

H₆ shifts ((MgClO₄)₂ > NaClO₄ > NaCl > NaOAc, TMAcI, TBACI). Variations in the magnitude of the effects observed for the four nucleoside and nucleotide molecules studied might be accounted for on the basis of minor differences in the local solvent structure about these molecules and/or small differences in the nonbonded interactions opposing the conformational change. The relative effectiveness of the various salts does not appear to correlate with the cation or the anion present in the solution. But, there appears to be a rough correlation with the solvent-structure "breaking" and "making" properties of the salts (Mg(ClO₄)₂ > NaClO₄ > NaOAc > NaCl > TMAcI > TBACI).^{13,14} These considerations suggest the possibility that the salts act indirectly through their effect on the water structure in influencing the rotational conformation of the uracil base about the glycosidic bond.

The results of this work indicate that electrolytes can have important effects on the conformation of nucleosides and nucleotides. The implications of these findings to the conformational properties of dinucleotides,

oligonucleotides, and to polynucleotide structure, however, remain to be ascertained, since the vertical base-stacking interactions presumably also play an important role in stabilizing the base orientations and the conformation of each furanose residue in these molecules. Recently, there has been some controversy over the nature of the intramolecular base-stacking interaction in several pyrimidine-pyrimidine dinucleotides.^{3,4} However, in these works, the molecules were examined under quite different experimental conditions of added electrolytes and ionic strengths. The observed discrepancies are therefore probably real rather than experimental artifacts, and may well reflect the effects of solvent structure on both the vertical stacking interaction and the conformational properties of the individual nucleotide units as demonstrated in this work. The intramolecular stacking interaction is generally considered to be weak in the pyrimidine-pyrimidine dinucleotides; hence subtle differences in the conformational properties of the nucleotide units might be expected to have a more profound influence on the overall conformation of the molecule.

Mechanisms of Photochemical Reactions in Solution.

LX.¹ Photochemical Isomerization of 2,4-Hexadiene *Via* a Quantum-Chain Mechanism

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Abstract: An investigation of the benzophenone-sensitized photoisomerization of 2,4-hexadiene has been carried out in an attempt to infer if the preferred configuration of the lowest lying triplet state of the diene is in the form of a "1,4-biradical," which would permit isomerization about both double bonds, or an "allyl-methylene" system, which would permit isomerization about only one double bond per excitation. During the course of the investigation it was found that a quantum-chain mechanism, heretofore unreported for the type of system, is operative during the early stages of photoisomerization. The chain-carrying species is believed to be an electronically excited state of the diene. Although the chain process appears to occur with isomerization of only one end of the diene, under conditions designed to minimize the chain process, the data are consistent with a "1,4-biradical" or rapidly equilibrating "allyl-methylene" system.

For a fuller knowledge of the photochemistry of unsaturated hydrocarbons, it is necessary to have a better understanding of the properties of their electronically excited states.⁴ Olson made a thorough theoretical study of the electronically excited states of *cis* and *trans* isomers of the substituted ethylenes, which is one of the first reported discussions in the nature of these species.⁵ In 1939, Lewis and Calvin presented the "loose bolt" theory, which discusses the conversion

of electronic oscillation to atomic vibrations and heat.⁶ In another paper, Lewis, Magel, and Lipkin discussed further the conversion of electronic energy into rotational and vibrational energy.⁷ They concluded that if ordinary *cis* and *trans* molecules are given increasing torsional vibration about the ethylenic double bond, the distinction between the two isomers will persist until the torsional energy approaches ΔH^\ddagger for thermal isomerization, above which true rotation will occur, and that it seems certain that *cis* isomers and some *trans* isomers excited to the lowest excited states will, before they decay to the ground state, probably acquire enough torsional energy to lose their identity

(1) Part LIX: G. S. Hammond, S. C. Shim, and S. P. Van, "Molecular Photochemistry," in press.

(2) Abstracted from the Ph.D. Thesis of H. L. Hyndman, California Institute of Technology, 1968.

(3) National Science Foundation Summer Fellow, 1965 and 1966.

(4) P. J. Wagner and G. S. Hammond, "Advances in Photochemistry," Vol. 5, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, New York, N. Y., 1968, p 21.

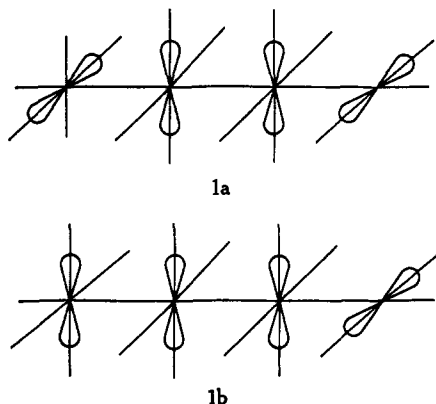
(5) A. R. Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

(6) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

(7) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).

as *cis* or *trans* molecules. In 1947, Mulliken and Roothan calculated by a molecular orbital method that the perpendicular form of the ethylene triplet should be more stable than the planar form by at least 20 kcal/mole.⁸ More recently, studies of the photochemical *cis-trans* isomerization of a variety of olefins have appeared.^{1,9} In general, these studies are compatible with the view that the lowest triplet is a twisted state which can decay to either of the two possible ground states.

