Orbital Symmetry and Steric Control in the Photorearrangement of 1,3,5-Hexatrienes to Bicyclo[3.1.0]hex-2-enes[1]

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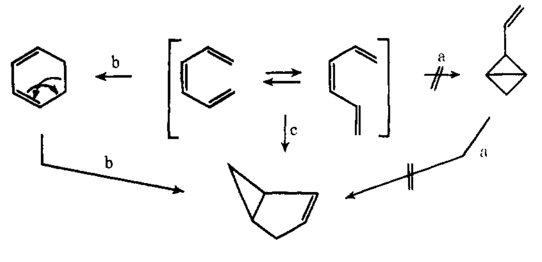
Abstract: Irradiation of (*Z,Z,E*)- or (*Z,Z,Z*)-1,2,6-triphenylhexa-1,3,5-triene (**6** or **13**, respectively) gave rise to 4-*exo*,6-*exo*- (**8**) and 4-*exo*,6-*endo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**17**), respectively. The formation of bicyclohexenes **8** and **17** from the (*Z,Z,E*)- and (*Z,Z,Z*)-trienes was shown to be a two-photon reaction involving initial cis–trans isomerization about the terminal C_1–C_2 bond followed by ${}_{\pi}4_s + {}_{\pi}2_a$ cycloaddition. Irradiation of *cis*- and *trans*-1,5,6-triphenylcyclohexa-1,3 diene also afforded *exo,exo*- (**8**) and *exo,endo*-bicyclohexenes (**17**), respectively. Secondary steric factors appear to control the direction of the conrotatory ring opening. The formation of the bicyclohexenes is in accord with the Woodward–Hoffmann predictions. The (1,5 + 4,6) bond closures are controlled by the nodal structure of the lowest π^* level of the most favorable ground-state conformation.

In 1958 Dauben and coworkers reported the first observations dealing with the photorearrangement of 1,3,5-hexatrienes to bicyclo[3.1.0]hex-2-enes,[3] a field which subsequently has been rather extensively studied.[4–18] This reaction has been discussed in terms of at least three mechanistic pathways:[19] (1) a vinylcyclopropane–cyclopentene rearrangement of a hypothetical 2-vinylbicyclo[1.1.0]butane intermediate (path a); (2) a prior photoisomerization to a 1,3-cyclohexadiene followed by a bond-switching process (path b); and (3) an electrocyclic, intramolecular photo-Diels–Alder reaction (path c). Meinwald and Mazzocchi[19] have shown, by deuteration experiments, that 1,1-dimethylhexatriene is photoisomerized to 6,6-dimethylbicyclo[3.1.0]hex-2-ene without passing through a vinylbicyclobutane intermediate. Consequently, pathway a can be discounted for this system and probably for closely related systems. In most cases it has been assumed that the corresponding 1,3-cyclohexadienes were not involved in the cyclization of 1,3,5-hexatrienes to bicyclo[3.1.0]hexenes, despite the fact that cyclohexadiene formation is a common and general photoreaction of hexatrienes.[20] In at least one case, however, a 1,3-cyclohexadiene has been shown to be the precursor of the bicyclohexene system.[21] There are some additional studies, however, which indicate that the bond switching process (*i.e.*, path b) is not the principal pathway involved in the isomerization of 1,3,5-hexatrienes to bicyclo[3.1.0]hexenes.[22] Specifically, optically active α-phellandrene[5a,22] is known to give inactive bicyclo[3.1.0]hex-2-enes as photoproducts. This result indicates that an intermediate in which chirality is lost is involved in the above transformation.



Orbital symmetry considerations and an acute sense of stereochemical requirements led Woodward and Hoffmann to view these rearrangements as examples of photochemical Diels–Alder reactions.[23] If concerted, this reaction can be considered as a 4 + 2 cycloaddition, in which case it should be either a (${}_{\pi}4_s + {}_{\pi}2_a$) or a (${}_{\pi}4_a + {}_{\pi}2_s$) process. Alternatively, it could be viewed as a 2 + 2 + 2 cycloaddition which would be photochemically allowed if antarafacial on all three components or on one. It is interesting to note that, in most of the cases where the hexatriene is sufficiently labeled to provide a test of these conclusions, the gross observations made are not in accord with orbital

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[1] Photochemical Transformations of Small Ring Compounds. XLI. For part XL see A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.* **94**, 5859 (1972). For a preliminary descripton of this work see A. Padwa and S. Clough, *J. Amer. Chem. Soc.*, **92**, 5803 (1970).

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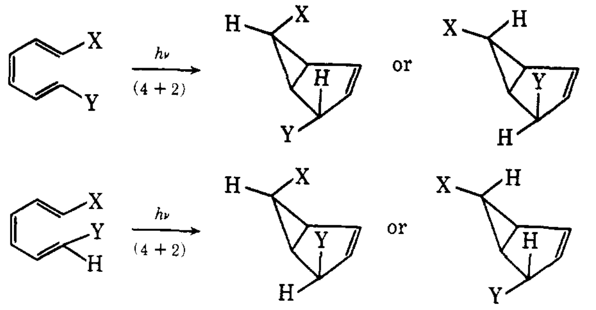
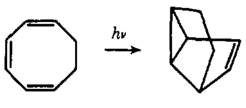
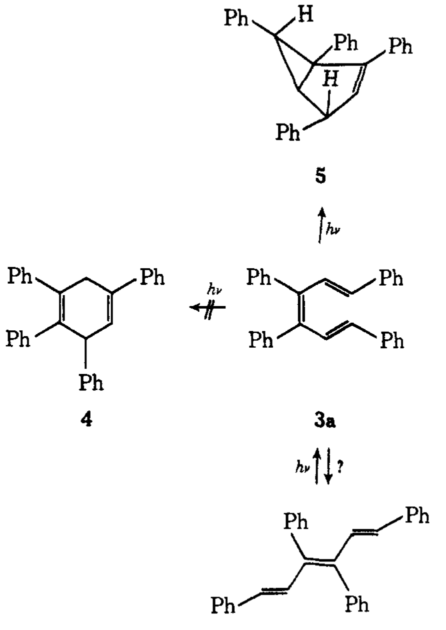


symmetry predictions. Chapman,[24] Roth,[25] and Winstein[26] have independently found that irradiation of 1,3,5-cyclooctatriene (**1**) produced tricyclo[5.1.0.0^{4,8}]-oct-2-ene (**2**) together with a number of other products. Irradiation of a *cis,cis,cis*-1,3,5-hexatriene (such as **1**) is not predicted to give a *endo,endo*-bicyclo[3.1.0]hex-2-ene (such as **2**) on the basis of orbital symmetry considerations. The fact that **2** is formed from **1** suggests that either an undetected cis–trans isomerization occurred, or else the reaction proceeds in a stepwise fashion and involves radical intermediates. Presumably, steric factors play an important role in this system. In a related case, Zimmerman and Iwamura have found that irradiation of cyclooctatetraene at −60° in isopentane with acetone as a sensitizer afforded semibullvalene as a major product.[27] These authors suggest that this transformation is a two-quantum process with the initially formed *trans,cis,cis,cis*-cyclooctatetraene absorbing the second photon and reacting more rapidly than it is formed, since no evidence for accumulation of an intermediate could be found in low-temperature infrared studies.



1 **2**

Another case where the assigned stereochemistry is opposite to the predictions is found in the photochemistry of 1,3,4,6-tetraphenylhexa-1,3,5-triene (**3**). Theis and Dessy originally reported that the irradiation of **3** gave rise to 1,2,3,5-tetraphenyl-1,4-cyclohexadiene (**4**).[28] In a subsequent report, Dauben and Smith concluded that the compound isolated was not **4** but rather 1,2,4,6-tetraphenylbicyclo[3.1.0]hex-2-ene (**5**).[29] The stereochemical assignment of the phenyl groups at C_4 and C_6 (exo,exo) is based on a very reasonable nmr interpretation and seems to be secure. Bicyclohexene **5** is not the expected product from **3a** according to orbital symmetry considerations. It is, however, the thermodynamically most favored bicyclic isomer. It should be pointed out that no definite assignment was made to the starting triene **3**,[29] although the material was drawn as the *E,E,E* isomer **3b**. In order for this process to proceed, the central double bond must be *Z* and therefore a photochemical inversion of at least one bond had to occur if starting triene had the *E,E,E* configuration.



5

4

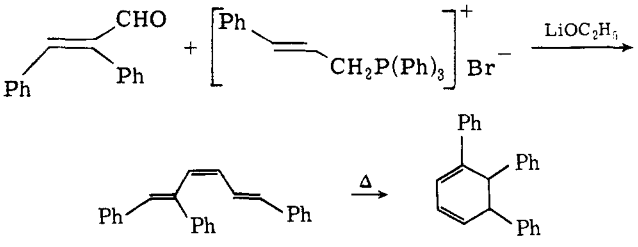
3a

3b

Several years ago Dauben and coworkers reported that irradiation of vitamin D_2 leads to two bicyclo[3.1.0]hex-2-enes, suprasterol I and suprasterol II.[3,23] In this system the stereochemistry about three of the four centers of the bicyclohexene was compatible with the orbital symmetry requirements. No information was available with regard to the fourth center and consequently it was not possible to discern whether the 4π system participates in the reaction in a suprafacial manner. With the hope of providing some additional data for understanding the stereochemical course of these reactions, we have investigated the photochemistry of a series of 1,2,6-triphenyl-1,3,5-hexatrienes. The results of our studies appear to be compatible with the theoretical predictions.

