tion, and the American Cyanamid Company is gratefully acknowledged. The Sherman Clarke Fund of the University of Rochester also provided funds. Two Faculty Research Grants from the California State University—Fresno are also gratefully acknowledged. It is a pleasure to acknowledge helpful discussions with Drs. L. E. Friedrich, Gary Schuster, W. H. Saunders, Jr., Kenneth G. Harbison, and J. A. Kampmeier.

A Novel Photochemical 1,4-Phenyl Migration. The Role of the Second π Bond in the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: In order to assess the role of the second π bond in the di-π-methane rearrangement, the photochemistry of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene was investigated. It was ascertained that neither the singlet nor the triplet of this tetraphenyl monoene rearranged in di-π-methane-like fashion. The absence of cyclopropane product contrasts dramatically with the known facile rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. While the triplet excited state of the tetraphenyl monoene was unreactive, the singlet rearranged to afford 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene in a novel 1,4-phenyl migration. Additionally, to a lesser extent, rearrangement occurred to afford 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane. The quantum yield for formation of the major product was $\phi = 0.00081$. That for the tetraphenyldimethylcyclopentane was $\phi = 0.0002$. An upper limit on the intrusion of any di-π-methane-type product could be set as 1/25th of this. Further, the low reactivity of the tetraphenylmonoene was found to derive from an inherently low rate of singlet rearrangement rather than a rapid excited-state decay. The rate of rearrangement of the singlet to give tetraphenyldimethylpentene was $k_r = 2.4 \times 10^7 \text{ sec}^{-1}$. This is indeed low compared with di-π-methane systems. The rate of all excited-state decay processes is $k_{dt} = 3.0 \times 10^{10} \text{ sec}^{-1}$. This, again, is low. From these data it is concluded that any di-π-methane-like rearrangement occurring must be even slower than the phenyl migration process. It is seen that the second π bond is a necessity for facile rearrangement.

Eight years ago we reported the rearrangement of barrelene to semibullvalene.[3] It was quickly recognized that the rearrangement mechanism was characteristic of molecules which have two π groups bonded to a central sp³-hybridized carbon atom; we thus termed the reaction the di-π-methane rearrangement.[3b,4] Since that time the rearrangement has proven extraordinarily general,[5-9] and an ever increasing number of examples are being reported.[10]

One example which has been thoroughly studied is that of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (1) which rearranges to give 1,1-diphenyl-2,2-dimethyl-3-(2',2'-diphenylvinyl)cyclopropane (2).[5] The mechanism we suggested[5] is shown in Chart I. This begins

Chart I. Mechanism for the Photochemical Rearrangement of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (1)
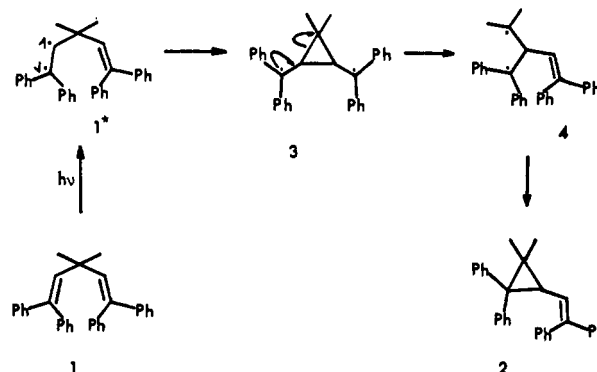
with bonding between the two π moieties of the singlet excited state. In contrast, Woodward and Hoffmann[11] have proposed that the reaction is a $_\sigma 2_a + _\pi 2_a$ or $_\sigma 2_s + _\pi 2_s$ process. In this mechanism only one π bond plays a role. The question posed then was whether the second π bond really is required for the reaction. An answer

(1) Paper LXXXIX of the series. For the previous paper on Mechanistic and Exploratory Organic Photochemistry, note H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 4630 (1974).

(2) For a preliminary communication describing some of these details, see H. E. Zimmerman and R. D. Little, *J. Amer. Chem. Soc.*, **94**, 8256 (1972).

(3) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, **89**, 3932 (1967).

(4) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

(5) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(6) (a) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970); (b) *ibid.*, **92**, 6267 (1970).

(7) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

(8) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

(9) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

(10) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 98–100.

seemed accessible from a study of the photochemistry of the dihydro derivative of the tetraphenyldiene **1**, namely 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene (**5**), since this latter compound differed only in the absence of the second double bond. Actually, the tetraphenyl monoene **5** should rearrange with greater facility than the tetraphenyldiene **1** if it is really correct that only σ bond 3,4, and not a second π bond, is involved in the di-π-methane rearrangement. This follows from the presence of a weaker 3,4-σ bond in tetraphenyl monoene **5** compared to the σ bond in tetraphenyldiene **1**. In the former the bond is sp³–sp³ compared to sp²–sp³ in the latter.

Synthesis of Tetraphenyl Monoene 5 and Its Potential Rearrangement Product. The synthesis of tetraphenyl monoene **5** began with the known six-ring lactone **6**. This on lithium–liquid ammonia reduction afforded 3,3-dimethyl-5,5-diphenylpentanoic acid (**7**). The corresponding methyl ester was treated with phenyllithium to give 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentanol (**8**) which was converted to the desired tetraphenyl monoene by p-toluenesulfonic acid dehydration. This approach is delineated in Chart II.

Chart II. Synthetic Route to the Tetraphenyl Monoene **5** and Its Potential Rearrangement Product
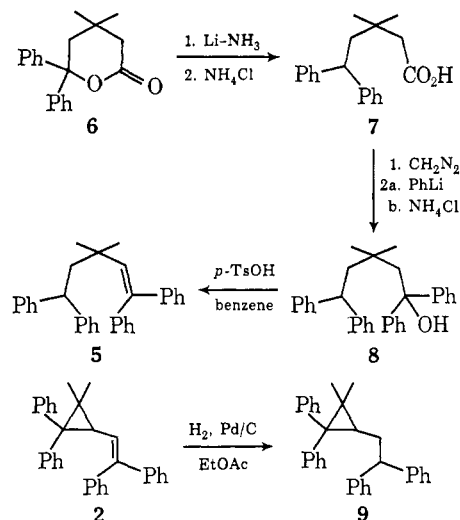
The potential product anticipated from a di-π-methane-like rearrangement is 1,1-dimethyl-2,2-diphenyl-3-(2',2'-diphenylethyl)cyclopropane (**9**), and this compound was synthesized by Pd/C catalyzed hydrogenation of the known[5] vinylcyclopropane **2**. This synthesis is also shown in Chart II.

Exploratory Photolyses and Product Structure Elucidation. It was found in exploratory photolyses that a major photoproduct **10**, a liquid, was formed. Additionally, a lesser product, mp 129–130°, was formed. In a typical run, irradiation of 1.00 g for 10 hr using a medium-pressure 450-W lamp afforded 152 mg of photoproduct **10**, 38 mg of minor photoproduct **11**, and 760 mg of recovered reactant monoene **5**.

Neither of the two photoproducts proved identical with the potential sigma plus π product **9** which had been synthesized (vide supra).

