The Photocyclization of 1,5-Diphenyl-1,4-pentadiene. A Simple Synthesis of Bicyclo[2.1.0]pentanes[1a,b]

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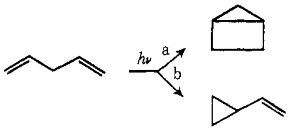
Abstract: Irradiation at 254 nm of a cyclohexane solution of *trans,trans*-1,5-diphenyl-1,4-pentadiene (**1**) affords, at low conversion, a mixture of *cis,anti*- and *trans*-2,3-diphenylbicyclo[2.1.0]pentane (respectively, **4** and **5**, with the former predominating); irradiation of the *cis,trans*-diene **2** under these conditions affords principally **5** while irradiation of the *cis,cis*-diene **3** gives a mixture of **5** and *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentane (**6**). These results demonstrate for the first time that *direct irradiation* of acyclic 1,4-dienes can lead to bicyclo[2.1.0]pentane formation instead of products resulting from a di-π-methane rearrangement. A mechanistic scheme is outlined involving singlet cis and trans 1,4 diradicals formed by vinyl–vinyl (2,4) bridging of dienes **1**–**3**. It is postulated that partial bond rotation precedes closure of the cis diradical or fragmentation of the trans diradical (regenerating diene).

A point of some interest in the application of orbital symmetry considerations to organic reactions is the molecular basis for selection between alternative symmetry-allowed processes.[2] The extensively investigated di-π-methane rearrangement[3] represents a particularly interesting case in point since this photochemical reaction, in the case of *direct irradiation of acyclic 1,4-dienes*, is reported to go exclusively by a symmetry-allowed ${}_{\pi}2_a + {}_{\sigma}2_a$ process[2–4,4a] giving vinylcyclopropanes (path b, eq 1) rather than by the alternative symmetry-allowed ${}_{\pi}2_s + {}_{\pi}2_s$ process to afford bicyclo[2.1.0]pentanes (path a, eq 1).[2] There exist a very limited number of examples of the simultaneous occurrence of processes a and b in mercury-photosensitized reactions of simple 1,4-dienes[5] (process b generally predominates here also) and photochemical reactions involving cyclic and bicyclic polyenes.[6] We shall describe here the first examples of the conversion of acyclic 1,4-dienes to bicyclo[2.1.0]pentanes by direct irradiation (path a).[7]



(1)

A number of studies have indicated that in photochemical reactions of acyclic nonconjugated dienes, electron delocalization in excited state species can play an important role in controlling directionality.[3,5a,8] The extensive studies by Zimmerman indicate, for example, the formation of the vinylcyclopropane J (Scheme I) consistent with the involvement of the more highly stabilized species of the pair G,H.[3] It is important to note that *all* of the acyclic 1,4-pentadienes studied by Zimmerman contain radical stabilizing substituents at C_3 (c in A or B) which should favor the sequences E → G → J and F → H → J (Scheme I). The di-π-methane rearrangement may be represented[3] in terms of a cyclic array of six orbitals (in Figure 1, d–e–f–g–h–i–) with a single sign inversion between orbitals i and d and is thus a Möbius system.[3] Zimmerman has argued that overlap between C_3 and C_5 (*i.e.*, orbital overlap g–h) in Figure 1 should lag behind the other processes shown, since, in the valence bond representation of Scheme I, bonding to the saturated sp^3-hybridized C_3 of diene A or B would not be expected without prior intervention of steps C → E → G

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[1] (a) We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 4109-B), and the University of Missouri-St. Louis for generous support of this work; (b) presented in part at the 7th Midwest Regional Meeting of the American Chemical Society, St. Louis, Missouri, Oct. 29, 1971; (c) National Science Foundation Undergraduate Research Participant, 1970.

[2] For examples, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[3] For studies involving acyclic dienes, see (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970); (c) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); (d) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971).

[4] A more sophisticated orbital representation for the di-π-methane rearrangement (presented below) may be preferred.

[4a] NOTE ADDED IN PROOF. Zimmerman has very recently presented evidence that formulation of the di-π-methane rearrangement as a $2_{\pi} + 2_{\sigma}$ process is in fact incorrect (H. E. Zimmerman and R. D. Little, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, ORGN 96).

[5] (a) J. Meinwald and G. W. Smith, *J. Amer. Chem. Soc.*, **89**, 4923 (1967); (b) R. Srinivasan and K. H. Carlough, *ibid.*, **89**, 4932 (1967).

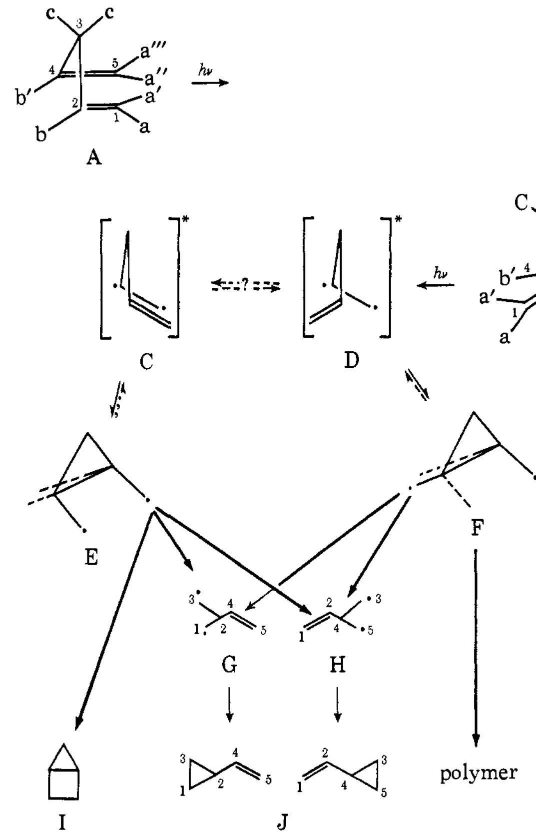
[6] (a) W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965); (b) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964); (c) I. G. Burstain, Ph.D. Thesis, U.C.L.A., 1967; (d) S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968).

[7] (a) We have previously reported a heterocyclic version of this process: E. Block and E. J. Corey, *J. Org. Chem.*, **34**, 896 (1969). (b) Subsequent to the completion of this work, Zimmerman has reported the detection of bicyclo[2.1.0]pentanes following direct irradiation of several 1,4-dienes. Thus *syn*-2,2,5,5-tetramethyl-3-phenylbicyclo[2.1.0]pentane is a lesser product in the direct irradiation of both *cis*- and *trans*-1-phenyl-3,3,5-trimethyl-1,4-hexadiene; the major product in each case results from a stereospecific di-π-methane rearrangement.[7c] Direct irradiation of 1,1,5,5-tetraphenyl-1,4-pentadiene gives very inefficiently 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane in addition to slightly larger amounts of the expected di-π-methane product. In this latter reaction, however, the bicyclopentane is shown to arise not from a ${}_{\pi}2_s + {}_{\pi}2_s$ process (which would give 2,2,3,3-tetraphenylbicyclo-[2.1.0]pentane) but rather by an initial 1,2 hydrogen sigmatropic shift (from C_3 to C_4) followed by 2,5 plus 1,3 bonding.[7d] The photochemical conversion of β,γ-unsaturated ketones to 2-oxabicyclo[2.1.0]pentane derivatives rather then the cyclopropyl ketones anticipated from an *oxa-di-π-methane rearrangement*[7e] has also been reported very recently.[7f] (c) H. E. Zimmerman, P. Baeckstron, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972). (d) H. E. Zimmerman and J. A. Pincock, *ibid.*, **94**, 6208 (1972). (e) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *ibid.*, **92**, 1786 (1970). (f) R. C. Cookson and N. R. Rogers, *Chem. Commun.*, 809 (1972).

[8] Other factors which may be important include kinetic factors of geometric origin[9a,b] and excited state orbital symmetry properties.[9b]

[9] (a) R. S. M. Liu and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 4936 (1967); (b) J. R. Scheffer and B. A. Boire, *ibid.*, **93**, 5490 (1971); (c) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

Scheme I[a]



[a] Substituents have been omitted in C–J.

