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[5]METACYCLOPHANE

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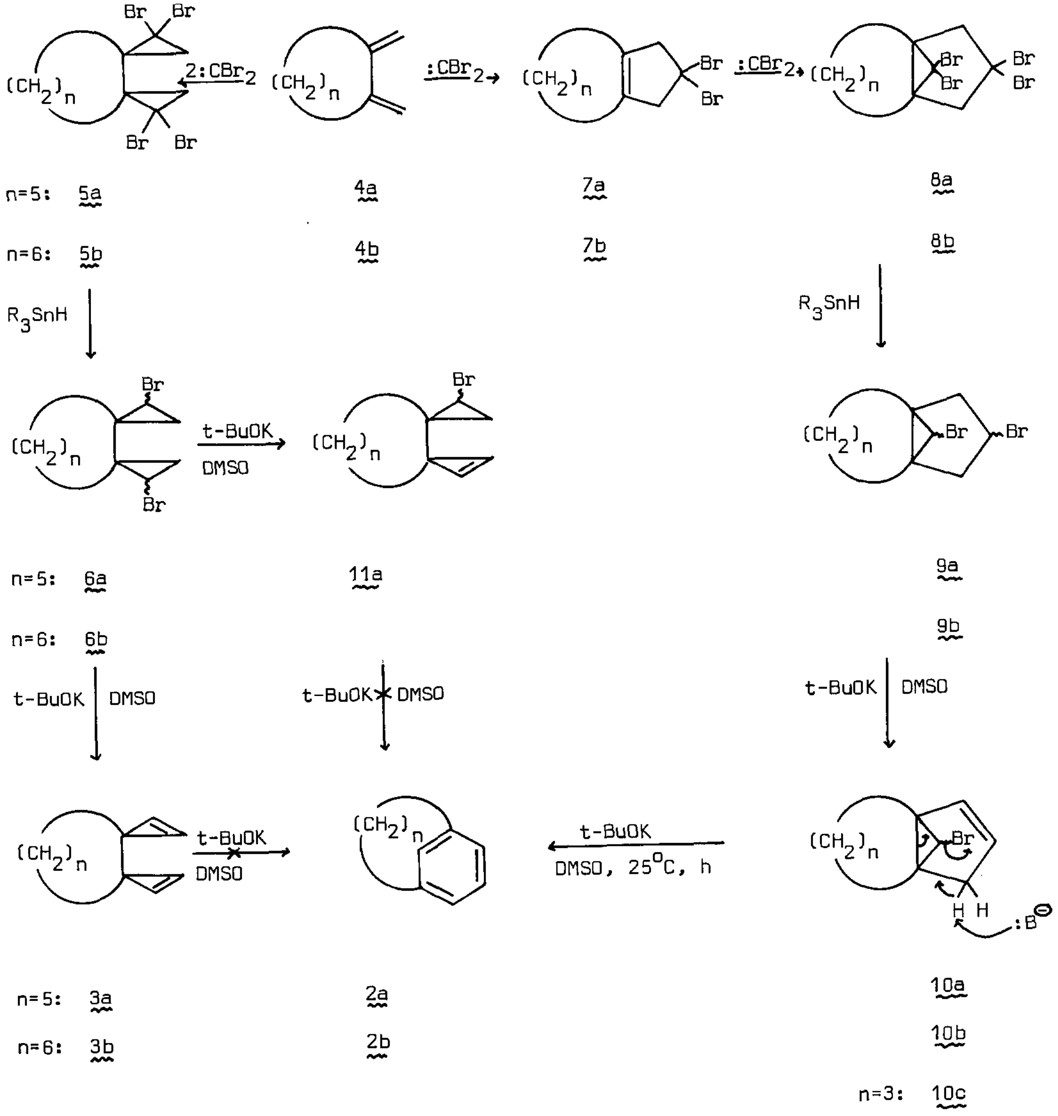
In both cyclophane series, the [6]bridged members, [6]paracyclophane (1b)[1] and [6]metacyclophane (2b)[2], respectively, are the lowest representatives known so far. Attempts to prepare [5]paracyclophane (1a) have been unsuccessful[3]. In this communication, we report on the formation and on some properties of [5]metacyclophane (2a).

