Acknowledgments. This work was supported by the U. S. Atomic Energy Commission and by the Danish NATO Committee for Advanced Studies. The authors are grateful to Mr. K. Philipson, Dr. J. Sutherland, Dr. R. Lawler, Mr. M. Kaplan, Dr. M. G. Ettlinger, and Mr. R. Bogomolni for many helpful discussions.

Duality of Mechanism in Photoracemization of Optically Active Biphenyls. Mechanistic and Exploratory Organic Photochemistry. LXV[1]

Howard E. Zimmerman* and David S. Crumrine

Contribution from the Department of Chemistry, the University of Wisconsin, Madison, Wisconsin 53706. *Received April 15, 1971*

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[2] 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;[3] for our study, 2,2′-dimethyl-6,6′-diethylbiphenyl (**1**) was selected.

Synthetic Aspects. A convenient starting material was 3-ethylbenzoic acid[4] (**2**), which was successively nitrated, reduced, diazotized, and coupled to give 6,6′-diethyldiphenic acid (**5**). This compound was resolved 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[3] 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).

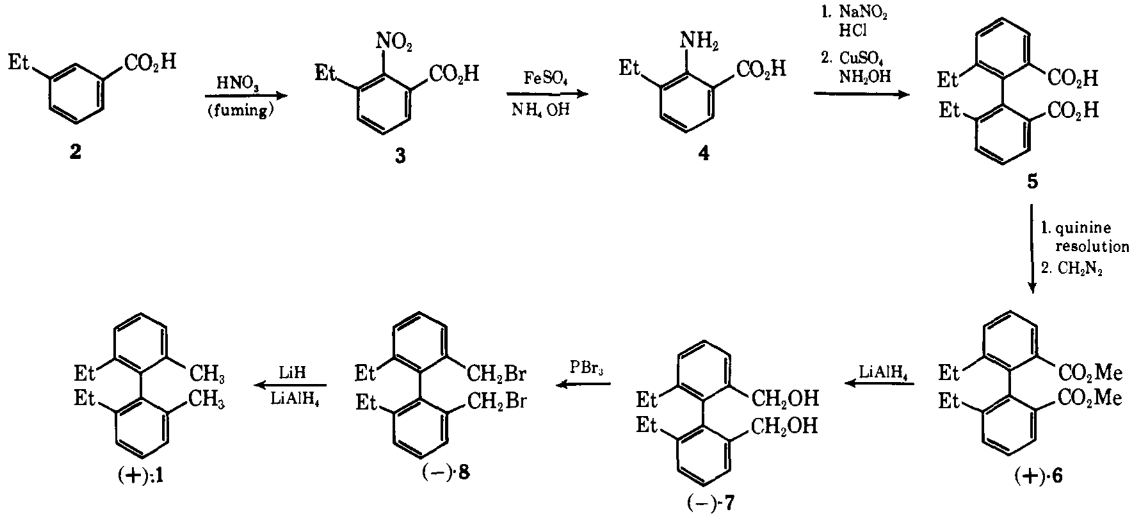
[2] (a) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June 1961, Abstracts, p 31; (b) H. E. Zimmerman, *Science*, **153**, 837 (1966); (c) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967); **86**, 1436 (1964); (d) H. E. Zimmerman, R. W. Binkley, J. J.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

Chart I. Synthesis of 2,2'-Dimethyl-6,6'-diethylbiphenyl (1)



aldehyde.[5] Hence a good part of the apparent photoracemization was due to side reaction.

Nevertheless, a real photochemical racemization did occur. Careful repetitive column chromatography afforded pure 2,2'-dimethyl-6,6'-diethylbiphenyl (1) which proved to be 17% racemized in 2 hr; note Table I.

Table I. Photolysis of Optically Active 2,2'-Dimethyl-6,6'-diethylbiphenyl

			%		
Solvent[a]	Temp, °C	Racemate, mmol	Racemization of 1	Isomers[f]	Oxidation products
Cyclohexane[b]	30	0.047	17.3	3.6	43
Dodecane[c]	30	0.044	16.9	4.1	31
Dodecane[d,e]	200	0.052	29.1	28	6
Dodecane[c]	195	0.075	28.4	38	

[a] All runs were for 2 hr in 500 ml with a Vycor-filtered 450-W Hanovia medium-pressure mercury lamp. [b] Water-cooled apparatus. [c] Vacuum-jacketed water-cooled apparatus (ref 6a). [d] Lamp cooled with nitrogen stream. [e] Part of material lost on distillation. [f] Vpc analysis.

Since a quantitative measure of the photoracemization was desired, quantum yields were measured on our black box apparatus as previously described.[1,6b] These results are included in Table II. A quantum yield of 0.0015 was obtained by extrapolation to 0% conversion. It was clear from the present studies that the extent of racemization could be seriously in error if one did not carefully separate all products before taking rotations; this was caused by the accumulation of inactive products from the parallel reactions.

Table II. Quantum Yields

			× 10³			
Run	Solvent–additive	mE/mmol	Φ_{disapp}	Φ_{rac}	Φ_{isomer}	Φ_{adduct}
D1	Cyclohexane	13.8	5.8	1.35	0.22	
D2	Cyclohexane	28.6	4.2	0.88	0.4	
D3	Cyclohexane	68.0	3.9	0.36	0.3	
D4	Methanol–HCl[a]	36.0	9.8	0.45	0.0	2.6
S1	Benzene–acetophenone[b]	6.0		0.0		
S2	Acetone	18.1		0.0	0.0	

[a] 0.2% concentrated hydrochloric acid by volume. [b] 0.067 *M* absorbing greater than 99% of the light.

The quantum yield of disappearance of optically active biphenyl 1 was *ca.* 0.005. It was found that the products formed were isomeric dimethyldiethylbiphenyls. Several authors[7] have reported analogous photoisomerizations. Since there are 99 such possible compounds isomeric with reactant, no attempt was made to identify these. However, vpc showed the presence of at least two of the four possible initial photoisomers. Nmr confirmed the presence of only aryl hydrogens, aromatic methyl absorption, and aromatic ethyl peaks; however, in addition to starting material peaks, a new methyl absorption and at least one more ethyl quartet were discernible in the chromatographic fractions of these isomers. High-resolution mass spectral analysis confirmed that this material was isomeric with reactant. The high-temperature photolyses (*vide infra*) produced further isomers which eluted later than the low-temperature products. These had a simple nmr spectrum but now at least four methyls were visible, and the presence of at least 20 compounds was revealed by vpc.

In addition to the isomeric biphenyl fractions, there was a product which derived from air oxidation of the photolyzed mixture. It was observed that this ketonic fraction was a mixture of isomers and was formed at the expense of isomeric biphenyl in the room temperature runs. At elevated temperatures (note Table I), little of this material was formed and the balance of the material appeared as biphenyl isomers. The material was observed to form in amounts increasing with time as the photolysis mixture from the room temperature runs was exposed to air. It was clear that benzvalene product was still present at the end of the photolysis and was susceptible to air oxidation. This has analogy in the findings of ref 5. When the photolysis was run in acidic methanol, biphenyl isomer formation

---

(6) (a) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970); (b) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

(7) (a) U. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970); (b) R. A. Finnegan and D. Knutson, *ibid.*, 3429 (1968); (c) R. A. Abranovitch and T. Takaya, *Chem. Commun.*, 1369 (1969).

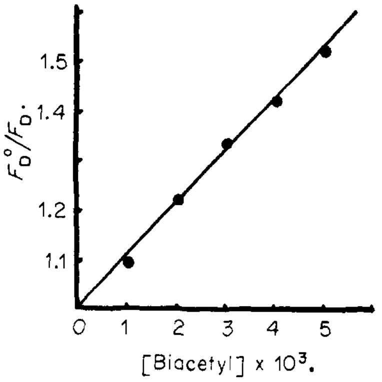


Figure 1. Fluorescence quenching by biacetyl in cyclohexane at 32° (excitation 247 nm).

was completely inhibited but photoracemization dropped only to $\Phi = 0.00045$. Finally, attempted sensitization by acetone and acetophenone (note Table II, runs S1 and S2) gave no discernible reaction.

