

Figure 1. Plot of  $\log 2k_t$  against molecular weight. Dashed line is gas-phase line from ref 30.

$(4\pi N/1000)(\sigma_A + \sigma_B)(D_A + D_B)$ , where  $D_A$  and  $D_B$  are the diffusion coefficients of the reactants  $A$  and  $B$  in the solvent medium and  $\sigma_A$  and  $\sigma_B$  are the molecular radii defined in terms of the distance across which reaction can take place between  $A$  and  $B$ . In the absence of diffusion coefficient data, it is common to use the Stokes-Einstein equation in the form  $D = kT/6\pi\eta r$  (or  $D = kT/4\pi\eta r$ )<sup>32</sup> and to identify the diffusion radius  $r$  with the radius for reaction in which case  $k_{diff} = 8RT/(3 \times 10^3\eta) M^{-1} \text{ sec}^{-1}$ . This equation implies that the diffusion-controlled rate constant for a

(32) E. McLaughlin, *Trans. Faraday Soc.*, 55, 28 (1959).

bimolecular reaction is independent of the size of the reactants. While this may be true of radicals in which the electron is completely delocalized so that reaction is equally probable at any location (e.g., certain aromatic  $\pi$  radicals) it cannot be true of saturated alkyl radicals and  $\sigma$ -type radicals. For these species the unpaired electron is localized and reaction can, therefore, only occur at a particular site on the radical. That is, as the size of these radicals increases, their diffusion radii continue to grow but their radii for reaction do not change appreciably. In consequence,  $2k_t$  decreases as the molecular weight (or any other measure of the size of the radical<sup>33</sup>) increases.

Only the trichloromethyl radical lies further from the line in Figure 1 than can be accounted for by experimental error or by minor steric effects. The divergence of this radical is surprising since the gas-phase correlation of  $2k_t$  with molecular weight fits alkyl and halogenated alkyl radicals, including  $\cdot\text{CCl}_3$ , equally well. The small value of  $2k_t$  for  $\cdot\text{CCl}_3$  radicals in solution is not due to steric factors since this radical is less hindered than the *tert*-butyl radical. The radical is not resonance stabilized to any great extent and so the low value of  $2k_t$  must be ascribed to polar factors. That is, to form  $\text{C}_2\text{Cl}_6$  requires that the positive ends of two dipoles,  $\text{Cl}_3^{\delta-}\text{C}^{\delta+}$ , be forced together and this must introduce some barrier that hinders the combination. It is not clear why such an effect does not appear to be operative in the gas phase.

(33) The correlation can be improved by plotting  $\log 2k_t$  against  $(\text{molecular weight})^{1/3}$  presumably because this function better represents the change in the size of the radicals.

## Absolute Asymmetric Synthesis. I. On the Mechanism of the Photochemical Synthesis of Nonracemic Helicenes with Circularly Polarized Light. Wavelength Dependence of the Optical Yield of Octahelicene

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**Abstract:** The synthesis of nonracemic yields of hexa-, hepta-, octa-, and nonahelicene with circularly polarized light was observed, and the structural and wavelength dependence of the induced optical yields was examined. The results obtained, together with a detailed consideration of the mechanism of helicene synthesis from the parent diarylolefins, indicate that the induced optical activity is due to selective reaction of enantiomeric conformations of the parent *cis*-diarylolefins by circularly polarized light.

Numerous attempts have been made to induce asymmetric synthesis in photochemical reactions by employing circularly polarized light.<sup>1-3</sup> Until

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recently, however, the rotations found were marginal, and in no case was the source of the rotation positively

