Photoisomerization and Related Processes in 1,2-Diphenylcyclopropane[1]

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The kinetics of the photoisomerization of 1,2-diphenylcyclopropane (I) have been studied in cyclohexane at 25 and 65°. Geometrical isomerization predominates over branching into side products by a ratio of 4:1. Product analysis has revealed that *cis*- and *trans*-1,3-diphenylpropene (II), 1-phenylindan, and a polymer are side products produced by direct photolysis at 2537 Å. Other possible side products such as 1-phenylindene, 1,3-diphenylpropane, 1,2-diphenylpropene, and 1,2-diphenylpropane have not been observed. With *cis*-I at 1.56×10^{-3} *M* initial concentration, the steady-state *cis–trans*-I mole ratio approaches 5.0:1, and, with *trans*-I at 1.74×10^{-3} *M* initial concentration, the steady-state *cis–trans*-I mole ratio approaches 0.90:1. The steady-state mole ratio of geometrical isomers was found to be independent of incident light intensity. No true photostationary state is attained even with variation in initial concentration by a factor of three. Attainment of a true photostationary state for I is prevented by the branching into side products. The rate of production of 1-phenylindan from *cis*-I is greater than that from *trans*-I. The independence of *cis–trans*-II mole ratio on I isomer indicates a common intermediate for these structural isomers. Postulation of a trimethylene diradical accounts for the geometrical and structural isomerization of I. The primary process was found to be independent of temperature over the range of temperature studied. The primary quantum yields for all processes except polymer formation have been measured.

The 1,2-diphenylcyclopropane molecule behaves in some respects like an olefin and undergoes cis–trans isomerization. The Raman spectra[3] of the stereoisomers of this compound have indicated considerable conjugation between the three-membered cyclopropyl ring and the phenyl rings. The effect is much weaker for the cis isomer, owing to steric hindrance.[4,5] Upon irradiation of the molecule, absorption of energy most probably occurs by a π–π^* transition.[6] Geometrical and structural isomerization has been induced in the molecule by a variety of methods: (1) thermal;[7-9] (2) photosensitization;[10-13] (3) direct photolysis;[14-16] and (4) radiolysis.[17]

Because of the current interest in cis–trans isomerization, this study was undertaken with the objective of determining kinetic and quantum yield information for the reaction processes resulting from the direct photolysis of *cis*- and *trans*-1,2-diphenylcyclopropane in solution and the formulation of a reasonable mechanism to account for the observed transformations.

Experimental Section

Materials.—The method of Beech, Turnbull, and Wilson,[18] employing the decomposition of 3,5-diphenyl-1-pyrazoline, was used to produce both *cis*- and *trans*-1,2-diphenylcyclopropane although other methods are known.[19-21] The cis-isomer fraction, bp 132–135° (4.5 mm) [lit.[22] bp 126.5–129° (3.8 mm)], and trans-isomer fraction, bp 150–152° (4.8 mm) [lit.[22] bp 144–145.3° (3.8 mm)], were retained. The samples were further purified by gas chromatography, using a $^3/_8$ in. o.d. × 10 ft 15% SE-30 column, operating at 170°. An F & M Model 5750 gas chromatograph equipped with flame ionization and thermoconductivity detectors was used in our work. The structures of the geometrical isomers were verified by their infrared spectra.[22-24]

The procedure described by Parham and Wright[25] was used to synthesize 1-phenylindene. The crude 1-phenylindene was transferred to a spining-band distillation column, and the middle fraction, bp 106–108° (0.38 mm) [lit.[25,26] bp 113–116° (0.40 mm)], was retained. The 1-phenylindene was further purified by gas chromatography. The collected fraction was a colorless oil which solidified to a white solid when stored at 0°.

A 1-phenylindan sample was prepared by the catalyzed hydrogen reduction of 1-phenylindene at room temperature, using 10% palladium–carbon catalyst. After reduction, the catalyst and cyclohexane solvent were easily removed, and the fraction, bp 99–100° (0.57 mm) [lit.[27] bp 103° (3 mm)], was collected. The sample, purified by gas chromatography, was 99.0% 1-phenylidan.[28]

The procedure incorporating a base-catalyzed condensation as described by Stoermer, Thier, and Laage[29] was employed for the synthesis of *trans*-1,3-diphenylpropene. The crude *trans*-1,3-diphenylpropene was purified by first chromatographing on an alumina column with *n*-hexane eluent followed by recrystallizing five times from *n*-hexane. The solvent was removed, and the *trans*-1,3-diphenylpropene was further purified by gas chromatography. The trans geometry was verified by the presence of the infrared absorption at 966 cm^{-1}.[30-32]

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A photochemical pocedure similar to that described by Raunio and Bonner[33] was found to be the most convenient route for preparing adequate quantities of *cis*-1,3-diphenylpropene. Purified *trans*-1,3-diphenylpropene in cyclohexane was photolyzed at 2537 Å in a degassed quartz tube. After photolysis, the solvent was removed, and the *cis*-1,3-diphenylpropene was then separated from the reaction mixture by preparatory gas chromatography.

Although other synthetic routes to 1,3-diphenylpropane are known[34-37] the catalyzed hydrogen reduction of 1,2-diphenylcyclopropane[38,39] was a convenient route for our purposes. Following reduction at room temperature, the 10% palladium-carbon catalyst and cyclohexane solvent were removed. The 1,3-diphenylpropane was separated from the residual *cis*-1,2-diphenylcyclopropane by preparatory gas chromatography.

