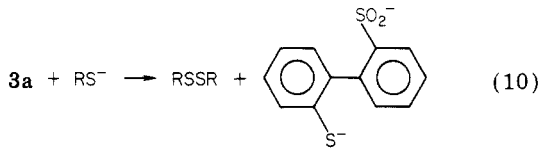
were of the highest degree of purity commercially available.

Procedure for Kinetic Runs. Measurement of k_{RS}. A 1.0×10^{-4} M solution of 1 (or 2) in 60% dioxane was placed in one of the reservoir syringes of a Durrum-Gibson stopped-flow spectrophotometer. In the other reservoir syringe was placed in a solution of the thiol (0.002–0.02 M) in 60% dioxane also containing 0.03 M K_2HPO_4 and 0.005 M KH_2PO_4. The reaction was initiated by mixing the two solutions by using the stopped-flow device, and the decrease in the absorbance at 296 nm (304 nm for 2) with time was recorded on a storage oscilloscope.

Measurement of k_{-RS}. A concentrated solution containing equal amounts of an alkanethiol (RSH) and the corresponding alkanethiolate (RS^-) was prepared by adding the calculated amount of 1 N standard sodium hydroxide to a solution of the thiol in 60% dioxane. A measured volume of this solution, containing an amount of thiolate at least sufficient to convert the thiolsulfonate completely to **3a** (or **4a**), was then added to a 1×10^{-4} M solution of 1 (or 2) in 60% dioxane. For certain thiols, mercaptoethanol and ethyl mercaptoacetate, it was important to use no more than the minimum amount (1×10^{-4} M) of thiolate ion needed to convert 1 quantitatively to **3a**. If significantly larger amounts of thiolate were added, the further reaction of **3a** with the thiolate (eq 10) began to create problems, particularly if the



(10)

solution was allowed to stand for any length of time before being acidified with a carboxylic acid buffer. With *t*-BuS^-, where reaction 10 is extremely slow due to the steric hindrance to attack on the sulfur adjacent to the *tert*-butyl group in **3a**, a large excess of thiolate ion over the minimum required to convert 1 to **3a** could be used. With *n*-BuS^- and $PhCH_2S^-$ up to a 2-fold excess of thiolate could be used, provided care was taken to perform the subsequent acidification of the solution promptly.

For the runs with 1 and all thiols except ethyl mercaptoacetate a 3.5-mL aliquot of the solution resulting from the addition of the 1:1 RS^-/RSH solution to the solution of 1 was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 UV spectrometer. To this was then added from 35–140 μL of a concentrated (1 M in each buffer component) 1:1 RCOOH/$RCOO^-$ buffer, using either chloroacetic or formic acid as the buffer acid, and the increase in the optical density of the solution at 296 nm was then monitored with time.

With ethyl mercaptoacetate the return of **3a** to 1 upon acidification was too rapid to be followed by conventional spectrophotometry, and the following stopped-flow procedure was employed. The solution resulting from the addition of the 1:1 RS^-/RSH solution to the solution of 1 was placed in one reservoir syringe of the stopped-flow spectrophotometer, a 1:1 RCOOH/$RCOO^-$ buffer ([RCOOH] = 0.02 M) in 60% dioxane was placed in the other syringe, and the reversion of **3a** to 1 was then initiated upon mixing the two solutions together in the stopped-flow apparatus. The reaction was followed at 296 nm. The same type of stopped-flow procedure was also used to follow the reversion of **4a** to 2. In this case a wavelength of 304 nm was used to follow the reaction.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. 1, 25331-82-2; 2, 40227-43-8; *t*-BuSH, 75-66-1; BuSH, 109-79-5; $HOCH_2CH_2SH$, 60-24-2; $PhCH_2SH$, 100-53-8; $EtOCOCH_2SH$, 623-51-8.

Photochemical Studies of Cyclopropenes and Cyclopentadienes. Mechanistic and Exploratory Organic Photochemistry[1,2]

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The photochemistry of two vinylcyclopropenes and one cyclopentadiene was investigated. Thus, 3-phenyl-3-(1-phenylvinyl)cyclopropene, 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene, and 2,5,5-triphenylcyclopentadiene were studied. The vinylcyclopropenes were designed with the vinyl moieties being the low-energy chromophores in contrast to previously studied examples where the cyclopropene π bond is lower in energy. As with previous vinylcyclopropenes, irradiation led to cyclopentadienes and indenes. 2,5,5-Triphenylcyclopentadiene was the main photoproduct of the irradiation of the (diphenylvinyl)cyclopropene. 3-(2,2-Diphenylvinyl)indene was a lesser product that was encountered. 1,2-Diphenylcyclopentadiene, 3-(1-phenylvinyl)indene, and 3,4-diphenyl-1,2,4-pentatriene were formed from direct photolysis of the styryl cyclopropene. Interestingly, the corresponding sensitized irradiation led exclusively to 1,2-diphenylcyclopentadiene. Quantum efficiencies were determined for these reactions. Direct irradiation of 2,5,5-triphenylcyclopentadiene led to a novel ring contraction to afford the (diphenylvinyl)cyclopropene. Additionally, phenyl migration was observed, leading to formation of 1,4,5-triphenylcyclopentadiene. Sensitized reaction of 2,5,5-triphenylcyclopentadiene led only to the phenyl migration product. Again, quantum yields were determined. The (diphenylvinyl)cyclopropene was labeled in order to ascertain the skeletal change in the rearrangement. Similarly, labeling studies were carried out with 2,5,5-triphenylcyclopentadiene, thus allowing delineation of the fate of each carbon. Additionally, studies were carried out independently to generate the 3,5,5-triphenylpentadienyl carbene. The (diphenylvinyl)cyclopropene was the major product along with 2,5,5-triphenylcyclopentadiene and 3-(2,2-diphenylvinyl)indene.

A major function of organic photochemistry is the search for new reactions. Once a new reaction has been uncovered, there is need for exploration of the generality, limitations, and mechanisms of the reaction. One type of reaction which has been of interest to us[3-5] is the photo-

(1) This is paper 133 of our "Mechanistic and Exploratory Organic Photochemistry" series.

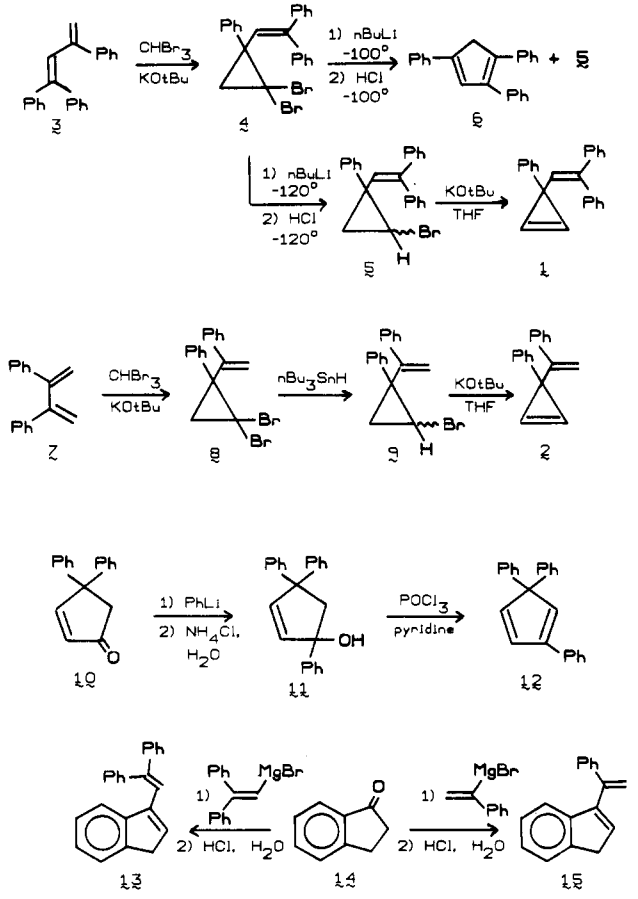
(2) For paper 132 of the series, see Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. Paper 131: Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128–2132. Paper 130: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980.

(3) (a) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

(4) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345.

