Table VII. Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Wavelength

λ, nm	*trans*-II, mg	Time, hr	Intensity × 10^{14} [a]	*cis*-II		Convn,[c] %	ϕ
				Obsd	Corr[b]		
246[d]	179.6	48	3.82 2.70 Av 3.26	1.6	1.6	0.9	0.13
254[e]							0.20
262	179.6	48	10.58 8.79 Av 9.68	8.8	9.2	4.9	0.25

[a] Photons/second. [b] Corrected for back-reaction. [c] Uncorrected. [d] The actual values are 246 ± 11 and 262 ± 11 nm. [e] This is the value from irradiation with the 2537-Å lamp, and is given here for comparison only.

Photoisomerization of *cis*-Piperylene. These experiments were conducted in a manner identical with the one above but in the absence of any sensitizer (the piperylene was purified immediately prior to use and the solvent was transparent in the uv). Conversions of *cis*- to *trans*-piperylene were 2–9%. Because all the incident 254-nm light is not absorbed under these conditions, the effective path length of the Vycor tubes was determined by actinometry using low concentrations of 6-phenyl-2-hexene and independently measured quantum efficiencies of product formation.[12] Although the tubes are 25 mm o.d., the effective path length was measured as 13.5 mm. This value was used to calculate the absorbance of the piperylene solutions and the ϕ's observed were 0.083, 0.086, and 0.094; av 0.087.

Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Concentration. Two 50-ml solutions of *trans*-1-phenyl-2-butene, 7.07×10^{-3} *M* (46.8 mg) and 2.55×10^{-2} *M* (168.8 mg), were prepared with spectral grade *n*-hexane. The *trans*-1-phenyl-2-butene was weighed into the Vycor tubes and the solutions were deoxygenated with argon 1 hr prior to irradiation with 2537 Å light in the turntable at 25.0 ± 1.0°. The standard was added, and the tubes were analyzed for *cis*-1-phenyl-2-butene on a 4% $AgBF_4$–16% Carbowax 20M column. The 7.07×10^{-3} *M* solution was photolyzed 32 min with a lamp intensity of 1.11×10^{17} photons/sec. Before correction for back-reaction, 7.7 mg (16.4%) of *cis*-1-phenyl-2-butene was detected; after correction the value became 9.1 mg, $\Phi = 0.195$. The 2.55×10^{-2} *M* solution was irradiated 41 min with 2537 Å light (1.11×10^{17} photons/sec). The 12.1 mg (7.7%) of *cis*-1-phenyl-2-butene measured by glpc was corrected for back-reaction, and the corrected value of 13.0 mg was obtained, $\phi = 0.218$.

Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Wavelength. The quantum efficiency of isomerization of *trans*-1-phenyl-2-butene at 246 ± 11 nm and 262 ± nm was examined. An 80-ml sample of 1.69×10^{-2} *M* *trans*-1-phenyl-2-butene in spectral grade *n*-hexane was cooled to 18–20° in a 6.6-cm path length water-jacketed cell, and the solution was deoxygenated with argon for 1 hr. A Bausch and Lomb "high intensity monochromator" was used to resolve the emission from the mercury–xenon lamp. Slit widths of 6.0 mm and 3.4 mm were used to obtain the maximum intensity. The optical density of the solutions was 2.0 over the entire band pass. Chemical actinometry was used to measure the lamp intensity before and after each experiment and then averaged. The results and conditions are summarized in Table VII.

Acknowledgment. The authors gratefully acknowledge the support of this research by the National Science Foundation.

Dual Reaction Pathways in an Open-Chain Cope Rearrangement

R. P. Lutz,*[1] S. Bernal, R. J. Boggio, R. O. Harris, and M. W. McNicholas[2]

Contribution from the Departments of Chemistry, Portland State University, Portland, Oregon 97207, and the University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received November 13, 1970

Abstract: *meso*-3,4-Diphenylhexa-1,5-diene rearranges with a half-life of about 15 hr at 120° to *cis,trans*-1,6-diphenylhexa-1,5-diene (63%) and *trans,trans*-1,6-diphenylhexa-1,5-diene (37%). The cis,trans isomer is formed through a transition state having four-center, chairlike geometry whereas the trans,trans isomer requires a six-center, boatlike transition state. The corresponding *dl*-3,4-diphenylhexa-1,5-diene is converted with a half-life of about 8 hr at 80° to 100% of the trans,trans isomer, a product which requires a four-center transition state. The "preferred" geometry for thermal Cope rearrangements is four centered, based on the known rearrangement stereochemistry of *meso*- and *dl*-3,4-dimethylhexa-1,5-diene. The exceptional behavior of the *meso*-diphenyl derivative appears to be a consequence of steric inhibition to coplanarity of contiguous phenyl and allyl groups in the four-center transition state derived from this molecule.

Transition-state geometries for the thermal Cope rearrangement[3] can generally be classified as either of two basic types—four-center, chairlike or six-center, boatlike. An example of the former is provided by the rearrangement of *meso*-3,4-dimethylhexa-1,5-diene (**1a**) at 225° to *cis,trans*-octa-2,6-diene (**3a**) as the virtually exclusive product (99.7%).[4] Of the two transition-state geometries, the four-center (**2a**) as shown accounts

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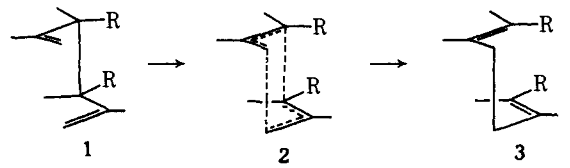
(1) To whom inquiries should be directed at Portland State University. Some of the preliminary experimental work was carried out at Harvard University, Cambridge, Mass.

