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PHOTOCYCLIZATION OF PROPENES TO CYCLOPROPANES

NOVEL PHENYL AND HYDROGEN MIGRATIONS IN π,π^* SYSTEMS

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The photocyclization of 1,3-diphenylpropene to *cis*- and *trans*-1,2-diphenylcyclopropane was recently reported (1). This cyclization is necessarily accompanied by either phenyl or hydrogen migration or both. The scope of this reaction is being defined, with emphasis on systems in which the identity of the migrating group may be deduced from the structure of the photoproduct.

In this paper, we report the photocyclization of five additional phenyl-substituted propenes to cyclopropanes, demonstrating that the reaction is reasonably general; furthermore, *cyclization is clearly associated with phenyl migration* in three cases and with *hydrogen migration* in another.

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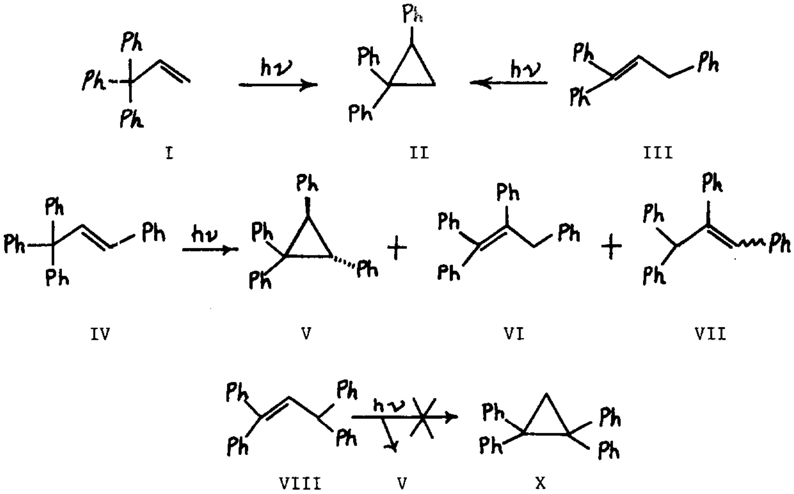
3,3,3-Triphenylpropene (I), (2,3), m.p. 75°; $\nu_{max}^{CS_2}$ (cm.$^{-1}$) 1190, 1036, 1005, 902, 753, 699, 676, 637, and 565, was irradiated with 2537 Å light in a degassed benzene solution (0.1$\underline{M}$) (4) for 50 hours. The major product, isolated by gas chromatography at 200° (5), was



1,1,2-triphenylcyclopropane (II), the result of cyclization and concomitant phenyl migration. In addition considerable starting material and a number of unidentified minor products were observed. The structure of II follows from the identity of its g.c. retention time and n.m.r. and I.R. spectra with those of a sample prepared (51%) by heating diphenyldiazomethane with styrene (3), m.p. 49.5-50.0°; $\nu_{max}^{CS_2}$ (cm.$^{-1}$) 1138, 1078, 1037, 777, 762, 747, 735, 698, 694, 575, and 550.

As anticipated II was also obtained in satisfactory yield by irradiation (17 hours) of 1,1,3-triphenylpropene (III) (6); the reaction mixture contained two additional minor products and starting olefin.

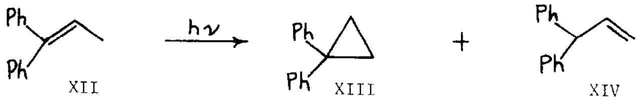
Upon irradiation for 5 hours, 1,3,3,3-tetraphenylpropene (IV) (2,3), m.p. 114.5-115°; λ_{max}^{EtOH} 220, 253 mu (ϵ 23,400, 16,500); $\nu_{max}^{CS_2}$ (cm.$^{-1}$) 1190, 1160, 1090, 1040, 915, 905, 767, 750, 700, 621, and 555, was transformed into 1,1,2,3-tetraphenylcyclopropane (V) in excellent yield; no starting material survived. Longer irradiation (24 hours) gave a most complex mixture, which included small amounts of V and olefins VI and VII, isolated by g.c. at 270°.

