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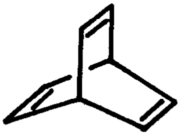
VALENCE ISOMERIZATION OF C_9H_{10}HYDROCARBONS: PHOTOCHEMICAL REACTIONS OF BICYCLO[3.2.2]NONA-2,6,8-TRIENE AND ITS DIHYDRO-DERIVATIVES[1)]

Tsutomu Kumagai, Kazuo Shimizu, Haruki Tsuruta,[2)] and Toshio Mukai
Department of Chemistry, Faculty of Science, Tohoku University
Aramaki, Sendai 980, Japan

Summary: The valence isomerization reaction of bicyclo[3.2.2]nona-2,6,8-triene (1), which photoisomerized to two homologues of semibullvalene, was discussed with the photoreactions of its dihydro-dreivatives, bicyclo[3.2.2]nona-6,8-diene (3) and bicyclo[3.2.2]nona-2,6-diene (4).

In connection with our continuing interest dealing with the potential energy hypersurface of various C_9H_{10}hydrocarbons[3)], we have investigated the photochemical behavior of bicyclo[3.2.2]nona 2,6,8-triene (1). Although some of the photochemistry of this system had already been described ,[4,5)] that of the parent molecule (1) had never been reported. This system is a homologue of barrelene (2)[6)] and possesses three types of di-π-methane chromophores; $C_3=C_2-C_1-C_7=C_6$, $C_6=C_7-C_1-C_8=C_9$, and $C_7=C_6-C_5-C_9=C_8$ dienes. Thus, it would be useful to explore the effect of geometrical alteration on the di-π-methane rearrangement of bicyclo[3.2.2]nonatriene. We now report the photochemical reaction of 1, which selectively isomerizes to the two homologues of semibullvalene, barbaralane (5) and tricyclo[4.3.0.0^{2,9}]nona-3,7-diene (6), on direct and sensitized irradiation. In addition, the photoreactions of bicyclo[3.2.2]nona-6,8-diene (3) and -2,6-diene (4) were investigated for comparison with that of the triene (1).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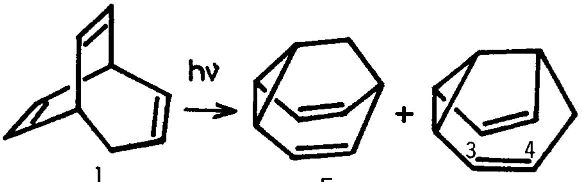

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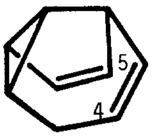