(2) National Science Foundation Undergraduate Research Participant.

(3) The traditional definition of the Cope rearrangement is assumed. For reviews, see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 867–869, and (b) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Vol. 1, Interscience, New York, N. Y., 1963, Chapter 11.

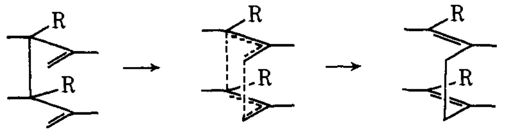
(4) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).



1 2 3

a, R = CH$_3$
b, R = C$_6$H$_5$

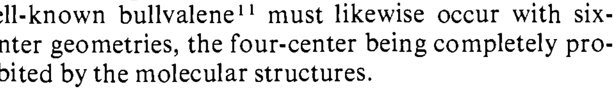
for the observed cis,trans isomer. Reaction through a six-center transition state would yield the trans,trans and/or cis,cis isomer. Hypothetical formation of the trans,trans (**5a**) is illustrated (**1a** → **4a** → **5a**). Rearrangement of the corresponding *dl*-3,4-dimethylhexa-1,5-diene to a mixture of the trans,trans and cis,cis isomers requires, by the same type of analysis,[5] four-center transition states (see below). Other rearrangements whose stereochemistry requires four-center transition states are those of optically active *trans*-3-methyl-3-phenylhepta-1,5-diene,[6] of *cis,trans*-cyclonona-1,5-diene,[7] and of *cis,trans*-cyclodeca-1,5-diene.[8]



1 4 5

a, R = CH$_3$
b, R = C$_6$H$_5$

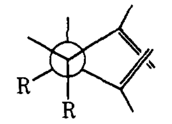
If the molecule undergoing rearrangement is so constructed that the four-center transition state leads to a product which is sterically strained, rearrangement can readily occur by the six-center route. *cis*-1,2-Divinylcyclobutane (**6**), for example, rearranges rapidly at 120° by a six-center transition state (**7**) to *cis,cis*-cycloocta-1,5-diene (**8**).[9] Rearrangement through a four-center transition state would give the highly strained *cis,trans*-cycloocta-1,5-diene. (Another conformation of the six-center transition state would give the unknown *trans,trans*-cycloocta-1,5-diene.) The facile, degenerate Cope rearrangements of 3,4-homotropilidene[10] and the well-known bullvalene[11] must likewise occur with six-center geometries, the four-center being completely prohibited by the molecular structures.



6 7 8

The four-center geometry apparently has the lower energy from the point of view of the unsubstituted hexa-1,5-diene carbon skeleton. If there is no steric barrier to reaction by either pathway, as in the 3,4-dimethylhexa-1,5-dienes, the four-center is preferred. The six-center is nevertheless energetically accessible when required. Several independent theoretical evaluations of the relative energies of the four- and six-center transition states (based either on orbital symmetry,[12] conformational energy calculations,[13] or molecular orbital calculations[14]) coincide with the experimental order.[15]

Orbital symmetry arguments, incidentally, suggest that a variation of the four-center arrangement is an "allowed" geometry for the transition state. In Woodward and Hoffmann's terminology, the two allylic units in either the four-center or six-center transition states shown above interact in a suprafacial manner. With somewhat more distortion, an allowed four-center antarafacial arrangement (*e.g.*, **9**) can be achieved.[16] The stereochemical consequences of the rearrangement of the isomeric 3,4-dimethylhexa-1,5-dienes by suprafacial or antarafacial four-center modes are the same, as Baldwin and Kaplan[17] have pointed out. The operation of a four-center antarafacial mode is rendered highly unlikely by the fact that a molecule constrained to react this way, 3,7-dideuteriobicyclo[3.3.0]octa-2,6-diene, does not rearrange in 85 min at 450°.[17] The one example of a reaction[18] which has been interpreted[16] as an antarafacial Cope rearrangement may well go by another route.[19]



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Given that the preference for the four-center transition state appears to be a moderate one, it is reasonable to expect that four- and six-center transition states for a particular rearranging molecule may have steric and electronic factors energetically balanced in such a way that both modes of rearrangement are used. *meso*-3,-4-Diphenylhexa-1,5-diene (**1b**) indeed behaves this way. It rearranges with a half-life of about 15 hr at 120° to give 63% *cis,trans*-1,6-diphenylhexa-1,5-diene (**3b**) and 37% *trans,trans*-1,6-diphenylhexa-1,5-diene (**5b**) as the kinetically controlled products. Neither the isomeric *cis,cis*-1,6-diphenylhexa-1,5-diene nor a compound incorrectly reported[20] to be a product of this rearrange-

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(5) Clearly described in ref 3 and 4.

(6) R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967).

(7) E. Vogel and W. Grimme, *Angew. Chem., Int. Ed. Engl.*, **2**, 739 (1963).

(8) P. Heimbach, *ibid.*, **3**, 702 (1964).

(9) (a) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958); (b) *cf.* G. S. Hammond and C. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(10) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(11) (a) Cover design, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968; also p 843 and references cited; (b) ref 3a, pp 886–889.

(12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 148–150.

(13) M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968).