For interpretation of the results as well as for general interest, the activation energy of the dark (*i.e.* thermal) racemization process was investigated. At 25° as well as at 300° there was no evidence of racemization. At 345° the reaction was found to have a $k_{rac} = 2.4 \times 10^{-3}$ hr^{-1} and a half-life of 283 hr. At 380° $k_{rac} = 2.8 \times 10^{-2}$ hr^{-1} and a half-life of 25 hr were observed. The temperature dependence affords a rough estimate of the activation energy of 56 kcal/mol. Thus, optically active biphenyl **1** is especially stable to thermal racemization.

Also of interest was the temperature dependence of the photochemical racemization, since this would allow calculation of any excited state activation energies encountered. Because of the high temperature used, relative quantum yields were obtained here rather than absolute ones. The runs were made with a Hanovia immersion well thermally insulated from the reaction vessel by a vacuum jacket as was utilized by us earlier in low-temperature studies.[6] The results are given in Table I and it is seen that the quantum yield increases by a factor of *ca.* 2 with a temperature increase from 30 to 195°.

Another facet needing attention was the singlet lifetime, since this information might allow a conclusion whether or not the excited singlet had time to thermally equilibrate with solvent. The method chosen to obtain the singlet lifetime was that of DuBois and Wilkinson[8a] and DuBois and Van Hemert.[8b] Both the quenching of the fluorescence of biphenyl **1** by biacetyl as well as the sensitization of biacetyl fluorescence by biphenyl **1** were investigated.

For the case of 2,2′-dimethyl-6,6′-diethylbiphenyl (**1**) emission with biacetyl quenching, the intensity of fluorescence is given by eq 1. Here (F_D^0/F_D) is the

$$\frac{d(F_D^0/F_D)}{d[A]} = k_{diff}(\tau_D^s) \qquad (1)$$

relative biphenyl fluorescence intensity, [A] is the concentration of biacetyl acceptor, k_{diff} is the rate of diffusion, and τ_D^s is the singlet lifetime of biphenyl **1**. A plot of F_D^0/F_D is given in Figure 1.

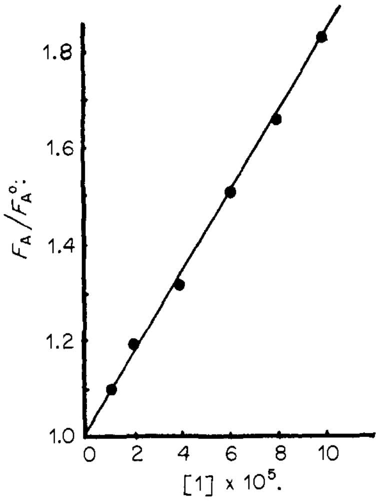


Figure 2. Sensitization of biacetyl (0.001 *M*) fluorescence in cyclohexane at 32° (excitation 265 nm).

With biacetyl as the acceptor and fluorescer, eq 2 is

$$\left[\frac{d(F_A/F_A^0)}{d[D]}\right]_{[D]\to 0} = \frac{\epsilon_D}{\epsilon_A}\left[\frac{k_{diff}(\tau_D^s)}{1 + k_{diff}(\tau_D^s)[A]}\right] \qquad (2)$$

applicable. However, here the plot is of (F_A/F_A^0), the relative biacetyl fluorescence, *vs.* biphenyl **1** concentration. From the slopes of these two plots, the molar extinction coefficients in eq 2, and the use of a rate of diffusion calculated from viscosity data,[9] the rate of unimolecular decay can be obtained. For both types of experiments, conditions were selected where over 93% of the light was transmitted. This is needed for use of eq 2. A plot of (F_A/F_A^0) is given in Figure 2.

The singlet lifetime and rate of unimolecular decay obtained by quenching of biphenyl **1** fluorescence were 1.2×10^{-8} sec and 8.3×10^7 sec^{-1}, respectively. The values obtained from sensitization of biacetyl were 2.2×10^{-8} sec and 4.5×10^7 sec^{-1}. Thus, agreement was quite good and an average singlet lifetime of 1.7×10^{-8} sec was obtained.

The fluorescence quantum yield of 0.12 was also obtained by measuring the amount of fluorescence from biphenyl **1** relative to biphenyl itself whose quantum yield of fluorescence is known.[11] In these experiments the same wavelength of excitation was employed and concentrations were adjusted so that both biphenyl **1** and biphenyl itself were absorbing the same amount of light.

Interpretative Discussion

The first point to be considered is the gross mechanism of the reaction. The diminution of the reaction efficiency by one-third by use of acidic methanol as a solvent together with the observation of benzvalene formation concomitant with the photoracemization provides evidence that *ca.* one-third of the photoracemization proceeds by way of benzvalene intermediates. It seems likely, because of the compressed size of the

---

(8) (a) F. Wilkinson and J. T. DuBois, *J. Chem. Phys.*, **39**, 377 (1963); (b) J. T. DuBois and R. L. Van Hemert, *ibid.*, 40, 923 (1964).

(9) A $k_{diff} = 8.4 \times 10^9$ sec^{-1} was calculated from the viscosity of cyclohexane[10] at 32° (0.80 cP).

(10) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p 235, Table 23c.

(11) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 92.

benzvalene ring, that having one benzvalene ring present allows more facile free rotation of the second aryl ring as needed for racemization. This is approximately equal to recognizing that in the original biphenyl, twisting of two ortho positions (*i.e.* carbons 2 and 6) together and out of plane will facilitate rotation of the other ring. In the benzvalene mechanism for photoracemization, however, it is seen that most of the benzvalene molecules formed proceed onward to rearrangement product rather than back to racemized reactant **1**.

Still to be considered is the mechanism of the major pathway for photoracemization. One possibility is the ground-state racemization of a vibrationally hot species formed by radiationless decay of excited state. Of available excited states, the singlet is indeed 106 kcal/mol above ground state and would provide maximum energy on radiationless decay. The Rice–Ramsperger–Kassel treatment of hot molecules has proven convenient for quantitative correlation of rates of hot gas-phase molecules and excess vibrational energy.[12–15] In eq 3, s is the number of effective degrees of freedom

$$k = A\left[\frac{E - E_0}{E}\right]^{s-1} \tag{3}$$

which can accept and dissipate excess energy, A is the frequency factor, E is the actual energy of the molecule, and E_0 is the normal activation energy. While for small molecules in the gas phase it is empirically found that a good approximation of the unimolecular rate results when s is taken to be half of $3N - 6$, for the present biphenyl this is less certain. Table III gives the predicted rate constants for varying numbers of effective vibrational modes s.

Table III. RRK Rate Prediction for Various Effective Vibrational Modes[a]

s	k, sec^{-1}	s	k, sec^{-1}
57	5.3×10^{-6}	11	5.5×10^{9}
31	1.6×10^{3}	6	1.5×10^{11}
26	6.9×10^{4}	5	4.9×10^{11}
21	3.0×10^{6}	4	1.0×10^{12}
16	1.3×10^{8}		

[a] A is taken as the usual 10^{13} sec^{-1}.

However, some information is available to assign limits for s. Thus, it is observed that the reaction quantum yield is approximately doubled at 195° *vs.* that at 30°. Use of eq 3 for each of these temperatures leads to

$$s - 1 = \log 2/\log\left[\frac{(E_{195} - 56)E_{30}}{(E_{30} - 56)E_{195}}\right] \tag{4}$$

Implicit in this reasoning is the assumption that the vibrationally hot ground-state molecule is cooled by solvent competitively with thermal racemization in order to account for a quantum yield of less than 0.87 (*i.e.* $1 - \Phi_{\text{fl}} - \Phi_{\text{benzv}}$). The extra kinetic energy imparted from an increased temperature derives from thermal equilibration of the excited state molecule. That equilibration is complete is seen from the relatively long lifetime of the singlet excited state, *i.e.* 1.7×10^{-8} sec and a modestly slow decay rate of $k_{\text{d}} = 0.59 \times 10^{8}$ sec^{-1}. This decay is small compared with a rate of collision with solvent of 10^{13} sec^{-1},[16] and there is ample time for equilibration of excited state molecules prior to thermal decay.

In contrast to ordinary excited kinetics, the quantum yield in the hot ground-state mechanism can be taken as directly linear with the reaction rate since the main process considered here, radiationless decay, is the one leading to reaction.

