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C_9H_{10} HYDROCARBONS : THE PHOTOCHEMISTRY OF TRICYCLO[3.2.2.$0^{2,4}$]-NONA-6,8-DIENES (HOMOBARRELENES)[1]

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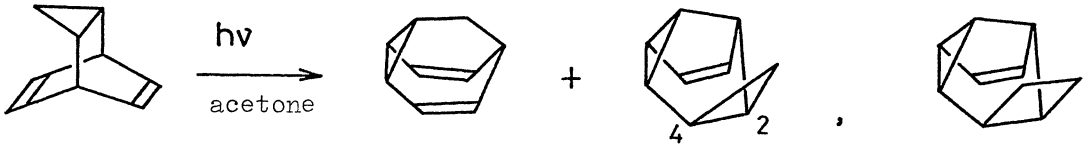
The photoreaction of homobarrelenes (1 and 6) was investigated; and the formation of novel photoproducts, 2,4-exo-homosemibullvalenes (3 and 7) was observed. The reaction path was discussed from a viewpoint of the di-π-methane rearrangement.

In 1968, Daub and Schleyer reported that tricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene (homobarrelene)(1), upon irradiation in the presence of acetone, gave barbaralane (2),[2)] but the reaction mechanism has not been completely clarified.[3)] In connection with the photochemistry of other C_9H_{10} hydrocarbons,[4)] we reinvestigated the photosensitized reaction of homobarrelene (1) and found that the main reaction was a di-π-methane rearrangement affording homosemibullvalene (3) rather than that giving 2. In addition, regiospecificities of the rearrangement were observed in the photoreaction of the substituted homobarrelene. These results are described here.

