by CH_3 in carbocations has clearly demonstrated that the substituent effect itself is strongly dependent upon the charge residing on the carbon to which the methyl is attached: G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3137 (1975).
(25) (a) The β-substituent effect was estimated from the difference in the C_4 shifts for **7**-CH_3 and **7**-*t*-Bu (23.5 ppm, Table II). (b) The γ-substituent effect was estimated from the $\delta\Delta_{ortho}$ value for **17** (9.8 ppm). Since there is such an interaction from *each tert*-butyl group at C_1 and C_3, this shielding factor is accordingly doubled. (c) Although our total correction factor of 40 ppm probably represents a maximum estimation, the value derived by the authors in ref 11g (13 ppm) is clearly much too low; they do not appear to have recognized the γ-substituent effect contribution.
(26) Ring inversion would probably be undetectable by NMR in this temperature range if the barrier to inversion in a symmetrical ion (such as **9a** or **5d**) was less than 4.5 kcal/mol or, in unsymmetrical ions such as **10**-H, **10**-Cl and **5**-Cl, if one of the conformers were as little as 1.5 kcal/mol more stable than the other since this would result in a population range of 93–99% for the major conformer.
(27) The relation between carbon-13 chemical shifts and p character is one of their most fundamental properties and is discussed extensively in ref 16.
(28) (a) J. B. Lambert and L. G. Greifenstein, *J. Am. Chem. Soc.*, **96**, 5120 (1974), and references cited therein. (b) R. S. Ozubko, G. W. Buchanan, and I. C. P. Smith, *Can. J. Chem.* **52**, 2493 (1974), and references cited therein.
(29) Reference 16a: (a) Chapter 5-1; (b) Chapter 10-1.
(30) $J_{4a,4b}$ was not resolved. Variation of this parameter in the line-shape analyses (see Appendix) suggested that $J_{4a,4b}$ values more positive than −17 Hz would not yield a resolvable splitting under these conditions.
(31) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969: (a) pp 94–101; (b) p 303.
(32) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Am. Chem. Soc.*, **91**, 3667 (1969). The data have been converted to parts per million relative to external Me_4Si as in ref 16a, p 91. The downfield shift of C_2 in **5**-H, relative to **23**, would be expected due to the β-substituent effect of C_4.
(33) K. Wuthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys.*, **52**, 230 (1970).
(34) E. J. Corey and W. H. Pirkle, *Tetrahedron Lett.*, 5255 (1967).
(35) It is assumed that there is a single minimum corresponding to **5d** = **5e**, and a single maximum corresponding to **5**-H.
(36) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974).
(37) D. A. Kleier and G. Binsch, *J. Magn. Reson.*, **3**, 146 (1970).
(38) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.
(39) R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964).

Conformation and Di-π-methane Reactivity. Mechanistic and Exploratory Organic Photochemistry[1]

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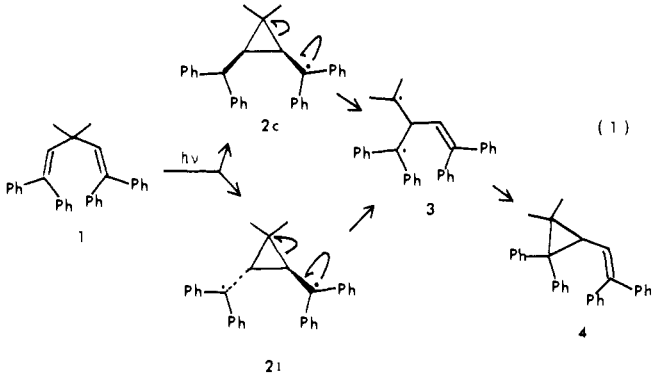
Abstract: In order to test the effect of conformation on the di-π-methane rearrangement, a number of dienes with fixed geometries were synthesized for study. 1-Phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, and 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene were used as dienes capable of bridging to form the *cis*-cyclopropyldicarbinyl diradical species. 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene was employed as a diene capable of leading on to a trans-bridged cyclopropyldicarbinyl diradical species. For these compounds, excited singlet and triplet reactions were investigated, and the di-π-methane rearrangement products encountered were identified by independent synthesis. Singlet and triplet quantum yields were obtained in order to assess reactivity. Additionally, the rates of excited singlet processes were investigated using single photon counting with deconvolution. The unimolecular rates of excited singlet rearrangement, rates of singlet decay, and rates of fluorescence were determined directly. Evidence was obtained that both cisoid and transoid diradical species can intervene successfully in the di-π-methane rearrangement. Rate differences are interpreted in terms of steric and electronic factors.

In our previous studies on the di-π-methane rearrangement, we have noted[2] that there are two a priori possible stereoisomers of the cyclopropyldicarbinyl diradical species engendered in the initial bridging step. These are the cisoid (**2c**) and transoid (**2t**) species of eq 1. There has been no

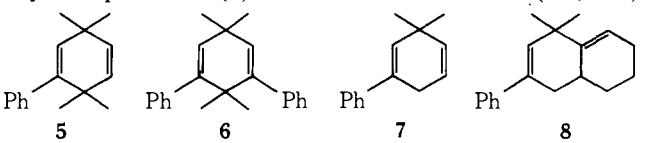


(1)

firm evidence bearing on this point. One suggestive observation[3] is that methyl substitution on the methane carbon (i.e., C-3) facilitates the rearrangement. In our previous reports,[3,4] we ascribed the requirement for methyl substitution to electronic effects which facilitate the opening of the cyclopropyldicarbinyl diradical **2** of eq 1. However, the central methyl effect, a priori, might be rationalized on the basis of such substitution enhancing formation of a conformer of diene reactant required for reaction. Thus, one could conceive of a Thorpe–Ingold effect[5] in which central methyl substitution would affect the probability of obtaining one of the two cyclopropyldicarbinyl diradical species (i.e., **2c** or **2t**).

Consequently, it seemed desirable to compare di-π-methane systems designed to permit generation of only cisoid or transoid cyclopropyldicarbinyl species (i.e., only **2c** or **2t**). With this approach, we could determine if one geometry was inherently unfavorable.

For this study, we selected 1-phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene (**5**), 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene (**6**), 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene (**7**), and 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene (**8**). Of these, the first three (i.e., **5**–**7**)



5 **6** **7** **8**

Chart I. Synthesis of Tetramethyl Monophenyl Diene 5

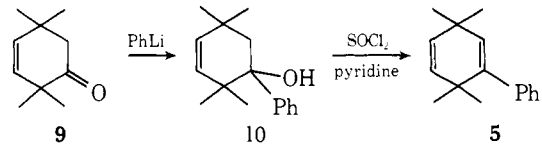


Chart II. Synthesis of Tetramethyl Diphenyl Diene 6

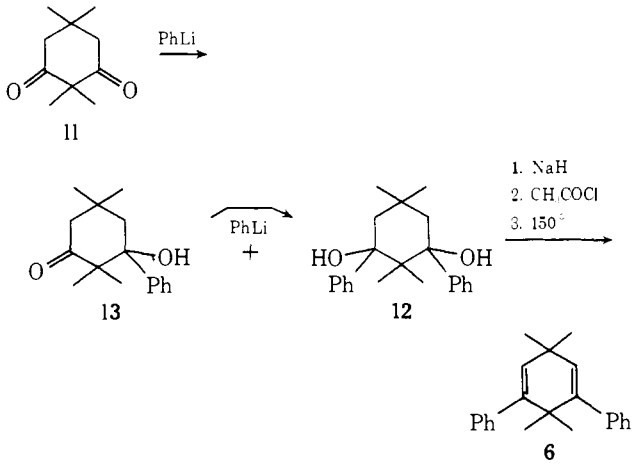
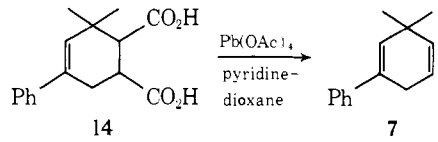


Chart III. Synthesis of Dimethyl Monophenyl Diene 7



can lead only to cisoid diradical species, while the last (i.e., **8**) can afford only a transoid diradical.

Results

Synthesis of Photochemical Reactants. The syntheses of the four dienes of interest (i.e., **5–8**) are outlined in Charts I–IV and detailed in the Experimental Section. Several synthetic aspects are noteworthy. One is the mode of dehydration of 1,3-diol **12** in which both thionyl chloride–pyridine and diacetate pyrolysis proved effective and avoided danger of 1,3-diol cleavage.[6] Rearrangement proved no problem in the case of alcohol **10** where *p*-toluenesulfonic acid proved as effective as thionyl chloride–pyridine.

Secondly, in the synthesis of the acyl azide from acid chloride **15,** it was determined that, in the dimethoxyethane solvent employed, azide formation did not occur unless water was added (0.1 equiv proved convenient). Presence or absence of adventitious water thus may lead to irreproducible results in such Curtius syntheses.

Finally, in the alkylation of enone **16,** spiroalkylation proved troublesome when direct alkylation was attempted. This was avoided by using carbomethoxy ketone **17** in the alkylation step. However, even in the saponification–decarboxylation of the alkylated material, formation of spiroketone **19** was encountered, and it proved necessary to run the saponification to part completion and then recycle unsaponified product **18.**

Synthesis of Anticipated Photochemical Products. Exploratory photochemical studies outlined below led us to concentrate our efforts on the syntheses of products expected from the di-π-methane rearrangement of dimethyl monophenyl diene **7** and bicyclic diene **8.**

These syntheses are delineated in Charts V and VI and are detailed in the Experimental Section. One step in Chart V meriting comment is the NBS bromination in which the allylic radical intermediate conveniently reacts with bromine selectively to give the primary bromide, presumably formation of the more substituted π bond being the driving force. Subsequent SN2 displacement with diethyl sodiomalonate led to diacid **23.** Also, we note that bicyclic ketone **26** was obtained by two routes, one of which was a one-step approach using the oxa-di-π-methane rearrangement.[7a,b] For the introduction of the π bond in the strained bicyclo[3.1.0] ring system of photoproduct, the Dauben reaction[8] proved especially useful.

The synthesis of bicyclic diene photoproduct (i.e., **32**) was straightforward. We do note that an oxa-di-π-methane rearrangement (**20** to afford **29**) was again a convenient way to generate the bicyclo[3.1.0]hexane ring system.

Exploratory Photochemical Efforts and Assignment of Product Structures. Our initial photolyses were run using a 450-W Hanovia immersion apparatus, a Corex filter, in *tert*-butyl alcohol solvent. Under these conditions, it was observed that tetramethyl monophenyl and diphenyl dienes **5** and **6** proved unreactive. This was the case even when the shorter wavelength Vycor filter was used in an attempt to utilize more light.

In the case of dimethyl monophenyl diene **7,** a smooth photochemical reaction was observed to give one product. This substance had vinyl absorptions at τ 4.30 and 4.48 in the NMR along with two nonequivalent methyl peaks at τ 9.03 and 9.14, suggesting the occurrence of a di-π-methane rearrangement.[9-11]

Unambiguous structure assignment was obtained by the independent synthesis of photoproduct **28** as outlined in Chart V. It was found that the photoproduct and the independently synthesized material were identical in all respects as is indicated in the Experimental Section.

