

2,5,7-TRIPHENYLNORCARADIENE AND RELATED CYCLOHEPTATRIENES

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Recently much attention has been focused on the valence tautomerization of norcaradienes and cycloheptatrienes. In this tautomerization, bridging C₁ and C₆ positions with three-atom bridge (1), incorporation of one or two double bonds into an condensed aromatic system (2), or introduction of negative groups at the C₇ position (3) favored the norcaradiene system. We find that the introduction of three phenyl groups into cycloheptatriene also leads to formation of a stable norcaradiene derivative. 2,5,7-Triphenylnorcaradiene (I), thus obtained, is the first example (4) of a simple norcaradiene having a hydrogen atom at the C₇ position. It exhibited interesting isomerization induced by heat and light and an outline of the results obtained will be reported.

Reaction of phenyl magnesium bromide with diphenyltropylium salts obtained from diphenylcycloheptatrienes (5) by hydride abstraction with triphenylmethyl fluoroborate (6), provided I, m.p. 170° (7), (yield 22 %) and oil (40 %). This oil, upon heating at 160° for 50 hr, afforded 1,3,6-triphenylcycloheptatriene (II, m.p. 132-133° (18 %). The structures of I and II were confirmed by the following evidence: mass spectra of I and II; m/e 320; ultraviolet spectra in cyclohexane; I, 245 and 364 m μ (log ϵ 4.46 and 4.03); II 272 and 340 m μ (log ϵ 4.61 and 4.14); nmr spectra in CDCl₃; I (60 Mc), τ 8.02 (H₇, triplet, J=5.2 cps). 6.12 (H₁ and H₆, doublet, J=5.2 cps), 3.25 (H₃ and H₄, singlet), and 2.4-2.8 (phenyl protons, multiplet); II (100 Mc), τ 6.70 (H₇, singlet), 3.40 (H₅, doublet, J=6.5 cps), 3.29 (H₂, broad singlet), 2.97 (H₄, double doublet, J=6.5 and 1.1 cps) and 2.4-2.9 (phenyl protons, multiplet). Ozonization of I gave 1,2-cis-dibenzoyl-3-trans-phenylcyclopropane (III), m.p. 153°, (80 %), which, in its nmr spectrum (100 Mc in CDCl₃), showed an AB₂ coupling pattern at τ 6.48 (H_A proton, J=6.0 cps) and

6.63 (B protons) (8).

As shown in Fig. 1. heating of I in chloroform at 121.0° in a sealed tube resulted in decrease of I and formation of 1,3,5-triphenylcycloheptatriene (IV) (9) followed by subsequent transformation to II. Finally, I disappeared completely and a 5 to 1 equilibrium ratio of II/IV was attained. Each step of this successive reaction (I \rightarrow IV \rightarrow II) was found to be unimolecular. The kinetic data shown in Tables I and II were obtained by measuring areas of the H_{1,6} signal of I and the H₇ signal of II and IV in their nmr spectra.

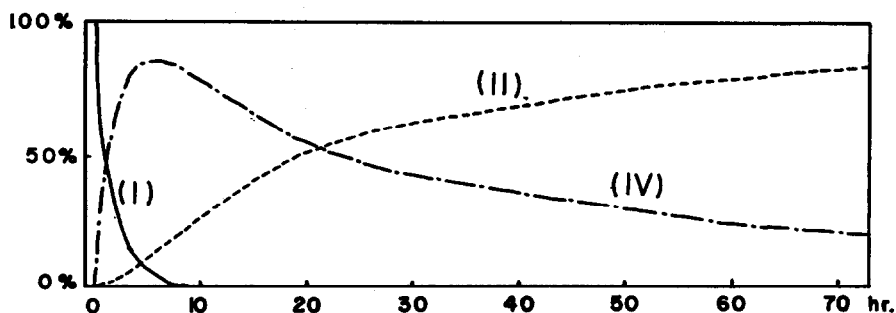


Fig. 1. Depletion of I and formation of IV and II during heating of I, at 121.0° C