The major photoproduct had an nmr spectrum which showed a 20-hydrogen multiplet centered at τ 2.84 (aromatic), a two-hydrogen singlet at 3.90 (vinyl hydrogens of the trans isomer), an AB quartet with τ_A 5.51 and τ_B 6.20 ($J = 11.5$ Hz, benzylic and benzhydryl hydrogens),

and two three-hydrogen singlets at 8.94 and 9.26 indicating that these methyl groups are diastereotopic. Unequivocal evidence in support of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene (**10**) as the structure for the major photoproduct was derived from independent synthesis as outlined in Chart III.

Chart III. Independent Synthesis of Photoproduct **10**
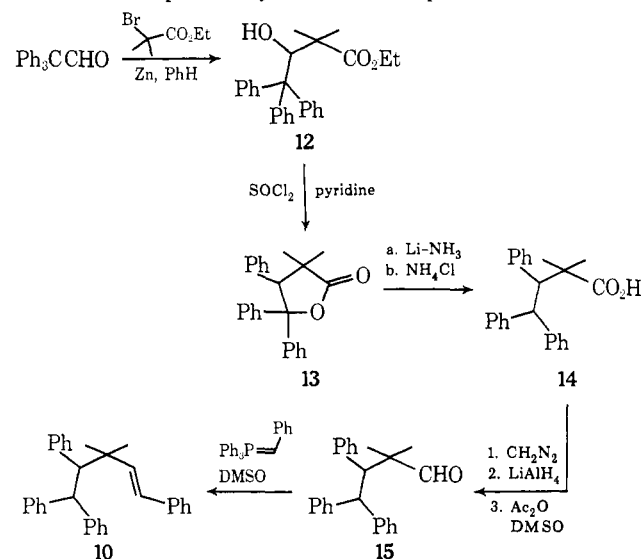
This synthesis began with the Reformatsky reaction of triphenylacetaldehyde and ethyl α-bromoisobutyrate to yield hydroxy ester **12**. It was anticipated that cationic elimination would result in phenyl migration, thus leading to the gross skeleton of photoproduct **10**. The product of thionyl chloride catalyzed elimination was lactone **13** whose structure rested on spectral evidence (note the Experimental Section), its elemental analysis, and on its subsequent transformation. The reaction mechanism is depicted in eq 1. Lactone **13** reacted smoothly with lithium–liquid ammonia to afford triphenylcarboxylic acid **14**. This product most likely arises from carboxylate expulsion from the benzhydryl carbon of the radical anion of lactone **13** followed by introduction of a second electron and protonation (note eq 2). Lithium aluminum hydride reduction of the
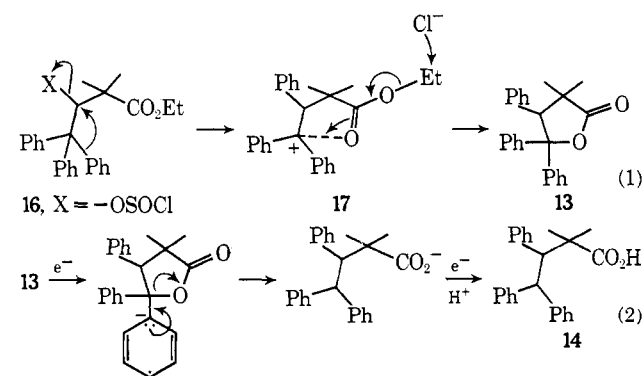
methyl ester of **14** followed by Albright–Goldman oxidation[12] of the resulting carbinol yielded aldehyde **15**. This reacted with benzylidenetriphenylphosphorane to give 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene (**10**) which proved identical with the major photoproduct.

(12) J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, **89**, 2416 (1967).

Attention was next turned toward the minor photoproduct. Elemental and mass spectral analysis showed this to be isomeric with tetraphenyl monoene reactant 5. The ultraviolet spectrum exhibited a peak at 257 nm (ϵ 2640) with vibrational structure. This was evidence against the presence of a conjugated phenyl group and was suggestive of four isolated phenyl groups. This view was supported by resistance to catalytic hydrogenation (note Experimental Section). The nmr spectrum revealed the expected 20 aromatic hydrogens. Additionally a sharp singlet at τ 6.02 suggested the presence of an isolated methine hydrogen. Two 3-hydrogen singlets showed the presence of two nonequivalent methyl groups. Finally, an ABC pattern was observed consisting of 12 peaks with the AB portion having nine absorptions in the τ 6–8 region and the C portion having 4 peaks centered at τ 5.86.

In order to check this interpretation, on-line nmr simulation was employed using the PDP8/I method described earlier.[13] The calculated results are compared with observation in Table I, and the agreement is seen to be excellent.

Table I. Comparison of Experimental and Theoretical Nmr for ABC Pattern of Minor Photoproduct 11

| Peak	Calcd shift[a,b]	Calcd intensity	Obsd shift	Obsd intensity
1	117.919	0.354	118	0.36
2	125.040	0.424	125	0.43
3	131.938	0.832	131	0.83
4	139.059	0.918	139	0.91
5	150.292	0.751	149.9	0.71
6	164.311	0.291	164	0.30
7	165.152	1	165	1
8	179.171	0.489	178.5	0.48
9	236.788	0.792	236.5	0.79
10	243.909	0.696	243	0.69
11	251.648	0.551	251	0.55
12	258.769	0.491	258	0.49
13	45.441	0.000	Not obsd	0.00
14	211.536	0.001	Not obsd	0.00
15	284.021	0.000	Not obsd	0.00

[a] Shift data are recorded in Hz downfield from TMS. [b] Calculation based on A, B, and C chemical shifts of 130, 164, and 247 Hz and $J_{AB} = 15$ Hz, $J_{AC} = 14$ Hz, $J_{BC} = 7$ Hz.

The mass spectrum of minor photoproduct 11 proved especially definitive and is summarized in Table II. The parent peak at 402 confirmed the molecular structure as isomeric with photochemical reactant monoene 5. A mass peak at 91 is assigned to a tropylium fragment which thus suggests the presence of Ph–CH.[14] Another intense peak, this at 167 mass, suggests the presence of a Ph_2C moiety. The strongest peak (note Table II) is of mass 256 which corresponds to the fragment $PhCH–CPh_2$. Another fragment which proves helpful in defining structure is of mass 56 and assigned structure as CH_2CMe_2 in view of the nmr. Finally, a mass 105 moiety corresponding to CH_2CH_2Ph was encountered.

This mass spectral pattern almost uniquely defines the

(13) (a) D. F. Juers, Ph.D. Thesis, University of Wisconsin, 1970. (b) Program available from Digital Equipment Computer Users Society, 8-194.
(14) The assignments given here and in Table II show original benzylic rather than rearranged tropylium structures since we are interested in formulating the structure of photoproduct 11 rather than mass spectral structures.
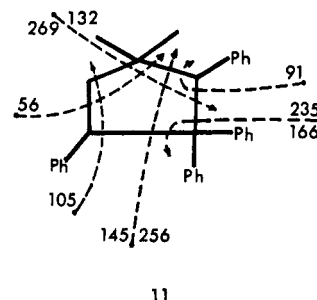

Figure 1.