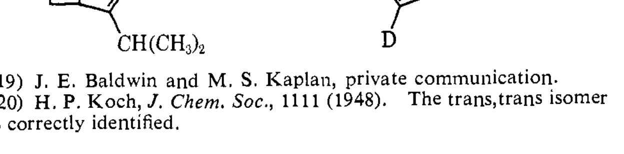
(14) (a) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, 251 (1966); (b) A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

(15) The experimental difference in free energy of activation based on relative rates at 225° is at least 5.7 kcal/mol (ref 4). Calculated enthalpy of activation differences are 5.3 (ref 13), 5–6 (ref 14a), and 6.6 kcal/mol (ref 14b).

(16) Reference 12, p 126. The geometry in **9** is exaggerated for clarity.

(17) J. E. Baldwin and M. S. Kaplan, *Chem. Commun.*, 1354 (1969).

(18) T. Miyashi, M. Nitta, and T. Mukai, [*Tetrahedron Lett.*, 3433 (1967)] observed the following transformation



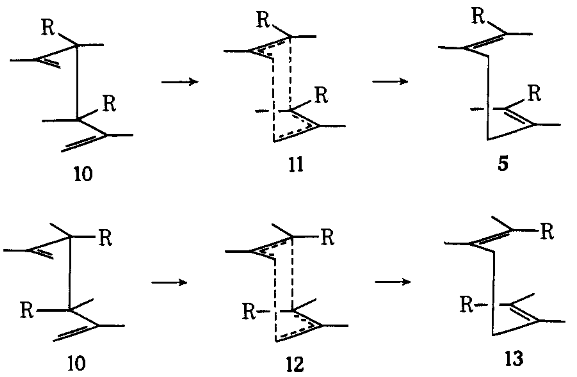
(19) J. E. Baldwin and M. S. Kaplan, private communication.

(20) H. P. Koch, *J. Chem. Soc.*, 1111 (1948). The trans,trans isomer was correctly identified.

ment, *trans*-1,4-diphenylhexa-1,5-diene, is produced to an extent greater than 0.2%. Product composition is based on relative peak areas obtained by gas-liquid partition chromatography (glpc).

The formation of the *cis,trans*-diene requires reaction by way of a transition state having the four-center geometry (**2b**), following the pattern observed in the rearrangement of Doering and Roth's *meso*-3,4-dimethylhexa-1,5-diene. The trans,trans isomer, on the other hand, must arise through a six-center transition state (**4b**), a reaction pathway which was clearly excluded in the case of the *meso*-dimethyl diene.

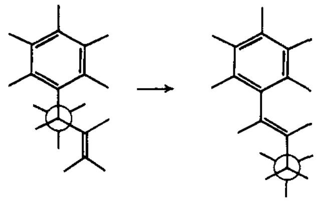
dl-3,4-Diphenylhexa-1,5-diene (**10b**) differs from its meso counterpart in that its rearrangement proceeds by a single pathway. At 80° it rearranges with a half-life of about 8 hr to 100% of the *trans,trans*-diene (**5b**) as the kinetically controlled product. Isomeric dienes are absent in proportions greater than 0.1%. In this case, not only does the reaction follow a four-center route rather than the six-center, but of the two possible four-center conformations, **11b** and **12b**, yielding the *trans,trans*-(**5b**) or the *cis,cis*-diene (**13b**), respectively, the one leading to the *trans,trans*-diene is followed exclusively. The analogous *dl*-3,4-dimethylhexa-1,5-diene (**10a**), on the other hand, rearranges through both four-center conformations, yielding 90% *trans,trans*- and 10% *cis,cis*-octa-2,6-diene (**5a** and **13a**) at 180°.[4]



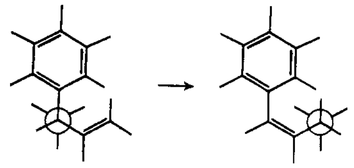
a, R = CH_3
b, R = C_6H_5

The contrasting stereochemical behavior of the diphenyl derivatives can be rationalized by considering the electronic and steric effects of the phenyl groups on transition state geometries. Phenyl groups clearly stabilize the transition state relative to unsubstituted or alkyl-substituted hexa-1,5-dienes,[21] through an interaction which requires that the phenyl group be coplanar, or nearly so, with the allylic moiety to which it is attached. The steric interaction between the phenyl and its allylic support will depend on whether the molecule is set to generate a trans double bond or a cis double bond. Scheme I shows the approximate geometry, based on Dreiding models, which must be assumed in generating a trans double bond. There are no severe steric interactions within this half of the molecule, nothing which might inhibit the change from taking place if the geometry were called for by other factors. Scheme II illustrates the sterically much less favorable formation of a cis double bond. One of the *o*-hydrogens is forced to interfere with a methylene hydrogen, an interaction which would prevent the type of coplanarity indicated.

Scheme I



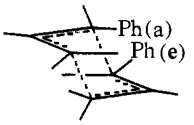
Scheme II



The reaction of the *meso*-diphenyl diene by both pathways can be explained by the above considerations. The preferred four-center transition state requires that the *meso*-diene yield exclusively the cis,trans product. However, the geometry leading to a cis double bond forces a phenyl group out of coplanarity with its allylic skeleton, so that part of the energetic advantage of the electronic interaction between the phenyl and allyl is lost. If the *meso*-diene rearranges by way of the six-center geometry to the *trans,trans*-diene, the energetic advantage of the four-center carbon skeleton is no longer available, but is partially compensated for by the fact that both phenyl groups may then be coplanar with their attached allylic units. The balance of factors still favors reaction through a four-center transition state, but the six-center is close enough in energy that a substantial fraction of the molecules rearranges by the latter route.[22]

The *dl*-diene has the potential for rearranging by way of a transition state which takes advantage of the four-center hexadiene skeleton as well as phenyl groups which are coplanar with the allylic units. The trans, trans isomer results. Any other arrangement, either a four-center one leading to cis,cis product or the six-center leading to cis,trans, would represent an increase in energy.