However, the energy imparted to the excited state molecule at elevated temperature is not known with precision. Table IV gives the number of effective degrees of freedom required by the quantum yield doubling with temperature increase for a series of possible electronic plus vibrational energies. Consideration of the liquid-phase heat capacity of *p*-xylene[17] and biphenyl[18] indicates that the excess heat content, ΔE, at 195° is between 14.8 and 18.4 kcal/mol. Table IV then gives s in the range of 5–6. It is seen that this value is even lower than the values for much less complex molecules; for example, the experimental values for cyclobutane and bicyclo[2.1.0]pentane are 18 ± 1[14] and 20,[15] respectively. Even for cyclopropane, s is determined as 13[12] and biphenyl **1** must have more degrees of freedom available than this simple molecule.

Table IV.[a] Effective Degrees of Freedom Corresponding to Increased Vibrational Energy of the Singlet Excited State

ΔE[b]	$E_s +$ ΔE	s	ΔE	$E_s +$ ΔE	s
1.5	107.5	46	15	121	6.2
3	109	24	20	126	5.2
5	111	15	30	136	4.1
10	116	8.5	35	141	3.8

[a] E_s is the excited singlet energy of 106 kcal/mol. [b] ΔE is the excess vibrational energy imparted at elevated temperature.

However, if one does use a low value of s, *e.g.*, 5–6, eq 3 gives a rate of hot molecule reaction of *ca.* 10^{11} sec^{-1} which might conceivably be enough to account for a probability of 0.001 (*i.e.* Φ) of reaction *vs.* solvent cooling. The main objection to this interpretation remains then to be the abnormally low number of accessible vibrational modes which would have to be present.

A simpler interpretation is that the reaction proceeds in the excited singlet with a small activation barrier of 0.89 kcal/mol corresponding to excited state twisting. The occurrence of benzvalene formation which is most probably a singlet reaction[19] shows the capability of the excited singlet to react. The sensitizers used (E_{T}, acetone, 80 kcal/mol: acetophenone, 74 kcal/mol) require close to isoenergetic transfer, and inefficient transfer is expected. The complete lack of sensitization suggests an unreactive triplet. One would expect a

---

(12) (a) J. N. Butler and G. B, Kistiakowsky, *J. Amer. Chem. Soc.*, **82**, 759 (1960); (b) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc., Ser. A*, **217**, 563 (1953).

(13) J. P. Chesick, *J. Amer. Chem. Soc.*, **82**, 3277 (1960).

(14) R. W. Vreeland and D. F. Swinehart, *ibid.*, **85**, 3349 (1963).

(15) T. F. Thomas, C. I. Sutin, and C. Steel, *ibid.*, **89**, 5107 (1967).

(16) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(17) R. J, Corruccini and D. C. Ginnings, *J. Amer. Chem. Soc.*, **69**, 2291 (1947).

(18) B. E. Walker, M. S. Brooks, C. T. Ewing, and R. R. Miller, *Chem. Eng. Data Ser.*, **3**, 280 (1958).

(19) (a) R. B. Cundall and A. J. R. Voss, *Chem. Commun.*, 902 (1968); (b) N. Leray, *J. Chim. Phys.*, **64**, 1390 (1967).

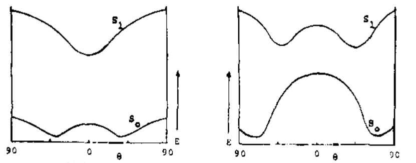


Figure 3. Energy barriers involved in twisting biphenyls.

MO	D_{2h}	D_2	Symmetry for planar conformer
ψ_9	a_u	a	AA
ψ_8	b_{1g}	b_1	AS
ψ_7	b_{3u}	b_3	SS
ψ_6	b_{2g}	b_2	SA
ψ_5	a_u	a	AA
ψ_4	b_{1g}	b_1	AS

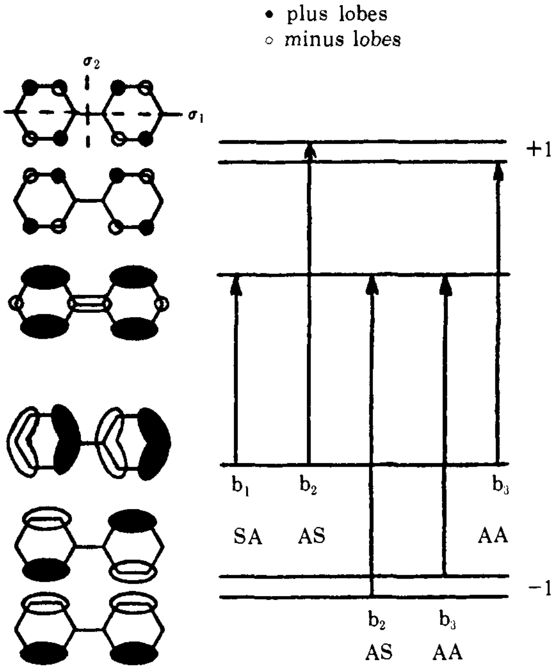


Figure 4. MO's and excitation processes for planar and twisted biphenyl.

lower energy barrier to racemization in the singlet excited state than in the ground state. It is reported by Hoffmann[20] that for ordinary biphenyl, configuration interaction calculations give an energy minimum for the planar conformation of the excited state singlet. In the present system, van der Waals interaction between ortho groups provides an energy barrier which counteracts this tendency toward planarity and leads to energy minima displaced somewhat from 90°. Hence one would expect an excited state rotation with lower energy than for the ground state. The two situations are depicted in Figure 3.

The electronic driving force facilitating excited state rotation is most readily understood by consideration of the nature of the MO's involved as depicted in Figure 4. It is seen that the excitation process involving promotion from the highest occupied to lowest vacant MO (*i.e.* $\psi_6 \rightarrow \psi_7$) removes an electron from an MO which is antibonding between the two phenyl rings and puts an electron in an MO which is centrally bonding. This excited state has the most enhanced central bond order and corresponds to the species calculated by Hoffmann as lowest in energy for the planar singlet. Figure 4 additionally reveals four excitation configurations of equal energy; these come in pairs. Two are of AS(b_2) symmetry and two are of AA(b_3) symmetry. In such a case one expects first-order configuration interaction to give two lower energy excited states and two higher energy ones. The lower energy ones are $\Phi = (\psi_5 \rightarrow \psi_7) - (\psi_6 \rightarrow \psi_8)$ and $\Phi = (\psi_4 \rightarrow \psi_7) - (\psi_6 \rightarrow \psi_9)$. These are degenerate and correspond to the excited states predicted by Hoffmann to be of lowest energy at perpendicularity. It is seen that such excited states are generated by removing an electron from an MO having no central bond order and putting it in an antibonding MO with a positive bond order or alternatively, taking an electron from an MO which is centrally antibonding and promoting to an MO which is centrally nonbonding. Such excited states then have lower bond orders than that formed by the $\psi_6 \rightarrow \psi_7$ excitation. Near planarity it is the $\psi_6 \rightarrow \psi_7$ excited state which is populated. This bond-order enhancement is responsible for the lowered barrier to planarity in the excited state.

Thus, the racemization of electronically excited biphenyl derives both from reversible benzvalene formation and from an enhanced excited state bond order lowering the potential energy barrier to interconversion of enantiomers.

Experimental Section[21]

***m*-Ethylbenzoic Acid.** The procedure of Newman[4] was used to give 124.5 g (70%) of *m*-ethylbenzoic acid, mp 46–47° (lit.[4] 47.0–47.6°).

2-Nitro-3-ethylbenzoic Acids. A 100.0-g (0.67 mol) portion of *m*-ethylbenzoic acid[4] was slowly added with stirring to 453.6 g of

---

[20] A. Imamura and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5379 (1968).

[21] All melting points were taken on a hot-stage apparatus and are corrected.

90% fuming nitric acid at −20° over 4 hr after the method of Müller.[22] After stirring for an additional 2 hr at −20°, the reaction mixture was quickly filtered through glass wool and the resultant yellow mass dried at 50° to give 64.1 g of crude nitro acid. The filtrate contained the other isomers which were not characterized. Recrystallization from methanol gave 30.66 g (24%) of 2-nitro-3-ethylbenzoic acid, mp 206–207°. The spectral data were: ir (KBr) 3.2–4.4 (broad OH), 5.93 μ (C=O); nmr (C_3D_6O) τ 2.0 (d of d, 1 H, ArH ortho to CO_2), 2.37 (m, 2 H, ArH), 3.54 (broad s, 1 H, OH), 7.40 (q, 2 H, CH_2), 8.78 (t, 3 H, CH_3).