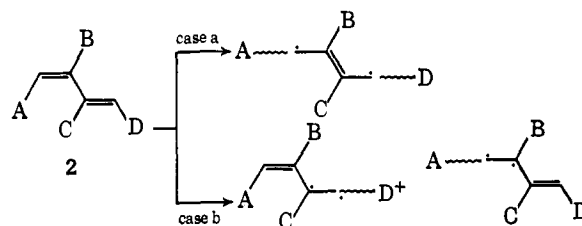
Extension of these ideas to conjugated systems is a nontrivial problem. In planar states produced by Franck-Condon excitation of ground-state molecules, the excitation energy is certainly spread over the entire π -electron system. However, vibrational relaxation of the planar forms is expected to produce nonplanar, excited species having some distortion similar to that of the vibrationally relaxed excited states of ethylene. Two limiting cases can be visualized. In the first, the excitation energy would still be spread symmetrically through the system with nonplanar distortions appearing at both ends as in **1a**, which we will call the "1,4-biradical" form. Alternatively, the distortion might be concentrated in one end as in **1b**, the "allyl-methylene form." These two cases are represented below.



In order to be more explicit, let us consider the generalized diene **2**. In case a, this diene gives a "1,4-biradical" in which the coulombic repulsion between the electrons is minimized by twisting the groups at the ends of the π system out of the planar form with the resulting loss of allyl resonance energy. On the other hand, if the diene forms an allyl-methylene-type triplet, case b, the allyl resonance energy is retained but the electronic repulsion will be greater.

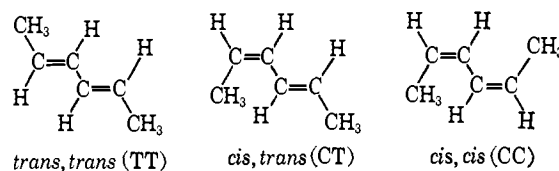
Several important mechanistic implications are now evident. An unsymmetrical diene, such as **2**, has two different triplets in case b (Scheme I). Further, for case a, a single quantum of energy can cause *cis-trans* isomerization at both double bonds whereas, in case b, a single quantum can cause isomerization of only one of the double bonds. This observation, of course, assumes that there is no rapid interconversion of the excited states in the case b triplet, and leads to the conclusion that the sums of the various quantum yields for isomerization in each case will be different. If the diene triplet is of type b, the quantum yields for the photochemical conversion of the *cis,cis*-diene to the

Scheme I. The Possible Excited Geometries for Conjugated Dienes



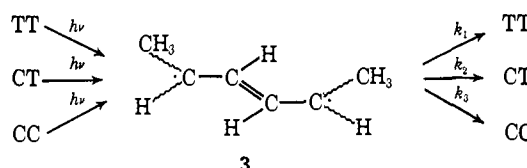
trans,trans and of the *trans,trans* to *cis,cis* must be zero since no direct isomerization can take place.

The chemical system which was selected for this investigation was 2,4-hexadiene. This system has the advantage over other systems which might be chosen of being easily obtainable and relatively easy to analyze using vapor phase chromatography. However, because of the symmetry of the 2,4-hexadiene molecule, it has only three geometrical isomers, instead of the four which would be present if the diene were not symmetrically substituted.¹⁰ The sum of the quantum yields for the case a and case b triplets may be calculated as follows.



In the following derivations for the photosensitized isomerizations, three explicit assumptions are made about the sensitizer: (a) the sensitizer absorbs all the light; (b) the singlet-triplet intersystem crossing quantum yield for the sensitizer is unity; (c) the triplet energy of the sensitizer is high enough so that the rate of energy transfer to the diene substrate is diffusion controlled or nearly so. With 3660-Å irradiation, 0.05 *M* benzophenone sensitizer satisfies all three conditions¹¹ (see Scheme II).

Scheme II. Model System Assuming a Common (Case a) Triplet



In the case of a common triplet (case a) capable of decaying to any of the three possible ground states, there are six possible interconversion and six possible quantum yields. These can be written as follows.

$$\phi_{TT \rightarrow CT} = \frac{k_2}{k_1 + k_2 + k_3} \quad (1)$$

$$\phi_{CT \rightarrow TT} = \frac{k_1}{k_1 + k_2 + k_3} \quad (2)$$

$$\phi_{CT \rightarrow CC} = \frac{k_3}{k_1 + k_2 + k_3} \quad (3)$$

(10) Although the analyses are simplified by the use of 2,4-hexadiene since only three isomers need be separated instead of four, the theoretical calculation for the sum of the quantum yields becomes somewhat more complex. The general case is discussed fully in ref 2.

(11) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(8) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(9) Reference 4, pp 70-75, and references contained therein.

$$\phi_{CC \rightarrow CT} = \frac{k_2}{k_1 + k_2 + k_3} \quad (4)$$

$$\phi_{TT \rightarrow CC} = \frac{k_3}{k_1 + k_2 + k_3} \quad (5)$$

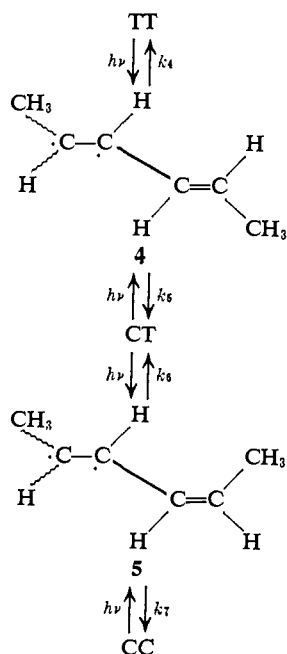
$$\phi_{CC \rightarrow TT} = \frac{k_1}{k_1 + k_2 + k_3} \quad (6)$$