0022-3263/82/1947-2060$01.25/0

Scheme I. Synthesis of Cyclopropene Photochemical Reactants and Potential Photoproducts



chemical rearrangement of vinyl- and allylcyclopropenes. Parallel efforts in this area are due to Padwa.[6]

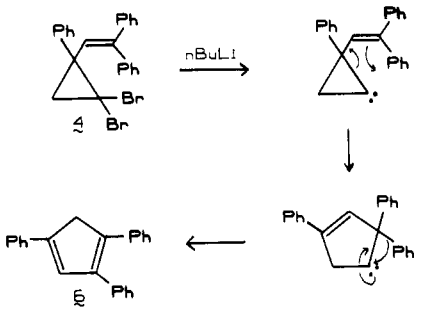
The present study began with the objective of investigating examples of the vinyl cyclopropene rearrangement where, in contrast to the previously studied cases, the low-energy chromophore is external to the three-membered ring. For this purpose, the photochemistry of 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene (1) and 3-phenyl-3-(1-phenylvinyl)cyclopropene (2) was investigated.

Results

Synthesis of Photochemical Reactants and Potential Photoproducts. Our syntheses of the (diphenylvinyl)cyclopropene 1 and the α-styrylcyclopropene 2 are outlined in Scheme I. Four aspects are worthy of comment.

First, the conversion of triphenylcyclopentenol 11 to 2,5,5-triphenylcyclopentadiene (12) proved difficult since under acidic conditions phenyl rearrangement led to the undesired 1,2,4-triphenylcyclopentadiene (6). However, phosphorous oxychloride–pyridine effected the elimination and afforded the desired unrearranged triphenylcyclopentadiene 12.

Second, the dibromo(diphenylvinyl)cyclopropane 4 proved unreactive toward tri-*n*-butylstannane. *n*-Butyllithium treatment at −120 °C, and protonation at this temperature proved necessary. Interestingly, when the butyllithium reaction was run at −100 °C, a rearrangement to afford 1,2,4-triphenylcyclopentadiene (6) occurred (note eq 1). This rearrangement is of some interest and has



(1)

precedent in the work of Skattebol,[7] who has proposed formation of a cyclopropyl carbene followed by ring expansion to an isomeric carbene. In the present instance, such a ring-expanded carbene would undergo phenyl migration to form the observed product (again note eq 1).

Third, the regioselective formation of one dibromocyclopropane (i.e., 4) from the reaction of triphenyl diene 3 is of some interest. This may derive both from the diminished steric hindrance to approach to the disubstituted, compared with the trisubstituted, double bond and also from a preferential electrophilic attack at the end of the diene allowing maximum phenyl delocalization. This has precedent.[8]

Finally, the dehydrobromination of bromocyclopropanes 5 and 9 proved equally successful on the different epimers, and in practice, the epimeric mixtures could be used.

Exploratory Photolysis of 3-Phenyl-3-(2,2-diphenylvinyl)cyclopropene. We turned first to the photochemistry of the (diphenylvinyl)cyclopropene 1.

In exploratory photolyses direct irradiation of 1 led to three photoproducts. The first was 2,5,5-triphenylcyclopentadiene 12 which had been synthesized as described in Scheme I. The second photoproduct, 16, also proved isomeric with the photoreactant. Additionally, the NMR spectrum exhibited a two-proton vinyl singlet at δ 6.76 and a one-proton singlet at δ 4.83 in addition to aryl absorption. The ^{13}C NMR spectrum revealed two different types of olefinic carbons and one aliphatic carbon in addition to the phenyl carbons (note the Experimental Section for details). The ultraviolet spectrum [λ_{max} 235 nm (ε 13 500), 349 (13 000)] was reminiscent of that of 1,4-diphenylcyclopentadiene (λ_{max} 237 nm (ε 13 000), 349 (20 000)[9]].

A second piece of evidence came from the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with this photoproduct (i.e., 16) to give an adduct with a single aliphatic peak at δ 4.14 and a two-proton vinyl singlet at δ 6.88, again supporting a structure having the two vinyl hydrogens symmetrically situated in a phenyl-substituted cyclopentadiene.

Finally, butyllithium treatment of 16 followed by quenching led to the known 1,2,3-triphenylcyclopentadiene, and sodium methoxide treatment effected a partial conversion to this cyclopentadiene.

This information led us to 1,4,5-triphenylcyclopentadiene (16) as the structure of the second photoproduct.

In addition, the third photoproduct was identified as 3-(2,2-diphenylvinyl)indene (13) by comparison with au-

(5) Zimmerman, H. E.; Bunce, R. A., submitted for publication in *J. Org. Chem.*

(6) (a) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344–2345. (b) *J. Org. Chem.* **1978**, *43*, 1481–1492. (c) For a general review of more recent papers by this author see: Padwa, A. *Org. Photochem.* **1979**, *4*, 261–326.

(7) (a) Holm, K. H.; Skattebol, L. *Tetrahedron Lett.* **1977**, 2347–2350. (b) Skattebol, L. *Tetrahedron* **1967**, *23*, 1107–1117.

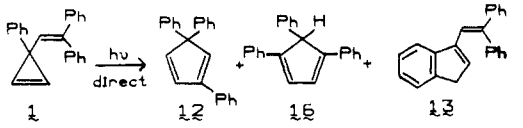
(8) Skattebol, L. *J. Org. Chem.* **1964**, *29*, 2951–2956.

(9) Bailey, P. S. "Sadtler Ultra Violet Spectra"; Sadtler Research Laboratories, Inc.: Philadelphia, 1964; Spectrum No. 2220U.

thentic material whose synthesis is included in Scheme I (vide supra). This photoproduct was obtained in very minor amounts.

In contrast, the photosensitized reaction, using xanthone and (dimethylamino)benzophenone as sensitizers, led to nonmonomeric products even at very low extents of conversion. NMR analysis established the absence of the singlet photoproducts. This provides evidence that the triplet behaves differently than the excited state involved in the direct irradiations which then can be identified as S_1.

The photochemistry of the (diphenylvinyl)cyclopropene 1 is depicted in eq 2.

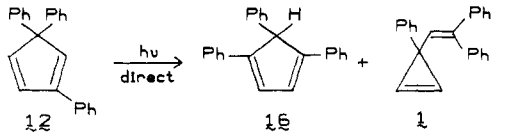


(2)

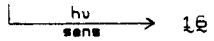
Photolysis of 2,5,5-Triphenylcyclopentadiene (12). Since reasonable one-step mechanisms (vide infra) thought to be involved in the photolysis of the (diphenylvinyl)-cyclopropene 1 plausibly led to 2,5,5-triphenylcyclopentadiene (12) but not to the 1,4,5-triphenylcyclopentadiene (16) which was also encountered, it seemed possible that the 1,4,5-isomer 16 arose from secondary photochemistry of the 2,5,5-cyclopentadiene 12. Hence it was important to investigate the photochemical behavior of 2,5,5-triphenylcyclopentadiene (12).

Irradiation of this compound (i.e., 12) did, indeed, effect a phenyl migration and formation of the 1,4,5-isomer 16 as shown in eq 3a.

Surprisingly, there was a second photoproduct, the known (diphenylvinyl)cyclopropene 1, in the irradiation of the triphenylcyclopentadiene 12. Thus although formed in small amount, it was very clear that the (diphenylvinyl)cyclopropene 1 was generated in a reaction which is formally the reverse of the (diphenylvinyl)cyclopropene 1 photochemistry. This rearrangement is included in eq 3a.



(3a)



(3b)

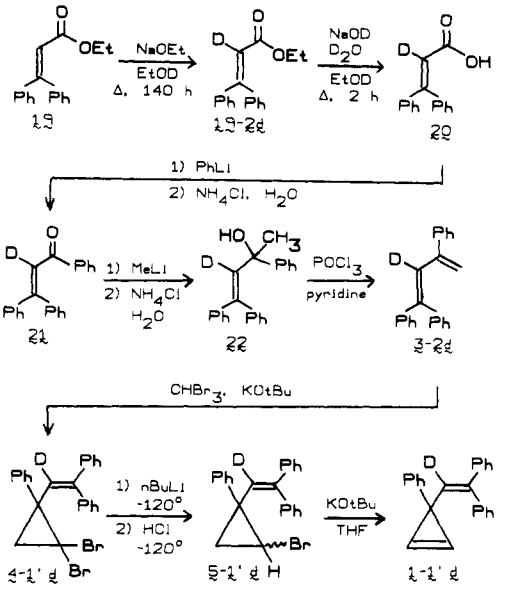
Finally, the sensitized irradiation of the triphenylcyclopentadiene 12 led exclusively to the phenyl-migrated cyclopentadiene isomer 16 as included in eq 3b.