Anal. Calcd for $C_9H_9NO_4$: C, 55.49; H, 4.65; N, 7.17. Found: C, 55.53; H, 4.69; N, 7.48.

2-Amino-3-ethylbenzoic Acids. A solution of 20.0 g (0.103 mol) of 2-nitro-3-ethylbenzoic acid in 230 ml of 5 *N* ammonium hydroxide was added dropwise, with stirring, over 2 hr, under nitrogen, to a refluxing solution of 220 g of ferrous sulfate heptahydrate in 530 ml of water. Then *ca.* 150 ml of concentrated ammonium hydroxide was added to make the solution basic. Refluxing was continued for another 15 min and then the solution was concentrated *in vacuo* to 500 ml. Acidification with acetic acid followed by cooling and filtration gave 13.99 g of yellow crystals. These were combined with ether extracts of the filtrate and concentrated *in vacuo.* Recrystallization from ether–hexane gave 16.56 g (99%) of 2-amino-3-ethylbenzoic acid, mp 153–154°. A sample was sublimed at 100° (0.5 mm) to give an analytical sample, mp 153–154°. The spectral data were: ir (KBr) 2.85, 2.95 (NH), 3.2–4.3 (broad OH), 6.02 μ (C=O); nmr (C_3D_8O) τ 2.27 (d of d, 1 H, ortho to CO_2, J_o = 8 Hz, J_m = 2 Hz), 2.85 (broadened d, 1 H, ortho to Et, J_o = 8 Hz), 3.49 (t, 1 H, para to NH_2, J_o = 8 Hz), 4.68 (broad, 3 H, NH_2 and OH), 7.45 (q, 2 H, CH_2), 8.81 (t, 3 H, CH_3).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.34; H, 6.50; N, 8.51.

6,6′-Diethyl-2,2′-diphenic Acid Dimethyl Ester. A solution of 8.50 g (0.123 mol) of sodium nitrite in 30 ml of water was added slowly with stirring to a suspension of 17.18 g (0.104 mol) of 2-amino-3-ethylbenzoic acid in 110 ml of 3 *N* hydrochloric acid. The reaction was carried out at 0–5° to give a clear solution of the diazonium salt. Then 9.0 g (135 mmol) of hydroxylamine hydrochloride in 40 ml of water plus a solution of 5.70 g (140 mmol) of sodium hydroxide in 20 ml of water were added in one portion, with vigorous stirring, to a solution of 37.0 g (147 mmol) of copper sulfate pentahydrate in 110 ml of water containing 62 ml of 15 *N* ammonium hydroxide in a 2-l. beaker. Finally, the diazonium salt solution was added *via* a small curved pipet which extended into the 0–5° copper solution. After stirring for an additional 5 min, the cooling bath was removed and the solution heated to boiling with a Meeker burner. Then 100 ml of concentrated hydrochloric acid was carefully added with stirring. After standing overnight, the reaction mixture was filtered and the yellow solid was extracted with 50 ml of hot acetone. Filtration and removal of solvent *in vacuo* gave 12.39 g of light tan carboxylic acid crystals which were esterified by refluxing overnight with 20 ml of methanol and 5.0 ml of concentrated sulfuric acid in 50 ml of dichloromethane. The reaction mixture was washed with water and sodium bicarbonate solution, dried, concentrated *in vacuo*, and distilled to give 13.00 g (38%) of 6,6′-diethyl-2,2′-diphenic acid dimethyl ester (bp 150–170° (0.2 mm); mp 38–39°). The spectral data were: ir (plate) 5.82 μ (C=O); nmr (CCl_4) τ 2.25 (d of d, 2 H, aryl H, ortho to CO_2, J_o = 6.5 Hz, J_m = 2.5 Hz), 2.64 (m, 4 H, aryl H), 6.55 (s, 6 H, CH_3O), 7.82 (q, 4 H, CH_2), 9.02 (t, 6 H, CH_3).

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.71; H, 6.89.

6,6′-Diethyl-2,2′-diphenic Acid. A 13.00-g (38.8 mmol) sample of 6,6′-diethyl-2,2′-diphenic acid dimethyl ester was refluxed overnight with 50 ml of 15% aqueous sodium hydroxide. The reaction mixture was ether extracted, and then the aqueous layer was acidified with 6 *N* hydrochloric acid. Filtration and recrystallization from ether–hexane afforded 11.20 g (97%) of 6,6′-diethyl-2,2′-diphenic acid, mp 213–214°. An analytical sample was sublimed (180° (0.1 mm)), mp 215–216°. The spectral data were: ir (KBr) 3.1–4.3 (broad OH), 5.95 μ (C=O); nmr (C_3D_6O) τ 2.13 (d of d, 2 H, aryl H ortho to CO_2, J_o = 6.4 Hz, J_m = 3.0 Hz), 2.49 (m, 4 H, aryl H), 4.27 (broad s, 2 H, OH), 7.80 (q, 4 H, CH_2), 8.99 (t, 6 H, CH_3).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.42; H, 5.90.

2,2′-Diethyl-6,6′-bis(hydroxymethyl)biphenyl.[23] A 513.0-mg (1.57 mmol) sample of 6,6′-diethyl-2,2′-diphenic acid dimethyl ester in 15 ml of dry ether was added dropwise to 136.0 mg (3.6 mmol) of lithium aluminum hydride in 20 ml of dry ether under nitrogen. After 30 min of reflux, the reaction mixture was cooled in an ice bath and saturated aqueous ammonium chloride was added dropwise. The ethereal solution was washed with 10% hydrochloric acid and water, dried, and concentrated *in vacuo* to give 614.5 mg of clear oil which was chromatographed on a 1 × 8 cm silica gel (Grace, 950, 60–200 mesh) column packed in chloroform. Elution with 500 ml of chloroform collecting 50-ml fractions gave: 1, nil; 2, 27 mg of uncharacterized yellow oil; 3–8, 395.5 mg (93%) of 2,2′-diethyl-6,6′-bis(hydroxymethyl)biphenyl, mp 92–94°. Recrystallization from ether–hexane gave 102.5 mg, mp 102.5–103°. The spectral data were: ir ($CHCl_3$) 3.0 μ (broad OH); nmr ($CDCl_3$) τ 2.72 (s, 6 H, aryl H), 5.95 (m of OH, singlet on CH_2, AB quartet, 6 H, J_{AB} = 12 Hz), 7.86 (q, 4 H, CH_2), 9.0 (t, 6 H, CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.08; H, 8.22.

2,2′-Diethyl-6,6′-bis(bromomethyl)biphenyl. A 0.41-ml sample of phosphorus tribromide in benzene (2.85 g in 10 ml) was added to 105.7 mg (0.39 mmol) of 2,2′-diethyl-6,6′-bis(hydroxymethyl)-biphenyl in 10 ml of dry benzene. After refluxing for 45 min, the reaction mixture was cooled, washed with water and 5% sodium bicarbonate, dried, and concentrated *in vacuo* to give 176.2 mg of 2,2′-diethyl-6,6′-bis(bromomethyl)biphenyl. Recrystallization from pentane gave 132.0 mg (86%), mp 67–68°. The spectral data were: nmr (CCl_4) τ 2.49 (pseudo s, 6 H, aryl H), 5.82 (s, 4 H, CH_2Br), 7.66 (q, 4 H, CH_2), 8.89 (t, 6 H, CH_3).

Anal. Calcd for $C_{18}H_{20}Br_2$: C, 54.57; H, 5.09; Br, 40.34. Found: C, 54.60; H, 5.01; Br, 40.29.