Turning to the exploratory photolysis of bicyclic diene **8,** we found a smooth, and even more facile, formation of a single photochemical product. Again, the appearance of two nonequivalent methyl NMR peaks, at τ 8.74 and 9.20, along with a simple vinyl absorption at τ 4.56 pointed to occurrence of a di-π-methane process. As before, the suggestive NMR evidence proved correct. Thus, independent synthesis of the photoproduct (note Chart VI) as discussed above led to material identical with the photoproduct **32.**[12]

Quantum Yield Determinations. These were obtained using the Black Box apparatus as well as the semimicro optical bench described by us earlier.[13] In quantum yield determinations, the usual precautions were taken. For general purposes, it is worthwhile making these following statements. (1) At the end of photolyses, ultraviolet spectra were determined to make certain that product light absorption was not leading to internal filter effects. (2) Lack of singlet self-quenching at the concentrations used was established. (3) Low enough conversions were used so that no secondary photochemistry was occurring, and runs were made to successively lower conversions to obtain a limiting quantum yield. (4) Concentrations and wavelength were adjusted to assure that minimal light passed through either actinometer or reactant,[14] and this was checked by use of a second, backup actinometer cell. Errors in correction for minor loss due to light transmission can lead to only minor relative errors. (5) In sensitized runs, low enough concentrations of reactant were employed so that the rate of singlet sensitizer decay would be fast enough to ensure that there was no singlet transfer; yet high enough concentrations of reactant were used to ensure essentially complete triplet capture.

To ascertain that singlet self-quenching is not occurring, one can determine quantum yields at decreasing concentrations to make certain that the efficiency has reached an asymptote. This was done (note Experimental Section) in the case of the monocyclic diene. However, a simpler test

Chart IV. Synthesis of Bicyclic Diene 8

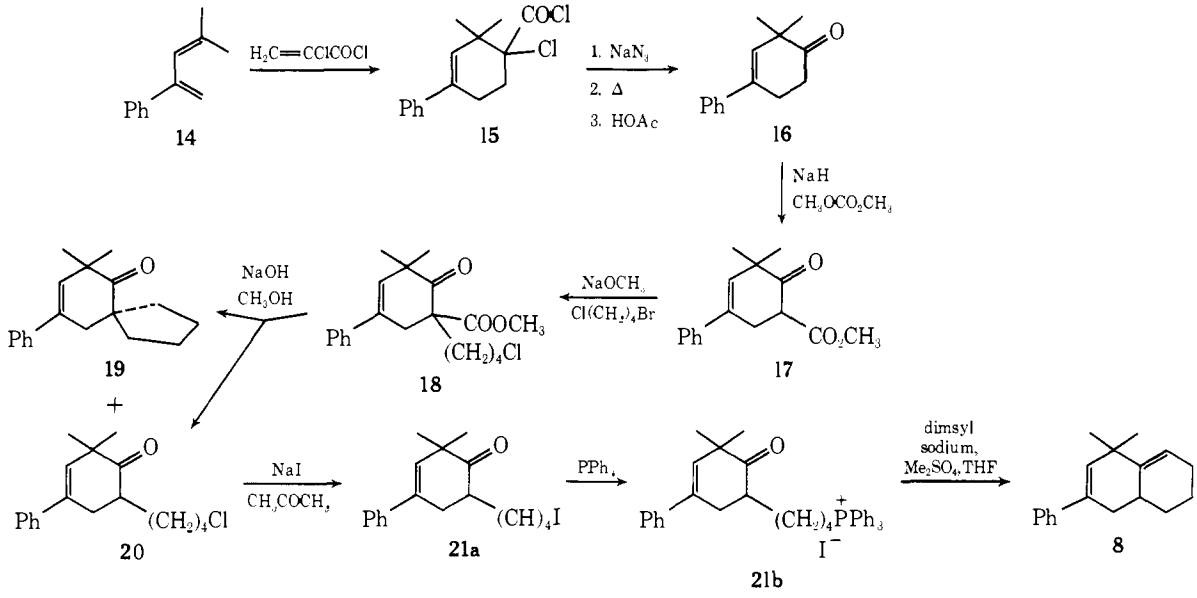


Chart V. Synthesis of Expected Photoproduct of Diene 7

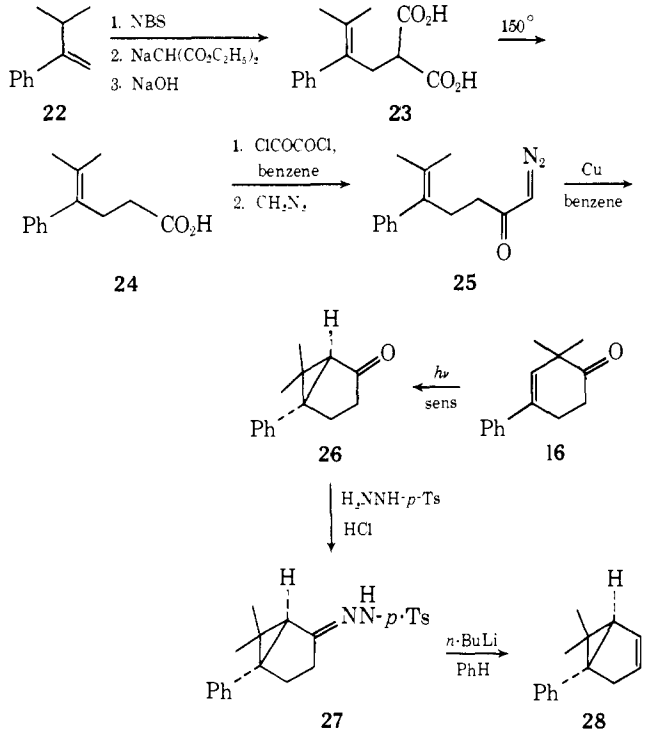
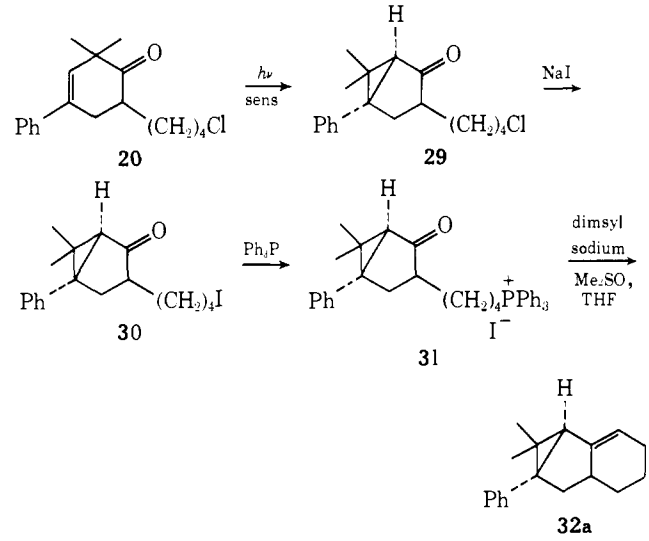


Chart VI. Synthesis of Photoproduct of Bicyclic Diene 8



seemed desirable, and such a test was predicated on checking for fluorescence quenching.

It is generally assumed that the intensity of fluorescence is given by eq 2.[15] However, this equation

$$I_t = I_0\phi_t(1 - 10^{-\epsilon cl}) \quad (2)$$

gives the total fluorescence emitted throughout the entire fluorescence cell. Most fluorimeters view fluorescence perpendicularly through a vertical slit placed halfway between the front face and rear of the fluorescence cell. The intensity of fluorescence emitted through such a slit is not given so simply. Beer's law and simple analytic geometry lead us to eq 3.

$$I_t = KI_0\phi_t A \times 10^{-(A/2)} \quad (3)$$

Here K is an instrumental, geometric proportionality constant, A is the solution absorbance, and I_0 gives the incident light intensity. I_f in eq 3 gives the fluorescence intensity for an idealized, infinitely narrow slit.

Hence, looking at eq 3, we do not expect the emission intensity, under practical experimental conditions, to follow eq 2. The intensity will increase initially as the preexponential term A is controlling, eventually reach a maximum, and then decrease. We have already noted[16] that maximum emission is expected at an absorbance of 0.87, and this is derivable from eq 3.

A test for lack of concentration quenching can then be predicated on eq 3. Thus in Figure 1, we have a plot of experimentally observed fluorescence intensity of dimethyl phenyl diene **7** vs. the function $A \times 10^{-(A/2)}$. This is a double valued furction with two values of A for each value of I_f. The near linearity shows lack of self-quenching; such quenching would decrease ϕ_f with increasing absorbance.

The results of the quantum yield and rate determinations are summarized in Table I and detailed in the Experimental Section.

Determination of Excited Singlet Rate Constants. In addition to the reaction quantum yields, the singlet excited state rates of decay and rates of rearrangement were desired. Additionally, it was of some interest to determine the natural rates of fluorescence.

Table I, Quantum Yield and Rate Determinations

Reactants	ϕ_r	$^1\tau$(ns)	$^1k_{dt}$	^3k_r	ϕ_f	k_f
Tetramethyl monophenyl diene 5	<0.0001	12.5	8.0×10^7	$<10^4$	0.033	2.6×10^6
Tetramethyl diphenyl diene 6	<0.0001	1.2	8.3×10^8	$<10^5$	0.0026	2.2×10^6
Dimethyl phenyl diene 7	0.015	4.3	2.3×10^8	3.4×10^6	0.079	1.8×10^7 46.0×10^7[a]
Bicyclic diene 8	0.097	0.29	3.4×10^9	3.3×10^8	0.0094	2.7×10^7 42.6×10^7[a]
Dimethyl phenyl diene 7 and acetophenone	0.0002					
Bicyclic diene 8 and acetophenone	0.0040					

[a] Determined via eq 6.

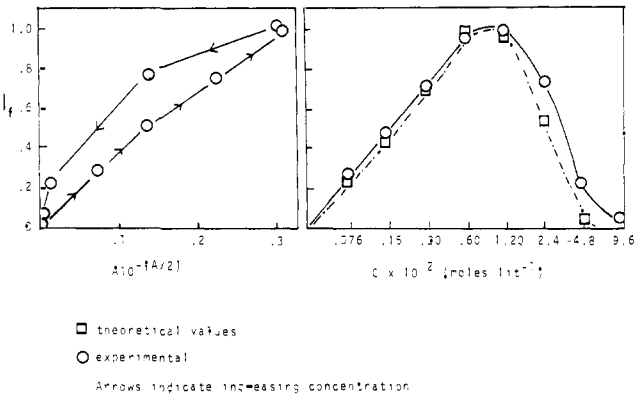


Figure 1. Plot of fluorescence intensity vs. $A \times 10^{-(A/2)}$ and vs. concentration.

Using our previously described method of single photon counting using an on-line minicomputer for data acquisition and indirect deconvolution,[17] we obtained the total rates of excited singlet decay (i.e., the $^1k_{dt}$'s) listed in Table I; also the results are given as lifetimes (τ's). In contrast to our previous studies on di-π-methane systems, the compounds presently investigated had sufficiently long lifetimes to allow determinations at room temperature.

With the $^1k_{dt}$'s available, along with the reaction quantum yields, eq 4 was employed to afford the unimolecular rates of excited state singlet rearrangement. These, too, are given in Table I.

$$\phi_r = k_r/(^1k_{dt}) \quad \text{or} \quad k_r = \phi_r(^1k_{dt}) \tag{4}$$

Using the same approach, the rates of fluorescence of the excited singlets were determined (note Table I), however, here using the quantum yields of fluorescence as in eq 5. These quantum yields were determined relative to a biphenyl standard.[18]

$$k_f = \phi_f(^1k_{dt}) \tag{5}$$

For interest's sake, an attempt was made to determine the k_f's by use of the Einstein relationship (note eq 6).[19]

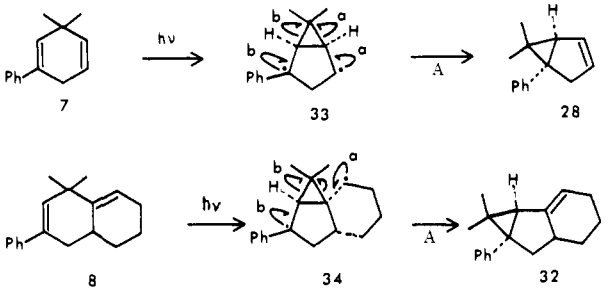
$$k_f = 2.88 \times 10^{-9} \bar{\nu}_{max}^2 n^2 \int \epsilon(\nu)\, d\nu \tag{6}$$

However, this requires integration of the absorption peak corresponding to the fluorescence emitted. Inspection of the ultraviolet absorption curves for the compounds of interest indicated an uncertainty of what portion should be considered as deriving from excitation to S_1. For dimethyl phenyl diene **7** and bicyclic diene **8**, integration of the peaks at 247 and 248 nm, respectively, afforded the values of k_f(calcd) given in Table I and compared with the directly measured values.