In the synthesis of the 3,3'-bridged bicyclopropenyls 3a[3] and 3b[4] from 4 (Scheme 1), we also obtained a mixture of byproducts from which, on careful gas chromatogrphic separation (glass column; 1.5 m; 10% SE-30; 60^{o}C) 2a (5% if calculated as being formed from 6a) and 2b[2] (13% if calculated for 6b) were isolated as colourless liquids, respectively. The structure of 2a follows from its spectral data; the mass spectrum ($M^{+\cdot}$ obsd. 146.1094, calcd. for $C_{11}H_{14}$ 146.1095) confirms its composition, the UV spectrum (C_6H_{12}; λ_{max} (log ε): 238 nm (shoulder; 3.5), 306.5 nm (2.4)) indicates the presence of a distorted benzene chromophor, the ^{1}H NMR spectrum ((CDCL$_3$):δ 7.85 (s, 1H), 7.23-6.75 (m, 3H), 3.10-2.40 (m,4H), 2.14-1.10 (m, 4H), 0.54-0.04 (m, 2H)) shows low field signals typical for aromatic protons in small metacyclophanes[2] (note the exceptionally low position of the signal of C(11)-H!) and a two proton signal at high field which , according to decoupling experiments

Scheme 1

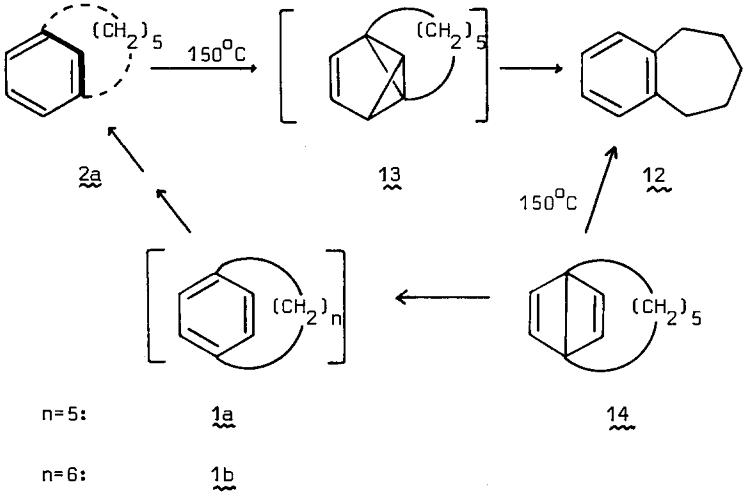


and to models, is due to two protons at the β carbon atoms located in the shielding region of the aromatic ring.

The formation of 2 was puzzling at first, as in separate experiments neither 3 nor 11a (one of the byproducts of 3a) gave rise to any 2 under identical reaction conditions. Eventually, 10a (($CDCl_3$):δ5.80-5.50 (m, 2H), 2.92 (s, 1H), 2.58 (m, 2H), 1.65 (m, 10H)) was identified as one of the other byproducts and shown to yield 2a on the usual base treatment. The formation of 10 on its turn can be rationalized (Scheme 1) by assuming 1,4-addition[5] of dibromocarbene to 4, followed by a second addition of dibromocarbene to yield 8. Separation of 8 from the isomeric main product 5 is difficult and apparently incomplete because of the instability of the (impure) products, their high boiling points and small quantities; the same holds for the reduction products 9 and 6. Thus, in the base treatment of 6, 9 is also present as an impurity and is converted to 10 which yields 2 as indicated by arrows. The same sequence of reactions has previously been postulated for the formation of the *syn*- and *anti*-isomers of 10c from 1,2-dimethylenecyclopentane[6].

The unusually high strain of 2a is reflected not only by its spectral properties, but also by its interesting thermal behaviour. Contrary to the characteristic temperature dependance of the ^{1}H NMR spectrum of 2b[2], the spectrum of 2a in d_6-DMSO was practically unchanged between -70°C and 150°C, pointing to a high degree of conformational rigidity of the pentamethylene chain. At about 150°C, 2a rearranged to its ortho isomer 12 (Scheme 2). This unprecedented and comparatively easy thermal rearrangement can best be rationalized by the intermediate formation[7] of a benzvalene (13), facilitated by the geometry and increased reactivity of the nonplanar benzene ring of 2a. Possibly, a similar mechanism, resulting in two consecutive 1,2-shifts, is involved in the thermal rearrangement of 14 (via 1a and 2a) to 12[3].

Scheme 2



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