Results and Discussion

The synthesis of 1,2,6-triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene (**6**),[30] mp 78–80°, utilized the Wittig reaction of *trans*-cinnamylphosphonium bromide and *cis*-2,3-diphenylacrolein. The preferential formation of the cis C_3–C_4 stereoisomer is in accord with literature reports on the geometric course of the Wittig reaction.[31] The structure assigned to triene **6** rests on the mode of preparation, its spectral data, and, finally, on the thermal electrocyclic ring closure to afford *cis*-1,5,6-triphenylcyclohexa-1,3-diene (**7**) (92%): mp 108–109°; nmr ($CDCl_3$) τ 6.25 (1 H, d, J = 8.0 Hz), 5.69 (t of



6 **7**

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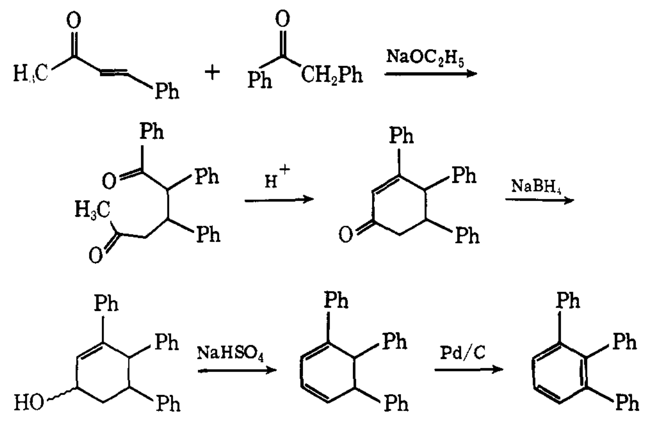

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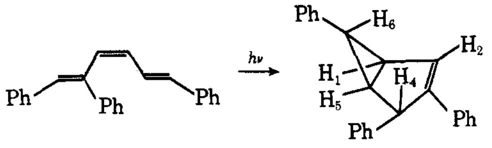
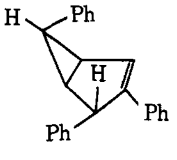
d, 1 H, J = 8.0 and 2.5 Hz), 4.32 (d of d, 1 H, J = 9.0 and 2.5 Hz), 3.85 (1 H, doublet of double doublets, 1 H, J = 9.0, 5.0, and 2.5 Hz), 2.75–3.50 (m, 16 H). The structure of *cis*-cyclohexadiene **7** was determined by oxidation to the known 1,2,3-triphenylbenzene[32] and by an independent synthesis; this is depicted above and described in the Experimental Section.



6 **8**

The photochemical studies were carried out with a 450-W medium-pressure immersion apparatus using a Pyrex filter. Irradiation of triene **6** (500 mg) in cyclohexane under nitrogen for 2.5 hr was found to afford one major product (77%), mp 104–106°, to which we have assigned the structure of *exo,exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**8**). The stereochemical assignment was based on the following nmr (CCl_4) data: τ 8.29 (t, 1 H, C_6H), 7.98 (double d, 1 H, C_5H), 7.69 (m, 1 H, C_1H), 5.59 (t, 1 H, C_4H), 3.20 (t, 1 H, C_2H), and 2.75 (m, 15 H, aromatic). Appropriate spin-decoupling experiments were performed which allowed the determination of the following coupling constants: $J_{1,5}$ = 6.3 Hz, $J_{1,6}$ = 2.3 Hz, $J_{5,6}$ = 3.6 Hz, $J_{1,4}$ = 2.4 Hz, $J_{2,4}$ = 1.6 Hz, and $J_{1,2}$ = 1.9 Hz. The magnitude of the coupling implies *trans*-cyclopropyl vicinal coupling[33,34] and thus requires that the C_6 phenyl group be exo. The absence of coupling between H_4 and H_5 implies trans vicinal coupling and fixes the C_4 phenyl group in the exo position. In support of this conclusion is the observation of other workers that the magnitude of trans C_4–C_5 vicinal coupling of bicyclo[3.1.0]hex-2-enes is close to zero,[5b,11a,29] while that for cis vicinal coupling is *ca.* 7 Hz.[12a] This is to be expected since molecular models show that the dihedral angle for the trans C_4–C_5 protons is about 110°, while that for the cis protons is approximately 0°.

The four symmetry-allowed products which might be expected from a concerted (4 + 2) cycloaddition of hexatriene **6** are shown in formulas **9–12**. It appears that the photochemistry of **6** in dilute solution parallels that of **3** in that the bicyclo[3.1.0]hexane obtained is not the expected product from orbital symmetry considerations but is the thermodynamically most favored isomer.



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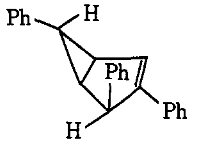

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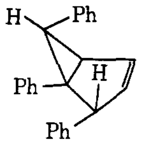

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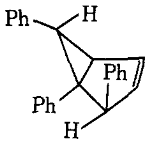
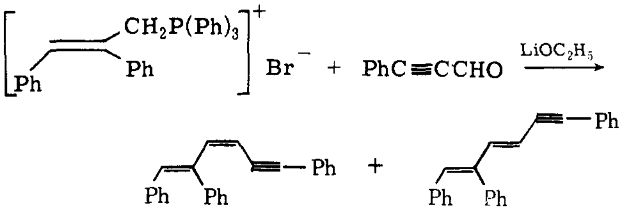


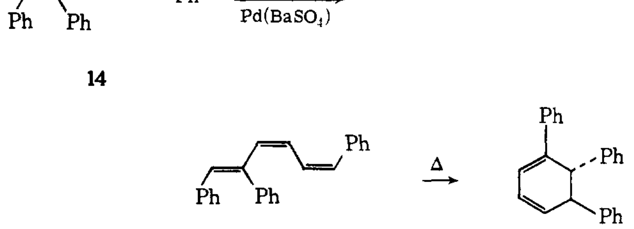
12

In order to determine whether the photoisomerization of a triphenyl-substituted hexatriene is subject to orbital symmetry interpretation, we have investigated the photochemistry of the isomeric 1,2,6-triphenyl-(*Z,Z,Z*)-hexa-1,3,5-triene (**13**). The *Z,Z,Z* isomer **13** was obtained from the catalytic hydrogenation of 1,2,6-triphenyl-(*Z,Z*)-hexa-1,3-dien-5-yne (**14**), mp 65–66°.



14 **15**

Dienyne **14** was in turn synthesized from the Wittig reaction of *cis*-α-phenylcinnamyltriphenylphosphonium bromide and phenylpropargyl aldehyde followed by fractional crystallization of the two isomeric dienynes, **14** (*Z,Z*) and **15** (*Z,E*). Structures **14** and **15** could readily be distinguished by their unique nmr spectra. The vinyl region of **14** was composed of doublets at τ 4.21 and 3.47 (J = 12.0 Hz) while dienyne **15** showed a one-proton doublet at τ 4.53 (J = 16.0 Hz). The two remaining vinyl protons of **15** appear under the aromatic multiplet. The larger coupling constant found with dienyne **15** is consistent with the trans stereochemistry about the C_3–C_4 double bond.[35] The identity of triene **13** was de-



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13 **16**

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[32] W. Polaczkowa, O. Achmatowicz, Jr., and J. Boehm, *Rocz. Chem.*, 31, 115 (1957).

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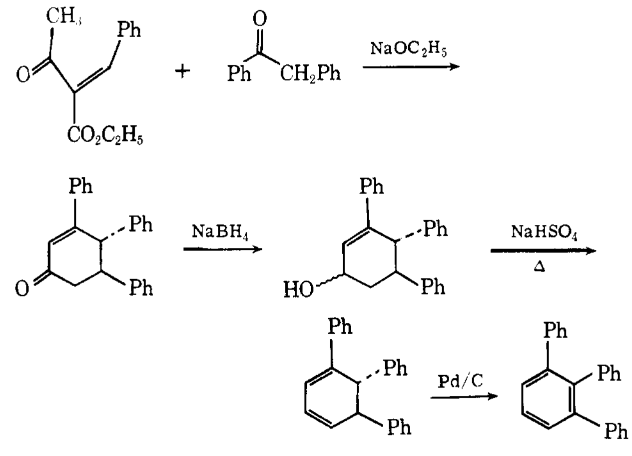
duced from the method of preparation, its spectral data, and by its thermal conversion to *trans*-1,5,6-triphenylcyclohexa-1,3-diene (**16**): nmr ($CDCl_3$) τ 6.30 (d of d, 1 H, J = 5.0 Hz), 5.92 (br s, 1 H), 4.31 (d of d, 1 H, J = 9.0 and 5.0 Hz), 3.78 (d of d, H, J = 9.0 and 4.0 Hz), 3.41 (d, 1 H, J = 5.0 Hz), 2.85–3.35 (m, 15 H). The structure of *trans*-cyclohexadiene **16** was established by oxidation to 1,2,3-triphenylbenzene and was further confirmed by comparison with an authentic sample synthesized in the manner outlined above.