A slightly different way to account for the stereochemical behavior of the 3,4-diphenylhexa-1,5-dienes makes use of the gross similarity between the four- and six-center transition states and the chair and boat conformations, respectively, of cyclohexane.[23] The four-center, chairlike transition state (**14**) for the rearrangement of the *meso*-diphenyl derivative places one of the phenyl groups in an equatorial position with the other forced to occupy the hindered axial position. The equatorial phenyl ends up in the product on the trans



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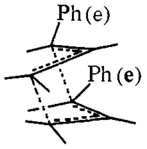

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[21] As indicated by the temperature required to effect rearrangement; *cf.* ref 3a.

[22] The difference in free energy of activation at 120° is about 0.4 kcal/mol (based on relative rearrangement rates).

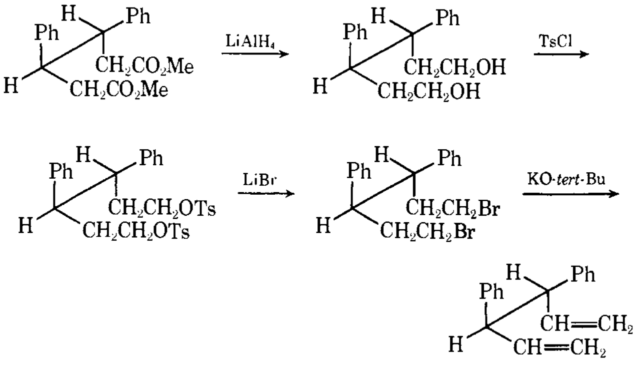
[23] A quantitative formulation of this approach is given by C. L. Perrin and D. J. Faulkner, *Tetrahedron Lett.*, 2783 (1969).

double bond whereas the axial phenyl becomes part of the cis double bond. The placement of phenyl in the unfavorable axial position is avoided in a six-center, boatlike transition state (**15**) where both phenyl groups occupy boat-equatorial positions and subsequently form trans double bonds. Another conformation of the boatlike transition state would place both phenyls in the hindered boat-axial positions leading to two cis double bonds in the product.

The chairlike transition state derived from the *dl*-diphenyl isomer has two conformations, with the phenyl groups either axial,axial or equatorial,equatorial. The former would lead to *cis,cis*-diene, the latter to the *trans,trans*-diene. The single possible conformation of the boatlike transition state, with one equatorial and one axial phenyl group, would give the *cis,trans*-diene. All factors recommend the four-center, equatorial,equatorial chairlike transition state as the lowest in energy.

The arguments cited above also account for the milder conditions under which the *dl*-diene rearranges with respect to the *meso*-diene, although part of the difference is undoubtedly due to a relatively higher ground-state energy for the *dl* isomer.

The *meso*- and *dl*-dienes were synthesized from the corresponding dimethyl esters of *meso*- and *dl*-β,γ-diphenyladipic acid. Both esters are obtained in moderate yield from the reductive coupling of methyl *trans*-cinnamate.[24] Transformation of the esters to the dienes is illustrated below for the meso isomer; *i.e.*, reduction to the diol with lithium aluminum hydride, conversion of the diol to the dibromide by way of the tosylate, followed by elimination from the dibromide using potassium *tert*-butoxide in a 1 : 1 (vol) mixture of dimethyl sulfoxide and *tert*-butyl alcohol. The choice of leaving group and base was suggested by a report[25] that this combination promotes elimination at the expense of substitution. It was found in this case, however, that the success of the elimination depended as well on the particular solvent mixture indicated. Neither *tert*-butyl alcohol nor dimethyl sulfoxide by itself proved to be satisfactory although this aspect of the reaction conditions was not extensively investigated.



The *meso*-diene was also available as a minor product in the Grignard coupling of *trans*-cinnamyl chloride.[20,26]

trans,trans-1,6-Diphenylhexa-1,5-diene is likewise a product of this coupling reaction. The unreported cis,cis and cis,trans isomers could be prepared, as a mixture with trans,trans, by a Wittig reaction using benzaldehyde and tetramethylenephosphonium bromide.[27] A more convenient procedure proved to be photosensitized (with benzil)[28] isomerization of the trans,trans isomer to a mixture of all three. The mixture was separated by preparative-scale glpc.

Experimental Section

Melting points are uncorrected and were obtained in capillary tubes. Infrared spectra were recorded on Perkin-Elmer spectrophotometers (Models 137, 237, or 337), ultraviolet spectra on Bausch and Lomb Spectronic 505, and nuclear magnetic resonance spectra (60 MHz) on Varian Model A60. Evaporation of solvents was carried out with a rotary evaporator at water aspirator pressure. Elemental analyses were by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Gas-Liquid Partition Chromatography. Analyses were carried out with either a Varian-Aerograph Autoprep 700 (thermal conductivity detector) or a Hewlett-Packard Model 5750 (dual flame detectors) gas chromatograph. Solids were injected as solutions in either chloroform or carbon tetrachloride. Successful resolution of the isomeric 1,6-diphenylhexa-1,5-dienes could be achieved with a cyanosilicone stationary phase; for example, 8 ft × 0.25 in. stainless steel with 5% XE-60 on 60–80-mesh acid-washed, silanized Chromosorb W. The column temperature was 220°, injector at 250°. No detectable isomerization of the 1,6-diphenylhexadienes took place under these conditions. The retention times increased in the order cis,cis, cis,trans, and trans,trans. The retention time of *trans*-1,4-diphenylhexa-1,5-diene was slightly shorter than that of the cis,cis isomer and a mixture of these two components was only partially resolved.