The 1,2-diphenylpropene was purchased from K & K Laboratories, under the name α-methylstilbene. This compound was stored in the dark in the solid form and was used without further purification.

The sample of several grams of bibenzyl was kindly furnished to us by Professor J. V. Swisher of our chemistry department. This bibenzyl sample was purified by recrystallizing three times from ethanol. The purified bibenzyl was stored in the solid form in the dark and was used as the internal standard for gas chromatographic analyses.

The cyclohexane used as the solvent in all photolyses was James Hinton spectrophotometric grade and was transparent to 2537 Å radiation. The cyclohexane was used as received without further purification.

Iodine was purified by sublimation before use in the radical scavenging experiments and was stored in a desiccator.

Two columns were used for analytical gas chromatography. The column used most was 0.25 in. o.d. × 10 ft 15% SE-30 on 60–80 mesh NAW Chromosorb P, and the more polar column was a 0.25 in. o.d. × 10 ft 20% Carbowax 20M on 60–80 mesh NAW Chromosorb P.

Optical Bench.—A standard single-rod optical bench was assembled in order to carry out our photolytic reactions in a carefully controlled manner. Aligned on the single-rod optical bench from left to right were the radiation source, a 2.75 in. diameter quartz lens, transmission filters, a thermostat, a 2 in. diameter focusing quatz lens at the exit collimator of the thermostat, and a detector. The temperature of the cell was controlled during photolysis to within 0.10° by circulating distilled water to the optical bench thermostat from a reservoir thermostat below the bench.

Light Source.—The light source for the photolytic reactions was a Hanovia spiral-quartz low-pressure mercury resonance lamp. The lamp was operated at 120 mA ac from a 5000-V transformer. The principle line emitted by this lamp was 2537 Å.

Transmission Filters.—Isolation of the 2537 Å line required a combination of transmission filters. The filtering system incorporated in series (a) a 10 cm path length × 5 cm o.d. quartz cell containing Cl_2 gas at 1 atm pressure, (b) a 10 cm path length × 5 cm o.d. quartz-window cell containing a solution of $NiSO_4$–$CoSO_4$,[40] and (c) a Corning CS 7-54 glass filter. The band width of the composite system was approximately 50 Å. Fresh $NiSO_4$–$CoSO_4$ filtering solution was added to the 10 cm path length cell for each 100 hr or less of exposure to the radiation source, depending on the sequence of experiments.

Radiation Detector and Recorder.—The detector used was an RCA 935 phototube. The dc signal from the phototube was fed through a Sencore R-C substitution unit into a Honeywell Electronik 17 strip chart recorder operated at 50 mV full-scale deflection. The recorder response to transmitted radiation at 2537 Å was calibrated by means of chemical actinometry.

Chemical Actinometry.—The potassium ferrioxalate system developed by Hatchard and Parker[41] was used for chemical actinometry in calibrating the recorder. Table I gives a summary of results for the calibration of the recorder response to 2537 Å radiation. These results are for 0.006 *M* $K_3Fe(C_2O_4)_3$ solution concentrations. The area of the cell windows exposed to the beam was 2.40 cm², and the recorder amplitude values in millivolts have been corrected for the cell absorptions.

TABLE I

SUMMARY OF CHEMICAL ACTINOMETRY CALIBRATION RESULTS

Time, min	Cell path length, mm	I_0^i, quanta, min^{-1}	Recorder amplitude, mV	I_0^i, quanta, mV^{-1} min^{-1}
90	1	5.456×10^{15}	20.60	2.649×10^{14}
40	2	5.087×10^{15}	18.80	2.706×10^{14}
45	2	4.429×10^{15}	16.70	2.652×10^{14}
70	2	5.742×10^{15}	22.00	2.610×10^{14}
			Av value =	2.654×10^{14}

Gas Chromatograph Calibration.—Bibenzyl, $PhCH_2CH_2Ph$, was chosen as the internal standard, and a calibration curve was produced by plotting the area ratio of component–bibenzyl *vs.* the mole ratio of component–bibenzyl for each component. The slope of the curve gives the factor for converting from area ratio to mole ratio.

Sample Preparation and Irradiation.—The cylindrical cells used for photolytic reactions were 22 mm o.d. × 1 mm and 2 mm path lengths with windows of "suprasil" quartz. Samples of 98.1% *trans*- and 94.4% *cis*-1,2-diphenylcyclopropane were used to make up starting solutions with cyclohexane solvent. The procedure was to begin with either cis or trans isomer and observe the growth of products with irradiation time. For each run an aliquot of starting solution was transferred to the cell. At the same time an aliquot of starting solution was taken and frozen down for later analysis to determine initial concentrations of solution components. The cell was then attached to a grease-free vacuum line and degassed five times by the freeze–pump–thaw procedure at a pressure of 5×10^{-6} Torr prior to sealing off under vacuum. The solutions were irradiated for varying times at 2537 Å on the optical bench with periodic mixing during photolysis.