(H) or D → F → H (G).[3] To the extent that g–h overlap is weak in the rate-limiting portion of the reaction, the orbital array h–i–d–e–f–g is linear and has been suggested to be roughly isoelectronic with 1,3,5-hexatriene.[3] Extension of this analogy permits the prediction that the hexatriene-like excited state for the di-π-methane rearrangement will be most stabilized by substitution at the *end* of the linear array, *i.e.*, at carbons 3 and 5, allowing conjugation with orbitals h and g.[3] Possible reaction rate enhancement for the di-π-methane rearrangement has been predicted for phenyl substitution at C_3.[3b] Alternative substitution (*i.e.*, at carbons bearing orbitals i, d, e, and f) would afford a cross-conjugated excited state of higher energy.[3] It is noteworthy that 2,5,5-trimethyl-1,3,6-heptatriene, a system which may be viewed as a C_3–C_5-substituted 1,4-pentadiene, undergoes the di-π-methane rearrangement[6a,9c] while analogous structures lacking the 5,5-dimethyl substituents do not.[9a]

The di-π-methane rearrangement may apparently be favored even in the complete absence of substituents or with substitution limited to *one* of the double bonds (*i.e.*, substitution at position 1 or 1 and 2 *only*).[10a] Other substitution patterns should favor the formation of products other than vinylcyclopropanes.[10b] In particular, it was anticipated that *simultaneous* radical stabilization at positions 1 and 5 (placing one substituent in a "cross-conjugated" position as described above) would improve the chances of closure of E to I (Scheme I) rather than rearrangement to G and H. The testing of this concept with 1,5-diphenyl-1,4-pentadiene provides the basis for our investigation as described herein.

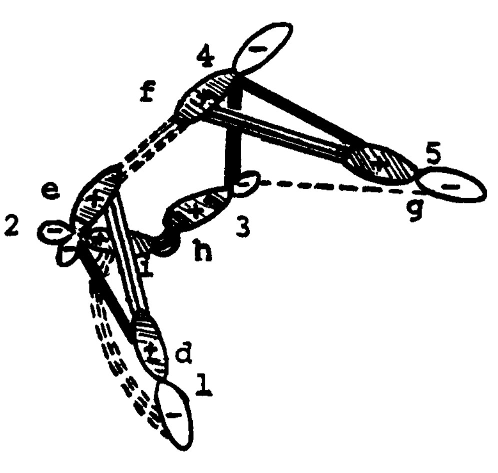
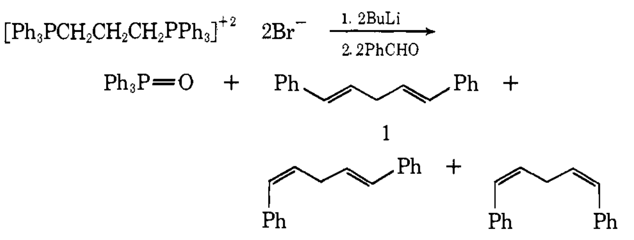


Figure 1. An orbital representation of the di-π-methane rearrangement[3]: ═══, bonds forming; ≡, bonds breaking; —, bonds unchanged.

Synthetic Aspects. The requisite dienes **1–3** were prepared as described by Wittig from the bisylide of trimethylene-1,3-bis(triphenylphosphonium) dibromide and benzaldehyde.[11] The three isomeric dienes **1**, **2**, and **3**, obtained in a ratio of *ca.* 1:3:6, respectively, were individually characterized following isolation by preparative glc. *trans,trans*-Diene **1** of 95% isomeric purity could be prepared by photoequilibration (at 350 nm) of the isomeric mixture **1–3** with diphenyl disulfide.[12] The spectral features of dienes **1–3**, summarized in Table I, are in good agreement with literature values for these compounds.[13]



$$[Ph_3PCH_2CH_2CH_2PPh_3]^{+2}\ 2Br^- \xrightarrow[2.\ 2PhCHO]{1.\ 2BuLi} Ph_3P{=}O + \mathbf{1} + \mathbf{2} + \mathbf{3}$$

1 **2** **3**

Preparative Photochemistry and Product Structure Proof. For preparative purposes a mixture of dienes **1–3** in *tert*-butyl alcohol was irradiated at wavelengths longer than 270 nm and the products isolated by chromatography on silver nitrate impregnated silica gel. In this manner there was isolated *cis,anti*-2,3-diphenylbicyclo[2.1.0]pentane (**4**; 15% yield), *trans*-2,3-diphenylbicyclo[2.1.0]pentane (**5**; 35% yield), and *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentane (**6**; 9% yield) in addition to a number of minor products and polymeric material. There was no evidence for vinylcyclopropane structures among the incompletely characterized minor products.[14]

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(10) (a) L. D. Hess and J. N. Pitts, *J. Amer. Chem. Soc.*, **89**, 1973 (1967). (b) We have limited consideration in Scheme I to processes initiated by 2–4 bonding. Initial bonding between carbons 2 and 5, 1 and 4, or 1 and 5 might also be favorable with appropriate substitution patterns (*cf.* ref 5, for example).

(11) G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).

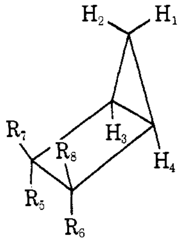
(12) C. Moussebois and J. Dale, *J. Chem. Soc. C*, 260 (1966).

(13) S. Brenner and J. Klein, *Israel J. Chem.*, 7, 735 (1969).

(14) (a) Certain phenyl-substituted vinylcyclopropanes have been reported to undergo photochemical rearrangement to bicyclo[2.1.0]-pentanes.[14b] However, the substitution pattern of the bicyclo[2.1.0]-pentanes predicted to be formed from the vinylcyclopropanes produced by di-π-methane rearrangement of **1–3** would be different from that obtained in these studies. (b) G. S. Hammond and H. Kristinsson, *J. Amer. Chem. Soc.*, **89**, 5970 (1967).

Table I. Comparison of Properties of Compounds **1–6**[a,b]

$(PhCH_a{=}CH_b)_2C(H_c)_2$



1, trans,trans
2, cis,trans
3, cis,cis

4, $R_5,R_6 = Ph;\ R_7,R_8 = H$
5, $R_5,R_8 = Ph;\ R_6,R_7 = H$
6, $R_7,R_8 = Ph;\ R_5,R_6 = H$

Compd	λ_{max}, nm (ϵ) (cyclohexane)[c]	Ir and near ir bands (μ; CCl_4)	Nmr spectra (in CCl_4)	
			Chemical shift (δ)	Coupling constant, Hz
1	260 (27,500), 285 (sh, 5200), 294 (sh, 2620), 300* (520), 350 (240)	10.31	H_a, H_b 5.85–6.55 (4 H), H_c 3.02 (2 H), H_{arom} 7.16 (10 H)	$J_{ab} = 15.8$, $J_{bc} = 5.4$, $J_{ac} < 0.5$
2	255 (21,400), 284 (sh, 2700), 293 (sh, 1600), 300* (510)	7.14, 10.31, 12.35	Superposition of nmr spectra of **1** and **3**	
3	248 (23,800), 280 (sh, 1090), 290 (sh, 475), 300* (186)	7.14, 12.35	H_a 6.46 (2 H), H_b 5.65 (2 H), H_c 3.28 (2 H), H_{arom} 7.18 (10 H)	$J_{ab} = 12$, $J_{bc} = 8$, $J_{ac} \simeq 2$
4	225 (5000), 262 (sh, 580), 272 (sh, 375)	2.225	H_1 1.08 (1 H), H_2 1.02 (1 H), H_3, H_4 2.00 (2 H), H_7, H, 3.28 (2 H), H_{arom} 6.95 (10 H)	$J_{48} = J_{37} = 0.01 \pm 0.22$
5	229 (5000), 264 (sh, 650), 271 (sh, 500)	2.221–2.225	H_1 0.87, H_2 0.79, H_3 1.84, H_4 2.06, H_6 3.55, H_7, 2.84 (1 H each), H_{arom} 7.05 (10 H)	$J_{46} = 4.57$, $J_{67} = 4.14$. $J_{37} = 0.60$
6	226 (5000)	2.224	H_1 0.79 (1 H), H_2 1.07 (1 H), H_3,H_4 1.97 (2 H), H_5,H_6 4.09 (2 H), H_{arom} 6.64 (10 H)	$J_{35} = J_{46} = 4.12$

