

PHOTOCHEMISTRY OF 2,5,7-TRIPHENYLNORCARADIENE AND 1,3,6-TRIPHENYL-
CYCLOHEPTATRIENE. EVIDENCE FOR VALENCE ISOMERIZATION BETWEEN
NORCARADIENE AND CYCLOHEPTATRIENE SYSTEMS (1)

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Thermal 1,5-sigmatropic carbon rearrangement in norcaradiene system has been established (2), whereas a few examples of photochemical 1,5-sigmatropic carbon rearrangement have been suggested in benzenorcaradiene derivatives (3, 4). We investigated photolysis of the titled compounds and found a possibility of the photo-1,5-sigmatropic carbon rearrangement in monocyclic norcaradiene system, in addition to carbene formation (3,5,6) and 1,7-sigmatropic hydrogen shift (1b, 7). Furthermore, our result could reasonably be explained by proposing an equilibrium of 2,5,7-triphenylnorcaradiene (I) and its valence isomer, 2,5,7-triphenylcycloheptatriene (Ia)(8).

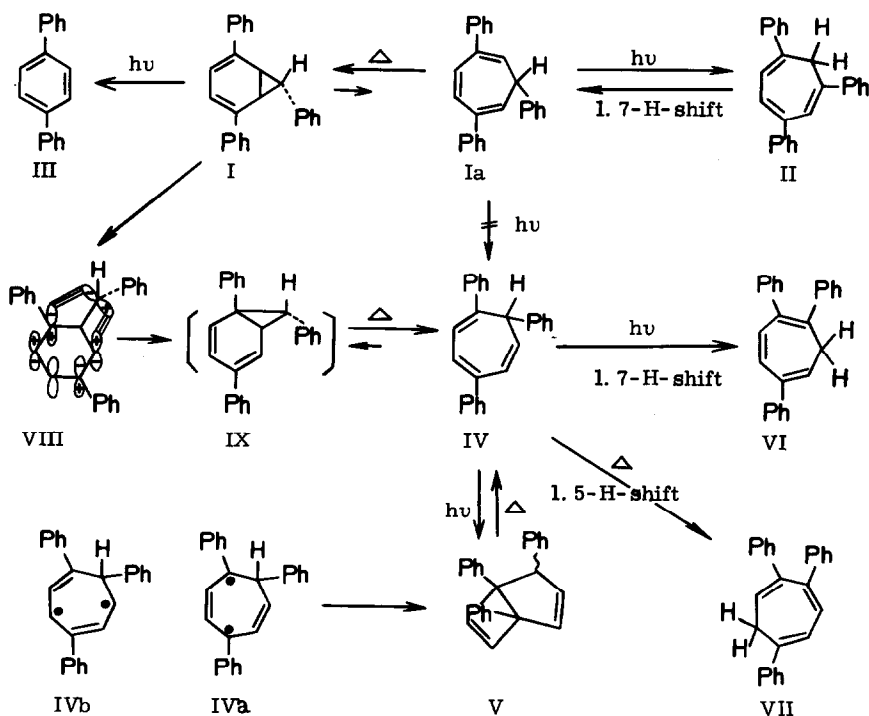
The photolysis of 2,5,7-triphenylnorcaradiene (I) (UV max in cyclohexane, 245 and 364 m μ) and 1,3,6-triphenylcycloheptatriene (II) (272 and 340 m μ) (8) was carried out in ethereal solution (10^{-2} M) using H.P. lamp (Toshiba H400-p) in Pyrex vessel for 5 hr and L.P. lamp (Ushio 6w) in quartz vessel for 7.5 hr. The results obtained are shown in Table I.

Table I

| Reactants & Conditions | | Products and their yield (%) | | | | | |
|------------------------|-----------|------------------------------|----|-----|----|----|----|
| | | I | II | III | IV | V | VI |
| I | H.P. lamp | 17 | 0 | 4 | 23 | 17 | 7 |
| | L.P. lamp | 16 | 34 | 3 | 15 | 0 | 7 |
| II | H.P. lamp | 12 | 15 | 3 | 32 | 8 | 7 |
| | L.P. lamp | 10 | 38 | 3 | 10 | 0 | 6 |

Product III is p-terphenyl and IV, oil, and V, m.p. 83°, were confirmed as 1,4,7-triphenylcycloheptatriene and 1,4,5-triphenylbicyclo[3.2.0]-hepta-