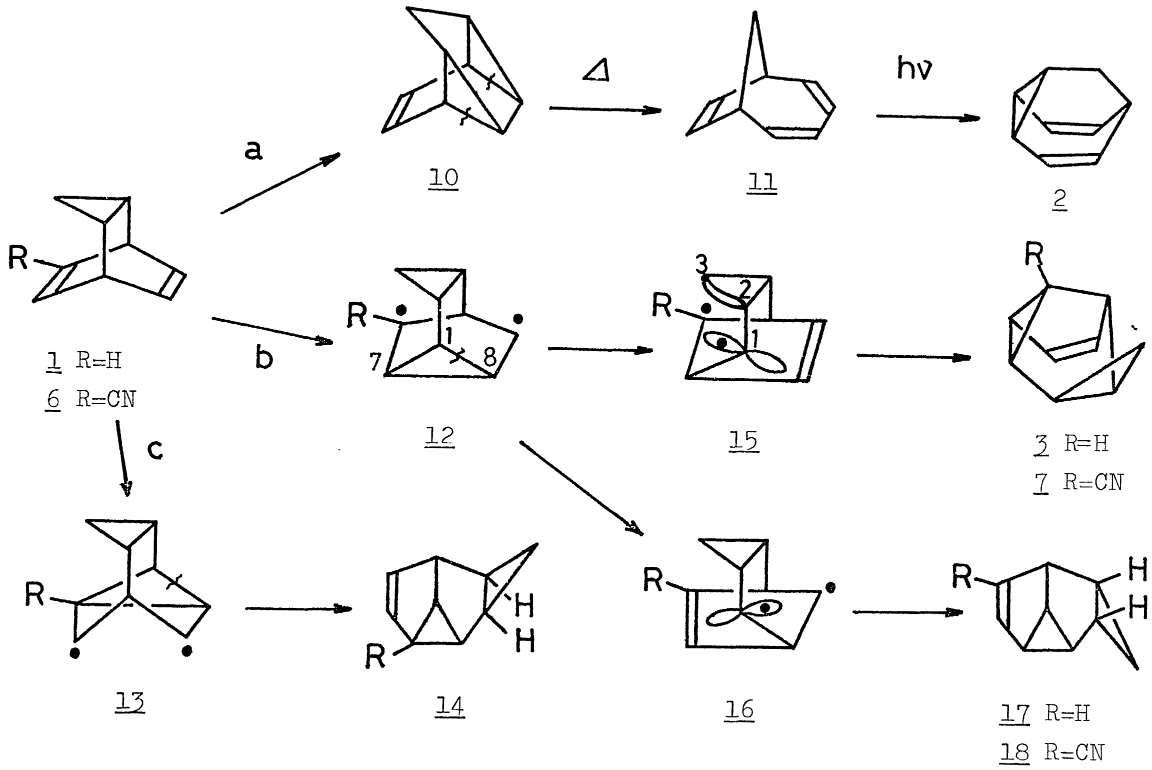


1 2 3 5

When a benzene-acetone (1:1 v/v) solution of 1 (5.7 x 10^{-3} M) was irradiated using a Rayonet photoreactor (RUL-3000 A) for 35 min, three photoproducts, 2, 3, and 4 were obtained as a volatile material in 0.9, 30.0 and 2.8 % yields, respectively, along with a recovery of 36.0 % of 1.[5)] Minor product 2 was identical with barbaralane in all respects. Major product 3 was not so stable and found to be labile to light. Thus, an additional 50 min-irradiation of 1 under the same condition afforded 1, 2, 3, and 4 in 9.6, 2.5, 18.4 and 5.7 % yields, respectively. The structural assignment of 3 is derived from analysis of its spectral data. The mass spectrum shows a molecular ion at m/e 118 and the uv spectrum in cyclohexane indicates an absorption maximum at 221.0 nm (ε 1960), which is coincident with that of a vinylcyclopropane of a similar system.$^{6)}$ The following nmr spectrum supports the exsistence of tricyclo[3.3.0.0^{2,8}]oct-3-ene$^{7)}$ and an additional cyclopropane ring ; (in CCl_4, 100 MHz), δ -0.02 (H_{3a}), 0.03 (H_{3b}), 0.96 (H_2), and 1.16 (H_4) for the cyclopropane and 1.59 (H_7), 1.77 (H_5), 1.87 (H_6), 3.14 (H_1), 5.44 (H_8), and 5.63 (H_9) for the tricyclo[3.3.0.0^{2,8}]octene moiety. The coupling constants were obtained by double and triple resonance experiments; $J_{1,6}$=5.2, $J_{1,9}$=1.9, $J_{2,3a}$=6.3, $J_{2,3b}$=3.6, $J_{2,4}$=5.7, $J_{3a,3b}$=5.6, $J_{3a,4}$=6.2, $J_{3b,4}$=4.5, $J_{5,6}$= 6.9, $J_{5,7}$=7.6, $J_{6,7}$=6.9, $J_{7,8}$=2.1, $J_{8,9}$=5.6 Hz. Thus, we propose 2,4-exo-tetracyclo[4.3.0.0^{2,4}.0^{5,7}]non-8-ene (exo-2,4-homosemibullvalene) for the structure of 3. Indeed, its uv and nmr spectra are similar to those of 2,5-exo-tetracyclo-[5.3.0.0^{2,5}.0^{6,8}]dec-9-ene (5), which is a 1,3-addition product of benzene and cyclobutene.$^{6)}$ The reason why the 2,4-exo configuration is assigned for 3 is due to the fact that the coupling constant between H_1 and H_2 or H_4 and H_5 is very small, nearly 0 Hz. If photoproduct 3 had 2,4-endo configuration, a larger value like 5 $\sim$ 7 Hz would be observed for the coupling constant between these protons, because the same situation was observed for the exo- and endo-isomers of 5.$^{6)}$ The structure of the third photoproduct, 4, could not be determined although its nmr spectrum ruled out a possibility of the 2,4-endo isomer of 3.

The irradiation of 6-cyanotricyclo[3.2.2.0^{2,4}]nona-6,8-diene (6)$^{8)}$ was carried out under the same condition, and after 60 min-irradiation only one product 7 was obtained in 26.8 % yield in addition to 11.5 % of the starting material and a considerable amount of non-volatile material. The structural determination of 7 is based on the following spectral properties ; uv max. (in cyclohexane), 219.5 nm (ε 2080) ; nmr spectrum (in CCl_4, 100 MHz), δ 0.23 (H_{3b}), 0.34 (H_{3a}), 1.18 (H_2), 1.31 (H_4), 2.41 (H_7), 2.51 (H_5), 3.99 (H_1), 5.51 (H_8), and 5.77 (H_9); $J_{1,9}$=2.20, $J_{2,3a}$=6.6, $J_{2,3b}$=4.7, $J_{2,4}$=5.9, $J_{3a,3b}$=5.5, $J_{3a,4}$=7.1, $J_{3b,4}$=3.6, $J_{5,7}$=7.4, $J_{5,9}$= 0.60, $J_{7,8}$=2.0, $J_{7,9}$=1.04, and $J_{8,9}$=5.82 Hz. It is noteworthy that no cyanobarbaralane (8) was detected in the photolysate of 6. For comparison, however, 8 could independently be synthesized by the irradiation of 3-cyanobicyclo[4.2.1]-nona-2,4,7-triene (9), which was obtained by the Rh-catalyzed reaction of 6.$^{8)}$

To rationalize the results obtained here, plausible mechanistic schemes (path a, b or c) are presented below. Since homobarrelene, 1 or 6, can be viewed as a typical constrained di-π-methane system, the formation of homosemibullvalene, 3 or 7, is ascribed to the normal photoreaction of the triplet state of 1 or 6 (see path b or c).9) On the other hand, the formation of barbaralane (2) is explicable by path a, which proceeds via 10 and 11. However, such a path involving [2π + 2σ] process seems difficult to occur compared with the normal di-π-methane rearrangement (path b).9) This is probably a reason why barbaralane (2) was a minor photoproduct. Additionally, a remarkable substituent effect and a high regiospecificity of the rearrangement should be noticed. Since the radical delocalization due to cyano group is expected to be more in diradical 12 than in 13, path b prefers to path c, thus leading not to the formation of 7-cyanohomosemibullvalene (14). With the most favorable path b, there would be two paths diverging from 12, affording diradicals 15 and 16, followed by the formation of 2,4-exo-homosemibullvalenes, 3 and 7, and their endo-isomers, 17 and 18, respectively. Nevertheless, the observed regiospecificity, i.e., the exclusive formation of the exo-isomers could only be explained with the intermediary of diradical 15. Compared with diradical 16, the perturbation of a bridged cyclopropane ring to a developing radical orbital may assist the C_1-C_8 bond cleavage.



This is probably due to the interaction between the C_2-C_3 banana bond and the C_1-radical orbital located in parallel.[10]

Further studies on the photochemistry of other substituted homobarrelene derivatives are in progress.

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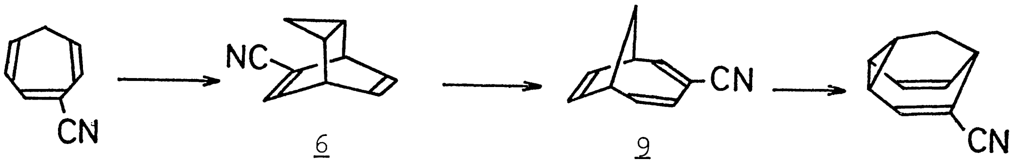
8) The following syntheses and spectral properties of 6, 8, and 9 will be reported elsewhere in detail.



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