ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All phosphorescence samples were degassed by several freeze-thaw cycles. Phosphorescence intensities with or without quencher were reproducible for different samples prepared from the same solution.

A Possible Photochemical ($_\pi 4_s + {}_\pi 2_a$) Diels-Alder Reaction. The Photodimerization of 6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone

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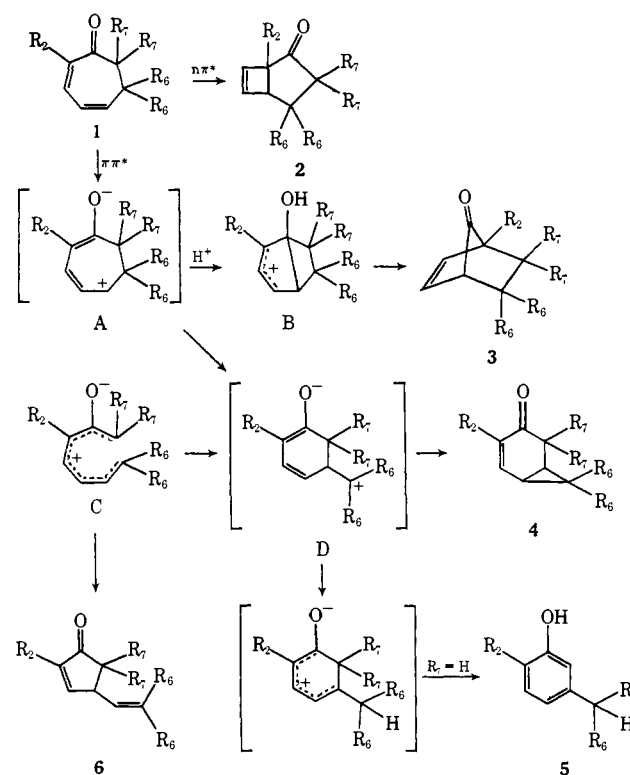
Abstract: Irradiation of the title compound **11** gave predominantly two stereoisomeric dimers, shown by chemical and X-ray crystal data to have the structures **16** and **17**, together with a small amount of a cyclobutane dimer (**19**?). A mechanism which rationalizes the major products involves the cycloaddition of the 4,5 double bond of one monomer unit to the styrene moiety of a second (structures E and F) to give intermediates G and H, followed by a 1,3-acyl shift to permit rearomatization. The major products have four chiral centers, yet only two diastereomers are formed. A preferred mechanism which explains the unique observed stereochemistry requires the cycloaddition to be antarafacial at the 4,5 double bond and suprafacial in the styrene moiety, with the 1,3-acyl shift suprafacial.

The Diels-Alder reaction is well known to occur by a ($_\pi 4_s + {}_\pi 2_s$) mechanism, although the possibility for a reaction antarafacial in both components also exists. To conserve orbital symmetry, a concerted *photochemical* Diels-Alder reaction would have to be suprafacial in one component and antarafacial in the other. The major obstacle to observing this reaction path experimentally is the much more accessible allowed photochemical ($_\pi 2_s + {}_\pi 2_s$) process. Consequently, intermolecular examples of the photochemical Diels-Alder reaction are rare or unknown. We wish to describe here a photodimerization which may proceed by this path. It was discovered accidentally in the following way.

The photoisomerization of 2,4-cycloheptadienones **1** leads to an exceptional variety of products (**2–6**) whose particular structures depend upon the substitution pattern, solvent polarity, acidity, and excitation wavelength. Scheme I[1] summarizes in a general way the structural changes which occur when 2,4-cycloheptadienones are irradiated, although it is an oversimplification which may require elaboration and modification as more is learned about mechanistic details.

Excitation of **1** to an nπ* state in a neutral medium leads to a bicyclo[3.2.0]hept-6-en-2-one (**2**);[2] singlet and triplet excited states have been implicated.[3] In the presence of acid either the excited state of the ketone

Scheme I

may become protonated or the ketone may be protonated prior to excitation; the sequence is not always clear and certainly depends in part on the acidity of the medium. It is also possible that polar media may lower the energy of the ππ* state relative to that of the nπ* state without protonation. Whatever the details, all the remaining products can be rationalized as stemming
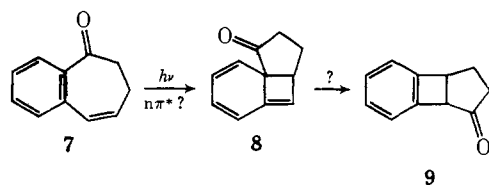
(1) H. Hart, *Pure Appl. Chem.*, **33**, 247 (1973).
(2) (a) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 443 (1960); (b) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962); (c) L. A. Paquette and O. Cox, *ibid.*, **89**, 5633 (1967); (d) K. E. Hine and R. F. Childs, *J. Chem. Soc. D*, 145 (1972); (e) D. I. Schuster and M. A. Tainsky, *Mol. Photochem.*, **4**, 437 (1972).
(3) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1657 (1970).

from A (or A–H⁺). If $R_6 = R_7 = H$, protonation and electrocyclic ring closure occur to give intermediate ion B which rearranges to a norbornenone 3.[2d] Ion B ($R_2 = R_6 = CH_3$, $R_7 = H$) has been trapped with methanol.[4] If R_6 and/or R_7 are effective at stabilizing an adjacent positive charge, the path to 3 becomes less important, and products are formed whose structures require the breaking of the C6–C7 bond. Intermediate C (or C–H⁺) is a convenient representation, though A (or A–H⁺) may proceed to the observed products 4–6 without the intervention of a discreet acyclic intermediate. When $R_6 = CH_3$ and $R_7 = H$ the products are 4 and 5,[5] whereas when $R_6 = H$ and $R_7 = CH_3$ the product is 6;[6] clearly the particular path depends on whether the cation-stabilizing substituents are located at C6 or C7.
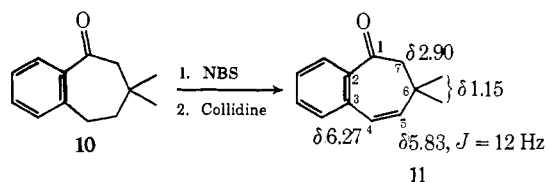
In the present paper we examine the effect of incorporating the 2,3 double bond of a 2,4-cycloheptadienone into a benzene ring on the ensuing photochemistry. From Scheme I, reaction via an $n\pi^*$ state would destroy the aromaticity of the benzene ring (7 → 8), although conceivably 8 might rearomatize to 9 as a con-

sequence of a 1,3-acyl shift. Alternatively, the 2,3-benzo ring might cause predominant reaction from a $\pi\pi^*$ state leading to benzo analogs of 4, 5, or 6. In the event, however, the reaction took a new and surprising course not previously observed with 2,4-cycloheptadienones themselves. We describe here the synthesis and irradiation of the title compound 11, chosen because it is the 2,3-benzolog of the widely studied cycloheptadienone eucarvone (1, $R_2 = R_6 = CH_3$, $R_7 = H$).

Results and Discussion

Synthesis of 11.[7] The desired ketone 11 was readily prepared in two steps (72% yield) from the known[8] 6,6-dimethyl-2,3-benzsuberone 10. The structure of 11 follows from its method of synthesis and spectro-

scopic properties. In particular, the pmr spectrum of 11 showed a methylene singlet at δ 2.90, a singlet at δ 1.15 for the gem-dimethyl group, and doublets at δ 6.27 and 5.83 ($J = 12$ Hz) for the vinyl protons at C4 and C5, respectively. Unfortunately, 11 was usually contaminated with a few per cent of unreacted 10, detected by

(4) K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, **95**, 6116 (1973).
(5) H. Hart and T. Takino, *J. Amer. Chem. Soc.*, **93**, 720 (1971); K. E. Hine and R. F. Childs, *ibid.*, **93**, 2323 (1971).
(6) H. Hart and A. F. Naples, *J. Amer. Chem. Soc.*, **94**, 3256 (1972).
(7) We are indebted to T. Takino for carrying out preliminary experiments on this synthesis.
(8) R. Huisgen, I. Ugi, E. Rauenbusch, V. Vossius, and H. Oertel, *Chem. Ber.*, **90**, 1946 (1957); S. C. SenGupta and P. K. Sen, *J. Indian Chem. Soc.*, **39**, 653 (1962).

pmr singlets at δ 1.05 and 2.65 for the gem-dimethyl group and the C7 methylene group, respectively. Recycling the product through the bromination–dehydrobromination procedure was unproductive, but it was possible, by a tedious liquid chromatographic separation, to obtain some pure 11. However, control experiments showed that purposeful addition of 10 to pure 11 did not affect the nature of the photoproducts obtained from 11; also, 10 was recovered unchanged from these irradiations. Consequently, all preparative photolyses were carried out on 11 contaminated with 5–10% of 10.

Irradiation of 11. The longest wavelength absorption band in the uv spectrum of 11 (in cyclohexane) occurs at 315 nm (log ϵ 3.27) and is bathochromically shifted in polar solvents (to 321 nm in CH_3OH, 325 nm in CF_3CH_2OH), suggesting that the excitation is principally $\pi\pi^*$ in character. Irradiation of 11 (Pyrex, 5×10^{-3} M in cyclohexane) led to its rapid conversion to photoproducts. Since 2,4-cyclohexadienones photoisomerize very slowly in nonpolar solvents ($n\pi^*$ reaction) but rapidly in polar solvents or when protonated ($\pi\pi^*$ reaction), this qualitative observation tends to affirm the notion that 11 was reacting via a $\pi\pi^*$ excited state.