Both *meso*- and *dl*-3,4-diphenylhexa-1,5-diene rearranged under the analysis conditions. The chromatogram of the meso isomer was a complex pattern of incompletely resolved peaks, with the greatest intensities centered at retention times corresponding to the isomers of 1,6-diphenylhexa-1,5-diene, the intensities decreasing in the order cis,trans > trans,trans > cis,cis. The *dl*-diene rearranged cleanly to give a chromatogram corresponding to that of the trans,trans isomer (see the section on *dl*-diene rearrangement).

Preparative-scale separations were carried out with the Autoprep 700, the column consisting of a 20 ft × $^3/_8$ in. aluminum tube packed with 20% XE-60 on Chromosorb W. The column temperature was 220°.

The proportion of isomers in the thermal rearrangement products was based on relative peak areas in the chromatograms. These did not vary significantly with changes in the detection systems.

***meso*-3,4-Diphenylhexane-1,6-diol.** Dimethyl *meso*-β,γ-diphenyladipate[29] (5.0 g, 0.015 mol) was suspended in 150 ml of anhydrous ether and added rapidly through an addition funnel to 1.1 g (0.030 mol) of lithium aluminum hydride in 50 ml of anhydrous ether. The mixture was protected with a drying tube and left overnight at room temperature with magnetic stirring. Excess hydride was then decomposed with 2 ml of ethyl acetate and the reaction mixture was hydrolyzed with water and 15% sulfuric acid until the aqueous phase was acid to litmus. The insoluble product

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[24] M. P. Oommen and A. I. Vogel, *J. Chem. Soc.*, 2148 (1930). The assignment of configuration was based on resolution of the derived *dl* acid by means of the brucine salt. The acid assigned the meso configuration could not be resolved with either of three optically active bases.

[25] P. Veeravagu, R. T. Arnold, and E. W. Eigenmann, *J. Amer. Chem. Soc.*, **86**, 3072 (1964).

[26] The assignment of a meso configuration was based on an X-ray crystallographic observation that the molecule was centrosymmetric: G. A. Jeffrey, H. P. Koch, and S. C. Nyburg, *J. Chem. Soc.*, 1118 (1948).

[27] A. Mondon [*Justus Liebigs Ann. Chem.*, **603**, 115 (1957)] reports preparation of the trans,trans isomer along with another isomer, mp 37°, which was not characterized but which we subsequently found was the cis,cis.

[28] The choice of photosensitizer was based on its behavior in the isomerization of *trans*-stilbene; *cf.* G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

[29] The procedure for synthesizing the ester was essentially that given in ref 24. It was found, however, that the preparation of the aluminum amalgam using household aluminum foil was nearly uncontrollably exothermic with considerable evolution of hydrogen, especially during treatment of the aluminum with sodium hydroxide. This could be done in a controlled manner by dipping batches of the foil into a large beaker of the base solution. Ice cooling of the wet amalgam was required at all times, including the initial stages of the coupling reaction, which was allowed to proceed for about 15 hr. The total yield of coupling products was 31%, of which 57% was the meso ester.

was separated from the three-phase mixture by suction filtration, then washed with water, followed by ether, and air dried. The ether layer of the filtrate was separated, dried over anhydrous potassium carbonate, and evaporated to dryness under vacuum to yield a small amount of residue which was discarded. The crude product (3.9 g, mp 178–180°) was recrystallized from tetrahydrofuran to give 3.4 g of material having mp 178.5–179° (lit. mp 178–179°,[30] 162.5–163.3° [31]) and a second crop of 0.11 g, mp 177.5–178.5°, for a total yield of 86%; ir (mineral oil) 2.98 (OH) and 9.78 μ (C–O). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.95; H, 8.22. Found: C, 79.81; H, 8.24.

***meso*-3,4-Diphenylhexamethylene *p*-Toluenesulfonate.** *p*-Toluenesulfonyl chloride (8.5 g, 0.044 mol, mp 67.5–69°)[32] was slowly added with stirring to an ice-cold solution of the *meso*-diol (3.0 g, 0.011 mol) in 70 ml of dry (molecular sieves) pyridine. This solution was allowed to stand in the refrigerator overnight. The resulting mixture, containing solid pyridine hydrochloride, was poured with stirring into about 450 g of ice water and the precipitated tosylate was filtered, washed with water, and dried. Recrystallization from 2:1 (vol) ethyl acetate–carbon tetrachloride gave 4.8 g (75%) of sample with mp 158–159°; ir ($CHCl_3$) 7.39 (RSO_2OR) and 8.55 μ (RSO_2OR).

***meso*-1,6-Dibromo-3,4-diphenylhexane.** Lithium bromide (2.5 g, 0.029 mol, 100% excess) was dissolved in 25 ml of acetone and the solution dried over molecular sieves, from which it was then separated by pressure filtration using dry nitrogen. *meso*-3,4-Diphenylhexamethylene *p*-toluenesulfonate (3.6 g, 0.0062 mol) was added and the resulting heterogeneous mixture was magnetically stirred and allowed to reflux overnight protected by a drying tube. After the mixture had cooled and the solvent evaporated under vacuum, water was added and the resulting slurry was suction filtered. The collected solid was dried and recrystallized from cyclohexane to give 1.9 g of material (77% yield) with mp 140–142°. (Better samples of the *meso*-dibromide had mp 144–144.5°.)