[a] All compounds show a parent peak in their mass spectra at *m/e* 220 and very similar fragmentation patterns. [b] Glc retention times (155°) relative to n-$C_{20}H_{42}$ = 35.2 min: **1,** 31.9; **2,** 23.5; **3**, 15.7; **4,** 11.9; **5**, 17.0; **6,** 14.7 min. [c] Extinction coefficients (ϵ) at wavelengths (λ) where there is no defined shoulder (sh) or maximum are indicated by an asterisk. Compare the values with those reported for phenyl-1-pentene (K. Yasufuku, S. Hirose, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jap.*, **40,** 2139 (1967)): cis, 242 (13,500), 291 (144) nm, and trans, 251 (17,000), 284 (1095), and 293 (758) nm.

The spectral features of compounds **4–6** are indicated in Table I. The structural assignments are based primarily on detailed nmr studies involving decoupling experiments and complete computer simulation of each spectrum using LAOCN3.[15a] The chemical shifts and coupling constants are in good agreement with those reported by Wiberg for *endo*-2-hydroxybicyclo[2.1.0]pentane.[15b] A detailed discussion of the nmr spectra of these compounds is the subject of a separate paper.[16] The structural assignments for **4–6** find additional support in the appearance of a band in the near infrared at 2.221–2.225 μ, characteristic of cyclopropyl hydrogens,[17] and absent in the near-infrared spectra of **1–3**.

Discussion of Results

The detailed results of direct irradiation studies on the isomeric 1,5-diphenyl-1,4-dienes **1–3** are given in Table II. In most cases *ca.* 0.02 *M* solutions of isomers **1–3** of good isomeric purity were irradiated in quartz tubes (254-nm light) or in Pyrex tubes (at 300 or 350 nm) with cyclohexane solvent in a merry-go-round equipped Rayonet Reactor. Product composition was determined using quantitative glc with eicosane (or docosane) as internal standard or, in several cases, by isolation *via* chromatography. Experimental difficulties (*i.e.*, glc peak overlap) prevented product determination in runs of less than *ca.* 10% conversion. In the low conversion runs at 254 nm, where product balance is good, it is seen that (1) double bond isomerization occurs at approximately the same rate as bicyclopentane formation, (2) the *dominant* bicyclopentane formed is that predicted for a concerted $_{\pi}2_s + {}_{\pi}2_s$ photocycloaddition (**1** → **4**, **2** → **5**, **3** → **6**), and (3) significant amounts of isomer **5** are formed in both runs 1 and 3. In simultaneous irradiation of equal concentrations of isomers **1–3**, the rate of disappearance was found to be **3** > **2** > **1**. In the low conversion runs at 300 nm the trends are similar to those at 254 nm except that the efficiency of bicyclopentane formation has significantly diminished in contrast to the efficiency of photoisomerization (which is essentially

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(15) (a) LAOCN3 program: A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, Chapter 3; (b) K. B. Wiberg and D. E. Barth, *J. Amer. Chem. Soc.*, **91,** 5124 (1969).

(16) E. Block, H. W. Orf, and R. E. K. Winter, *Tetrahedron*, **28,** 4483 (1972).

(17) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31,** 295 (1966).

Table II. Product Distribution from Direct Photolysis of Dienes **1–3**

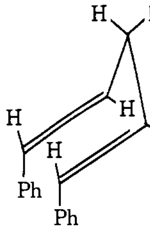
Run	Diene	λ (nm) of irrad	Total diene consumed, %	Absolute yields: Dienes % **1**	% **2**	% **3**	Bicyclopentanes % **4**	% **5**	% **6**	Material balance, %	Total yield of **4–6**[a]
				Low Conversion Runs							
1	**1**[b]	254	18	75.9	6.6	Negl	3.9	2.1	Negl	89	35
2	**2**[b]	254	15	5.7	77.2	2.0	0.6	6.3	0.2	92	47
3	**3**[b]	254	12	3.0	9.3	75.7	0.3	5.8	5.9	100	100
4	**1**[c]	300	24	53.9	21.8	0.9	0.55	0.36	Negl	78	4
5	**2**	300	9	3.9	82.3	5.2	0.2	2.9	Negl	95	36
6	**3**	300	14	1.8	9.2	75.2	0.3	2.1	2.7	91	37
				Higher Conversion Runs							
7	**1**[b]	254	86	6.7[d]	7.7[d]	Negl	13.7[d]	11.6[d]	Negl	92[e]	30
8	**2**	254	83	6.5	11.0	Negl	6.3	7.3	1.4	53	42
9	**3**	254	81	4.2	11.7	2.6	5.6	24.3	17.4	66	59
10	**1** + **2** + **3**	>270	82	4.8[d]	6.1[d]	7.2[d]	11.4[d]	27.8[d]	6.8[d]	67[f]	56
11	**1**[c]	300	84	7.1	6.4	3.0	1.9	2.1	Negl	21	5
12	**2**	300	79	5.4	9.0	6.7	0.9	9.2	Negl	31	13
13	**3**	300	97	2.0	1.5	Negl	1.2	7.4	10.5	23	20
14	**1** + **2** + **3**	300	80	Not determined (total = 20%, major = **3**)			5.1	11.0	Negl	36	20
15	**1**	350	64	20.0	11.9	3.5	Negl	1.1	Negl	36	1.7

[a] Corrected for unreacted starting material. [b] >98% pure by glc. [c] 85% **1** + 15% **2**. [d] Isolated. [e] Includes 19% of an unknown photoproduct (see Experimental Section) and 33% isolated polymer. [f] Includes 2.7% of benzylbenzoate, a contaminant of the original diene mixture; an additional 15% of six other products was obtained (see Experimental Section).

Table III. Quantum Yields in the Irradiation of Dienes **1–3**

Run	Diene	λ (nm) irrad	% diene consumed	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_{polymer}[a]
1	**1**	254	16	0.34[b]	0.10	Negl	0.065	0.034	Negl	0.14
2	**2**	254	27	0.108	0.37[b]	0.020	0.012	0.134	Negl	0.096
3	**3**	254	26	0.063	0.19	0.71[b]	Negl	0.13	0.056[c]	0.23
4	**1** + **2** + **3**	254	~30				0.032	0.105		
5	**1** + **2** + **3**	300	~50				0.003	0.023		

[a] Estimated (see Experimental Section). [b] $\Phi_{\text{disappearance}}$. [c] Minimum value (peak overlap prevented more accurate analysis); maximum value, 0.26.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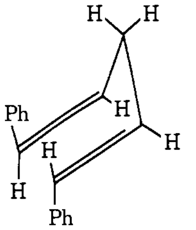
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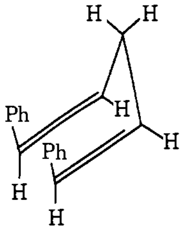
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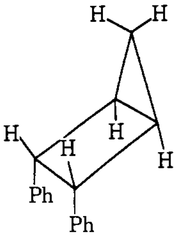
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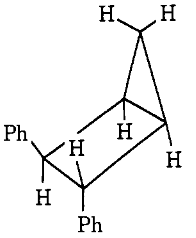
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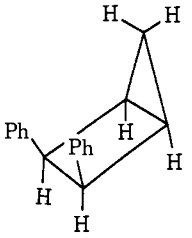
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unchanged). Irradiation at 350 nm leads to the formation of only very minor amounts of bicyclopentane **5** while extensive polymer formation occurs. At higher conversions, monomeric material balance, the stereoselectivity and the total bicyclopentane yield all decrease, while considerable polymeric material is formed. Photoproducts **4–6** are stable under the conditions of the irradiation studies and do not interconvert, although decomposition occurs on extended irradiation at all wavelengths used.