Summing the quantum yield expressions gives

$$\Sigma \phi = \frac{2k_1 + 2k_2 + 2k_3}{k_1 + k_2 + k_3} = 2 \quad (7)$$

Although for case b there are only four possible conversions and four possible quantum yields, the problem is somewhat more difficult since there two different triplets to consider (Scheme III). The

Scheme III. Model System Assuming Two Different (Case b) Triplets



trans,trans- and *cis,cis*-dienes can each give only a singlet triplet because in each case the two double bonds are identical. However, the *cis,trans*-diene can give either triplet depending on to which double bond the energy is transferred. Therefore, the rate of energy transfer to the *cis* double bond (k_{cis}) and the rate of energy transfer to the *trans* double bond (k_{trans}) of the *cis,trans*-diene must be considered. The quantum yields may now be written as follows.

$$\phi_{TT \rightarrow CT} = \frac{k_5}{k_4 + k_5} \quad (8)$$

$$\phi_{CT \rightarrow TT} = \left(\frac{k_{cis}}{k_{cis} + k_{trans}} \right) \left(\frac{k_4}{k_4 + k_5} \right) \quad (9)$$

$$\phi_{CT \rightarrow CC} = \left(\frac{k_{trans}}{k_{cis} + k_{trans}} \right) \left(\frac{k_7}{k_6 + k_7} \right) \quad (10)$$

$$\phi_{CC \rightarrow CT} = \frac{k_6}{k_6 + k_7} \quad (11)$$

When these expressions are added, the following sum is obtained.

$$\Sigma \phi = 1 + \frac{k_{trans}k_5k_6 + k_{trans}k_5k_7 + k_{cis}k_4k_6 + k_{cis}k_5k_6}{(k_{cis} + k_{trans})(k_4 + k_5)(k_6 + k_7)} \quad (12)$$

Unfortunately, the individual rate constants in the second term are not available, nor are they likely to be as can be imagined from the complexity of the proposed mechanism for this case. However, it can be seen upon expansion of the denominator that this term must be less than unity, thus making the sum of the quantum yields less than 2. It was estimated that this sum should be in the range of 1.2–1.5.

From the above discussion three criteria for differentiating between the case a and case b triplet are evident. The isomerization mechanism described in case a requires that the sum of the quantum yields of isomerization be exactly 2, while in that described in case b the sum should be in the range 1.2–1.5. For a case a triplet $\phi_{CC \rightarrow TT}$ and $\phi_{TT \rightarrow CC}$ will have the same values as $\phi_{CT \rightarrow TT}$ and $\phi_{CT \rightarrow CC}$, respectively, but for case b the former two quantum yields will be zero. In case a, $\phi_{TT \rightarrow CT}$ and $\phi_{CC \rightarrow CT}$ must have the same value while in case b they need not be the same.

Experimental Section

Materials. Reagent grade benzene (Baker and Adamson) was stirred over concentrated sulfuric acid for 6 days. The acid was changed every 2 days. Then it was washed three times with dilute sodium bicarbonate, dried over magnesium sulfate, and distilled from phosphorus pentoxide. Reagent grade *n*-hexane was purified by the same method as benzene except that it was heated at reflux over the acid. Spectrograde acetonitrile (Eastman) was distilled three times from phosphorus pentoxide, once from anhydrous sodium carbonate, and once with no drying agent. Reagent grade benzophenone (Matheson Coleman and Bell) was recrystallized twice from ligroin (boiling range 60–70°). Triphenylene was recrystallized twice from ethanol.

The three isomers of 2,4-hexadiene were obtained from either K & K Laboratories or Columbia Organic Chemicals Co. and were used without further purification. Each batch was analyzed by vapor phase chromatography prior to use and was found to have greater than 99.9% chemical purity and greater than 93% isomeric purity except for the *cis,cis* isomer which sometimes has as much as 3% isomeric impurity. The measured quantum yields were corrected for the small amount of other isomers present.

Measurement of Quantum Yields. Hexane solutions of diene and sensitizer were delivered by calibrated syringe into constricted Pyrex test tubes which had been cleaned by soaking overnight in alcoholic potassium hydroxide, rinsed in distilled water, and oven-dried at about 110°. The tubes were kept wrapped during the entire degassing procedure. The samples were degassed by three freeze–pump–thaw cycles on a vacuum line with pumping to less than 5×10^{-4} mm on each cycle and sealed over with the stopcocks open to vacuum. The tubes were frozen in liquid nitrogen during the pumping cycles. All degassed sample tubes were stored in the dark before and after irradiation.

Irradiation of the samples was carried out in a “merry-go-round” which ensured equal amounts of radiation incident on each sample. The lamp used was a 450-W Hanovia medium-pressure mercury arc in a quartz immersion well for cooling. The filter system employed with benzophenone sensitizer consisted of Corning 737 and 052 filter plates. This system admits only a very narrow band of light of wavelengths of 3650 ± 50 Å. For the few samples using triphenylene as a sensitizer the 313-m μ region of the spectrum was isolated by a two-compartment filter consisting of a 1.5-cm path length of an aqueous solution of 26 g of cobaltous sulfate heptahydrate per 100 ml and a 0.6-cm path length of 0.127 g of potassium chromate in 250 ml of 1% aqueous sodium carbonate. For all measurements potassium ferrioxalate actinometry was used to determine the intensity in einsteins per minute of the particular wavelength of light being used.¹²

(12) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956). This procedure was modified slightly by the use of stock solutions of ferrioxalate instead of preparing it by precipitation.