To our surprise, no monomeric photoisomers of 11 were formed. The two major products were crystalline dimers, designated I (mp 208–210°) and II (mp 199–200°). They were separated by column chromatography from a mixture which also contained traces of minor products, not all of which have been identified. The formation of dimers I and II was readily quenched by 1,3-cyclohexadiene or piperylene, suggesting that the dimers are $\pi\pi^*$ triplet products of 11.
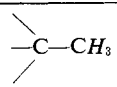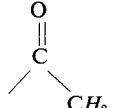
The Gross Structures of Dimers I and II. It was immediately apparent from the infrared spectra of the dimers that they were *not* simply cyclobutane dimers (12), since each dimer had one *nonconjugated* carbonyl

12hh   12ht
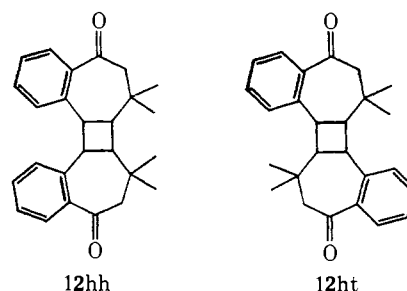
group (1730 cm⁻¹), as well as a conjugated carbonyl group (1661 cm⁻¹ in I, 1673 cm⁻¹ in II). In support of this conclusion, the mass spectral fragmentation patterns of I and II did not contain a major peak at half the parent mass. The presence of a nonconjugated carbonyl group required that *a phenyl–carbonyl bond be broken at some stage during the reaction*. Since this type of cleavage is most exceptional for a photoreaction of aryl ketones, we were spurred on to determine the structures of the dimers.

Table I shows the pmr spectra of the dimers. Many features of the spectra suggested that I and II had closely related gross structures and were probably stereoisomers. For example, each dimer had two methylene groups with chemical shifts which indicated that they were adjacent to a carbonyl group, as in 11. One of these appeared as a fairly sharp singlet, the

Table I. Pmr Spectra of Dimers I and II and Three Derivatives (δ from TMS)

| Assignment	Dimer I (16)	Dimer II (17)	i-I (18)	Dehydro-i-I (14)	Dehydro-II (15)
\—C—CH₃/	0.42 (3, s)	0.70 (3, s)	0.22 (3, s)	0.75 (3, s)	1.15 (3, s)
	0.96 (3, s)	0.84 (3, s)	1.10 (3, s)	1.20 (3, s)	1.18 (3, s)
	1.02 (3, s)	1.36 (3, s)	1.13 (3, s)	1.40 (3, s)	1.53 (3, s)
	1.10 (3, s)	1.40 (3, s)	1.30 (3, s)	1.45 (3, s)	1.58 (3, s)
O‖C/\CH₂	2.30 (2, s)	2.26 (2, s)	2.40 (2, s)ᵃ	2.57 (2, s)	2.51, 2.53 (2)
	2.80 (1, d, J = 13)	2.57 (1, d, J = 16)	2.12 (1, d, J = 11.5)	2.28 (1, d, J = 12)	2.73 (1, d, J = 13)
	3.25 (1, d, J = 13)	3.14 (1, d, J = 16)	2.92 (1, d, J = 11.5)	3.23 (1, d, J = 12)	3.47 (1, d, J = 13)
Ha	3.45 (1, d, J = 10)	3.55 (1, d, J = 7)	3.93 (1, d, J = 10)		
Hb	2.40 (1, d, J = 10)	2.80 (1, d of d, J = 7, 5)	2.53 (1, d, J = 10)		
Hc	1.80 (1, d, J = 5.5)	2.53 (1, d of d, J = 5, 11)	2.55 (1, d, J = 3)	2.89 (1, d, J = 4)	2.78 (1, d, J = 7)
Hd	4.90 (1, d, J = 5.5)	4.70 (1, d, J = 11)	4.06 (1, d, J = 3)	4.53 (1, d, J = 4)	4.45 (1, d, J = 7)
Arom	7.20–7.60 (6, m)	6.45–6.65 (1, m)	6.70–6.95 (1, m)	6.60–6.80 (1, m)	7.00–7.53 (6, m)
	7.85–8.30 (2, m)	7.00–7.50 (6, m)	7.05–7.60 (6, m)	7.18–7.72 (5, m)	8.16–8.36 (1, m)
		7.50–7.75 (1, m)	7.70–8.05 (1, m)	8.15–8.35 (2, m)	8.63–8.85 (1, m)

ᵃ This signal was split slightly in the 100-MHz spectrum.

other as a pair of geminally coupled doublets. Since neither set was further split, both methylenes were presumably still adjacent to a quaternary carbon atom, as in the starting ketone. The pmr spectrum of each dimer contained four sharp singlets corresponding to two *gem*-dimethyl groups. Each spectrum also showed four protons (Ha–d), one each on four different carbon atoms (these protons presumably arise from the vinyl protons in **11**), and eight aromatic protons.

To confirm the presence of methylene groups adjacent to the carbonyls, each dimer was treated at room temperature with NaOCH₃ in CH₃OD. The dimers were recovered unchanged, except that the peaks assigned to the methylene groups were absent from the pmr spectrum. Also absent from each spectrum was the one-proton doublet designated Ha in Table I. Consequently, Ha must be adjacent to the nonconjugated carbonyl group. Ha must also be adjacent to another methine proton, Hb, with which it is coupled in both dimers. These data require that the partial structures be present in each dimer.
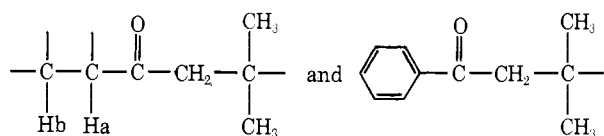

The pmr spectrum of dimer II contained a readily interpretable series of peaks for four adjacent methine protons, starting with the proton adjacent to the nonconjugated carbonyl group. Thus the partial structure of dimer II is readily extended to
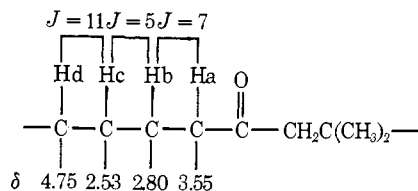

Dimer I also contained four methine protons with chemical shifts similar to those in dimer II, but the coupling pattern was deceptively simple, each signal appearing as a doublet. Chemical transformations to be described prove that the four methine protons in dimer

I are adjacent, as in dimer II, and that the lack of coupling between Hb and Hc in I must be due to the dihedral angle between them. The partial structure of dimer I is therefore extended to
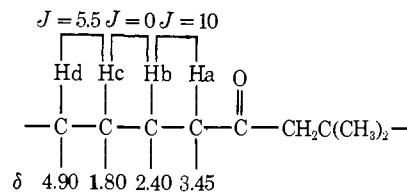
The only fragment which remained to be located in each structure was the second aromatic ring. The key to this problem was the low-field proton Hd which, since it is not adjacent to a carbonyl group (not rapidly exchanged in base), must be located adjacent to both aryl groups. Indeed even a methine proton α to two benzene rings might not appear at sufficiently low field to be entirely consistent with the observed chemical shift of Hd.[9] However, if one of the aryl groups also contained an ortho carbonyl substituent, the chemical shift of Hd could be adequately rationalized. Thus the
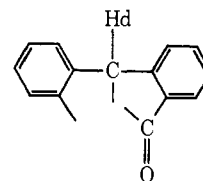
presence of the moiety in the dimers seemed likely, in view of the structure of the starting material **11**.

The only structure which accommodates all of these features is **13**; the presence of four chiral centers is a
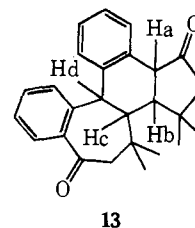
13

(9) The methine proton of 1,1-diphenylethane, for example, appears at δ 4.06: A. Jung and M. Brini, *Bull. Soc. Chim. Fr.*, 587 (1965).

matter to which we will return. Since structure **13** was deduced primarily from spectroscopic data[10] it seemed desirable to obtain supporting chemical evidence.

Isomerization of Dimer I. Although dimer I was recovered unchanged (except for the exchange of Ha and the four methylene protons) when treated with $NaOCH_3$ in CH_3OD at room temperature, it was converted in high yield to an isomer, designated *i*-I, by sodium hydroxide in methanol at reflux (N_2 atmosphere, 1 hr). *i*-I, mp 214–215°, still had both a nonconjugated (1730 cm⁻¹) and a conjugated (1680 cm⁻¹) carbonyl group and a pmr spectrum similar to those of dimers I and II (Table I). Although the chemical shifts in *i*-I differ from those in dimer I, the coupling pattern is nearly the same, including the lack of coupling between Hb and Hc.

When dimer I was isomerized to *i*-I in a deuterated solvent, the signal for Hd was absent from the pmr spectrum of the product. This proton did not exchange, however, when *i*-I was subjected to the isomerization conditions. *Therefore the transformation I → i-I presumably involves epimerization at the carbon atom bearing Hd.* Proton Hd should be weakly acidic since it is conjugated, through a benzene ring, with a carbonyl group.

Similar treatment of dimer II with sodium hydroxide in refluxing methanol did not result in any isomerization; II was recovered in high yield.

Dehydrogenation of the Dimers. Dimer II gave a crystalline dehydro product (mp 204°, *m/e* 370), designated dehydro-II, when treated at room temperature with *o*-chloranil in acetonitrile or with palladium on charcoal in refluxing ethyl acetate. Dehydro-II was clearly an α,β-unsaturated cyclopentenone from its uv and ir spectra. Its pmr spectrum (Table I) showed only two mutually coupled methine protons, Hc and Hd (the four methyl singlets, two methylene groups, and eight aromatic protons were still present).

i-I also readily gave a crystalline dehydro derivative (mp 213–214°, *m/e* 370), designated dehydro-*i*-I, on treatment with *o*-chloranil. The ir, uv, and pmr spectra of the two dehydro dimers were very similar (see Table I and the Experimental Section).