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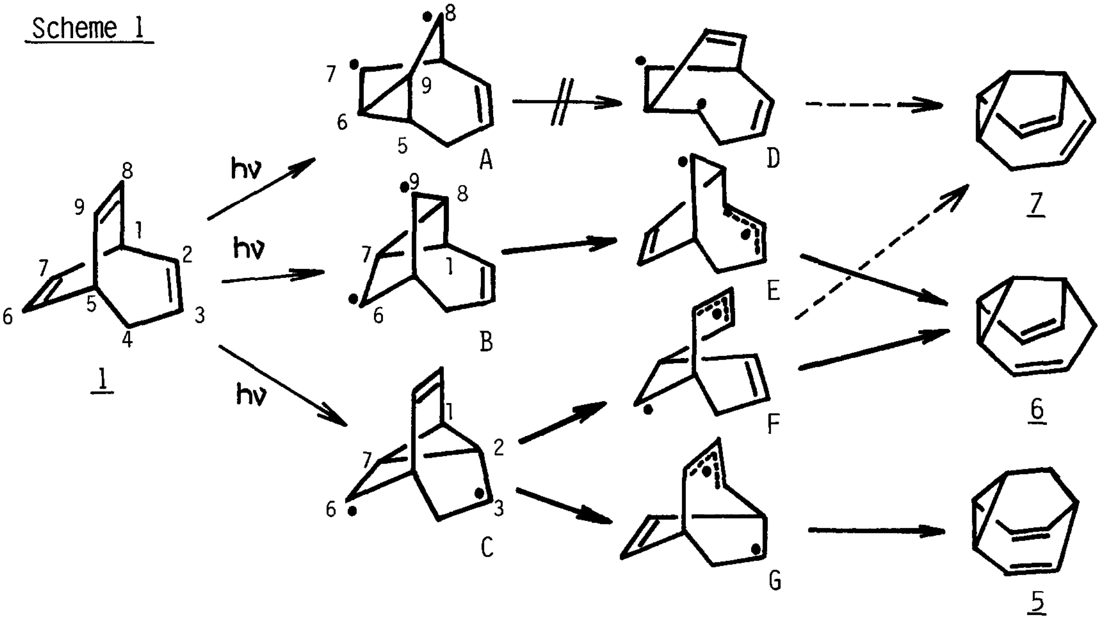
When an acetone-benzene solution of bicyclo[3.2.2]nonatriene (1) was irradiated with Rayonet photoreactor using RUL-3000Å lamps (43W) in a quartz vessel for 160 min under an argon atmosphere, two isomeric photoproducts, barbaralane (5) and the tricyclic diene (6) were obtained in 10.8 % and 53.5 % yield with a recovery of starting triene (16 %). On direct irradiation of 1, the formation of the same products 5 and 6 was observed in 2 and 5 % yield, respectively, accompanied by 85 % of 1 after 15 hr. The photoproducts could be separated by preparative vapor phase chromatography using a 1/4 in. x 5 M column containing 20 % DC-11 on Chromosorb-W at 80°. The minor product 5 was found to be identical with tricyclo[3.3.1.0^{2,8}]nona-3,6-diene (barbaralane) in all aspects including spectral and chemical properties.7) The structural assignment of the main product 6 was based on its spectral data, which were completely identical with those of tricyclo[4.3.0.0^{2,9}]nona-3,7-diene synthesized by the Huang-Minlon reduction of bicyclo[4.2.1]nonatrienone.8)

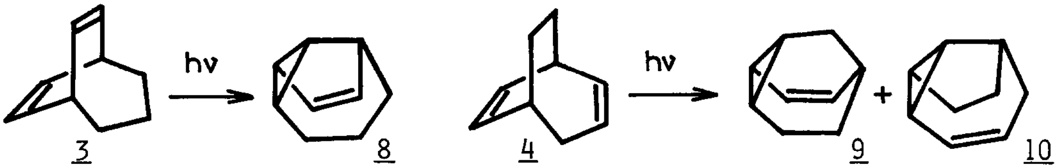
The formation of 5 and 6 can be explained by di-π-methane rearrangements which were summarized in Scheme 1. Why is the other possible semibullvalene homologue (7) absent in the photolysate of 1 ? One possible explanation is the reflection of the geometrical differences in the di-π-methane

Scheme 1



chromophores, i.e., $C_3{=}C_2{-}C_1{-}C_7{=}C_6$ diene has an arrangement which favors the di-π-methane rearrangement and thus gives both products, 5 and 6, via the diradical intermediate (C). On the other hand, the $C_6{=}C_7{-}C_1{-}C_8{=}C_9$ and $C_7{=}C_6{-}C_5{-}C_9{=}C_8$ dienes overcome disadvantages inherent in the geometry. In order to elucidate the influence of geometry on the 1,4-diene chromophores of 1, we examined the photoreactions of the dihydro derivatives 3 and 4 as model compounds.

After irradiation of 20 hr under acetone sensitized conditions, bicyclo[3.2.2]nona-6,8-diene (3) gave tricyclo[4.3.0.0^{2,9}]non-7-ene (8) in 63.0 % yield. Under the same conditions bicyclo [3.2.2]nona-2,6-diene (4) isomerized to dihydrobarbaralane (9) and tricyclo[4.3.0.0^{2,9}]non-3-ene



(10) in 5.6 % and 50.0 % yields. The direct irradiation of 3 and 4 also produced the same product 8, 9 and 10 but in very poor yields. The structures of these photoproducts were deduced by comparison with authentic samples which were synthesized by the procedures of Gardner and Musso.9,10) Quantum yields for each photoreaction under acetone sensitized conditions were shown in Table 1.11)