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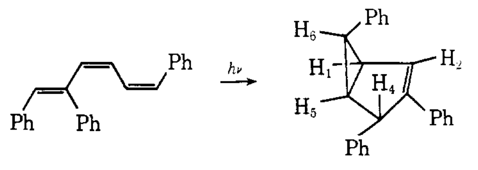
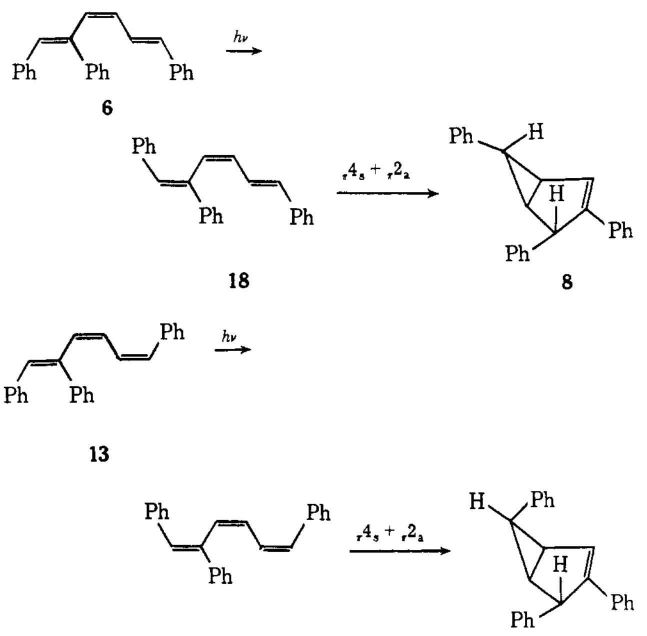
Irradiation of hexatriene **13** in cyclohexane gave a new bicyclo[3.1.0]hex-2-ene (mp 132–133°) whose structure is assigned as 4-*exo*,6-*endo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**17**) on the basis of its nmr spectrum: τ 7.99 (d of d, 1 H, C_5H), 7.50 (m, 2 H, C_1H and C_6H), 6.22 (t, 1 H, C_4H), 3.68 (m, 1 H, C_2H), and 3.2–2.7 (m, 15 H, aromatic). Appropriate spin-decoupling experiments showed that $J_{1,2} = J_{1,4} = J_{2,4}$ = 2.0 Hz, $J_{1,5}$ = 6 Hz, and $J_{5,6}$ = 8.0 Hz. The magnitude of the *cis*-cyclopropyl vicinal coupling requires that the C_6 phenyl group be endo. In accord with this assignment is the observation that H_6 is no longer shielded by the anisotropy of the double bond and appears 0.8 ppm downfield from C_6H in the exo,exo isomer **8**. Again, $J_{4,5}$ = 0 Hz, requiring that the C_4 phenyl group be exo.



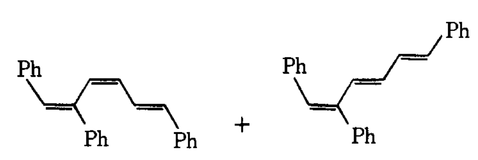
13 **17**

The fact that only **17** was isolated from the irradiation of **13** implies that the stability of the bicyclo[3.1.0]hex-2-ene is not the major factor governing the photoisomerization. These results indicate that orbital symmetry control may be important in these systems.[36] It should be pointed out, however, that **17** *is not the isomer that would be predicted to be formed from the irradiation of* **13**. The above observations can be rationalized if it is assumed that the above reactions (*i.e.*, **6** → **8** and **13** → **17**) are two photon reactions involving initial cis–trans photoisomerization about the C_1–C_2 double bond followed by $_{\pi}4_s + _{\pi}2_a$ cycloaddition to the bicyclic isomer.

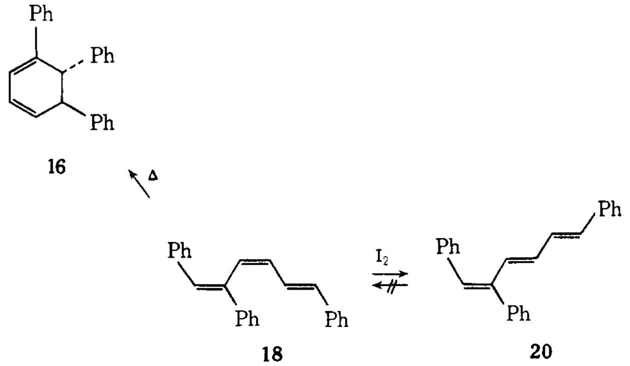


6 **18** **8** **13** **19** **17**

In order to gain further evidence for the above suggestion, the photochemistry of the (*E*,*Z*,*E*)- (**18**) and (*E*,*Z*,*Z*)- (**19**) trienes was examined. The requisite (*E*,*Z*,*E*)-triene (**18**) was synthesized from the Wittig reaction of *trans*-α-phenylcinnamyltriphenylphosphonium bromide with *trans*-cinnamaldehyde. The mixture of trienes formed was separated by silica gel chromatography. The structure of the (*E*,*Z*,*E*)-triene **18** was based on its facile iodine-catalyzed isomerization to **20**. The formation of *trans*-1,5,6-triphenylcyclohexa-1,3-diene (**16**) from the thermolysis of **18** is also consistent with the assignment.



18 **20**



16 **18** **20**

The synthesis of the *E*,*Z*,*Z* isomer **19** was realized by the catalytic hydrogenation of 1,2,6-triphenyl-(*E*,*Z*)-

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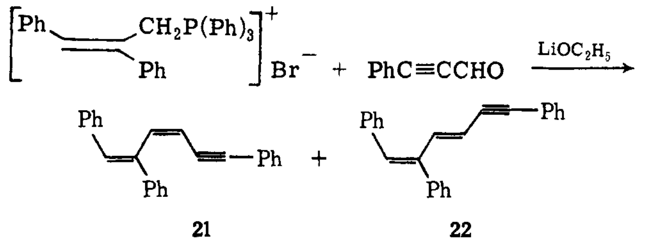
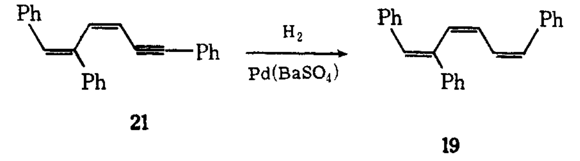
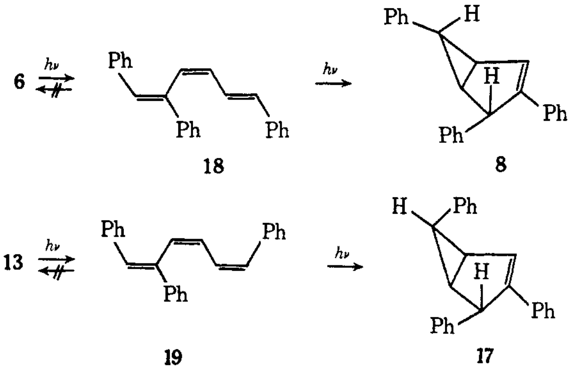
(36) See, however, W. Th. A. M. van der Lugt and L. J. Oosteroff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969), for criticism of the applicability of the Woodward–Hoffmann rules in photochemical reactions.



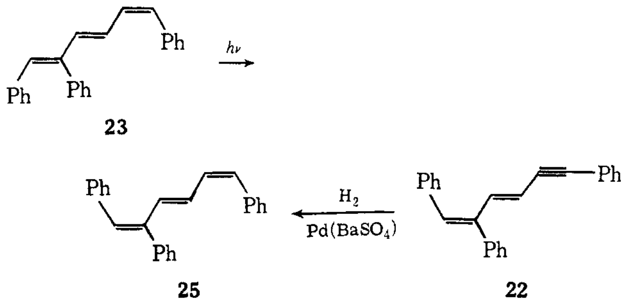


hexa-1,3-dien-5-yne (**21**). Dienyne **21** was obtained from the Wittig reaction of *trans*-α-phenylcinnamyltriphenylphosphonium bromide with phenylpropargyl aldehyde followed by chromatographic separation of the two isomers. This sequence is described below and is detailed in the Experimental Section. Dienynes **21** and **22** could be distinguished by the magnitude of the vinyl coupling in the nmr (*i.e.*, J = 11.5 Hz for **21**; J = 15.5 Hz for **22**).