Exploratory Photolysis of 3-Phenyl-3-(1′-phenylvinyl)cyclopropene. Turning to the styrylcyclopropene 2, we observed the irradiation to afford three photoproducts.

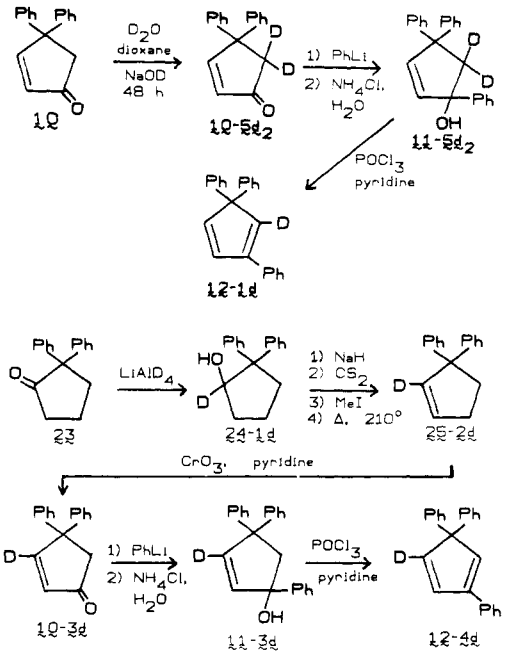
The major product proved to be 3-(1-phenylvinyl)indene (15) which had been synthesized as noted in Scheme I. Also formed was the known[10] 1,2-diphenylcyclopentadiene (17). A third product, 18, proved to be isomeric with styrylcyclopropene reactant 2. The infrared spectrum of 18, with a band at 1935 cm^{-1}, suggested the presence of an allenic moiety. Similarly, the ^1H NMR spectrum consisted of two absorptions in addition to the aryl signals. The first was a two-hydrogen singlet at δ 5.05 and the second was composed of two one-hydrogen peaks only weakly coupled and centered at δ 5.44. This suggested two $=CH_2$ groups.

(10) Rio, G.; Charifi, M. *Bull. Chim. Soc. Fr.* **1970**, 3585–3593.

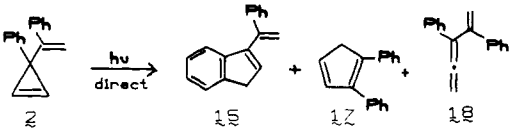
Scheme II. Synthesis of Deuterium-Labeled (Diphenylvinyl)cyclopropene



Scheme III. Synthesis of Labeled Cyclopentadienes



This led to assignment of 3,4-diphenyl-1,2,4-pentatriene (18) as the structure of the third photoproduct. This photochemistry is summarized in eq 4a.



(4a)

(4b)

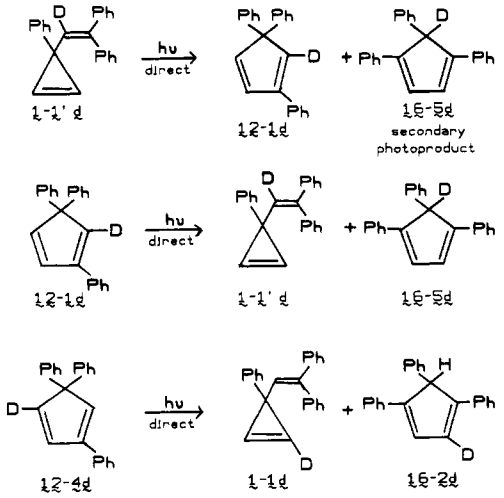
Interestingly, the sensitized irradiation of styrylcyclopropene 2 led exclusively to 1,2-diphenylcyclopentadiene (17; note eq 4b).

Synthesis of Deuterium-Labeled Reactants. For our studies the (diphenylvinyl)cyclopropene 1 labeled in the side chain was required. Scheme II summarizes the synthetic methods used.

Table I. Summary of Quantum Yield Determinations

reactant	sensitizer	photoproducts (quantum yields)
1	none	12 (0.17 ± 0.02), 13 (0.018 ± 0.002)
12	none	16 (0.097 ± 0.010), 1 (0.0038 ± 0.0004)
	4-(dimethylamino)benzophenone	16 (0.018 ± 0.004), 1 (0.0000)
2	none	15 (0.099 ± 0.010), 17 (0.095 ± 0.010), 18 (0.056 ± 0.012)
	xanthone	15 (0.000), 17 (0.018 ± 0.004), 18 (0.000)

Scheme IV. Photolysis of Deuterium Labeled Compounds



Also, we required the triphenylcyclopentadiene 12 labeled with deuterium at two sites, carbons 1 and 4. The approach to these compounds is outlined in Scheme III.

Photochemistry of Deuterium-Labeled Compounds. It was necessary to determine the fate of the deuterium label in the cyclopropene and cyclopentadiene rearrangements.

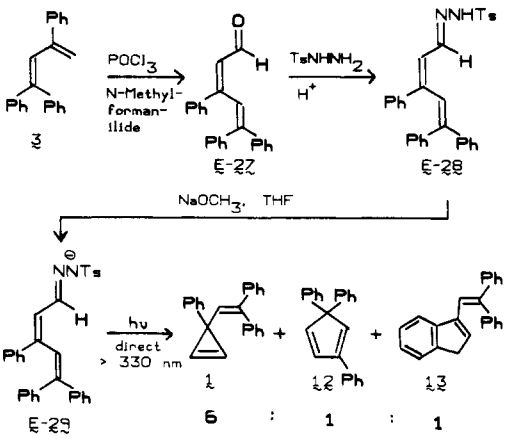
In the case of the labeled (diphenylvinyl)cyclopropene 1-*1'-d* (i.e., labeled at position 1') the photolysis led to deuterium located at C-1 in the triphenylcyclopentadiene product 12-*1*-*d*. The deuterium distribution was established by comparison of the photoproduct with the independently synthesized labeled compounds (vide supra). Additionally, the label in the minor amount of secondary product was found by ^1H NMR analysis to be at C-5. Finally, recovered diphenylvinyl cyclopropene 1-*1'-d* had the deuterium label unscrambled. Scheme IV depicts these rearrangement results.

In the case of photolysis of the C-1 and C-4 labeled triphenylcyclopentadienes 12-*1*-*d* and 12-*4*-*d* the product label distribution was determined similarly and was as indicated in Scheme IV.

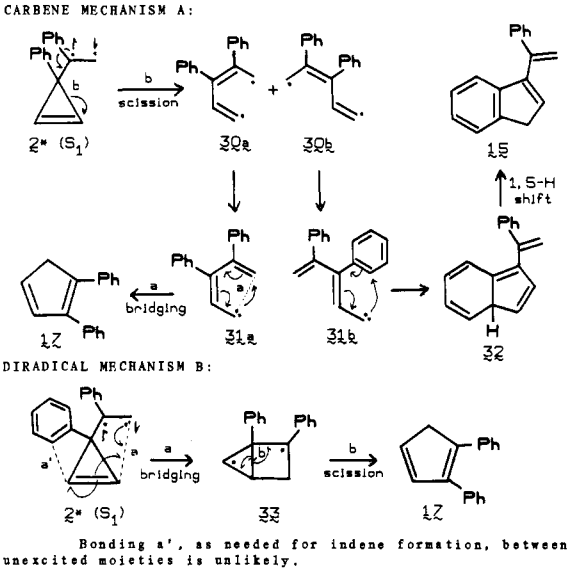
Independent Carbene Generation Studies. For comparison purposes it was of interest to investigate the behavior of the 3,5,5-triphenylpentadienyl carbene **26**. The tosylhydrazone precursor (i.e., (*E*)-**28**) was obtained as outlined in Scheme V, and the photochemical carbene generation is also described in this chart. Products anticipated from both the *E* and the *Z* isomers of **28** were observed. At this point it is relevant only to note that all of the photochemical reactants and primary products of our study in the diphenylvinyl system were encountered.

Quantum Yield Determinations. Quantum yield determinations were carried out as described in the Experimental Section. The variation of the observed efficiencies with the extent of conversion was appreciable in some of the direct irradiations. Hence, it was necessary to obtain efficiencies for a number of runs of varying conversions and extrapolate to zero reaction. In the case of sensitized runs where this dependence was smaller, several low-conversion runs were used. The final quantum yields obtained are summarized in Table I.