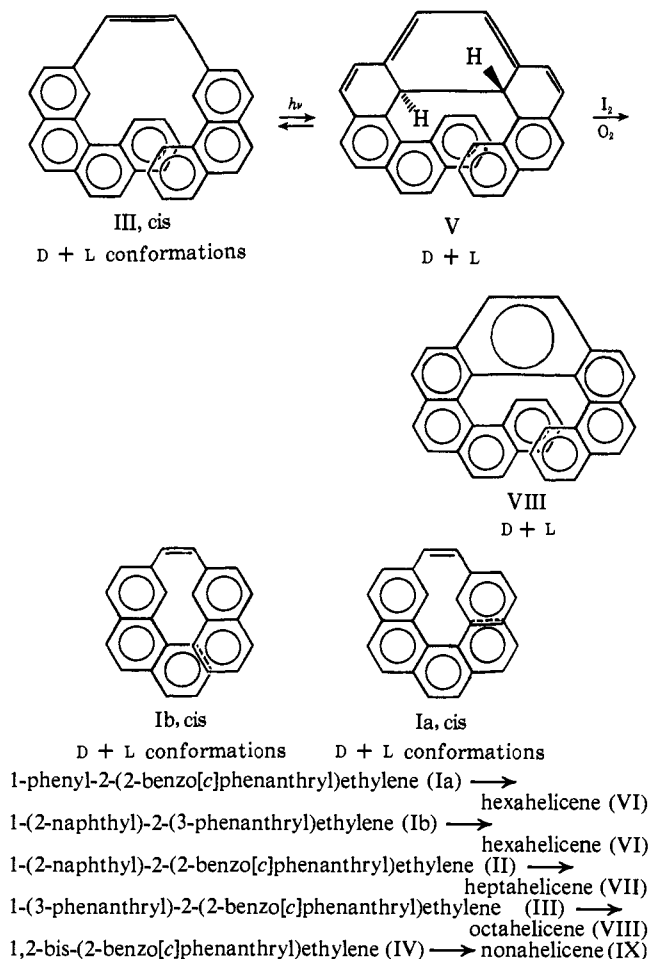
- (1) P. Boldt, W. Thielecke, and H. Lutke, *Chem. Ber.*, 104, 353 (1971).
- (2) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 81ff.
- (3) (a) T. L. V. Ulbricht, *Quart. Rev., Chem. Soc.*, 13, 48 (1969);

identified. Furthermore, in only one experiment<sup>4</sup> were opposing rotations found with right and left circularly polarized light (RCL and LCL), and in this case the optical activity disappeared upon prolonged irradiation. Recent attempts to reproduce many of these results have failed.<sup>1,5</sup>

After the work reported here was completed, Moradpour, *et al.*,<sup>6</sup> reported that irradiation of compounds Ia and Ib leads to nonracemic yields of hexahelicene.

We wish to report irradiations of the 1,2-diarylethylenes (I-IV) in the presence of iodine to the helicenes VI-IX with LCL and RCL.<sup>7-10</sup> All resulted in the formation of an unequal mixture of enantiomers of the respective helicenes (Scheme I).

Scheme I



## Results and Discussion

With each of the substrates I-IV, two samples were irradiated under otherwise identical conditions with RCL and LCL, and except for the marginal optical

(b) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971. References 1-3 all review the earlier literature.

(4) G. Karagunas and C. Drikos, *Z. Phys. Chem. Abt. B*, **26**, 928 (1934).

(5) Professor A. I. Scott, Yale University, personal communication.

(6) A. Moradpour, J. F. Nicould, G. Balavoine, H. Kagan, and G. Tsoucaris, *J. Amer. Chem. Soc.*, **93**, 2353 (1971).

(7) M. Flammang-Barbieux, J. Nasielsky, and R. H. Martin, *Tetrahedron Lett.*, 743 (1967).

(8) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *ibid.*, 3507 (1968).

(9) R. H. Martin, G. Morren, and J. J. Schurter, *ibid.*, 3683 (1969).

(10) VI-IX simply refer to helicenes with the corresponding number of rings, *i.e.*, VII corresponds to heptahelicene.

activity reported for irradiation of Ia, significant optical activity was observed.

Equal and opposite rotations were obtained in the products resulting from irradiation with RCL and LCL, and the compounds responsible for the optical activity were identified by chromatography and by the characteristic shape of the induced ORD and CD curves as the expected helicenes (Table I).

Table I. Irradiation of 1,2-Diarylethylenes with Circularly Polarized Light<sup>a</sup>

Starting material <sup>b</sup>	Max rotation, deg, between $\lambda_1$ and $\lambda_2$ , nm <sup>c</sup>	Time irradiated, min		% completion of photolysis <sup>d,e</sup>	
		$\lambda_1$	$\lambda_2$		
Ia <sup>f</sup>	0.0007 ± 0.0004	500	400	30	50
Ib	0.0086 ± 0.0004	500	370	30	20
II	0.0044 ± 0.0004	520	385	20	30
II	0.0100 ± 0.0004	520	385	45	60
II	0.0132 ± 0.0004	520	385	90	80
III	0.0174 ± 0.0004	500	410	60	30
III <sup>g</sup>	0.0320 ± 0.0004	500	410	120	30
IV	0.0144 ± 0.0004	500	415	120	15

