The Photochemical Reaction of 1,3,4,6-Tetraphenylhexatriene

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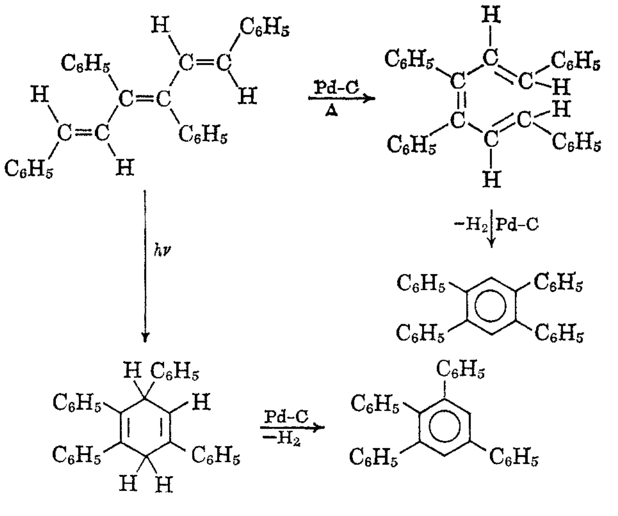
Substituted hexatrienes have been cyclized to 1,3-cyclohexadienes both by irradiation[1] and by passing over hot aluminum oxide.[2-4] We wish to report the photochemical cyclization and rearrangement of 1,3,4,6-tetraphenylhexatriene to 1,2,3,5-tetraphenyl-1,4-cyclohexadiene. 1,3,4,6-Tetraphenylhexatriene was synthesized from 1,4-dibromo-2,3-diphenylbutadiene and benzaldehyde, employing a double Wittig[5-7] reaction (see the Experimental Section).

In order to obtain conclusive proof for the structure of 1,3,4,6-tetraphenylhexatriene, the compound was refluxed in mesitylene over 10% palladium-charcoal to cyclize and dehydrogenate it to 1,2,4,5-tetraphenylbenzene. The tetraphenylbenzene produced had the same melting point, mixture melting point, and ultraviolet spectrum as those of an authentic sample prepared according to the Dilthey method.[8] When 1,3,4,6-tetraphenylhexatriene was irradiated in the sunlight or with a Westinghouse sunlamp, the compound cyclized and also rearranged to yield 1,2,3,5-tetraphenyl-1,4-cyclohexadiene. Kinetic studies showed that the process was a first-order one. The reactions may be summarized as shown in Scheme I.

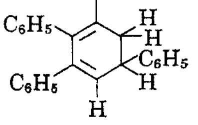
SCHEME I



The position of the phenyl groups in the rearranged product was established by dehydrogenation to yield 1,2,3,5-tetraphenylbenzene which had the same melting point, mixture melting point, and ultraviolet spectrum as that of an authentic sample synthesized by the procedure employed by Woods.[9]

The structure of the photoproduct was established by its nmr spectrum and elimination of the other possible isomeric structures. The nmr spectrum exhibited 20 phenyl protons centered around τ 3.0, a vinyl proton (doublet) at 4.3, a C_6H_5CH proton (doublet) at 5.9, and two equivalent methylene protons (singlet) at 7.7.

The structures of the other possible tetraphenylcyclohexadiene isomers are listed below.



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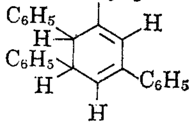
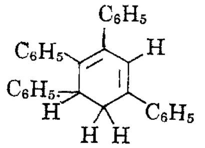
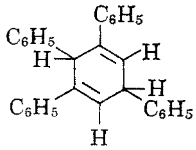


II



III



IV

Compounds I and II have previously been reported by Woods.[9,10] Compound I is a yellow oil. Compound II has a melting point of 143–145° which is similar to that of the cyclohexadiene isolated in the present work. It was prepared according to Woods' method[9] and showed a depressed mixture melting point with the photoproduct. The nmr spectra were also different. Structure III was eliminated on the basis of the ultraviolet spectra of the photoproduct which has λ_{max} 238 mμ (ϵ 23,800). Structure III has the *s-cis* 1,4-diphenylbutadiene chromophore which should have a higher λ_{max} and molar extinction coefficient. The nmr spectrum is also inconsistent with structure III. The methylene protons in the nmr spectrum of the photoproduct exhibit a singlet, whereas in structure III they would produce a doublet.