Table II. Most Intense Mass Spectral Peaks for Minor Photoproduct 11

Rel intensity	Mass	Formula	Structural assignment[a]
100	256	$C_{20}H_{16}$	$PhCHCPh_2$
95	269	$C_{21}H_{17}$	$CH_2=C(Ph)CPh_2$
58	402	$C_{31}H_{30}$	
48	235	$C_{18}H_{19}$	$PhCH=CHCMe_2CHPh$
45	91	C_7H_7	$PhCH_2$
29	145	$C_{11}H_{13}$	$Me_2C=CHCHPh$
19	167	$C_{13}H_{11}$	Ph_2CH
16	105	C_8H_9	CH_2CH_2Ph
13	132	$C_{10}H_{12}$	Me_2CCHPh
2.4	56	C_4H_8	Me_2CCH_2

[a] The assignments given are those of the parent molecule rather than those of the actual mass spectral ion.

structure of photoproduct 11. However, we now remember that the nmr spectrum required the presence of an isolated methine hydrogen and a separated ABC three-hydrogen system. Accordingly, the mass spectral and nmr data lead uniquely to 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane as the structure of minor photoproduct 11. The different modes of cleavage are indicated in Figure 1 and are seen to conform to the mass spectral fragments listed in Table II.[15]

The photochemical rearrangement of monoene 5 can now be formulated as

$$\text{(3)}$$

5   10   11
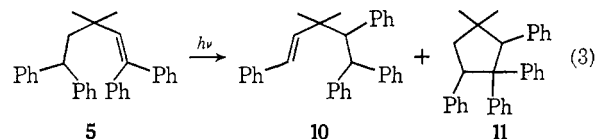
Determination of Reaction Efficiency, Multiplicity, and Reaction Rates. Results. The quantum yields of reaction of monoene 5 to form both major and minor photoproducts were determined using the Black Box apparatus described earlier.[16] Solution filters[16] with a band pass of 245–305 nm and ferrioxalate actinometry[17] were employed. Products were assayed using high-speed liquid chromatography. Runs were made to *ca.* 4–5% conversion in order to prevent light capture by the photoproducts. The results of these determina-

(15) Further mass spectral peaks, whose structures are not uniquely defined, are included in Table II and are seen to be consistent with the assigned structure.
(16) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).
(17) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. B*, **140**, 470 (1953).

Table III. Quantum Yield Determinations[a]

Run	Reactant concn	mEin-steins	% conversion	Quantum yields Ph-migr. prod.	Cyclopent. prod.
1	0.00914	30.96	4.3	0.00077	0.0002
2	0.00914	34.22	5.4	0.00085	0.0002
3	0.000891	1.39	<0.009	Too little to detect	

[a] All photolyses were conducted in tert-butyl alcohol.

tions are listed in Table III. Further details are described in the Experimental Section.

It was next necessary to determine the multiplicity of the species leading to the two photoproducts. To determine if a triplet excited state could give rise to the observed photoproducts, benzophenone sensitization was employed under conditions where only the benzophenone absorbed light. Because of the very low reactivity observed, a 450-W Hanovia immersion apparatus with Pyrex filter was employed for these runs. In a second, parallel photolysis benzophenone was run alone with benzhydrol, while in a third irradiation a benzophenone–benzhydrol mixture was photolyzed with monoene 5 at the 0.008 M concentration used in the run with just added benzophenone.[18] The benzophenone–benzhydrol experiments provided evidence for the interception of benzophenone triplets[19] by monoene 5 since complete quenching of the benzophenone–benzhydrol reaction to form benzopinacol was observed. Additionally, benzophenone–benzhydrol formed a rough actinometer under the conditions and hence allowed some conclusion about the upper limit of any triplet reactivity. A very conservative estimate indicates that any products resulting from the triplet were formed in quantum yields less than 1% of the efficiencies in the direct irradiations. Previous experience[1,8] indicates that benzophenone triplet is not only intercepted by molecules with a styryl moiety but also transfers triplet excitation to these molecules. Therefore, we can conclude that in these sensitized runs the triplet excited state of monoene 5 is being formed but that this is unreactive. This suggests that in the direct irradiations it is the singlet excited state which gives rise to phenyl migrated product 10 and cyclopentane product 11.

In addition to reaction efficiencies, we were interested in obtaining the unimolecular rate constants for reaction of the excited singlet. For this, we employed single photon counting with our recently published method[20] of systematic reiterative convolution and use of an on-line PDP8/I computer both as a multichannel analyzer and for computation.

It was found that the rate of decay at room temperature was too rapid for direct measurement, and lifetimes were therefore measured at liquid nitrogen temperature.

(18) (a) Recently Schuster[18b] has noted the danger of benzophenone triplet self-quenching. However, under the present conditions (i.e., 0.13 M benzophenone) a pseudounimolecular quenching rate of 16.4 × 10⁴ sec⁻¹ is calculated using Schuster's data and the approximation that quenching in the present tert-butyl alcohol will not be faster than in the benzene solvent employed by Schuster. This source of loss of benzophenone triplets is then only ca. 10% of the natural decay which is known[19] to be 5.2 × 10⁵ sec⁻¹. Thus this is not a problem presently. (b) D. I. Schuster and T. M. Weil, J. Amer. Chem. Soc., 95, 4091 (1973).
(19) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, J. Amer. Chem. Soc., 83, 2789 (1961); (b) H. L. J. Baeckstrom and K. Sandros, Acta Chem. Scand., 14, 48 (1960).
(20) (a) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, J. Amer. Chem. Soc., 95, 5094 (1973); (b) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, ibid., 96, 439 (1974).

Table IV. Single Photon Counting and Derived Rate Data for Monoene 5

Run	k_{dt}^{77}	τ_{77}, nsec	k_{dt}^{298} [a]	τ_{298}, psec[a]	k_r^{298}, sec⁻¹ [b]
1	1.96×10^8	5.11	2.94×10^{10}	34.0	2.97×10^7
2	1.98×10^8	5.04	2.98×10^{10}	33.6	3.01×10^7
3	1.98×10^8	5.05	2.97×10^{10}	33.7	3.00×10^7
4	2.00×10^8	4.99	3.00×10^{10}	33.3	3.03×10^7
Av	1.98×10^8	5.05	2.97×10^{10}	33.7	3.00×10^7

[a] Determined using an average multiplier value of 150 (note Experimental Section). [b] This is the sum of the rates of formation of the two photoproducts.

These measurements are summarized in Table IV. An average lifetime at 77°K of 5.0 nsec was measured. The temperature dependence of fluorescence intensity was determined to be that given by

$$M = k_{dt}^{298}/k_{dt}^{77} = 150 \qquad (4)$$

Use of this magic multiplier[20] in conjunction with the low temperature rate of decay (i.e., $k_{dt}^{77} = 1.98 \times 10^8$ sec⁻¹) affords an average value of $k_{dt}^{rt} = 3.0 \times 10^{10}$ sec⁻¹. This corresponds to a room temperature lifetime of only 34 psec! This does emphasize the power of the present single photon counting–reiterative convolution technique. Using this value for the room temperature rate of singlet decay in conjunction with the definition (eq 5a) and value of the room temperature

$$k_r = \phi_r k_{dt} \qquad (5a)$$

quantum yields, we were then able to derive the room temperature rates of excited singlet unimolecular rearrangement. A summary of the rate data is given in Table IV and eq 5b and 5c.

$$k_r(\text{phenyl migrated prod. } 10) = 2.4 \times 10^7 \text{ sec}^{-1} \qquad (5b)$$

$$k_r(\text{cyclopentane prod. } 11) = 5.9 \times 10^6 \text{ sec}^{-1} \qquad (5c)$$

Interpretative Discussion of Results Relating to the Di-π-methane Rearrangement. The first result to be noted is the very low reaction efficiency ($\phi_{tot\ react} = 0.0010$) of the photochemistry of monoene 5 compared with the corresponding diene 1 ($\phi_{rearr} = 0.080$).[5] Thus even superficially there is suggestive evidence that the second π bond plays a role in the di-π-methane rearrangement. Secondly, in the absence of the second π bond a totally different reaction course intercedes, and one may therefore conclude that the second π bond is an essential feature of the di-π-methane rearrangement. In this connection we notice that the rates we have compared are for the di-π-methane rearrangement in the case of diene 1 but for totally different rearrangements by monoene 5. This means that the comparison is particularly conservative, since any di-π-methane-like (or σ plus π) rearrangements occurring from monoene 5 would have to be still an order of magnitude slower than 3×10^7 sec⁻¹ in order not to be discerned.