Dimer I was recovered unchanged from dehydrogenation conditions which were highly effective in dehydrogenating dimer II and *i*-I. When the reaction conditions were made more vigorous, however, some dehydrogenation occurred. The product was dehydro-II! Since dimers I and II give the same dehydro product, the stereochemical relationship between Hc and Hd in the two dimers must be identical.

Finally, treatment of dehydro-II at room temperature with sodium methoxide in methanol converted it to dehydro-*i*-I in high yield. This result provides a structural link between dimers I and II and shows that they are stereoisomers. When the base-catalyzed isomerization of dehydro-II was carried out in a deuterated solvent, the low-field methine proton Hd was exchanged, showing that epimerization occurred at that carbon atom.
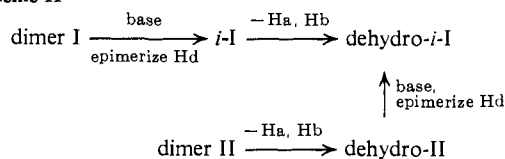
The Stereochemistry of the Dimers.[11] The results of

the two previous sections are summarized in Scheme II.

Scheme II

dimer I $\xrightarrow[\text{epimerize Hd}]{\text{base}}$ *i*-I $\xrightarrow{-\text{Ha, Hb}}$ dehydro-*i*-I

$\uparrow$ base, epimerize Hd

dimer II $\xrightarrow{-\text{Ha, Hb}}$ dehydro-II

It is clear that dehydro-*i*-I and dehydro-II must be the cis and trans isomers **14** and **15**, with dehydro-*i*-I being

14   15

the more stable isomer. The particular assignments can be made by using the coupling constants for the methine protons Hc and Hd. Dreiding models, though not entirely satisfactory because they tend to be too rigid in polycyclic structures of this type, show that the dihedral angle for these protons should be about 135–170° in the trans isomer (**15**) and about 40–60° in the cis isomer (**14**). The pmr data in Table I therefore indicate that dehydro-*i*-I has the structure **14** ($J = 4$ Hz) whereas dehydro-II must have the structure **15** ($J = 7$ Hz). The models also show that steric interaction between the *gem*-dimethyl groups on the five- and seven-membered rings is more severe in the trans isomer than in the cis isomer, consistent with the direction which was observed for the base-catalyzed epimerization.[12]

The geometric relationship between Hc and Hd must be the opposite in dimer I from what it is in *i*-I (since *i*-I is formed by epimerizing Hd in I). Since Hc and Hd are cis in dehydro-*i*-I, they must be cis in *i*-I and trans in I. Since Hc and Hd are trans in dehydro-II, they must also be trans in II. Consequently, Hc and Hd must have the same relative geometry, trans, in dimers I and II, and this conclusion explains the observation that both dimers gave the same dehydro product, **15**.

The dehydrogenation results, which require that Hc and Hd be trans in both dimers, therefore limit the possibilities for the structures of dimers I and II to the four diastereomers shown.[13]

Ha–Hb	Hb–Hc	Hc–Hd
c	c	t
c	t	t
t	c	t
t	t	t

Further delineation of the structures is more speculative, although one can come to some conclusions by using the coupling constants of the methine protons. For example, of the four possibilities with Hc–Hd trans, the ctt geometry best fits the very striking lack of coupling between Hb and Hc in dimer I. If dimer I has

(10) Note that the $\nu_{C=O}$ of the nonconjugated carbonyl group, 1730 cm⁻¹, is consistent with its presence in a five-membered ring.
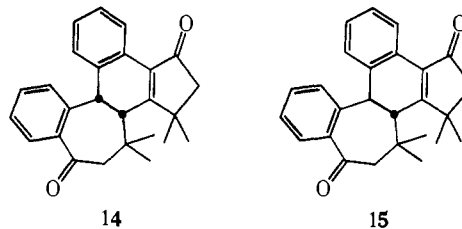
(11) The stereochemistries assigned to the dimers in a preliminary account of this work (ref 1) are incorrect, as is the mechanism which was based on those stereochemical assignments.

(12) Although Hc and Hd are each conjugated with a carbonyl group, the labeling result which showed that the epimerization involves only Hd can be rationalized. The adjacent *gem*-dimethyl group and possibly also the *gem*-dimethyl group in the five-membered ring probably block attack by the base on Hc, whereas Hd is in a relatively exposed position.

(13) The c and t stand for cis and trans, respectively. In the remaining discussion, the sequence Ha–Hb, Hb–Hc, Hc–Hd is always used in describing these relative geometries.

the ctt geometry, then *i*-I must have the ctc geometry (since the epimerization involved Hd). Models indicate that here too the dihedral angle between Hb and Hc is such that coupling should be small or zero. If the facile dehydrogenation of *i*-I and II by palladium on charcoal implies that Ha and Hb have a cis relationship, then dimer II must be cct. These relationships are outlined in Scheme III. In support of these as-

Scheme III

16
(dimer I)

17
(dimer II)

18
(*i*-I)
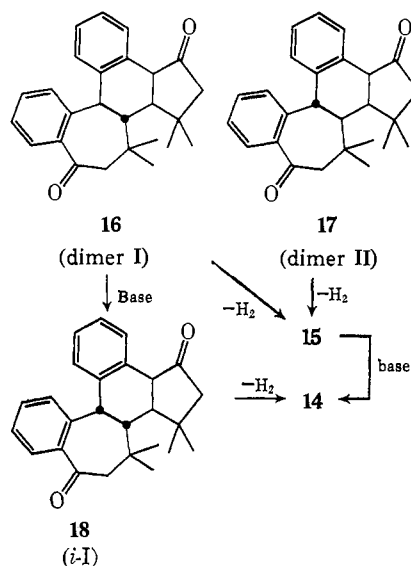
signments, dimer II was not epimerized by base; the product of such an epimerization at Hd would have an all-cis geometry, which models show to be particularly unfavorable, involving a serious interaction between the *gem*-dimethyl groups. Also consistent with these assignments, models of **18** show that one of the methyl groups in the seven-membered ring is forced into the shielding region of a benzene ring, accounting for the high-field methyl signal (δ 0.22, Table I).

It was clear at this point in our investigation that although the gross structure of the dimers was on firm ground[14] the stereochemical assignments rested largely on the correlation of pmr coupling constants with models and that deductions of this type or those made on mechanistic grounds may be misleading.[11] Consequently X-ray crystallographic data were obtained to solve the stereochemical problems unequivocally. Details are presented in a separate paper.[15] In this way structures **16** and **17** were firmly established for dimers I and II, respectively.[16]

(14) Additional chemical evidence, described later in this paper, was in hand which confirmed these structures, although it did not shed any light on the stereochemical problem.

(15) B. L. Barnett, C. G. Biefeld, and H. A. Eick, *Acta Crystallogr.*, in press.

(16) The dihedral angles between the methine protons, as determined from the X-ray structures, and the predicted (R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd Ed., Wiley, New York, N. Y., 1967, p 132) and observed coupling constants are as follows

Dimer		Ha–Hb	Hb–Hc	Hc–Hd
I	$\angle$, deg	35	85	124
	J(pred)	5.5	0	4.8
	J(obsd)	10	0	5.5
II	$\angle$, deg	49	45	146
	J(pred)	3.3	4.0	8.0
	J(obsd)	7	5	11

Agreement between predicted and observed coupling constants is good except for Ha–Hb, which is somewhat larger than predicted. The lack of coupling between Hb and Hc in dimer I is nicely explained.

Irradiation of Labeled 11. The structural relationship between **11** and its photodimers **16** and **17** is fairly obvious with regard to the benzo-seven-membered ring. The relationship of the "upper" fragment to **11**
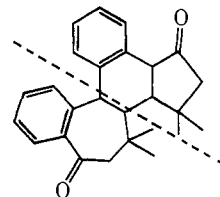
is not as obvious; it appears to have been formed *via* a 1,3 shift of the carbonyl group from the aryl ring to the carbon atom of the double bond. If this is correct,
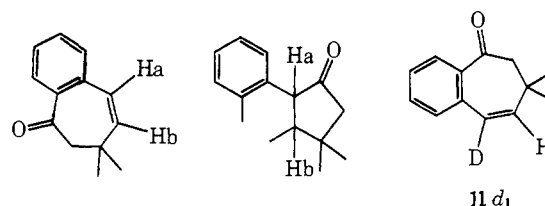
11 d_1

and one were to irradiate **11**-d_1, one would expect to find the deuterium at Ha and Hd in the resulting dideuterated dimers. Accordingly, **11**-d_1 was synthesized (see Experimental Section for details) and irradiated. The pmr of the resulting dimers fully confirmed this supposition.

11·d $\xrightarrow{h\nu}$

I and II, d_2
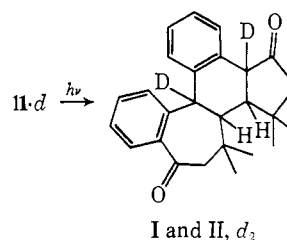
The Dimerization Mechanism. The fact that only two of the eight possible diastereomeric forms of **13** are produced in the photodimerization suggests that stereoelectronic factors probably weigh heavily in the reaction mechanism. Two structural features of **16** and **17** are particularly significant: (1) Ha and Hb are cis in both structures, and (2) Hc and Hd are trans in both structures. The two dimers differ only in the relative orientations of Hb and Hc. Also noteworthy, from the experiments with **11**-d_1, is that Hb and Hc are derived from the double bond carbon that is β to the aryl ring in **11** (C5), whereas Ha and Hd arise from the corresponding α carbon (C4).