<sup>a</sup> The ORD spectra of VII-IX and the CD spectra of VII and IX were generously donated by Professor R. H. Martin (University of Brussels). A sample of optically pure VI was donated by Dr. Lin Tsai (National Institutes of Health). <sup>b</sup> 1 mg/ml except when otherwise stated. <sup>c</sup> Recorded with the Cary-60 recording spectropolarimeter in the ORD mode. The rotations are expressed as the difference between the two curves equalized at  $\lambda_1$ , from the samples irradiated with LCL and RCL, respectively. *E.g.*, the last entry in the table indicates that the scan for both samples was started at the same ordinate on the chart at 500 nm ( $\lambda_1$ ), and that at 415 nm ( $\lambda_2$ ) the curve of the sample irradiated with LCL was 0.0144° above the one of the sample irradiated with RCL. All rotations were measured in a 2-cm quartz vessel. <sup>d</sup> Per cent completion was estimated with tlc by comparison of the intensity of olefinic and helicenic spots, ±15%. Samples could not be run to completion due to the light and heat sensitivity of the PL-40 polarizing plate. <sup>e</sup> The helicenes were identified by their uv spectra and by comparison of their ORD spectra with those of authentic samples. Also, the CD spectra of hexa-, hepta-, and nonahelicene were compared with those of authentic samples (W. Kuhn, *Trans. Faraday Soc.*, **46**, 293 (1930)). <sup>f</sup> Ia was irradiated in benzene solution, Ib-IV in toluene. <sup>g</sup> 2 mg/ml.

In each case it was found that irradiation with LCL led to a positive rotation, whereas irradiation with RCL led to a negative rotation.

*A priori* three mechanisms could be invoked to explain the observed asymmetric formation of helicenes. (1) Primary formation of racemic helicenes with subsequent light-induced asymmetric destruction. (2) Primary light-induced formation of racemic mixtures of dihydrohelicenes, *e.g.*, compound V, with subsequent light-induced asymmetric ring opening to the starting olefin, *i.e.*, partial photoresolution<sup>11</sup> of the dihydrohelicene, this intermediate being oxidized at a slower rate to give the optically active (nonracemic) helicenes. (3) The diarylolefin precursors, which exist in conformational D and L forms in rapid equilibrium at room temperature, give rise when irradiated with circular light to different amounts of excited D and L forms, which ring close at a faster rate than they racemize in the excited state.

(11) K. L. Stevenson and J. F. Verdick, *Mol. Photochem.*, **2**, 271 (1969).

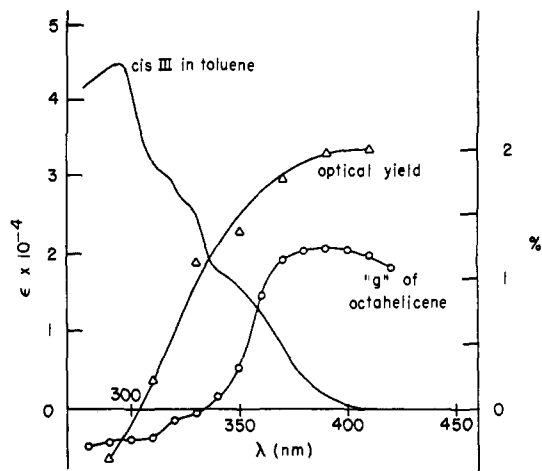


Figure 1.

Had mechanism 1 been operative, long-wavelength irradiation of the olefin with LCL would have resulted in the development of negative long-wavelength optical activity (ORD and CD), while RCL would have resulted in positive optical activity. The opposite is observed.

In order to further examine the applicability of mechanism 1, asymmetric destruction of racemic hepta- and octahelicene was attempted under identical experimental conditions; no rotations were developed. (Indeed, upon prolonged irradiation of hexahelicene with RCL and LCL, Moradpour, *et al.*,<sup>6</sup> found small rotations opposite to those induced by synthesis of hexahelicene with RCL and LCL.)