Table I. Quantum Yields as a Function of Diene Concentration

[Diene], <i>M</i>	$\phi_{TT \rightarrow CT}$	$\phi_{CC \rightarrow CT}$	$\phi_{CT \rightarrow TT}$	$\phi_{CC \rightarrow TT}$	$\phi_{CT \rightarrow CC}$	$\phi_{TT \rightarrow CC}$
0.005	0.84 ± 0.02	0.85 ± 0.01	0.69 ± 0.00	0.55 ± 0.12	0.14 ± 0.00	0.28 ± 0.05
0.010	1.04 ± 0.02	1.5 ± 0.1	0.50 ± 0.09	0.30 ± 0.03	0.20 ± 0.00	0.40 ± 0.07
0.050	1.52 ± 0.03	5.2 ± 0.1	2.4 ± 0.1	0.5 ± 0.1	0.52 ± 0.05	0.35 ± 0.15
0.100	2.0 ± 0.2	5.5 ± 0.2	3.2 ± 0.1	0.6 ± 0.1	2.0 ± 0.0	0.42 ± 0.10
0.150	2.1 ± 0.2	8.4 ± 0.2		0.9 ± 0.1		0.40 ± 0.15
0.250	3.7 ± 0.3		12.6 ± 0.8		2.9 ± 0.3	0.46 ± 0.06
0.500	10.6 ± 0.6	31.8 ± 0.6	11.5 ± 0.6	0.3 ± 0.1	3.0 ± 0.3	0.74 ± 0.06
0.750	7.1 ± 0.2	44.5 ± 0.9	10.5 ± 0.5	0.9 ± 0.2	2.3 ± 0.1	0.66 ± 0.19
1.00	5.3 ± 1.1	56.3 ± 4	9.0 ± 1.7	0.6 ± 0.2		0.62 ± 0.12

Analysis of the irradiated samples was carried out by vapor phase chromatography using an Aerograph Model 600 B instrument with a flame ionization detector and an integrating recorder. The column used consisted of (1) 15 ft (0.25 in. o.d.) of 10% triethylene glycol saturated with AgNO₃ on Chromosorb P (60–80, acid-washed) and (2) 10 ft (1/8 in. o.d.) of 25% β,β-oxydipropionitrile on Chromosorb P (80–100). At least three, and sometimes four, aliquots of each sample were analyzed. The quantum yields are given as averages of three determinations plus or minus the standard deviation from that average.

Equimolar solutions of the three isomers of 2,4-hexadiene showed equal response, and the percentage composition of the irradiated sample could be readily calculated by dividing the peak area of the product isomer by the total peak area. In calculation of the quantum yields the per cent conversions were corrected for the small amounts of isomeric impurity present in the starting diene.

Effect of Room Light. A set of sample tubes containing 0.2 *M* *cis,cis*-hexadiene and 0.5 *M* benzophenone in hexane was prepared as above. There were left in the room light for 20 hr, analyzed, and compared with samples that were wrapped in aluminum foil during preparation and wrapped in black cloth and stored in a cupboard until analysis.

Measurement of Photostationary States. In the measurement of the photostationary states, samples were prepared in the same way as for the measurement of quantum yields, except that the tubes were not wrapped in aluminum foil. The irradiation was conducted in a stationary system immersed in a water bath using the same lamp and immersion wells which was used for the quantum yield determinations. The glass filters were replaced by an uranium glass filter sleeve (0.25-mm thickness) which cuts off all light whose wavelength is less than 340 mμ. It was found that under these conditions 36 hr of irradiation was sufficient to achieve a photostationary state although after as much as 1 week of irradiation the samples remained colorless and no solid deposits were formed. The samples were analyzed as described above.

Electron Paramagnetic Resonance. Sample tubes were degassed by three freeze–pump–thaw cycles with a forepump, followed by two such cycles with a diffusion pump with pumping to 3×10^{-6} mm on the final cycle, and sealed off. Irradiation was carried out in the apparatus that has been previously described.¹³ A 0.050 *M* benzophenone solution in hexane exhibited a weak signal for which hyperfine analysis was not possible. A similar solution that was 1.00 *M* in *cis,cis*-hexadiene and 0.05 *M* in benzophenone had no observable signal.

Examination of Surface Effect. This experiment was carried out by using specially constructed Pyrex tubes which could be used more than once. Two of these tubes were prepared as usual and irradiated for 44 hr under conditions described for photostationary-state measurements. The tubes were rotated by hand periodically in an attempt to get equal irradiation on all the glass surfaces. They were then opened, emptied, refilled, degassed, sealed, and then exposed to measured irradiation for quantum yield measurement and quantum yields determined as above.

Results and Discussion

The quantum yields of isomerization for each of three isomers of hexadiene were measured as a function of diene concentration using 0.050 *M* benzophenone in hexane solution. The results are given in Table I. The indicated errors are calculated from the deviation

(13) S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 1659 (1968); S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).

of three or four vpc analyses of the irradiated tubes. It should be noted that, although $\phi_{TT \rightarrow CC}$ and $\phi_{CC \rightarrow TT}$ have been written as one-step processes, they might well be two-step processes which could be more appropriately described as $\phi_{TT \rightarrow CT \rightarrow CC}$ and $\phi_{CC \rightarrow CT \rightarrow TT}$, respectively. In any case, the data in this and subsequent tables actually represent the measured quantum yield of formation of the final product from the starting material.

