the hexamethylene chains of Ia-Id appeared in part at higher field than δ 1.0, which is ascribed to the magnetic anisotropy of the heteroaromatic rings.[1] Whereas the base peaks of methyl-substituted 5-membered heteroaromatics are often found at M-1,[8] those of the present heterophanes are molecular peaks, M-1 peaks being of *ca*. 30% relative abundance. Supposedly the steric strain of the system would acount for the preference of the hexamethylene chain cleavage.

Table 1. Properties and Spectrometric Data of [6](2,4)Heterophanes

Compd	B.p. °/mm	IR (cm^{-1}) (neat)	NMR (δ ppm) aromatic	NMR (δ ppm) Me	MS m/e (rel abundance) M^+	M-15	M-29
Ia	68-74° at 3	3022, 1605, 1513	6.54 (CCl_4)	2.27	180[a] (100)	165 (48)	151 (60)
Ib	114-116° at 0.08	3075, 3050, 1596, 1528, 1502	6.53 ($CDCl_3$)	2.15	239[b] (100)	224 (12)	210 (28)
Ic[c]	129-130° at 2	3078, 3046, 1604, 1578, 1527, 1502	6.29 ($CDCl_3$)	2.02 1.89	253 (100)	238 (55)	224 (46)
Id[c]	128-129° at 0.65	3026, 1611, 1520	6.47 ($CDCl_3$)	2.40 2.14	253[d] (100)	238 (19)	224 (48)

[a] Exact MS: 180.095. Calcd: 180.097. [b] Exact MS: 239.163. Calcd: 239.167. [c] See footnote 4. [d] Exact MS: 253.176. Calcd: 253.182.

Footnotes and References

[1] For previous papers, see S. Fujita, T. Kawaguti and H. Nozaki, Bull. Chem. Soc. Japan, **43**, 2596 (1970) and literature cited therein.

[2] A [6]heterophane having a condensed heteroaromatic part has been reported, see W. E. Parham, R. W. Davenport and J. B. Blasotti, J. Org. Chem., **35**, 3775 (1970). For attempted synthesis of [6](3,5)pyrazolophane, see W. E. Parham and J. F. Dooley, J. Org. Chem., **33**, 1476 (1968).

[3] M. Bertrand, M. Santelli and R. Maurin, Bull. Soc. Chim. France, 998 (1967).

[4] All the new compounds gave correct analyses.

[5] Attempted synthesis of 8-methyl[6](2,4)pyrrolophane (I, X = NH) proved futile.

[6] J. Sice, J. Org. Chem., **19**, 70 (1954).

[7] B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y. (1964).

[8] V. Hanus and V. Cermack, Collection Czech. Chem. Comm., **24**, 1602 (1959).

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