These results can be accommodated by a mechanism involving a ($_\pi 4_s + _\pi 2_a$) cycloaddition, a process which is photochemically "allowed."[17] The 4π (or 8π) component is the cisoid styrene moiety in **11**. The 2π component is the carbon–carbon double bond, and it is apparent from the trans relationship of Hc and Hd in both dimers that the reaction must be antarafacial in this component. Only two orientations of the monomers (**11**) with respect to one another are possible if one places the further restriction that each C5 of the monomer units is covalently bound to the other in the dimer. These orientations are shown in E and F.

(17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 79.

E   F
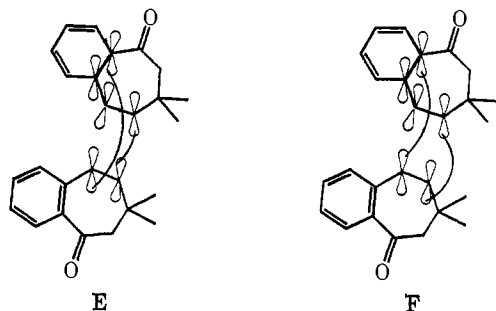
Suprafacial addition in the styrene moiety and antarafacial addition at the C4–C5 double bond, orienting the two units so that only C5–C5 bonding occurs, yield the two methylenecyclohexadienes G and H. It is ob-


E   F

G   H

ctt (16, dimer I)   cct (17, dimer II)
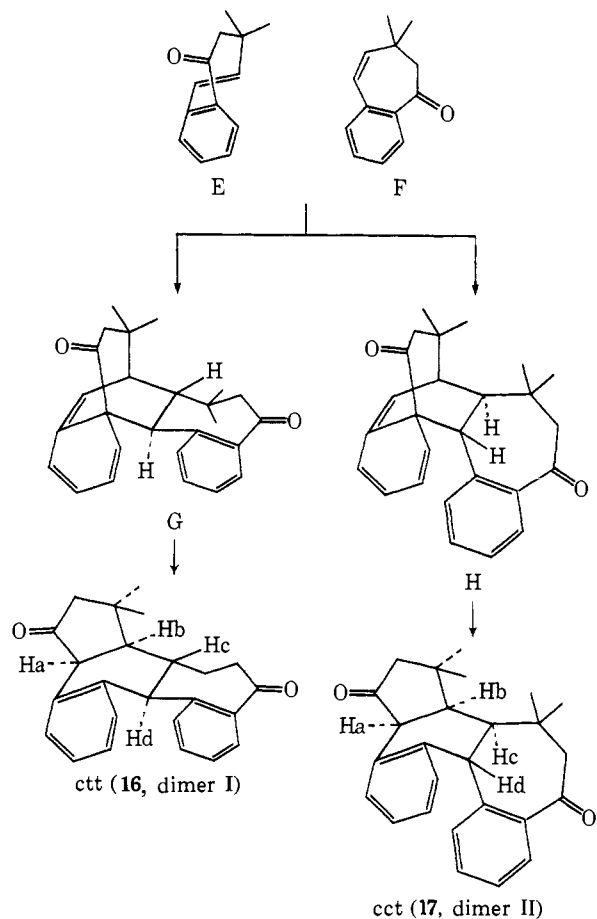
vious from the structures of G and H that they could have been formed by an alternative mechanism, isomerization of the carbon–carbon double bond in 11 followed by a ($_\pi 4_s$ + $_\pi 2_s$) cycloaddition of the resulting *trans*-cycloheptene to the styrene moiety of a second molecule of 11. This alternative cannot be ruled out by the present data; it would require the formation of a ground state *trans*-cycloheptene with five sp² carbon atoms.

Structures G and H can readily rearomatize by a suprafacial 1,3-acyl shift. The products have the stereochemistries observed in dimers I (16) and II (17), respectively.

Several features of this mechanism are worthy of comment. One might have expected that dimers could arise from ($_\pi 2_s$ + $_\pi 2_s$) reactions, giving cyclobutane dimers of the type 12 hh, *i.e.*, 19 and 20.[17a] In fact one of

the reaction products was a cyclobutane dimer (mp 225–226°, *m/e* parent peak at 372 with a base peak at 186;

19   20
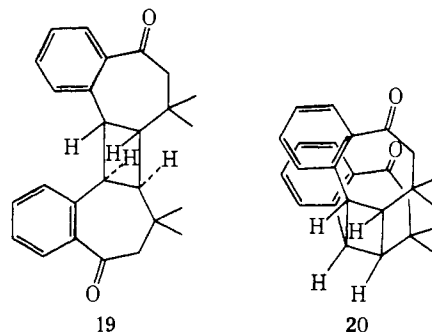
for further structural details, see Experimental Section), but it was formed in only minor amounts. Although steric factors might be significant in preventing the formation of a dimer such as 20, such effects would be less severe in 19 and in and of themselves they cannot explain the preference for (4 + 2) over (2 + 2) cycloaddition.

There are two other arrangements of the 4π and 2π moieties than those shown in E and F. These would have the two aryl rings remote from rather than close to one another and would lead to two diastereomers of the general structure 21. These would involve forming a carbon–carbon bond between C5 in the 4π component

21
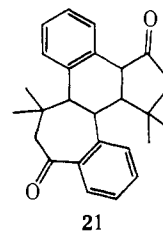
and C4 in the 2π component. This reaction path was not observed. One can rationalize this result since C5–C5 bonding leaves both π systems fully conjugated, whereas C5–C4 bonding would leave an isolated p orbital at C5 in the 2π component of the cycloaddition reaction. Consequently, no products of the type 21 are formed.

The stereochemistry observed in the dimers is nicely accounted for by the ($_\pi 4_s$ + $_\pi 2_a$) mechanism. Models show that it would be just as easy, perhaps easier, for the reaction to be suprafacial in both components (see E and F). If the first stage of the reaction were not concerted but stepwise, perhaps involving diradical intermediates as might be expected for a triplet state reaction, one might have expected ($_\pi 4_s$ + $_\pi 2_s$) products to be formed (if the 1,3-acyl shift were still suprafacial, these products would have ccc and ctc geometries[18]). The absence of such products argues against a diradical mechanism. Finally, the transition states leading to the alternative concerted paths ($_\pi 4_a$ + $_\pi 2_s$) seem impossibly strained compared with the ($_\pi 4_s$ + $_\pi 2_a$) paths.

We conclude that a plausible reaction path which accounts for the stereochemistry of the observed dimers involves a concerted ($_\pi 4_s$ + $_\pi 2_a$) cycloaddition, followed by a suprafacial 1,3-acyl shift; an alternative mech-

(17a) NOTE ADDED IN PROOF. Structures in which the hydrogens from a monomeric unit are trans are also possible. Indeed, an example has recently been found, and will be reported separately (unpublished result with M. Suzuki).

(18) This was, in fact, the mechanism previously proposed when the stereochemistry of the products was still in doubt (ref 1).

anism involving a *trans*-cycloheptene can also rationalize the observed stereochemistry.

Autoxidation of 16 and 18. During chemical work on the structure elucidation of the dimers, an interesting autoxidation was observed. As noted above, dimer I (**16**) can be converted to *i*-I (**18**) by reflux in sodium hydroxide in methanol *in a nitrogen atmosphere*. If the epimerization of Hd is attempted in the presence of air, the reaction mixture becomes deep red and leads to a crystalline acid (mp 190–191°) which contains two more oxygen atoms than dimer I (m/e 372 + 32 = 404). The same acid can be obtained in better yield starting with *i*-I (**18**). The carbonyl absorptions of the acid (1700 and 1680 cm⁻¹) indicated that the cyclopentanone moiety was no longer present. The acid gave a crystalline ester (mp 128–129°) which showed only ester (1730 cm⁻¹) and conjugated carbonyl bands (1675 cm⁻¹).

The structure of the ester can be assigned from these data and its nmr spectrum, which showed two isolated methylene groups α to carbonyl groups (doublets at δ 2.21 and 2.79, $J = 12.5$ Hz, and at δ 2.37 and 2.94, $J = 15.5$ Hz), four methyl groups (singlets at δ 0.63, 1.04, 1.17, and 1.23), and three methine protons (in addition to the methoxyl and eight aromatic protons). The methine protons are designated Hb, Hc, and Hd, respectively, to indicate their relationship to the methine protons in dimers I and *i*-I. The structures of the acid and ester, and the route to them, are shown in Scheme IV.

Scheme IV
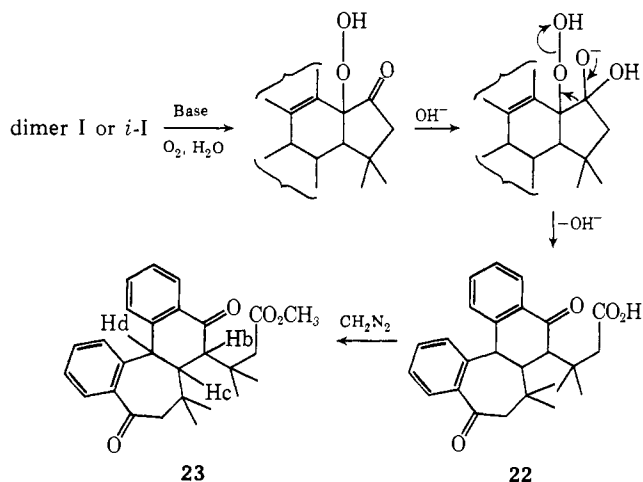
The change in chemical shift of Hb (from about δ 2.5 in I or *i*-I to δ 3.32) is consistent with location of this proton adjacent to a carbonyl group. The remaining methine protons appeared as mutually coupled doublets at δ 2.72 (Hc) and 5.17 (Hd), $J = 3.5$ Hz. The chemical shift of Hc is similar to its value in *i*-I; the downfield shift of Hd is consistent with its conjugation with two carbonyl groups. The lack of coupling between Hb and Hc and the small coupling between Hc and Hd suggest that the stereochemistry of the three methine protons is the same in **23** as it is in *i*-I (**18**), but this question was not examined further.