Photocyclization to V in good yield also occurred upon irradiation (24 hours) of 1,1,3,3-tetraphenylpropene (VIII) (3,7), in another case of cyclization with a phenyl shift. The reaction mixture appeared to contain little else with the exception of some starting material; it was analyzed by both gas (270°) and elution chromatography. Neither cis-1,1,2,3-tetraphenylcyclopropane (IX) (8) nor 1,1,2,2-tetraphenylcyclopropane (X) was detected. Since X, the product expected from cyclization with hydrogen migration, was not found, it is likely although not certain (9) that hydrogen migration was negligible (10).

The structure of V, m.p. 130-131°; λ_{max}^{EtOH} 227 mu; $\nu_{max}^{CS_2}$ (cm.$^{-1}$) 3100, 3080, 3030, 1070, 1030, 910, 773, 752, 740, 695, 570, 550; n.m.r., τ 6.58 (2 H singlet), τ 2.75-3.18 (20 H) (3), was painstakingly established by degradation and by two independent syntheses. Chromic acid oxidation in acetic acid at 60° gave both benzophenone and benzoic acid. Ozonolysis in 95% acetic acid (oxidative work up) (11) followed by esterification with diazomethane afforded trans-1,1,2,3-tetracarbomethoxycyclopropane, identified by the correspondence of its I.R. spectrum and retention time with those of authentic material (12). The trans cyclopropane V was synthesized quantitatively from its cis isomer IX (8) by heating to 260° for 6 minutes as well as by passing it through a gas chromatograph at 270°. Decomposition of diphenyldiazomethane in the presence of cis-stilbene also gave V (13). The identity of V from the photochemical reactions with that from the other syntheses was confirmed by mixture melting points and by comparing their I.R. spectra and retention times.

The olefins VI and VII were identified by the conformity of their retention times and I.R. spectra with those of authentic samples (*vide infra*). 1,1,2,3-Tetraphenylpropene (VI), m.p. 139.5-140° (14); $\lambda_{\max}^{\mathrm{EtOH}}$ 227, 270 mu (ϵ 20,000, 11,600); $\nu_{\max}^{\mathrm{CS_2}}$ (cm.$^{-1}$) 1078, 1033, 962, 914, 795, 775, 763, 727, 699, 630, 620, 610, 580, and 540; n.m.r., τ 6.18 (2 H singlet), 2.60-3.15 (20 H), was obtained by iodine-catalyzed dehydration of 1,1,2,3-tetraphenylpropanol (XI) (15), in refluxing benzene.

When XI or VI is heated with iodine in refluxing xylene the product is *trans*-1,2,3,3-tetraphenylpropene (VII), m.p. 131.5-133° (14), $\lambda_{\max}^{\mathrm{EtOH}}$ 220, 305 mu (ϵ 21,800, 14,200), $\nu_{\max}^{\mathrm{CS_2}}$ (cm.$^{-1}$) 1075, 1031, 903, 833, 787, 770, 758, 746, 738, 697, 630, 600, 588, 522, and 495; n.m.r., τ 4.93 (1 H singlet), 2.50-3.15 (21 H).



After irradiating a solution of 1,1-diphenylpropene (XII) for 30 hours, the products isolated by gas chromatography (5) included 1,1-diphenylcyclopropane (XIII), $\nu_{\max}^{\mathrm{CS_2}}$ (cm.$^{-1}$) 1325, 1130, 1080, 1055, 1025, 936, 825, 755, and 698, and 3,3-diphenylpropene (XIV), $\nu_{\max}^{\mathrm{CS_2}}$ (cm.$^{-1}$) 1025, 990, 912, 755, 734, 698, and 530. The reaction mixture also contained starting material and a number of unidentified compounds. The cyclopropane XIII was identified by comparison (I.R., retention time) with a sample made by Bumgardner

(16a). The structure of the olefin XIV was confirmed by its I.R. and n.m.r. spectra, which agreed with published values (16b,17) and by direct comparison of its retention time and I.R. spectrum with those of a sample prepared by reaction of 3,3-diphenylpropyltrimethylammonium iodide (16a) with sodium hydride.

