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C_9H_{10} HYDROCARBONS. THE PHOTOCHEMISTRY OF BARBARALANE[1)]

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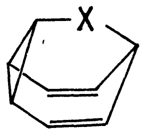
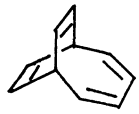
Irradiation of barbaralane (1c) afforded four products (3, 4, 5 and 6). The formation of 3, 4 and 5 suggests that 1c initially rearranges to bicyclo[4.2.1]nona-2,4,7-triene (7), which then converts into these products. This suggestion was supported by control experiments. The possible mechanistic pathways for these photochemical rearrangements were outlined.

The thermal behavior of the bridged homocycloheptatrienes (1) depends on the nature of the bridge: bullvalene (1a), dihydrobullvalene (1b) and barbaralane (1c), upon heating, rearrange to cis-9,10-dihydronaphthalene,[2)] bicyclo[3.3.2]deca-2,7,9-triene[3)] and 7-vinylcycloheptatriene[4)] respectively. In contrast, the photochemical behavior of 1, apart from their reaction mechanisms, seems to be independent of the nature of the bridge, since the same type of photochemical interconversion took place between 1a and bicyclo[4.2.2]deca-2,4,7,9-tetraene (2)[5)] and between semibullvalene (1d) and cyclooctatetraene.[6)] We wish to describe here the photoreaction of barbaralane (1c) which adds some knowledges on the energy surface of the excited molecule of the C_9H_{10} hydrocarbons.



1a X= CH=CH , **1c** X= $(CH_2)_1$
1b X= $(CH_2)_2$, **1d** X= $(CH_2)_0$



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When a solution of 1c (1.8×10^{-2} M) was irradiated using a Rayonet photoreactor (MGR 2537 A) at room temperature, four products shown in Table were formed. The products 3 and 4 exhibit nmr spectra characteristic of exo- and endo-tricyclo-[4.2.1.$0^{2,5}$]nona-3,7-dienes and their structures were determined by comparison of retention time in vpc and nmr spectra with those of authentic samples.[7)]

Table

starting materials	irradiation time	products and yields (%)					
		1c	3	4	5	6	7
1c	5 hr	28.6	5.9	14.0	14.9	9.2	-
7	18 min.	30.7	7.9	23.7	25.1	-	3.3
	3 hr	5.9	9.5	28.0	30.6	trace	-
7*	2.5 hr	63.0	-	-	-	-	1.0
1c*	12.0 hr	41.8	-	-	-	-	-

* benzophenone-sensitized irradiation

The nmr spectrum of product 5 (M^+ 118) shows eight groups of peaks; δ 1.32 (m, 2H), 1.79 (q, J=12.0, 1.9 Hz, 1H), 2.06 (m, 1H), 2.11 (m, 1H), 2.79 (m, 2H), 3.10 (m, 1H), 5.36 (q, J=5.9, 2.8 Hz, 1H) and 5.85 (q, J=5.9, 2.4 Hz, 1H). The coupling constant (5.9 Hz) of the olefinic protons indicates the presence of the cyclopentene ring and the ir spectrum (ν_{max}^{neat} 3040, 1630, 1600, 1009 and 746 cm^{-1}) suggests the existence of a cyclopropane ring and a cis-double bond. The decoupling experiments which clarified the situation of all protons, coupled with the reaction mechanisms described below, enable us to determine the structure of 5 as tetracyclo[$4.2.1.0^{4,8}.0^{5,7}$]nona-2-ene. Osmium tetroxide selectively oxidized the olefinic bond affording the corresponding diol (mp 80-83°),[8] whose nmr spectrum showed that the other parts of molecule 5 remains unchanged.

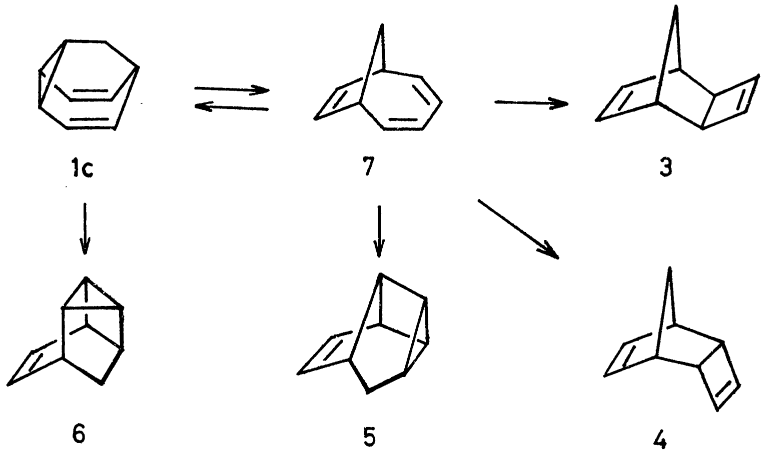
Despite of the difficulty in isolation of pure 6 due to proximate retention time of 5 and 6 in vpc, the nmr spectrum of a mixture (5 and 6) made possible to assign the following signals to 6; a pair of olefinic protons at δ 6.34 and 5.73 (both, splitted q, J=8.4, 6.5, 1.5 Hz), and geminal methylene protones at δ 1.75 (m, 1H, overlapped with one of the cyclopropyl protons) and 0.57 (q, J=9.7, 2.0 Hz, 1H). Appearance of one geminal methylene proton in such a high field shows that it suffers from the shielding effect due to the double bond. Thus, the structure of 6 was assigned as tetracyclo[$4.3.0.0^{4,8}.0^{5,7}$]nona-2-ene by comparison of its nmr spectra with that of tetramethoxycarbonyl derivative of 6 which was synthesized by Eberbach and Prinzbach.[9] Molecular model indicates that one of the geminal protons is located above the olefinic bond.