Interpretative Discussion

The Rearrangements and Their Regiospecificity. Considering first the photochemistry of dienes **7** and **8**, we note that these rearrange via a di-π-methane mechanism. This is outlined in Chart VII.

Chart VII. Mechanism of Di-π-Methane Rearrangement of Dimethyl Monophenyl Diene **7** and Bicyclic Diene **8**

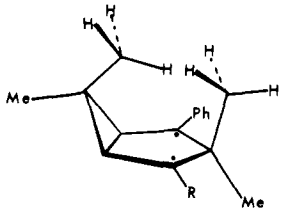


We note that, in each case, the cyclopropyldicarbinyl diradical species (i.e., **33** and **34**) has the a priori possibility of reacting further in two different ways. Thus each reactant has two di-π-methane products as possibilities. However, with complete regiospecificity each diene led only to that product expected on the basis discussed by us earlier.[11,20] Accordingly, in Chart VII, the three-membered ring opening preferred is pathway A (arrows a) since this minimizes loss of excited state delocalization. The alternative pathway B (arrows b) utilizes a diffuse benzylic electron which is thus not too available, and such utilization leads to loss of benzylic delocalization in the ring opening.

One point of interest is that there are two conceivable stereoisomers which might arise in the di-π-methane rearrangement of bicyclic diene **8**, namely **32a** and **32b** (the C-6 epimer of **32a**). Although definitive proof is not available, strong evidence is provided by lack of base catalyzed epimerization of ketone **29** which was a synthetic precursor to photoproduct **32**. It is seen that the exo stereoisomer of **29** has the chlorobutyl side chain more distant from the *endo*-methyl group at C-6, and that this is the stereoisomer which should not epimerize. This then suggests that both in the di-

π-methane rearrangement of **8** and in the oxa-di-π-methane rearrangement of **20**, π–π bridging occurs stereoselectively, giving the bridged species **33** and **34**. This does seem reasonable since this bonding stereochemistry leads to minimization of steric interactions between the *endo*-methyl at C-6 and the chloroalkyl side chain.

A final, yet striking, observation needing comment is the lack of reactivity observed for the tetramethyl monophenyl diene **5** and tetramethyl diphenyl diene **6**. In view of the occurrence of the di-π-methane rearrangement in the very closely related dimethyl phenyl diene **7**, we have concluded that the lack of reactivity of **5** and **6** is due to flagpole methyl–methyl interactions in the bridged species (note **35**)



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which would have to be engendered from these two nonreactive dienes. This is clear from consideration of Dreiding models. The corresponding representation **35** also gives an indication of the proximity of methyls after such bridging.[21]

Multiplicity and Efficiencies. The first point to be noted is that both the singlet and triplet excited states of the dimethyl phenyl diene **7** and the bicyclic diene **8** undergo the di-π-methane rearrangement. However, the direct quantum yields are considerably greater (ca. 25 to 50-fold; note Table I) than the sensitized efficiencies. Two points can be deduced from this evidence. First, since the sensitized runs define the reactivity of the triplet, and this is low, we can conclude that the higher efficiency observed on direct irradiation derives from an inherently high reactivity of the singlet rearrangement; any appreciable intervention of intersystem crossing and subsequent triplet rearrangement would lead only to the characteristically low quantum yields of the triplet. Actually, the ratio of the sensitized to the direct irradiation efficiencies provides an upper limit for the fraction of excited triplet intervention in the direct irradiations, and the direct quantum yields provide a lower limit for singlet state efficiencies.

The second conclusion possible is that, for the systems at hand, reactivity is thus minimally 25- to 50-fold greater for the singlet than for the triplet. This difference may reflect a high singlet rate rather than a low triplet efficiency. Thus, our earlier generalization[10,11,23] that constrained systems, such as monocyclic ones, prefer to utilize the triplet for the di-π-methane rearrangement derives from the frequent availability of a rapid, competitive electrocyclic process available to and preferred by the singlet. No such process is presently competitive, and thus it is not surprising that the di-π-methane rearrangement dominates efficiently.

Excited Singlet Rates. In our previous studies on the di-π-methane rearrangement,[17] we have noted a parallelism between the rates of singlet unimolecular rearrangement to product and the rates of total singlet decay to ground state reactant. This was interpreted to mean that the major decay process and the rearrangement mechanism had some common mechanistic feature, susceptible in the same way to structural variations in the singlet excited state. The common step was taken as vinyl–vinyl bridging since both decay and rearrangement were accelerated by addition of terminal stabilizing groups on the di-π-methane system.

However, we note that, in the present study, the rates of decay of the two tetramethyl dienes, **5** and **6**, and that of the dimethyl phenyl diene **7** all fall into a range of one order of magnitude (i.e., from 8.0×10^7 to 8.3×10^8 sec^{-1}) despite varying rates of rearrangement. Furthermore, this rate of decay is not only slow compared with the previously studied di-π-methane systems but also is suggestively close to that observed by us earlier[16] for the excited singlet of 1-phenylcyclohexene where no bridging is involved; the 1-phenylcyclohexene k_{d_t} was 6.9×10^8 sec^{-1}.[16] This, taken together with the observation of the failure of the tetramethyl dienes **5** and **6** to react, provides evidence that all of these dienes decay primarily by routes which are characteristically 1-phenylcyclohexene-like and which do not involve vinyl–vinyl bridging. In fact, the absence of this bridging has already been concluded (vide supra) for dienes **5** and **6**. This does not mean that a minor component of the decay of dimethyl phenyl diene **7** is not bridging, but it does mean that there is a leveling effect on these rates due to bridging having become too slow. Typically, with $k_r = 1.4 \times 10^6$ sec^{-1} and with typical quantum yields of ca. 0.1, k_{d_t} for dimethyl phenyl diene **7** would be ca. 3.4×10^7 sec^{-1}. But this would indeed be unobserved in the present total decay.

With the total singlet decay rates then due to normal phenylcyclohexene type decay and being largely unrelated to bridging, we can understand a lack of the usual ratio between decay and reaction rates for dimethyl phenyl diene **7**.

Turning now to ${}^1k_r$ for dimethyl phenyl diene **7** and bicyclic diene **8**, we find that the former is one of the slowest di-π-methane rearrangement rates encountered thus far. Comparison of the rates for the previously studied systems suggests that a terminal phenyl group enhances the rate relative to that of a system with only a terminal methyl group by a factor of ca. 5 per such phenyl vs. methyl replacement. Similarly, methyl speeds up the rate relative to hydrogen by a factor of ca. 3.[24a] Thus, we can make a very rough prediction of rates for the two dienes (i.e., **7** and **8**) in absence of nonelectronic effects. We obtain[24b] a rate inhibition of 15-fold relative to 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**36**) whose k_r was found[17] to be 6.9×10^9 sec^{-1}; this leads to $k_r = 5 \times 10^8$ sec^{-1}.

Our conclusion is that the rate of rearrangement of bicyclic diene **8** is perfectly normal, but that for dimethyl phenyl diene **7** is somewhat inhibited. This is reasonable when one considers the related failure of the tetramethyl dienes **5** and **6** to react at all, ascribed to flagpole–flagpole interactions, and also the considerable strain incurred on vinyl–vinyl bridging in the three monocyclic systems as a consequence of having two sp^2-hybridized carbons in the bicyclo[3.1.0]hexane ring system; note structure **35**. Bicyclic diene **8**, in contrast, has only one sp^2-hybridized carbon in the strained [3.1.0] ring system. In both the case of bicyclic diene **8** and dimethyl phenyl diene **7**, there may be some residual flagpole–flagpole van der Waals interaction between methyl and hydrogen.

Thus, except for effects on the excited singlet rates deriving from the usual substituent and from steric factors, we find no demand for either a cisoid or a transoid cyclopropyldicarbinyl diradical system; rather both are seen capable of rearranging. This then also confirms the view that the central methyl effect, in which this substitution facilitates the di-π-methane rearrangement, does derive from electronic stabilization and not from conformational effects.

In conclusion, we note with some awe that the di-π-methane rearrangement is impressively consistent in its operation. It seems to be one of those reactions which is willing to afford a rational pattern of behavior on intensive investigation. Also, it is a reaction of considerable synthetic utility.

Experimental Section[25]

1-Phenyl-2,2,5,5-tetramethylcyclohex-3-en-1-ol. A solution of 12.9 g (85.0 mmol) of 2,2,5,5-tetramethylcyclohex-3-en-1-one[26] in

100 ml of anhydrous ether was treated with 200 ml of a 2.0 *M* solution of phenyllithium in ether. After refluxing for 2 hr, the mixture was decomposed with water, ether extracted, dried, and concentrated. The residue, containing ca. 60% of starting ketone (NMR analysis), was again subjected to the phenyllithium treatment. Repetition of the work-up yielded a brown oil which was distilled. Collection of the fraction boiling at 80–85° (1.0 mmHg) afforded 17.4 g (75.6 mmol, 89%) of the desired 1-phenyl-2,2,5,5-tetramethylcyclohex-3-en-1-ol as a clear, colorless oil, 99% pure by NMR.

The spectral data were: ir (neat) 2.78, 2.85 (OH), 6.28 (C=C), 6.94, 7.37, 8.58, 13.24, 14.32 μ; NMR ($CDCl_3$) τ 2.20–2.99 (m, 5 H, arom), 4.62 (AB q, 2 H, J = 10 Hz, vinyl), 7.54 (d, 1 H, J = 14 Hz, CH_2), 8.10 (s, 1 H, OH), 8.36 (d, 1 H, J = 14 Hz, CH_2), 8.86 (s, 3 H, CH_3), 8.92 (s, 3 H, CH_3), 9.11 (s, 3 H, CH_3), 9.22 (s, 3 H, CH_3); mass spectrum (calcd for $C_{16}H_{22}O$, 230.167) *m/e* 230.167.

2-Phenyl-3,3,6,6-tetramethylcyclohexa-1,4-diene. A solution of 12.2 g (53.0 mmol) of 1-phenyl-2,2,5,5-tetramethylcyclohex-3-en-1-ol in 200 ml of dry pyridine was treated with 6.30 g (53.4 mmol) of thionyl chloride over 5 min. After refluxing for 30 min, the cooled mixture diluted with 200 ml of ether was washed with 10% hydrochloric acid and dried over magnesium sulfate. The residue after concentration was purified by passing through a 5 × 50 cm silica gel column (MCB Grade 62). The first 1000 ml of hexane eluent yielded 9.50 g (44.8 mmol, 85%) of 2-phenyl-3,3,6,6-tetramethylcyclohexa-1,4-diene as a clear, colorless oil.

The spectral data were: ir (CCl_4) 3.23, 3.26, 3.31, 3.37, 3.41, 3.48, 6.73, 6.83, 7.39, 14.29 μ; NMR ($CDCl_3$) τ 2.83 (s, 5 H, arom), 4.57 (s, 1 H, vinyl), 4.58 (s, 1 H, vinyl), 4.73 (m, 1 H, styryl), 8.93 (s, 6 H, CMe_2), 8.95 (s, 6 H, CMe_2); uv (EtOH) 250 nm sh (1250).

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.49. Found: C, 90.35; H, 9.31.