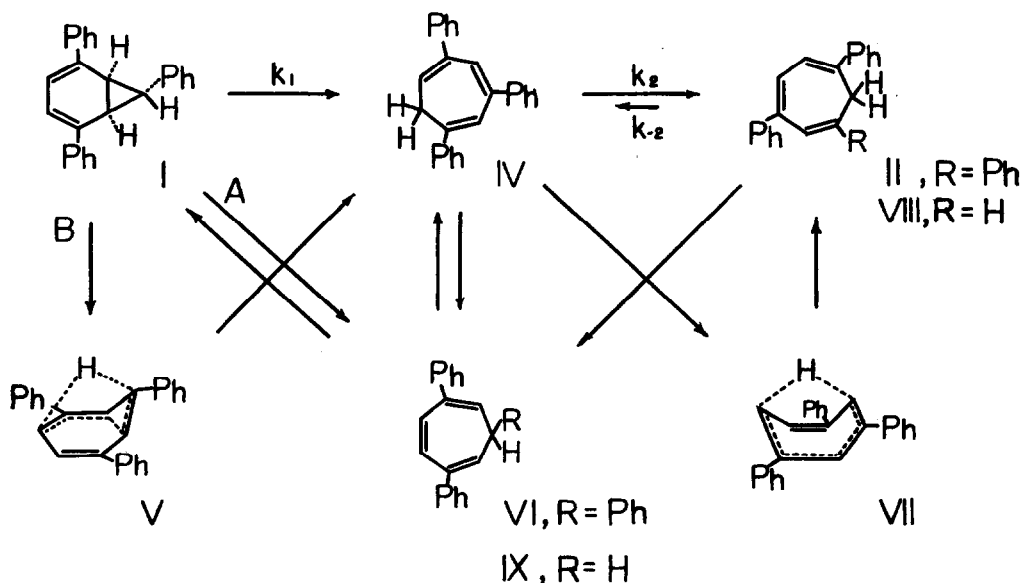


TABLE I. Rate Constants (sec^{-1}) of the Isomerization

Temp., $^{\circ}\text{C}$	$K_1(\text{I} \rightarrow \text{IV})$	$K_2(\text{IV} \rightarrow \text{II})$	7-Phenylcycloheptatriene \rightarrow 3-Isomer	1,4-Bis(7-cycloheptatrienyl)benzene \rightarrow 3-Isomer
110.5	6.50×10^{-5}	3.4×10^{-6}		
121.0	1.64×10^{-4}	9.3×10^{-6}	3.6×10^{-5} (Ref.10a)	3.33×10^{-5} (Ref.10b)
131.5	4.03×10^{-4}	2.3×10^{-5}		

TABLE II. Activation Parameters of the Isomerization *

	I \rightarrow IV	IV \rightarrow II	7-Phenylcycloheptatriene \rightarrow 3-Isomer	1,4-Bis(7-cycloheptatrienyl)benzene \rightarrow 3-Isomer
ΔE_a (Kcal/mol)	26.0	27.8	27.6	30.6
ΔH^* (Kcal/mol)	25.2	27.2	26.9 (Ref.10a)	29.8 (Ref.10b)
ΔS^* (e.u.)	-12.7	-13.4	-11.7	-3.9

* In this work, calculation was made from data at 121°C

The isomerization of IV to II seems to proceed by 1,5-hydrogen shift through transition state VII (11,12). The kinetic parameters are very similar to those of the thermal isomerization of 7-phenylcycloheptatriene to 3-isomer (Table I and II) (10). For the rearrangement I \rightarrow IV, one of the most likely pathways is via intermediate VI (path A). That is, norcaradiene I is in equilibrium with cycloheptatriene VI (13), which then proceeds to IV by 1,5-hydrogen shift. However, it should be noted that the rate of I \rightarrow IV is faster than IV \rightarrow II ($K_1 > K_2$) or than the rate of the thermal 1,5-hydrogen shift of other cycloheptatrienes (Table I) (10). If the rate from the intermediate VI to IV is assumed to be comparable with that of the thermal isomerization of others, path B may also be possible as an alternative one, in which V represents the likely transition state (14,15). The rigidity and electronic state of the transition state V are not so different from the transition state VII of the step IV \rightarrow II. The activation parameters of the steps I \rightarrow IV shown in Table II are similar to those of the steps IV \rightarrow II.