2,2′-Dimethyl-6,6′-diethylbiphenyl. A 132.0-mg (0.334 mmol) sample of 2,2′-diethyl-6,6′-bis(bromomethyl)biphenyl in 5 ml of dry tetrahydrofuran was added to a mixture of 31.0 mg (0.76 mmol) of lithium aluminum hydride and 8.5 mg (0.77 mmol) of lithium hydride (90% technical grade) in 20 ml of dry tetrahydrofuran. After refluxing for 1 hr, the reaction mixture was chilled in an ice bath, excess hydride was destroyed with saturated aqueous ammonium chloride, and the reaction mixture was ether extracted. The ethereal solution was dried and concentrated *in vacuo* to give 90.4 mg of a clear oil which was filtered through a 1.5 × 9 cm silica gel (*vide supra*) Norit column eluting with pentane and collecting the first 70 ml. Concentration *in vacuo* gave 70.4 mg (88%) of 2,2′-dimethyl-6,6′-diethylbiphenyl as a clear oil. The spectral data were: ir (plate) 3.25, 3.31, 3.37, 3.40, 3.48, 6.26, 6.90, 7.30, 12.80 (broad), 13.27 μ (broad); nmr (CCl_4) τ 2.85 (s, 6 H, aryl H), 7.79 (q, 4 H, CH_2), 8.10 (s, 6 H, aryl CH_3), 8.95 (t, 6 H, CH_3); uv (cyclohexane) 246 min (470), 263 max (820), 320 nm (1.6).

Anal. Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.30. Found: C, 90.59; H, 9.24.

Resolution of 6,6′-Diethyl-2,2′-diphenic Acid. A mixture of 29.837 g (0.1 mol) of racemic 6,6′-diethyl-2,2′-diphenic acid, 37.921 g (0.1 mol) of (−)-quinine, and 150 ml of 95% ethanol was heated on a steam bath until solution occurred and then filtered and allowed to stand overnight, yielding 23.009 g of white crystalline salt, mp 155–158°, $[\alpha]^{30}_{589}$ −123°[24] (*c* 0.66, MeOH). An additional crystallization gave 18.431 g, mp 158–159°, $[\alpha]^{30}_{589}$ −137° (*c* 0.77, MeOH). A portion of this salt on hydrolysis (6 *N* HCl) gave acid with mp 170–172°, $[\alpha]^{30}_{589}$ +6.9° (*c* 1.85, MeOH). Further recrystallization of the salt did not improve these values. A 14.49-g sample of salt, hydrolyzed to 5.243 g of acid, mp 170–172°, $[\alpha]^{30}_{589}$ +7.1° (*c* 0.70, MeOH). Two crystallizations from ether–hexane gave 4.535 g (15.2%) of 6,6′-diethyl-2,2′-diphenic acid, mp 170–172°, $[\alpha]^{30}_{589}$ +7.1° (*c* 0.70, MeOH), with no further change in rotation on crystallization. The ir and nmr spectra were identical with those of racemic material; ORD max at 300 nm, intercept at 260 nm, $[\alpha]^{30}_{300}$ +460° (*c* 0.05, MeOH). Treatment of the resolution mother liquors with acetone at 0° and removing three crops of crystals gave a fourth crop of 1.3760 g of salt, mp 140–150°, $[\alpha]^{30}_{589}$ −76° (*c* 0.67, MeOH). A portion of this salt on hydrolysis (6 *N* HCl) gave acid with mp 178–180°, $[\alpha]^{30}_{589}$ −6.7° (*c* 0.47, MeOH), with no further change in rotation on recrystallization.

---

(22) E. Müller, *Chem. Ber.*, 42, 423 (1909).

(23) W. L. Meyer and R. B. Meyer, *J. Amer. Chem. Soc.*, **85**, 2170 (1963).

(24) All quantitative work was done on a Perkin-Elmer Model 141 spectropolarimeter with thermostatted 1-dm cells. We thank Professor Goering for the use of this instrument.

Optically Active 6,6′-Diethyl-2,2′-diphenic Acid Dimethyl Ester. A 4.53-g (15.2 mmol) sample of 6,6′-diethyl-2,2′-diphenic acid $[\alpha]^{30}_{589}$ +7.1° in 80 ml of dry ether was added dropwise over 30 min to a stirred 0° solution of tenfold excess distilled ethereal diazomethane. After stirring for an additional 30 min, the excess diazomethane was blown off with nitrogen leaving 5.1822 g of a light yellow oil which was chromatographed on a 2.5 × 250 cm column of deactivated silica gel slurry packed in 10% ether–hexane. Elution with 1 l. of 10% ether–hexane and collection of 250-ml fractions gave: 1, 54.9 mg of impure diester; 2–4, 4.8739 g (98%) of 6,6′-diethyl-2,2′-diphenic acid dimethyl ester as a crystallizing oil, mp 27–28°, $[\alpha]^{30}_{589}$ +30.8° (*c* 2.86, MeOH). The ir and nmr spectra were identical with those of racemic material; ORD max at 300 nm, intercept at 260 nm, $[\alpha]^{26}_{300}$ +470° (*c* 0.05, MeOH).

Optically Active 2,2′-Diethyl-6,6′-bis(hydroxymethyl)biphenyl. A 4.8739-g (15.0 mmol) sample of 6,6′-diethyl-2,2′-diphenic acid dimethyl ester $[\alpha]^{30}_{589}$ +30.8° in 60 ml of dry ether was added dropwise over 25 min under nitrogen to 1.502 g (39.8 mmol) of lithium aluminum hydride in 100 ml of ether. After refluxing for 1 hr, the reaction mixture was cooled to 0° and hydrolyzed with 50 ml of saturated aqueous ammonium chloride solution, and ether extracted. The ethereal solution was dried and concentrated *in vacuo* to give 4.0243 g (99%) of crystalline 2,2′-diethyl-6,6′-bis(hydroxymethyl)biphenyl, mp 95–96.5°. Recrystallization from ether–hexane gave clear plates, mp 97–98°, $[\alpha]^{30}_{589}$ −33.8° (*c* 1.03, MeOH). The ir and nmr spectra were identical with those of racemic material; ORD was a plain curve with relative max at 284 nm, $[\alpha]^{26}_{284}$ −204°. The rotations were not improved on further crystallization.

Optically Active 2,2′-Diethyl-6,6′-bis(bromomethyl)biphenyl. A 6.4-ml (13.4 mmol) sample of phosphorus tribromide in benzene (2 ml, 5.70 g in 10 ml of benzene solution) was added to 3.462 g (12.8 mmol) of 2,2′-diethyl-6,6′-bis(hydroxymethyl)biphenyl, $[\alpha]^{30}_{589}$ −33.8° in 75 ml of dry benzene. After refluxing for 1.3 hr under nitrogen the reaction mixture was cooled, hydrolyzed with 50 ml of water, and ether extracted. The ethereal solution was washed with aqueous sodium bicarbonate and with water and then dried. Removal of solvent *in vacuo* afforded 4.9574 g, mp 48–52°, of white crystals which were recrystallized from pentane to give 2.5892 g (52%) of 2,2′-diethyl-6,6′-bis(bromomethyl)biphenyl, mp 52–53°, $[\alpha]^{30}_{589}$ −10.3° (*c* 1.52, cyclohexane). The ir and nmr spectra were identical with those of racemic material; ORD max at 238 nm, intercept at 228 nm, $[\alpha]^{26}_{238}$ −2900° (*c* 0.006, cyclohexane).

Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. A 2.291-g (5.64 mmol) sample of 2,2′-diethyl-6,6′-bis(bromomethyl)biphenyl, $[\alpha]^{30}_{589}$ −10.3°, in 15 ml of dry tetrahydrofuran was added to a mixture of 421 mg (11 mmol) of lithium aluminum hydride and 98 mg (11 mmol) of lithium hydride (90% technical grade) in 100 ml of dry tetrahydrofuran. After refluxing for 1.2 hr, the reaction mixture was cooled to 0°, excess hydride was destroyed with saturated aqueous ammonium chloride, and the reaction mixture was ether extracted. The ethereal solution was washed with saturated aqueous sodium chloride solution and dried. Removal of solvent *in vacuo* gave 1.3349 g of a clear oil which was chromatographed on a 1.5 × 12 cm silica gel–Norit column slurry packed with pentane. Elution with pentane and collection of 40-ml fractions gave: 1, nil; 2–4, 1.1770 g (86%) of 2,2′-dimethyl-6,6′-diethylbiphenyl as a clear oil, $[\alpha]^{30}_{589}$ +14.8°, $[\alpha]^{30}_{578}$ +15.5°, $[\alpha]^{30}_{546}$ +17.7°, $[\alpha]^{30}_{436}$ +31.3°, $[\alpha]^{30}_{365}$ +52.3° (*c* 1.338, cyclohexane). The ir and nmr spectra were identical with that of racemic material; ORD max at 268 nm, intercept at 248 nm, $[\alpha]^{26}_{268}$ +190° (*c* 0.063, cyclohexane).