The quantum yields for bicyclopentanes **4–6** given in Table III and determined using a merry-go-round and potassium ferrioxalate or benzhydrol–benzophenone actinometry compare favorably with those reported by Zimmerman[3] and indicate moderately efficient photoprocesses at 254 nm. The formation of both *cis*- and *trans*-bicyclo[2.1.0]pentanes under conditions of direct irradiation to low conversion of pure isomers **1** or **3** (runs 1 and 3, Table II, respectively) implies that intermediates of sufficient lifetime for partial loss of stereochemistry are involved. The photoisomerization of the diene double bonds at rates competitive to rates of photocyclization suggests either the involvement of common intermediates for both these processes or else separate processes occurring with comparable overall rate constants.

The ultraviolet spectra of the 1,5-diphenyl-1,4-pentadienes as given in Table I indicate the absence of appreciable vinyl–vinyl interaction, suggesting no significant homoconjugation either in the ground state or during a vertical excitation process.[18] The spectra of *trans,trans*-diene **1** and *cis,cis*-diene **3** are very similar

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(18) Zimmerman has reached a similar conclusion from the ultraviolet spectra of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene.[8b] Also see ref 6c for studies on cyclic 1,4-dienes.

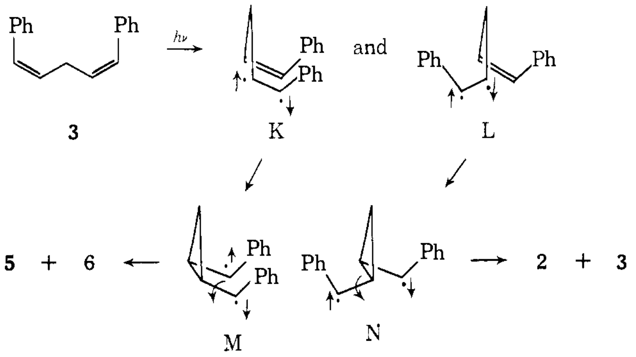
to the ultraviolet spectra of the corresponding isomers of 1-phenyl-1-pentene[19] and related compounds, differing only in the occurrence of a 6–10-nm bathochromic shift in compounds **1** and **3** compared to the latter model compounds. There is no evidence for hyperchromicity in **1–3** (compared to the model compounds) in contrast to the somewhat analogous "homoconjugated" structure, 1,4-diphenyl-3-buten-1-one.[20]

We may therefore use styrene and β-substituted styrenes as reasonable models in discussions of the photochemistry of dienes **1–3**.

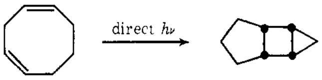
Current evidence suggests that the dimerization of styrene and β(alkyl)-substituted styrenes on direct irradiation is singlet derived[21] while photoisomerization of the alkyl-substituted styrenes under these conditions may be entirely singlet or may have a singlet and triplet component.[21c,22] There is ample evidence for the facile photopolymerization of styrene and derivatives in solution[21a,c,23,24] as well as the photopolymerization and easy oxidation of 1,4-pentadienes.[5,6c,25]

We propose that direct photolysis at 254 nm of the isomeric 1,5-diphenyl-1,4-pentadienes, which molecular models suggest may exist preferentially in the anti rather than syn form, produces the corresponding vertical singlets K and L (Scheme II; illustrated for the cis,cis compound **3** only) which with minimal geometric distortion could close to syn and anti diradicals M and N.[26] We suggest that *singlet* species M might possess a sufficient lifetime to permit some bond rotation because of (a) the stabilizing effect of the phenyl groups and (b) the fact that bringing the spin centers close enough to permit bond formation must involve development of some of the exceptional ring strain found in the bicyclo[2.1.0]pentane system.[27] We further suggest that singlet species N, which is obviously incapable of ring closure, might dissipate some of its energy by free rotation and then return to the ground state by a fragmentation process (effectively internal conversion). Some of the photoisomerization is also explicable in terms of a direct process involving species K and L. The lifetimes of radicals M and N are apparently not sufficiently long to permit complete randomization with respect to rotation about the methylene single bonds.[28,29] Thus we can account for most of the observations associated with direct irradiation at 254 nm with radicals M and N. A parallel photolysis of isomer **2** in the presence and absence of piperylene (2 *M*) at 254 nm (entries 2 and 1, Table IV, respectively) indicated no difference in the ratio nor amounts of dienes **1–3**, indicating that if triplet species are involved in this isomerization they are very short lived. Bicyclopentane formation was quenched to the extent of 36% (there was, however, no change in the ratio of the bicyclopentanes). This observation indicates that there may be a quenchable triplet component for the photocyclization process; it is also possible that some chemical reactions are occurring involving the piperylene and the singlet syn radical M (but not the anti radical N) forming adducts. This latter proposal finds support in the observation of glc peaks in run 2 but not run 1 with retention times as high as that of the internal standard *n*-docosane. Other aspects of the cophotolysis of dienes **1–3** and piperylene are discussed below.

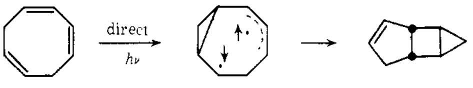
Scheme II



The proposal involving diradicals M and N developed above find support and precedence in a variety of studies. Thus, it is reported that direct irradiation of 1,4-cyclooctadiene (**7**) affords the syn tricyclic structure **8** (shown to be the thermodynamically *less* stable structure) with $>99\%$ stereospecificity at low conversion[6c,d] while direct irradiation of 1,3,6-cyclooctatriene (**9**) affords the anti structure **11**.[6ab,c] Tricyclic structures of type **11** (or its syn isomer) are not formed during sensitized irradiation of the cyclooctatriene. It is suggested that the extra double bond in **9** stabilizes the singlet intermediate **10** sufficiently to permit it to collapse to the sterically less crowded, thermodynamically more stable anti tricyclic olefin **11**.[6c] The isomerization of the 1,3,6-heptatrienes studied by Hammond[9a] is postulated to involve triplet diradicals analogous to M and N, Scheme II.[9c] The fragmentation of diradical **13**, produced in the gas phase by photolysis of bicyclo[3.1.0]hexan-3-one (**12**),



7 8



9 10 11

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[19] See Yasufuku, *et al.*, footnote *c*, Table I.

[20] D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, 93, 1153 (1971).

[21] (a) W. G. Brown, *ibid.*, 90, 1916 (1968); (b) H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *Tetrahedron*, 24, 2183 (1968); (c) J. R. Pajak, Ph.D. Thesis, Purdue University, 1971; *Diss. Abstr.*, *B*, 32, 839 (1971).

[22] Certain observations by Zimmerman[3c] are also suggestive of photoisomerization *via* a singlet excited state[3b] in aryl olefin systems. Also see (a) A. Padwa and F. Albrecht, *J. Amer. Chem. Soc.*, 94, 1000 (1972) and (b) J. Saltiel and E. D. Megarity, *ibid.*, 94, 2742 (1972).

[23] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 505.

[24] F. R. Mayo, *J. Amer. Chem. Soc.*, 90, 1289 (1968).

[25] G. Wittig and B. Obermann, *Chem. Ber.*, 68, 2214 (1935).

[26] Hammond has argued that "cyclization of triplet biradicals to form three-membered rings appears to be competitive with rotation rates."[9a] Such arguments might also be applied to sufficiently long-lived singlets.

[27] For a discussion of the strain energy of bicyclo[2.1.0]pentane, see R. B. Turner, *et al.*, *J. Amer. Chem. Soc.*, 90, 4315 (1968).

[28] From pyrolysis studies involving somewhat analogous singlet diradicals Hammond has concluded that "rates of ring closure are only modestly smaller than the rates of internal rotation": G. S. Hammond and C. D. DeBoer, *ibid.*, 86, 899 (1964).