The comparison of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (1) and its dihydro derivative (i.e., monoene 5) is justified, since evidence has been adduced that monoene 5 utilizes its singlet for rearrangement as has been shown[5] to be the case for diene 1.

Nevertheless, comparison of quantum yields of different reactants, even when from the same multiplicity state, is not meaningful. It is quite possible for

an inherently successful reaction having exceedingly high excited-state reactivity to give a very low quantum yield because of an excessively rapid rate of radiationless decay to ground state. Therefore, a more suitable criterion for comparison of excited-state reactivity is found in the rate constants for the excited-state processes of interest.

The reactions of monoene **5** and diene **1** are compared in eq 6a and 6b. It is seen that the singlet excited state

(6a)
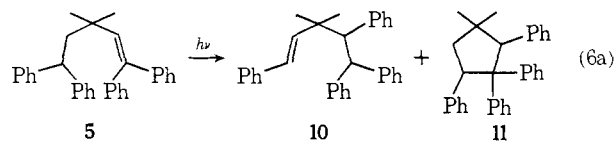
$$k_r = 3.0 \times 10^7 \text{ sec}^{-1} \qquad \phi_r = 0.0010$$
$$k_{dt} = 2.97 \times 10^{10} \text{ sec}^{-1} \qquad M = 150$$
$$\tau_{RT} = 33.7 \text{ psec}$$

(6b)
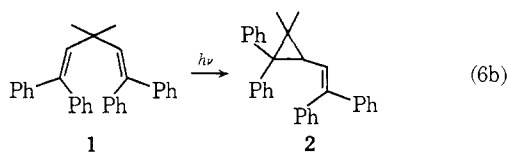
$$k_r = 1.4 \times 10^{11} \text{ sec}^{-1} \qquad \phi_r = 0.080$$
$$k_{dt} = 1.8 \times 10^{12} \text{ sec}^{-1} \qquad M = 225$$
$$\tau_{RT} = 0.55 \text{ psec}$$

of monoene **5** reacts 5000-fold more slowly than the excited singlet of diene **1**. Thus, the difference in behavior of the two compounds does derive from a difference in inherent excited-state reactivity.

In this connection we might question the validity of the comparison. If we were to envisage the di-π-methane rearrangement as a σ plus π rearrangement, then in the case of the diene **1** it is an sp²-sp³ σ bond which has to be added. We do note that the weaker σ bond is the sp³-sp³ σ bond of monoene **5**. Thus, any diminished reactivity cannot derive from hybridization factors, and the comparison is indeed valid.

As a consequence, we can indeed conclude that the second π bond plays an important role in the di-π-methane rearrangement.

This does not mean, however, that σ plus π rearrangements are inherently impossible. 1-Aryl-3,3-dimethyl-1-butenes (**18**) are known to rearrange to 1-aryl-2,3-trimethylcyclopropanes (**19**).[21-23] However, the reaction efficiencies seem to be very low[22] and it seems likely that the rates cannot be high either.

We now turn attention to two *a priori* models. One is a $_\pi 2_a + _\sigma 2_a + _\pi 2_a$ mechanism which is equivalent to the resonance picture presented earlier. The other is the $_\sigma 2_a + _\pi 2_a$ process which is mentioned earlier. These pathways are depicted in Chart IV.

The two pathways really differ only subtly. To begin with, the overall skeletal change is identical for the two.

The two different orbital arrays can be seen in both instances to provide orbitally allowed mechanisms for

(21) (a) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966); (b) J. J. Brophy and G. W. Griffin, *Tetrahedron Lett.*, 493 (1970).

(22) (a) S. S. Hixson and T. P. Cutler, *J. Amer. Chem. Soc.*, **95**, 3031, 3032 (1973).

(23) Other cases of interest include the ring expansion of vinylcyclopropanes to give housanes as reported by H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5970 (1967) and also the methyl migration reported by L. B. Jones and V. K. Jones, *ibid.*, **89**, 1880 (1967); **90**, 1540 (1968), in the case of 3,7,7-trimethyltropylidene which rearranges to give 1,5,7-trimethyltropylidene.

Chart IV. Orbital Arrays Involved in the Two *A Priori* Mechanisms

$\sigma 2_a + \pi 2_a + \pi 2_a$, Möbius 6ε

$\sigma 2_a + \pi 2_a$, Hückel 4ε

=== bonds forming; === bonds breaking
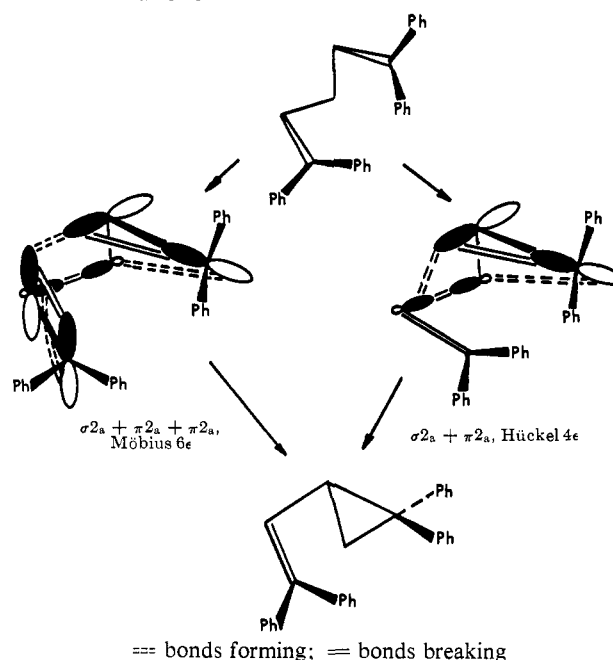
an excited-state transformation. The six orbital array is Möbius (*i.e.*, an odd number of sign inversions) and with six electrons is excited state allowed.[24] The four orbital array is Hückel (*i.e.*, zero or an even number of inversions between basis orbitals) and with its four delocalized electrons is excited state allowed as well.[24] Thus the two versions are not distinguished by orbital allowedness.

Further, the six-orbital array and the four-orbital array have nonbonding degeneracies which point to crossing of bonding and antibonding MO's. This has been noted to provide a mechanism for excited states of reactant getting to ground states of product.[25] Again, we find no distinction between the two mechanisms.

Similarly, the two routes predict the same stereochemical outcome. Hence prior to the present study little basis for differentiation was available.