***meso*-3,4-Diphenylhexa-1,5-diene.** Potassium *tert*-butoxide (2.0 g, 0.021 mol) was dissolved with magnetic stirring in 18 ml of 1:1 (vol) *tert*-butyl alcohol and dry (molecular sieves) dimethyl sulfoxide. The *meso*-dibromide (1.0 g, 0.0025 mol) was then added to give a mixture containing some undissolved bromide. The mixture was stirred at room temperature for 30 min during which period the amount of solid increased. The mixture was poured over about 100 g of ice, precipitating a white solid, and immediately neutralized to a phenolphthalein end point with 18% hydrochloric acid. When the ice had melted, the mixture was extracted with 50 ml of dichloromethane in three portions. The extracts were combined, washed once with water, dried over anhydrous magnesium sulfate, and evaporated to dryness to yield 0.62 g of crude *meso*-diene. This sample was combined with 0.68 g of equivalent material from another reaction run on a 0.0033-mol scale and the total was purified by dry-column chromatography[33] on 240 g of silica gel (Woelm dry-column grade, 0.5% inorganic fluorescent indicator). The column was developed with hexane, with the progress of separation followed with ultraviolet light. The portion of the column suspected of retaining the *meso*-diene was washed with hexane until no more solid was removed. The hexane washings were evaporated under vacuum to yield about 0.6 g of white solid which recrystallized from ethanol to give 0.40 g (29%): mp 86–87°; ir (CCl_4) 6.10 ($C{=}C$), 10.19 ($CH{=}CH_2$), and 10.97 μ ($CH{=}CH_2$); nmr (CCl_4) δ 7.15 (doublet, 4.7, C_6H_5), 5.8 (broad multiplet, 1.0, $CH{=}CH_2$), 4.8 (pattern of three doublets, 1.9, $CH{=}CH_2$), and 3.6 ppm (multiplet, 1.0, $ArCH$). This sample was identical (melting point, ir, nmr) with *meso*-diene previously obtained as a minor product in the Grignard coupling of *trans*-cinnamyl chloride.[20]

***dl*-3,4-Diphenylhexane-1,6-diol.** Dimethyl *dl*-β,γ-diphenyladipate[29] (6.8 g, 0.021 mol) was suspended in 200 ml of dry ether (it was only partially soluble) and added in portions through an addition funnel to a magnetically stirred suspension of lithium aluminum hydride (1.6 g, 0.042 mol) in 75 ml of dry ether. The reaction mixture was protected by a drying tube and allowed to stir overnight.

Water was then cautiously added to decompose excess hydride, followed by more water and 15% sulfuric acid until the aqueous phase was pH 1. The ether layer was separated and the aqueous phase was washed with several portions of ether. The combined ether solutions were dried over anhydrous magnesium sulfate and evaporated under vacuum, leaving 5.2 g of a crystalline white solid having mp 98.5–100° (cloudy melt). The crude sample was partially purified by adding acetonitrile, which dissolved the alcohol and left an insoluble substance subsequently removed by filtration. The filtrate was evaporated to dryness under vacuum and the residue recrystallized from benzene to yield 4.3 g (76%) of material with mp 99–100° (lit.[31] mp 103.6–104.7°); ir ($CHCl_3$) 2.78 (OH), 2.93 (OH···O), and 9.78 μ (C–O). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.95; H, 8.22. Found: C, 79.84; H, 8.16.

***dl*-3,4-Diphenylhexamethylene *p*-Toluenesulfonate.** *dl*-3,4-Diphenylhexane-1,6-diol (4.3 g, 0.016 mol) was dissolved in 95 ml of pyridine previously dried over molecular sieves and the solution was brought to 0° in an ice bath. To this was added 12.4 g (0.065 mol) of freshly purified *p*-toluenesulfonyl chloride,[32] slowly and with stirring, keeping the temperature as close to 0° as possible. The resulting solution was placed in the refrigerator overnight, during which time pyridine hydrochloride precipitated. The reaction mixture was then poured over ice, stirred, and warmed to room temperature. The aqueous phase was decanted and the gummy product taken up in dichloromethane. The dichloromethane solution was washed once with water, dried over anhydrous magnesium sulfate, and evaporated on the rotary evaporator followed by application of full oil-pump vacuum for several hours. The residual clear gum was caused to solidify by trituration in warm hexane. The solid was filtered and dried to yield 7.8 g (84%) of material with mp 97–100.5°, which was used without further purification in the preparation of the dibromide. A small portion recrystallized from methanol had mp 99.5–101.5°; ir (CCl_4) 7.29 (RSO_2OR) and 8.40, 8.48 μ (doublet, RSO_2OR).

***dl*-1,6-Dibromo-3,4-diphenylhexane.** Lithium bromide (4.7 g, 0.054 mol, 100% excess) was dissolved in 50 ml of acetone and the solution was dried over molecular sieves, from which it was subsequently removed by pressure filtration with dry nitrogen. *dl*-3,4-Diphenylhexamethylene *p*-toluenesulfonate (7.6 g, 0.013 mol) was added, and the resulting solution allowed to reflux overnight, with magnetic stirring, protected by a drying tube. (A precipitate began to form about 0.5 hr after reflux was started.) The reaction mixture was then cooled to room temperature and evaporated to dryness under vaccum. Water was added to the residue, leaving an insoluble gum which solidified after being rubbed with a spatula. The solid was separated by suction filtration, washed with water, and dried. Recrystallization from methanol gave 3.0 g, mp 62–63.5°, and a second crop weighing 0.7 g, mp 61–64°. The two crops represented a yield of 72%.