Structure IV was also eliminated on the basis of the nmr spectra. This structure has two vinyl protons (doublet) and two C_6H_5CH protons (singlet and triplet).

Of the possible mechanisms which could lead to the rearranged product, two involve formation of intermediate V, which then would react further to produce the observed product (Scheme II).

Pathway A involves tautomerization to a 1,3-cyclohexadiene, followed by a "bond switching" rearrangement similar to that reported by Barton[11] and Evanega.[12]

Pathway B involves a direct tautomerization to V, which then can undergo a free-radical reaction to produce 1,2,3,5-tetraphenyl-1,4-cyclohexadiene.

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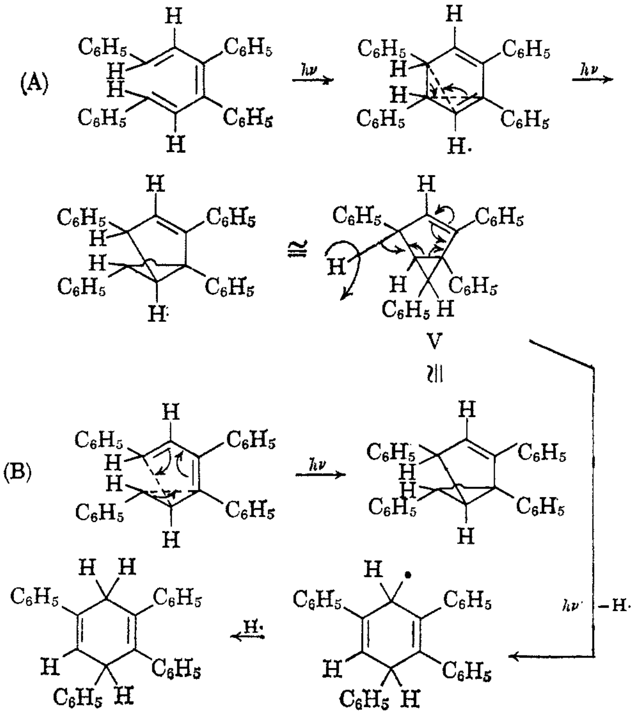
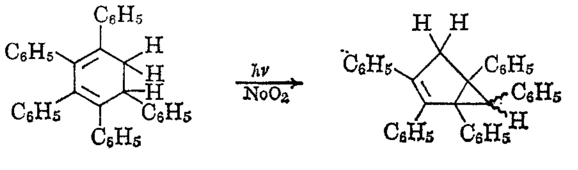
SCHEME II



Evanega[12] has reported the photochemical rearrangement of 1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene to produce a compound analogous with the proposed intermediate V, but which apparently was stable to further irradiation. The driving force for further reaction of the proposed intermediate V may be the formation of the conjugated stilbene moiety in the product.



Experimental Section

Preparation of 1,3,4,6-Tetraphenylhexatriene.—2,3-Diphenyl-2,3-butanediol was prepared by the reaction of benzil with 2 equiv of methylmagnesium iodide according to the procedure of Johlin.[13] The butanediol was converted into 2,3-diphenylbutadiene by vacuum distillation from potassium hydrogen sulfate.[14]

2,3-Diphenylbutadiene was then brominated to yield bisbromomethyl stilbene according to the method of Allen.[15]