1,3-Diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol. A solution of 19.2 g (0.114 mol) of 2,2,5,5-tetramethylcyclohexane-1,3-dione[27] in 250 ml of anhydrous ether was added over 30 min to 1.0 mol of phenyllithium in 1000 ml of ether. After 6 hr at room temperature, the mixture was treated with water and ether extracted, and the extracts were dried and concentrated to yield 25 g of a slightly yellow solid. The solid was recrystallized from 50% ether–hexane to yield 12.3 g (0.052 mol) of 3-hydroxy-3-phenyl-2,2,5,5-tetramethylcyclohexan-1-one, mp 179.0–181.5°, 6.50 g of a mixture of the keto alcohol and 1,3-diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol, and finally 3.40 g (0.011 mol, 10%) of 1,3-diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol as colorless prisms, mp 224.0–227.0°.

The spectral data for 3-hydroxy-3-phenyl-2,2,5,5-tetramethylcyclohexan-1-one were: ir (KBr) 2.95, 3.23, 3.25, 3.27, 3.32, 3.38, 3.42, 3.48, 5.92, 6.82, 6.95, 7.05, 7.22, 7.29, 7.41, 7.79, 7.86, 8.00, 8.30, 8.43, 8.61, 8.74, 9.21, 9.35, 9.69, 9.88, 10.36, 10.47, 10.92, 11.67, 12.48, 13.08, 13.99, 14.21, 15.33 μ; NMR ($CDCl_3$) τ 2.40–2.76 (m, 5 H, arom), 7.16 (d, 1 H, J = 13 Hz, CH_2) 7.28 (d, 1 H, J = 7.13 Hz, CH_2), 7.76 (d of d, 1 H, J = 13 and 2 Hz, CH_2), 8.40 (d of d, 1 H, J = 13 and 2 Hz, CH_2), 8.76 (s, 3 H, CH_3), 8.84 (s, 3 H, CH_3), 8.96 (s, 3 H, CH_3), 9.07 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.80; H, 8.93.

The spectral data for 1,3-diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol were: ir (KBr) 3.14, 3.35, 3.39, 6.29, 6.72, 6.88, 7.32, 7.41, 8.19, 8.33, 8.48, 8.60, 8.30, 8.83, 9.38, 9.73, 10.21, 10.98, 11.30, 11.77, 13.16, 14.24 μ; NMR ($CDCl_3$) τ 2.30–2.84 (m, 10 H, arom), 5.90 (s, 2 H, OH), 7.34 (d, 2 H, J = 16 Hz), 8.30 (d, 2 H, J = 16 Hz), 8.56 (s, 3 H, CH_3), 8.83 (s, 3 H, CH_3), 9.16 (s, 3 H, CH_3), 9.29 (s, 3 H, CH_3).

Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.43; H, 8.70. Found: C, 81.26; H, 8.68.

The keto alcohol could be recycled to produce the diol in 54% yield by treating it with 4 equiv of phenyllithium under the same conditions.

1,5-Diphenyl-3,3,6,6-tetramethylcyclohexa-1,4-diene. A mixture of 1.06 g (24.7 mmol) of 56% sodium hydride suspension in mineral oil, 25 ml of anhydrous ether, and 1.90 g (6.01 mmol) of 1,3-diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol was refluxed for 10 hr after which 1.8 ml (25.0 mmol) of acetyl chloride was added. The mixture was then refluxed for 4 more hr, decomposed with water, and ether extracted. The ether layer was washed with water, dried over magnesium sulfate, concentrated under vacuum, and triturated with hexane, leaving 1.95 g of crude 1,3-diphenyl-2,2,5,5-tetramethylcyclohexane-1,3-diol diacetate as a pasty solid.

The spectral data were: ir ($CHCl_3$) 2.78, 2.89, 3.35, 3.40, 3.47, 5.73, 6.70, 6.92, 7.21, 7.27, 7.39, 8.7, 9.00, 9.34, 9.64, 9.80, 14.27 μ.

The crude material was pyrolyzed at 150° for 15 min and then chromatographed on a 2.5 × 100 cm silica gel column (MCB grade 62) with hexane to remove nonhydrocarbon impurities. The resulting 0.470 g of white solid was recrystallized from methanol to yield 0.411 g (1.43 mmol, 24%) of colorless needles, mp 119.0–119.5°.

The spectral data were: ir (KBr) 3.25, 3.27, 3.32, 3.37, 3.42, 3.49, 6.25, 6.71, 6.82, 6.94, 7.22, 7.37, 8.29, 8.49, 8.92, 9.32, 9.72, 10.30, 10.78, 10.98, 11.40, 11.80, 14.2, 15.1 μ; NMR (CCl_4) τ 2.82 (s, 10 H, arom), 4.65 (s, 2 H, –CH=), 8.84 (s, 6 H, CMe_2), 8.93 (s, 6 H, CMe_2); uv (EtOH) 230 nm sh (5700).

Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.54; H, 8.27.

2,2-Dimethyl-4-phenyl-1,2,5,6-tetrahydrophthalic Anhydride. The reaction described by Alder[28] was run under more convenient conditions. To a solution of 73.0 g (0.493 mol) of 4-methyl-2-phenylpenta-1,3-diene[29] in 400 ml of 4:1 benzene–hexane was added 51.0 g (0.520 mol) of maleic anhydride in 200 ml of the same solvent. The solution was refluxed for 24 hr, diluted with 1.0 l of hexane, again brought to reflux, and allowed to cool. The white crystalline precipitate was collected, washed quickly with 100 ml of cold ether, and dried for 24 hr at 40–50° to yield 121.6 g (0.494 mol, 100%) of the anhydride as white prisms, mp 114.5–115.5° (reported[4] 116°).

2,2-Dimethyl-4-phenyl-1,2,5,6-tetrahydrophthalic Acid. A 33.0-g (0.134 mol) portion of 2,2-dimethyl-4-phenyl-1,2,5,6-tetrahydrophthalic anhydride was heated in 100 ml of 10% aqueous sodium carbonate until no solid remained. The solution was cooled, then neutralized with 10% aqueous hydrochloric acid to a Methyl Orange end point. The resulting white solid was filtered, washed with 100 ml of ether, and dried 48 hr at 40° to yield 24.9 g (0.095 mol, 70%) of 2,2-dimethyl-4-phenyl-1,2,5,6-tetrahydrophthalic acid as a white solid, mp 178.0–179.2° (reported[29] mp 180°). Recrystallization from acetone did not change the melting point.

1-Phenyl-3,3-dimethylcyclohexa-1,4-diene. To a mixture of 24.9 g (90.8 mmol) of 2,2-dimethyl-4-phenyl-1,2,5,6-tetrahydrophthalic acid, 12.1 ml (150 mmol) of pyridine, and 200 ml of anhydrous dioxane was added 27.8 g (67.0 mmol) of 90% lead tetraacetate in acetic acid. The resulting red solution was heated at 60° until evolution of carbon dioxide had ceased (ca. 45 min). The reaction was quenched with 10 ml of ethylene glycol and then treated with 200 ml of 10% sodium hydroxide. This mixture was pentane extracted. The extracts were washed with 10% hydrochloric acid, followed by 10% sodium bicarbonate.

The residue remaining after drying and concentrating was passed through a 3.0 × 25 cm silica gel column (MCB grade 62) to yield 1.80 g (9.75 mmol) of a clear, colorless oil. Crystallization at Dry Ice temperature from an equal volume of ether afforded 1.65 g (8.98 mmol, 9.8%) of 1-phenyl-3,3-dimethylcyclohexa-1,4-diene as a colorless oil.

The spectral data were: ir (neat) 3.24, 3.26, 3.32, 3.43, 3.49, 3.56, 6.25, 6.70, 6.93, 7.25, 7.38, 8.82, 9.76, 10.70, 11.50, 13.25, 13.75, 14.40 μ; NMR (CCl_4) τ 2.42–2.96 (m, 5 H, arom), 6.16 (d of t, 1 H, J_t = 1.5, J_d = 1.8 Hz, styryl), 4.32 (d of t, 1 H, J_d = 10.0, J_t = 3.0 Hz, C-5 vinyl), 4.46 (d of t, 1 H, J_d = 10.0, J_t = 1.6 Hz, C-4 vinyl), 7.05 (m, 2 H, CH_2), 2.89 (s, 6 H, CH_3); uv (EtOH) 247 nm (13,900).

Anal. Calcd for $C_{14}H_{16}$: C, 91.24; H, 8.75. Found: C, 91.12; H, 8.86.

2,2-Dimethyl-4-phenylcyclohex-3-en-1-one. The general method of Corey[30] for masked ketene 1,4 cycloaddition was used with some modification. A 5.07-g portion (40.6 mmol) of 2-chloroacrylyl chloride[31] was stirred in 50 ml of anhydrous ether at 0° to which had been added 6.65 g (42.1 mmol) of 2-phenyl-4-methyl-1,3-pentadiene.[29] The solution was stirred at 0° for 2 hr and then allowed to warm to room temperature. The ether was removed under vacuum to obtain 11.7 g (40.6 mmol, 100%) of 1-chloro-2,2-dimethyl-4-phenylcyclohex-3-ene-1-carboxyl chloride as a colorless oil.

The spectral data were: NMR (CCl_4) τ 2.53–2.95 (m with s at

7.23, 5 H, arom), 4.42 (t, 1 H, J = 1 Hz), 7.35–7.74 (m, 4 H, CH_2CH_2), 8.57 (s, 3 H, CH_3), 8.74 (s, 3 H, CH_3); ir (neat) 3.24, 3.27, 3.30, 3.36, 3.40, 3.48, 5.67, 6.29, 6.71, 6.94, 7.21, 7.34, 9.39, 9.72, 10.56, 11.34, 11.64, 13.00 13.35, 14.47 μ. The oil was dissolved in 150 ml of freshly distilled dimethoxyethane to which had been added 4.48 g (69.0 mmol) of sodium azide and 0.10 ml (5.5 mmol) of water. After 3 hr, the salt was filtered, and the filtrate was refluxed 3 hr. Then 60 ml of a 2:1 mixture of acetic acid–water was added to the cooled mixture which was heated at 65° for 3 hr (note that this is longer than the 45 min used by Corey[30]). The reaction was worked up by concentrating the mixture to 100 ml in vacuo, taking up the mixture in 1000 ml of pentane, and washing with 1 sodium bicarbonate. After drying over magnesium sulfate and concentrating, the crude product was chromatographed on a 150 × 5 cm silica gel column (MCB grade 62, 60–200 mesh) to give 500-ml fractions: 1–3 (hexane) nil; 4–6 (5% ether–hexane) 3.98 g (19.9 mmol, 47%) 2,2-dimethyl-4-phenylcyclohex-3-en-1-one as a clear, colorless oil.

The spectral data were: NMR (CCl_4) τ 2.60–2.95 (m, 5 H, arom), 4.18 (t, 1 H, J = 1.2 Hz), 7.02–7.62 (m, 4 H, CH_2CH_2), 8.82 (s, 6 H, CH_3); ir (neat) 3.22, 3.24, 3.26, 3.29, 3.37, 3.41, 3.49, 5.86, 6.31, 6.72, 6.77, 6.86, 6.95, 7.28, 7.39, 8.37, 9.09, 9.34, 9.71, 10.43, 12.87, 13.32, 13.60, 14.40 μ.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.95; H, 8.05. Found: C, 83.88, H, 7.99.

Methyl 3,3-Dimethyl-2-oxo-5-phenyl-4-cyclohexenecarboxylate. A slurry consisting of 2.50 g (50.0 mmol) of a 50% suspension of sodium hydride in mineral oil was stirred and refluxed with 4.5 ml (50 mmol) of dimethyl carbonate in 50 ml of anhydrous ether. A solution of 5.02 g (25.1 mmol) of 2,2-dimethyl-4-phenylcyclohex-3-en-1-one in 25 ml of ether was added over 2 hr. After 24 hr of refluxing, the mixture was quenched with water and ether extracted, and the extracts were dried over magnesium sulfate, concentrated, and chromatographed on a 3 × 80 cm silica gel column. Elution with 2 l. of hexane removed the mineral oil; elution with 4 l. of 1% ether–hexane and recrystallization from methanol yielded 4.74 g of colorless crystalline product (18.3 mmol, 73.3%), mp 64.5–65.5°.