Ample precedent exists for the base-catalyzed autoxidation of α-phenyl ketones shown in Scheme IV.[19]

(19) F. G. Bordwell, R. G. Scamehorn, and A. C. Knipe, *J. Amer. Chem. Soc.*, **92**, 2172 (1970); W. E. Doering and R. M. Haines, *ibid.*, **76**, 482 (1954).

The reaction may have some stereochemical requirements, however, since dimer II (**17**) was not readily oxidized under similar conditions.

Experimental Section[20]

3,3-Dimethyl-5-phenylpentanoic Acid.[21] To a solution of potassium hydroxide (120 g, 2.14 mol) in 500 ml of ethylene glycol was added a solution of 3,3-dimethyl-4-benzoylbutanoic acid[8] (114. 8 g, 0.477 mol) in 300 ml of the same solvent. The solution was cooled to room temperature and hydrazine hydrate (95 ml, 97.8 g, 1.95 mol) was slowly added. The solution was stirred and slowly brought to 200°; all volatile components boiling below 200° were removed by distillation. The mixture was refluxed for 10 hr, cooled to room temperature, and poured into ice–water containing 360 ml of concentrated HCl, affording 3,3-dimethyl-5-phenylpentanoic acid as a yellow oil which gave off-white crystals: mp 50–51° (93.5 g, 96%); pmr (CCl₄) δ 1.10 (s, 6 H, *gem*-dimethyl), 1.4–2.0 (m, 2 H, C4 methylene), 2.25 (s, 2 H, C2 methylene), 2.3–2.9 (m, 2 H, C5 methylene), 7.03 (s, 5 H, arom).

6,6-Dimethyl-2,3-benzo-2-cycloheptenone (10). From 69.5 g (0.338 mol) of 3,3-dimethyl-5-phenylpentanoic acid and polyphosphoric acid (700 g of P₂O₅ in 435 ml of phosphoric acid) there was obtained[8] 56.3 g (89%) of **10**, recrystallized as colorless plates from 30–60° petroleum ether: mp 55–55.5°; ir (CCl₄) 3090, 2970, 2890, 1680, 1600, 1470, 1320, 1310, 1245 cm⁻¹; pmr (CCl₄) δ 1.05 (s, 6 H, *gem*-dimethyl), 1.58–1.85 (m, 2 H, C5 methylene), 2.65 (s, 2 H, C7 methylene), 2.90–3.15 (m, 2 H, C4 methylene), 7.05–7.45 (m, 3 H, arom), 7.70–7.90 (m, 1 H, arom).

6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone (11). To a solution of **10** (10.0 g, 0.053 mmol) in 200 ml of CCl₄ was added 0.35 g of benzoyl peroxide[22] and 9.58 g (0.053 mmol) of freshly recrystallized *N*-bromosuccinimide (NBS). The mixture was refluxed until the NBS was consumed.[23] The yellow reaction mixture was cooled to room temperature and filtered to remove the succinimide, and the solvent was removed by rotary evaporation. 2,4,6-Collidine (10 g, 0.10 mol, freshly distilled) was added to the residue and the mixture was heated at 115–120° for 12 hr. The cooled reaction mixture was triturated with CCl₄ (300 ml) and the CCl₄ layer was washed with 10% hydrochloric acid (3 × 100 ml) and water (3 × 100 ml) and dried (MgSO₄). Removal of the solvent under reduced pressure and vacuum distillation afforded 6.91 g (72%) of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone (**11**), bp 84–86° at 0.15 Torr. The product was shown, by nmr integration, to be contaminated with 5–10% of unreacted **10**: ir (neat) 3080, 3030, 2970, 1670, 1640, 1595, 1490, 800, 760 cm⁻¹; uv (cyclohexane) λ_{max} 315 nm (ϵ 3480), 276, 267, 259 (sh), 235; (acetonitrile) 318 (3530); (methanol) 320 (3360); (acetic acid) 323 (3360); (2,2,2-trifluoroethanol) 325 (2750); (absorbed on silica gel–cyclohexane) 327 nm; pmr (CCl₄) δ 1.15 (s, 6 H, *gem*-dimethyl), 2.90 (s, 2 H, methylene), 5.75 (d, 1 H, $J = 12$ Hz, C5 vinyl), 6.18 (d, 1 H, $J = 12$ Hz, C4 vinyl), 6.9–8.0 (m, 4 H, aryl).[24] Treatment of 352 mg of **11** with a solution of 540 mg of sodium methoxide in 7 ml of CH₃OD at room temperature for 1.5 hr gave on work-up 324 mg of **11**-d_2 whose nmr spectrum lacked the singlet at δ 2.90 but was otherwise identical with that of undeuterated **11**.

In addition to **11**, there was recovered about 1.0 g of a higher boiling product (110° at 0.15 Torr) believed to be 4-bromo-6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone: ir (neat) 1672 cm⁻¹; m/e 264 and 266, equal intensity; pmr (CDCl₃) δ 1.15 (s, 6 H, *gem*-dimethyl), 2.90 (s, 2 H, methylene), 6.90 (s, 1 H, vinyl), 7.25–8.10 (m, 4 H, arom).

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(20) Melting points are uncorrected. Ir spectra were calibrated against a polystyrene film; pmr spectra are referenced against tetramethylsilane. Mass spectra reported here were run on a Hitachi Perkin-Elmer RMU6. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(21) This acid was previously described as an oil (ref 8); since we obtained this precursor of **10** as low-melting crystals and in improved yield, we include the procedure here.

(22) Azobis(isobutyronitrile) (0.2 g) may be used in place of benzoyl peroxide.

(23) Usually 6–7 hr; the reaction can be followed readily since the NBS sinks to the bottom of the reaction mixture whereas the succinimide which is formed floats.

(24) Compound **11** was not subjected to elemental analysis since it was clear that an analysis of its nmr spectrum was a far more sensitive criterion of its purity (*i.e.*, >20% of **10** could be present in **11** and still give an elemental analysis which would be within satisfactory limits of error). Comparison of the relative areas of the *gem*-dimethyl peaks at δ 1.05 (in **10**) and δ 1.15 (in **11**) provided the best analytical method.

Irradiation of 11. A solution of 1.00 g (5.37 mmol) of **11** in 80 ml of spectrograde cyclohexane was degassed and irradiated under nitrogen (Hanovia 450 W, Pyrex) for 4 hr. The resulting yellow solution was concentrated under reduced pressure to a taffy-like semisolid, which was dissolved in a minimum quantity of anhydrous ether and chromatographed on 80–100 mesh neutral alumina. Elution with ether–carbon tetrachloride (1:9) afforded 170 mg of unreacted **11**. The eluent ratio was changed to 3:17 to yield 250 mg of dimer I (**16**),[25] mp 208–210° (methanol). The eluent ratio was changed to 1:4, affording 236 mg of dimer II (**17**),[26] mp 199–200° (methanol), and 50 mg of a cyclobutane dimer (**19** ?), mp 225–226° (methanol). The residue on the column was not further investigated. Vpc examination of the crude reaction product showed no volatile compounds except for recovered **11**.

The dimers had the following properties. **16**: ir (KBr) $\nu_{C=O}$ 1728, 1663 cm^{-1}; λ_{max}^{MeOH} 252 nm (ϵ 11,300), 295 (2640); pmr, see Table I;[27] mass spectrum (70 eV) m/e (rel intensity)[28] 372 (78), 316 (19), 298 (18), 288 (21), 283 (25), 272 (86), 245 (27), 232 (82), 231 (100), 215 (29), 202 (48). **17**: ir (KBr) $\nu_{C=O}$ 1730, 1673 cm^{-1}; λ_{max}^{MeOH} 250 nm (ϵ 10,050), 290 (2210); pmr, see Table I; mass spectrum (70 eV) m/e (rel intensity)[28] 372 (40), 288 (13), 272 (10), 245 (28), 232 (62), 231 (100), 215 (20), 202 (23). Cyclobutane dimer (**19** ?): ir (CCl$_4$) $\nu_{C=O}$ 1660 cm^{-1}; pmr (CDCl$_3$) δ 0.90 (s, 6 H, methyls), 1.08 (s, 6 H, methyls), 2.54 (d of d, J = 7.0 and 1.5 Hz, 2 H, methine adjacent to gem-dimethyl group), 2.74 (d, J = 9 Hz, 2 H, methylene), 3.25 (d, J = 19 Hz, 2 H, methylene), 3.64 (d of d, J = 7.0 and 1.5 Hz, 2 H, methine adjacent to aryl ring), 6.69–6.82 (m, 2 H, aryl), 7.11–7.32 (m, 4 H, aryl), 7.69–7.82 (m, 2 H, aryl); mass spectrum (70 eV) m/e (rel intensity) 372 (2), 186 (100), 171 (75), 144 (67), 128 (28), 115 (22).