A mixture of 6.0 g (0.016 mole) of bisbromomethylstilbene and 5.5 g (0.033 mole) of triethylphosphite was heated to a slow reflux for 1 hr. A small amount of ethyl bromide was then distilled off, and the pot temperature was raised to 190–200° for 1 additional hr. The yellow solution was cooled to room temperature, 40 ml of dimethylformamide was added, and the contents of the flask were poured into a 125-ml flask containing 1.9 g of sodium methoxide (0.035 mole). The deep red solution formed was cooled in an ice bath with swirling for 5 min. Benzaldehyde (3.5 g, 0.033 mole) was added dropwise with continued cooling. The reaction flask was then allowed to stand at room temperature for 25 min. A solution of 10 ml of methanol and 20 ml of water was then added to the reaction mixture and the flask was shaken for 1 min. The resulting yellow solid was filtered, washed with water and methanol, and recrystallized from methylcyclohexane to yield 3.7 g (48% based on bisbromomethyl stilbene) of pale yellow crystals, mp 176–178°.

Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol wt, 384. Found: C, 93.61; H, 6.13; mol wt (osmometer, diphenyl mercury in monoglyme standard), 350, 361.

The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 247 mμ (ϵ 13,6000), 253 (13,300), 270 (14,600), 353 (49,000), 368 (65,600), and 386 (50,000).

Cyclodehydrogenation of 1,3,4,6-Tetraphenylhexatriene.—A mixture of 0.2 g of 1,3,4,6-tetraphenylhexatriene and 0.05 g of 10% palladium–charcoal was refluxed in mesitylene for 20 hr. The solution was filtered and the solvent was evaporated. The solid residue was recrystallized from benzene–methanol to yield 0.12 g of 1,2,4,5-tetraphenylbenzene, mp 270–271°. The melting point, mixture melting point, and ultraviolet absorption spectrum were identical with those of an authentic sample prepared according to the method of Dilthey[8] from 3,4-diphenylcyclopentadienone and diphenylacetylene. The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 253 mμ (ϵ 56,000).

Irradiation of 1,3,4,6-Tetraphenylhexatriene.—A solution of 1.0 g of 1,3,4,6-tetraphenylhexatriene in 400 ml of methylcyclohexane was set in the sunlight in a stoppered Pyrex flask for 8 days during which time the yellow solution became nearly colorless. Evaporation of the solvent yielded a faintly yellow solid which was recrystallized from ethanol to yield 0.82 g of 1,2,3,5-tetraphenyl-1,4-cyclohexadiene as colorless crystals, mp 144–145°. Concentration of the mother liquor yielded an additional 0.05 g of the same material, yield 87%.

Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol wt, 384. Found: C, 93.50; H, 6.36; mol wt (osmometer, diphenylmercury in monoglyme standard), 364.

The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 238 mμ (ϵ 23,800). The nmr spectrum (ppm) gave phenyl protons centered about τ 3.0, doublet at 4.3, doublet at 5.9, and a singlet at 7.7; integration 20:1:1:2.

The irradiation was also carried out with a Westinghouse sunlamp for 40 hr, and produced the same results.

Dehyrogenation of 1,2,3,5-Tetraphenyl-1,4-cyclohexadiene.—A mixture of 0.3 g of 1,2,3,5-tetraphenyl-1,4-cyclohexadiene and 0.1 g of 10% palladium–charcoal was refluxed in 15 ml of mesitylene for 17 hr. The solution was filtered and the solvent was evaporated. The residue was taken up in 5 ml of ethanol and warmed to dissolve some dark residue. The remaining tan crystals were filtered and recrystallized from benzene–methanol to yield 0.13 g of 1,2,3,5-tetraphenylbenzene, mp 224–225°. The melting point, mixture melting point, and ultraviolet absorption spectrum were identical with those of an authentic sample prepared according to the methods of Woods.[9]

Acknowledgment.—The authors wish to thank the National Science Foundation for its support and encouragement in the form of Grant GP 1984.

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The Electron Spin Resonance Spectrum of the 9-Nitrotriptycene Anion Radical

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The question of transannular interaction between the benzene rings in triptycene has prompted several workers[1–3] to examine the ultraviolet spectrum of the compound. While an electron spin resonance (esr) spectroscopic study of the triptycene anion radical would have an obvious bearing on this question such a study has not been reported. DeGroot and van der Waals[4] have studied the lowest triplet state of triptycene by magnetic resonance and report that

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