The spectral data were: NMR (CCl_4) τ 0.00 (d, 1 H, J = 1 Hz, enol H), 2.52–2.90 (m, 5 H, arom), 4.28 (t of d, 1 H, J_t = 2, J_d = 1 Hz, styryl), 6.28 (s, 3 H, OCH_3), 6.75 (d, 2 H, J = 2 Hz, CH_2), 8.69 (s, 6 H, CH_3); ir ($CHCl_3$) 3.33, 3.37, 3.41, 3.44, 3.48, 3.52, 5.97, 6.05, 6.20, 6.70, 6.80, 6.90, 7.24, 7.38, 7.44, 7.67, 7.78, 8.00, 8.81, 9.32, 9.76, 10.50, 10.8, 11.5, 14.2, 15.1 μ.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.02; H, 6.99. Found: C, 74.18; H, 7.04.

Methyl 1-(4-Chlorobutyl)-3,3-dimethyl-5-phenyl-2-oxo-4-cyclohexenecarboxylate. To a solution of sodium methoxide made from 50 ml of anhydrous methanol and 0.80 g (35 mmol) of sodium was added 4.98 g (20.0 mmol) of methyl 3,3-dimethyl-2-oxo-5-phenyl-4-cyclohexenecarboxylate. The ester was stirred for 1 hr and then 4.6 ml (6.84 g, 40.0 mmol) of 1-chloro-4-bromobutane was added. The reaction mixture was refluxed for 48 hr, decomposed with water, ether extracted, and dried over magnesium sulfate. Chromatography on a 3 × 100 cm silica gel column slurry packed in hexane yielded the following (125-ml fractions): 1–4 (2% ether–hexane), 1.28 g of starting ester; 5–6 (3% ether–hexane), nil; 7–18 (5% ether–hexane), 3.73 g (10.7 mmol) of methyl 1-(4-chlorobutyl)-3,3-dimethyl-5-phenyl-2-oxo-4-cyclohexenecarboxylate. The yield based on recovered starting material was 77%.

The spectral data were: NMR (CCl_4) τ 2.50–2.96 (m, 5 H, arom), 4.24 (d, 1 H, J = 2 Hz, –CH═), 6.43 (s, 3 H, CH_3O–), 6.56 (t, 2 H, J = 6 Hz, CH_2Cl), 6.72 (d, 1 H, J = 17 Hz, CH_2), 7.44 (d of d, 1 H, J = 17 and 2 Hz, CH_2), 7.90–8.80 (m, 6 H, aliph), 8.80 (s, 3 H, CH_3), 8.82 (s, 3 H, CH_3); ir (neat) 3.28, 3.32, 3.36, 3.38, 3.42, 3.49, 5.76, 5.85, 6.26, 6.95, 7.26, 7.39, 7.62, 7.81, 8.18, 8.56, 8.95, 11.61, 13.24, 14.34 μ.

Anal. Calcd for $C_{20}H_{25}O_3Cl$: C, 68.86; H, 7.22. Found: C, 69.08; H, 7.16.

6-(4-Chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one. Treatment of 3.31 g (9.51 mmol) of methyl 1-(4-chlorobutyl)-3,3-dimethyl-5-phenyl-2-oxo-4-cyclohexenecarboxylate with 25 ml of 10% sodium hydroxide in anhydrous methanol for 4 hr at room temperature was followed by ether extraction and water washing. The dried extracts were chromatographed on a 5 × 75 cm silica gel column, eluting with 1% to 5% ether–hexane, to yield: (250-ml fractions) 1–4 (nil); 0.249 g (1.0 mmol) of 3,3-dimethyl-5-phenylspiro[5.4]non-4-en-2-one; 6–9, 1.27 g (4.40 mmol) of 6-(4-chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one; 10–12, 0.326 g of starting ester.

The spectral data for 3,3-dimethyl-5-phenylspiro[5.4]non-4-en-2-one were: ir (neat) 2.22, 2.25, 2.29, 2.36, 3.47, 5.88, 6.26, 6.70, 6.81, 6.92, 7.25, 7.38, 7.99, 8.42, 8.91, 9.31, 9.70, 10.12, 13.29, 14.42 μ; NMR (CCl_4) τ 2.74 (m, 5 H, arom), 4.12 (t, 1 H, J = 1.5 Hz, vinyl), 7.33 (d, 2 H, J = 1.5 Hz, CH_2), 8.21–8.54 (m, 8 H, cyclopentyl), 8.80 (s, 6 H, CH_3); MS (70 eV) m/e 254, 226, 211, 158, 143, 128.

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.92; H, 8.55.

The spectral data for 6-(4-chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one were: NMR (CCl_4) τ 2.60–2.85 (m, 5 H, arom), 4.19 (d, 1 H, J = 2 Hz, vinyl), 6.50 (t, 2 H, J = 6 Hz, CH_2Cl), 7.00–7.62 (m, 3 H, CH_2CH), 7.90–8.75 (m, 6 H, aliph), 8.75 (s, 3 H, CH_3), 8.84 (s, 3 H, CH_3); ir (neat) 3.24, 3.34, 3.28, 3.35, 3.39, 3.47, 5.85, 6.26, 6.69, 6.82, 6.92, 7.24, 7.37, 7.77, 8.38, 9.00, 9.20, 10.18, 13.24, 13.85, 14.40 μ; uv (EtOH) 243 nm (11,100).

Anal. Calcd for $C_{18}H_{23}ClO$: C, 74.33; H, 7.97. Found: C, 74.12; H, 8.04.

6-(4-Iodobutyl)-2,2-dimethyl-4-phenylcyclohex-3-enone. To 2.20 g (14.8 mmol) of anhydrous sodium iodide dissolved in 50 ml of anhydrous acetone, 1.70 g (5.87 mmol) of 6-(4-chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one was added, and the solution was brought to reflux. The reflux was maintained for 48 hr, the acetone stripped off, and the solid washed with ether. The ether washings were concentrated to yield 2.36 g (6.18 mmol, 100%) of 6-(4-iodobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one as a slightly yellow oil. This oil was used without purification in the next step.

The spectral data were: ir (neat) 3.22, 3.24, 3.27, 3.33, 3.37, 3.46, 5.83, 6.25, 6.67, 6.32, 6.40, 7.21, 7.33, 8.23, 8.51, 9.68, 11.54, 13.23, 14.40 μ; NMR (CCl_4) τ 2.48–2.98 (m, 5 H, arom), 6.90 (t, 2 H, J = 7 Hz, CH_2I), 7.20–7.62 (m, 1 H, COCH), 7.80–8.88 (m, 11 H, with s at τ 8.66, CH_2 and CH_3), 9.08 (s, 3 H, CH_3); mass spectrum (calcd for $C_{18}H_{23}OI$, 382.0795) m/e 382.0795.

4-(2,2-Dimethyl-1-oxo-4-phenylcyclohex-3-en-6-yl)butyltriphenylphosphonium Iodide. To 2.36 g (6.18 mmol) of 6-(4-iodobutyl)-2,2-dimethyl-4-phenylcyclohex-3-enone equipped with an efficient mechanical stirrer was added 1.53 g of triphenylphosphine. The mixture was heated to 75° for 2 hr. The cooled pasty mixture gave a glass which was dissolved in methylene chloride and precipitated with ether to form 3.70 g (5.75 mmol, 93%) of 4-(2,2-dimethyl-1-oxo-4-phenylcyclohex-3-en-6-yl)butyltriphenylphosphonium iodide as a colorless solid, mp 157.0–158.5°. This proved pure without further treatment.

The spectral data were: ir (KBr) 3.28, 3.32, 3.35, 3.39, 3.43, 3.50, 5.90, 6.34, 7.00, 7.62, 8.50, 9.03, 9.35, 9.76, 10.10, 13.39, 13.64, 13.90, 14.38, 14.52 μ; NMR ($CDCl_3$) τ 1.92–2.90 (m, 20 H, arom), 4.20 (d, 1 H, J = 2 Hz), 6.0–6.50 (m, 3 H, cyclohexyl), 8.00–8.67 (m, 8 H, aliph chain), 8.77 (s, 3 H, CH_3), 8.87 (s, 3 H, CH_3).

Anal. Calcd for $C_{36}H_{38}POI$: C, 67.08; H, 5.94. Found: C, 67.09; H, 5.95.

1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene. To 10 ml of dimethyl sulfoxide was added 0.20 g (4.0 mmol) of 50% sodium dispersion in mineral oil. The mixture was heated to 70° for 45 min, the resulting sodium methylsulfinylmethide solution was cooled to 0°, and 25 ml of anhydrous tetrahydrofuran added. To this stirred mixture was added 2.01 g (3.20 mmol) of 4-(2,2-dimethyl-1-oxo-4-phenylcyclohex-3-en-6-yl)butyltriphenylphosphonium iodide, which immediately produced a deep red color. The solution was allowed to warm to room temperature and then refluxed for 2 hr. Work-up by ether extraction and water washing yielded a colorless oil which was passed through a 3 × 20 cm silica gel column to yield 0.553 g (2.33 mmol, 73%) of 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene, pure by VPC and NMR.

The spectral data were: ir (CCl_4) 3.36, 3.42, 3.49, 6.95, 7.27, 8.96, 9.35, 14.40 μ; NMR (CCl_4) τ 2.15–2.60 (m, 5 H, arom), 4.50 (m, 1 H, styryl), 4.74 (t of d, 1 H, J_d = 1.2, J_t = 3.7 Hz, –CH═), 7.24–8.58 (m, 9 H, aliph), 8.79 (s, 3 H, CH_3), 8.83 (s, 3 H, CH_3); uv (EtOH) 245 nm (12,500); mass spectrum (calcd for

$C_{18}H_{22}$, 238.172) *m/e* 238.172.

4-Phenyl-5-methylhex-4-enoic Acid. To 250 ml of dry carbon tetrachloride were added 35.4 g (0.243 mol) of α-isopropylstyrene, 20.0 g (0.112 mol) of *N*-bromosuccinimide, 2.0 g of benzoyl peroxide, and 0.20 g of azobis(isobutyronitrile). The stirred mixture was refluxed while maintained under the illumination of a clear tungsten-filament 100-W lamp for 4 hr.

The mixture was cooled and then filtered and concentrated to ca. 50 ml. NMR analysis of this mixture showed two methyl resonances at τ 8.12 and 8.43. A solution of diethyl sodiomalonate prepared from 3.0 g of sodium (0.131 mol), 100 ml of anhydrous ethanol, and 17.1 ml (0.113 mol) of diethyl malonate was added slowly to the carbon tetrachloride solution. The mixture was refluxed for 2 more hr after which it was poured into 250 ml of water and ether extracted.

The extract was dried over magnesium sulfate and evaporated in vacuo to yield a brown oil, which was refluxed in 100 ml of 10% sodium hydroxide for 30 min, ether extracted, and washed with water. The aqueous layer was reacidified with 10% hydrochloric acid and reextracted with ether. The extract was dried over magnesium sulfate and decolorized with Norite. Filtration and concentration yielded 20.5 g (83.2 mmol, 73.5%) of 2-carboxy-4-phenyl-5-methylhex-4-enoic acid. A solid product, mp 145–146° dec, was obtained by extensive chromatography and recrystallization from chloroform–heptane. The spectral data for this solid product were indistinguishable from those of the crude material, and the decarboxylation could most conveniently be carried out without further purification.