Scheme V. Synthesis of the Pentadienyl Carbene and Its Reactivity



Scheme VI. Two Alternative Mechanisms for Rearrangement of S_1 of the Styrylcyclopropene 2



Interpretative Discussion

Possible Mechanisms for Rearrangement of S_1 of the Styrylcyclopropene 2. A priori, one can consider both carbene and diradical mechanisms for the direct irradiation. Both have been considered in our earlier studies[3,4] and in the work of Padwa and co-workers.[6] The two mechanisms are outlined in Scheme VI for the present rearrangement.

The carbene mechanism (mechanism A) involves opening of the cyclopropene three-membered ring. This is understood in qualitative bond terms as depicted from S_1 in Scheme VI. Thus, it is seen that the carbene mechanism is not contingent on having excitation localized within the three-membered ring and its substituents. Also it is understood that the carbene mechanism may well be a "vinyl diradical-like" process, since the S_1 surface is initially followed, and this corresponds to incipient generation of

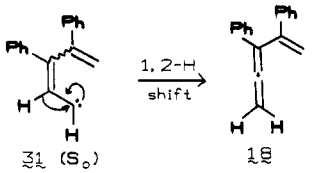
a vinyl diradical as in Scheme VI. It is likely but not certain that such a vinyl diradical (i.e., S_1 of the rearranging species) decays to the lower energy[11-13] S_0 carbene prior to complete rearrangement.

Also, it is seen that the carbene mechanism rationalizes the formation of both cyclopentadiene- and indene-type products (i.e., **17** and **15**) in Scheme VI.

For cyclopentadiene formation the alternative housane diradical mechanism differs only in the chronology of bond a formation and bond b scission. The carbene mechanism begins with bond b scission and follows with bond a formation, while the housane diradical mechanism has these reversed. As has been noted earlier,[4] gradations between these two extremes are not only possible but also likely.

However, in contrast to previous examples where electronic excitation was in the three-membered ring, the present molecule's rearrangement to afford indene product (i.e., **15**) is not readily explicable in terms of a housane diradical mechanism, since such a mechanism involves[3,4] bridging between an excited cyclopropene bond and the ortho position of the 3-phenyl group.

One strong piece of evidence for carbene intervention is the observation of 3,4-diphenyl-1,2,4-pentatriene (**18**) as one of the photoproducts. Thus, the rearrangement to the styrylallene **18** is characteristic of a ground-state (i.e., S_0) carbene such as **31** (note eq 5). Still, a mechanism with



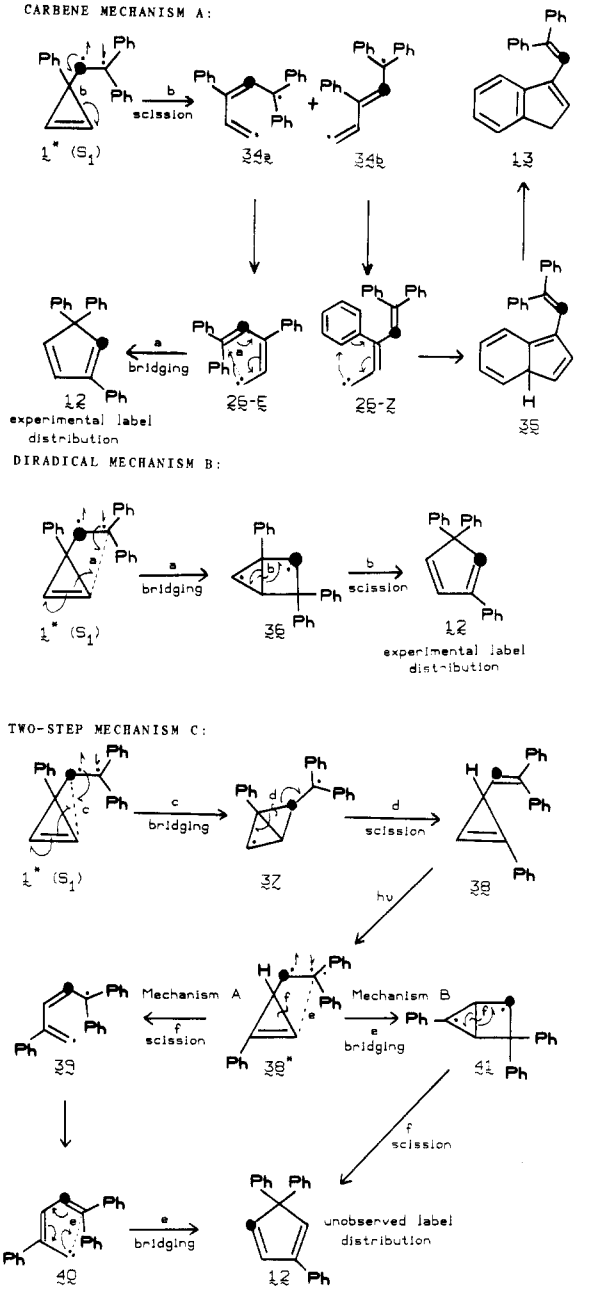
31 (S_0) 18 (5)

bonding characteristics between that of the two extreme possibilities could nevertheless afford some carbene which would then rearrange to allene **18**.

Mechanisms for the S_1 Photochemistry of the (Diphenylvinyl)cyclopropene 1. The carbene and housane diradical mechanisms are applied in Scheme VII to account for the photochemical rearrangement of the (diphenylvinyl)cyclopropene **1**. In Scheme VII the positions labeled with deuterium are indicated. It is seen that both the carbene and diradical pathways are consistent with the final label disposition in cyclopentadiene product. However, a third possibility (mechanism C) is not in accord with the observed labeling. This two-step mechanism involves a prior walk rearrangement[14] to afford 1-phenyl-3-(2,2-diphenylvinyl)cyclopropene (**38**) followed by a subsequent diradical or carbene pathway. Since the isomeric cyclopropene **38** has two strongly absorbing chromophores, the nonobservation of this isomer might, a priori, have arisen from a facile further reaction.

Hence the (diphenylvinyl)cyclopropene **1** rearrangement is primarily of value in demonstrating, again, that the chromophore external to the three-membered ring permits the usual rearrangement.

Scheme VII. Mechanisms for Rearrangement of S_1 Diphenylcyclopropene (• = D-Labeled Carbon)



Mechanism of S_1 Rearrangement of the Triphenylcyclopentadiene 12. For this rearrangement, two mechanisms which are somewhat similar to the cyclopropene processes are a priori possibilities. Note Scheme VIII. One involves scission of the 1,5 or 4,5 σ bond of the cyclopentadiene ring to afford a vinyl diradical or carbene. The other mechanism involves 1,3- or 2,4-bridging to afford the same housane diradical-type species considered in the cyclopropene reactions. The two mechanisms are outlined in Scheme VIII. It is seen that the bridging mechanism predicts a nonobserved deuterium distribution. Thus 1,3-bridging of the cyclopentadiene excited state would be anticipated to afford the more delocalized diradical **41**, arising from 1,3-bridging, rather than diradical **36** which derives from 2,4-bridging. However, as can be seen in Scheme VIII, only 2,4-bridging leads to the observed (diphenylvinyl)cyclopropene product **1**. 1,3-Bridging, which would be expected to be preferred, leads to 1-phenyl-3-(2,2-diphenylvinyl)cyclopropene (**38**) which was not encountered.