However, the two mechanisms do differ in their predictions of the kind of structural change likely to affect the excited-state reaction rate. The σ plus π mechanism would predict a more rapid rate for the rearrangement shown in Chart IV in absence of the 4,5-π bond due to the hybridization effects noted above. This σ plus π mechanism would certainly not predict the dramatic rate inhibition observed in absence of the second π bond. The σ plus π plus π route by its nature demands the second π bond for its occurrence.
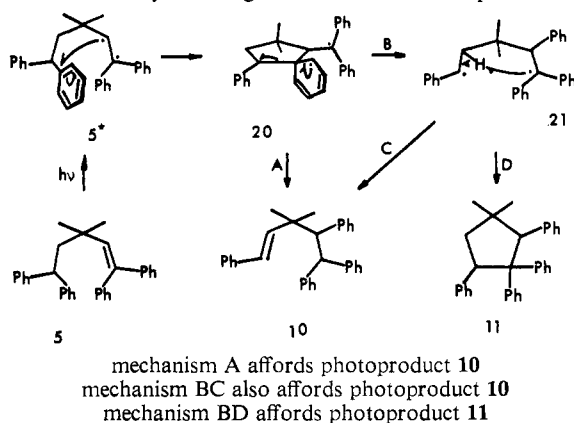
Interpretative Discussion. The Nature of the Observed Rearrangements. The first aspect needing comment is the occurrence of the two new photochemical processes encountered, the first leading to a phenyl migrated monoene (*i.e.*, **10**) and the second affording a cyclopentane product (*i.e.*, **11**).

Next we need to consider the pathways leading to these products. The first step postulated (note Chart V) is bridging between diphenylvinyl and phenyl groups in the excited singlet of reactant. Excited-state

(24) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *Accounts Chem. Res.*, **4**, 272 (1971).

(25) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1566 (1966); (b) H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 8749 (1972).

Chart V. Pathways Leading to the Observed Photoproducts

mechanism A affords photoproduct **10**
mechanism BC also affords photoproduct **10**
mechanism BD affords photoproduct **11**

bridging between π systems attached 1–3 on a carbon chain has precedent in the elegant work of Binkley.[26] This leads presently to diradical **20**. Completion of the migration leads to the 1,5-diradical **21** which on σ bond formation leads to the observed cyclopentane product **11**. This is referred to as pathway BD in Chart V.

Diradical **21** can be seen to be a reasonable precursor to product monoene **10** as a result of disproportionation as shown in Chart V (*i.e.*, mechanism BC). Conceivably, steps B and C could be concerted, and this is shown in Chart V as process A.

One fascinating feature of the disproportionation process, whether it proceeds by mechanism A or by BC, is the regiospecificity resulting in exclusive formation of product monoene **10**. An *a priori* equally plausible product of mechanism BC is the nonobserved monoene **22**. This product could arise by an equivalent hydrogen abstraction process as shown in eq 7. Yet, no monoene

$$(7)$$
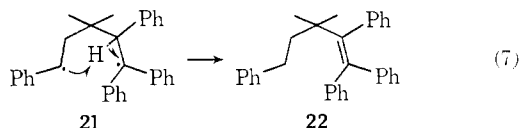
22 was encountered and this remarkable regiospecificity requires examination.

Analysis of the situation in mechanism BC reveals that the basic question is which mode of a disproportionation, of those depicted in eq 8a and 8b, is kinetically pre-

ferred. This question is equivalent to asking whether more transition-state stabilization results from placement of delocalizing groups on the center abstracting the hydrogen, corresponding to a preference for the disproportionation mode in eq 8a, or instead whether more stabilization derives from the delocalizing groups
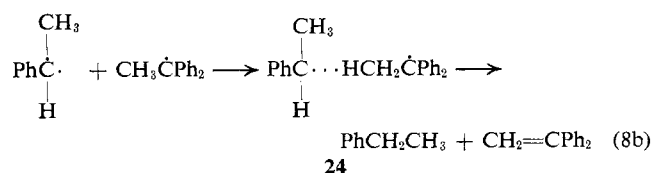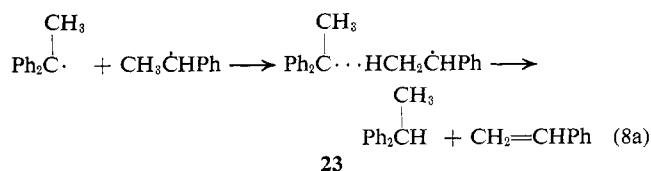
(26) R. W. Binkley and W. C. Schumann, *J. Amer. Chem. Soc.*, **94**, 1769 (1972).

being on the carbon adjacent to that bearing the hydrogen atom being abstracted as in eq 8b. Intuitively, one might favor the latter. Yet some minor literature precedent favors the former.[27]

In order to resolve this question we have compared the transition states **23** and **24** by calculations including only the delocalized portion of the system and ignoring σ bonds not involved in the reaction. The precise systems used as models were those shown in eq 8a and 8b, since these are quite similar to process C in Chart V and the reaction in eq 7 which were of direct interest.

We did assume, using Hammond's postulate,[28] that the transition states **23** and **24** come early along the reaction coordinate and thus that new carbon–hydrogen bond formation is weak and the old C–H bond being broken is still strong. While the resonance integrals chosen are only qualitatively valid, the calculation proved to be independent of these.

The basic quantum mechanical question is which end of a butadienoid array, with four orbitals (1–2–3–4) having weak 1–2 overlap, is most in need of stabilization by delocalization. Even simple Hückel calculations of butadiene with bond 1–2 stretched reveal that the highest occupied MO has a concentration of electron density at atom 1 (Table V).

In the case of transition states **23** and **24**, the total delocalized electron energy favored **23**. Additionally, when equal resonance integrals were used for systems such as **23** and **24**, there was a lower bond order observed between the carbon bearing the extra phenyl and the atom adjacent, thus indicating that, if one bond is to be weakened, it should be at this site. Thus it appears that there is a unique, but still unrecognized phenomenon in disproportionation reactions.

It is thus seen from these considerations that the regiospecificity in the disproportionation of diradical **21** in the present photochemistry is that expected on electronic grounds. The potential presence of diradical **21** is supported by the observation of cyclopentane **11** as one of the two photoproducts.

Nevertheless, there is another possible rationale for the formation of monoene **10** and no monoene **22**, namely the concerted formation of monoene **10** by mechanism A (note Chart V) which does not proceed *via* the discrete diradical **21**. It is seen in eq 9 that the

$$(9)$$
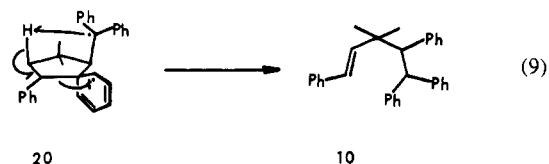
phenyl bridged species **20** has a benzhydryl free radical center situated 1,5 to a hydrogen atom whose removal leads directly to photoproduct. There is no operational basis for distinction between the two mechanisms leading to monoene **10** and these differ primarily in the extent to which completion of phenyl migration and hydrogen abstraction overlap in time.