The spectral data were: NMR ($CDCl_3$) τ 0.84 (s, 2 H, CO_2H), 2.45–2.95 (m, 5 H, arom), 6.50–7.11 (m, 3 H, $-CH_2CH-$), 8.21 (s, 3 H, CH_3), 8.49 (s, 3 H, CH_3); ir (KBr) 3.25–4.12 (OH), 5.88, 7.11, 7.96, 10.02, 12.02, 12.90, 14.28 μ.

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.69; H, 6.44.

Pyrolysis of the crude diacid followed by decolorization with Norite gave 16.1 g (78.9 mmol) of 4-phenyl-5-methylhex-4-enoic acid as a light yellow oil, bp 108–110° (0.25 Torr).

The spectral data were: NMR (CCl_4) τ 0.84 (s, 1 H, CO_2H), 2.40–3.15 (m, 5 H, arom), 7.06–7.97 (m, 4 H, CH_2CH_2), 8.15 (s, 3 H, CH_3), 8.46 (s, 3 H, CH_3); ir ($CHCl_3$) 2.8–4.2, 5.90, 6.96, 7.11, 7.30, 7.74, 8.93, 11.05, 14.31 μ.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.59; H, 7.88.

4-Phenyl-5-methylhex-4-enoyl Chloride. To a solution of 5.81 g (28.5 mmol) of 4-phenyl-5-methylhex-4-enoic acid in 200 ml of anhydrous benzene was added 4.85 ml (56.9 mmol) of oxalyl chloride followed by 0.05 ml of dimethylformamide. After 2 hr at 25°, the benzene was removed in vacuo, and the resulting brown oil was distilled to yield 2.70 g (12.2 mmol, 43%) of 4-phenyl-5-methylhex-4-enoyl chloride as a clear colorless oil, bp 68–70° (0.1 Torr), with a penetrating odor. The 1.20-g fraction, bp 70–80°, consisted of less pure acid chloride.

The spectral data were: NMR (CCl_4) τ 2.57–3.12 (s, 5 H, arom), 7.28 (s, 4 H, CH_2CH_2), 8.16 (s, 3 H, CH_3), 8.47 (s, 3 H, CH_3); ir ($CDCl_3$) 3.25, 3.30, 3.33, 3.41, 3.48, 5.59, 6.01, 6.95, 12.67 μ.

Anal. (the compound was analyzed as the methyl ester) Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.90; H, 8.20.

1-Diazo-5-phenyl-6-methylhept-5-en-2-one. To distilled diazomethane prepared from 25 g (70. mmol) of *N,N'*-dinitroso-*N,N'*-dimethylterephthalamide (Du Pont EXR 101) in 700 ml of ether was added with stirring 10.8 g (48.7 mmol) of 4-phenyl-5-methylhex-4-enoyl chloride. After 45 min at 0° followed by 45 min at room temperature, the excess diazomethane was removed in a dry nitrogen stream, and the solution was concentrated in vacuo to yield 10.7 g (47.4 mmol, 97%) of 1-diazo-5-phenyl-6-methylhept-5-en-2-one as a clear yellow oil.

The spectral data were: NMR (CCl_4) τ 2.52–3.14 (m, 5 H, arom), 5.00 (s, 1 H, $COCHN_2$), 7.09–8.06 (AA'BB', 4 H, CH_2CH_2), 8.17 (s, 3 H, CH_3), 8.48 (s, 3 H, CH_3); ir (neat) 3.23, 3.30, 3.34, 3.42, 3.49, 4.75, 5.63, 5.79, 6.11, 6.72, 6.95, 7.33, 7.52, 8.76, 9.15, 9.34, 9.81, 13.08, 14.25 μ.

6,6-Dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one. Method A. To a solution of 10.7 g (47.7 mmol) of 1-diazo-5-phenyl-6-methylhept-5-en-2-one in 50 ml of anhydrous benzene was added 0.108 g of copper–bronze powder (Luco brand, 99.9% Cu). The solution was refluxed for 1 hr and then filtered through Celite and the filtrate concentrated to yield 9.95 g of a product containing ca. 80% of the desired material. The product was obtained in 95% purity (NMR analysis) by refluxing for 10 min in 10% sodium hydroxide to remove Wolff products, then ether extracting to yield, after drying and concentrating, 7.96 g (38.8 mmol, 81%) of 6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one as a clear, colorless oil. Samples of >99% purity were obtained by microdistillation at below 50° (0.050 Torr).

The spectral data were: NMR (CCl_4) τ 2.85 (br s, 5 H, arom), 7.44–8.11 (m, 4 H, CH_2CH_2), 8.67 (s, 3 H, CH_3), 9.12 (s, 3 H, CH_3); ir ($CHCl_3$) 3.32, 3.37, 3.48, 5.83, 6.02, 6.24, 6.70, 6.92, 7.21, 7.27, 7.38, 8.32, 9.05, 9.90, 14.20, 14.52 μ.

Method B. A solution of 5.00 g (25.0 mmol) of 2,2-dimethyl-4-phenylcyclohex-3-en-1-one and 2.40 g of acetophenone in 200 ml of *tert*-butyl alcohol was photolyzed with the 450-W Hanovia lamp through a 2-mm Pyrex filter for 14 hr. The solvent was removed in vacuo, the acetophenone removed at 60° at 0.5 Torr, and the residue was molecularly distilled at 50° (0.050 Torr) to yield 2.54 g (12.7 mmol) of a clear, colorless oil having identical spectral properties with those described above; mass spectrum (calcd for $C_{14}H_{16}O$, 200.120) *m/e* 200.120.

6,6-Dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one *p*-Toluenesulfonylhydrazone. A solution consisting of 1.17 g (5.10 mmol) of 6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one, 1.10 g (5.9 mmol) of *p*-toluenesulfonylhydrazine, and 0.05 ml of concentrated hydrochloric acid in 50 ml of anhydrous ethanol was refluxed for 3 hr and then cooled, after which 200 ml of water was added dropwise. The resulting precipitate was dissolved in 10 ml of methanol and crystallized to yield 1.31 g (3.56 mmol, 70%) of the desired hydrazone as colorless prisms, mp 175–179° dec.

The spectral data were: NMR ($CDCl_3$) τ 2.04–3.00 (m, 9 H, arom), 7.64 (s, 3 H, tosyl CH_3), 7.36–8.80 (m, 5 H, aliph), 9.01 (s, 3 H, cyclopropyl CH_3), 9.18 (s, 3 H, cyclopropyl CH_3); ir ($CHCl_3$) 3.03, 3.11, 3.33, 3.39, 3.42, 3.46, 3.48, 6.08, 6.24, 6.70, 6.93, 7.22, 7.39, 7.46, 7.66, 8.31, 8.55, 9.17, 9.75, 10.45 μ.

Anal. Calcd for $C_{21}H_{24}N_2SO_2$: C, 68.44; H, 6.56. Found: C, 68.19; H, 6.54.

6,6-Dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene. To a solution of 0.781 g (2.12 mmol) of 6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one *p*-toluenesulfonylhydrazone in 20 ml of benzene was added 4.0 ml (5.72 mmol) of 1.43 *M* *n*-butyllithium in *n*-hexane. After 2 hr at reflux, the mixture was taken up in ether and washed with water. The dried extracts were concentrated and then chromatographed on a 20 × 20 cm preparative silica gel plate to yield 0.238 g (1.29 mmol, 53%) of 6,6-dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene as a colorless oil. Exceptionally pure material was obtained by microdistillation at 25° (0.005 Torr) to yield 0.149 g (0.810 mmol).

The spectral data were: NMR (CCl_4) τ 2.88 (s, 5 H, arom), 4.30 (m, 1 H, vinyl), 4.48 (m, 1 H, vinyl), 7.48 (br s, 2 H, allyl CH_2), 8.01 (br s, 1 H, cyclopropyl), 9.03 (s, 3 H, CH_3), 9.14 (s, 3 H, CH_3); ir ($CHCl_3$) 3.25, 3.32, 3.41, 3.47, 6.23, 6.66, 6.89, 7.26, 7.40, 8.24, 8.97, 9.30, 9.70, 9.88, 10.2, 10.7, 14.3 μ.

Anal. Calcd for $C_{14}H_{16}$: C, 91.24; H, 8.75. Found: C, 91.13, H, 8.69.

3-(4-Chlorobutyl)-6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one. A solution of 1.10 g (3.80 mmol) of 6-(4-chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one, 1.25 g (9.61 mmol) of acetophenone, and 200 ml of *tert*-butyl alcohol was purged for 30 min with vanadous purified nitrogen and then photolyzed for 4 hr using a 450-W medium-pressure mercury lamp with Pyrex filter. The solvent was removed in vacuo, and excess acetophenone was removed on a hot water bath (80°) at 1.0 mmHg. The yield of light yellow 3-(4-chlorobutyl)-6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one was 1.10 g (3.79 mmol, 100%). Residual color was removed by microdistillation [24 hr at 100° (0.050 Torr)] to yield 0.725 g (2.50 mmol, 66%).

The spectral data were: NMR (CCl_4) τ 2.85 (m, 5 H, arom), 6.57 (t, 2 H, J = 6 Hz, CH_2Cl), 7.40 (d of d, 1 H, J = 7.5, J' = 12 Hz, cyclopentyl), 7.90–8.92 (m, 9 H, aliph, cyclopentyl, and cyclopropyl), 8.66 (s, 3 H, CH_3), 9.08 (s, 3 H, CH_3); ir ($CHCl_3$) 3.25, 3.29, 3.33, 3.40, 3.48, 5.90, 6.25, 6.70, 6.92, 7.27, 7.36, 7.90, 8.30, 9.04, 9.60, 9.72, 10.81, 15.05 μ; mass spectrum (calcd for $C_{18}H_{23}OCl$, 290,144) *m/e* 290.144.

3-(4-Iodobutyl)-6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one.

A 0.950-g (3.26 mmol) portion of 6-(4-chlorobutyl)-2,2-dimethyl-4-phenylcyclohex-3-en-1-one was refluxed in 50 ml of anhydrous acetone to which had been added 1.08 g (7.20 mmol) of dry sodium iodide. After 48 hr, the solvent was removed and the residue washed with ether. The ether extract was concentrated to yield 1.15 g (3.02 mmol, 93%) of 3-(4-iodobutyl)-6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one as a slightly yellow oil. The oil was used without purification in the next step.

The spectral data were: NMR (CCl_4) τ 2.48–2.96 (m, 5 H, arom), 6.90 (t, 2 H, J = 7 Hz, CH_2I), 7.38 (d of d, 1 H, J = 8 and J' = 13 Hz, α-ketocyclopentyl), 7.80–8.80 (m with s at 8.66, 13 H, aliph and CH_3), 9.08 (s, 3 H, CH_3); ir ($CHCl_3$) 3.30, 3.33, 3.39, 3.47, 5.86, 6.23, 6.67, 6.92, 7.27, 7.36, 7.71, 7.94, 8.39, 9.06, 14.2, 15.1 μ; mass spectrum (calcd for $C_{18}H_{23}OI$, 382.0795) m/e 382.0795.

4-(6,6-Dimethyl-5-phenyl-2-oxobicyclo[3.1.0]hex-3-yl)butyltriphenylphosphonium Iodide. To 1.01 g (2.65 mmol) of 3-(4-iodobutyl)-6,6-dimethyl-5-phenylbicyclo[3.1.0]hexan-2-one was added 0.670 g (2.56 mmol) of triphenylphosphine. The mixture was heated with stirring to 60° and maintained at this temperature for 3 hr. The resulting glassy solid was triturated with ether to yield 0.995 g (1.55 mmol, 58%) of 4-(6,6-dimethyl-5-phenyl-2-oxobicyclo-[3.1.0]hex-3-yl)butyltriphenylphosphonium iodide as a colorless solid, mp 88–91°.

