Anomalous Hydrolysis Behaviour of [*n.n*] Paracyclophanediazonium Salts: a New Route to Bridged Benzobarrelenes

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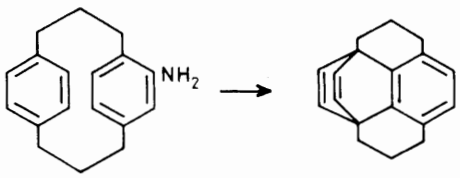
The hydrolysis of diazotized 5-amino-[3.3]paracyclophane and *anti*-4-amino-[2.2](1,4)naphthalenoparacyclophane gives products having a barrelene structure, presumably *via* an aryne mechanism.

In general, reactions of ordinary arenediazonium salts in aqueous solution proceed exclusively *via* an aryl cation mechanism, not *via* an aryne one.[1] This is demonstrated by the absence of rearranged products or cycloadducts. We report here the unexpected results that some [2.2]- and [3.3]-paracyclophanediazonium salts in aqueous solution give bridged benzobarrelenes in low but significant yield.† Diazotization and subsequent hydrolysis of 5-amino-[3.3]paracyclophane (**1**)[2] (61 mg) in a mixture of $MeCO_2H$ (2.5 ml), H_2O (2 ml), and H_2SO_4 (0.5 ml) gave a bridged benzobarrelene (**3**)[3] in 14% yield (6 mg) and 5-hydroxy- and 5-acetoxy-[3.3]paracyclophanes[2] in 84% yield (42.4 mg). On the contrary, 4-amino-[2.2]paracyclophane[4] gave only the corresponding 4-substituted products.

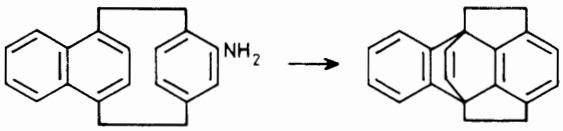
Similar treatment of *anti*-4-amino-[2.2](1,4)naphthalenoparacyclophane (**2**)[5] (88 mg) in dilute H_2SO_4 gave a novel bridged dibenzobarrelene (**4**)‡ in 37% yield (14 mg, m.p. 137—139 °C) and the corresponding 4-hydroxycyclophane[5] in

† Each aminocyclophane was diazotized in aqueous acid with $NaNO_2$, stirred for 2—3 h at room temperature, then worked up in the usual manner. The product distribution was determined by g.c. and each product was then isolated by t.l.c. or h.p.l.c. on silica gel.

‡ The structure of (**4**) was based upon extensive ^1H n.m.r. (400 MHz) and mass spectral characterization and was supported by an *X*-ray crystal structure determination, details of which will be reported elsewhere.



(1) (3)



(2) (4)

61% yield (20 mg). This is in sharp contrast to the isomeric *syn*-4-aminocyclophane,[5] where (**4**) is not obtained, but the corresponding *syn*-4-hydroxy- and the isomeric 17-hydroxycyclophane are obtained in 61% and 38% yield, respectively.

The formation of (**3**) and (**4**) from diazotized (**1**) and (**2**) cannot be explained by the generally accepted aryl cation mechanism of arenediazonium salt hydrolysis,[1] so an aryne mechanism is suggested: compound (**3**) can also be obtained by transannular cycloaddition of the aryne generated from 5-bromo-[3.3]paracyclophane.[3] Therefore, our results provide a new route to this and other bridged benzobarrelenes.

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