(27) (a) Thus, disproportionation of *tert*-butyl and 4,4-dimethyl-2-pentyl radicals has been reported to give abstraction preferentially by the *tert*-butyl radical.[27b] (b) C. W. Larson and B. S. Rabinovitz, *J. Chem. Phys.*, **52**, 5181 (1970). (c) Note M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973), for recognition of a general tendency of more substituted alkyl radicals to abstract than to donate hydrogen; this was attributed to steric effects.
(28) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

Table V. Results of Hückel Calculations

| Case | H_{12} | H_{23} | Results for Stretched Butadienoids |||||||
| | | | Bond orders and electron densities for HOMO | | | | | | |
			p_{12}	p_{23}	p_{34}	$2c_1{}^2$	$2c_2{}^2$	$2c_3{}^2$	$2c_4{}^2$
$C_1\cdots H_2\text{-}C_3\text{-}C_4$	-0.5	-1.5	0.2558	-0.0604	0.0977	0.9470	0.2764	0.0528	0.7236
$C_1\text{-}H_2\cdots C_3\text{-}C_4$	-1.5	-0.5	0.1202	-0.1307	0.3439	0.4584	0.1262	0.5414	0.8736

Results for Transition States **23** and **24** and Symmetrical Analog

Case	H_{rs}	$E_{\pi,i}$	Bond orders
$Ph\text{-}C_1\cdots H_2\text{-}C_3\text{-}C_4Ph_2$	$H_{12} = -0.5$ $H_{23} = -1.5$	-29.8596	$p_{12} = 0.5069$ $p_{23} = 0.7984$ $p_{34} = 0.5268$
$Ph\text{-}C_1\text{-}C_2\text{-}H_3\cdots C_4Ph_2$	$H_{23} = -1.5$ $H_{34} = -0.5$	-29.8980	$p_{12} = 0.5726$ $p_{23} = 0.7859$ $p_{34} = 0.4730$
$Ph\text{-}C_1\text{-}C_2\text{-}H_3\cdot\cdot C_4Ph_2$	$H_{12} = H_{23} =$ $H_{34} = -1.0$	-29.8252	$p_{12} = 0.7658$ $p_{34} = 0.7125$

A final point which is of considerable interest is the rate of radiationless decay of the present photochemical reactant (*i.e.*, monoene **5**). With $k_{dt} = 3.0 \times 10^{10}$ sec⁻¹, this is slower by two orders of magnitude than the decay[20] of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**)[5] and slower than all the comparably substituted di-π-methane systems whose rates of singlet decay were recently reported.[20] This supports the view[20] that radiationless decay of the di-π-methanes is so very rapid by virtue of reversible vinyl–vinyl bridging, a process not available to the singlet excited state in the present photochemical system.

Conclusion

The present study has provided a unique phenyl migration process occurring from the excited singlet and also has given quantitative support for the mechanistic intervention of the second π bond in the di-π-methane rearrangement.

Experimental Section[29]

3,3-Dimethyl-5,5-diphenylpentanoic Acid. *Ca.* 150 ml of lithium dried ammonia in a dry flask was distilled into a second dry, nitrogen-flushed flask equipped with a Dry Ice condenser. To this solution, maintained at $-78°$, was added 0.164 g (23.6 mg-atoms) of lithium. The Dry Ice-acetone bath was removed and 2.00 g (7.15 mmol) of 5-hydroxy-3,3-dimethyl-5,5-diphenylpentanoic acid lactone in 2.0 ml of dry ether and 2.0 ml of dry tetrahydrofuran was added. After 1.0 hr at refluxing liquid ammonia temperature, the reaction was quenched by the addition of 1.3 g (24 mmol) of ammonium chloride. The white solid which remained after ammonia evaporation was dissolved in ice–water and acidified with 10% hydrochloric acid to pH 2. Ether extraction, drying, and concentration *in vacuo* afforded 1.97 g (98%) of a white, crystalline material, mp 83–84.5°.

The spectral data were: ir (CHCl₃) broad CO₂H from 2.83 to 4.18, 3.40, 5.89, 6.24, 6.70, 6.90, 7.10, 7.20, 7.30, 7.66, 7.98, 8.67, 8.99, 9.26, 9.71, 14.46, 15.50 μ; nmr (CDCl₃) τ 9.05 (s, 6 H, CH₃), 7.86 (s, 2 H, CH₂CO₂H), 7.73 (d, 2 H, $J = 6.9$ Hz, C-4 CH₂), 5.90 (t, 1 H, $J = 6.9$ Hz, benzylic), 2.73 (m, 10 H, arom), 1.53 (s, 1 H, CO₂H).

Anal. Calcd for C₁₉H₂₂O₂: C, 80.85; H, 7.80. Found: C, 80.57; H, 7.56.

Methyl 3,3-Dimethyl-5,5-diphenylpentanoate. Diazomethane was prepared from 5.71 g of EXR-101 (*N,N'*-dinitroso-*N,N'*-dimethylterephthalamide) and 75 ml of 30% aqueous sodium hydroxide and was distilled directly into a solution of 1.89 g (6.70 mmol) of 3,3-dimethyl-5,5-diphenylpentanoic acid in 100 ml of dry ether. After removal of the excess diazomethane in a nitrogen stream and concentration *in vacuo*, the desired methyl ester was obtained as a clear, colorless oil.

The spectral data were: ir (NaCl) 3.22, 3.25, 3.28, 3.36, 3.39, 3.46, 5.78, 6.27, 6.33, 6.70, 6.82, 6.90, 6.98, 7.19, 7.32, 7.40, 7.54, 8.26, 8.71, 8.99, 9.28, 9.71, 9.87, 12.77, 13.46, 14.31 μ; nmr (CDCl₃) τ 9.05 (s, 6 H, *gem*-CH₃), 7.86 (s, 2 H, C*H₂*CO₂CH₃), 7.73 (d, 2 H, $J = 6.9$ Hz, C-4 CH₂), 5.90 (t, 1 H, $J = 6.9$ Hz, benzylic), 2.90 (m, 10 H, arom).

1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentanol. To 16.3 mmol of phenyllithium in 20.0 ml of ether at 0° under nitrogen was added 1.93 g (6.53 mmol) of methyl 3,3-dimethyl-5,5-diphenyl pentanoate in 20 ml of ether over 55 min. The reaction mixture was then maintained at 0° for another 65 min, warmed to room temperature, stirred for 2 hr, and finally refluxed for 5 hr. The reaction mixture was poured onto an ice–ammonium chloride solution, ether extracted, dried over magnesium sulfate, and concentrated *in vacuo* to afford 4.25 g of yellow, crystalline material which was chromatographed on a 106 × 2.5 cm Vycor column slurry packed with silica gel in 10% ether in hexane and washed with one column volume of hexane. Elution, with 3 l. of hexane, gave 805.7 mg of biphenyl; 1 l. of 5% ether in hexane, 2 l. of 10%, and 2 l. of 15% afforded 2.76 g of a slightly yellow alcohol which was passed through a 50 × 8 cm 1:1 silica gel–Norite column to remove the color. This gave 2.73 g (99.6%) of pure alcohol, mp 115–117°. Ether recrystallization gave mp 117–118°.

The spectral data were: ir (NaCl) 2.79, 2.84, 3.22, 3.26, 3.29, 3.38, 3.47, 6.28, 6.73, 6.86, 6.93, 7.22 (sh), 7.33, 7.61, 8.51, 8.96, 9.29, 9.46, 9.72, 10.01, 10.29, 11.08, 11.38, 11.90, 12.86, 13.49, 14.41, 15.33 μ; nmr (CDCl₃) τ 9.21 (s, 6 H, CH₃), 8.68 (s, 1 H, OH), 7.86 (d, 2 H, $J = 6.9$ Hz, C-4 CH₂), 7.71 (s, 2 H, C-2 CH₂), 5.92 (t, 1 H, $J = 6.9$ Hz, benzylic), 2.79 (br s, 20 H, arom).