The spectral data were: NMR (acetone-d_6) 1.96–2.96 (m, 20 H, arom), 6.10–6.56 (br m, 2 H, CH_2P), 7.20–7.40 (m, 2 H, cyclopentyl), 8.12–8.68 (m, 10 H, aliph and cyclopentyl), 8.70 (s, 3 H, CH_3), 9.14 (s, 3 H, CH_3); ir ($CHCl_3$) 3.26, 3.32, 3.40, 3.48, 5.86, 6.24, 6.28, 6.74, 6.95, 7.27 (br), 8.27 (br), 9.00, 10.06, 10.40 μ.

Anal. Calcd for $C_{36}H_{38}POI$: C, 67.08; H, 5.94. Found: C, 67.28; H, 6.09.

3,3-Dimethyl-4-phenyltricyclo[4.4.0.0^{2,4}]dec-1(10)-ene. A solution of dimsyl sodium was prepared by heating 0.100 g (4.1 mmol) of sodium hydride 50% dispersion at 70° in 5.0 ml of anhydrous dimethyl sulfoxide under nitrogen. The mixture was cooled to 0°, and then 0.675 g (1.05 mmol) of 4-(6,6-dimethyl-5-phenyl-2-oxobicyclo[3.1.0]hex-3-yl)butyltriphenylphosphonium iodide was added. The mixture was allowed to warm to room temperature, during which the solution became deep red. After 8 hr, the reaction was quenched with water, ether extracted, and chromatographed on a 40-g silica gel thin layer plate. Removal of the hydrocarbon fraction yielded 29.7 mg (0.178 mmol, 17%) of 3,3-dimethyl-4-phenyltricyclo[4.4.0.0^{2,4}]dec-1(10)-ene as a colorless oil.

The spectral data were: NMR (CCl_4) τ 2.89 (m, 5 H, arom), 4.56 (m, 1 H, vinyl), 7.40–9.16 (m, 12 H with sharp s at 8.74 for 3 H, aliph and CH_3), 9.20 (s, 3 H, CH_3); ir ($CHCl_3$) 3.24, 3.26, 3.33, 3.37, 3.49, 3.56, 6.02, 6.24, 6.70, 6.85, 6.93, 7.23, 7.34, 7.73, 8.27 (br), 9.30, 9.69, 10.1, 10.45, 10.75, 11.10, 11.45, 11.60, 14.4, 15.1 μ.

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.31. Found: C, 91.16; H, 9.31.

Exploratory Photolysis of 3,3,6,6-Tetramethyl-1-phenyl-1,4-cyclohexadiene. A solution of 0.470 g of 3,3,6,6-tetramethyl-1-phenyl-1,4-cyclohexadiene (0.00201 M) in 200 ml of *tert*-butyl alcohol under deoxygenated nitrogen was irradiated for 4 hr using a 450-W Hanovia lamp equipped with a 1-mm Corex filter. The *tert*-butyl alcohol was removed in vacuo, and the resulting oil was chromatographed on a 20 × 20 cm silica gel thick layer plate, eluting with hexane. Removal of the only mobile band yielded 0.406 g (86%) of a clear colorless oil which was identical in all respects to unreacted 2,2,5,5-tetramethyl-1-phenyl-1,4-cyclohexadiene.

Sensitized Photolysis of 3,3,6,6-Tetramethyl-1-phenyl-1,4-cyclohexadiene. A solution of 0.551 g of 3,3,6,6-tetramethylphenylcyclohexadiene (0.0130 M) and 0.501 g of xanthone was purged with deoxygenated nitrogen for 1.0 hr prior to and during the photolysis. Irradiation (Pyrex) for 6 hr using a 450-W Hanovia lamp afforded, after concentration and chromatography of the residue on a 20 × 20 cm preparative silica gel plate, 0.506 g (92%) of unreacted 3,3,6,6-tetramethyl-1-phenyl-1,4-cyclohexadiene. Repetition of the experiment using acetophenone and benzophenone sensitizer again gave only unreacted starting diene.

Exploratory Photolysis of 1,5-Diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene. A solution of 54.3 mg (1.51×10^{-3} M) of 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene in 125 ml of *tert*-butyl alcohol under deoxygenated nitrogen was irradiated for 4 hr using a 450-W Hanovia lamp equipped with a 1-mm Corex filter. Removal of the solvent in vacuo yielded 0.0628 g of a residue which was chromatographed on a 20 × 20 cm preparative silica gel plate to yield 47.3 mg of 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, identified by NMR and VPC (3% Carbowax).

Sensitized Photolysis of 1,5-Diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene. A solution of 0.120 g of 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene and 0.500 g of acetophenone in 125 ml of *tert*-butyl alcohol was photolyzed for 8 hr with the 450-W Hanovia lamp using a 2-mm Pyrex filter. After removal of the solvent in vacuo, chromatography of the residue through a 2 × 20 cm silica gel column (MCB Grade 62) yielded 0.100 g (84%) of pure starting material, identified by NMR and VPC (3% Carbowax).

Exploratory Photolysis of 3,3-Dimethyl-1-phenyl-1,4-cyclohexadiene. A solution of 0.448 g of 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene (0.0122 M) in 200 ml of *tert*-butyl alcohol was purged with deoxygenated nitrogen for 1.0 hr prior to and during photolysis. Photolysis for 10 hr with a 450-W Hanovia immersion well lamp equipped with a 2-mm Corex filter was followed by removal of the solvent through a 50-cm column of glass helices. The residue was chromatographed through a 200 × 2 cm silica gel (MCB grade 62) column, packed and eluted with hexane. Collection of 25-ml fractions yielded: fractions 1–30 (nil); 31–35 (73.9 mg of a mixture of 6,6-dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene and an unidentified secondary photoproduct); 36–39 (130 mg of pure 6,6-dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene); 40–42 (93.1 mg of a mixture of the above photoproduct and starting diene); 43–48 (30.4 mg of pure 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene). The NMR and ir spectra for 6,6-dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene, as well as the retention times on 20% Apiezon, 15% Carbowax, and 5% QF-1 chromatographic columns, were in all respects identical with those of independently synthesized material (vide supra).

Sensitized Photolysis of 3,3-Dimethyl-1-phenyl-1,4-cyclohexadiene. A solution of 0.480 g of 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene (1.30×10^{-2} M) and 0.562 g of *m*-methoxyacetophenone in 200 ml of deoxygenated *tert*-butyl alcohol was photolyzed for 30 hr with the 450-W Hanovia lamp using a 2-mm Pyrex filter. Removal of the solvent in vacuo, followed by chromatography on a 2.5 × 100 cm silica gel column, yielded 0.227 g (47%) of a mixture of starting diene and 6,6-dimethyl-5-phenylbicyclo[3.1.0]hex-2-ene in a ratio of 2:1 (NMR and VPC analysis).

Exploratory Photolysis of 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene. A solution of 0.417 g of 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene (0.00876 M) in 200 ml of nitrogen-purged *tert*-butyl alcohol was photolyzed for 2 hr with a 450-W Hanovia immersion lamp through a 2-mm Corex filter. Removal of the solvent through a 2 × 50 cm column of glass helices was followed by chromatography on a 2 × 200 cm silica gel (MCB grade 62) column packed and eluted with hexane and collected in 25-ml fractions. The results were: fractions 1–30 (nil); 31–39 (50.5 mg of 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene); 40–45 (145.3 mg of a mixture of 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene and 3,3-dimethyl-4-phenyltricyclo[4.4.0.0^{2,4}]dec-1(10)-ene); 46–54 (99.3 mg of 3,3-dimethyl-4-phenyltricyclo[4.4.0.0^{2,4}]dec-1(10)-ene). The NMR and ir spectra and also VPC retention times on a 20% Apiezon, 3% Carbowax, and 5% QF-1 columns of 3,3-dimethyl-4-phenyltricyclo[4.4.0.0^{2,4}]dec-1(10)-ene were identical in all respects with those of independently synthesized material.

Photolysis Equipment and Quantum Yield Determinations. Quantum yield irradiations were performed on the "Black Box" apparatus or on the microoptical bench.[13] Light output was monitored by ferrioxalate actinometry, and the light absorbed in the reaction cell was determined by the splitting ratio technique.

For the microoptical bench runs, the monochromator inlet slit was set at 5.4 mm and the exit slit at 3 mm, giving a band pass of 22 nm at half-peak height. For direct "Black Box" irradiation, the solution filters used were: filter A, (a) 2 M nickel sulfate hexahydrate in 5% sulfuric acid; (b) 0.8 M cobalt sulfate heptahydrate in 5% sulfuric acid; (c) 3×10^{-4} M bismuth(III) chloride in 10% hydrochloric acid. This combination (2.4-cm thickness for each of three cells) gave a transmission maximum at 282 nm (30% transmission) and was opaque above 310 nm and below 250 nm. In the sensitized runs, filter B, 0.1 M cupric sulfate replaced the bismuth chloride solution. This combination was opaque below 290 nm and above 345 nm and had a maximum transmission of 33% at 322 nm.

Quantum Yields. 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydro-

naphthalene. Quantum yield photolyses were run on the optical bench apparatus. Ca. 10^{-3} *M* solutions in 40.0 ml of purified *tert*-butyl alcohol under deoxygenated nitrogen at 31° were photolyzed with the monochromator set at 280 nm for the direct runs and 320 nm for the sensitized runs. Analysis was by vapor phase chromatography using a 4 ft × 0.25 in. column packed with 3% Carbowax 20M on 80–100 Varaport 30. Fluorene was used as an internal standard. Data for the individual quantum yields are as follows.

Run 1-D. Starting diene used, 0.169 mmol; 0.152 mEinstein absorbed; vinylcyclopropane product formed, 1.44×10^{-2} mmol; Φ = 0.095, 8.6% conversion.

Run 2-D. Starting diene, 0.190 mmol; 0.0284 mEinstein; vinylcyclopropane, 2.73×10^{-3} mmol; Φ = 0.0959; 1.5% conversion.

Run 3-D. Starting diene used, 0.195 mmol; 0.0565 mEinstein absorbed; vinylcyclopropane product formed, 5.34×10^{-3} mmol; Φ = 0.0945; 2.74% conversion.

Run 1-S. Starting diene, 0.110 mmol; sensitizer, 0.400 mmol of acetophenone; 0.114 mEinstein absorbed; vinylcyclopropane, 4.58×10^{-4} mmol, Φ = 0.0040; 0.42%.

Run 2-S. Starting diene, 0.148 mmol; sensitizer, 0.791 mmol of acetophenone; 0.176 mEinstein absorbed; vinylcyclopropane, 6.89×10^{-4} mmol, Φ = 0.0039; 0.46%.

Quantum Yields. 3,3-Dimethyl-1-phenyl-1,4-cyclohexadiene. Direct quantum yields were run on the "Black Box" apparatus in 750 ml of *tert*-butyl alcohol purged with purified nitrogen 1.0 hr before and then during photolysis. Filter combination A (vide supra) was used in the direct runs; filter B was used in the sensitized runs.

Quantum yield runs were analyzed by vapor phase chromatography at 140–160° on a 4 ft × 0.25 in. column packed with 15% Carbowax 20M on 80–100 Chromosorb W and calibrated with naphthalene standard.

The data are reported as follows.

Run 4-D. Starting diene, 1.03 mmol; 5.98 mEinsteins absorbed; vinylcyclopropane product formed, 9.34×10^{-2} mmol; Φ = 0.0156; 6.8% conversion.

Run 5-D. Starting diene, 1.78 mmol; 7.86 mEinsteins; vinylcyclopropane, 0.112 mmol; Φ = 0.0143; 6.3% conversion.

Run 3-S. Starting diene, 2.03 mmol; sensitizer, 1.00 g (8.33 mmol) of acetophenone; vinylcyclopropane, 3.87×10^{-3} mmol; Φ = 0.00032; 1.9% conversion.