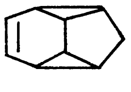
These photoroducts (3, 4, 5 and 6) did not interconvert each other under the thermal (vpc) and photochemical conditions,[10] indicating thus those to be primary products.

The formation of 3, 4 and 5 suggests that 1c initially converts into bicyclo-[4.2.1]nona-2,4,7-triene (7), which in turn affords 3, 4 and 5. While 3 and 4 are products originated from the $[_{\pi}2 + {}_{\pi}2]$ cycloaddition in the diene part of 7, the formation of 5 could be explained in terms of the $[_{\pi}2 + {}_{\pi}2]$ cycloaddition between an isolated olefinic bond and a double bond in the diene moiety.[11]

To confirm the intermediacy of 7, the photoreaction of 7 was carried out under the same condition as that of 1c. As expected, the reaction proceeded rapidly. After only 18 min. of irradiation, 97% of the starting material was consumed and four products 3, 4, 5 and barbaralane (1c) were obtained (see Table). The formation of 3, 4 and 5 should support our previous assumption. Furthermore, it is noteworthy that barbaralane (1c) was produced by the direct irradiation of 7. This suggests that a concerted $[_{\sigma}2 + {}_{\pi}2 + {}_{\pi}4]$ process would be involved in the photoreaction of 7 in addition to the well documented di-π-methane rearrangement. Absence of 6 in the photolysate of 7 (at least at an early stage of the irradiation) illustrates that 6 is originated from 1c presumably via a $[_{\sigma}2 + {}_{\pi}2]$ cycloaddition, but not from 7.

Contrary to the direct irradiation, 1c was a sole product in benzophenone-sensitized reaction of 7 and 1c remained unchanged even after prolonged irradiation under this condition (see Table).

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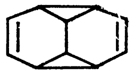
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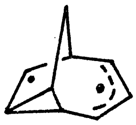
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In connection with the photochemistry of bullvalene (1a), the formation of 7 from 1c is a subject to discussion. The present results will cover at least three interpretations for this rearrangement: i) A direct concerted rearrangement of 1c via $[_{\sigma}2 + {}_{\pi}2 + {}_{\sigma}2 + {}_{\pi}2]$ process. ii) A two-step pathway; Initial conversion of 1c to a thermally labile intermediate (8)[12] followed by retro $[_{\sigma}2 + {}_{\sigma}2 + {}_{\pi}2]$ cycloreversion. The intermediate (8) could be formed either via the manner analogous to the formation of the thermally labile compound (9) from bullvalene (1a)[5b,13] or via some alternatives. iii) A pathway via a radical intermediate (10) which can be interconvertible to either 1c or 7. The similar transient was proposed in the photointerconversion between 1a and 2.[5c] However, it is uncertain at present whether the photorearrangement of 1c to 7 proceeds via single or via the combination of these pathways.

References

1) Organic Photochemistry XXXI: Part XXX; M. Nitta and T. Mukai, submitted to Heterocycles.

2) W. von E. Doering and J.W. Rosenthal, J. Amer. Chem. Soc. 88, 2078 (1966); G. Schröder, Chem. Ber., 97, 3140 (1964).

3) J.N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, J. Amer. Chem. Soc., 89, 612 (1967).

4) H. Tsuruta, T. Kumagai, and T. Mukai, Chem. Lett., 981 (1972).

5) a) M. Jones, Jr., S.D. Reich, and L.T. Scott, J. Amer. Chem. Soc., 92, 3118 (1970); b) S. Masamune and N. Derby, Accounts Chem. Res., 5, 272 (1972); c) L.T. Scott and M. Jones, Jr., Chem. Rev., 72, 181 (1972) and references therein.

6) H.E. Zimmerman and H. Iwamura, J. Amer. Chem. Soc., 92, 2015 (1970).

7) L.G. Cannell, Tetrahedron Lett., 5967 (1966).

8) Satisfactory elemental analysis were obtained for all new compounds.

9) W. Eberbach and H. Prinzbach, Helv. Chem. Acta., 50, 2490 (1967).

10) Compound 5 slowly affords 3 and 4 (less than 3% yield). Upon prolonged irradiation (over 25 hr), it yielded other polycyclic compounds. For example aceton-sensitized irradiation of 4 was shown to give homocubane. L.A. Paquette and J.C. Stowell, J. Amer. Chem. Soc., 92, 2584 (1970).

11) J. Zirner and S. Winstein, Proc. Chem. Soc., 235 (1964); W.R. Roth and B. Peltzer, Angew. Chem., 76, 378 (1964).

12) H. Tsuruta, K. Kurabayashi, and T. Mukai, Bull. Chem. Soc. Japan, 45, 2822 (1972); E. Vedejs, R.A. Gabel, and P.D. Weeks, J. Amer. Chem. Soc., 94, 5842 (1972).

13) H. Hojo, R.T. Seidner, and S. Masamune, ibid., 92, 6641 (1970).

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