From the data given in Table I it is readily apparent that $\Sigma\phi$ is much greater than the expected value (*vide supra*). These very large values which increase with increasing diene concentration are suggestive of a chain mechanism of some sort. However, before this conclusion could be reached it was necessary to eliminate other possible sources of high per cent isomerization by appropriate controls. Four sources of high measured conversion are possible: (1) isomerically impure starting materials; (2) stray light, causing actinometrically unmeasured isomerization; (3) thermal catalysts present in the solvent, causing thermal isomerization; (4) loss of starting material *via* dimerization or polymerization.

To check the effect of isomeric (geometrical, not structural) impurities in the starting material, the various samples of "pure" isomer were analyzed before sensitizer was added. Since this factor varied with each batch of purchased material, it is sufficient to note that this variable was checked prior to each quantum yield experiment, and the samples were found to have less than 3% total isomeric impurity. This small amount of impurity, while technically significant, is not sufficient to account for the large effect observed. It was felt that energy transfer to this small amount of impurity was negligible and that the quantum yields could be corrected by simply subtracting the initial percentage from the final percentage of isomer after photolysis to obtain the true per cent conversion. All the values in Table I have been so corrected.

To demonstrate the actual effect of stray light from the room, an experiment was conducted in which samples of *cis,cis*-diene were prepared, left out in the room light for 20 hr, and analyzed. These were compared with samples prepared in an identical manner, except that they were wrapped in aluminum foil during preparation and were wrapped in black cloth and stored in a cupboard until they were analyzed (the results are given in Table II). Thus it can be seen that approximately 1.5% conversion occurred after 20 hr of exposure to room light. However, this small amount of conversion is not nearly enough, in

itself, to account for the observed effect. Furthermore, in the quantum yield experiments the samples were never exposed to room light for more than about 2 or 3 hr and then only during the degassing stage. During this phase, they were wrapped in foil and for the most part in the solid state at 77°K. Since the diene has no significant ($\epsilon > \sim 1$) uv absorption at wavelengths greater than 280 m μ and since benzophenone only transfers triplet energy to its nearest neighbor at liquid nitrogen temperature, it can be assumed that almost no light energy is being put into the diene, either directly or indirectly during this phase. Therefore the possibility of stray room light was discarded as a reasonable explanation of the high quantum yields.

Table II. Effect of Stray Room Light^a

Sample	Exposed to room light	% CT	% TT
1	Yes	4.26 \pm 0.05	0.15 \pm 0.05
2	Yes	4.30 \pm 0.05	0.18 \pm 0.05
3	No	2.82 \pm 0.05	...
4	No	2.87 \pm 0.05	...
Starting diene		2.92 \pm 0.05	...

^a *cis,cis*-Hexadiene initial concentration = 0.20 M; benzophenone sensitizer concentration = 0.050 M.

Since the solvents were purified over sulfuric acid, it was thought that hydrogen ion might be present in the solvent. This could bring about chemical isomerization which was attributed to photoisomerization in the calculation of quantum yields. To test the possibility samples were prepared for photostationary-state measurements, irradiated for 1 week, and left standing for nearly 3 weeks awaiting analysis. It was felt that if any nonphotochemical isomerization were taking place the solutions would come to a thermal rather than a photochemical equilibrium since Döring and Hauthal¹⁴ found that the thermal stationary state of 2,4-hexadiene is reached within a maximum of 30–36 hr using iodine (approximately 10⁻³M) as catalyst in heptane solvent. The photostationary state was measured starting from *trans,trans*- and *cis,trans*-diene as well as from a diene mixture corresponding to the thermal equilibrium. The results are shown in Table III. These data indicate that thermal or hydrogen-catalyzed isomerization is not an important factor and thus is not responsible for the observed high quantum yields.

Table III. Comparison of Thermal and Photostationary States

	% TT	% CT	% CC
Thermal (at 20.2°) ^a	65.5	30.7	3.8
Photo			
From TT	33.2	50.5	16.3
From CT	33.3	50.8	15.9
From thermal mixture	34.0	50.0	16.0
After 3 weeks standing	33.5	50.3	16.2

^a From ref 14.

(14) C.-E. Döring and H. G. Hauthal, *J. Prakt. Chem.*, **24**, 27 (1964).

Probably the most important consideration that must be made in attempting to identify the cause of this unusual effect is that of loss of starting material. Loss of starting material, caused by dimerization or more extensive polymerization, would make the size of the peak of the predominant isomer in the vapor phase chromatogram smaller than expected, thereby making the peak of the product isomer seem relatively larger. Photosensitized dimerization of conjugated dienes has been extensively investigated.¹⁵ Polymerization of dienes such as butadiene is a well-known reaction and could be particularly important in this case if free radicals were present particularly since benzophenone can produce free radicals by hydrogen abstraction.¹⁶

The first obvious observation that was made was that samples of relatively high diene concentration (1.0 M) irradiated for approximately 1 week (to photostationary state) showed no physical evidence of polymerization. The samples remained colorless and no solid deposits were formed. The first way in which this problem was investigated was to analyze solutions for loss of diene monomer. Samples were prepared and the total integrated peak areas from the vpc trace of the diene isomers from irradiated and unirradiated solutions were compared using carefully controlled sample sizes (10- μ l. syringe with a Cheney adapter). The total peak areas were constant to within experimental error (1.15 %).