Mechanism 2 involves the establishment of a  $\text{III} \rightleftharpoons \text{V}$  photostationary state with an unequal distribution of the enantiomers of V resulting from their unequal absorption of circular light. Nonracemic yields of helicenes would reflect this "partial photoresolution" of V. Muszkat and Fischer<sup>12</sup> have shown for a group of substituted stilbene-dihydrophenanthrene systems that the rates of the forward ( $\text{III} \rightarrow \text{V}$ ) and reverse ( $\text{V} \rightarrow \text{III}$ ) photolyses are comparable, and that the dihydrophenanthrenes aromatize quite rapidly at even low concentrations of oxidant ( $\text{V} \rightarrow \text{VIII}$ ). Since many of the photolyses described below required several days, even in the presence of a relatively powerful oxidant (molecular iodine with atmospheric exposure), the rate of the forward reaction to the dihydrohelicene must be slow from the cis compound. (The  $\text{trans} \rightarrow \text{cis}$  conversion is rapid compared to succeeding steps.) Since the reverse reaction is of comparable rate,<sup>12</sup> no dihydrohelicene can accumulate for its photoreversal back to the diarylolefin to occur. Thus, if the results of Muszkat and Fischer may be applied here, it appears that mechanism 2 is highly unlikely.

In order to further clarify the above mechanistic possibilities, compound III (cis + trans) was irradiated at seven different wavelengths. The relative optical yields are plotted on Figure 1. Note that the sign of induced optical activity changes at *ca.* 305 nm. The sample irradiated with LCL at 410 nm was 2.7% resolved with reference to an octahelicene sample partially resolved by crystallization by Professor R. H. Martin.<sup>13</sup> Since the actual purity of the crystallized

(12) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

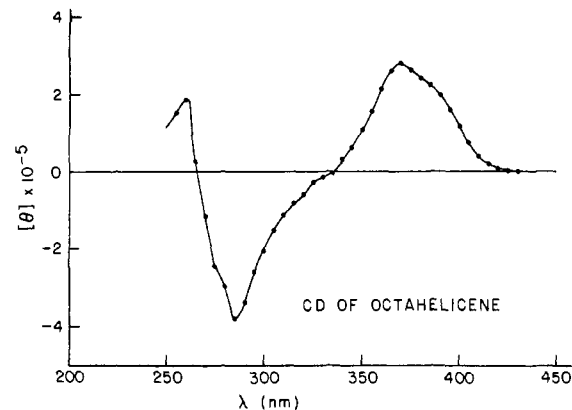


Figure 2.

sample is not known, the true optical yield of the 410-nm sample may be significantly lower than 2.7%. This, taken together with an extrapolation to octahelicene from the CD of hexahelicene, led us to assume an optical yield of 2.0% for the 410-nm sample.

From our optically active octahelicene solutions the CD of octahelicene (based on the assumed 2.0% resolution of VIII in the 410-nm sample) was obtained (Figure 2). Had mechanism 1 been operative, the wavelength dependency of the optical yield of VIII would have followed the anisotropy<sup>14</sup> factor [ $g = (\epsilon_1 - \epsilon_2)/(\epsilon_{\text{total}})$ ] of octahelicene and the induced optical activity would have changed sign at *ca.* 335 nm; it does not (Figure 1).

The wavelength-dependence data are quite consistent with the absorption spectrum of the cis isomer of compound III, isolated by chromatography from the synthesized cis-trans mixture. Compound V, on the other hand, would in all probability have many transitions well out into the visible, if studies of the absorption of 4a,4b-dihydrophenanthrenes<sup>12</sup> are applicable here. Thus, if mechanism 2 were valid, one would expect a change in sign of the induced optical activity, reflecting a change in the sign in the CD of V, well above 305 nm where it actually occurs. A final result which is inconsistent with mechanism 2 is the observation by Moradpour, *et al.*, that irradiation of Ib gives approximately four times the optical yield of hexahelicene as the irradiation of Ia.<sup>6</sup> Our data indicate this difference to be even greater (see Table I). Both Ia and Ib should form similar dihydrohelicene structures, and it is reasonable to expect them to have similar capabilities for asymmetric destruction.