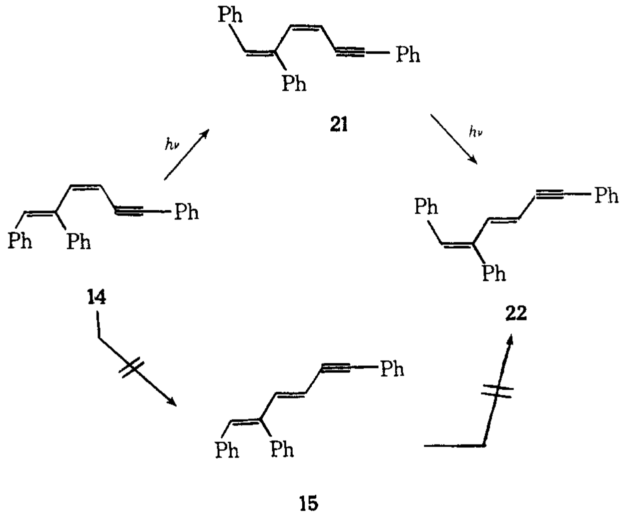
The irradiation of (*E*,*Z*,*E*)-hexatriene **18** was found to give a single photoisomer. This product was found to be identical with the *exo*,*exo*-bicyclohexene **8**. The alternate bicyclohexene (**17**) was shown by nmr to be missing. When the (*E*,*Z*,*Z*)-triene (**19**) was subjected to irradiation, only bicyclohexene **17** was formed. The stereoselectivity observed with these trienes supports the two-photon sequence outlined earlier. In order to provide additional support for this path, we sought to establish conditions under which **18** might be detected in the photolysis of **6**. Irradiation of **6** (0.5 g) for 9 min produced only traces of bicyclohexene **8**, the major product being the (*E*,*Z*,*E*)-triene **18**. Similarly, in the partial photolysis of **13** (9 min), the presence of **19** could be readily detected by nmr spectroscopy. However, in the partial irradiation of **18** (or **19**) no detectable quantities of **6** (or **13**) were found.[37] These results strongly suggest that the major pathway from **6** to **8** (or **13** to **17**) in our system is the two-photon route involving the intermediacy of **18** (or **19**). Thus, it appears that photoisomerization about the 1,2-double bond to relieve cis diphenyl nonbonded interactions is rapid relative to symmetry-allowed cyclization.



Liu and Butt have recently demonstrated that excited state bond orders cannot be used to predict the direction of photoisomerization about a substituted 1,3,5-hexatriene.[38] Although MO calculations on 1,3,5-hexatriene give significantly lower central bond orders as compared with that of the terminal bond,[39] the experimental results encountered by Liu and Butt with 2,6-dimethyl-2,4,6-octatriene are more consistent with isomerization about the terminal double bond. In our case, the results are also consistent with Liu's finding of preferential isomerization about the terminal double bond. In order to provide additional support for rapid terminal bond rotation in the 1,2,6-triphenylhexatriene system, we have studied the photochemistry of (*Z*,*E*,*Z*)-hexatriene (**23**), mp 152–154°, and (*Z*,*Z*)-dienyne (**14**), mp 65–66°. The synthesis of these compounds is outlined in the Experimental Section. We note that irradiation of (*Z*,*E*,*Z*)-triene **23** produced a single photoisomer which was shown to be the (*E*,*E*,*Z*)-triene (**25**), mp 109–110°, by comparison with an authentic sample. Triene **25** was independently synthesized from the catalytic hydrogenation of 1,2,6-triphenyl-(*E*,*E*)-hexa-1,3-dien-5-yne (**22**). One can conclude, therefore, that rotation about the 1,2-double bond to relieve cis diphenyl nonbonded interactions is more favorable than rotation about the 5,6-double bond.



When dienyne **14** was irradiated in cyclohexane it was photoisomerized to the (*E*,*E*)-dienyne (**22**). Analysis of the reaction mixture indicated that the (*E*,*Z*)-dienyne (**21**) was also a product. Under conditions where the (*E*,*E*)- (**22**) and (*E*,*Z*)- (**21**) dienynes are produced, no detectable quantities of the (*Z*,*E*)-**15** isomer were found. These results clearly indicate



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[37] This observation implies that the excited state of **18** (or **19**), in contrast to triene **6** (or **13**), prefers to cyclize to bicyclohexene **8** (or **17**) rather than photoisomerize about the C–C double bond. This may be related to secondary steric factors.

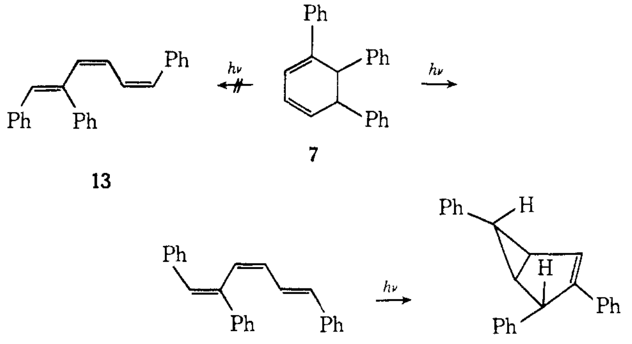
[38] R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971).

[39] H. E. Simmons, *Progr. Phys. Org. Chem.*, **7**, 1 (1970).

that photoisomerization about the C_1–C_2 double bond is the preferred process in these systems. The observed differences in rate of rotation about the various double bonds are surely due to the phenyl groups which not only perturb the π system but also add considerable nonbonded interactions.

In a further attempt to evaluate the role of steric factors in the bond reorganization of 1,3,5-hexatrienes and 1,3-cyclohexadienes, we have investigated the photochemistry of *cis*- and *trans*-1,5,6-triphenylcyclohexa-1,3-diene (**7** and **16**, respectively). Irradiation of **7** in cyclohexane at 25° gave *exo,exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**8**) in high yield (71%). No other stereoisomeric bicyclohexenes could be detected by nmr spectroscopy. *trans*-Cyclohexadiene (**16**), upon irradiation, rearranges stereospecifically to give 4-*exo*,6-*endo*-3,4,5-triphenylbicyclohexene (**17**) in good yield (65%). Again, no other stereoisomeric bicyclohexenes could be detected by nmr spectroscopy.

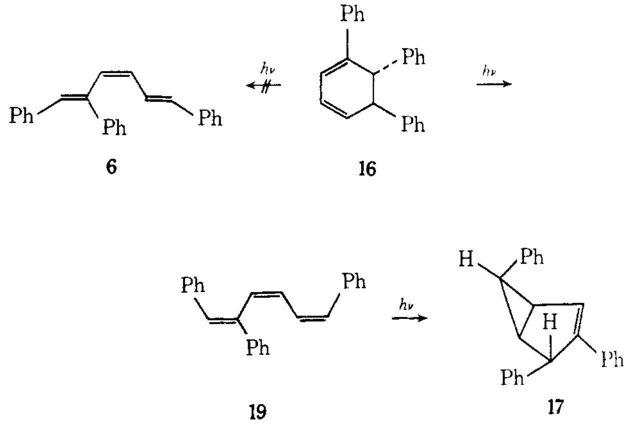
The exclusive formation of **8** from the irradiation of **7** probably follows a photochemically induced electrocyclic ring opening[40,41] of **7** to 1,2,6-triphenyl-(*E,Z,E*)-hexa-1,3,5-triene (**18**) followed by subsequent closure to **8**. In fact, in the partial photolysis of **7**, the presence of **18** could be detected by nmr spectroscopy. We have previously shown that **18** rearranges to **8** on irradiation. The isomeric (*Z,Z,Z*)-hexatriene (**13**), if formed, would have cyclized to **17**.