Anal. Calcd for C₃₁H₃₂O: C, 88.57; H, 7.62. Found: C, 88.68; H, 7.55.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene. A solution of 1.096 g (2.61 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethylpentanol and 50 mg of *p*-toluenesulfonic acid in 25.0 ml of tetrahydrofuran was refluxed for 3.0 hr. The tetrahydrofuran was removed *in vacuo* and the residue taken up with ether, water washed, dried over magnesium sulfate, concentrated *in vacuo*, and chromatographed on a 108 × 3 cm silica gel (Matheson Coleman and Bell, Grade 62, 60–200 mesh) column slurry packed with 5% ether in hexane and washed with hexane. Elution with 5 l. of 1% ether in hexane gave 0.841 g (2.09 mmol, 80%) of product olefin, mp 76–78°, after crystallization from pentane at Dry Ice temperature. Recrystallization from 95% ethyl alcohol gave mp 80–81°.

The spectral data were: nmr (CDCl₃) τ 9.14 (s, 6 H, CH₃), 7.77 (d, 2 H, $J = 6.9$ Hz, CH₂), 5.87 (t, 1 H, $J = 6.9$ Hz, benzylic), 4.04 (s, 1 H, vinyl), 2.99 (s, 6 H, arom), 2.86 (br s, 14 H, arom); uv max (cyclohexane) 250 nm (ϵ 13,700).

Anal. Calcd for C₃₁H₃₀: C, 92.54; H, 7.46. Found: C, 92.20; H, 7.55.

Ethyl 3-Hydroxy-2,2-dimethyl-4,4,4-triphenylbutanoate. Granular zinc (0.560 g, 8.6 mmol) was activated by treatment with 10% hydrochloric acid, three 50-ml washings with absolute ethanol, three 50-ml washings with benzene, and finally dried by distillation of the benzene. A mixture of 2.0 g (7.35 mmol) of triphenylacetaldehyde,[30] mp 105.0–105.5°, and 1.13 ml (7.71 mmol) of

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(29) All melting points were taken on a hotstage apparatus calibrated with known compounds.

(30) A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **80**, 2844 (1958).

on a 107 × 2.5 cm Vycor column slurry packed with alumina using hexane. The eluent was scanned at 260 nm and 40-ml fractions were collected. Elution with hexane gave: fractions 390–405, 40.1 mg of the trans isomer; fractions 407–420, 39.5 mg of the cis isomer. These compounds were identical with those obtained from independent synthesis (*vide supra*).

The spectral data for 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane (mp 129–130°) were: ir (CHCl₃) 3.36, 3.41, 3.49, 6.28, 6.71, 6.88, 7.35, 9.30, 14.41 μ; uv (95% EtOH) 252 nm (ϵ 2320), 257 (2640), 264 (2305); nmr (CDCl₃) τ 2.98 (m, 20 H, arom), 6.02 (s, 1 H benzylic), τ_A 7.83, τ_B 7.27 (8 line AB portion of an ABC pattern, 2 H, J_{AB} = 15 Hz, J_{BC} = 7 Hz, CH₂), τ_C 5.88 (4 line C portion of an ABC pattern, 1 H, J_{AC} = 14 Hz, PhHCH₂), 8.68 (s, 3 H, CH₃), 8.95 (s, 3 H, CH₃); mass spectrum (70 eV) m/e (rel intensity) 402 (58), 269 (95), 256 (100), 235 (48), 167 (19), 145 (19), 132 (13), 105 (16), 91 (45), 56 (2.4).

Anal. Calcd for C₃₁H₃₀: C, 92.54; H, 7.46. Found: C, 92.40; H, 7.57.

Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene. Test for Energy Transfer by Benzophenone. Photoreduction of Benzophenone by Benzhydrol. A solution of 6.000 g (33.00 mmol) of benzophenone and 2.000 g (10.98 mmol) of benzhydrol in 230 ml of *tert*-butyl alcohol was purged with purified nitrogen[31] for 1 hr before and during the photolysis. Irradiation for 22 min using a 450-W Hanovia medium-pressure lamp equipped with a Pyrex glass filter afforded, after concentration *in vacuo*, 8.178 g of a slightly yellow oil which was chromatographed on a 147 × 2.5 cm Vycor column slurry packed with silica gel using hexane. The eluent was scanned at 260 nm and 40-ml fractions were collected. The material was eluted using 200 ml of hexane, 1.5 l. of 0.5% ether in hexane, 1 l. of 1%, 3.5 l. of 1.5%, 1 l. of 2.5%, 1 l. of 5%, and 3 l. of 7% ether in hexane. Fractions 49–85 gave 4.000 g of benzophenone, mp 47–48°; 86–139 gave 0.381 g of benzopinacol, mp 68–69°; 202–288 gave 1.839 g of benzhydrol, mp 191–194°.

Photoreduction of Benzophenone by Benzhydrol in the Presence of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene. Irradiation of a solution of 6.000 g (33.00 mmol) of benzophenone, 2.000 g (10.9 mmol) of benzhydrol, and 0.7356 g (1.83 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene under the same conditions as described above gave, after concentration *in vacuo*, 10.25 g of an oil which was chromatographed on a 147 × 2.5 cm Vycor column slurry packed with silica gel in hexane. The eluent was scanned at 260 nm and 40-ml fractions were collected. The material was eluted using 5 l. of hexane, 1 l. of 0.5% ether in hexane, 2 l. of 1.5%, 1 l. of 2%, 1 l. of 5%, 1 l. of 10%, and 1 l. of 12% ether in hexane. Fractions 63–110 gave 0.735 g of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene, mp 80–81°; 157–214 gave 6.00 g of benzophenone, mp 47–48°; 265–290 gave 1.99 g of benzhydrol, mp 68–69. No benzopinacol was isolated.

Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene. A solution of 5.999 g (33.00 mmol) of benzophenone and 0.736 g (1.83 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene in 230 ml of *tert*-butyl alcohol was purged with purified nitrogen[31] for 1.5 hr before and during photolysis. Irradiation for 10 hr using a 450-W Hanovia medium-pressure lamp equipped with a Pyrex glass filter afforded, after concentration *in vacuo*, a slightly yellow oil which was chromatographed on a 147 × 2.5 cm Vycor column slurry packed with silica gel using hexane. The eluent was scanned at 260 nm and 40-ml fractions were collected. The material was eluted using 5 l. of hexane, 3 l. of 0.5% ether in hexane, 1 l. of 1.5%, 1 l. of 3%, 1 l. of 5% ether in hexane. Fractions 22–90 gave 0.696 g of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene, mp 80–81°; 91–160 gave 5.976 g of benzophenone, mp 47–48°. No 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene or 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane, mp 129–130°, was detected or isolated.