2,6-diene from the following spectral and chemical evidence. Mass spectra of IV and V; 320 (M^+). UV max in methanol in $m\mu$ ($\log \epsilon$); IV, 244 (4.30) and 325 (4.18); V, end absorption only. NMR spectrum in $CDCl_3$ (100 MHz) (9); IV, δ 4.76 (C_7 -H, d, $J=9.0$ Hz), 5.93 (C_6 -H, t, $J=9.0$), 6.53 (C_5 -H, d, $J=9.0$), 6.63 (C_2 & C_3 -H, not clear) and 7.2 (phenyl-H); V, δ 4.33 (C_4 -H, dd, $J=2.0$ & 2.5 Hz), 5.83 (C_6 or C_7 -H, d, $J=3.2$), 6.04 (C_2 -H, dd, $J=6.1$ & 2.5), 6.33 (C_3 -H, dd, $J=6.1$ & 2.0), 6.66 (C_6 or C_7 -H, d, $J=3.2$) and 7.1 (phenyl-H). Appearance of the C_7 -H signal of IV at lower field (δ 4.76) and large coupling constant (9 Hz) between C_6 and C_7 protons indicate that a conformer with axial 7-phenyl group is more stable than that with equatorial 7-phenyl group, in which two phenyl groups at the C_1 and C_7 positions have nonbonded interactions (10,11). Although product VI could not be isolated in a pure state (12), its nmr spectrum showing a peak of C_7 -H at δ 2.96 (d, $J=7.5$ Hz) and the fact that irradiation of IV with H.P. lamp afforded V and VI with recovery of IV support that the structure of VI is 1,2,5-triphenylcycloheptatriene. When V was heated at 110° for 10 min, it isomerized to IV quantitatively. Such an easy ring opening of the cyclobutene



ring in compound V, although the disrotatory opening is not thermally allowed, was attributed to nonbonded interaction of two phenyl groups located at the C₁ and C₅ positions and is explained by the stabilization effect of benzyl radicals which have resulted from this process. Thermal isomerization of IV at 137° afforded 1,4,5-triphenylcycloheptatriene (VII), m.p. 140°, which possesses the following spectra: 320 (M⁺); UV max in methanol in mμ (log ε), 251 (4.06) and 317 (4.04); NMR in CDCl₃ (60 MHz), δ 2.96 (C₇-H, d, J=7.5 Hz), 5.86 (C₆-H, t, J=7.5), 6.59 (C₂-H, d, J=6.0) and 7.3 (C₃-H and phenyl-H). Catalytic hydrogenation of IV and VII produced the identical triphenylcycloheptane, m.p. 81-84°.

The mechanism for the formation of the photo-products shown in Table I was discussed in the scheme above. Occurrence of the photo-equilibrium between I and II, upon irradiation of I or II with L.P. lamp, could be explained by proposing the thermal valence isomerization between I and Ia (8,13) and the photo-1,7-hydrogen shift of Ia or II. Since Ia should not absorb UV light longer than 300 mμ, as supported from the fact that 2- and 7-phenylcycloheptatrienes do not absorb at such a wavelength, irradiation of I with H.P. lamp resulted in no formation of II, but in other photo-reactions giving III and IV etc. Although phenylcarbene could not be trapped, the formation of III is an accepted photo-reaction of the norcaradienes (3,5,6). The product IV should not be originated from photo-1,7-phenyl migration (14) of Ia, but from the excitation of I itself, because the photo-products III-VI were formed, even though upon irradiation of I with H.P. lamp, without the formation of II, i.e., without the excitation of Ia. Thus the formation of IV from I might proceed via norcaradiene (IX) which was brought by the 1,5-carbon rearrangement of I. If the skeletal reorganization to IX is a concerted process, the stereochemistry of IX would be determined by the slither-mechanism of cyclohexadienyl radical (VIII), which is figured out as L.V.M.O. (ψ_4). Because IX is unstable and immediately transformed into its stable valence isomer IV, it is impossible to speculate about the stereochemistry of IX by considering the isomer IV. The products V and VI are secondary photoproducts from IV as shown in the experiment mentioned above. However, it should be noted that V was not obtained by the irradiation of I and II with L.P. lamp. There are two possible modes of

the photocyclization of IV, i.e., formation of V from the excited state IVa and an isomer from IVb. Although V has severe nonbonded interaction between two phenyl groups, a preferable formation of V may be ascribed to the contribution of the stability of two benzyl-type radicals included in IVa.

The photo-transformation of I was not quenched in the presence of oxygen as shown in Table II. This result indicates that the photo-reaction of I might proceed through a singlet state of the concerned species (7).

Table II

| Conditions ^a | Products and their yield (%) | | | | | | |
|----------------------------|------------------------------|----|-----|----|---|----|----------------|
| | I | II | III | IV | V | VI | X ^b |
| H.P. lamp + O ₂ | 18 | 0 | 2 | 24 | 7 | 2 | 14 |
| H.P. lamp + N ₂ | 15 | 0 | 4 | 24 | 9 | 2 | 0 |

- a) In acetone ($10^{-2}M$) and in Pyrex vessel for 8 hr under stream of O₂ or N₂.
 b) Product X is a photo-oxidation product, m.p. 149-150°, having C₂₅H₂₀O₂.

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