Run 4-S. Starting diene, 1.36 mmol; sensitizer, 0.431 g (2.91 mmol) of 3-methoxyacetophenone; vinylcyclopropane, 1.51×10^{-3} mmol; Φ = 0.00014, 1.11% conversion.

Emission Studies. Purification of Solvent. Isopentane and methylcyclohexane were purified by repeated washing with 10% fuming sulfuric acid until the washings were colorless, then with water, 5% potassium hydroxide, drying over calcium chloride, and distillation. The solvent was then passed through a 2.5 × 80 cm alumina column containing 10% of silver nitrate.[32] The early and late fractions were discarded, and the solvent was redistilled. Solvents prepared in this way were transparent in the ultraviolet and fluorescence free.

Determination of Relative Fluorescence Quantum Yields. An Aminco-Keirs spectrofluorimeter, equipped with an Hanovia 901C-1 xenon lamp, was used to obtain the relative fluorescence quantum yields for the dienes. The emission maxima for the compounds were: 1-phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 305 nm; 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 320 nm; 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene, 305 nm; 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene, 310 nm.

The fluorescence standard was biphenyl, ϕ_f = 0.18,[18] selected because of the close similarity between its absorption and emission and those of the phenylcycloalkenes. The emission monochromator slits were set wide enough that the structured biphenyl emission merged into a smooth envelope nearly identical with the phenylcycloalkene fluorescence. Rates of fluorescence were calculated from the Einstein relationship as modified by Bowen and Wokes.[19] Absorption spectra were measured on a Beckman DK-2A or a Cary 14 recording ultraviolet spectrometer. Solutions of the dienes and biphenyl were of equivalent (0.90) optical densities at the excitation wavelength. No significant solvent effect was observed on the fluorescence quantum yields. Results are as follows.

1. 1-Phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, ϕ_f^{rel} 0.185, ϕ_f = 0.033.

2. 1,5-Diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, ϕ_f^{rel} = 0.0145, ϕ_f = 0.0026.

3. 3,3-Dimethyl-1-phenyl-1,4-cyclohexadiene, ϕ_f^{rel} = 0.439, ϕ_f = 0.079.

4. 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene, ϕ_f^{rel} = 0.0524, ϕ_f = 0.0094.

Single Photon Counting. The apparatus and procedure have been described previously.[17] The experiments were run for a time sufficient to collect a minimum of 2000 counts in the highest channel (about 300,000 counts total in 512 channels), when collecting at 5% of the 20 kHz lamp frequency. The 5% factor assures that few double photons are collected. Excitation was generally at 250 nm, and emission was monitored by an RCA 8850 photomultiplier at 310 nm. Optical densities were adjusted to 1.0–2.0 at the excitation wavelength. Different choices of excitation and emission wavelength produced no significant change in the observed decay rate of all compounds investigated. All runs were performed at room temperature. The data are reported as follows: compound, average lifetime, average rate of decay, number of runs, estimated error in rates.

1. 1,5-Diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 1.20 nsec, $k_{dt} = 8.3 \times 10^8$, five runs (20%). For this run only, the method of magic multipliers was used to give a rate of 1.10 nsec at room temperature.

2. 1-Phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 12.5 nsec, $k_{dt} = 8.0 \times 10^7$ sec^{-1}, four runs (10%).

3. 3,3-Dimethyl-1-phenyl-1,4-cyclohexadiene, 4.3 nsec, $k_{dt} = 2.3 \times 10^8$ sec^{-1}, six runs (5%).

4. 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene, .29 nsec, 3.5×10^9 sec^{-1}, eight runs (20%).

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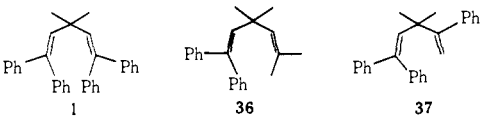
References and Notes

(1) (a) This is paper 97 of our photochemical series. (b) For the previous paper, see H. E. Zimmerman and C. J. Samuel, *J. Am. Chem. Soc.*, **97**, 4025 (1975).
(2) H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Am. Chem. Soc.*, **96**, 4630 (1974).
(3) H. E. Zimmerman and J. A. Pincock, *J. Am. Chem. Soc.*, **95**, 2957 (1973).
(4) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Am. Chem. Soc.*, **95**, 2155 (1973).
(5) (a) This would derive from the central substituents favoring conformations particularly suitable for the bridging step. See ref 5b–g for discussion of the effect: (b) R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 107, 1080 (1915); (c) C. K. Ingold, *ibid.*, 119, 305 (1921); (d) P. v. R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961); (e) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960); (f) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 197–202; (g) K. Mislow, *Tetrahedron Lett.*, 1415 (1964). Here quantitative information is given on the extent to which rehybridization effects control bond angles.
(6) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2285, 2291, 2294 (1954); F. Brutcher and J. English, Jr., *ibid.*, **74**, 4279 (1952).
(7) (a) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969); (b) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Am. Chem. Soc.*, **92**, 1786 (1970).
(8) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Am. Chem. Soc.*, **90**, 4762 (1968).
(9) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).
(10) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).
(11) For a review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(12) The literature seems to contain increasing use of spectral data for structure elucidation without support of the more classical, synthetic methods. While NMR analysis proves exceedingly useful in telling one what to synthesize, there is some danger in relying on NMR alone. Thus, in a set of photochemical investigations involving 25 new compounds, there is a 22% chance of one compound of the set having an erroneous structure assigned even if the probability of any single error being made is only one in a hundred.
(13) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).
(14) In general an actinometer solution, no matter how carefully selected, will not have exactly the same absorption curve as reactant. Thus, one cannot safely assume that cells of the same geometry and containing solutions of the same absorbance at the wavelength maximum will capture the same amount of light unless the light used is close to mono-

chromatic. The problem arises because of the wavelength dependence of most lamps.
(15) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966.
(16) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **97**, 3718 (1975).
(17) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974).
(18) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1965.
(19) E. J. Bowen and F. Wokes, "Fluorescence of Solutions", Longmans, Green and Co., London, 1953.
(20) H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 6267 (1970).
(21) It is known[22] that 3,3,6,6-tetramethyl-1,4-cyclohexadiene does undergo the di-π-methane rearrangement on mercury photosensitization in the gas phase. However, the point has been made,[11] that di-π-methane rearrangements which do not proceed readily in solution sometimes do occur under the strenuous conditions of gas phase mercury photosensitization.
(22) W. Reusch and D. W. Frey, *Tetrahedron Lett.*, 5193 (1967).
(23) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972).
(24) (a) For replacement of methyl by phenyl $K_{CH_3\rightarrow Ph} = [k_{d_r}(\mathbf{1}) = k_{d_r}[(\mathbf{36})]^{1/2} = 4.5$. For replacement of hydrogen by methyl, $K_{H\rightarrow CH_3} = [k_{d_r}(\mathbf{36})/k_{d_r}(\mathbf{37})]^{1/2} = 3.5$



1 36 37

(b) $k_{d_r}(\text{calcd})(\mathbf{8}) = k_{d_r}(\mathbf{36})/(K_{CH_3\rightarrow Ph}\ K_{H\rightarrow CH_3})$.
(25) All melting points were taken on a hot-stage apparatus calibrated with known compounds.
(26) Y. Gaoni and E. Wenkert, *J. Org. Chem.*, **31**, 3809 (1966).
(27) G. M. Whitesides and W. J. Ehman, *J. Org. Chem.*, **35**, 3565 (1970).
(28) K. Alder and J. Haydn, *Justus Liebigs Ann. Chem.*, **570**, 201 (1950).
(29) V. I. Esafov, *Zh. Obsch. Khim.*, **27**, 2711 (1967).
(30) E. J. Corey, T. Ravindranathan, and S. Terashima, *J. Am. Chem. Soc.*, **93**, 4326 (1971).
(31) C. S. Marvel, J. Dec, H. G. Cooke, Jr., and J. C. Cowan, *J. Am. Chem. Soc.*, **62**, 3495 (1940).
(32) E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

Propellanes. X. The Dimerization of 9,9-Dichlorotricyclo[4.2.1.0^{1,6}]non-3-ene[1]

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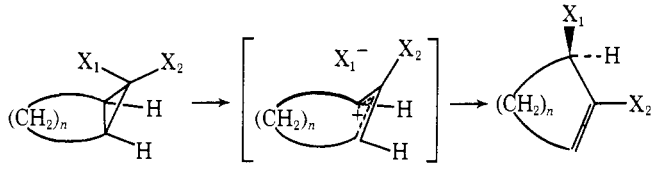
Abstract: The syntheses and subsequent dimerization of 9,9-dichlorotricyclo[4.2.1.0^{1,6}]non-3-ene and 9,9-dichlorotricyclo[4.2.1.0^{1,6}]nonane are reported. Both dimerizations occur via the intermediacy of a bridgehead olefin (comparable to a *trans*-cycloheptene). In the former case, this olefin has been trapped as a Diels–Alder adduct with furan. The double bond of the first above-mentioned dichloride exerts a retarding effect on the ring-opening (leading to dimerization) reaction, either via a rather large inductive effect, or a bishomoantiaromatic (electronic) effect.

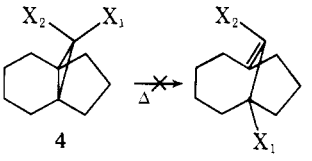
It has long been known that bicyclic dihalocyclopropanes are subject to ring opening to give vinyl allylic dihalides (eq 1).[3] The rate of the reaction is a function of the strain relief



1 2 3 (1)

inherent in the transformation and generally requires $n \leq 4$ in order to occur at moderate temperatures. The reaction meets all the criteria for ionicity (including Ag^+ promotion) and may be formulated as proceeding through an allylic ion (**2**). When this ring opening is monitored for its stereochemistry, it is found to follow the Woodward–Hoffmann–De Puy rules[4] (i.e., **1** gives **3** when n is small).

When the dihalocyclopropane unit is contained within a propellane structure (e.g., **4**), the ring-opening reaction is not expected to occur easily since the product would necessarily contain a bridgehead double bond[5] (in the case of **5**,



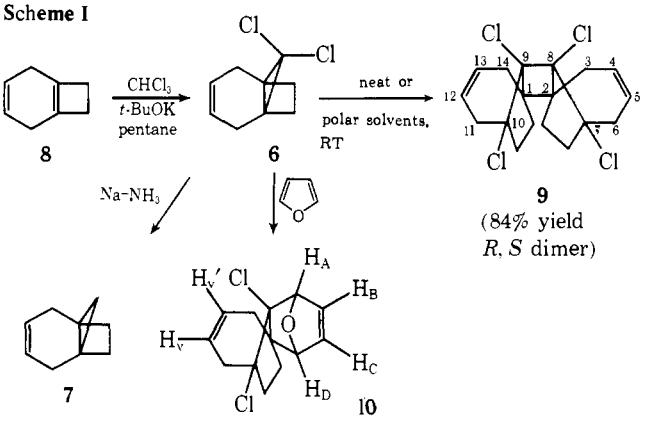
4 5 (2)

comparable to a trans double bond in a seven-membered ring[5c]). Thus **4** ($X_1 = X_2 = Br$) is thermally stable, unless heated in polar solvents.[6] It was thus initially surprising when we found[7] that 9,9-dichlorotricyclo[4.2.1.0^{1,6}]non-3-ene (**6**) was thermally unstable with respect to ring opening.

Results and Discussion

Our synthesis of **6** stemmed from our desire to study the chemistry of the corresponding [4.2.1]propell-3-ene[8] (**7**). Upon our first attempt to isolate **6** following dichlorocarbene addition to dihydrobenzocyclobutene (**8**), the oil obtained after rotoevaporation of the pentane solvent suddenly underwent an exothermic reaction upon warming to room temperature. A white, crystalline material (**9**) was simultaneously deposited (Scheme I). Subsequently, we found the

Scheme I



8 6 9 (84% yield *R, S* dimer)

7 10