Tetrahedron Letters No. 50, pp 4499 - 4502 1975. Pergamon Press. Printed in Great Britain

SYNTHESIS AND THERMOLYSIS OF 1,4-PENTAMETHYLENE(DEWAR BENZENE)

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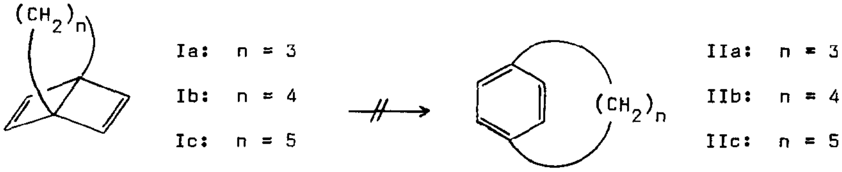
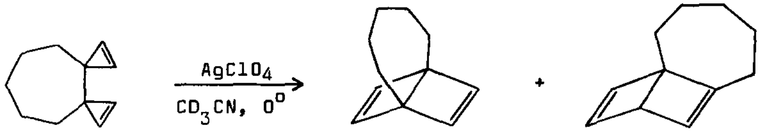
(Received in UK 13 October 1975; accepted for publication 3 November 1975)

Attempts to prepare the lower [n]-paracyclophanes from the corresponding 1,4-bridged Dewar benzenes have failed so far. Thus Ia was thermally stable[1], presumably because aromatization would have lead to excessive strain in [3]-paracyclophane (IIa), whereas Ib[2,3] on pyrolysis gave an escape reaction to p-xylylene[2] and ethylene.



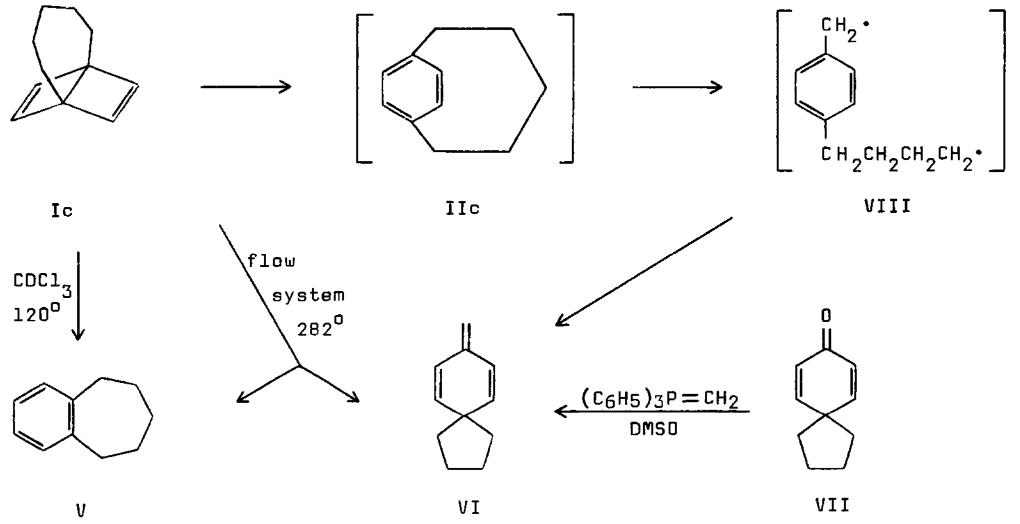
It was conceivable that these adverse factors were not operative for n = 5, and that [5]-paracyclophane (IIc), the next smaller homolog of the known [6]-paracyclophane[4], could be obtained in this way. Therefore, the synthesis and investigation of the thermal behaviour of 1,4-pentamethylene(Dewar benzene) (Ic) was undertaken[5].

1,1'-Pentamethylenebicyclopropenyl (III)[6] [NMR ($CDCl_3$): δ 7.08 (s, 4H), 1.60 (m, 10H); IR (neat): 3140 (w), 1630 (m), 1000 (m) cm^{-1}] was obtained from 1,2-dimethylenecycloheptane[6,7] in 5% overall yield as described previously[2]. Treatment of III in CD_3CN at 0° with a catalytic amount of $AgClO_4$ yielded the expected[1,2] Ic and its 1,2-isomer IV



III Ic IV

nearly quantitatively (ratio 2 : 3). IV[6] [NMR ($CDCl_3$): δ 6.75 (m, 1H), 6.58 (m, 1H), 6.07 (m, 1H), 3.36 (bs, 1H), 2.25 (m, 2H), 1.90 - 1.30 (m, 8H)] was thermally more stable than its lower homologs[1,2], which is to be expected if conformational strain is the major cause for instability of 1,2-bridged Dewar benzenes; in $CDCl_3$ at 49° it cleanly rearranged ($t_{1/2}$ ca. 60 min) to benzocycloheptene (V). As is generally observed[1,2], Ic[6] [NMR ($CDCl_3$): δ 6.53 (s, 4H), 1.88 (m, 4H), 1.50 (m, 6H)] was thermally considerably more stable than its 1,2-isomer IV, but it was less stable than Ia and Ib. In $CDCl_3$ at 120° it decomposed ($t_{1/2}$ ca. 88 min); surprisingly, V was the major product besides some smaller unidentified side products. Pyrolysis in a flow system[2] (N_2, 282°) yielded, besides polymeric material and V, the spiro compound VI[6]. The structure of VI follows from its spectral data [NMR ($CDCl_3$): δ 6.20, 5.78 (AB, 2 two-line m, J = 10 Hz, 4H), 4.83 (bs, 2H), 1.69 (m, 8H); IR (neat): 860 (s) cm^{-1} ($=CH_2$)] and from independent synthesis from VII[8] by a Wittig reaction.



The formation of VI can most easily be explained by invoking the intermediacy of the diradical VIII. The thermal stability of Ia together with the observation that thermolysis of both Ib and Ic involves bond breakage at a "benzylic" position, makes it highly probable that the latter is a consequence of preceding aromatization to IIb and IIc, respectively.

The formation of V from Ic is quite unexpected, because so far the Dewar benzene ⟶ benzene aromatization was usually not accompanied by rearrangement of substituents[1,2,9]. Rearrangement could occur at the Dewar benzene stage, e.g. by a 1,3-shift of the 1,2-bond; a similar interpretation was proposed for the rearrangements observed in the diazine series, which constitutes the only other example of thermal topological scrambling[10]. Another possibility would be rearrangement at the stage of the strained aromatic compound IIc, e.g. via a triplet state[11]. Rationalization must be speculative for the present.

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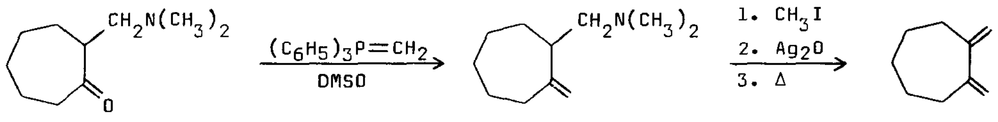
5. Prof. Dr. K. Weinges has kindly informed us that he has achieved the synthesis of Ic along a different route.
6. The compound gave a high resolution mass spectrum and other spectral data in agreement with the proposed structure.
7. 1,2-Dimethylenecycloheptane was obtained in 22% overall yield from 2-dimethylaminomethylcycloheptanone [W. Treibs and M. Mühlstadt, Chem. Ber., 87, 407 (1954)] as follows:



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