Product Analysis.—In some of the early experiments light products were sought by reattaching the cell to the grease-free vacuum line after irradiation. The analysis section of the vacuum line was equipped with a LeRoy still, a McLeod gauge, and a Toeppler pump. After light-product analysis, a measured quantity of bibenzyl solution was added to the irradiated solution, and the heavy product concentrations were determined from the gas chromatograph area ratios, using the calibrated conversion factors. The final component concentrations were corrected for the values determined from the aliquot of initial solution.

Quantum Yield Calculations.—With prolonged irradiation heavy products accumulate in solution which also absorb part of the incident light. The quantity of light absorbed by the starting substrate alone can be calculated by a method described by Ishakawa and Noyes.[42] Corrections were also made for any decrease in incident light intensity during a run. The primary-quantum yields were calculated from the corrected product concentrations and the total quanta absorbed by the substrate for runs with less than 4% conversion of the initial substrate.

Results and Discussion

Photolysis of *cis*-1,2-Diphenylcyclopropane.—Samples of 1.74×10^{-3} *M* *cis*-1,2-diphenylcyclopropane in cyclohexane were photolyzed in a 2 mm path length cell with 2537 Å radiation. The growth of products during irradiation was followed from short exposure times, and the product yields shown at each interval in subsequent figures represent a separate irradiation with a fresh sample. Figure 1 shows the results for the photolytic reaction of *cis*-1,2-diphenylcyclopropane at room temperature. Because the incident light intensity varied significantly over the course of our work as a result of aging of the lamp, the exposure intervals were converted from hours to total quanta absorbed by the

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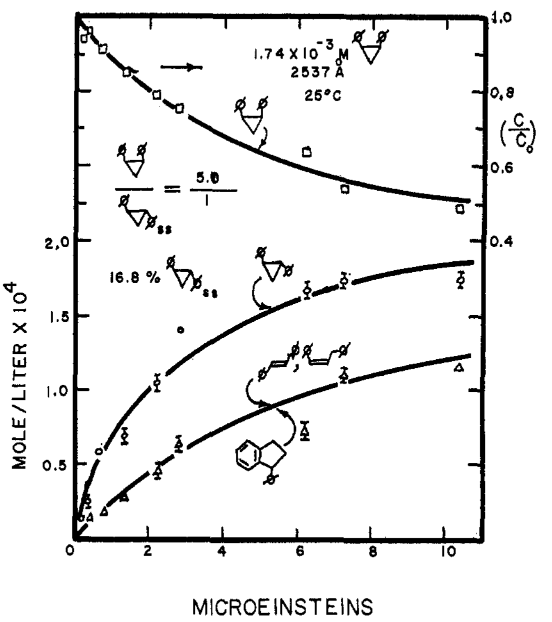


Figure 1.—Photolysis of 1.74 × 10^{-3} *M* *cis*-1,2-diphenylcyclopropane in cyclohexane at 25° with 2537 Å radiation.

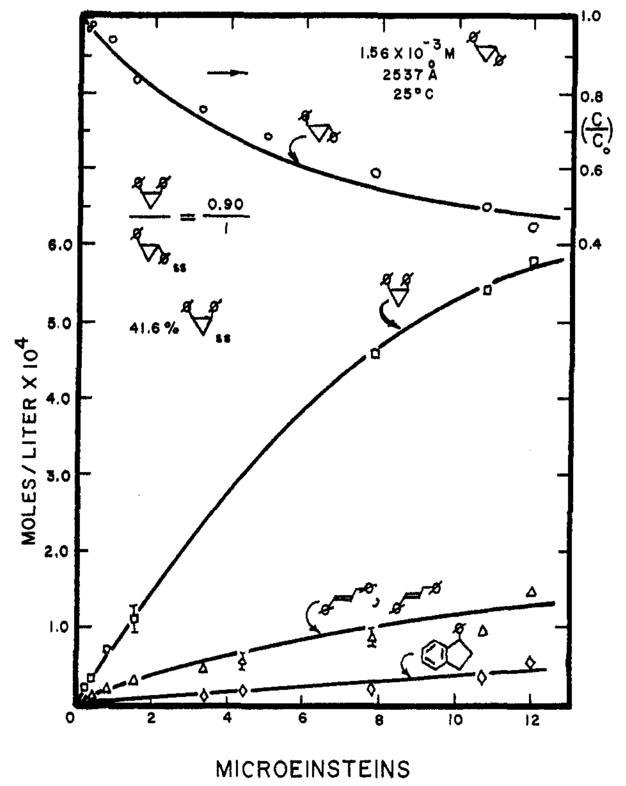


Figure 2.—Photolysis of 1.56 × 10^{-3} *M* *trans*-1,2-diphenylcyclopropane in cyclohexane at 25° with 2537 Å radiation.

photolyzed substrate. This procedure corrected product yields for the variation in incident light intensity.

The disappearance of *cis*-1,2-diphenylcyclopropane is displayed in Figure 1 in terms of the ratio of the concentration at the termination of an exposure interval to the initial concentration (C/C_0). Both *cis*- and *trans*-1,2-diphenylcyclopropane may be observed to asymptotically approach steady-state concentrations with continued irradiation. The steady-state cis–trans mole ratio is 5.0:1 for 1,2-diphenylcyclopropane, and at this level the solution contains 16.8% *trans*-1,2-diphenylcyclopropane (relative to the total soluble products present).