13 **7**

18 **8**

Two modes of conrotatory motion are possible in the ring opening of **7**. The results indicate that the process leading to **18** is followed exclusively. We attribute this high degree of stereospecificity to secondary forces operative during the bond reorganization step. Thus, as bond rotation in **7** commences toward triene **13**, two phenyl groups are brought into a *cis*-stilbene relationship. The steric factors generated in this maneuver are apparently sufficient to raise the activation to a level which permits operation of the alternate rotation which leads to triene **18** (*trans*-stilbene relation). Similarly, two modes of conrotatory motion in **16** are possible; movement in one direction leads to the (*E,Z,Z*)-triene (**19**) while movement in the other direction will give the (*Z,Z,E*)-triene (**6**). Triene **19** has been shown to cyclize to **17** whereas **6** gives **8** on irradiation. In the partial photolysis of **16**, the presence of **19** could be detected by nmr spectroscopy. Again it appears as though secondary steric factors control the bond reorganization of *trans*-cyclohexadiene (**16**). In a related system, Courtot and Rumin have reported that secondary steric factors control the direction of the photochemical ring opening of 1,4-diphenyl-5,6-dimethylcyclohexa-1,3-diene.[41]



6 **16**

19 **17**

Recent investigations have shown that conformational factors can influence the direction of both photo and thermal electrocyclic reactions.[42–46] In cases where two modes of ring opening or ring closing are possible, the stereoselectivity of the reaction can often be explained or predicted from consideration of the ground-state conformer populations. This phenomenon is not without precedent as conformational restraints have been demonstrated to have a profound effect on the rate of Diels–Alder reactions, where adduct formation is known to parallel the accessibility of the required s-cis conformation.[47–50] In the case of the 1,3,5-hexatriene system, photoisomerization to one or another type of bicyclohexene might also be controlled by differences in ground-state geometry of the different hexatrienes. The present investigation demonstrates that the photochemical cycloaddition reaction of 1,3,5-hexatrienes is a highly stereoselective process. It has been previously noted by Zimmerman that 1,5 bonding in the excited state of a polyene system is especially favorable energetically and that 4,6 bonding is just somewhat less likely.[51] Our results indicate that bicyclohexenes **8** and **17** are both genuine primary products and are formed photochemically from trienes **18** and **19** by (1,5 + 4,6) bonding. In both cases the *cyclization is observed to occur only via the* ${}_{\pi}4_s + {}_{\pi}2_a$ *route*. This can be explained in terms of the populations of the ground-state conformations by considering the structure of the substituted 1,3,5-hexatrienes. For steric reasons, the most favored reactive conformer of the (*E,Z,E*)-triene (**18**) should be **18c**, since conformers **18a** and **18b** will be destabilized relative to **18c** as a result of phenyl–hydrogen nonbonded interactions. According to the Woodward–Hoffman rules, this conformer (**18c**) should cyclize photochemically to give the geometry of the *exo,exo*-bicyclohexene (**8**). The formation of this isomer is expected since the (1,5 + 4,6) bond closure will be controlled by the nodal

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(40) W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964).

(41) P. Courtot and R. Rumin, *Bull. Soc. Chim. Fr.*, **10**, 3665 (1969); *Tetrahedron Lett.*, 1849 (1970).

(42) J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 6444 (1969).

(43) G. A. Doorkian and H. H. Freedman, *ibid.*, **92**, 399 (1970).

(44) C. W. Spangler and R. P. Hennis, *Chem. Commun.*, 24 (1972).

(45) W. G. Dauben, *Chem. Weekbl.*, **60**, 381 (1964).

(46) J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291, 301 (1966).

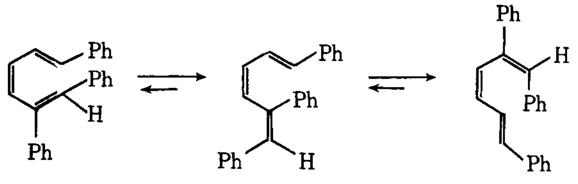
(47) B. Eisler and A. Wassermann, *J. Chem. Soc.*, 979 (1953).

(48) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961).

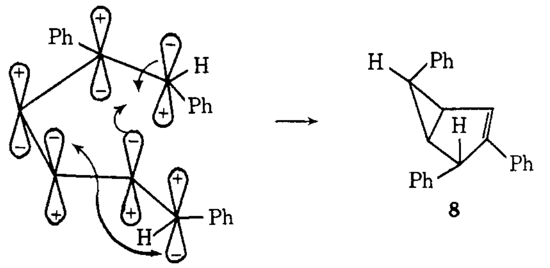
(49) J. Sauer, *Angew. Chem.*, **79**, 76 (1967).

(50) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(51) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1566 (1966).

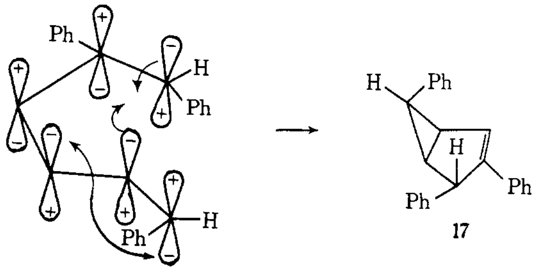


18a **18b** **18c**



8

structure of the lowest π* level. An additional and contributing factor for this system is that the $_{\pi}4_a + {}_{\pi}2_s$ process will lead to a severely strained *endo,endo*-bicyclohexene. Similarly, the major and reactive conformer of the (*E,Z,Z*)-triene (**19c**) will give bicyclohexene **17** by a $_{\pi}4_s + {}_{\pi}2_a$ route. The formation of this particular bicyclohexene is undoubtedly a reflection of the greater steric interactions involved in the alternate ($_{\pi}4_a + {}_{\pi}2_s$) path.[52]



19c **17**

In conclusion, it is gratifying to know that the original premise for this study has been confirmed.[53a] The specificity of the cycloaddition supports the proposition[42] that the ground-state geometry of a molecule subjected to photolytic excitation may determine the structure and stereochemistry of the photoproduct.

Experimental Section[54]

Materials. *cis*-2,3-Diphenylacrolein was prepared by the base-catalyzed condensation of phenylacetaldehyde and benzaldehyde, mp 92–93° (lit.[55] 94°). *cis*-2,3-Diphenylallyl alcohol was prepared by the lithium aluminum hydride reduction of *cis*-2,3-diphenylacrolein, mp 70–70.5° (lit.[56] 68–69°). *trans*-2,3-Diphenylallyl alcohol was prepared by the lithium aluminum hydride reduction of *trans*-phenylcinnamic acid[57] (mp 136–137°) according to the procedure of Axenrod, *et al.*,[58] mp 73–74° (lit.[59] 73–74°).

***cis*-2,3-Diphenylallyl Bromide.** A solution of phosphorous tribromide (2.15 g) in anhydrous ether (10 ml) was added to an ice-cooled solution of *cis*-2,3-diphenylallyl alcohol (5.0 g) in anhydrous ether (50 ml). The resulting solution was left at room temperature for 12 hr, and then placed on a steam bath for 15 min. Ether (100 ml) was added and the resulting solution was washed with aqueous sodium hydroxide (10%). The ether layer was dried over magnesium sulfate and the ether evaporated to an oil which partially crystallized on standing to give 6.2 g (96%) of crude *cis*-2,3-diphenylallyl bromide which was not further purified: ir (KBr) 6.71, 6.95, 7.20, and 8.32 μ; nmr (CCl_4) τ 5.75 (s, 2 H), 3.26 (s, 1 H), and 3.0 and 2.75 (s, 10 H).

Triphenyl-*cis*-2,3-diphenylallylphosphonium Bromide. *cis*-2,3-Diphenylallyl bromide (5.0 g) and triphenylphosphine (4.8 g) were refluxed in benzene (125 ml) for 4 hr. The resulting slurry was cooled to room temperature and filtered to give 8.4 g (85%) of the colorless phosphonium salt: mp 250–255°; ir (KBr) 6.78, 6.99, 7.15, and 9.05 μ.

Triphenyl-*trans*-2,3-diphenylallylphosphonium Bromide. A solution of phosphorous tribromide (1.9 g) in ether (10 ml) was added to a solution of *trans*-2,3-diphenylallyl alcohol (4.4 g) in ether (50 ml). The resulting solution was stirred at room temperature for 6 hr, washed with 10% sodium hydroxide, dried over magnesium sulfate, and evaporated to an oil. The oil was dissolved in a solution of triphenylphosphine (5.5 g) in benzene and the mixture was refluxed overnight. On cooling, 7.5 g (67%) of the colorless phosphonium salt was obtained on filtration: mp 210–212°; ir (KBr) 6.71, 6.93, 7.10, and 9.02 μ.

Triphenyl-*trans*-cinnamylphosphonium Bromide. *trans*-Cinnamyl bromide (1.34 g) and triphenylphosphine (1.8 g) were refluxed in benzene (25 ml) for 2 hr. The resulting slurry was cooled to room temperature and filtered to give 2.0 g (65%) of the colorless phosphonium salt: mp 245–250°; ir (KBr) 6.95, 7.12, 9.02, and 10.11 μ.

1,2,6-Triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene (6). A solution of lithium ethoxide (prepared by dissolving 0.1 g of lithium wire in absolute ethanol) was added to a stirred slurry of triphenyl-*trans*-cinnamylphosphonium bromide (6.0 g) and *cis*-2,3-diphenylacrolein (2.76 g) in absolute ethanol (60 ml), and the resulting slurry was stirred at room temperature overnight. The mixture was then concentrated to about 20 ml to precipitate 3.13 g (77%) of a yellow solid identified as 1,2,6-triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene (**6**): mp 78–80°; ir (KBr) 6.70, 6.92, 7.12, 10.15, 10.51, 10.89, and 11.30 μ; nmr (CCl_4) τ 3.60 and 3.18 (m) and 2.4–2.9 (m); uv (95% ethanol) 353 and 372 nm (ϵ 37,400 and 29,700); *m/e* 308 parent. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.44; H, 6.55.