On irradiation in dioxane at room temperature for 5 hr using low pressure mercury lamp (Ushio 6W), I afforded a mixture of II (43 %), I (21 %), p-terphenyl (ca 1 %) and an unseparable oil. Irradiation of II in the same manner yielded I (12 %), II (31 %) and an oil. These preliminary results suggest the occurrence of a photo-equilibrium between I and II. A possible pathway from I to II is via

disrotatory process giving VI (16), followed by the 1,7-hydrogen shift (12). On the other hand, the isomerization of II to I can be explained by a photo-1,7-hydrogen shift affording VI (12), followed by thermal isomerization of VI to I (11). Compared with the photoisomerization of II, it should be noted that the irradiation of 1,4-diphenylcycloheptatriene (5) (VIII) afforded 2,5-diphenylcycloheptatriene (IX), oil (yield 30 %) and 3,7-diphenylcycloheptatriene (X), m.p. 57° (50 %); nmr spectra in CDCl_3 (60 Mc): IX, τ 7.58 (H_7 , triplet, $J=7.0$ cps), 4.35 (H_1 and H_6 , triplet, $J=7.0$ cps), 3.02 (H_3 and H_4 , singlet) and 2.3-2.9 (phenyl protons, multiplets); X, τ 7.15 (H_7 , broad triplet, $J=5.5$ cps), 4.50 (H_1 and H_6 , multiplets), 3.70 (H_2 and H_5 , broad triplet), 2.95 (H_4 , doublet, $J=6.2$ cps) and 2.2-2.9 (phenyl protons, multiplets). Norcaradiene derivatives could not be detected in the product by nmr spectroscopy (17). This fact leads to the suggestion that the irradiation of II gives rise to VI as intermediate, and the resulting cycloheptatriene VI proceeds to its valence tautomer I at ordinary temperature; that is, the introduction of the third phenyl group into the C_7 position plays an important role in the formation of stable norcaradienes.

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REFERENCES AND FOOTNOTES

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4. We have learned recently that compound (I) has been synthesized by the similar method to ours by A. Cairncross, however, no thermal or photochemical reaction was investigated: PhD thesis of Yale University, 1963 (under Dr. Doering's supervision); private communication from Dr. Cairncross to Prof. T. Nozoe, to whom the authors are indebted for the information about Dr. Cairncross work.

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7. Satisfactory elemental analyses were obtained for all new compounds.
8. B. M. Trost, J. Am. Chem. Soc., 89, 138 (1967).
9. Compound(IV) could not be isolated in pure state, but its structure was elucidated without doubt from the following nmr spectra in $CDCl_3$: (60 Mc) τ 7.03 (H_7 , doublet, $J=7.5$ cps), 4.16 (H_6 , triplet, $J=7.5$ cps) 3.30 (H_2 , singlet), 2.3-2.9 (H_4 and phenyl protons, multiplet).
10. (a) A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chem., 82, 741 (1963); (b) R. W. Murry and H. L. Kaplan, J. Am. Chem. Soc., 88, 3527 (1966).
11. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).
12. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 2511 (1965).
13. The activation energy for valence tautomerization in the norcaradiene-cycloheptatriene system was estimated to be quite low (< 10 Kcal/mole) cf (a) K. N. Klump and J. P. Chesick, J. Am. Chem. Soc., 85, 130 (1963); (b) F. A. L. Anet, ibid., 86, 458 (1964).
14. Activation energies should be compared, but comparison cannot be made because ΔE_a for $I \rightarrow IV$ is the sum of $VI \rightarrow IV$ and ΔH between I and VI.
15. There is some evidence against path B (Huisgen and Juppe, Ref. 2a); 7-carboethoxy-2,3-benzonorcaradiene underwent thermal rearrangement to give 6-carboethoxy-1,2-benzocycloheptatriene. However, this isomerization also can be explained by path B followed by 1,5-hydrogen shift.
16. Photochemically, this process is unfavorable by Woodward-Hoffmann's rule (11). However, if a thermal equilibrium $I \rightleftharpoons IV$ are possible at room temperature this pathway is favorable. As other pathway, a concerted one, in which cleavage of the three membered ring and hydrogen shift takes place simultaneously or process giving diradical can not be discarded at present.
17. Details will be reported elsewhere.