In agreement with Griffin, *et al.*,[14] *cis*- and *trans*-1,3-diphenylpropene and 1-phenylindan were observed as side products resulting from the direct photolysis of *cis*-1,2-diphenylcyclopropane. The yields of 1,3-diphenylpropenes and 1-phenylindan were found to be equal within experimental error. Under the conditions of our experiments, 1-phenylindene was not observed. Other products not observed were *cis*- and *trans*-1,2-diphenylpropene, 1,2-diphenylpropane, and 1,3-diphenylpropane. Griffin and coworkers[14] did not observe these same products when the 1,2-diphenylcyclopropanes were irradiated at 2537 Å in benzene; however, they did observe a trace amount of 1-phenylindene. This product may arise as a unique result of benzene sensitization of the reaction. With the columns and flame ionization detectors used, it was possible to detect components to a lower limit of 1 × 10^{-6} *M* concentration, corresponding to a lower limit of 10^{-4} for the quantum yields of products.

Analyses of solutions photolyzed for several hours were carried out in the grease-free vacuum system. By mass spectrometric analysis no light products such as H_2 or C_1–C_4 hydrocarbons were observed.

Authentic samples were used to identify observed products by retention times and infrared spectra, and a deliberate search was made for the unobserved heavy products. Since the retention time of 1-phenylindan and 1,3-diphenylpropane are the same on SE-30 columns, analyses of some photolyzed solutions were made on a more polar Carbowax 20M column in an effort to resolve the 1-phenylindan elution peak. The 1-phenylindan peak did not resolve on the Carbowax 20M column.

The mass balance deficiency increased with prolonged irradiation. After 65 hr of continuous photolysis, a mass deficiency of 14% was noted. This deficiency is attributed to the formation of a polymer. This polymer was not detected in our analyses since the retention time, if indeed the polymer would elute, would be significantly longer than our analysis times. As it is, the last product to elute from the SE-30 column, *trans*-1,3-diphenylpropene, has a retention time greater than 1 hr at the column temperatures used. Products with significantly longer retention times were searched for but not observed.

Photolysis of *trans*-1,2-Diphenylcyclopropane.—The reverse reaction, that of the photolysis of *trans*-1,2-diphenylcyclopropane, was carried out by the same procedure. Samples of 1.56 × 10^{-3} *M* *trans*-1,2-diphenylcyclopropane in cyclohexane were photolyzed in a 1 mm path length cell. Figure 2 presents the results for the photolytic reaction of *trans*-1,2-diphenylcyclopropane at room temperature. Both the trans substrate and the *cis*-1,2-diphenylcyclopropane again asymptotically approach steady-state levels, but these steady-state concentrations are not the same as those observed in the photolysis of *cis*-1,2-diphenylcyclopropane. At the steady state, the solution contains 41.6% *cis*-1,2-diphenylcyclopropane (of the total soluble products present), and the cis–trans mole ratio is 0.90:1 for the 1,2-diphenylcyclopropane isomers.

The data of Figure 2 indicate that equal yields of the 1,3-diphenylpropene isomers are again observed, but the yield of 1-phenylindan is significantly lower. Comparing Figures 1 and 2, one observes a lower rate of production of 1-phenylindan from *trans*-1,2-diphenylcyclopropane than from the cis isomer. The 1-phenylindan appears to accumulate as irradiation progresses. The 1,2-diphenylpropenes, 1,2-diphenylpropane, 1,3-diphenylpropane, and 1-phenylindene were searched for again as possible products of photolysis but were not observed within the stated limits of detectability.

Increased mass deficiency with prolonged irradiation was again observed. This deficiency is attributed to the production of polymer. Visible quantities of polymer were actually observed when preparatory-scale quantities of substrate were irradiated at room temperature. This polymer was not characterized. Most probably the polymer formation is an irreversible reaction so that once the polymer is produced, it does not photolytically react to any appreciable extent. This continued removal of available substrate from the solution produces an increased mass depletion of soluble components with prolonged irradiation.

When the photoisomerization of 1,2-diphenylcyclopropane was promoted by sensitizers added to the solution, no side products were observed if the absorption was carefully restricted to that by the sensitizer.[12,13] Brown[17] also observed a different product distribution when the photoisomerization of 1,2-diphenylcyclopropane in benzene solutions was promoted by γ radiation. He did find the 1,3-diphenylpropenes as side products but did not detect 1-phenylindan. He also did not find 1,2-diphenylpropene, 1,2-diphenylpropane, or 1,3-diphenylpropane in agreement with our results. The photosensitized reactions and the reactions promoted by γ radiation may proceed by mechanisms different than those operative in direct photolysis.

Optical Density Variation during Photolysis.—Since highly absorbing products such as the 1,3-diphenylpropenes were accumulating in solution during irradiation, the question arose as to whether or not the photoreaction of the 1,2-diphenylcyclopropanes was slowing down or stopping as a result of the incident light being absorbed by the products to the exclusion of the initial substrate. If this were the case, it might account for the fact that the same steady-state levels were not being attained upon prolonged irradiation of the *cis*- and *trans*-1,2-diphenylcyclopropane isomers. A plot of the variation of optical density of solution components *vs.* microeinsteins of light absorbed by the substrate is shown in Figure 3 for the case of *trans*-1,2-diphenylcyclopropane photolysis.