Thermal Racemization Experiments. Solutions of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in distilled dodecane were degassed and sealed in heavy wall glass tubes. An insulated Wood's metal bath was used and temperatures were ±1° as measured on a calibrated thermocouple. Samples were opened and examined polarimetrically at 578, 546, and 436 nm in a 1-dm cell at 25°. The results were plotted as log (α_0/α_t) *vs.* time; good straight-line relationships resulted (±10%). There were at least four points at each temperature, the last point being taken at a time somewhat greater than one half-life. Some decomposition was noted in the last point (= 15% by nmr), but no isomers were formed (vpc of crude and nmr of chromatographed material). At 345° (*c* 1.74, dodecane), α_{436} +0.481 at t_0 gave a rate of 2.4 ± 0.2 × 10^{-3} hr^{-1} and at 380° (*c* 2.26, dodecane) α_{436} +0.748 at t_0 gave a rate of 2.8 ± 0.2 × 10^{-2} hr^{-1} for an activation energy of 56 ± 4 kcal/mol.

Solvents and Reagents. Cyclohexane, methylcyclohexane, isopentane, and dodecane for photolytic studies were washed with 30% fuming sulfuric acid, water, and saturated aqueous sodium bicarbonate. They were then dried, distilled from calcium hydride, and checked for uv transparency. Benzene was treated similarly except that concentrated sulfuric acid was used. Biacetyl was vacuum distilled and stored in the dark under nitrogen at 0°. Reagent grade acetophenone was vacuum distilled and stored under nitrogen. Reagent grade acetone was distilled from Drierite (anhydrous calcium sulfate) and used immediately. Biphenyl was recrystallized from ethanol and dried *in vacuo*.

Phosphorescence and Fluorescence Studies. All studies were carried out on an Aminco-Kiers spectrophosphorimeter. Both monochromators were calibrated and all spectra were calibrated with a mercury pen lamp. Solvent blanks were checked. Spectra are not corrected for photomultiplier response.

The phosphorescence spectra were run at 77°K (liquid nitrogen) in 4:1 (v/v) methylcyclohexane–isopentane, 7 × 10^{-3} *M*, with λ_{excit} 280 nm. There were two maxima (394 (73 kcal/mol) and 462 nm (62 kcal/mol)) with the onset of emission at 344 nm (83 kcal/mol). An approximation taking the 0–0 band 20% of the way toward the maximum gives 81 kcal/mol.

Fluorescence work was done on nondegassed cyclohexane solutions (5.7 × 10^{-4} *M*), and the excitation wavelength was varied. With 256-nm excitation the emission maximum is 285 nm (101 kcal/mol); with the onset of emission at 260 nm (110 kcal/mol) overlap of absorption and emission occurs at 272 (106 kcal/mol).

The fluorescence quantum yield at this concentration and wavelength relative to that of biphenyl (Φ_{fl} = 0.18[11]) is Φ_{fl} = 0.12. This value was determined from the ratio of the integrated areas under the emission curves; the equivalence of the optical densities at 256 nm was checked.

Determination of Singlet Lifetime. The singlet lifetime was determined from fluorescence quenching with biacetyl and from sensitization of biacetyl fluorescence after the methods of Dubois and Wilkinson.[8] Figures 1 and 2 give experimental conditions and results. The results of the sensitization of biacetyl fluorescence with biphenyl agreed with those of Dubois and Wilkinson.[8a]

Exploratory Photolysis of Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. A solution of 159.8 mg (0.688 mmol) of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in 500 ml of cyclohexane was purged with purified[25] nitrogen for 1 hr before and during the photolysis. After 2 hr of irradiation with a Vycor-filtered, water-cooled 450-W Hanovia medium-pressure mercury lamp, the solvent was removed *in vacuo*. The residue, 190 mg of light yellow oil, was chromatographed on a 1.5 × 120 cm silica gel column (Grace 950, 60–200 mesh), slurry packed in 0.5% ether–hexane. Collection of 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–60, 0.5% ether–hexane, 12.2 mg of uncharacterized saturated hydrocarbon; 61–74, 1% ether–hexane, 4.1 mg of uncharacterized oil; 75–85, 1% ether–hexane, 125.2 mg (77%) of a light yellow oil which was shown by nmr and the rotation of separate fractions to be predominantly starting material; fractions 86–91, 1% ether–hexane, nil; and fractions 92–128, 10% ether–hexane, 40.1 mg (25%) of a dark yellow oil which was shown by ir to contain oxidation products.

Fractions 75–85 were collected and rechromatographed on a 1.5 × 120 cm silicic acid (Mallnckrodt Silicar-CC7) column slurry packed in hexane. Elution with hexane while scanning the eluent at 263 nm and collecting 40-ml fractions gave: fractions 1–8, 2.3 mg of uncharacterized oil; 9–42, 92.6 mg (68%) of light yellow oil which was shown by nmr to be a mixture of starting material and some isomers; 43–55, nil; 56–62, 38.9 mg (24%) of dark yellow oil shown by ir to contain oxidation products; 63–67, nil.

Fractions 9–42 were combined and rechromatographed on an identical column. Fractions 1–9 gave 2.3 mg of uncharacterized oil; 10–19, 70.2 mg (44%) of 2,2′-dimethyl-6,6′-diethylbiphenyl which was shown by rotations of fractions 10–12 to be 17% racemized while vpc[26] showed not more than 2% of isomers. Vpc showed the presence of at least two isomers which were concentrated in fractions 13–19. Vpc analysis gives 64.7 mg (40%) of starting material, and 5.4 mg (3.6%) of the initial photoisomers.

Characterization of Initial Photoisomers. Vpc[26] analysis of fractions 13–19 showed two new peaks with relative retention volumes of: starting material, 1.00; peak A, 1.12; peak B, 1.23. Fractions 13–14, 19.3 mg, had 12.2% of these isomers by vpc analysis. The spectral data were: ir (plate) identical with that of starting

---

(25) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(26) All vpc analyses were done on a 100-ft capillary column loaded with 5% SE-30 and operated at 110° with 60 ml/min of helium. The injector block was 190° and the detector was 200°. Relative retention volumes are: starting material, 1.00 (11 min); peak A, 1.12; peak B, 1.23; all later isomers, 1.4–6.5.

material; nmr (100 MHz, CCl_4) τ 2.95 (s, 6 H, aryl H), 7.56–7.95 (m, 4 H, CH_2), 8.12 (s, rel integ 1, aryl CH_3), 8.15 (s, rel integ 4.95, aryl CH_3), 8.98 (t, 6 H, J = 7 Hz, ethyl CH_3); mass spectrum m/e (per cent of base) 238 (100), 224 (11), 223 (58), 209 (14), 179 (17); high-resolution mass determination, calcd, 238.1720; found, 238.1755.

Characterization of Oxidation Products. The yellow material obtained from 10% ether–hexane elution of the silica gel columns had the following spectral data: ir (neat) 2.8–3.1 (broad OH), 5.8 (strong C=O), 6.9 and 7.2 μ (CH_3 bend); uv (hexane) tailing only (log ϵ) 220 (4.1), 263 (3.0), 300 nm (2.4); nmr (CCl_4) τ 2.5–3.6 (broad m, vinyl H, rel integ 1), 8.2–9.4 (structured m, CH_2 and CH_3, rel integ 8); mass spectrum m/e (per cent of base), 256 (parent, 3), 238 (39), 223 (20), 209 (35), 149 (35), 56 (110), 43 (89), 41 (100).