1,2,6-Triphenyl-(*Z,Z*)- and -(*Z,E*)-hexa-1,3-dien-5-yne (14 and 15). Lithium ethoxide (0.245 g) was added to a stirred solution of phenylpropargyl aldehyde (4.53 g), triphenyl-*cis*-2,3-diphenylallylphosphonium bromide (18.7 g), and lithium bromide (3.0 g) in 125 ml

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(52) Treatment of the above reaction as a ($_{\pi}4 + {}_{\pi}2$) process raises some difficulties when one tries to treat the process in the usual cycloaddition fashion. For the ($_{\pi}4 + {}_{\pi}2$) process, one usually assumes two basic sets. In the above system, the two sets will be the olefin and diene portions of the hexatriene. Usually, these sets are independent of each other. If this were the case, the conformation of the triene should play no role in the photo-Diels–Alder reaction. However, if one uses the formalism of the cycloaddition but puts on the restriction that the two sets are not independent but are related to the π* level (as discussed above), then the conformation of the triene will be expected to play a role in determining the stereochemistry of the final product.[53]

(53) We wish to acknowledge Professor W. G. Dauben for helpful discussion in regard to the above point.

(53a) NOTE ADDED IN PROOF. In a recent publication D. A. Seeley (*J. Amer. Chem. Soc.*, **94**, 4378 (1972)) reported that the labile benzohexatrienes produced from the irradiation of *cis*- or *trans*-1,2-dihydro-1,2-dimethylnaphthalene cyclize to bicyclohexenes without any apparent stereospecificity. Similarly, Dauben and coworkers have found that the photo-Diels–Alder reaction of a cycloundeca-1,3,5-triene could not be accounted for in terms of a $_{\pi}4 + {}_{\pi}2$ cycloaddition: W. G. Dauben, Plenary Lecture presented at the 4th IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 1972. In view of our data and the very different results encountered by Seeley and Dauben, it would appear that the stereospecificity of the cycloaddition is a function of the particular triene used. Consequently, one should not necessarily depend on orbital symmetry control of stereoselectivity in this reaction.[36]

(54) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco-MH-100 spectrometer.

(55) K. Alder, J. Haydin, K. Heinbach, and K. Neufang, *Justus Liebigs Ann. Chem.*, **586**, 128 (1954).

(56) H. E. Zimmerman, L. Singer, and B. S. Thyagarjan, *J. Amer. Chem. Soc.*, **81**, 108 (1959).

(57) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1957, p 182.

(58) T. Axenrod, E. Bierig, and L. H. Schwartz, *Tetrahedron Lett.*, 2181 (1965).

(59) R. E. Lutz and E. H. Rinker, *J. Amer. Chem. Soc.*, **77**, 368 (1955).

of dimethylformamide.[60] The resulting solution was stirred overnight at room temperature. Ether was added (75 ml) and the resulting solution was washed three times with water, dried over magnesium sulfate, and concentrated. Triphenylphosphine oxide was precipitated by the addition of heptane and removed. The solution was evaporated to an oil, taken up in hot ethanol, and allowed to cool to give 5.4 g (51%) of crude 1,2,6-triphenyl-(*Z,E*)-hexa-1,3-dien-5-yne. Recrystallization from 95% ethanol gave 3.2 g (30%) of pure 1,2,6-triphenyl-(*Z,E*)-hexa-1,3-dien-5-yne (**15**): mp 92–93°; ir (KBr) 6.74, 6.97, 7.20, 10.55, 13.35, 14.20, and 14.60 μ; nmr ($CDCl_3$) τ 4.53 (d, 1 H, J = 16.0 Hz), 3.30 (br s, 1 H), 2.4–3.0 (broad m, 16 H); uv (95% ethanol) 337 nm (ϵ 46,000); *m/e* (parent) 306. *Anal.* Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.90; H, 5.96.

The filtrate was allowed to stand for several days at which time 2.2 g (20%) of 1,2,6-triphenyl-(*Z,Z*)-hexa-1,3-dien-5-yne (**14**) precipitated. This material was recrystallized from 95% ethanol to give pure **14**: mp 65–66°; ir (KBr) 6.21, 6.70, 6.80, 9.30, 9.70, 10.80, 11.32, 13.21, 13.30, and 14.81 μ; nmr (CCl_4) τ 4.21 (d, 1 H, J = 12 Hz), 3.47 (d, 1 H, J = 12 Hz), and 2.7–3.1 (m, 16 H); uv (95% ethanol) 339 nm (ϵ 28,300); *m/e* (parent) 306. *Anal.* Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.74; H, 5.84.

1,2,6-Triphenyl-(*Z,Z,Z*)-hexa-1,3,5-triene (13). Hydrogen (39 ml at 20°) was added to a stirred slurry of 5% palladium on barium sulfate (50 mg), quinoline[61] (2 drops), and 1,2,6-triphenyl-(*Z,Z*)-hexa-1,3-dien-5-yne (0.5 g) in absolute ethanol (50 ml). The catalyst was removed by filtration, and the filtrate was concentrated to a yellow oil which was chromatographed on a silica gel column using 20% benzene–petroleum ether to give 450 mg (90%) of 1,2,6-triphenyl-(*Z,Z,Z*)-hexa-1,3,5-triene (**13**) as a pale yellow oil; ir (liquid film) 6.28, 6.72, 6.96, 9.38, 9.75, 10.91, 11.34, 13.24, and 14.40 μ; nmr (CCl_4) τ 3.65 (m), 3.14 (m), and 2.6–3.0 (m); uv (95% ethanol) 335 and 265 nm (ϵ 56,400 and 28,400); *m/e* (parent) 308.

1,2,6-Triphenyl-(*Z,E,Z*)-hexa-1,3,5-triene (23). Hydrogen (24 ml at 20°) was added to a stirred slurry of 5% palladium on barium sulfate (100 mg), quinoline (2 drops), and 1,2,6-triphenyl-(*Z,E*)-hexa-1,3-dien-5-yne (**15**) (0.3 g) in ethanol (50 ml). The catalyst was removed by filtration and the filtrate was concentrated to 15 ml at which time 186 mg (60%) of 1,2,6-triphenyl-(*Z,E,Z*)-hexa-1,3,5-triene (**23**) precipitated as pale yellow needles: mp 152–154°; ir (KBr) 6.71, 6.90, 7.15, 9.76, 10.51, 10.84, and 14.40 μ; nmr ($CDCl_3$) τ 3.67 (m), 3.32 (s, 1 H), and 2.9 (br m); uv (95% ethanol) 364 and 343 nm (ϵ 27,200, 47,500); *m/e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.20; H, 6.62.

1,2,6-Triphenyl-(*E,E,E*)- and -(*E,Z,E*)-hexa-1,3 5-trienes (20 and 18). A solution of lithium ethoxide (prepared by dissolving 0.026 g of lithium wire in about 5 ml of absolute ethanol) was added to a stirred solution of *trans*-cinnamaldehyde (0.49 g) and triphenyl-*trans*-2,3-diphenylallylphosphonium bromide (2.0 g) in absolute ethanol (25 ml). The resulting solution was stirred at room temperature overnight. On scratching, 0.16 g (14%) of a yellow solid precipitated and was identified as 1,2,6-triphenyl-(*E,E,E*)-hexa-1,3,5-triene (**20**): mp 160–161°; ir (KBr) 6.71, 6.90, 10.05, 10.91, 13.10, 14.22, and 14.51 μ; nmr ($CDCl_3$) signals due to vinyl protons at τ 3.8, 3.54, 3.4, and 3.3, and aromatic signals at 2.5–3.2; uv (95% ethanol) 372, 353, 337, and 325 nm (ϵ 45,800, 67,400, 53,800, 33,000); *m/e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.23; H, 6.56.

The filtrate was evaporated to an oil and then hexane was added to precipitate the triphenylphosphine oxide. The filtrate was then evaporated to an oil and chromatographed on a silica gel column using 20% benzene–hexane. A fraction containing 250 mg (21%) of an oil consisted of 1,2,6-triphenyl-(*E,Z,E*)-1,3,5-triene (**18**): ir (film) 3.40, 6.27, 6.95, 10.1, 13.10, 13.42, 14.0, and 14.40 μ; nmr ($CDCl_3$) τ 3.3–3.9 (m) and 2.6–3.4 (m); uv (95% ethanol) 370, 352, 338, 282, and 237 nm (ϵ 26,500, 46,200, 46,100, 19,000, 16,000); *m/e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.45; H, 6.54. Found: C, 92.99; H, 6.82.