In Figure 3 it may be seen that, although *cis*- and *trans*-1,3-diphenylpropene absorb in the range of 10–15% of the incident light upon prolonged irradiation of *trans*-1,2-diphenylcyclopropane, this quantity of light absorption by the products cannot account for the magnitude of leveling of the substrate concentration observed in Figure 1 and 2. The absorption by 1-phenylindan is insignificant. Figure 3 then is some evidence that the reaction is not stopping because light is prevented from reaching the substrate, so that other parameters were tested to determine what steady state the system tends to approach with continued irradiation of the initial isomer.

Concentration Dependence.—To test the concentration dependence of the 1,2-diphenylcyclopropane cis–trans mole ratio, the initial *trans*-1,2-diphenylcyclopropane concentration was decreased by a factor of three. For the same total exposure of the substrate, the cis–trans mole ratio was 0.19:1 for a 3.9×10^{-4} *M* *trans*-1,2-diphenylcyclopropane solution and 0.18:1 for 1.56×10^{-3} *M* solution. The invariance of the photoisomerization process with concentration change implies that no second-order processes are operative during photolysis.

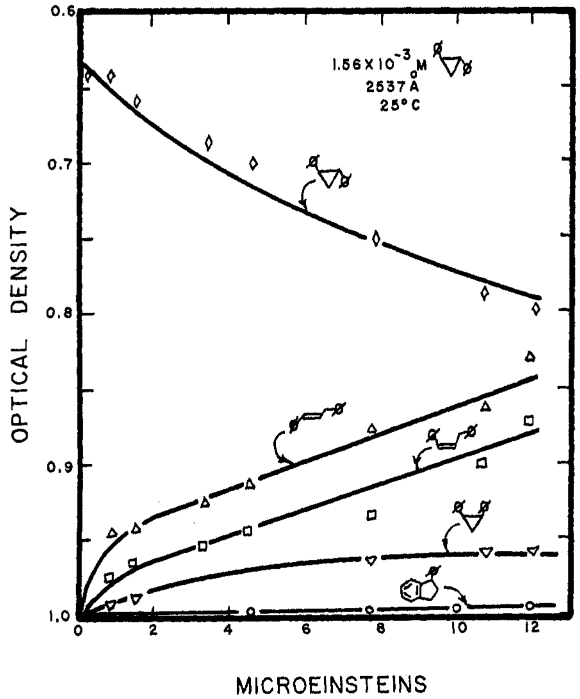


Figure 3.—Variation of the optical density of solution components during photolysis of *trans*-1,2-diphenylcyclopropane.

Light Intensity Dependence.—No specific experiments were run in which the incident intensity was deliberately decreased with a neutral density filter, but over the course of the time during which the photolytic reactions of 1,2-diphenylcyclopropane were studied, the light intensity of the lamp decreased by a factor of three due to aging of the lamp. Over this range of intensity variation, no significant deviation from a smooth curve was observed in plots of the cis–trans mole ratio of 1,2-diphenylcyclopropane *vs.* irradiation time for the series of experiments conducted. No corrections for the variation in incident intensity were made in these plots as was done in Figures 1 and 2 so that from this it may be concluded that the steady-state cis–trans mole ratio for 1,2-diphenylcyclopropane is not light intensity dependent.

Mixtures of Isomers.—Attempts were made to answer two questions: (1) is the photoisomerization of an isomer sensitized by the presence of the other geometrical isomer, and (2) what factors determine the steady-state ratio of isomers?

A solution was made up in cyclohexane with an initial cis–trans mole ratio of 1.08:1. Aliquots of this solution were photolyzed for 3 hr and 57 hr to determine the mole ratios for short and long exposures. At 3 hr the cis–trans mole ratio had increased to 1.16:1 and, after 57 hr this ratio had grown to 1.33:1. The photolysis of mixtures of the 1,2-diphenylcyclopropane isomers did not show noticeably increased rates of photoisomerization compared to photolysis of solutions of initially pure isomers. The conclusion reached was that the photoisomerization of 1,2-diphenylcyclopropane was not self-sensitized.

It is not likely that the side products can sensitize the photoisomerization since spectral studies indicate that λ_{max} (*cis*-1,3-diphenylpropene) equals 2430 Å and λ_{max} (*trans*-1,3-diphenylpropene) equals 2520 Å. These maxima correspond to singlet–singlet transitions for these molecules. They are all lower energy transitions than those of the isomers of 1,2-diphenylcyclopropane which have λ_{max} (*cis*-1,2-diphenylcyclopropane) equals 2260 Å and λ_{max} (*trans*-1,2-diphenylcyclopropane) equals 2300 Å. While the triplet states of the side products may be higher than those of the 1,2-diphenylcyclopropane isomers, no data are available at this time concerning the magnitude of splitting of the various levels, so that it is not possible to state conclusively that no significant triplet energy transfer from the side products to 1,2-diphenylcyclopropane takes place during photolysis. Our kinetic data, however, do not show an apparent rate change for photoisomerization of 1,2-diphenylcyclopropane as the side-product concentrations increase with continued irradiation.

Initially, the ratio of absorbances of cis–trans was $A_C/A_T = 0.0246$. After 3 hr $A_C/A_T = 0.0263$, and, after 57 hr, $A_C/A_T = 0.0299$, a change of over 20% from the initial value. The mole ratio of geometrical isomers for 1,2-diphenylcyclopropane appeared to be determined by the quantity of light absorbed by the isomers.