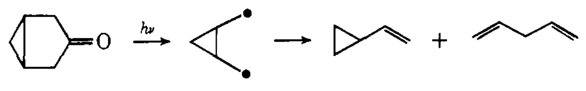
[29] L. A. Paquette and J. A. Schwartz (*ibid.*, 92, 3215 (1970)) and W. R. Roth and M. Martin (*Tetrahedron Lett.*, 3865 (1967)) have both presented examples of loss of stereochemistry during the fragmentation of singlet 1,4 diradicals; also see C. P. Casey and R. A. Boggs, *J. Amer. Chem. Soc.*, 94, 6457 (1972).

Table IV. Photolysis of Dienes **1–3** in the Presence of Piperylene[a,b]

Run	Substrate[c]	λ (nm) of irrad	% diene consumed[d]	Dienes[f]			Bicyclopentanes[f]		
				% **1**	% **2**	% **3**	% **4**	% **5**	% **6**
1	**2**[e]	254	37	18	42	2.6	3	28	1.3
2	**2**[e] + 2 *M* P	254	39	16	42	2.7	1.9	18	<0.7
3	**1** + **2** + **3**	300	80				6.4	13.8	
4	**1** + **2** + **3** + 0.01 *M* P	300	80				6.4	16.0	
5	**1** + **2** + **3** + 0.05 *M* P	300	80				7.6	20.6	
6	**1** + **2** + **3** + 0.1 *M* P	300	80				9.4	25.0	
7	**1** + **2** + **3** + 0.5 *M* P	300	80				9.6	25.6	
8	**1** + **2** + **3** + 1 *M* P	300	80				9.1	22.8	
9	**1** + **2** + **3** + 1.5 *M* P	300	80				9.6	22.2	
10	**1** + **2** + **3** + 2 *M* P	300	80				8.5	20.6	
11	**1** + **2** + **3** + 4 *M* P	300	80				7.8	17.8	
12	**1** + **2** + **3** + neat P (10 *M*)	300	80				6.0	11.9	

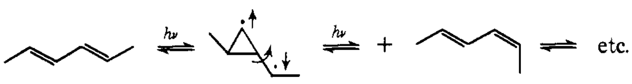
[a] Runs 1 and 2 and runs 3–12 each done simultaneously in a merry-go-round. The solvent, except in run 12, is cyclohexane; the concentration of **2** in runs 1 and 2 is 0.0063 *M* while the concentration of **1** + **2** + **3** in the remaining runs is 0.0133 *M*. Yields were determined by quantitative glc with docosane as internal standard. [b] In runs 2 and 4–12 but not in runs 1 and 3 glc peaks with retention times as high as that of docosane were observed. [c] P = piperylene. [d] Given as total diene **1** + **2** + **3** reacted. [e] 99.5% **2** + 0.5% **3**. [f] Weight of **1–6** (separately) divided by weight of dienes **1–3** originally present at beginning of photolysis.

has been reported by Pitts.[30] The photoisomerization



12 13

of 2,4-hexadienes on direct irradiation is postulated to involve bond rotation in the cyclic *singlet* species **14**.[31]



14

Excimers[32] have been invoked to explain the remarkable stereospecificity of the photodimerization of styrene and 1-*p*-methoxyphenyl-1-propene to give predominantly or exclusively the cis head-to-head dimers.[21a,b] Although intramolecular excimer formation[33] may be possible for dienes **1–3**, examination of molecular models indicates that attainment of a parallel arrangement of the styryl groups (believed necessary for excimer formation in general) cannot be achieved.

In order to explain the observed wavelength dependency of bicyclopentane and polymer formation, we suggest that these processes involve different excited states populated by absorption processes with maxima at different wavelengths. Spectroscopic studies on styrene and derivatives indicate that there are two bands at longer wavelengths: a band at about 280 nm ($\epsilon \sim 10^2$–10^3) which is relatively insensitive to conjugation effects, and a more intense band at about 250 nm ($\epsilon \sim 10^4$) which is much more strongly shifted by conjugation. The first band (variously represented as a ^1L_b, $^1B_{2u}$, or B band) is best considered as arising from a local excitation within the benzene ring while the second band (labeled a ^1L_a, $^1B_{1u}$, or K band) is viewed as an extensively delocalized $\pi \rightarrow \pi^*$ band.[34] In benzene the lowest triplet state can mix with the $^1B_{2u}$ state.[34] We propose that the photocyclization and photoisomerization processes are derived primarily from the second $^1B_{1u}$ band while polymerization (at least in part) is a consequence of population of the first $^1B_{2u}$ band. An attractive possibility is that a triplet diradical, produced by intersystem crossing from the singlet corresponding to excitation of the $^1B_{2u}$ band, is primarily responsible for the destruction of dienes **1–3** by polymerization or other radical processes. In order to test this possibility, dienes **1–3** were irradiated at 300 nm in the presence of varying concentrations of piperylene (Table IV). We observed a 75% increase in the yield of bicyclopentanes (without any significant change in the stereoselectivity) in the presence of 0.1 *M* piperylene and lesser increases above or below this concentration level. In the glc traces for reactions carried out in the presence (but not in the absence) of piperylene, peaks were observed with retention times as high as that of the internal standard, *n*-docosane ($C_{22}H_{46}$). Irradiation at 350 nm in the presence of 0.5 *M* piperylene greatly reduced the rate of disappearance of dienes **1–3** compared to a parallel run carried out in the absence of piperylene. It would appear that the piperylene is trapping to some extent the species responsible for the destruction of dienes **1–3**. At higher concentrations the piperylene may be capable of undergoing photochemical reactions with these dienes, accounting in part for the poor product balance.[35]

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(30) See ref 10a.

(31) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **92** 3227 (1970).

(32) For a general discussion, see J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970.

(33) See, for example, S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 507 (1972).

(34) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963.

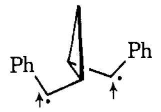
(35) For a possibly related example of the enhancement of a photochemical reaction by piperylene, see R. O. Campbell and R. S. H. Liu, *J. Chem. Soc. D*, 1191 (1970).

Table V. Product Distribution from Sensitized Irradiation of Dienes **1–3**[a]

Run	Diene (concn, M)	% diene consumed[b]	Senst[d] (concn), M	Irrad time, min	Dienes[c] % **1**	Dienes[c] % **2**	Dienes[c] % **3**	Bicyclopentanes[c] % **4**	Bicyclopentanes[c] % **5**	Bicyclopentanes[c] % **6**
1–5	**1** + **2** + **3**	0		0	19	33	48			
1	**1** + **2** + **3** (0.012 M)	20	None	600	18	28	34	Negl	0.6	Negl
2	**1** + **2** + **3** (0.012 M)	43[e]	TA (0.11 M)[f]	600	24	19[e]	14	Negl	5.9	1.8
3	**1** + **2** + **3** (0.0088 M)	16	TA (0.0072 M)[g]	85	31	39	31	Negl	1.5	Negl
4	**1** + **2** + **3** (0.008 M)	~100	TA (0.0016 M)	8640	Negl	Negl	Negl	Negl	25[h]	4[h]
5	**1** + **2** + **3** (0.0104 M)	38	TE (0.0051 M)	150	29	20	13	Negl	5.7	Negl
6–7	**1**	0		0	95	3	2			
6	**1** (0.0074 M)	15	None	114	76	6	3	Negl	Negl	Negl
		26[i]	None	250	62	9	3	Negl	Negl	Negl
7	**1** (0.0135 M)	18	TE[j] (0.0029 M)	30	74	8	Negl	Negl	Negl	Negl
		27[i]	TE[j] (0.0029 M)	114	53	17	3	Negl	0.3	Negl
		40	TE[j] (0.0029 M)	250	35	19	6	Negl	1.1	Negl

[a] Irradiation at 350 nm in cyclohexane as solvent at 35°. [b] Given as total diene **1–3** reacted. [c] Weight, as determined by glc, of **1–6** present at the time indicated divided by weight of total amount of diene **1–3** originally present at the beginning of photolysis. [d] TA = triphenylamine, TE = triphenylene. [e] Estimated value; overlap of sensitizer peak in glc prevented accurate determination. [f] Sensitizer is absorbing >99% of incident radiation. [g] Sensitizer is absorbing >90% of incident radiation. [h] Isolated yields; overall yield of **5** on extended *direct* irradiation at 350 nm of **1–3** is only *ca.* 5%. [i] Graphically determined. [j] Solvent is benzene.