However, mechanism 3 can account for this difference. Hammond has noted<sup>15</sup> that in the lowest excited singlet ( $S_1$ ) state of unsymmetrical stilbenes, from which all stilbene photoclosures presumably take place, the excitation is "localized" in the aryl group with the lower  $S_1$  energy. Thus, in the  $S_1$  state of *cis*-Ib, we would expect rotation up to  $180^\circ$  about the naphthyl-ethylene bond to be nearly free, the excitation being localized on the larger phenanthryl group. Similarly, we would expect rotation about the phenyl-ethylene bond in  $S_1$  *cis*-Ia to be nearly free. Due to the symmetry of the phenyl group, rotation

(13) See Table I, footnote a.

(14) See Table I, footnote e.

(15) G. S. Hammond, S. C. Shim, and S. P. Van, *Mol. Photochem.*, 1, 99 (1969).

Table II

Wavelength irradiated, nm	% circularity of light	Time irradiated, hr	Grating, slit width (mm), dispersion (nm)	$\theta$ , deg at 385 nm	Helicene conc $\times 10^{-4} M$	Rel optical yield, %
410	75	48	Vis, 2, 12.8	+0.0247	2.38	2.00
390	75	36	Vis, 2, 12.6	+0.0236	2.34	1.96
370	75	12	Vis, 2, 12.6	+0.0231	2.53	1.77
350	75	195	Uv, 4, 12.8	+0.0156	2.22	1.37
330	75	94	Uv, 4, 12.8	+0.0138	2.36	1.14
310	75	48	Uv, 4, 12.8	+0.0030	2.48	0.21
290	75	86	Uv, 4, 12.8	-0.0054	2.51	(-) 0.42

about the phenyl-ethylene bond ( $\sim 180^\circ$ ) in *cis*-Ia results in interchange of its enantiomeric conformations, whereas corresponding rotation about the naphthyl-ethylene bond in *cis*-Ib does not, due to the dissymmetry of the 2-naphthyl group.

Thus, if mechanism 3 is operative, it can be seen that although irradiation of *cis*-Ia with circular light excites its enantiomeric conformations unequally, this imbalance of the D and L excited forms is greatly reduced through the above-described bond rotation. Unequally excited *cis*-Ib, on the other hand, cannot similarly racemize in the excited state, and thus produces a more nonracemic yield of dihydrohexahelicene, which forms nonracemic hexahelicene. The same is true for the III-V-VIII system, and all of the other systems here studied.

However, the different optical yields of VI from Ia and Ib may also be due to differences in the CD spectra between *cis*-Ia and *cis*-Ib in the wavelength region employed for irradiation.

Experiments to further clarify the mechanism of nonracemic helicene production with circular light are under way.

## Experimental Section

**Synthesis of I-IV.** 2-Naphthylmethyltriphenylphosphonium bromide (40 g) was dissolved in 120 ml of 1 *N* LiOMe-MeOH, and 10 g of *p*-tolualdehyde was added slowly. The mixture was stirred vigorously for 10 min and filtered. Crystallization from benzene-ethanol gave 8 g (39%) of 1-(2-naphthyl)-2-(*p*-tolyl)-ethylene (X), mp 188-189°. Compound X (2 g) was irradiated for 12 hr in a Rayonet reactor (3500-Å lamps) in 2 l. of cyclohexane with a few crystals of iodine added under exposure to the atmosphere. The volume was reduced to ca. 10 ml, and the mixture was chromatographed (cyclohexane on neutral alumina). The solvent was removed from the first fraction. The residue was crystallized from ethanol-water (by saturation by addition of water at room temperature and slow cooling to  $-40^\circ$ ), yielding 1.0 g (51%) of 2-methylbenzo[*c*]phenanthrene (XI), mp 80-81° (lit.<sup>17</sup> 80-81°). Compound XI (1.0 g) was dissolved in 20 ml of reagent grade CCl<sub>4</sub>. NBS (0.8 g) and a trace of dibenzoyl peroxide were then added, and stirred at a gentle reflux for 3 hr. The succinimide was filtered off, the solvent was removed from the filtrate by rotary evaporation, and the residue of crude 2-bromomethylbenzo[*c*]phenanthrene (XII) was dissolved with 1.2 g of triphenylphosphine in 20 ml of xylene, and stirred vigorously at reflux for 45 min. The nearly colorless, high melting (mp  $>300^\circ$ ) powder, 2-benzo[*c*]phenanthrylmethyltriphenylphosphonium bromide (XIII), was filtered off, and washed with xylene and petroleum ether (yield, 2.32 g, 96%). Addition of compound XIII to equimolar amounts of 1 *N* LiOMe-MeOH and benzaldehyde, 2-naphthaldehyde, 3-phenanthraldehyde, or 2-benzo[*c*]phenanthraldehyde, and work-up and purification as in the preparation of X gave Ia (50%, mp 144-145°, lit.<sup>8</sup> 144-145°), II (60%, mp 200-202°, lit.<sup>8</sup> 200-201°), III (65%, mp 176-178°, lit.<sup>8</sup> 199-200°), and IV (40%, mp 230-232°, lit.<sup>8</sup> 229-230°; the samples obtained by this method were shown by chromatography (benzene on neutral alumina) to consist