Anal. Calcd for C$_{26}$H$_{28}$O$_2$: C, 83.83; H, 7.58. (**16**) Found: C, 83.68; H, 7.52. (**17**) Found: C, 83.75; H, 7.61. (**19** (?)) Found: C, 83.91; H, 7.55.

Solutions of **11** (50 μl) in cyclohexane (5 ml) or in cyclohexane (4 ml) to which was added 1 ml of 1,3-cyclohexadiene, piperylene, or styrene were irradiated simultaneously in a merry-go-round apparatus (200-W Hanovia lamp, Pyrex, 2.5 hr). The mixture was examined for the presence of **16** and **17** by thin-layer chromatography. Styrene did not affect dimer formation, but piperylene decreased the dimer yield and with cyclohexadiene no dimers of **11** were formed.

Deuteration of 16, 17, and the Cyclobutane Dimer. A solution of **16** (60 mg, 0.16 mmol) in CH$_3$OD (15 ml) containing 86 mg (1.6 mmol) of sodium methoxide was stirred at room temperature for 3 hr, then poured into an ice–hydrochloric acid mixture and extracted with benzene (3 × 50 ml). The combined benzene extracts were washed with water (3 × 25 ml), dried (MgSO$_4$), and rotary evaporated. The residue was recrystallized from methanol to give 45 mg (75%) of **16**-d_5: pmr (CDCl$_3$) δ 0.42, 0.96, 1.02, 1.10 (s, 3 H each, methyls), 1.80 (d, J = 5.5 Hz, 1 H, Hc), 2.40 (s, 1 H, Hb), 4.90 (d, J = 5.5 Hz, 1 H, Hd), 7.20–7.60 (m, 6 H, arom), 7.85–8.30 (m, 2 H, arom); mass spectrum (70 eV) m/e (rel intensity) 377 (62), 319 (15), 301 (13), 291 (20), 286 (15), 273 (22), 272 (67), 261 (16), 247 (15), 234 (15), 233 (70), 232 (100), 231 (32), 216 (18), 205 (33), 204 (30), 203 (48).

An identical procedure with **17** gave 51 mg (85%) of **17**-d_5: pmr (CDCl$_3$) δ 0.70, 0.84, 1.36, 1.40 (s, 3 H each, methyls), 2.53 (d of d, J = 5 and 11 Hz, 1 H, Hc), 2.80 (d, J = 5 Hz, 1 H, Hb), 4.70 (d, J = 11 Hz, 1 H, Hd), 6.45–7.75 (m, 8 H, arom as in Table I); mass spectrum (70 eV) m/e (rel intensity) 377 (33), 319 (4), 291 (12), 256 (13), 248 (11), 247 (22), 234 (15), 233 (59), 232 (100), 231 (32), 216 (15), 205 (10), 204 (20), 203 (23).

The same exchange procedure applied to the cyclobutane dimer (**19** ?) gave **19**-d_4: pmr (CDCl$_3$) δ 0.90, 1.08 (s, 6 H each, methyls), 2.54 (d of d, J = 7.0 and 1.5 Hz, 2 H, methine), 3.64 (d of d, J =

7.0 and 1.5 Hz, 2 H, methine), 6.69–7.82 (m, 8 H, arom as in unlabeled compound); mass spectrum (70 eV) m/e (rel intensity) 376 (2), 188 (44), 187 (23), 173 (66).

Isomerization of 16 to 18. To a solution of **16** (50 mg, 0.134 mmol) in 25 ml of methanol was added a solution of sodium hydroxide (1.2 g, 30 mmol) in 5 ml of water, and the resulting yellow solution was refluxed in a N$_2$ atmosphere for 5 hr. The cooled solution was diluted with 200 ml of water and extracted with ether (3 × 50 ml). The combined ether layers were washed with water and dried (MgSO$_4$), and the solvent was evaporated to leave a residue which, recrystallized from methanol, gave 38 mg (76%) of **18** as colorless crystals, mp 214–215° (red melt): ir (KBr) $\nu_{C=O}$ 1720 and 1660 cm^{-1}; λ_{max}^{MeOH} 243 nm (ϵ 6590), 286 (1435); pmr, see Table I; mass spectrum (70 eV) m/e (rel intensity) 372 (37), 316 (15), 298 (20), 288 (7), 283 (24), 272 (100), 260 (21), 245 (11), 232 (55), 231 (100), 215 (23), 202 (43).[29]

The isomerization of **16** was also carried out using deuterated base and solvent. To a solution of **16** (55 mg, 0.148 mmol) in 25 ml of CH$_3$OD at reflux under N$_2$ was added a solution of 2.04 g (33 mmol) of sodium oxide in 5 ml of D$_2$O. The yellow solution was refluxed for 4 hr, cooled to 0°, and diluted with 100 ml of water. The mixture was washed with ether and the combined ether extracts were washed with water, dried (MgSO$_4$), and evaporated to leave a residue which, on recrystallization from methanol, gave 27 mg (49%) of pure **18**-d_5: pmr as in Table I, except that the peaks at δ 2.12, 2.40, 2.92 (methylenes) and 4.06 (Hd) were absent, and the peak at δ 2.55 (Hc) became a singlet;[30] mass spectrum (70 eV) m/e (rel intensity) 377 (20), 376 (14), 375 (10), 320 (5), 319 (9), 318 (8), 302 (6), 301 (11), 300 (13), 299 (8), 298 (3), 286 (11), 285 (13), 284 (9), 274 (17), 273 (60), 272 (60), 262 (12), 261 (19), 260 (5), 248 (8), 247 (7), 234 (23), 233 (59), 232 (100), 231 (54), 217 (15), 216 (15), 205 (20), 204 (23), 203 (22), 202 (16).

A solution of **16** (25 mg, 0.067 mmol) in 7 ml of methanol containing 81 mg (1.5 mmol) of sodium methoxide was refluxed for 5 hr, N$_2$ atmosphere, then worked up as above. Dimer **16** was recovered nearly quantitatively (ir, nmr). Therefore sodium hydroxide, not sodium methoxide, is necessary to isomerize **16** to **18**.

Deuteration of 18. A solution of **18** (38 mg, 0.102 mmol) in 15 ml of CH$_3$OD containing 50 mg (0.93 mmol) of sodium methoxide was stirred at room temperature for 10 hr and then poured into an ice–hydrochloric acid mixture and extracted with ether (3 × 25 ml). The combined ether layers were washed with water and dried (MgSO$_4$). Removal of the solvent under reduced pressure and recrystallization of the residue from methanol gave 27 mg (71%) of **18**-d_4: nmr (CDCl$_3$) as in Table I except for the absence of the signals at δ 2.12, 2.40, and 2.92 (methylene protons). Neither Ha nor Hd exchanges under these conditions.

Attempted Isomerization of 17. Treatment of **17** with aqueous methanolic sodium hydroxide in a N$_2$ atmosphere, exactly as described from the isomerization of **16** to **18**, gave only recovered **17**.

Dehydrogenation of 17. A solution of **17** (100 mg, 0.269 mmol) and o-chloranil (250 mg, 1.02 mmol) in acetonitrile (25 ml) was kept in the dark at room temperature for 24 hr (the reaction was followed by tlc, alumina, 15% ether–85% CCl$_4$). Solvent was removed under reduced pressure and the residue was taken up in ether and subjected to preparative tlc (alumina, 20% ether–80% CCl$_4$). The product band was extracted with ether and the solvent evaporated to give 65 mg of crude **15** which, recrystallized from methanol, gave colorless crystals (50 mg), mp 204°: ir (Nujol) 1691, 1665 cm^{-1}; λ_{max}^{MeOH} 238 nm (ϵ 24,800), 245 (22,800), 292 (8900); pmr, see Table I; mass spectrum (70 eV) m/e (rel intensity) 370 (37), 355 (22), 315 (34), 314 (100), 313 (54), 299 (51), 271 (45).

Anal. Calcd for C$_{26}$H$_{26}$O$_2$: C, 84.29; H, 7.07. Found: C, 84.18; H, 7.13.

An identical product (mp, pmr, mass spectrum, tlc R_f) was obtained in good yield when a solution of **17** (20 mg) in ethyl acetate (30 ml) was refluxed for 23 hr with 200 mg of 5% Pd on charcoal.[31]

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(25) Possible names are 1,1,10,10-tetramethyl-4,5:6,7-dibenzo-1,2,3a(α),5a(α),10a(β),10b(α)-hexahydrocyclohept[e]inden-6-en-3,8-dione or 7a,7a,15,15-tetramethyl-11,12-benzo-13-epi-18-nor-B-homo-estra-1,3,-5(10),11-tetraene-6,17-dione.

(26) Alter the names in ref 25 to 5a(β),10a(α) or to 14-epi.

(27) Decoupling experiments were carried out on dimers I, II, and i-I (Table I) to verify the various assignments.

(28) The mass spectra were studied in much greater detail than presented here, in collaboration with S. Meyerson (Standard Oil Company, Ind.). In general the results support the fact that **16** and **17** are stereoisomers which fragment similarly but not identically. Analysis of the [M − CH$_3$]$^+$ peak intensities indicates that methyl crowding is more severe in **17**. Both compounds undergo some thermal dehydrogenation in the inlet system at high temperatures, **16** more extensively than **17**.

(29) An elemental analysis was considered unnecessary since all the spectral data clearly showed that **18** was a stereoisomer of **16**.

(30) Apparently Ha does not exchange under the conditions which isomerize **16** to **18**. However, if **18** is refluxed for a longer time under the same conditions, Ha also exchanges.