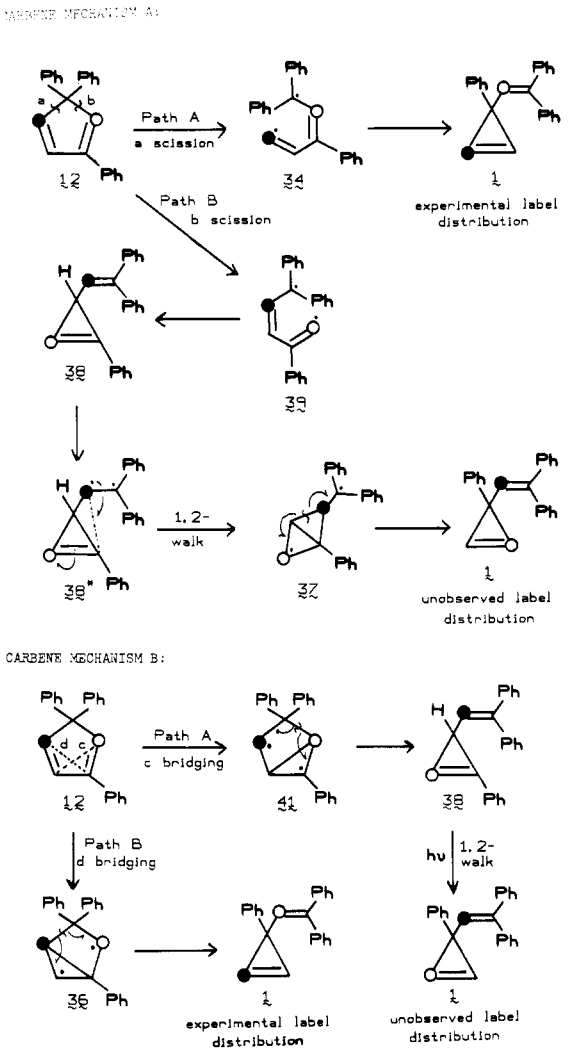
(11) Sevin, A.; Arnaud-Danon, L. *J. Org. Chem.* **1981**, *46*, 2346–2352. These authors have derived a correlation diagram in which S_0 leads to S_0 carbene with the usual two electrons in an sp^2 hybrid and two electrons in the π system. Similarly, S_1 cyclopropene leads to S_1 carbene with three electrons in the π system and one in the sp^2 orbital.

(12) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482–2491. Earlier calculations by these authors are qualitatively similar.

(13) Note also calculations by: Davis, J. H.; Goddard, W. A.; III; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427–2434. Here avoided crossings are not included despite apparent inclusion of CI and lack of symmetry in the cyclopropene to carbene rearrangement.

(14) Such walk rearrangements of vinylcyclopropenes have been previously encountered.[3,4]

Scheme VIII. Mechanisms for Rearrangement of S_1 of Triphenylcyclopentadiene 12 to Cyclopropene 1[a]



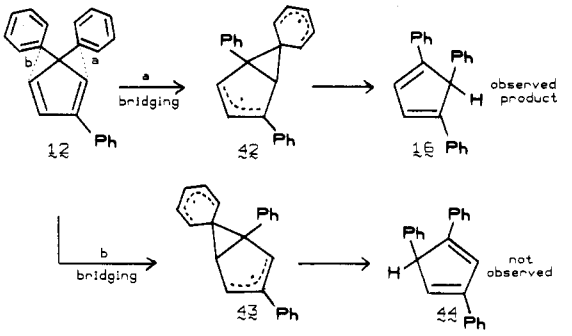
[a] • and ○ = D-labeled carbons arising from the 4-deuterio- and 1-deuteriocyclopentadiene isomers respectively.

One further possibility is that cyclopropene **38** had been formed and rapidly consumed in the 1,2-vinyl shift process (vide supra). However, as Scheme VIII reveals, the deuterium label resulting is different from that observed experimentally.

Turning to the carbene mechanism, we find the first interesting point in the regioselectivity required for this type process. Thus a preference for selective fission of bond 4,5 (i.e., process A) over bond 1,5 (process B) must be accounted for. To the extent that the initial fission affords a diradical-like species or a molecule in transition such as **34** and **39**, one can see that species **34** has five π electrons, a nonbonding MO, and extra delocalization due to positioning of a phenyl group at the center of a pentadienyl π moiety. This extra delocalization is lacking in the diradical counterpart **39**. The pathway predicted to be preferred (i.e., A) leads to the correct product with the experimentally encountered deuterium distribution. The alternative pathway B leads to the nonobserved cyclopropene product **38**. Again, the possibility exists that a 1,2-shift of this product might afford the observed cyclopropene **1**. However, as Scheme VIII reveals, an unobserved deuterium distribution would result.

Hence, we conclude that the rather novel cyclopentadiene fragmentation mechanism, affording a vinyl diradical (i.e., a carbene state), provides the pathway for

Scheme IX. Mechanism and Regioselectivity of the S_1 Triphenylcyclopentadiene Phenyl Migration



the cyclopentadiene to cyclopropene rearrangement.

The second rearrangement observed from S_1 of the triphenylcyclopentadiene **12** is a unique phenyl migration to afford the isomeric 1,4,5-triphenylcyclopentadiene (**16**). This has some analogy in the rearrangement of 1,1-diarylindenes to 1,2- and 2,3-diarylindenes studied by Griffin,[15] Wilson,[16] and McCullough,[17] a reaction observed to occur both on direct and sensitized irradiation.

Of particular interest is the regioselectivity of the triphenylcyclopentadiene rearrangement. A priori, the phenyl group might undergo a 1,2-shift in either direction as outlined in Scheme IX. That this is an S_1 rearrangement is justified below.

It is seen that the observed rearrangement involves formation of a phenyl-bridged diradical with extra delocalization effected by the phenyl group at carbon 2.

Another aspect of interest is that, in contrast to the indene examples, where the initial product of phenyl migration rearranges with aromatization, the triphenylcyclopentadiene rearrangement affords the primary product of the phenyl shift.

Behavior of the Styrylcyclopropene Triplet. There are several striking points to be noted in considering the triplet behavior of the styryl cyclopropene. The first is that the styrylallene **18** and the styrylindene **15**, observed in the direct irradiations, are no longer encountered. The allene, especially, was a product characteristic of a rearranging carbene (vide supra).

However, the same 1,2-diphenylcyclopentadiene (**17**) as was observed in the direct irradiation is formed, although with lower efficiency. This latter observation allows one to set limits on the amount of 1,2-cyclopentadiene (**17**) which arises from S_1 in the direct irradiation. Thus, the direct quantum yield of a reaction is given as in eq 6a or

$$\phi_{DIR} = {}^1\phi + (\phi_{ISC})({}^3\phi) \quad (6a)$$

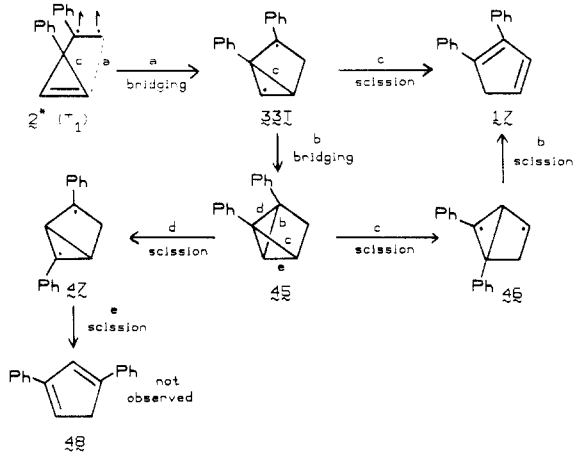
$${}^1\phi = \phi_{DIR} - (\phi_{ISC})({}^3\phi) \quad (6b)$$

$$\phi_{DIR} - {}^3\phi \leq {}^1\phi \leq \phi_{DIR} \quad (7)$$

in rearranged fashion as in eq 6b. With the recognition that ϕ_{isc} must be between 0 and 1.0, we arrive at eq 7 which sets limits on the amount of singlet reaction in cases where a sensitized irradiation affords a product with a lower quantum efficiency than in the corresponding direct

(15) Griffin, G.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2951–2958.
(16) Pettit, W. A.; Wilson, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 6372–6379.
(17) (a) McCullough, J. J. *Can. J. Chem.* **1968**, *46*, 43–47. (b) Kamal de Fonseka, K.; Manning, C.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 8257–8261. (c) McCullough, J. J.; McClory, M. R. *Ibid.* **1974**, *96*, 1962–1963.

Scheme X. Mechanism for Rearrangement of T_1 Styrylcyclopropene 2



photolysis. Equation 7 is of general utility for such cases.[18]

Thus, using the values from Table I and inserting these into eq 7, we establish that the singlet quantum efficiency, $^1\phi$, is between 0.077 and 0.095.

Another point which is particularly intriguing is the knowledge that triplet cyclopropenes seem generally not to rearrange to ring opened carbenes.[4,5] Yet one does observe the 1,2-diphenylcyclopentadiene (17) from the sensitized irradiation of styrylcyclopropene **2**. This signifies that another mechanism must be operating. This seems most likely to be the triplet counterpart of the singlet housane diradical mechanism B of Scheme VI. This is depicted in Scheme X. One might be tempted to argue that the mechanism for the triplet process affording a given photoproduct would be favored by the singlet as well in affording the same product. However, since the presence of the carbene seems certain in the direct irradiations, a more reasonable conclusion is that the singlet and triplet rearrangements afford the same 1,2-diphenylcyclopentadiene by different pathways. As noted above, the difference may well be just in gradations of bond formations and breakage and thus quantitative rather than qualitative.