The conversion of XII to XIII appears to be the first clear case of photocyclization of an olefin to a cyclopropane in solution in which hydrogen migration is required. The formation of the olefin XIV from XII is notable in that two successive 1,2-hydrogen migrations (or an even less likely 1,3-hydrogen shift) are apparently needed, even if XIII is an intermediate.

trans-1,2,3-Triphenylpropene (XV), m.p. 62-63°; $\nu_{max}^{CS_2}$ 3110, 3080, 3000, 1070, 1027, 915, 775, 745, 718, 690, 640, 610, 545, 520, and 505, (18) and 1,1,2,3-tetraphenylpropene (VI), which possess stilbene chromophores, fail to undergo photocyclization to cyclopropanes. Perhaps trace amounts of phenanthrenes, known to be formed from such systems, quench cyclopropane formation (19). After irradiation of solutions of VI for 144 hours, nothing but unchanged VI was detected by gas chromatography. Irradiation of XV apparently resulted only in partial conversion to the cis isomer which was separated by gas chromatography, $\nu_{max}^{CS_2}$ (cm.$^{-1}$) 3110, 3080, 3000, 1060, 1017, 905, 763, 745, 715, 690, 553, 530, and 505. The structures of XV and its cis isomer were assigned on the basis of U.V. data (trans, λ_{max}^{EtOH} 275 mu; cis λ_{max}^{EtOH} 220, 260 mu) using cis- and trans- stilbene and their α-methyl analogs as models (20).

A discussion of the mechanisms of these reactions will be deferred until the results of labeling, kinetic, and quenching experiments currently in progress may be reported. Cyclization with alkyl migration is also under investigation.

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2. I and IV were synthesized by the Wittig reaction, involving treatment of triphenylacetaldehyde with the appropriate alkylidenetriphenylphosphorane. Satisfactory elemental analyses have been obtained for all new compounds described. Details of syntheses will appear in a later paper.

3. The n.m.r. spectrum, for which we are much indebted to Mr. Gordon Boudreaux of the Southern Regional Research Laboratory, U. S. Department of Agriculture, was consistent with this structure.

4. All irradiations were carried out in quartz vessels containing rigorously degassed benzene solutions (0.1M). An air cooled (35-40°) Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 low pressure mercury lamps was employed as a light source. Little or no effort to find optimum conditions for cyclopropane formation has been made for most of these reactions.

5. A 210 x 0.6 cm. i. d. glass column packed with 30% silicone gum (SE-30) on 60-80 mesh acid- and base- washed Chromosorb P was employed in all g.c. work except for the separation of 1,1-diphenylcyclopropane, for which a similar column with Carbowax 20M as the liquid phase was used.

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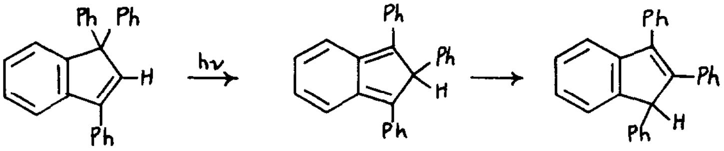
8. We thank Professor M. A. Battiste, University of Florida, for a generous sample of IX, prepared from 1,2,3,3-tetraphenylcyclopropene by reduction with diimide. He will publish details of its preparation and of its thermal isomerization.

9. While X is quantitatively isomerized to VIII in 5 minutes at 300°, and was unstable to gas chromatography at 240°, the results of preliminary experiments indicate that it is relatively stable to irradiation under the reaction conditions.

10. A related transformation occurred when 1,3,3-triphenylindene XVI was irradiated. Conversion to 1,2,3-triphenylindene XVIII was observed. It is inviting to propose that phenyl migration gives 1,2,3-isoindene (XVII) (an o-xylylene) which in a subsequent "dark reaction" isomerizes to the indene. Attempts to trap the suggested intermediate are in progress. Alternatively successive migrations of a phenyl group and hydrogen atom cannot be discounted at this stage.



XVI XVII XVIII

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