1 2,6-Triphenyl-(*E,Z*)- and -(*E,E*-hexa-1,3-dien-5-yne (21 and 22). Lithium ethoxide (0.05 g) was added to a stirred solution of triphenyl *trans*-1,2-diphenylallylphosphonium bromide (2.5 g), phenylpropargyl aldehyde (0.62 g), and lithium bromide (0.41 g) in dimethylformamide (40 ml), and the resulting solution was stirred overnight at room temperature. Ether was added and the solution was washed with water, dried over magnesium sulfate, and evaporated to an oil. Triphenylphosphine oxide was precipitated by the addition of hexane and removed by filtration. Evaporation of the filtrate gave an oil which was subjected to silica gel chromatography using 30% benzene–hexane. The early fractions consisted of the *E,E* isomer (**22**) as an oil: ir (film) 4.61, 6.25, 6.71, 6.92, 9.20, 9.71, 10.40, 10.85, 13.20, 13.62, and 14.31 μ; nmr ($CDCl_3$) τ 4.29 (d, 1 H, J = 15.5 Hz), 3.55 (br s, 1 H), and 2.7–3.0 (m, 16 H); *m/e* (parent) 306; uv (95% ethanol) 337 nm (ϵ 41,700).

The later fractions consisted of the *E,Z* isomer (**21**) as an oil (156 mg, 11%): ir (film) 4.59, 6.23, 6.71, 6.91, 9.70, 10.89, 13.23, 13.81, and 14.30 μ; nmr (CCl_4) τ 4.39 (d, 1 H, J = 11.5 Hz), 2.6–3.5 (m, 17 H); *m/e* (parent 306).

1,2,6-Triphenyl-(*E,E,Z*)-hexa-1,3,5-triene (25). Hydrogen (14 ml at 20°) was added to a stirred slurry of 5% palladium on barium sulfate (50 mg), quinoline (2 drops), and 1,2,6-triphenyl-(*E,E*)-hexa-1,3-dien-5-yne (179 mg) in ethyl acetate (50 ml). The catalyst was removed by filtration and the filtrate was concentrated to an oil which was recrystallized from 95% ethanol to give 60 mg (30%) of 1,2,6-triphenyl-(*E,E,Z*)-hexa-1,3,5-triene (**25**) as a colorless solid: mp 109–110°; ir (KBr) 6.71, 6.90, 7.12, 9.25, 9.71, 10.03, 10.46, 10.75, 11.71, 12.20, 12.81, 13.05, 13.35, 13.61, 14.10, and 14.30 μ; nmr ($CDCl_3$) τ 3.64 (br, s, 1 H), 3.44 (br s, 1 H), 2.7–3.2 (m, 18 H); uv (95% ethanol) 235 nm (ϵ 25,600); *m/e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.25; H, 6.54.

1,2,6-Triphenyl-(*E,Z,Z*)-hexa-1,3,5-triene (19). Hydrogen (12 ml at 20°) was added to a stirred slurry of 5% palladium on barium sulfate (50 mg), quinoline (2 drops), and 1,2,6-triphenyl-(*E,Z*)-hexa-1,3-dien-5-yne (160 mg) in ethyl acetate (50 ml). The catalyst was removed by filtration and the filtrate was evaporated to give a clear oil (125 mg, 77%): ir (film) 6.29, 6.71, 6.95, 9.35, 9.70, and 10.91 μ; nmr ($CDCl_3$) τ 3.6 (br s), 2.6–3.2 (m).

Isomerization of 1,2,6-Triphenylhexa-1,3,5-trienes with Iodine. A representative example consists of heating 1,2,6-triphenyl-(*E,Z,E*)-hexa-1,3,5-triene (**18**) (1.0 g) in ethanol (25 ml) with several crystals of iodine for 2.5 hr. The resulting solution was cooled, the solvent was evaporated, and the residue was taken up in ether. The ethereal layer was washed with an aqueous thiosulfate solution, dried over magnesium sulfate, and evaporated under reduced pressure to give 1,2,6-triphenyl-(*E,E,E*)-hexa-1,3,5-triene (**20**), as a yellow solid, mp 161–162°. In this way the following trienes were all isomerized to the (*E,E,E*)-triene which is the most thermodynamically stable isomer: *Z,Z,E*; *Z,E,Z*; *E,E,Z*; and *Z,Z,Z*.

***cis*-1,5,6-Triphenylcyclohexa-1,3-diene (7).** A 2.0-g sample of 1,2,6-triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene (**6**) was heated at reflux in toluene (50 ml) for 3 hr. The resulting solution was cooled and evaporated to an oil which was taken up in hot ethanol. Colorless needles (1.85 g, 92%) precipitated on cooling and were identified as *cis*-1,5,6-triphenylcyclohexa-1,3-diene (**7**): mp 108–110°; ir (KBr) 6.28, 6.71, 6.90, 9.25, 11.30, 12.91, 13.35, 13.62, and 14.53 μ; nmr ($CDCl_3$) τ 6.25 (d, 1 H, J = 8.0 Hz), 5.69 (t of d, 1 H, J = 8.0 and 2.5 Hz), 4.32 (d of d, J = 9.0 and 2.5 Hz, 1 H), 3.85 (1 H, d of d of d, 1 H, J = 9.0, 5.0, and 2.5 Hz), 2.75–3.50 (m, 15 H); uv (95% ethanol) 372, 316, and 233 nm (ϵ 1,500, 13,000, and 13,000); *m/e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.45; H, 6.57.

An authentic sample of **7** could also be prepared by the sodium bisulfate dehydration of *cis*-3,4,5-triphenyl-2-cyclohexenol.[62] A mixture of 250 mg of *cis*-3,4,5-triphenyl-2-cyclohexenol and 200 mg of fused anhydrous sodium bisulfate in 20 ml of benzene was heated for 50 hr at reflux. At the end of this time the benzene layer was separated from the solids and was washed with 10% sodium bicarbonate, followed by water. The benzene extracts were dried over sodium sulfate and then concentrated under reduced pressure to give a crude solid, mp 100–105°. Recrystallization of this material from ethanol gave white crystals, mp 108–109°. The infrared and nmr spectra of this material were identical with the product obtained from the thermolysis of 1,2,6-triphenyl-(*Z,Z,E*)-hexa-1,4,6-triene (**6**).

Further chemical confirmation was obtained by the oxidation of **7** to the known 1,2,3-triphenylbenzene. A 100-mg sample of **7** was refluxed in 25 ml of xylene which contained 10 mg of palladium on charcoal, for 16 hr. The resulting solution was cooled to room temperature, filtered to remove the catalyst, and evaporated to an oil. The oil was crystallized from ethanol to give 72 mg (72%) of 1,2,3-triphenylbenzene, mp 156–157° (lit.[32] 158–159°).

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[60] For the use of polar solvents and added lithium bromide to increase the relative yield of cis olefins in the Wittig reaction see L. L. Bergelson and M. M. Shemyakin, *Tetrahedron*, **19**, 149 (1963).

[61] For the use of quinoline as a poison see D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

[62] G. F. Woods, *U. S. Dep. Commerce, Office Tech. Serv., P. B. Rep.*, **161** (508), 86 (1959).

trans-**3,4,5-Triphenyl-2-cyclohexenol.** To a mixture of 11 g of *trans*-3,4,5-triphenyl-2-cyclohexenone[63] in 300 ml of methanol was added 1.5 g of sodium borohydride. After 12 hr of standing, 10 ml of a 20% hydrochloric acid solution was added. The solution was concentrated under reduced pressure and then extracted with ether. The ethereal extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent left a crude solid which was recrystallized from 95% ethanol to give 8.1 g (74%) of *trans*-3,4,5-triphenyl-2-cyclohexenol: mp 165–168°; ir (KBr) 2.95, 6.28, 6.75, 6.96, 9.01, 9.35, 9.62, 11.50, 13.22, and 14.45 μ; nmr ($CDCl_3$) τ 7.69 (2 H, q, $J = 4.5$ Hz), 6.68 (m, 1 H), 6.05 (1 H, d, $J = 8.0$ Hz), 5.32 (m, 1 H), 3.84 (1 H, d of d, $J = 5.0$ and 1.5 Hz), 2.8–3.3 (m, 15 H). *Anal.* Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.08; H, 6.72.

trans-**1,5,6-Triphenylcyclohexa-1,3-diene (16).** A mixture of fused anhydrous sodium bisulfate (3.2 g) and *trans*-3,4,5-triphenyl-2-cyclohexenol (4.0 g) in 300 ml of benzene was refluxed for 50 hr. An additional 3.2 g of sodium bisulfate was added after 20 hr of reflux. At the end of the reflux period, water was added and the benzene layer was removed. The aqueous layer was extracted twice with benzene and the combined benzene extracts were washed once with water, three times with saturated sodium bicarbonate solution, and finally with water. After drying the solution over sodium sulfate and filtering, concentration of the benzene solution yielded 3.8 g (98%) of a pale yellow oil: ir (film) 3.35, 6.20, 6.75, 6.95, 8.51, 9.35, 9.70, 11.02, 11.35, 13.01, 13.92, and 14.31 μ; nmr ($CDCl_3$) τ 6.3 (d of d, 1 H, $J = 6.0$ Hz), 5.92 (br s, 1 H), 4.31 (d of d, 1 H, $J = 9.0$ and 5.0 Hz), 3.78 (d of d, 1 H, $J = 9.0$ and 4.0 Hz), 3.41 (d, 1 H, $J = 5.0$ Hz), 2.85–3.35 (m, 15 H); uv (95% ethanol) λ_{max} 306 nm (ϵ 36,200); *m*/*e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.44; H, 6.81.

trans-1,5,6-Triphenylcyclohexa-1,3-diene (**16**) could also be prepared by heating a sample of the(*Z*,*Z*,*Z*)- or (*E*,*Z*,*E*)-hexatriene in toluene for 18 or 30 hr. The nmr and ir of the material obtained by this fashion were identical with the product described above.