of mixtures of *cis* and *trans* olefins. These compounds gave elemental analyses consistent with their expected composition. Degassed solutions of the isolated *cis* and *trans* compounds were shown by tlc to give approximately the same *cis*-*trans* photostationary ratio upon irradiation. In addition, both compounds exhibited uv spectra characteristic of *cis*- and *trans*-stilbenes, respectively.<sup>18</sup> (Nmr spectra proved inconclusive, as the aromatic resonances masked those of the olefinic protons.) Fractional crystallization of the mixture of *cis* and *trans* III from benzene yielded pure *trans* compound, giving a melting point close to that reported by Martin. 2-Benzo[*c*]phenanthraldehyde was prepared by the procedure of Angyal, *et al.*,<sup>18</sup> from crude XII. 3-Phenanthraldehyde was similarly synthesized from 3-bromomethylphenanthrene. Condensation of 3-phenanthraldehyde with 2-naphthylmethyltriphenylphosphonium bromide in 1 *N* LiOMe-MeOH and crystallization from benzene-ethanol gave Ib (mp 213-215°).

**Irradiation Procedure.** The light source used in all work was an SP-200 super high pressure mercury lamp. For all experiments except the wavelength dependence the beam was collimated with a fused silica lens and passed through a chemical filter<sup>18</sup> to give light of wavelengths 340-400 nm. The beam was then passed through an ultraviolet polarizing filter (Polacoat Inc., PL-40) followed by a quarter wave plate centered at 390 nm (Gaertner Inc.), followed by the sample.

For the wavelength-dependence studies the lamp was attached to a monochromator (Bausch & Lomb, 33-86-25) with uv and visible gratings (Bausch & Lomb, 33-86-25-01 and 33-86-25-02, respectively). The beam was collimated with a fused silica lens and passed through a PL-40 plate and fused silica fresnel rhomb (Karl Lambrecht Inc.). The circularity of the light was calculated as the ratio of minimum to maximum intensity of the beam transmitted by a rotating PL-40 plate. Irradiations were performed at 410, 390, 370, 350, 330, 310, and 290 nm. The following data were obtained for irradiation of III with this apparatus (Table II).

In all work except the wavelength studies, the diarylolefins were irradiated at a concentration of 1.0 mg/ml unless otherwise noted, with a trace of iodine and exposure to the atmosphere. The vessel used was a cylindrical quartz cell with a capacity of 6.5 ml and a 2-cm optical path. Unless otherwise noted, toluene was used as a solvent. For the wavelength dependence, irradiations were performed in a similar vessel at a concentration of 0.1 mg/ml in toluene-I<sub>2</sub>.

All samples were chromatographed (benzene on neutral alumina), and the helicene (first) fraction was concentrated for ORD or CD analysis in a 2-cm quartz cell. Since the parent *cis*-olefin cannot be separated from the respective helicene under these conditions, it was difficult to judge the helicene concentration by uv analysis, unless the reaction was carried to completion. (The wavelength studies demanded accurate determination of helicene concentration for the calculation of relative optical yields; thus, these reactions were irradiated to completion.)

Asymmetric destructions of heptahelicene (0.42 mg/ml and 0.12 mg/ml) and of octahelicene (0.57 mg/ml) were attempted by irradiation for 30 and 60 min, respectively, under identical conditions as those employed in the asymmetric syntheses recorded in Table I.

Uv spectra were taken on a Cary-14 spectrophotometer and CD and ORD spectra on a Cary-60 recording spectropolarimeter.

(16) S. J. Angyal, J. R. Tetaz, and J. G. Wilson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 691.

(17) J. Hewett, *J. Chem. Soc.*, 1289 (1938).