Table V summarizes the results of sensitized irradiation of isomers **1–3**. Irradiation of **1–3** at 350 nm in the presence of acetone (used as solvent), acetophenone, diphenylamine, or chlorobenzene as sensitizer led to the destruction of **1–3**; irradiation in the presence of dibenzofuran was ineffectual, while irradiation in the presence of triphenylamine and triphenylene led to the formation of bicyclopentane **5** (minor amounts of **6** were also formed in some runs). Triphenylamine led to the formation of bicyclopentanes **5** and **6** in a total yield that was *ca.* 50% of the best yield of **4**, **5**, and **6** obtained by direct irradiation at 254 nm while triphenylene-sensitized irradiation led to a far poorer yield of bicyclopentanes. Both photosensitized runs appeared to be of very poor efficiency requiring several days of irradiation for completion of the reaction. It is apparent that photoisomerization and photocyclization can occur by a triplet pathway. It is less apparent why there is principally destruction of **1–3** on direct irradiation at long wavelength (*i.e.*, 350 nm) while sensitized irradiation under these same conditions can lead to reasonable yields of bicyclopentanes, since according to our postulates *both* processes should involve triplet species. One possibility is that the (triplet) radical species presumed to be responsible for destruction of starting material (**15**) might be trapped by a reducing agent such as *N*-phenyl-11,12-dihydrocarbazole, postulated as an intermediate formed on irradiation of triphenylamine.[36] Indeed, under the conditions of sensitized irradiation with triphenylamine, the amine is rapidly consumed when low concentrations are used. The decreased effectiveness of triphenylene might then be a consequence of its inability to trap **15**. Destruction of **1–3** by the carbonyl sensitizers may reflect chemical reactions (*e.g.*, at reactive C-3)[37] while the action of chlorobenzene may be a consequence of the photochemical production of hydrogen chloride.[3a]



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Summary

Our results indicate that, with the appropriate substitution pattern, bicyclo[2.1.0]pentanes are as accessible as vinylcyclopropanes from the direct photolysis of acyclic 1,4-dienes. Worthy of further study is the apparent action of piperylene and by-products from the photolysis of triphenylamine as quenchers of radical species, a possibility which should be borne in mind when using these substances in photochemical studies. This effect might in fact be advantageously employed to minimize destructive radical processes in other photochemical reactions.

Experimental Section[38]

1,5-Diphenyl-1,4-pentadiene Isomers 1–3. The procedure of Wittig[11] was followed with minor modifications. Thus, to a sus-

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(36) (a) See, for example, H. Shizuka, Y. Takayama, T. Morita, S. Matsumoto, and I. Tanaka, *J. Amer. Chem. Soc.*, **93**, 5987 (1971). (b) We cannot at this time exclude the alternative possibility that triphenylamine is acting as a *singlet* sensitizer.

(37) See T. R. Evans, *Tech. Org. Chem.*, **14**, 297 (1969).

(38) Melting points are corrected. Analyses were carried out by Chemalytics, Tempe, Ariz. The infrared spectra were recorded on Perkin-Elmer Model 137 and 337 spectrometers. The near-infrared spectra and ultraviolet spectra were recorded on a Perkin-Elmer Model 450 spectrometer; nmr determinations were made on Varian T-60 and HA-100 instruments in CCl_4 solvent with chemical shifts, δ, reported in parts per million downfield from internal tetramethylsilane standard. Mass spectra were determined on an AEI Model MS-12 mass spectrometer using a direct inlet. Gas–liquid chromatography (glc) was accomplished on a Hewlett Packard Model 5750 instrument (flame ionization detector). A $^1/_8$ in. × 6 ft column of 10% silicone rubber UC-W98 on 80–100 mesh Chromosorb W and a $^1/_4$ in. × 4 ft column

pension of 50 g of trimethylene-1,3-bis(triphenylphosphonium) dibromide[11] (69 mmol; mp 333–335°) in 400 ml of anhydrous ether in a 1-l. flask equipped with addition funnel, thermometer, magnetic stirrer, and condenser with nitrogen inlet was added under nitrogen 141 ml of 0.97 *M* *n*-butyllithium (138 mmol) in hexane. The brick red mixture was stirred for 2 hr, cooled to 0°, and then treated with 14.6 g of freshly distilled benzaldehyde (138 mmol). The dark solution was heated at 65° for 6.5 hr after which time the solution was light yellow with a white precipitate. The mixture was filtered; the yellow filtrate was washed several times with 350-ml portions of 0.01 *N* HCl and then 100 ml of saturated brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* affording 10.4 g of crude yellow liquid. Distillation of the latter gave as the main fraction 6.6 g (44%) of a colorless distillate, bp 105–120° (0.005 mm), showing three peaks on glc analysis at 15.7 (57%), 23.5 (33%), and 31.9 (10%) min compared to a retention time of 35.2 min for *n*-eicosane (155° on the $^{1}/_{8}$-in. silicone rubber column). The mixed isomers were used directly in photolyses or the individual isomers were isolated by preparative glc. The physical constants are recorded in Table I.

Preparation of *trans,trans*-1,5-Diphenyl-1,4-pentadiene (1). A solution of 384 mg of mixed isomers **1–3** and *ca.* 400 mg of diphenyl disulfide in 70 ml of cyclohexane was irradiated for 90 min at 350 nm in a Rayonet photoreactor according to the procedure of Moussebois and Dale.[12] Analytical glc indicated the enhancement of the 31.9-min peak at the expense of the 15.7- and 23.5-min peaks. The latter peaks were practically gone after 60 min of irradiation. Dry column chromatography[39] on Woelm alumina (24 × 1.25 in. nylon column) with *n*-heptane as developing solvent afforded 115 mg of a colorless liquid which was purified further by molecular distillation at high vacuum. Analysis by glc indicated a single major peak of retention time 31.9 min with only minor amounts of the isomers with shorter retention times. The spectral properties of this compound, characterized as *trans,trans*-1,5-diphenyl-1,4-pentadiene (**1**), are recorded in Table I.

The stereoisomers could also be separated by preparative glc on a 3-ft UC-W98 column at 180°. Analysis by uv, ir, nmr, and mass spectral methods, as summarized in Table I, allowed the assignment of the 15.7-, 23.5-, and 31.9-min glc peaks as *cis,cis*-, *cis,trans*-, and *trans,trans*-1,5-diphenyl-1,4-pentadiene (**3**, **2**, **1**), respectively.

Anal. Calcd for *cis,cis*-1,5-diphenyl-1,4-pentadiene (**3**), $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.47; H, 7.14.

Isomers **1–3** had significant mass spectral fragments at *m/e* 220 (parent), 129 ($P - C_7H_7$), 128 ($P - C_7H_8$), 143–141, 117–115, 92, 91, 77, and 205–202. Since the isomeric dienes **1–3** turned yellow and became viscous on standing at room temperature (with the trans,-trans isomer **1** apparently being the most labile) they were stored under argon at −20° until needed.