***dl*-3,4-Diphenylhexa-1,5-diene.** Potassium *tert*-butoxide (7.2 g, 0.074 mol) was dissolved with magnetic stirring in 65 ml of a 1:1 (vol) mixture of *tert*-butyl alcohol and dry (molecular sieves) dimethyl sulfoxide. *dl*-1,6-Dibromo-3,4-diphenylhexane (3.6 g, 0.0091 mol) was added to give a solution which was magnetically stirred at room temperature protected from atmospheric moisture. A precipitate began to form after about 5 min. The mixture was stirred for an additional 30 min, then mixed with about 200 g of ice in a separatory funnel. Excess base was immediately neutralized with 18% hydrochloric acid to a phenolphthalein end point. When the ice had melted the mixture was extracted with four 40-ml portions of dichloromethane which were subsequently combined, washed once with water, dried over anhydrous magnesium sulfate, and evaporated under vacuum to yield 2.1 g of pale yellow oil.

The crude diene was purified by dry-column chromatography[33] on 417 g of silica gel (Woelm dry-column grade, 0.5% inorganic fluorescent indicator). The column was developed with hexane, and the progress of the separation was followed with uv light. The portion of the column containing the suspected *dl*-diene was washed with hexane until no more solid was removed. The combined hexane washings were evaporated under vacuum to yield 1.23 g of colorless solid with mp 27–34°. Recrystallization from ethanol with ice cooling (suction filtration was carried out in a cold room at 4°) gave 0.74 g of sample with mp 35.0–35.2° (35% yield). Further recrystallization of this material gave 0.57 g with mp 35.1–35.4°; ir (CCl_4) 6.11 ($C{=}C$), 10.13 ($-CH{=}CH_2$), and 10.92 μ ($-CH{=}CH_2$); nmr (CCl_4) δ 7.0 (broad singlet, 5.2, C_6H_5), 6.1

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(30) O. Dann and G. Hauck, *Arch. Pharm.* (*Weinheim*), **293**, 187 (1960); *Chem. Abstr.*, **55**, 3554*b* (1961).

(31) A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953). The discrepancy between the reported melting point of the *meso*-diol and that observed in our work as well as ref 30 is unaccounted for. The source of the *meso*-diol was lithium aluminum hydride reduction of the meso diester, with recrystallization out of di-*n*-butyl ether. We find that recrystallization of our pure *meso*-diol out of this solvent does not affect the melting point. The recrystallization solvent for the *meso*-diol in ref 30 was ethanol–water.

(32) Purification according to L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1179.

(33) B. Loev and M. M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

(broad multiplet, 1.0, C*H*=CH_2), 5.0 (pattern of three doublets, 2.0, CH=CH_2), and 3.6 ppm (multiplet, 1.0, ArC*H*). *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H. 7.74. Found: C, 92.02; H, 7.69.

Isomeric 1,6-Diphenylhexa-1,5-dienes. *trans,trans*-1,6-Diphenylhexa-1,5-diene (7.6 g), prepared by the Grignard coupling of *trans*-cinnamyl chloride,[20] was dissolved in 300 ml of benzene along with 0.79 g of benzil and irradiated for 40 hr at 3500 Å in a Rayonet photochemical reactor[34] to give a mixture containing all three isomers in the ratio of about one part trans,trans to three parts cis,trans to two parts cis,cis. The proportion of trans double bonds could be reduced by further irradiation, but the reaction was stopped at the point indicated to optimize the subsequent isolation of the cis,trans isomer with minimal contamination by other isomers. The solvent was removed under vacuum and the residual oil was distilled without fractionation at 0.05 mm to yield 6.2 g of oil which was combined with 4.3 g of similar material obtained from a previous reaction. The total was diluted with two parts (vol) benzene and separated by preparative glpc.

The cis,cis isomer was recrystallized from ethanol to yield 1.7 g of sample having mp 34.5–36° (lit.[27] mp 37°). The analytical sample was further recrystallized from methanol, giving mp 36.5–37°. *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.76.

The cis,trans isomer was distilled without fractionation in two batches at 120–128° (0.1 mm) to give a total of 2.6 g of material which remained an oil at room temperature. The sample which was used for characterization purposes and comparison with the Cope rearrangement products was greater than 97% pure by glpc. *Anal.*[35] Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.86.

The assignment of configurations was based on ultraviolet and infrared spectra. For trans,trans: uv max (95% C_2H_5OH) 258 mμ (ε 32,700) [lit.[36] 255 mμ (ε 33,000, *n*-hexane)]; ir (CCl_4) 6.08 (C=C), 10.38 (*trans*-CH=CH), and 14.5 μ (sharp, C_6H_5R). For cis,trans: uv max[35] (95% C_2H_5OH) 251 mμ (ε 26,800); ir (CCl_4) 6.05 (very weak, C=C), 10.36 (*trans*-CH=CH), 14.35 (*cis*-CH=CH), and 14.5 μ (C_6H_5R). For cis,cis: uv max (95% C_2H_5OH) 246 mμ (ε 24,900); ir (CCl_4) 6.07 (very weak, C=C) and 14.3 μ (broad, *cis*-CH=CH and unresolved C_6H_5R).