To test this, a nearly equiabsorbing mixture of 1,2-diphenylcyclopropane was made up in cyclohexane with an initial cis–trans mole ratio of 3.65:1. The ratio of the extinction coefficients for trans–cis is 4.42:1. An aliquot of the solution was photolyzed in a 1-mm path length cell of 144 hr. After this period, the cis–trans mole ratio was 3.37:1. When the limits of error of our method are taken into consideration, the change in the mole ratio can be considered insignificant for 144 hr of continuous irradiation. Griffin and coworkers[14] state that irradiation at 2537 Å of 0.1 *M* *cis*- or *trans*-1,2-diphenylcyclopropane solutions promoted photoisomerization in which the cis isomer was favored. They note that a cis–trans mole ratio of 1.54:1 was approached, and state that this value was determined by irradiating mixtures approaching this composition.[14] However, our results suggest that the quantity of light absorbed by each isomer tends to determine the steady-state ratio approached by the geometrical isomers with prolonged irradiation. Apparently, failure to reach the steady state can be accounted for by the degradative process of branching into side products which depletes the geometrical isomers with prolonged exposure.

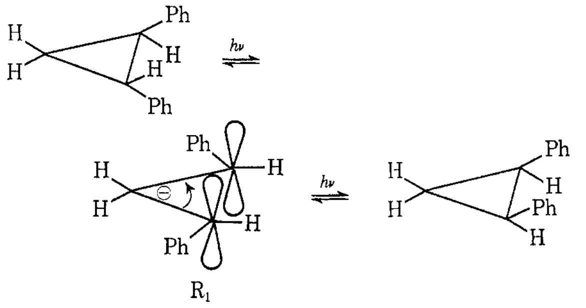
Primary Quantum Yields for 1,2-Diphenylcyclopropane Reactions.—The primary quantum yields for product formation were determined at less than 4% conversion of the initial substrates. Runs for 1 hr or less total irradiation time were used for determining the primary quantum yields by the procedure discussed previously. The results shown in Table II are the average of four runs and reflect the initial slopes of the product yield curves.

TABLE II
PRIMARY QUANTUM YIELDS FOR 1,2-DIPHENYLCYCLOPROPANE REACTIONS

cis-1,2-Diphenylcyclopropane photolysis		*trans*-1,2-Diphenylcyclopropane photolysis	
Product	Φ	Product	Φ
T[a]	0.084 ± 0.004	C[a]	0.089 ± 0.005
c-P[b]	0.022 ± 0.002	c-P[b]	0.023 ± 0.002
t-P[b]	0.022 ± 0.002	t-P[b]	0.023 ± 0.002
I[c]	0.022 ± 0.002	I[c]	3×10^{-3}

[a] C and T are *cis*- and *trans*-1,2-diphenylcyclopropane. [b] c-P and t-P are *cis*- and *trans*-1,3-diphenylpropene. [c] I is 1-phenylindan.

The products observed can be rationalized as arising from the cleavage of the 1,2 C–C bond on the cyclopropane ring of 1,2-diphenylcyclopropane followed by rearrangement. The primary step can be visualized as taking place by the production of a diradical intermediate of the type R_1 shown in reaction 1, but we have no information from our kinetic data which will enable us to deduce with certainty which state is being populated by the intermediate diradical; however, it is probably a triplet state. The primary quantum yields indicate that geometrical isomerization is favored over branching by a ratio of 4:1.



(1)

The data of Table II indicate that the rates of production of either geometrical isomer from the common intermediate R_1 are equal. Since the trans isomer absorbs four times more energy than the cis isomer, and it is known from the quantum yields that the trans isomer is not produced four times faster from the intermediate than the cis isomer, the excess energy may be accounted for by considering the radiative processes operative. The radiative lifetime of an excited state bears an inverse relation to the transition probability of that state. As an approximation, the radiative lifetimes of absorbing compounds are found to be inversely proportional to their extinction coefficients,[43] so that one expects a shorter radiative lifetime for the trans isomer of 1,2-diphenylcyclopropane. Hence, one would expect an emission yield from the trans isomer four times greater than that from the cis isomer. At present no information is available on the radiationless processes operative in this system.

Equal yields of *cis*- and *trans*-1,3-diphenylpropene observed during the photolysis of both geometrical isomers of 1,2-diphenylcyclopropane implies a common intermediate for the 1,3-diphenylpropenes and also implies equal rates of formation of the 1,3-diphenylpropenes from this intermediate. Once this intermediate is formed, it appears to go cis or trans without preference. Although thermodynamically one would expect the trans isomer to dominate, this system is not at thermodynamic equilibrium and this result probably simply demonstrates kinetic control during photolysis.

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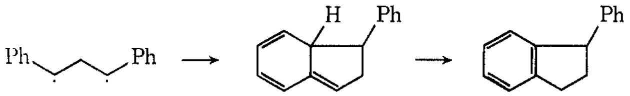
(43) Reference 6, p 174.