Preparative Photolysis of Mixed Isomers 1–3 at 270 nm. A sample of 1.5039 g of mixed isomers **1–3** was dissolved in 500 ml of reagent *tert*-butyl alcohol through which solution was bubbled rigorously deoxygenated nitrogen[40] for 30 min. The sample was then irradiated at 25° for 6.5 hr with continued nitrogen bubbling using a 450-W Hanovia lamp equipped with a Corex filter. Removal of the *tert*-butyl alcohol *in vacuo* left 1.5169 g of a slightly yellow, turbid oil of which 0.1080 g was chromatographed on a 10.6 × 1.25 cm column containing 15 g of silica gel–silver nitrate. The absorbant was prepared by slurrying 200 g of 100–200 mesh silica gel (Davison Chemical) and 10 g of Celite 545 in a solution containing 100 g of silver nitrate in 180 ml of distilled water in a 2-l. flask, removing most of the water on a rotary evaporator at 50–60° for 3 hr and then air drying the pulverized product at 120° overnight. Elution was with pentane (150 ml, 10-ml fractions 1–14, no products) followed by 100 ml of 10:1 pentane–methylene chloride (fractions 15–22), 400 ml of 5:1 pentane–methylene chloride (fractions 23–55), 300 ml of 1:1 pentane–methylene chloride (fractions 56–85), and finally 250 ml of pure methylene chloride (fractions 86–100). Fractions were combined following glc analysis of each fraction; removal of the solvent afforded the following weights (given as combined fraction no., fractions combined, weight): no. 1, 28–32, 1.38 mg; no. 2, 35–46, 28.71 mg; no. 3, 47–50, 7.45 mg; no. 4, 51–56, 5.17 mg; no. 5, 58–60, 3.2 mg; no. 6, 62–85, 25.67 mg; no. 7, 86–90, 4.12 mg; no. 8, 91–99, 12.30 mg. The weight of total recovered material was 88.1 mg (81% recovery).

Combined fraction no. 8 from a larger scale silver nitrate chromatography was recrystallized from absolute ethanol at −15° affording a colorless crystalline solid, mp 78–78.5°, characterized as *cis,anti*-2,3-diphenylbicyclo[2.1.0]pentane (**4**) by spectral means as summarized in Table I. The molecular weight determined mass spectrometrically was 220.1252 (calcd for $C_{17}H_{16}$, 220.1252).

Combined fraction no. 2 from a larger scale silver nitrate chromatography was further purified by preparative glc at 149° on an 18 × 0.25 in. silicone rubber column. The major component was characterized by spectral methods as *trans*-2,3-diphenylbicyclo-[2.1.0]pentane (**5**), as summarized in Table I.

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.25; H, 7.36.

Combined fraction no. 5 (together with fractions from a larger scale chromatography) was subjected to preparative glc as above yielding a practically colorless low melting solid characterized as *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentane (**6**) by spectral methods (see Table I). The molecular weight determined mass spectrometrically was 220.1250 (calcd for $C_{17}H_{16}$, 220.1252). From this same fraction there was also isolated a small amount of a colorless liquid characterized by nmr, ir, and mass spectral analysis as benzyl benzoate (in particular its infrared spectrum was identical with that of authentic material).

Combined fraction no. 6 from a larger scale silver nitrate chromatography afforded on preparative glc under the above conditions pure samples of starting dienes **1**, **2**, and **3** in addition to some photoproduct **6**.

Analysis by glc and nmr of each combined fraction allowed the following analysis to be made of total product composition (given as product, weight, retention time relative to $n\text{-}C_{20}H_{42}$ = 35.2 min (at 155°), and, in the case of photoproducts **4–6**, yield based on unrecovered **1–3**): **1**, 5.16 mg, 31.9 min; **2**, 6.60 g, 23.5 min; **3**, 7.83 mg, 15.7 min; **4**, 12.36 mg, 11.9 min, 14.5%; **5**, 30.0 mg, 17.0 min, 35%; **6**, 7.4 mg, 14.7 min, 8.7%; benzyl benzoate (a contaminant present in the original mixture of dienes **1–3**), 2.90 mg, 10.9 min; A, 2.06 mg, 11.9 min; B, 1.38 mg, 14.7 min; C, 0.80 mg, 20.0 min; D, 6.79 mg, 20.0 min; E, 4.76 mg, 23.5 min; F, 0.22 mg, 38 min. The weights of **1–6** were determined gas chromatographically using an internal standard and authentic samples of pure **1–6** to calibrate the instrument; the weights of unknown products A, B, C, D, E, and F are estimated from nmr analysis and glc peaks areas (assuming similar response factors as for **1–6**). The most reproducible glc results were achieved using high flow rates and keeping the column temperature below 175° where photoproduct **4–6** decomposition begins.

Unknown peak A showed nmr bands at δ 2.6–3.0 (m, 2 H), 3.0–3.4 (m, 1 H), 3.84 (m, 1 H), 5.83 (sym, m of >13 peaks, 2 H), and 7.10 (s, 10 H). It is unlikely that this compound is a vinylcyclopropane in view of the absence of peaks at higher field than δ 2.6. Unknown peak B appeared to be a mixture of compounds probably incorporating the solvent or a solvent contaminant, since the integrated area in the δ 0.8–3.0 region was larger than the area in the aromatic region (δ 7.0–7.2). There was no evidence for olefinic protons (no bands between δ 4.0 and 7.0). Peaks D and E were incompletely separated from photoproduct **5**. Nmr of the mixture indicated nmr bands of **5** with an additional sharp singlet at δ 1.27 and enhanced absorption at δ 2.03. There were no olefinic proton bands in the region δ 4.0–7.0.

Direct (254-nm) Irradiation of *trans,trans*-1,5-Diphenyl-1,4-pentadiene (1). A solution of 62.8 mg of diene **1** and 19.6 mg of eicosane ($C_{22}H_{46}$) in 18 ml of cyclohexane was irradiated in quartz at 254 nm using a Rayonet Model RPR-100 photochemical reactor. After irradiation for 2 hr, the solution was concentrated *in vacuo* and the reaction products isolated by preparative tlc on silver nitrate impregnated silica gel with methylene chloride as elutant. The tlc plates were prepared from 165 g of Merck PF_{254} silica gel and a solution of 82.5 g of silver nitrate in 350 ml of distilled water; the 1.5 mm thick plates were air dried in the dark at room temperature overnight. The following fractions were isolated (corrected for aliquots removed for glc analysis): R_f 0.92, 19.8 mg, pure eicosane; R_f 0.80, 21.8 mg, mixture of *trans*-2,3-diphenylbicyclo[2.1.0]pentane (**5**, estimated weight 6.9 mg = 13% yield based on unrecovered diene), unknown photoproducts (nmr very similar to spectrum of unknown products D and E; estimated weight 11.9 mg), and *cis,-trans*-diene **2** (3.1 mg); R_f 0.65, 8.2 mg of a mixture of dienes **1–3**; R_f 0.43, 17 mg which on recrystallization twice from 95% ethanol afforded 8.6 mg of crystalline *cis,anti*-2,3-diphenylbicyclo[2.1.0]-pentane (**3**, 17% yield); R_f 0.21, 7.8 mg of yellow-brown polymeric material. An additional 13 mg of cyclohexane-insoluble polymer

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of 20% UC-W98 on 45–60 mesh Chromosorb W were used for analytical and preparative purposes, respectively. All chromatography solvents were distilled from P_2O_5 prior to use.

(39) B. Loev and M. M. Goodman, *Intra-Sci. Chem. Rep.*, 4 (4), 283 (1970).

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

was collected prior to beginning the tlc (40% total yield of polymer based on unrecovered diene). The total weight accounted for represents 96% of the weight of **1** used.

Quantum Yields for Isomeric 1,5-Diphenyl-1,4-pentadienes 1–3. Dilute solutions of individual or mixed diene isomers **1–3** in cyclohexane (*ca.* 0.001–0.002 *M*) were irradiated in a merry-go-round used in conjunction with a Rayonet Model RPR-100 photochemical reactor (Southern New England Ultraviolet Co.) containing four (instead of 16 possible) lamps. From the manufacturer's specifications it was determined that 91.5% of the light output was in the 254-nm region. Optically opaque diene samples were irradiated to about 25% conversion simultaneously with a potassium ferrioxalate actinometer.[23,27] Runs 1–3 (see Table V) were done simultaneously. Mass analyses for dienes **1–3** and bicyclo[2.1.0]pentanes **4–6** were by quantitative glc on $^1/_8$-in. silicone rubber columns using docosane as an internal standard after calibration with authentic samples of **1–6**. Data for individual quantum yield determinations are listed as follows: mass starting material, solvent, light input, mass of photoproducts and dienes, conversion, and quantum yields. The difference between the quantum yield for the disappearance of the starting diene and the sum of the quantum yields for the appearance of the other dienes and photoproducts **4–6** is reported as the quantum yield of polymer formation.