Table 1 Quantum Yields of Photoreactions

Quantum Yield for Disappearance	Quantum Yield for Formation
Φ_1= 0.76	Φ_5= 0.06 Φ_6= 0.47
Φ_3= 0.15	Φ_8= 0.047
Φ_4= 0.17	Φ_9= 0.007 Φ_{10}= 0.038

Photoreactions of the model compounds and the determination of the quantum yields indicate that 1,4-dienes 3 and 4 rearrange to vinylcyclopropane moieties with almost the same efficiencies (Φ_8= 0.047 and Φ_{9+10}= 0.045) under acetone sensitized conditions. This result suggests that the geometrical differences between the $C_3=C_2-C_1-C_7=C_6$ and the $C_6=C_7-C_1-C_8=C_9$ (or $C_7=C_6-C_5-C_9=C_8$) diene unit do not influence the di-π-methane rearrangement pathways of bicyclo[3.2.2]nonatriene (1). An efficiency of photorearrangement of 1, 11-12 times larger than that of 3 or 4, reveals that the allyl stabilization in diradical intermediate E and F (in Scheme-1) significaltly accelerates the di-π-methane rearrangement. The formation of 7 *via* intermediate D which lacks allyl stabilization was never observed in the photoreactions of 1. This is probably due to the fact that intermediate A does not revert to D since both radical centers can not be stabilized by interaction with the double bond. Although the formation of 7 is also possible from diradical F, 7 could not be detected in the irradiation of 1. We think the diradical intermediate F readily rebonds to give photoproduct 6 in preference to 7 and this is different from the di-π-methane rearrangement of barrelene because of stereochemical reasons. It has been demonstrated by Zimmerman the corresponding diradical species is involved and plays an important role in the photoreaction of barrelene.6) The formation of 6 can be reasonably derived from intermediates B and C in almost equal ratio without any geometrical influences of the 1,4-diene moieties in 1.

Our experimental results afford new knowledge about the energy surface of the excited states of C_9H_{10} hydrocarbons and further work using labeling experiments will be carried out in the future for the full elucidation of the photochemistry of **1**.

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8) The NMR spectrum of **6**, δ^{ppm}(100MHz, CCl_4) 1.26(H_2,d.d.d.d.t.), 1.55($H_{5\text{-endo}}$, d.d.d.), 1.81(H_1, t.d.), 2.04(H_9, t.d.d.), 2.31($H_{5\text{-exo}}$, m.), 3.02(H_6,m.), 5.33(H_8,d.d.d.d.t.), 5.45(H_3, m.), 5.48 (H_8, m.), 5.75(H_4, d.d.d.d.), $J_{1,2}$= 6.4, $J_{1,6}$= $J_{1,9}$= 7.5, $J_{2,3}$= 3.8, $J_{2,4}$= 0.6, $J_{2,5\text{-exo}}$= 1.9, $J_{2,6}$= 0.6, $J_{2,9}$= 7.5, $J_{3,4}$= 9.8, $J_{3,5\text{-exo}}$= $J_{4,5\text{-exo}}$= 1.9, $J_{4,5\text{-endo}}$= 6.1, $J_{5\text{-exo},5\text{-endo}}$= 16.4, $J_{5\text{-exo},6}$= 3.8, $J_{5\text{-exo},7}$= 2.0, $J_{5\text{-endo},6}$= 2.6, $J_{6,7}$= 1.0, $J_{7,8}$= 5.6, $J_{7,9}$= 1.9, $J_{8,9}$= 0.7 Hz. Other spectral data were identical with those of the authentic sample, which was synthesized by the procedure of Sakai, M. Sakai, D. L. Harris, and S. Winstein, *Chem. Commun.*, 861 (1970). Compound **7** was independently synthesized by the procedure of Berson, J. A. Berson, R. R. Boettcher, and J. J. Vollmer, *J. Am. Chem. Soc.*, **93**, 1540 (1971), but it was not detected in the photolysate of **1**.
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