Photolysis Equipment and Quantum Yield Determinations. The quantum yield irradiations were performed on the Black Box apparatus described previously.[16] Light output was monitored by ferrioxalate actinometry[17] and the light absorbed in the reaction cell was determined by the splitting ratio technique described previously.[16] The filter solutions employed for direct irradiations were: (a) 1.0 M nickel sulfate pentahydrate in 5% sulfuric acid; (b) 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; (c) 2 × 10⁻⁴ M bismuth(III) chloride in 10% hydrochloric acid. This combination (2.4 cm thickness for each of the three cells) showed a transmission maximum at 283 nm and was opaque above 305 nm and below 245 nm. The quantum yields for product formation were determined by high-pressure liquid chromatography using a 4 ft × ⅛ in. column packed with high-speed, Woelm alumina (particle size 18–30 μ). Naphthalene was used as an internal standard for calibra-

tion of the Waters high-pressure liquid chromatographic system with respect to *trans*-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene and 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane; 5% methylene chloride in hexane was used as the eluting solvent; a 0.3 ml/min flow rate was employed. Retention times were: naphthalene, 73 min; 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene, 126 min; 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentene, 89 min; *trans*-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene, 426 min.

Summary of Quantum Yields. Data are listed as follows: starting monoene (mmol), light absorbed, *trans*-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene formed (mmol), 1,2,2,3-tetraphenyl-4,4-dimethylcyclopentane formed (mmol), quantum yield (olefin, cyclopentane), per cent conversion.

Run 1: monoene (0.67 mmol), 1.39 mEinsteins, amount of photoproduct formed was too small to be detected, less than 0.009%.

Run 2: monoene (0.686 mmol), 30.96 mEinsteins, olefin (2.38 × 10⁻² mmol), ϕ = 0.00077, cyclopentane (6.1 × 10⁻³ mmol), ϕ = 0.0002, 4.3%.

Run 3: monoene (0.686 mmol), 34.22 mEinsteins, olefin (2.95 × 10⁻² mmol), ϕ = 0.00085, cyclopentane, (6.9 × 10⁻³ mmol), ϕ = 0.0002, 5.4%.

Single Photon Counting. Determination of the Rate of Excited Singlet State Rearrangement of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene. Purification of Solvent. Isopentane was used for emission studies. Reagent grade solvent was purified by stirring 500 ml with 50 ml of 15% fuming sulfuric acid for 6 hr, washing with water, drying over calcium chloride, and distilling. Finally, the solvent was passed through a 2.5 × 40 cm column of alumina containing 10% of silver nitrate as described by Murray and Keller.[32] The early and late fractions were discarded. Solvent prepared in this way was transparent in the ultraviolet and was fluorescence free.

Purification of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1-pentene for Emission Studies. Samples of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene were crystallized five times from pentane and then five times from 95% ethanol prior to preparing two solutions of the olefin in isopentane (solution A, OD (250 nm) = 0.83; solution B, OD (250 nm) = 1.02). All samples were degassed five times using alternate freeze–thaw cycles; liquid nitrogen was used for freezing the samples.

Magic Multiplier. The fluorescence spectrum was recorded at 298° and 77°K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W Xenon lamp. Concentrations were adjusted to give an optical density in the range of 0.8–1.5 (solutions A and B) to minimize scatter. Self-quenching was shown to be unimportant at this concentration (<10⁻⁴).

The magic multiplier was obtained from a single sample by integrating the emission intensities obtained at 77 and 298°K. The magic multiplier thus obtained was M = 150.

Single Photon Counting Procedure. The optical density at the excitation wavelength was maintained between 1.8 and 2.0, thus minimizing scatter. Excitation and emission monochromators were employed. To avoid counting double photon pulses the monochromator slits were narrowed to the point at which the rate of photon counting was less than 1/20th of the lamp frequency,[33] which was kept at 2–3 kHz in these runs. Collection was continued until the maximum number of counts per channel was 1100–1200. The lamp flash curve was obtained from a run using pure solvent in the sample cell; this run was made contiguous in time with the sample measurement. It was found that the same lamp flash resulted with use of an empty cell.

Summary of Single Photon Counting Data. For each run the following are given in order: temperature, solution, excitation wavelength, emission wavelength, time resolution in sec/channel, lifetime after time axis shifting,[20] ratio SSQR/SSQP[20] gives a measure of the fit with 1 representing a perfect fit; see ref 34.

Run 1: 77°K, B, 270 nm, 310 nm, 8.2 × 10⁻¹¹, 5.11 nsec, 1.04.
Run 2: 77°K, B, 255 nm, 310 nm, 8.2 × 10⁻¹¹, 5.04 nsec, 1.14.
Run 3: 77°K, B, 255 nm, 325 nm, 8.2 × 10⁻¹¹, 5.05 nsec, 1.19.
Run 4: 77°K, B, 270 nm, 325 nm, 8.2 × 10⁻¹¹, 4.99 nsec, 1.20.

Hückel Molecular Orbital Calculations. Molecular orbital

(32) E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).
(33) W. R. Ware, Office of Naval Research Technical Report No. 3, March 1969.
(34) A. E. W. Knight and B. K. Seliger, *Spectrochim. Acta, Part A*, **27**, 1223 (1971).

calculations were carried out using a PDP8/I computer. Resonance integrals were taken to be β for adjacent atoms, 0 for nonadjacent atoms, 1.5β for a strong bonding interaction, and 0.5β for a weak bonding interaction. The result of Jacobi diagonalization of the resulting H-matrix afforded a list of eigenvalues, eigenfunctions, and a bond-order matrix.

Preparation of Chiral Compounds with High Optical Purity by Irradiation with Circularly Polarized Light, a Model Reaction for the Prebiotic Generation of Optical Activity[1]

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Abstract: The partial photodecomposition of racemic α-azido-N,N-dimethylpropionamide and of camphor with circularly polarized light was investigated. The evolution of the enantiomeric yield during the course of the photolysis is reported. The experimental results are in good agreement with theoretical values obtained from a computer simulation of the chemical system. The highest enantiomeric yield achieved yet in an asymmetric transformation induced by circularly polarized light is reported; namely, by carrying the photodecomposition of racemic camphor to 99% completion, the residual starting material had an enantiomeric purity of 19.9 ± 2%. Calculations show that by carrying the reaction to 99.99% completion the residual camphor would be 35.5% enantiomerically pure. It is shown that the obtention of very high optical purity is therefore possible by this way. The relationship between the significance of these results and the prebiotic generation of optical activity is discussed.

The way by which optical activity was generated and propagated on Earth is not yet fully understood and several processes could be postulated. This is a fascinating problem which is closely related to the origin of life, and Pasteur[3] regarded the generation of optical activity as having a cosmic origin, as a consequence of the dissymmetry of the Universe.

Discussions and speculations about the appearance and propagation of optical activity can be found very early in the literature. For example, Le Bel[4a] and Van't Hoff[4b] considered circularly polarized light as a way to create the optical activity found in living systems. The propagation and increase of a small optical activity in living systems has been discussed by Mills.[5] Prebiotic chemistry has recently received much attention and optical activity remains one of the points to be clarified. Several recent articles have reviewed the different theories and the experimental evidence.[6-12] A

part of this material was recently reinvestigated[13,14] and the review by Vigneron[15] seems to be the most complete to date.

To achieve the synthesis of a living system in one enantiomeric form two questions need in general to be considered: (a) the initial creation of a racemic mixture slightly enriched in one antipode and (b) the chemical evolution giving rise to the optically pure material. Chemical evolution which does not need the help of a new chiral auxiliary was recently discussed from a theoretical point of view and some models were proposed[16-18] involving autocatalysis.

Several ways to initiate optical activity were suggested, such as spontaneous resolution[10] and preferred crystallization of either one enantiomer[19] or a labile chiral compound.[20,21] Photochemistry with circularly polarized light[22-25] was also considered for achieving the partial destruction or the optical activation[26] of a race-

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