Run 1. Diene **1** (1.58 mg, 98% **1** and 2% **2**, 0.00719 mmol); 3 ml of cyclohexane; 0.00442 mEinstein; 0.063 mg (0.000286 mmol) of photoproduct **4**, 0.033 mg (0.000150 mmol) of photoproduct **5**, 1.22 mg (0.00555 mmol) of unreacted diene **1**, and 0.097 mg (0.000441 mmol; corrected for 0.009 mg originally present) of diene **2**; conversion (total diene consumed), 16%; $\Phi_{\text{disappearance of 1}} = 0.34$, $\Phi_2 = 0.10$, $\Phi_4 = 0.065$, $\Phi_5 = 0.034$, $\Phi_{\text{polymer}} = 0.14$.

Run 2. Diene **2** (0.84 mg, 98% **2** and 2% **3**, 0.00377 mmol); 3 ml of cyclohexane; 0.00442 mEinstein; 0.105 mg (0.0004777 mmol) of diene **1**, 0.47 mg (0.00214 mmol) of unreacted diene **2**, 0.0193 mg (0.000088 mmol) of diene **3** (corrected for 0.0137 mg of **3** originally present), 0.0117 mg (0.000053 mmol) of photoproduct **4**, 0.13 mg (0.000591 mmol) of photoproduct **5**; conversion (total diene consumed), 27%; $\Phi_1 = 0.108$, $\Phi_{\text{disappearance of 2}} = 0.37$, $\Phi_3 = 0.020$, $\Phi_4 = 0.012$, $\Phi_5 = 0.134$, $\Phi_{\text{polymer}} = 0.096$.

Run 3. Diene **3** (1.75 mg, 0.00795 mmol); 3 ml of cyclohexane; 0.00442 mEinstein; 0.061 mg (0.000277 mmol) of diene **1**, 0.1825 mg (0.000830 mmol) of diene **2**, 1.06 mg (0.00482 mmol) of unreacted diene **3**, 0.125 mg (0.000568 mmol) of photoproduct **5**, 0.054 mg (0.000245 mmol)[41] of photoproduct **6**; conversion (total diene consumed), 26%; $\Phi_1 = 0.063$, $\Phi_2 = 0.19$, $\Phi_{\text{disappearance of 3}} = 0.71$, $\Phi_5 = 0.13$, $\Phi_6 = 0.056$, $\Phi_{\text{polymer}} = 0.27$.

Run 4. Mixed dienes **1–3** (1.35 mg, 0.00603 mmol); 3 ml of cyclohexane; 0.00578 mEinstein; 0.135 mg (0.000603 mmol) of photoproduct **5**, 0.041 mg (0.000186 mmol) of photoproduct **4**; estimated conversion *ca.* 30%; $\Phi_4 = 0.032$, $\Phi_5 = 0.105$.

Run 5 (Quantum Yields for the Isomeric 1,5-Diphenyl-1,4-pentadienes 1–3 at 300 nm). A solution of 22.1 mg (0.100 mmol) of mixed dienes **1–3** and 7.13 mg of eicosane in 5 ml of *tert*-butyl alcohol was irradiated in a merry-go-round at 300 nm in the Rayonet reactor simultaneously with benzophenone–benzhydrol actinometer solutions (prepared as described by Moore and Ketchum[42] except substituting *tert*-butyl alcohol instead of benzene as solvent). The optically opaque samples in quartz tubes were irradiated using 4 instead of 16 lamps for 130 min and then analyzed by quantitative glc. The absorption of 0.478 mEinstein produced 2.39 mg (0.0109 mmol) of photoproduct **5** and 0.32 mg (0.00146 mmol) of photoproduct **4** at an estimated diene conversion of 50% giving quantum yields of $\Phi_5 = 0.023$ and $\Phi_4 = 0.003$.

Photolysis of Isomeric Dienes 1–3 in the Presence of Piperylene. At 254 nm. Two solutions were prepared each containing 5.40 mg of *cis,trans*-1,5-diphenyl-1,4-pentadiene (**2**) and 2.09 mg of docosane in 1.5 ml of spectrograde cyclohexane. In one case the solution was 2.0 *M* in piperylene. After 17 min irradiation at 254 nm in the Rayonet RPR-100 reactor, the solutions were analyzed by glc. The results are summarized in Table IV (runs 1 and 2).

At 300 nm. A series of solutions was prepared each containing 8.8 mg of mixed dienes **1–3**, 3.64 mg of docosane, varying concentrations of piperylene (0.01–10 *M* and a sample lacking piperylene), and sufficient cyclohexane to give a total volume of 3 ml. The solutions (0.0133 *M* in **1–3**) were irradiated simultaneously in Pyrex tubes at 300 nm in a merry-go-round-equipped Rayonet RPR-100 reactor for a total of 24 hr with periodic analysis by quantitative glc. Data for each run at 80% conversion (as determined graphically; all solutions were quite close to 80% conversion after 25 hr) are listed in Table IV (runs 3–12).

Triphenylamine-Sensitized Irradiation of Dienes 1–3. Analytical Run. From ultraviolet absorption spectra it was determined that at 350 nm the extinction coefficient of triphenylamine is at least ten times that of dienes **1–3**. In order to ensure absorption by the triphenylamine of 99% of the light, a tenfold excess of sensitizer was employed. Thus, a solution was prepared in 15 ml of spectrograde cyclohexane containing 38.3 mg of dienes **1–3** (0.17 mmol; 19% **1**, 33% **2**, 48% **3**), 406.7 mg of triphenylamine (1.7 mmol), and 18.4 mg of *n*-docosane as internal standard. Another solution was prepared containing in 15 ml of cyclohexane 36.7 mg of dienes **1–3** along with 20.1 mg of *n*-docosane. The solutions were irradiated in Pyrex tubes simultaneously at 350 nm in a merry-go-round-equipped Rayonet Model RPR-204 reactor for 10 hr. Glc analysis of the unsensitized run at this time indicated 18% **1**, 28% **2**, 34% **3**, 0.6% **5**, and negligible **4** and **6** (percentages are relative to **1** + **2** + **3** = 100% before irradiation); 20% total diene had been consumed. Glc analysis of the sensitized run indicated 24% **1**, 19% **2** (estimated; bad overlap with Ph_3N peak), 14% **3**, negligible **4**, 5.9% **5**, 1.8% **6**; an estimated 43% of the total diene has been consumed.

Preparative Run. A solution of 60 ml of cyclohexane 0.008 *M* in dienes **1–3** and 0.0016 *M* in triphenylamine was irradiated in a Pyrex tube for 144 hr in the above photochemical apparatus. The solution was then filtered, concentrated *in vacuo*, and chromatographed on a silver nitrate impregnated tlc plate (prepared as previously described) using 5:1 pentane–methylene chloride as elutant. The fastest moving band (R_f 0.8) gave 25 mg (25% yield) of *trans*-2,3-diphenylbicyclo[2.1.0]pentane (**5**) of good purity as determined by glc and nmr. In addition, the fractions of lower R_f contained an estimated total of 4 mg of the cis,syn photoproduct **6** as indicated by glc and nmr. No attempt was made to isolate **6** in pure form from these fractions. The results of sensitized irradiation of dienes **1–3** are summarized in Table V.

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[41] Overlap of the glc peak due to **6** with a peak due to a minor impurity in **3** prevented an exact determination of the amount of **6** produced. The number given is the minimum amount of **6** present; the maximum possible amount is 0.25 mg (0.00113 mmol; $\Phi_6 = 0.26$ for this weight of **6**).

[42] W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).