Exploratory High-Temperature Photolysis of Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. A solution of 143 mg (0.60 mmol) of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in 500 ml of dodecane was purged with purified[25] nitrogen for 1 hr before and during photolysis. The irradiation was carried out for 2 hr using a Vycor-filtered 450-W Hanovia medium-pressure mercury lamp in the usual quartz immersion well but with only a stream of nitrogen for cooling. A solvent temperature of 200 ± 5° was maintained with a silicone oil bath around the sample flask. Removal of solvent *in vacuo* gave 286.4 mg of yellow oil which was chromatographed on a 1.5 × 120 cm silica gel (*vide supra*) column slurry packed in hexane. Elution of 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–10, hexane, 116.6 mg of residual dodecane; 11–50, 1% ether–hexane, 8.3 mg of uncharacterized oil; 51–56, 2% ether–hexane, 0.5 mg of uncharacterized oil; 57–65, 2% ether–hexane, 91.1 mg (64%) of light yellow oil which was shown by rotation of separate fractions to contain starting material; 66–70, 2% ether–hexane, 1.6 mg of uncharacterized oil; and 71–100, 10% ether–hexane, 8.9 mg of yellow oil which was shown by ir to contain oxidation products.

Fractions 57–65 were combined and rechromatographed on a 1.5 × 120 cm silicic acid column slurry packed in hexane. Elution with hexane while scanning the eluent at 263 nm and collecting 40-ml fractions gave: fractions 1–11, 5.8 mg of saturated hydrocarbon oil; 12–15, 41.8 mg of a clear oil which contained 85.5% starting material, 12.3% initial photoisomers, and 2.6% other isomers, but 29.3% racemized; 16–17, 8.9 mg of a mixture of 38.2% starting material, 25.0% initial photoisomers, and 38.6% other isomers; 18–33, 29.3 mg of an isomer mixture of many biphenyls (nmr and high-resolution mass spectral analysis of various fractions); 34–66, 0.7 mg of uncharacterized oil.

Characterization of the Polybiphenyl Mixture. Vpc analysis showed at least 20 discrete peaks. The spectral data were: ir (plate) 3.30–3.45 (CH), 6.28, 6.90, 9.45, 11.38, 11.70, 12.20, 14.26; nmr (100 MHz, CCl_4) τ 2.70–3.19 (m, 6 H, aryl H), 7.28–7.53 (complex m, 4 H, CH_2), 7.68 (s, rel integ 9.3, aryl CH_3), 7.72 (s, rel integ 6.8, aryl CH_3), 7.83 (s, rel integ 1.9, aryl CH_3), 7.85 (s, rel integ 1.0, aryl CH_3), 8.69–8.81 (m, 6 H, ethyl CH_3); mass spectrum m/e (per cent of base) 238 (100), 224 (12), 223 (62), 209 (10), 179 (12); high-resolution mass determination, calcd, 238.1720; found, 238.1720.

Relative Quantum Yield at 30° of Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. A solution of 157.5 mg (0.66 mmol) of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in 500 ml of dodecane was purged with purified[25] nitrogen for 1 hr before and also during photolysis. The 2-hr irradiation was accomplished with a Vycor-filtered, water-cooled 450-W Hanovia medium-pressure mercury lamp which had a vacuum jacket surrounding the immersion well.[6] The sample flask was immersed in a silicone oil bath and the solvent temperature remained at 30 ± 2°. Removal of solvent *in vacuo* gave 3.389 g of yellow oil which was chromatographed on a 1.5 × 120 cm silica gel (*vide supra*) column slurry packed in hexane. Collection of 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–25, hexane, 3.158 g of dodecane; 26–63, 2% ether–hexane, 5.4 mg of an uncharacterized oil; 64–90, 2% ether–hexane, 132.2 mg (83%) of light yellow oil which was shown by nmr and rotation of fractions to contain starting material; 91–96, 10% ether–hexane, 9.7 mg of dark yellow oil which was shown by ir to be oxidation product; 97–141, 50% ether–hexane, 13.9 mg of dark yellow oil which was shown by ir and mass spectral analysis to contain oxidation products.

Fractions 26–90 were collected and rechromatographed on a 1.5 × 120 cm silicic acid column (*vide supra*) slurry packed in hexane. Collection of 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–10, hexane, 9.9 mg of uncharacterized oil which contained a small amount of starting material; 11–34, hexane, 87.9 mg of a light yellow oil which was shown by vpc and rotation of separate fractions to contain starting material (fraction 12, the purest fraction, showed *ca.* 21% racemization); 35–60, 10% ether–hexane, 16.1 mg of dark yellow oil which was shown by ir to contain oxidation products.

Fractions 1–34 were collected and rechromatographed on an identical silicic acid column. Collection of 40-ml fractions gave: fractions 1–8, hexane, 4.9 mg of uncharacterized oil; 9–11, hexane, 5.1 mg of clear oil which was 29% starting material by vpc; 12, hexane, 4.3 mg of pure starting material by vpc; 13, hexane, 22.9 mg of a clear oil which was 98% starting material (16.9% racemized) and 2% initial photoisomers; 14, hexane, 22.1 mg of a clear oil which contained 94% starting material and 6% of initial photoisomers (apparent racemization 20.6%); 15–17, hexane, 14.7 mg of a clear oil which was 83% starting material and 17% initial photoisomers; 18–25, hexane, 3.2 mg of clear oil which was 23% starting material, 20.2% initial photoisomers, and 57% other photoisomers; 34–36, 10% ether–hexane, 3.0 mg of uncharacterized oil; 37–40, 10% ether–hexane, 7.2 mg of yellow oil which was shown by ir to contain oxidation products.

Relative Quantum Yield at 195° of Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. A solution of 157.5 mg (0.66 mmol) of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in 500 ml of dodecane was purged with purified[25] nitrogen for 1 hr before and also during photolysis. The 2-hr irradiation was accomplished with a Vycor-filtered, water-cooled 450-W Hanovia medium-pressure mercury lamp which had a vacuum jacket surrounding the immersion well.[6] The solvent was maintained at 195 ± 2° by immersing the sample flask in a silicone oil bath. Removal of solvent *in vacuo* gave 5.17 g of clear oil which was chromatographed on a 1.5 × 120 cm silica gel (*vide supra*) column slurry packed in hexane. Collection of 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–25, hexane, 5.0146 g of dodecane; 26–59, 2% ether–hexane, 4.2 mg of uncharacterized oil; 60–77, 2% ether–hexane, 147.3 mg (93.5%) of a clear oil which was shown by nmr and rotation of fractions to contain starting material.

Fractions 60–77 were collected and rechromatographed on a 1.5 × 120 cm silicic acid (*vide supra*) column slurry packed in hexane. Elution with hexane while scanning the eluent at 263 nm and collecting 40-ml fractions gave: fractions 1–9, 2.7 mg of uncharacterized oil; 10–11, 14.4 mg of a clear oil which was 30% racemized, 97.6% starting material, and 2.4% initial photoisomers; 12–13, 55.4 mg of clear oil which was 28% racemized, 78.5% starting material, 20.4% initial photoisomers, and 1% other isomers by vpc; 14–15, 14.8 mg of a clear oil which was about 68% racemic, 39.6% starting material, 27.9% initial photoisomers, and 32.6% other isomers by vpc; 16–17, 13.6 mg of clear oil which had no rotation and was 96.4% other isomers by vpc; and 18–38, 24.5 mg which was all other isomers by vpc, nmr, and spectral analysis.

Quantum Yield Apparatus and Equipment. The light source for the macrophotolysis apparatus was a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter. The light was filtered by a cell containing three water-cooled compartments. These compartments (2.4 cm thick and 12 cm in diameter) were separated by gasketed quartz disks.

The photolysis cell contained two identical compartments each 12 cm i.d. diameter with a 5-cm optical path and aliphatic epoxy (uv transparent and nonfluorescent) cemented quartz faces. The cells were equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, and nitrogen inlet. An actinometer cell (26 mm i.d. × 10 cm optical path) was situated perpendicular to the main optical path to receive the light from a beam splitter consisting of a 4.6 × 4.6 × 0.2 cm quartz plate mounted at 45° to the light path. This side cell was used to monitor light input. Before and during irradiation vanadous-purified nitrogen[25] was bubbled through the photolysis solution.