The second way in which this matter was investigated was by looking specifically for the presence of diene dimers in solution. In this experiment, various solutions of diene were injected onto a 20% Carbowax 20M vpc column used to separate cyclohexadiene dimers.¹⁷ With the injection block at 220°, a 1.0 M solution of diene was analyzed and a new peak appeared. As the temperature of the injection block was lowered to room temperature, this peak decreased and disappeared with the injection block at 30°. In addition, the retention time of this new peak is approximately the same as that observed under the same conditions for the cyclohexadiene dimers.¹⁷ It was concluded that the new peak could be attributed to hexadiene dimers formed thermally on the injection block. A 1.0 M solution of diene which had been irradiated to photostationary state (conditions which would have allowed the most extensive dimerization) was analyzed (with the injection block at 30°). No peak was observed at the retention time attributed above to hexadiene dimers. Further, since Σ_0 is nearly a factor of 10 greater than the expected value, 90% of the starting diene and none of the product dienes would have to be lost to account for the observed effect solely on this basis. Thus, with the data from these two experiments and the original observation, it was concluded that loss of material was unable to account for the high observed quantum yields.

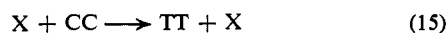
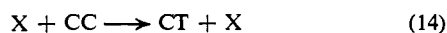
Having eliminated other possible explanations, we conclude that a chain process of some sort is operative in the *cis-trans* isomerization of 2,4-hexadiene. Since

(15) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965), and references contained therein.

(16) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965), and references contained therein.

(17) G. F. Vesley, Ph.D. Thesis, California Institute of Technology, 1968.

some chain initiation and propagation steps of the type



X is the chain-carrying species

must be present in the mechanism, a dependence of the quantum yield of isomerization on diene concentration is implied. As mentioned above, the data given in Table I indicate that there is very pronounced concentration effect on the quantum yield. A chain process of some sort seems confirmed since the previously studied mechanism for *cis-trans* isomerization¹⁸ does not predict a significant dependence of the quantum yield on olefin concentration, nor has it been observed in previously reported cases.

Further support for a chain mechanism was provided by an experiment in which piperylene was added to the reaction mixture as a potential scavenger for X. In this experiment, *trans*-piperylene was present in a 1:10 ratio with *cis,cis*-hexadiene, and the quantum yields for isomerization of the hexadiene were measured. The results are given in Table IV. Based on the relative concentrations of piperylene and hexadiene, one would expect approximately 10% quenching of sensitizer triplets by piperylene, which, in a classical decay mechanism, should result in 10% quenching of the hexadiene isomerization. However, by comparison with the results given in Table I, one can see that this isomerization is about 60–90% quenched by the piperylene. Also azulene in 0.5% concentration relative to that of hexadiene completely quenched the diene isomerization. (In this case, azulene absorbs only about 1.5% of the light directly.) Apparently the chain-carrying species must be destroyed by interaction with piperylene and azulene.

Table IV. Quantum Yields Measured in the Presence of Piperylene

[CC], M	[<i>t</i> -Piperylene], M		$\phi_{CC \rightarrow CT}$	$\phi_{CC \rightarrow TT}$
0.010	0.001		0.51 ± 0.01	0.33 ± 0.06
0.100	0.011		1.7 ± 0.0	0.33 ± 0.01
1.004	0.111		6.7 ± 0.0	0.95 ± 0.03

Several experiments designed to identify the chain-carrying species were carried out. Since no thermal catalysis was observed in control experiments, we concluded that this species must be generated photochemically. The first possibility considered was the photochemical formation of free radicals possibly generated *via* hydrogen abstraction by benzophenone triplet.¹⁶ Although this did not seem to be a likely explanation since any free radicals should initiate formation of other products including low polymers, the examination of various irradiated solutions of sensitizer and diene in hexane by electron paramagnetic resonance was carried out. A 0.05 M benzophenone solution in hexane did, indeed, exhibit a weak epr signal. Although the signal was so weak under these

(18) G. S. Hammond, J. Saltiel, A. A. Lamola, N. S. Turro, H. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

conditions that no hyperfine analysis was possible, it seems safe to conclude that the signal observed was that of the benzophenone ketyl radical, especially as benzopinacol formation was also observed and benzophenone is known to abstract from hydrocarbons.¹⁶ When a similar solution which was also 1.00 M in *cis,cis*-hexadiene was analyzed, no signal whatsoever was observed. Apparently the diene inhibits the formation of benzophenone ketyl radical. This is expected since we expect efficient energy transfer from sensitizer triplets to the dienes.

Additional quantum yield determinations were carried out with triphenylene as sensitizer since its triplet is a $\pi-\pi^*$ triplet and is not expected to abstract hydrogen atoms. Since it was necessary to use benzene rather than hexane for these determinations, the quantum yields were also determined with benzophenone sensitizer in benzene. These results are given in Table V. Although these data vary somewhat from similar data in Table I, it is apparent that both sensitizers initiate chain reactions. Therefore, it was concluded that free radicals are not the chain-carrying species.

Table V. Quantum Yields as a Function of Diene Concentration in Benzene Solution

[CC] ₀ , M	$\phi_{CC \rightarrow CT}$	
	$\phi_{\text{benzophenone}}$	Triphenylene ^a
0.005	1.52 ± 0.10	0.58 ± 0.08
0.010	0.72 ± 0.06	2.38 ± 0.00
0.050	3.86 ± 0.06	7.17 ± 0.06
0.100		9.13 ± 0.03
0.150	9.79 ± 0.13	22.74 ± 0.08
0.200	9.12 ± 0.32	28.81 ± 0.23
0.750	24.04 ± 0.09	77.95 ± 0.78
1.000		93.90 ± 0.93

^a In this case, wavelength of incident light was 3130 Å.