From the quantum yield results, it is apparent that the production of observable products by direct photolysis is a highly inefficient process with less than 10% of the absorbed energy being utilized for geometrical isomerization. Hammond and Cole[11] also noted the inefficiency of this process. It is apparent that less than 15% of the absorbed energy is accounted for in terms of products. Of the remainder of the energy of the system, some is probably lost through radiative and radiationless processes. Since the yield of polymer was not determined quantitatively, it is not possible to estimate the quantity of energy consumed in producing polymer.

Cleavage of the 1,3 C–C bond of the cyclopropane ring of 1,2-diphenylcyclopropane would lead to *cis*- or *trans*-1,2-diphenylcyclopropene as products of photolysis. These products were not observed. If they are produced at all under our experimental conditions, their quantum yields are less than 10^{-4}. It may be that an unsymmetrical diradical intermediate produced by 1,3 bond cleavage has so much less resonance stabilization than the symmetric intermediate R_1 produced by 1,2 bond cleavage that its lifetime is considerably shortened and presents a highly unfavorable path for reaction.

The rate differences noted for the production of 1-phenylindan from *cis*- and *trans*-1,2-diphenylcyclopropane are also consistent with a diradical of the type R_1. From molecular models of the geometrical isomers of 1,2-diphenylcyclopropane one observes that, after removal of an H atom from the proper site on the benzene ring, there are four ways to cyclize to 1-phenylindan from *cis*-1,2-diphenylcyclopropane which require minimum rotation compared to only two easy routes from the trans isomer. Griffin[44] suggests that cyclization to 1-phenylindan may proceed as shown in reaction 2.

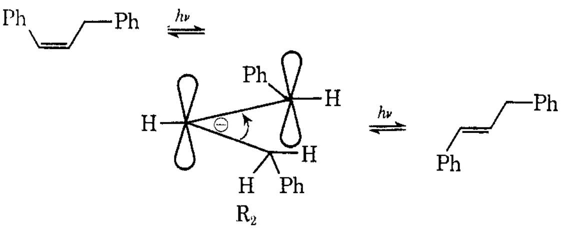


(2)

How much the solvent participates in the rearrangement process is unknown at the present time.

The photolytic reactions of 1.74 × 10^{-3} M *cis*-diphenylcyclopropane were run at 65° for irradiation time intervals up to 10 hr to compare the results with room temperature experiments. The trans isomer yields were 3.89 × 10^{-5} M and 7.06 × 10^{-5} M at 4.8 and 10.0 hr, respectively, and were plotted in the same manner as in Figure 2. Although the absolute yield of trans isomer was somewhat greater, the initial slopes of the curves for 25 and 65° were equal within experimental error. It is concluded that the primary process for geometrical isomerization does not appear to be temperature dependent over the range of temperatures studied. It can also be stated that since the yield of trans isomer was within experimental error of the expected value, the secondary processes appear to exhibit temperature invariance over the temperature range studied.

Photolysis of *cis*- and *trans*-1,3-Diphenylpropene.—We investigated the importance of back reactions from the 1,3-diphenylpropenes to 1,2-diphenylcyclopropane during photolysis. Aliquots of 10^{-4} M solutions of *cis*- and *trans*-1,3-diphenylpropene in cyclohexane were photolyzed under the same conditions as employed in the irradiation of 1,2-diphenylcyclopropane. Direct photolysis at 2537 Å did promote geometrical isomerization. The reaction can be most easily visualized as proceeding through a diradical intermediate R_2 shown in reaction 3.



(3)

Cyclization to 1,2-diphenylcyclopropane was also observed to accompany geometrical isomerization during the irradiation of 1,3-diphenylpropene in agreement with Griffin and coworkers,[14] but the cyclization yields were small under our experimental conditions. Equal yields of *cis*- and *trans*-1,2-diphenylcyclopropane were observed from either initial 1,3-diphenylpropene isomer and were produced with primary quantum yields of 5 × 10^{-3}. The production of 1,2-diphenylcyclopropane probably proceeds through a radical intermediate of type R_1, and the slow step in the formation of R_1 from R_2 may be hydrogen or phenyl migration.[45] The role of solvent participation in the radical rearrangement is at present unknown. No 1-phenylindan, 1-phenylindene, 1,2-diphenylpropenes, 1,2-diphenylpropane, or 1,3-diphenylpropane were observed within the limits of detectability of our method.

The rate of increase of mass deficiency was greater for the photolytic reactions of the 1,3-diphenylpropenes than that observed for the reactions of the 1,2-diphenylcyclopropanes. This increased rate of mass deficiency is attributed to the higher rate of polymer fromation from R_2 than from R_1. The back reaction from polymer is probably insignificant since the mass deficiency becomes quite pronounced with continued irradiation.

Photolysis of 1-Phenylindan.—Aliquots of 1.73 × 10^{-3} M 1-phenylindan in cyclohexane were irradiated at room temperature with 2537 Å radiation to determine the products of photolysis. After 16 hr of continuous irradiation, no detectable products were observed by gas chromatography. It appears that 1-phenylindan is highly unreactive under these conditions. This result is consistent with our observations on the photolytic reactions of 1,2-diphenylcyclopropane that 1-phenylindan accumulates during irradiation and also agrees with Brown's results.[17] From the remarks above it is evident that under the experimental conditions employed in our study the contribution of back reactions from the products to 1,2-diphenylcyclopropane during photolysis is negligible.