Actinometry. Each determination required three runs: (1) actinometer solution in the main sample cell and in the side cell; (2) reactant solution in the main cell and actinometer solution in the back cell and the side cell; and (3) actinometer solution in the main cell and the side cell. In runs 1 and 3 the ratio of light transmitted to light reflected was determined and this ratio along with the amount of light reflected to the side cell during run 2 was used to calculate the lamp output during run 2. This value was checked by averaging the lamp outputs determined in runs 1 and 3. Available light was corrected for light transmitted to the back cell during run 2. Potassium ferrioxalate actinometry was employed.[27]

Filter Solutions. For preparation of filter solutions, nickel sulfate hexahydrate and cobalt sulfate heptahydrate were used in 10% sulfuric acid for filter A and 5% sulfuric acid for filters B and C. Stannous chloride dihydrate and bismuth trichloride were each used in 10% hydrochloric acid. Filter transmission was measured in a cell containing three 2.4-cm optical path compartments balanced against a 7.2-cm cell containing water: filter A, cell I, 90 g of nickel salt/l.; cell II, 200 g of cobalt salt/l.; cell III, 10.2 g of tin salt/l.; transmission (275–365 nm, max at 317 nm) 220–275 0%; 292 nm, 30%; 317 nm, 60%; 342 nm, 30%; 365–400 nm, 0%; filter B, cell I, 263 g of nickel salt/l.; cell II, 225 g of cobalt salt/l.; cell III, 0.03 g of bismuth salt/l.; transmission (245–310 nm and 337–355 nm) 220–245 nm, 0%; 263 nm, 30%; 277 nm, 60%; 295 nm, 30%; 310–337 nm, 0%; 343 nm, 4%; 355–400 nm, 0%; filter C, cell I, 263 g of nickel salt/l.; cell II, 225 g of cobalt salt/l.; cell III, distilled water; transmission (225–350 nm) 220–225 nm, 0%; 230–240 nm, 10%; 252 nm, 20%; 275–310 nm, 40%; 330 nm, 20%; 350–400 nm, 0%.

Quantum Yields for Optically Active 2,2′-Dimethyl-6,6′-diethylbiphenyl. Dilute solutions of 0.0009–0.0017 *M* optically active 2,2′-dimethyl-6,6′-diethylbiphenyl were irradiated on the macroapparatus. Although there was no change in optical density in the sensitized runs, the optical density at 263 nm did increase somewhat (<30%) in the direct runs, and did not decay overnight in a stoppered cell. The quantum yield of racemization was extrapolated to 0% conversion. Photolyzed solutions were concentrated *in vacuo* and then subjected to chromatography on at least one of two columns. Column A was a 1.5 × 10 cm deactivated silica gel (Grace grade 950, 60–200 mesh which was swamped with water, filtered, and dried for 18 hr at 50°) slurry packed with pentane. Elution with pentane while collecting 50-ml fractions gave: fraction 1, a saturated hydrocarbon oil; 2–3, 2,2′-dimethyl-6,6′-diethylbiphenyl which was contaminated with various isomers in some runs; 4, nil. Column B was a 1.5 × 115 cm deactivated silica gel (*vide supra*) column slurry packed with hexane. Elution with hexane while scanning at 263 nm and collecting 40-ml fractions gave: fractions 1–26, nil; 27–36, 2.2′-dimethyl-6,6-′diethylbiphenyl; 37–48, 2,2′-dimethyl-6,6′-diethylbiphenyl which showed the presence of some isomers in the cyclohexane runs. Data for individual quantum yields are listed as follows: mass starting material, added reagent if any, solvent, filter, light input, columns used, mass of recovered starting material, per cent racemization,[24] quantum yield for disappearance of starting material, quantum yield of racemization, mass of isomers, quantum yield of isomer formation.

QY-D1. Starting biphenyl (229.0 mg, 0.962 mmol); 750 ml of cyclohexane; filter B, 13.3 mEinsteins; columns A and B; 186.0 (0.782 mmol) of recovered biphenyl; 2.3% racemized; $\Phi_{\text{disapp}} = 5.8 \times 10^{-3}$; $\Phi_{\text{rac}} = 1.35 \times 10^{-3}$; 0.68 mg of isomers; $\Phi_{\text{isom}} = 2.2 \times 10^{-4}$.

QY-D2. Starting biphenyl (299.0 mg, 1.25 mmol); 750 ml of cyclohexane; filter B; 36.0 mEinsteins; columns A and B; 246.9 mg (1.04 mmole) of recovered biphenyl; 3.0% racemized; $\Phi_{\text{disapp}} = 4.2 \times 10^{-3}$; $\Phi_{\text{rac}} = 8.8 \times 10^{-4}$; 3.45 mg of isomers; $\Phi_{\text{isom}} = 4 \times 10^{-4}$.

QY-D3. Starting biphenyl (177.0 mg, 0.745 mmol); 750 ml of cyclohexane; filter C; 50.9 mEinsteins; columns A and B; 131.1 mg (0.551 mmol) of recovered biphenyl; 3.3% racemized; $\Phi_{\text{disapp}} = 3.9 \times 10^{-3}$; $\Phi_{\text{rac}} = 3.6 \times 10^{-4}$; 3.60 mg of isomers; $\Phi_{\text{isom}} = 3 \times 10^{-4}$.

QY-S1. Starting biphenyl (262.0 mg, 1.10 mmol); acetophenone 6.004 g (50.0 mmol); 750 ml of benzene; filter A; 6.61 mEinsteins; column A; 246.8 mg (1.04 mmol) of recovered biphenyl; 0% racemized; $\phi_{\text{rac}} = 0$.

QY-S2. Starting biphenyl (183.2 mg, 0.770 mmol); 750 ml of acetone; filter B; 14.0 mEinsteins; column B; 167.5 mg (0.704 mmol) of recovered biphenyl; 0% racemized; $\Phi_{\text{rac}} = 0$; no detectable isomers; $\Phi_{\text{isom}} = 0$.

Photolysis in Methanolic Hydrochloric Acid (D4). A 161.8-mg (0.680 mmol) sample of optically active 2,2′-dimethyl-6,6′-diethylbiphenyl in 750 ml of 0.2% by volume of hydrochloric acid in methanol was irradiated in the macrophotolysis apparatus using filter B until 24.4 mEinsteins of light had been absorbed. The photolyzed solution was diluted with ether, neutralized by standing overnight over anhydrous potassium carbonate, washed with saturated salt solution, dried over sodium sulfate, and concentrated *in vacuo* to give 159.3 mg of light yellow oil which was chromatographed on a 1.5 × 120 cm silicic acid (*vide supra*) column slurry packed with hexane. Elution in 40-ml fractions while scanning the eluent at 263 nm gave: fractions 1–9, hexane, nil; 10–18, hexane, 100.5 mg (0.422 mmol) of 2,2′-dimethyl-6,6′-diethylbiphenyl which was 2.6% racemized, $\Phi_{\text{rac}} = 4.5 \times 10^{-4}$, but showed no trace of isomers; 19–35, 1% ether–hexane, 1.3 mg of uncharacterized oil; 36–42, 10% ether–hexane, nil; 43–50, 10% ether–hexane, 17.7 mg of methoxy-containing products as a light yellow oil; 51–85, 50% ether–hexane, 17.1 mg of light yellow oil which was shown by ir and nmr to contain oxidation products; 86–100, ether, 22.2 mg of orange oil which was shown by ir and nmr to contain oxidation products.

Characterization of Methoxy Adducts. The spectral data were: ir (plate) 3.25, 3.35, 3.39, 3.47 (CH stretch), 6.80, 7.25, 9.05, (broad), 12.80 (broad), 13.20 μ (broad); nmr (100 MHz, CCl_4) τ 2.80–3.21 (m, 4 H, aryl H and one vinyl), 4.70–4.85 (m, 1 H, vinyl H), 5.86–6.04 (m, 1 H, benzylic cyclopropyl), 6.60–6.78 (m, 3 H, OCH_3), 7.40–7.64 (m, 4 H, ethyl CH_2), 7.80–7.94 (m, 6 H, aryl and vinyl CH_3), 8.64–8.82 (m, 7 H, ethyl CH_3 and cyclopropyl); mass spectrum *m/e* (per cent of base) 270 (78, parent), 255 (27), 241 (100), 209 (58); high-resolution mass determination, calcd, 270.1979; found 270.1992.

Acknowledgment. Support of this research by the National Science Foundation, the U. S. Army Research Office (Durham), and by a predoctoral National Institutes of Health Fellowship to D. C. is gratefully acknowledged.

---

(27) C. G, Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).