The possibility of an ionic species was also considered although the formation of ions or radical ions would be very difficult to rationalize under the conditions employed in these quantum yield measurements. Nevertheless, if this were the case, the quantum yields should be strongly dependent on solvent polarity. It has already been shown that the change of solvent from hexane to benzene does not greatly affect the quantum yields. Quantum yield determinations were carried out in acetonitrile, a polar solvent. These data are given in Table VI. It is apparent from Table VI that the quantum yields are certainly no larger than in any other solvent.

Table VI. Quantum Yields as a Function of Diene Concentration Using Acetonitrile as Solvent

[CC] ₀ , M	$\phi_{CC \rightarrow CT}$
0.005	0.49 ± 0.05
0.050	1.79 ± 0.02
0.500	3.10 ± 0.03

Thus far, it has been assumed that all reactions occur homogeneously, despite the fact that the glass-liquid interface is a possible site for occurrence of surface catalytic effects. It was felt that if catalytic sites were formed photochemically on the surface of the glass by

one means or another, they might be formed by prior irradiation and used to increase the quantum yield in a subsequent measured irradiation. Irradiations were carried out in tubes used in previous experiments, and the measured quantum yields were compared with those measured from irradiations carried out in a parallel set of new tubes. These results are given in Table VII. Since these results are nearly identical, it was concluded that catalytic sites on the surface of the Pyrex tube do not play any part in causing the high quantum yields.

Table VII. Effect of Preirradiated Tubes on the Quantum Yields^a

Preirradiated tubes	$\phi_{CC \rightarrow CT}$	Average
Yes	30.78	30.56
No	32.22	
No	28.45	30.33

^a $[CC]_0 = 1.80 M$, $[\phi_2CO] = 0.050 M$ in hexane.

From these experiments, it was concluded that the only species which was generated photochemically and had a sufficient lifetime to have multiple interactions with ground-state diene was the diene triplet. Although such a quantum-chain process in which a triplet state is the chain-carrying species has never been observed before, it is not unreasonable since the transfer of triplet energy from a molecule in its triplet state to a diene to produce the ground state of the first molecule and the diene triplet is a well-known energy-transfer process.^{14,15,18} In this case the diene acts as both sensitizer and quencher so that the energy is passed from one molecule to another. Such a process, occurring intramolecularly, was considered by Crandall and Mayer for the isomerization of 1,5,9-cyclododecatriene, a cyclic and nonconjugated olefin, and discarded on the basis of unfavorable energetics.¹⁹

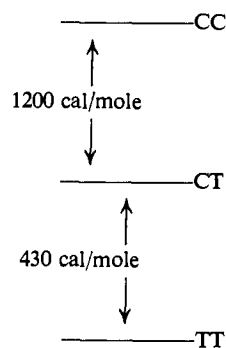
Since the triplet energies of both "sensitizer" and "quencher" in this chain process are the same, the energy transfer will be nearly isoenergetic and may possibly be of the nonvertical type. Thus it may well be that a "relaxed" or "phantom triplet" rather than the spectroscopic one that is the chain-carrying species.¹⁸ Any conclusions about the nature of the diene triplet drawn from the kinetics of the chain mechanism are subject to this limitation.

Examination of the thermodynamics of the 2,4-hexadiene system shows that this type of interaction is, indeed, capable of producing a chain process. Döring and Hauthal¹⁴ report the following relative free-energy relationships for the ground states of the three 2,4-hexadiene isomers (Scheme IV).

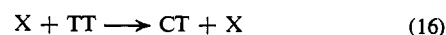
If X, the chain-carrying intermediate, is a triplet, decay of X to the *cis,trans* isomer releases 1200 cal/mole of energy in excess of that needed to produce X from the *cis,cis* isomer. If decay produced the *trans,trans* isomer, the energy excess would be 1630 cal/mole. Similarly the conversion of CT to TT produces 430 cal/mole. The data in Table I show that the largest

(19) J. K. Crandall and C. F. Mayer, *J. Am. Chem. Soc.*, **89**, 4374 (1967).

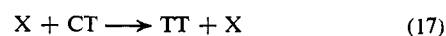
Scheme IV. Free-Energy Relationships for the Ground States of the Three 2,4-Hexadiene Isomers



quantum yield in experiments at high concentration is associated with the $CC \rightarrow CT$ process. The chain process also makes a considerable contribution to the $CT \rightarrow TT$ process. However, $\phi_{CC \rightarrow TT}$ increases very little with increasing concentration indicating that reaction 14 must be far more efficient than reaction 15 if the above mechanism is correct. Furthermore, considerable chain character is developed by the slightly endothermic $TT \rightarrow CT$ reaction. The latter observation is not really disturbing since the endothermicity in reaction 16 would be only 430 cal. Since



the value of RT at 30° , the temperature of the experiments, is approximately 600 cal/mole, reaction 16 might have a very rapid rate so that reactions 16 and 17 would behave as a partially reversible pair.



This simply points up the fact that any chain mechanism can only drive the system in the direction of thermodynamic equilibrium. If we assume that there is a chain reaction for conversion of CT to TT, the reverse connection must also exist, and in an experiment starting with pure CT, the chain reaction *must* give net conversion to TT until thermodynamic equilibrium is established.