A final point of real interest derives from the real possibility that the housane diradical **33T** in Scheme X has the a priori possibility of closing to give a tricyclic intermediate, **45**. Such a closure, of course, would require intersystem crossing to match spins. However, the resultant tricyclic molecule **45** seems much more likely to undergo fission of bond d than of bond c due to extra phenyl stabilization. Since bond d fission leads to the nonobserved 1,3-diphenylcyclopentadiene (48) while bond c fission leads to the 1,2-diphenylcyclopentadiene product (17), we can conclude that the triplet housane diradical **33T** does not close. This point is of importance, since for allyl cyclopropenes, such [2 + 2] cycloadditions have been observed.[5,6]

Sensitized Rearrangement of 2,5,5-Triphenylcyclopentadiene (12). The first point to be made is that the same gross mechanism as presented in Scheme IX for the S_1 rearrangement applies for the presently discussed T_1 reaction.

The second point is that we were indeed justified in assuming (vide supra) that the direct irradiation process primarily occurred via the excited singlet. Thus, we can again apply the bracketing reasoning derived from eq 7. This rule states that where the same product results from direct and sensitized irradiations, but in lower quantum yield from the sensitized runs, the lower limit for $^1\phi$ is given by the difference $\phi_{DIR} - {}^3\phi$ and the upper limit by the direct irradiation quantum yield ϕ_{DIR}. This places $^1\phi$ between 0.079 and 0.097.

Significance of the Independent Carbene Generation. The main significance of these experiments is that they demonstrate that all the (diphenylvinyl)cyclopropene photolysis products, the triphenylcyclopentadiene **12** and the (diphenylvinyl)indene **13**, are formed. Additionally, one finds the (diphenylvinyl)cyclopropene 1 as the major product. The ratio of cyclopentadiene **12** to indene **13** differs in the cyclopropene and carbene experiments, but this seems due to the possibility for formation of two stereoisomeric carbenes, (*E*)-**26** and (*Z*)-**26**. The former is capable of proceeding onward to form cyclopentadiene **12** while the latter has proximate phenyl and carbene centers and can lead to indene **13**. The predominance of cyclopropene product 1 most likely derives from an entropy effect in which 1,3-related centers have a high probability of bonding due to their proximity and lack of requisite special conformations.

Conclusion. It is seen that the photochemistry of cyclopropenes is not contingent upon the excited chromophore residing in the three-membered ring but that similar reactivity arises with an external chromophore. The photochemistry of the singlets seems most likely to arise either from a carbene or from a species which is a composite of a bridged diradical and the excited carbene. The triplet photochemistry is understood best on the basis of $\pi-\pi$ bridging to afford diradical species which then react in chemically reasonable ways.

Experimental Section[19]

Purification of Solvents. Tetrahydrofuran (Fisher, histological grade) was stored over solid potassium hydroxide and then distilled successively from calcium hydride, lithium aluminum hydride, and benzophenone ketyl. Benzene used in photolysis experiments was washed with concentrated sulfuric acid, 5% aqueous acidic potassium permanganate, water, 10% aqueous sodium hydroxide, water, and brine, dried over anhydrous magnesium sulfate, and distilled from calcium hydride under a nitrogen atmosphere. Cyclohexane and pentane for photolysis experiments were washed with a 1:1 mixture of concentrated sulfuric and nitric acids, water, 10% sodium hydroxide, saturated sodium bicarbonate, water and brine, dried over anhydrous calcium chloride, and distilled from calcium hydride under a nitrogen atmosphere.

General Experimental Procedures. All reactions were run under an atmosphere of dry nitrogen. Standard workup A involved dilution with water, ether extraction, and washing of the extracts with water, saturated sodium bicarbonate, and brine, followed by drying and concentration in vacuo. Workup B omitted the bicarbonate wash.

(18) This useful expression has been termed "the singlet bracketing rule" in our laboratories. A "generalized bracketing rule"[5] is given by: $\phi_{X\text{-}DIR} - (\phi_{Y\text{-}DIR})({}^3\phi_X)/{}^3\phi_Y \leq {}^1\phi_X \leq \phi_{X\text{-}DIR}$. This sets the limits on the singlet quantum yield for product X when a second product, Y, is formed with a lower $\phi_{DIR}/{}^3\phi$. A corollary is that the amount of product X formed in the direct irradiation from the triplet is given by $0 \leq {}^3\phi_{X\text{-}DIR} \leq (\phi_{Y\text{-}DIR})({}^3\phi_X)/{}^3\phi_Y$.

(19) Melting points were determined by using a calibrated hot-stage apparatus. Mass spectra were obtained by using an AEI MS-902 mass spectrometer at 70 eV. ^{1}H NMR spectra were obtained by using a JEOL MH-100 or a Bruker WH-270 spectrometer. ^{13}C NMR spectra were obtained by using a JEOL FX-60 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

HPLC was performed on a Waters ALC-100 liquid chromatograph employing a LDC 254-nm UV detector and polished stainless-steel columns. Column chromatography was performed on silica gel (Matheson Colemand and Bell, grade 62, 60–200 mesh) packing mixed with Sylvania 2282 phosphor and slurry packed into quartz columns with monitoring with a UV lamp. Preparative TLC was carried out by using MN-Kieselgel G/UV-254 silica gel (Machery Nagel and Co.).

1,1-Dibromo-2-phenyl-(2,2-diphenylvinyl)cyclopropane. By use of a modification of the general method of Yakuskina and Bolesov,[20] 17 mL (49 g, 0.19 mol) of bromoform was added dropwise to a stirred slurry of 30 g (0.11 mol) of 1,1,3-triphenylbutadiene[21] and 21 g (0.19 mol) of potassium *tert*-butoxide in 150 mL of dry hexane at 0 °C. The dark slurry was stirred for 15 h and poured onto ice. Workup B gave 20.8 g (43%) of a tan solid, mp 126–129 °C. The solid was dissolved in 200 mL of 50% benzene in hexane and decolorized by filtration through a 3.5 × 25 cm column of alumina packed in hexane. Elution with 500 mL of 5% benzene in hexane and 250 mL of hexane followed by concentration of the combined eluents in vacuo gave 18.3 g (38%) of a colorless solid, mp 130–131 °C. Recrystallization from hexane gave 16.7 g (35%) of the dibromocyclopropane as colorless needles, mp 130–131 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.20–7.40 (m, 13 H, arom), 6.96–7.08 (m, 2 H, arom), 6.64 (s, 1 H, vinyl), 2.09 (d, J = 8 Hz, 1 H, CH_2), 1.50 (d, J = 8 Hz, 1 H, CH_2); IR (KBr) 3084, 3060, 3030, 1600, 1492, 1448, 1418, 1360, 1075, 1069, 1032, 1004, 995, 948, 916, 883, 869, 782, 763, 737, 715, 695 cm^{-1}; MS m/e 451.9780 (calcd for $C_{23}H_{18}Br_2$ m/e 451.9775).

Anal. Calcd for $C_{23}H_{18}Br_2$: C, 60.82; H, 3.99. Found: C, 60.95; H, 4.03.

1-Bromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane. A modification of the general method of Seyferth and co-workers[22] was used. In each of four runs, a solution of 3.0 g (6.6 mmol) of 1,1-dibromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane in 40 mL of tetrahydrofuran was cooled to −120 °C [pentane, acetone, 2-propanol (4:1:1)/liquid N_2],[23] and 4.5 mL (6.7 mmol) of a 1.5 M solution of *n*-butyllithium in hexane was added dropwise. The solution was stirred for 1 min at −120 °C, and 1.0 mL of concentrated hydrochloric acid was added dropwise. The cold bath was removed and 10 mL of water was added after 2 min. The stirred mixture was warmed slowly to room temperature. The workup of the combined reaction mixture from the four runs following method A afforded 10.5 g of a yellow oil. Crystallization from dichloromethane in hexane gave 2.65 g (27%) of primarily one epimer of the bromocyclopropanes as colorless crystals, mp 105–117 °C. Concentration of the mother liquors and recrystallization gave an additional 5.0 g (50%) of primarily the other epimer, mp 87–90 °C.

Further recrystallization of the first crop from dichloromethane in hexane gave 1.93 g (19%) of pure epimer A, mp 134–136 °C. Recrystallization of the second crop from hexane gave 3.62 g (36%) of pure epimer B, mp 92–94 °C.