(31) Curiously, when **17**-d_5 (methylenes and Ha deuterated) was dehydrogenated with chloranil and purified by tlc, the product **15** contained one deuterium. The pmr spectrum was as in Table I except that the peak at δ 3.27 was a singlet and that at δ 2.73 was absent (m/e 371 (M$^+$)). Apparently one of the methylene protons in the five-membered ring in **15** is specifically prevented from back exchange (via enolates) during the purification on alumina.

Dehydrogenation of 18. A solution of **18** (56 mg, 0.15 mmol) and *o*-chloranil (191 mg, 0.78 mmol) in 25 ml of spectrograde acetonitrile was refluxed in a dark apparatus (wrapped with aluminum foil) for 3 days. The solvent was evaporated under reduced pressure and the resulting red residue was dissolved in a few milliliters of 85% CCl_4–15% ether and chromatographed on neutral alumina using the same solvent as eluent. There was obtained 29 mg (52%) of **14** as colorless crystals, mp 213–214°: ir (KBr) 1698, 1670, 1623 cm^{-1}; λ_{max}^{MeOH} 263 nm (ϵ 22,800), 288 (7500); pmr (CDCl$_3$) see Table I; mass spectrum (70 eV) *m/e* (rel intensity) 370 (21), 355 (5), 315 (32), 314 (100), 299 (40), 271 (26).

Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.32; H, 6.98.

Attempted Dehydrogenation of 16. Treatment of **16** with chloranil or with 5% Pd–C exactly as described for the dehydrogenation of **17** gave mainly recovered **16**, but traces (~5%) of **15**, identified by ir and pmr.

Isomerization of 15 to 14. An oxygen-free solution of **15** (65 mg, 0.176 mmol) in 200 ml of methanol containing 150 mg (0.277 mmol) of sodium methoxide was allowed to stand at room temperature under nitrogen for 24 hr. The mixture was poured into an ice–hydrochloric acid mixture, most of the methanol was removed by rotary evaporation, and the residue was extracted with benzene. Combined benzene layers were washed with water and dried (MgSO$_4$). Evaporation of the benzene and recrystallization of the residue from methanol gave colorless crystals (45 mg, 69%) of **14**, mp 214°, identical (ir, pmr, uv, mass spectrum) with the dehydrogenation product of **18**.

When this reaction was carried out using CH$_3$OD in place of ordinary methanol, the product was **14**-d_4 (*m/e* 374 (M$^+$)). The pmr spectrum was as listed in Table I with the exception that peaks at δ 2.28, 2.57, and 4.53 were absent, and the peaks at δ 3.23 and 2.89 were singlets.[32]

Synthesis of 11-d_1. **6,6-Dimethyl-2,3-benzocyclohept-2-en-1-ol-1-d.** To a suspension of lithium aluminum deuteride (0.67 g, 16 mmol) in 80 ml of absolute ether under N$_2$ at 10° was slowly added a solution of **10** (6.0 g, 32 mmol) in 40 ml of ether. The mixture was refluxed for 3 hr. Ethyl acetate was added to the cooled mixture to destroy excess lithium aluminum deuteride. Following hydrolysis with 20 ml of hydrochloric acid, the organic layer was separated, washed with water (3 × 25 ml), and dried (MgSO$_4$). Removal of the ether under reduced pressure and recrystallization of the residue from hexane afforded 5.8 g (97%) of 6,6-dimethyl-2,3-benzocyclohept-2-en-1-ol-1-d as colorless crystals, mp 102–103°: pmr (C$_6$D$_6$) δ 0.72, 0.87 (s, 3 H each, methyls), 1.24 (m, 2 H, C5 methylene), 1.56 (br s, 2 H, C7 methylene), 2.00 (s, 1 H, OH), 2.52 (m, 2 H, C4 methylene);[33] ir (Nujol) 3300 cm^{-1}, no $\nu_{C=O}$; *m/e* 191 (M$^+$). **7,7-Dimethyl-3,4-benzo-1,3-cycloheptadiene-2-d.** To a solution of 6,6-dimethyl-2,3-benzocyclohept-2-en-1-ol-1-d (6.1 g, 32 mmol) in 80 ml of benzene was added 14 g (0.1 mol) of phosphorus pentoxide, and the mixture was refluxed for 2 hr. The cooled mixture was filtered and the filtrate was washed with water (3 × 30 ml), dried (MgSO$_4$), and distilled under reduced pressure to give 5.0 g (91%) of 7,7-dimethyl-3,4-benzo-1,3-cycloheptadiene-2-d, bp 71–72° at 0.12 Torr; ir (neat) 2950, 1710 (weak), 780, 750 cm^{-1}; pmr (CCl$_4$) δ 1.05 (s, 6 H, *gem*-dimethyl), 1.55–1.75 (m, 2 H, C6 methylene), 2.52–2.78 (m, 2 H, C5 methylene), 5.55 (br s, 1 H, Cl vinyl);[34] *m/e* 173 (M$^+$). **6,6-Dimethyl-2,3-benzo-2,4-cycloheptadien-1-ol-4-d.** Benzylic bromination of 7,7-dimethyl-3,4-benzo-1,3-cycloheptadiene-2-d and hydrolysis of the resulting bromide were performed in sequence without purification of the intermediate. To a solution of the deuterated benzocycloheptadiene (5 g, 29 mmol) in 100 ml of carbon tetrachloride was added 7.12 g (40 mmol) of *N*-bromosuccinimide and a few mg of azobis(isobutyronitrile). The mixture was refluxed for 12 hr, cooled and filtered to remove the succinimide, and concentrated under reduced pressure to give 8.8 g of a yellow oil. To the oil was added 100 ml of 10% aqueous sodium carbonate, and the mix-

ture was refluxed for 5 hr. The cooled mixture was acidified with dilute aqueous hydrochloric acid and extracted with ether, and the combined ether layers were washed with water and dried (MgSO$_4$) and the solvent evaporated to leave 5.3 g of a brownish oil. The oil was dissolved in a little benzene and chromatographed through silica gel. With benzene as eluent there was obtained 2.8 g of a hydrocarbon fraction shown by nmr to be 25% recovered starting material and 75% 7,7-dimethyl-3,4-benzo-1,3,5-cycloheptatriene-2-d: pmr (CCl$_4$) δ 1.03 (s, 6 H, methyls), 5.4–5.65 (m, 2 H, Cl and C6 vinyls), 6.36 (d, J = 12 Hz, 1 H, C5 vinyl), 6.95–7.15 (m, 4 H, arom). Further elution with ether gave 2.0 g (36%) of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadien-1-ol-4-d as a yellow oil, bp 44–45° (1 Torr): ir (neat) 3450 cm^{-1}; pmr (CDCl$_3$) δ 0.88, 1.06 (s, 3 H each, methyls) 1.8–2.0 (m, 2 H, methylene), 3.68 (br s, 1 H, OH), 4.7 (m, 1 H, Cl proton), 5.51 (s, 1 H, C5 vinyl), 6.9–7.5 (m, 4 H, arom). **6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone-4-d** (**11-d_1**). To a solution of the secondary alcohol from the previous step (2.0 g, 11 mmol) in 30 ml of acetone at 0–5° was added a slight excess of 1.67 *M* Jones' reagent.[35] The resulting brown solution was stirred for 10 min, quenched with saturated aqueous sodium bisulfite, diluted with water, and extracted with ether. The combined ether layers were dried (MgSO$_4$) and evaporated and the resulting oil was vacuum distilled to give 1.6 g (80%) of **11-d_1**, bp 87–90° (0.6 Torr), *m/e* 187 (M$^+$). The pmr spectrum was identical with that of authentic **11** except that the signal at δ 6.18 was absent and that at δ 5.75 was a singlet.

Irradiation of 6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone-4-d (**11-d_1**). The procedure was as described for unlabeled **11**. The resulting dimer I (**16**) had the following properties: pmr (CDCl$_3$) as in Table II except that signals at δ 3.45 and 4.90 were absent, and those at δ 1.80 and 2.40 were singlets; mass spectrum (70 eV) *m/e* (rel intensity) 374 (48), 359 (6), 318 (13), 301 (6), 300 (10), 299 (6), 290 (16), 285 (16), 275 (15), 274 (30), 273 (75), 272 (20), 263 (7), 262 (18), 261 (10), 248 (15), 247 (26), 246 (15), 235 (25), 234 (75), 233 (100), 232 (75). The resulting dimer II (**17**) had the following properties: pmr (CDCl$_3$) as in Table I except that the signal at δ 4.70 was absent and that at δ 2.53 was a doublet, J = 5 Hz;[36] mass spectrum (70 eV) *m/e* (rel intensity) 373 (32), 290 (8), 289 (17), 288 (5), 275 (7), 274 (12), 273 (8), 254 (20), 247 (17), 246 (32), 245 (8), 234 (30), 233 (77), 232 (100), 231 (48), 217 (10), 216 (21), 215 (8), 205 (16), 204 (23), 203 (26), 202 (14).