Further confirmation of the structure of **16** was obtained by its oxidation to 1,2,3-triphenylbenzene using palladium on charcoal in refluxing toluene.

Photolysis of 1,2,6-Triphenyl-(*Z*,*Z*,*E*)- and -(*E*,*Z*,*E*)-hexa-1,3,5-trienes. A solution of the (*Z*,*Z*,*E*)-triene (500 mg) in cyclohexiene (500 ml) was irradiated for 2.5 hr with a 450-W Hanovia lamp fitted with a Pyrex filter. The resulting solution was evaporated to a yellow oil which after crystallization from ethanol gave 380 mg (76%) of *exo*,*exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**8**): mp 104–106°; ir (KBr) 6.23, 6.71, 6.90, 9.31, 9.45, 9.68, and 9.79 μ; nmr ($CDCl_3$) τ 8.29 (t, 1 H), 7.98 (d of d, 1 H), 7.69 (m, 1 H), 5.59 (t, 1 H), 3.20 (t, 1 H), and 2.75 (m, 15 H). Spin coupling experiments allowed the determination of the following coupling constants: $J_{1,5} = 6.3$ Hz, $J_{1,6} = 2.3$ Hz, $J_{5,6} = 3.6$ Hz, $J_{1,4} = 2.4$ Hz, $J_{2,4} = 1.6$ Hz, and $J_{1,2} = 1.9$ Hz; uv (95% ethanol) 272 nm (ϵ 17,800); *m*/*e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.21; H, 6.60.

The filtrate was concentrated under reduced pressure and was analyzed by nmr and tlc. The filtrate consisted of a mixture of unreacted (*Z*,*Z*,*E*)- and (*E*,*Z*,*E*)-trienes.

Irradiation of a 300-mg sample of (*Z*,*Z*,*E*)-hexatriene in cyclohexane for 9 min gave a pale yellow oil after removal of the solvent. An nmr spectrum of the oil showed signals due to the (*E*,*Z*,*E*)-hexatriene as well as recovered starting material. Only a trace of *exo*,*exo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene was observed.

Irradiation of 120 mg of 1,2,6-triphenyl-(*E*,*Z*,*E*)-hexa-1,3,5-triene (**18**) in cyclohexane for 1.5 hr resulted in the formation of *exo*,*exo*-bicyclohexene **8**. Under these conditions no detectable quantities of (*Z*,*Z*,*E*)-hexatriene **6** or *endo*,*exo*-bicyclohexane **17** were observed.

Irradiation of *cis*-1,5,6-Triphenyl-1,3-cyclohexadiene. A solution of *cis*-cyclohexadiene **7** (400 mg) in cyclohexane (500 ml) was irradiated for 4 hr with a 450-W Hanovia mercury lamp fitted with a Pyrex filter. The solvent was removed under reduced pressure and the residue was crystallized from ethanol to give 283 mg (71%) of colorless needles identified as *exo*,*exo*-3,4,6-triphenylbicyclo-[3.1.0]hex-2-ene by matching ir and nmr spectra. A mixture melting point was undepressed. The mother liquors contained unreacted starting material (5%) and 90 mg of 1,2,6-triphenyl-(*E*,*Z*,*E*)-hexa-1,3,5-triene (**18**).

Irradiation of a solution of *cis*-cyclohexadiene **7** (300 mg) in cyclohexane (200 ml) for only 45 min resulted in the formation of (*E*,*Z*,*E*)-hexatriene (30%) as well as unreacted starting material. Only trace amounts of the *exo*,*exo*-bicyclohexene were formed under these conditions.

Irradiation of 1,2,6-Triphenyl-(*Z*,*Z*,*Z*)- and -(*E*,*Z*,*Z*)-hexa-1,3,5-trienes. A solution of the (*Z*,*Z*,*Z*)-triene (285 mg) in cyclohexane (500 ml) was irradiated with a 450-W Hanovia lamp fitted with a Pyrex filter for 4 hr. The resulting solution was evaporated to a tan solid which was recrystallized from ethanol to give 77 mg (27%) of *exo*,*endo*-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**17**): mp 132–133°; ir (KBr) 6.21, 6.71, 6.90, 9.32, 9.70, 10.22, 11.55, 12.02, 13.21, and 14.45 μ; nmr ($CDCl_3$) τ 7.99 (d of d, 1 H), 7.50 (m, 2 H), 6.22 (t, 1 H), 3.68 (m, 1 H), and 2.7–3.2 (m, 15 H). Appropriate spin decoupling experiments showed that $J_{1,2} = J_{1,4} = J_{2,4} = 2.0$ Hz, $J_{1,5} = 6$ Hz, and $J_{5,6} = 8.0$ Hz; uv (95% ethanol) 269 nm (ϵ 11,000); *m*/*e* (parent) 308. *Anal.* Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.36; H, 6.54.

The filtrate was concentrated under reduced pressure and was analyzed by nmr and showed the presence of the *exo*,*endo*-bicyclohexene (**17**) as well as the *E*,*Z*,*Z* isomer. No significant quantities of the *exo*,*exo*-bicyclohexene **8** (*i.e.*, less 2%) were detected.

Irradiation of 150 mg of 1,2,6-triphenyl-(*E*,*Z*,*Z*)-hexa-1,3,5-triene in the manner described above gave 38 mg (28%) of the *exo*,-*endo*-bicyclohexene **17**. Under these conditions no detectable quantities of (*Z*,*Z*,*Z*)-hexatriene **13** or *exo*,*exo*-bicyclohexene **8** were observed.

When a solution of 50 mg of the (*Z*,*Z*,*Z*)-triene was irradiated in cyclohexane (100 ml) for 9 min, the nmr of the residue showed recovered starting material (40%) as well as the *E*,*Z*,*Z* isomer (50%). Only a small amount of *exo*,*endo*-bicyclo[3.1.0]hexene **17** was detected in the nmr (*ca.* 10%).

Irradiation of *trans*-1,5,6-Triphenyl-1,3-cyclohexadiene. A solution of *trans*-cyclohexadiene **16** (700 mg) in cyclohexane (500 ml) was irradiated for 4 hr with a 450-W Hanovia lamp fitted with a Pyrex filter. The solvent was removed under reduced pressure and the residue was crystallized from ethanol to give 455 mg (65%) of *exo*,*endo*-bicyclohexene **17** as shown by its nmr and ir spectra. The mother liquors contained mostly (*E*,*Z*,*Z*)-hexatriene (**19**).

Irradiation of a solution of *trans*-cyclohexadiene **16** (330 mg) in cyclohexane (500 ml) for only 45 min resulted in the formation of (*E*,*Z*,*Z*)-hexatriene **19** (40%) as well as unreacted starting material. Only trace quantities of the *exo*,*endo*-bicyclohexene isomer were formed under these conditions.

Photoisomerization of (*Z*,*E*,*Z*)- to (*E*,*E*,*Z*)-Hexatriene. A 200-mg sample of (*Z*,*E*,*Z*)-hexatriene **23** was irradiated through a Pyrex filter using a 450-W Hanovia lamp in cyclohexane (500 ml) for 20 min. Evaporation of the solvent under reduced pressure and crystallization of residue from 95% ethanol afforded 180 mg (90%) of 1,2,6-triphenyl-(*E*,*E*,*Z*)-hexa-1,3,5-triene, mp 109–100°.

Photoisomerization of (*Z*,*Z*)-1,2,6-Triphenylhexa-1,3-dien-5-yne. A solution containing 100 mg of the (*Z*,*Z*)-dienyne in 500 ml of cyclohexane was irradiated for 12 min with a 450-W Hanovia lamp fitted with a Pyrex filter. The solvent was removed under reduced pressure and the residue was analyzed by nmr spectroscopy. The nmr spectrum of the crude residue showed the presence of the (*E*,*E*)-dienyne (**22**) (80%), recovered starting material (10%), and (*E*,*Z*)-dienyne **21** (10%). There was no detectable quantities of the (*Z*,*E*)-dienyne **15**. When the irradiation of the (*Z*,*Z*)-dienyne was interrupted after 5 min of irradiation, the major product was the (*E*,*Z*)-dienyne (70%). Again, no detectable amounts of the (*Z*,*E*)-dienyne (**15**) were found.

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[63] M. M. Robinson, W. G. Pierson, L. Dorfman, and B. F. Lambert, *J. Org. Chem.*, **31**, 3213 (1966).