(18) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 734, Table 7-7.

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## Duality of Mechanism in Photoracemization of Optically Active Biphenyls. Mechanistic and Exploratory Organic Photochemistry. LXV<sup>1</sup>

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**Abstract:** Optically active 2,2'-dimethyl-6,6'-diethylbiphenyl was synthesized. This molecule was found to be exceptionally stable to thermal racemization with half-lives of 283 and 25 hr at temperatures of 345 and 380°, respectively. The Arrhenius activation energy found was 56 kcal/mol. This biphenyl was found to racemize photochemically with a quantum yield of 0.0015. Accompanying the photoracemization there was observed an isomerization proceeding *via* benzvalene type intermediates. The benzvalene intermediates could be intercepted with methanolic hydrochloric acid but the racemization was inhibited only by one-third. A temperature dependence of the photoracemization was found with photoracemization being enhanced by increased temperature. The evidence points to two mechanisms for photoracemization of biphenyls. One is a direct reaction of the excited state and is not affected by benzvalene interceptors as methanolic HCl while the other involves reversible benzvalene formation with a lowered barrier for enantiomer interconversion due to the decreased size of the benzvalene ring compared to the original aromatic one. The possibility of intervention of a reacting hot ground state is discussed. Interconversion of enantiomers in the excited state is understood on an MO basis as deriving from an enhanced excited state central bond order.

In our earlier publications<sup>2</sup> we noted that in photochemistry molecular reactivity can be understood as excited state molecules tending to deform in such a way that atoms having a positive bond order attempt to bond even more strongly and those with negative bond orders avoid one another. We have applied this concept to a number of photochemical rearrangements. To further delineate the importance of this concept, it appeared of interest to initiate a quantitative study of the photochemical racemization of optically active biphenyls, a system where the central bond order in the excited state should differ from that in the ground state. An early interesting report of photochemical racemization of bridged biphenyls had already appeared in the literature;<sup>3</sup> for our study, 2,2'-dimethyl-6,6'-diethylbiphenyl (**1**) was selected.

**Synthetic Aspects.** A convenient starting material was 3-ethylbenzoic acid<sup>4</sup> (**2**), which was successively nitrated, reduced, diazotized, and coupled to give 6,6'-diethyldiphenic acid (**5**). This compound was re-

solved with quinine, the methyl ester reduced with lithium aluminum hydride, and the resulting diol converted to 2,2'-diethyl-6,6'-bis(bromomethyl)biphenyl (**8**). Dibromide **8** was then reduced to afford the desired 2,2'-dimethyl-6,6'-diethylbiphenyl (**1**). The synthetic route is outlined in Chart I and detailed in the Experimental Section.

### Results

In confirmation of the earlier work<sup>3</sup> involving photolysis of optically active biphenyls a dramatic loss in optical activity was observed in exploratory photolyses. Thus, in a 2-hr photolysis with a 450-W medium-pressure lamp a massive 49% racemization of a 159.8-mg sample was observed. However, it was quickly established that a large fraction of this loss in optical activity derived from a process different than simple enantiomerization. In fact, the primary process occurring was benzvalene formation. The benzvalenes formed afforded at least 20 of the 99 theoretically possible diethyldimethylbiphenyls. The reaction mixture was analyzed by vpc and column chromatography; the products were established as isomers by nmr and mass spectral analysis. Note the Experimental Section. Also, the benzvalenes were found to be sufficiently stable so that in absence of heat or acidic treatment (*vide infra*) the photolysis mixture reacted with air to give ketonic products. Details are given in the Experimental Section. The reaction of benzvalene itself with air is known to give cyclopentadienecarbox-

(1) For paper LXIV of the series note H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3662 (1971).

(2) (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June 1961, Abstracts, p 31; (b) H. E. Zimmerman, *Science*, **153**, 837 (1966); (c) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967); **86**, 1436 (1964); (d) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).

(3) (a) K. Mislow and A. J. Gordon, *ibid.*, **85**, 3521 (1963); (b) note also J. J. Dannenberg and A. L. Blackwood (Abstracts, the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORG-86) for another example where biphenyl photoracemization has been noted.

(4) M. S. Newman and E. K. Easterbrook, *J. Amer. Chem. Soc.*, **77**, 3763 (1955).

(5) L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **93**, 3819, 3821 (1971).