The spectral data for epimer A were as follows: NMR ($CDCl_3$) δ 7.3–6.9 (m, 15 H, arom), 6.44 (s, 1 H, vinyl), 3.16 (dd, J = 8, 6 Hz, 1 H, CH), 1.64 (t, J = 8 Hz, 1 H, CH_2), 0.96 (dd, J = 8, 6 Hz, 1 H, CH_2); IR (KBr) 3080, 3060, 3035, 1600, 1498, 1491, 1450, 1446, 1292, 1221, 1078, 1042, 1030, 1015, 925, 902, 880, 858, 780, 770, 755, 735, 720, 698 cm^{-1}; MS (no parent at low eV) m/e 295.1493 [$(M - Br)^+$] (calcd for $C_{23}H_{19}^+$ m/e 295.1487).

The spectral data for epimer B were as follows: NMR ($CDCl_3$) δ 7.28–6.92 (m, 15 H, arom), 3.10 (dd, J = 8, 5 Hz, 1 H, CH), 1.44 (br t, J = 5 Hz, 1 H, CH_2), 1.24 (t, J = 8 Hz, 1 H, CH_2); IR (thin film) 3082, 3060, 3030, 1600, 1495, 1444, 1270, 1200, 1072, 1050, 1029, 925, 865, 775, 768, 758, 728, 698 cm^{-1}; MS m/e 374.0658 (calcd for $C_{23}H_{19}Br$ m/e 374.0670).

3-Phenyl-3-(2,2-diphenylvinyl)cyclopropene. A mixture of 1.07 g (2.85 mmol) of 1-bromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane and 1.3 g (11.6 mmol) of potassium *tert*-butoxide in 35 mL of tetrahydrofuran was stirred for 20 h at room temperature. Workup B afforded 900 mg of an orange oil. Chromatography on a 2.5 × 40 cm silica gel column packed in and eluted with hexane in 150-mL fractions gave, in fractions 3–6, 437 mg (52%) of the cyclopropene as a colorless solid, pure by NMR, mp 107–116 °C dec. Recrystallization from cold hexane gave 323 mg (38%) of colorless needles, mp 112–119 °C dec. Further recrystallization from cold benzene in hexane gave 216 mg (20%) of analytically pure cyclopropene, mp 117–119 °C dec. The spectral data were as follows: NMR ($CDCl_3$) δ 7.20 (m, 15 H, arom), 6.66 (s, 1 H, vinyl), 6.42 (s, 2 H, cyclopropenyl); IR ($CHCl_3$) 3070, 3050, 2995, 1638, 1598, 1490, 1443, 1358, 1190, 1140, 1110, 1078, 1060, 1032, 988, 950, 925, 870 cm^{-1}; UV (EtOH) λ_{max} 227 nm (ε 19000), 260 (14000); MS m/e 294.1412 (calcd for $C_{23}H_{18}$ m/e 294.1409).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.74; H, 6.20.

In this run a mixture of bromocyclopropane epimers was used. However, in separate runs the two separate epimeric bromides were found to afford the same product under the above conditions.

1,1-Dibromo-2-phenyl-2-(1-phenylvinyl)cyclopropane. A modification of the general procedure of Yakuskina and Bolesov[20] was used. To a mechanically stirred solution of 9.0 g (44 mmol) of 2,3-diphenyl-1,3-butadiene[24] in 100 mL of dry hexane at 0 °C was added 8.2 g (73 mmol) of potassium *tert*-butoxide. To the cold suspension was then added dropwise a solution of 6 mL (17.3 g, 68 mmol) of bromoform in 20 mL of hexane. When the addition was complete, the tan slurry was stirred for 1 h at 0 °C, warmed to room temperature, stirred for 14 h, and poured onto ice. Workup B afforded 19 g of an oily brown solid. Trituration with cold hexane and filtration gave 12 g (71%) of a tan solid (mp 118–121 °C) which was dissolved in 100 mL of benzene and decolorized by filtration through a 4 × 14 cm alumina column packed in 10% benzene in hexane. Elution with an additional 500 mL of 10% benzene in hexane and concentration of the combined eluents gave 11 g of a pale tan solid which was recrystallized from 10% benzene in hexane to afford 10.0 g (59%) of 1,1-dibromo-2-phenyl-2-(1-phenylvinyl)cyclopropane as colorless needles, mp 123–124 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.20–7.50 (m, 10 H, arom), 5.62 (s, 2 H, vinyl), 2.35 (ν_a of AB q, J = 8 Hz, 1 H, CH_2), 2.16 (ν_b of AB q, J = 8 Hz, 1 H, CH_2); IR ($CHCl_3$) 3090, 3060, 3010, 1628, 1608, 1580, 1500, 1450, 1432, 1325, 1312, 1115, 1090, 1072, 1025, 1010, 985, 922 cm^{-1}; MS m/e 375.9468 (calcd for $C_{17}H_{14}Br_2$ m/e 375.9462).

Anal. Calcd for $C_{17}H_{14}Br_2$: C, 54.00; H, 3.73. Found: C, 54.23; H, 3.69.

1-Bromo-2-phenyl-2-(1-phenylvinyl)cyclopropane. A modification of the general method of Sydnes[25] was used. To a solution of 10 g (26 mmol) of 1,1-dibromo-2-phenyl-2-(1-phenylvinyl)cyclopropane in 55 mL of tetrahydrofuran at 0 °C was added dropwise 7.6 mL (8.36 g, 29 mmol) of tri-*n*-butylstannane.[26] After being stirred for 2 h at 0 °C, the solution was warmed to room temperature and stirred for 42 h, followed by addition of 200 mL of 20% potassium fluoride. The resultant slurry was stirred for 2 h and filtered, and the filtrate was ether extracted. The extract was dried and concentrated in vacuo to afford 12.4 g of an oily yellow solid which was chromatographed on a 4 × 100 cm silica gel column packed in hexane. Elution with hexane in 150-mL fractions gave the following: fractions 15–18, 1.36 g (16%), colorless oil, identified by NMR as a mixture of the epimeric 1-bromocyclopropanes contaminated with ca. 5% of the starting dibromide; fractions 19–31, 4.65 g (60%), colorless oil, a mixture of the epimeric 1-bromocyclopropanes.

The spectra data for the epimeric mixture of 1-bromo-2-phenyl-2-(1-phenylvinyl)cyclopropanes were as follows: NMR ($CDCl_3$) δ 7.18–7.64 (m, 10 H, arom), 5.96 (s, 0.4 H, vinyl), 5.61 (s, 0.6 H, vinyl), 5.55 (s, 0.4 H, vinyl), 5.46 (s, 0.6 H, vinyl), 3.83 (t, J = 6 Hz, 0.4 H, CH), 3.66 (dd, J = 8, 4 Hz, 0.6 H, CH), 1.58–1.90 (m, 2 H, CH_2); IR (thin film) 3085, 3060, 3030, 1625, 1605, 1582, 1500, 1450, 1430, 1330, 1312, 1255, 1182, 1053, 1037, 918, 788, 763, 718, 708 cm^{-1}; MS m/e 298.0360 (calcd for $C_{17}H_{15}Br$ m/e 298.0357).

Anal. Calcd for $C_{17}H_{15}Br$: C, 68.24; H, 5.05. Found: C, 68.20; H, 5.26.