Autoxidation of 18. To a solution of **18** (33 mg, 0.089 mmol) in 20 ml of methanol was added 4.5 ml of 20% aqueous sodium hydroxide. The yellow solution was refluxed (in air) for 4 hr. The resulting red solution was cooled, diluted with 100 ml of water (turns green), and extracted with ether (3 × 25 ml). The combined ether extracts were washed with water, dried (MgSO$_4$), and evaporated, leaving no residue whatever. The aqueous layer was acidified with hydrochloric acid and again extracted with ether (3 × 100 ml). Combined ether layers were washed with water, dried (MgSO$_4$), and evaporated to dryness affording a semisolid residue which, on recrystallization from methanol, gave 28 mg (79%) of acid **22**, mp 190–191°: ir (KBr) 3500–2850 (br), 1700, 1680 cm^{-1}; λ_{max}^{MeOH} 293 nm (ϵ 960), 252 (4190), 210 (8400); pmr (CDCl$_3$) δ 0.60, 1.02, 1.20, 1.28 (s, 3 H each, methyls), 2.11–3.35 (m, 6 H, 4 methylene and 2 methine protons), 5.21 (br s, 1 H, methine Hd), 6.67–6.90 (m, 1 H, arom), 7.20–7.70 (m, 5 H, arom), 7.80–8.20 (m, 2 H, arom); mass spectrum (70 eV) *m/e* (rel intensity) 404 (9), 397 (30), 396 (100), 372 (5), 371 (17), 345 (11), 344 (32), 331 (20), 330 (70), 315 (24), 313 (15), 289 (13), 288 (51), 287 (34), 271 (29), 269 (14), 248 (31), 247 (100), 246 (17), 245 (15), 231 (24), 226 (29).

Esterification of 22. To a solution of **22** (50 mg, 0.124 mmol) in 10 ml of absolute ether was added an ether solution of diazomethane until nitrogen ceased to be evolved and the yellow color persisted. Evaporation of the solvent and recrystallization of the residue from methanol gave an essentially quantitative yield of ester **23**, mp 128–129°: ir (CCl$_4$) 1730, 1675 cm^{-1}; λ_{max}^{MeOH} 293 nm (ϵ 2300), 248 (10,000); pmr (CDCl$_3$) δ 0.63, 1.04, 1.17, 1.23 (s, 3 H each, methyls), 2.21 d, J = 12.5 Hz, 1 H, methylene), 2.37 (d, J = 15.5 Hz, 1 H, methylene), 2.72 (d, J = 3.5 Hz, 1 H, Hc), 2.79 (d, J = 12.5 Hz, 1 H, methylene), 2.94 (d, J = 15.5 Hz, 1 H, methylene), 3.32 (s, 1 H, Hb), 3.65 (s, 3 H, methoxyl), 5.17 (d, J = 3.5 Hz, Hd), 6.65–6.88

(32) Apparently Hd is isomerized in the conversion of **15** to **14**; also exchanged under these conditions are three of the four methylene protons (2 H at δ 2.57 and 1 H at δ 2.28). To test this conclusion, **14** was subjected to the isomerization conditions, using CH$_3$OD. The same three methylene protons exchanged, but Hc and Hd remained as mutually coupled doublets. The mass spectrum of the product had an M$^+$ peak at *m/e* 373. The reason why only three of the four methylene protons exchange under these conditions is not known.

(33) The multiplet at δ 4.75 corresponding to the Cl proton in unlabeled alcohol was absent in the deuterated product.

(34) Peaks at δ 5.9–6.2 due to the C2 vinyl proton in the unlabeled benzocycloheptadiene were absent in the deuterated product.

(35) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 142.

(36) The product obviously contained only one deuterium, at Hd, rather than the two deuteriums expected. We conclude that the other methine deuterium must have been at Ha and that this was lost during the chromatographic purification. Experiments with **17**-d_5 showed that Ha could be exchanged easily under such conditions.

(m, 1 H, arom), 7.28–7.45 (m, 5 H, arom), 7.85–8.20 (m, 2 H, arom), coupling constants verified by decoupling experiments; mass spectrum (70 eV) m/e (rel intensity) 418 (40), 387 (15), 386 (37), 261 (11), 248 (35), 247 (100), 231 (13), 219 (13).

Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23. Found: C, 77.31; H, 7.08.

A solution of **23** (11 mg, 0.026 mmol) in 11 ml of CH_3OD containing 14 mg (0.26 mmol) of sodium methoxide was refluxed for 6 hr under a nitrogen atmosphere. The cooled solution was neutralized with 5 ml of D_2O containing CF_3CO_2D and then diluted with water (50 ml) and extracted with ether (3 × 25 ml). The combined ether layers were washed with water, dried ($MgSO_4$), and evaporated, and the residue was recrystallized from methanol to give 7 mg (64%) of **23-d_4**: pmr ($CDCl_3$) as for **23** except that the four methylene signals at δ 2.21, 2.37, 2.79, and 2.94 were absent;[37]

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(37) Hb does not exchange under these conditions; approach by the base to Hb may be hindered, or formation of the enolate anion at that site would bring the bulky ester side chain in a position which interacts severely with the *gem*-dimethyl group on the seven-membered ring.

mass spectrum (70 eV) m/e (rel intensity) 422 (9), 391 (8), 390 (15), 248 (49), 247 (100).

When the autoxidation of **18** was carried out as described above but using CH_3OD and Na_2O in D_2O and the resulting acid was esterified directly with diazomethane, the resulting **23** contained six deuterium atoms (mass spectrum), the four methylene protons, and the methine protons Hb and Hd being labeled.

Autoxidation of 16. When **16** (85 mg, 0.228 mmol) was autoxidized using exactly the procedure described for the oxidation of **18**, there was isolated only 9 mg (10%) of the acid **22** (identical by ir and nmr with the autoxidation product of **18**), the remainder of the material being neutral. However, when **16** was first treated as described for the isomerization of **16** to **18** (*vide supra*) and the reaction mixture was subsequently refluxed for an additional 4 hr with air rather than nitrogen bubbling through the solution, acid **22** was isolated in 80% overall yield.

Arylcyclopropane Photochemistry. The Photochemical Addition of Amines to 1,2-Diarylcyclopropanes

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Abstract: Photolysis of 1,2-diphenylcyclopropane (**1**) in primary or secondary amines resulted in addition of the N–H bond of the amine across the C-1–C-2 bond of the cyclopropane. Irradiation of dibenzotricyclo[3.3.0.0^{2,8}]-octadiene (**15**) in cyclohexylamine produced a 4:1 mixture of *syn-* and *anti-*4-cyclohexylaminodibenzobicyclo[3.3.0]-octadienes (**16** and **17**), indicating a preference for the formation of the more hindered isomer. Sensitization studies indicate that the additions to diphenylcyclopropane do not occur *via* the lowest triplet state. No isotope effect was found when the efficiencies of addition of *n*-butylamine and *n*-butylamine-*N,N-d₂* to *trans*-1,2-diphenylcyclopropane (**1**) were compared. Quantum yield studies of the addition of *n*-butylamine to **1** were carried out at various amine concentrations. A discussion of the reactive excited state of **1** and a reaction mechanism are presented.

Investigations carried out over the last several years by several groups,[1] most notably that of Griffin,[1a–d] have revealed that *trans*-1,2-diphenylcyclopropane (**1**) is from the photochemical standpoint an exceedingly diverse molecule. This is illustrated in Scheme I which shows the paths taken by **1**, probably the most thoroughly studied of all arylcyclopropanes, when irradiated in methanol.[1a,b]

Thus, like stilbene, **1** undergoes trans–cis isomerization upon both direct[1a,e] and triplet-sensitized[1f,g] irradiation. In addition, however, the singlet excited state of **1** undergoes migration of hydrogen and of carbon to form **3–5**,[1a,e] cleavage to give phenylcarbene **6**,[1c,d,2,3] and addition of methanol to provide ether **8**.[1b]

(1) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, 87, 1410 (1965); (b) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinnson, C. S. Aaron, G. W. Griffin, and G. J. Boudreau, *ibid.*, 88, 5675 (1966); (c) H. Kristinnson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind. (London)*, 1562 (1966); (d) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968); (e) E. W. Valyocsik and P. Sigal, *J. Org. Chem.*, 36, 66 (1971); (f) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, 86, 2532 (1964); (g) C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966; (h) G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, 87, 3256 (1965); (i) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, 90, 2957 (1968); (j) R. S. Cole, Ph.D. Thesis, California Institute of Technology, 1968; (k) T. A. Matzke, Ph.D. Thesis, University of Texas at Austin, 1971.

(2) G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, 10, 529 (1971).

(3) S. S. Hixson, *J. Amer. Chem. Soc.*, 95, 6144 (1973).

Scheme I. Photolysis of *trans*-1,2-Diphenylcyclopropane in Methanol
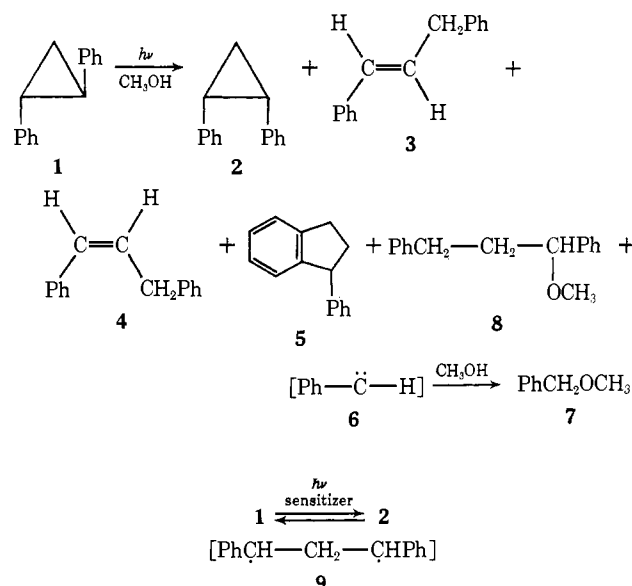
The formation of products **2–7** in the direct photolysis of **1** has been rationalized[1a,e,2] as occurring *via* an intermediate diradical **9**, though the exact nature of **9** remains unclear.[4]