Thermal Rearrangement of *meso*-3,4-Diphenylhexa-1,5-diene. A 1.0-g sample of the *meso*-diene was sealed into an evacuated (~0.1 mm) Pyrex tube and heated at 120° for 93 hr. (In an earlier run, a sample dissolved in carbon tetrachloride was heated at 120° in a sealed nmr tube and the rearrangement was followed by periodically cooling the sample and examining its nmr spectrum. The half-life was calculated to be about 15 hr.) The crude rearrangement product was a colorless semisolid. Ninety-three hours corresponds to about six half-lives; *i.e.*, 1.5% of the diene remained unreacted. Analysis of the crude rearrangement mixture by glpc showed that it consisted of 62.7% *cis,trans*-1,6-diphenylhexa-1,5-diene and 36.9% trans,trans isomer. The remaining 0.4% was accounted for by three minor components, one of which (0.2%) had the same retention time as *trans*-1,4-diphenylhexa-1,5-diene[37] but was not further characterized. The cis,cis isomer was not present in the mixture.

A 390-mg portion of the crude rearrangement product was chromatographed on 250 g of Woelm neutral alumina, Grade 1, using 200 ml of hexane, 2400 ml of 15% (vol) benzene in hexane, and 250 ml of benzene, in that order, for elution. Fractions (20 ml) containing essentially pure cis,trans isomer, which eluted first, were combined and evaporated under vacuum to give 205 mg of oil which was then distilled at 0.2 mm without fractionation (most of the sample distilled with an oil bath temperature of 125–130°) to yield 180 mg of colorless oil which analyzed by glpc as greater than 99.5% of the cis,trans isomer. Its infrared spectrum was virtually identical with that of material obtained by the photosensitized isomerization of the trans,trans isomer.

Fractions from the chromatography on alumina which contained mainly the trans,trans isomer were combined and evaporated under vacuum to give 126 mg of solid, mp 72–75°. It was recrystallized from methanol to yield 60 mg of sample with mp 78.1–78.5°; mmp with authentic (mp 78.5–79.0°) *trans,trans*-diene, 78.5–79.0°. The infrared spectrum of the material obtained from the rearrangement was virtually identical with that of authentic *trans,trans*-diene.

Thermal Rearrangement of *dl*-3,4-Diphenylhexa-1,5-diene. A 106-mg sample of the *dl*-diene (mp 35.1–35.4°) was sealed into an evacuated (~0.1 mm) Pyrex tube and maintained at 80° for 47 hr. (The rearrangement conditions were previously established by nmr spectroscopy, as with the *meso*-diene. The *dl* isomer has a half-life of about 8 hr at 80°.) The crude rearrangement product was a colorless solid with mp 79–80°. Its nmr spectrum in carbon tetrachloride corresponded to that of *trans,trans*-1,6-diphenylhexa-1,5-diene, with no detectable unrearranged *dl*-diene at a sensitivity setting which kept the largest peak in the spectrum (corresponding to phenyl) just on scale. A reaction time of 47 hr corresponds to about six half-lives, which means that 1.5% of the diene remained unreacted. The composition of the crude product, by glpc, was 99.1% *trans,trans*-1,6-diphenylhexa-1,5-diene and 0.9% of a component thought to be an impurity in the starting material (see below). A base-line inflection (less than 0.1% relative area) at a retention time close to that of the cis,trans isomer was the only other peak in the chromatogram. The cis,cis isomer as well as *trans*-1,4-diphenylhexa-1,5-diene could not be detected under conditions where about 0.1% would be observed.

Recrystallization of the crude product from methanol gave material having mp 79.0–79.5° which, on mixing with authentic (mp 79.0–79.5°) *trans,trans*-diene, gave an undepressed melting point, 79.2–79.8°. An infrared spectrum of the recrystallized material was virtually identical with that of authentic *trans,trans*-diene.

The component occurring to the extent of 0.9% in the crude rearrangement product is thought to represent an impurity in the original *dl*-diene for the following reasons. The component is also observed to the extent of 0.9% in the chromatogram of the original *dl*-diene, where the main peak corresponds to the trans, trans isomer because the *dl*-diene rearranges under the analysis conditions. The mother liquor which deposited the *dl*-diene contains the unknown component to the extent of 1.7% of the combined peak areas with the trans,trans peak. If the *dl*-diene used for the reaction is further recrystallized from ethanol, the new material (mp 35.4–35.7°) exhibits the unknown to the extent of 0.8%. Hence the amount of this component appears to be a function of the purity of the *dl*-diene.

Thermal Stability of 1,6-Diphenylhexa-1,5-diene Isomers. About 15 mg of the cis,cis isomer was sealed into an evacuated (~0.1 mm) Pyrex tube and heated at 120° for 48 hr. Simultaneous comparison of the melting points of the heated sample with unheated material gave the following results: unheated material, mp 36.3–36.8°; heated material, mp 36.2–36.8°. The glpc chromatogram of the heated material was unchanged from that of the original material, under conditions where 0.5% conversion to the other isomers would have been detected easily.

A sample of the trans,trans isomer was treated in an identical manner. Unheated sample had mp 78.8–79.2°; heated material had mp 78.7–79.2°. Analysis by glpc showed that heating effected no change in the composition of the sample.

The cis,trans isomer was subjected to the same reaction conditions as the other isomers. Investigation by glpc showed that the original sample, which analyzed as greater than 99.5% cis,trans, suffered no change on heating. The infrared spectra of heated and unheated material were identical.

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[34] Southern New England Ultraviolet Co., Middletown, Conn.

[35] The specific sample used for this determination was the *cis,trans*-diene (~99.5% pure) obtained in the rearrangement of *meso*-3,4-diphenylhexa-1,5-diene.

[36] H. P. Koch, *J. Chem. Soc.* (*London*), 1123 (1948).

[37] One of the products of reductive coupling of *trans*-cinnamyl chloride, ref 20.