

[4]Paracyclophane: Electronic Absorption Spectrum and Trapping by Alcohols

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[4]Paracyclophane (**2**) is generated photochemically from 1,4-tetramethylene Dewar benzene; its electronic absorption spectrum and trapping reaction by alcohols are reported.

Geometrically distorted unsaturated compounds have attracted considerable interest in recent years.¹ Paracyclophanes having a short bridge have presented a particular challenge in this field and efforts to prepare [*n*]paracyclophanes having very short bridges have led to the recent generation of [5]paracyclophane which is stable at low temperature in solution, but not isolable.² The substantially reduced stability of [5]paracyclophane compared to that of the [6]homologue³ suggested that [4]paracyclophane would be extremely reactive if it were generated. We report here the observation of the electronic absorption spectrum of [4]paracyclophane (**2**), which should have a severely bent benzene ring, and the trapping of (**2**) by alcohols.

Irradiation of a dilute methanolic solution of (**1**)⁴ by a high pressure Hg lamp through Pyrex led to the formation of a single product, whose structure was readily elucidated as (**3a**) (61% yield).^{†‡} Photolysis of (**1**) in ethanol analogously produced (**3b**) in 47% yield. The photochemical addition of the less acidic propan-2-ol, however, was efficient only in the presence of acid [(**3c**), 57% yield from (**1**) in 0.25 M CF₃CO₂H in propan-2-ol]. In sharp contrast, photolysis of (**4**)⁵ in methanol gave only (**8**) and none of the corresponding methanol adduct (**6a**) was detected in the photolysate.

The formal addition of alcohols to the central σ bond of (**1**) seems to be best explained in terms of the intermediate formation of [4]paracyclophane (**2**). Addition of alcohols to distorted double bonds, such as anti-Bredt bridgehead alkenes, is well documented¹ and generally subject to acid catalysis as observed in the present reaction. The photochemical inertness of (**4**) towards methanol is also in accord with the intermediacy of (**2**). Owing to the additional ethano bridge, the five-bonds-bridge in (**4**) is shorter than that in (**1**). Therefore the benzene ring in (**5**), if it were formed, would suffer more severe bending than that in (**2**). This is readily confirmed by examination of molecular models. Isomerisation to (**5**) being inhibited, (**4**) would undergo the relatively slow 1,3-shift of its double bond giving (**7**) and subsequent aromatisation to (**8**).[§]

The generation of (**2**) was further substantiated by the development of an electronic absorption having maxima at *ca.* 260 and 340 nm upon irradiation of (**1**) in an ethanol matrix at 77 K with a low pressure Hg lamp. The generated species appeared to be stable at 77 K, but underwent complete decomposition when the matrix was briefly thawed at 173 K.

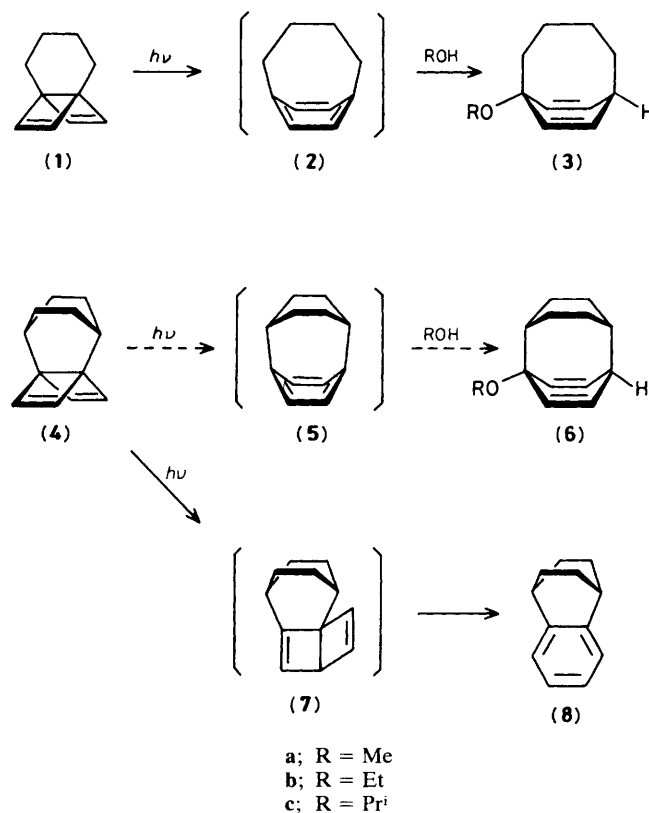
[†] In a personal communication, we learned that Professor F. Bickelhaupt made a similar observation independently. We thank him for this information prior to his publication.