The low values of $\phi_{CC \rightarrow TT}$ in comparison with $\phi_{CC \rightarrow CT}$ must be accounted for on other grounds. The specific rate of reaction 14 must be greater than that of (15) for some reason not directly related to energetics, since the more exothermic of the reactions must be assigned the lower rate as will be noted later.

One problem which was very bothersome for a time was that of the photostationary states. Since a chain mechanism can only drive the system to thermodynamic equilibrium, the photostationary state should represent the same equilibrium mixture as in the thermal stationary state. However, this problem was fairly easily solved when the quantum yields in Table VIII were available, since they show that the chain process, in essence, disappears as the products of the isomerization appear. This indicates that, long before the solutions have reached a photostationary state, the chain process has disappeared and the quantum yields have become conventional ones (that is to say, less than unity). This sort of behavior accounts for the relatively poor reproducibility of the quantum yields since no special effort was made to carry every reaction to the same conversion.

Table VIII. Quantum Yield as a Function of Time^a

Irradiation time, min	$\phi_{CC \rightarrow CT}^b$
15	164.31 \pm 0.0
30	61.78 \pm 0.70
45	53.34 \pm 2.34
60	21.65 \pm 0.47
90	8.16 \pm 0.71
120	7.17 \pm 0.54
240	5.60 \pm 0.00
480	3.84 \pm 0.00
720	0.93 \pm 0.00
1440	0.62 \pm 0.00

^a $[CC]_0 = 1.00 M$. ^b Maximum per cent conversion was 5.8%.

In principle it should be possible to extrapolate the data in Table I to infinite dilution to obtain the quantum yields in the absence of the chain process, but this cannot be done with confidence owing to the irreproducibility of the values noted above. However, examination of the data suggests important conclusions. First, there is no indication that $\phi_{CC \rightarrow TT}$ approaches zero. This seems especially important because the $CC \rightarrow TT$ reaction shows at most a small contribution from the chain process in even the most concentrated solutions. We also note that values of $\phi_{CC \rightarrow CT}$ and $\phi_{TT \rightarrow CT}$ may well be approaching a common limiting value and that the same could conceivably be true of $\phi_{CT \rightarrow CC}$ and $\phi_{TT \rightarrow CC}$. In short, the data are semi-quantitatively in agreement with case a.

This conclusion appears to be at variance with indications read from the characteristics of the chain reaction if we adopt the view that X, the chain-carrying intermediate, is a diene triplet or family of triplets. The strong tendency of the chain process to show preference for selective production of CT is most easily rationalized if the triplet undergoing deactivation has an unsymmetrical structure. We can see at least three ways to extricate ourselves from this dilemma.

1. Selection rules may control the deactivation of a symmetrical triplet so that unimolecular decay and decay by energy transfer show different symmetry preferences.

2. Unsymmetrical triplets may be rather rapidly interconverted so that in dilute solutions, where lifetimes are longest, a group of isomeric triplets behave as though they were a single species.

3. Isomerization may involve some entirely different mechanism, such as a Schenck mechanism.^{20, 21}

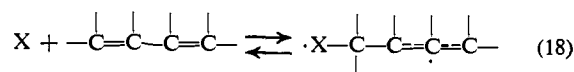
Extensive discussion of the possibilities is inappropriate without more discriminating experimental information. The first alternative simply recognizes the fact that the conservation of orbital symmetry²²

(20) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chem. Belges*, **71**, 781 (1962).

(21) N. C. Yang, J. I. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3265 (1968).

(22) R. Hoffman and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

may apply to nonradiative decay of excited states. Since we are very uncertain as to the symmetry of the excited states involved in the present case, better systems must be found to allow study of special symmetry requirements. The substance of the second alternative is self-evident. Furthermore, we can readily conceive of facile interconversion of stereoisomeric radicals of the b class by transfer of the nonplanar distortion from one end of the molecule to the other.²³ Interconversion of isomeric triplets could provide part of the explanation of the difference between the decay ratios observed in the chain reaction and at low concentration when the chain reaction has largely, or completely, disappeared. As concentrations are increased, the chain-carrying reactions, (14) and so on, would become more rapid, decreasing the lifetime of triplets. Under these circumstances, isomeric triplets might not be equilibrated during their lifetimes. The third possibility is somewhat attractive because it automatically introduces a possible bias in the direction observed. The mechanism could be written as



Reversible addition would supply a mechanism for isomerization of only one of the centers of isomerism in the substrate molecule. As written eq 18 is somewhat unrealistic because we would expect that the biradical should also dissociate to form ground-state molecules from X triplets from the other portion. This would simply be one of the possible detailed mechanisms for energy transfer. Inclusion of the step would still require partial preservation of the original stereochemistry in the allylic portion of the newly formed triplet during its lifetime.

Conclusions

A chain process believed to involve electronically excited states of the diene as chain-carrying species has been discovered for the photochemical isomerization of 2,4-hexadiene. Although the chain process appears to occur with isomerization of only one end of the molecule (case b), under conditions designed to minimize the chain process the data are consistent with the view that the diene triplets have configuration **1a** or the different forms of **1b** rapidly interconvert.

Acknowledgments. This study was supported by the National Science Foundation and the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Contract No. AF 49(638)-1479. We wish to thank Dr. S. A. Weiner for determination of the esr spectra.

(23) The process should be more facile than stereoisomerization of allylic radicals, since loss in resonance energy by turning the terminal carbon atom of the allylic system out of plane would be partially compensated by the synchronous twisting of the methylene unit at the other end of the molecule into the plane of the two central carbon atoms of the diene.