Radical Scavenging Attempts.—A solution 1.04 × 10^{-3} M in *cis*-1,2-diphenylcyclopropane plus 1.05 × 10^{-3} M in iodine in cyclohexane was made up for experiments designed to attempt the scavenging of radical intermediates during photolysis. Aliquots of this solution were irradiated in the manner described above for up to 6 hr to determine the effect of I_2 on product yields. Solution analyses by the usual gas chromatographic methods revealed no new peaks re-

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[44] G. W. Griffin, private communication.

[45] G. W. Griffin, A. F. Marcantonio, and H. Kristinsson, *Tetrahedron Lett.*, 2951 (1965).

sulting from radical trapping by I_2. When correction was made for the quantity of light absorbed by the iodine, the product yields were shown to be within the experimental limits of those expected for irradiation of pure solutions of *cis*-1,2-diphenylcyclopropane of the same concentration for the same exposure.

During photolysis, it appears that, when the cyclopropane ring is opened to produce the diradical, the rotation rate of the p orbital about the C–C single bond is sufficiently greater than the rearrangement into side products that geometrical isomerization is favored. The average lifetime of this diradical intermediate must be at least longer than the rotation rate of the p orbitals about the C–C single bond but shorter than the reaction with I_2 since geometrical isomerization takes place but scavenging of the intermediate with I_2 is unsuccessful. Cookson, Nye, and Subrahmanyan[46,47] also attempted to intercept the trimethylene diradical. Griffin, *et al.*,[14] and Hammond and Cole[11] reported no success in trapping intermediates.

Photolyses of 1,2-diphenylcyclopropane samples not degassed prior to irradiation were performed. The scatter in the product yields was such as to render the results inconclusive, presumably since reproducibility of the O_2 content was a problem. The construction of the cells was such as to preclude the application of high pressures of O_2 over the solutions prior to sealoff.

Mechanism.—Our kinetic data indicate that the photoisomerization of 1,2-diphenylcyclopropane is not consistent with a mechanism involving a path through the 1,3-diphenylpropenes, *i.e.*

$$\mathrm{C} \xrightarrow{h\nu} \mathrm{P} \longrightarrow \mathrm{T}$$

A chain reaction mechanism for the photoisomerization is also highly improbable when one considers the low quantum yields of products.

A mechanism is presented below which is consistent with our results. If one considers the arguments presented above and the difference in the rates of polymer formation from the 1,3-diphenylpropenes and the 1,2-diphenylcyclopropanes, the data can be correlated by postulating at least two diradical intermediates of types R_1 and R_2. C and T are *cis*- and *trans*-1,2-diphenylcyclopropane, c-P and t-P are *cis*- and *trans*-1,3-diphenylpropene, and I is 1-phenylindan.

$$\mathrm{C} + h\nu \longrightarrow \mathrm{R_1} \tag{4}$$

$$R_1 \xrightarrow{k_5} \mathrm{T} \tag{5}$$

$$\mathrm{R_1} \xrightarrow{k_6} \mathrm{C} \tag{6}$$

$$\mathrm{T} + h\nu \longrightarrow \mathrm{R_1} \tag{7}$$

$$\mathrm{R_1} \xrightarrow{k_8} \mathrm{I} \tag{8}$$

$$\mathrm{R_1} \xrightarrow{k_9} \mathrm{R_2} \tag{9}$$

$$\mathrm{R_2} \xrightarrow{k_{10}} \mathrm{R_1} \tag{10}$$

$$\mathrm{R_2} \xrightarrow{k_{11}} \text{t-P} \tag{11}$$

$$\mathrm{R_2} \xrightarrow{k_{12}} \text{c-P} \tag{12}$$

$$\text{c-P} + h\nu \longrightarrow \mathrm{R_2} \tag{13}$$

$$\text{t-P} + h\nu \longrightarrow \mathrm{R_2} \tag{14}$$

$$\mathrm{R_2} \xrightarrow{k_{15}} \text{polymer} \tag{15}$$

The equal yields of the isomers of 1,3-diphenylpropene during photolysis of 1,2-diphenylcyclopropane implies that $k_{11} = k_{12}$. Similarly, the equal yields of the 1,2-diphenylcyclopropanes from 1,3-diphenylpropene irradiation suggests that $k_5 = k_6$. If $k_{10} < k_{11}, k_{15}$, this is consistent with the higher yields of geometrical isomerization and polymer formation over cyclization to 1,2-diphenylcyclopropane during 1,3-diphenylpropene photolysis. The slow step in the conversion of R_2 to R_1 may involve phenyl or hydrogen rearrangements. Since $k_8 < k_5$, this is consistent with the fact that no 1-phenylindan is observed as a cyclization product when the 1,3-diphenylpropenes are photolyzed.

Registry No.—*cis*-1,2-Diphenylcyclopropane, 1138-48-3; *trans*-1,2-diphenylcyclopropane, 1138-47-2; *cis*-1,3-diphenylpropene, 1138-83-6; *trans*-1,3-diphenylpropene, 3412-44-0; 1-phenylindan, 26461-03-0.

Acknowledgment.—One of us (E. W. V.) would like to thank the National Science Foundation for financial support under a traineeship held during the period 1966–1969.

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(46) R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc., London*, 144 (1964).

(47) We thank Professor G. W. Griffin for calling our attention to ref 46.