[‡] The electronic absorption spectrum of (**1**) extends to the 300 nm region. Irradiation without the filter brought about faster consumption of (**1**), but resulted in an appreciably lower yield of (**3a**) and the increased formation of amorphous material. Satisfactory spectral and analytical data were obtained for all new compounds.

[§] Photolysis of (**1**) proceeded more than six times faster than that of (**4**) in methanol. Therefore, the inability of (**4**) to give (**6**) is not the result of a fast 1,3-shift giving (**7**) which inhibits the isomerisation of (**4**) to (**5**).

The development of a similar absorption was also observed in ether-pentane-ethanol (5:5:2) or pentane-isopentane (1:1) at 77 K (Figure 1). When irradiated with 366 nm light, the newly developed absorption was quickly bleached and the original spectrum was almost restored, suggesting efficient photochemical reversion of the generated species to (**1**).

Evidence that the absorption was due to [4]paracyclophane was provided by the following experiment. Irradiation of (**1**) in ethanol containing 1% of sulphuric acid at 77 K apparently led to development of the same absorption as observed in neutral ethanol. The formation of (**3b**) was confirmed by g.l.c. and g.l.c.-mass spectrometry following ten freeze-irradiation-thaw cycles.[¶] When the developed absorption was bleached with 366 nm light each time before the matrix was thawed, however, the yield of (**3b**) fell to *ca.* one tenth. Thus the species exhibiting the absorption is undoubtedly the direct precursor of (**3b**), most probably (**2**). The possibility that (**3**) was produced by the addition of the alcohol to excited (**1**)^{*} or a



[¶] Compound (**1**) was stable in this acidic ethanolic solution and did not give (**3b**) in the dark. The intensity of the developing absorption at 260 and 340 nm reached a plateau after a short period of irradiation and prolonged irradiation only induced secondary photolysis. The matrix was thawed before the secondary photoreaction proceeded to a significant extent. Even after ten cycles, the conversion of (**1**) was quite low.

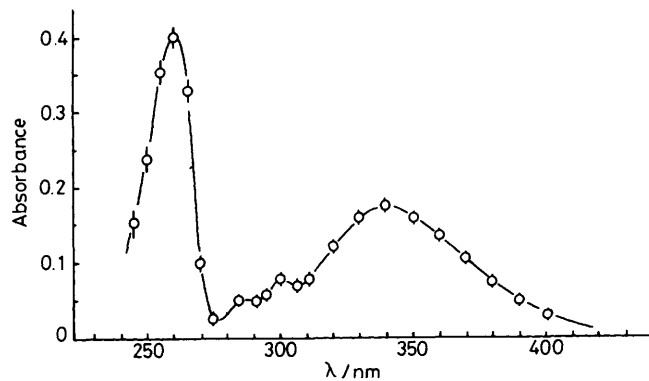


Figure 1. Electronic absorption spectrum obtained by subtracting the absorption due to (1) from the spectrum exhibited when (1) in pentane-isopentane (1 : 1) was irradiated with a low pressure Hg lamp at 77 K. This spectrum is probably due to [4]paracyclophane (see text). Small peaks at 285 and 300 nm are due to a secondary photoproduct.

prismane intermediate is definitely ruled out. In accord with the photochemical inertness of (4) towards methanol, no detectable absorption developed in the 300–400 nm region when (4) in ethanol was irradiated with 254 nm light at 77 K. Thus it may be concluded that (2) was photochemically generated from (1) and reacted with alcohols to give (3).

Aromatization of 1,4-bridged Dewar benzenes has provided a major means of access to [n]paracyclophanes with short bridges.⁶ The inability of (4) to give (5) photochemically appears to indicate that the isomerisation of (1) to (2) may represent a limiting case of this methodology.

Received, 27th January 1987; Com. 102

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