3-Phenyl-3-(1-phenylvinyl)cyclopropene. A mixture of 3.0 g (10 mmol) of epimeric 1-bromo-2-phenyl-2-(1-phenylvinyl)-cyclopropanes and 4.4 g (39 mmol) of potassium *tert*-butoxide

(20) (a) Yakuskina, N. I.; Bolesov, I. G. *J. Org. Chem.* USSR (*Engl. Transl.*) **1979**, *15*, 853–859. (b) Bovin, N. J.; Surimina, L. S.; Yakuskina, N. I.; Bolesov, I. G. *Ibid.* **1977**, *13*, 1749–1755.
(21) Freeman, J. P. *J. Org. Chem.* **1957**, *22*, 1608–1611.
(22) Seyferth, D.; Lambert, R. J., Jr.; Massol, M. J. *J. Organomet. Chem.* **1975**, *88*, 255–286.
(23) Neuman, H.; Seebach, D. *Tetrahedron Lett.* **1976**, 4839–4842.
(24) Dodson, R. M.; Srinivasan, V.; Sharma, K. S.; Sauers, R. F. *J. Org. Chem.* **1972**, *37*, 2367–2372.
(25) Sydnes, L. K. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 47–55.
(26) Van der Kerk, G. J. M.; Moltes, J. G.; Luitjan, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

in 125 mL of tetrahydrofuran was stirred for 2 h at 0 °C and 14 h at room temperature. Workup B afforded 2.5 g of a brown oil. Chromatography on a 2.5 × 90 cm silica gel column packed in and eluted with hexane in 150-mL fractions gave, in fractions 4–9, 1.78 g (81%) of the cyclopropene as a colorless oil, pure by NMR. Crystallization from methanol at −20 °C gave 1.22 g (56%) of colorless crystals, mp 32–34 °C. Recrystallization from cold methanol–ether gave 1.04 g (48%) of product, mp 34–36 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.7–7.1 (m, 10 H, arom), 7.44 (s, 2 H, cyclopropenyl), 5.68 (s, 1 H, vinyl), 5.30 (s, 1 H, vinyl); IR (thin film) 3090, 3075, 3050, 3020, 1642, 1620, 1602, 1585, 1495, 1443, 1078, 1032, 1000, 978, 904, 800, 785, 760, 705, 662, 618 cm^{-1}; UV (EtOH) λ_{max} 241 nm (ε 12 500), λ_{sh} 289 (1140); MS *m/e* 218.1095 (calcd for $C_{17}H_{14}$ *m/e* 218.1092).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.43; H, 6.45.

1,4,4-Triphenylcyclopent-2-en-1-ol. To an ice-cooled solution of 1.8 g (7.7 mmol) of 4,4-diphenylcyclopent-2-en-1-one[27] in 40 mL of anhydrous ether was added dropwise 10.2 mL (12.2 mmol) of a 1.2 M phenyllithium solution in ether. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature, refluxed for 2 h, cooled, and quenched by dropwise addition of 1.2 mL of saturated ammonium chloride. Workup B gave 2.4 g of a yellow oil. Chromatography on a 2.5 × 30 cm silica gel column, packed in 5% ether in hexane and eluted with 5–10% ether in hexane in 200-mL fractions, gave, in fractions 4–6, 1.89 g (79%) of the triphenylcyclopentenol as a nearly colorless oil containing ca. 5% of the starting enone by NMR. In general, the cyclopentenol was used without further purification.

In one run, a portion of the crude alcohol was retreated twice with fresh phenyllithium and worked up as above to afford analytically pure cyclopentenol as a nearly colorless oil. The spectral data were as follows: NMR ($CDCl_3$) δ 7.5–7.0 (m, 15 H, arom), 6.54 (d, *J* = 6 Hz, 1 H, vinyl), 6.02 (d, *J* = 6 Hz, 1 H, vinyl), 3.13, 2.80 (ν_a, ν_b of AB q, J_{ab} = 14.5 Hz, 2 H, CH_2), 2.0 (br s, 1 H, OH); IR (thin film) 3545, 3410, 3080, 3050, 3020, 2970, 1598, 1578, 1492, 1448, 1346, 1335, 1235, 1190, 1160, 1100, 1068, 1045, 1028, 1002, 988, 922, 840 cm^{-1}; MS *m/e* 312.1505 (calcd for $C_{23}H_{23}O$ *m/e* 312.1349).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.57; H, 6.38.

2,5,5-Triphenylcyclopentadiene. To an ice-cooled solution of 3.5 g (11 mmol) of 1,4,4-triphenylcyclopent-2-en-1-ol in 100 mL of pyridine was added dropwise 4.5 mL of phosphorus oxychloride. After being stirred for 15 min at 0 °C, the mixture was heated at 60–70 °C for 2.5 h, cooled, and poured into ice–water. The crude product was diluted with water and ether extracted. The extracts were washed with 10% hydrochloric acid, water, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 2.75 g of a brown oil. Chromatography on a 4 × 30 cm silica gel column packed in and eluted with hexane in 100-mL fractions gave, in fractions 6–8, 1..3 g (60%) of the triphenylcyclopentadiene as a colorless solid, mp 96–97 °C. Recrystallization from dichloromethane in methanol gave 1.64 g (51%) of colorless crystals, mp 96–97.5 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.64 (m, 2 H, arom), 7.24 (m, 13 H, arom), 7.05 (t, *J* = 1.6 Hz, 1 H, vinyl), 6.96 (dd, *J* = 5 Hz, 1.8 Hz, 1 H, vinyl), 6.82 (dd, *J* = 5, 1.5 Hz, 1 H, vinyl); IR ($CHCl_3$) 3070, 3015, 1605, 1580, 1495, 1450, 1362, 1190, 1150, 1115, 1080, 1040, 940, 910, 875, 825 cm^{-1}; UV (EtOH) λ_{max} 232 nm (ε 26 000), 268 (5100), 286 (6000); MS *m/e* 294.1414 (calcd for $C_{23}H_{18}$ *m/e* 294.1408).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.94; H, 6.18.

3-(2,2-Diphenylvinyl)indene. To a refluxing solution of (2,2-diphenylvinyl)magnesium bromide,[28] prepared from 830 mg (34 mmol) of magnesium turnings and 9.0 g (35 mmol) of 1-bromo-2,2-diphenylethylene[29] in 25 mL of tetrahydrofuran, was added dropwise a solution of 3.0 g (23 mmol) of 1-indanone[30] in 25 mL of tetrahydrofuran. The mixture was refluxed for 2 h, cooled, and poured into 100 mL of concentrated hydrochloric acid and ice. Workup A afforded a yellow oil which partially crystallized on standing. Trituration with hexane and filtration gave 3.86 g (57%) of a slightly yellow solid, mp 78–80 °C. Further recrystallization of 1.8 g of the above from methanol afforded 1.7 g of analytically pure indene as colorless needles, mp 84–85 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.3 (m, 14 H, arom), 6.96 (m, 1 H, vinyl), 5.72 (m, 1 H, vinyl), 3.20 (m, 2 H, CH_2); IR ($CHCl_3$) 3060, 3002, 2880, 1610, 1500, 1465, 1452, 1400, 1218, 1085, 1040, 1030, 980, 950, 925, 890 cm^{-1}; UV (EtOH) λ_{max} 254 nm (ε 33 500), 307 (10 700); MS *m/e* 294.1412 (calcd for $C_{23}H_{18}$ *m/e* 294.1408).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.75; H, 6.20.

1,2-Diphenyl-1,3-cyclopentadiene. By use of procedure of Rio and Charifi,[10] 4-chloro-3,4-diphenylcyclopent-2-en-1-one[31] was reduced with lithium aluminum hydride to afford the cyclopentadiene in 2.5% yield (lit.[10] 15% maximum) after chromatography as a colorless oil which crystallized on standing at −20 °C, mp 70–72 °C (lit.[10] mp 72–74 °C).

3-(1-Phenylvinyl)indene. To a solution of 1-styrylmagnesium bromide,[28] prepared from 5 g (27 mmol) of 1-bromostyrene[32] and 0.68 g (28 mmol) of magnesium turnings in 10 mL of tetrahydrofuran, was added dropwise a solution of 2.64 g (20 mmol) of 1-indanone[30] in 15 mL of tetrahydrofuran. The mixture was refluxed for 3 h, cooled, poured into 25 mL of concentrated hydrochloric acid and ice, and stirred for 0.5 h. Workup A afforded an oily brown solid which was triturated with hexane and filtered to afford 2.52 g of a brown solid. Recrystallization from methanol gave 1.8 g (42%) of tan crystals, mp 76–79 °C. Further recrystallization gave 1.3 g (30%) of colorless needles, mp 81–82 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.5–7.0 (m, 9 H, arom), 6.44 (m, 1 H, vinyl), 5.56 (br s, 1 H, styryl), 5.49 (br s, 1 H, styryl), 3.44 (br s, 2 H, CH_2); IR ($CHCl_3$) 3070, 3005, 2885, 1620, 1608, 1575, 1498, 1463, 1449, 1400, 1285, 1278, 1220, 1080, 1032, 1020, 972, 912 cm^{-1}; UV (EtOH) λ_{max} 245 nm (ε 17 600); MS *m/e* 218.1093 (calcd for $C_{17}H_{14}$ *m/e* 218.1096).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.49; H, 6.53.

Ethyl 2-Deuterio-3,3-diphenyl-2-propenoate. A modification of the procedure of Hauser and co-workers[33] was used. To a solution of sodium ethoxide in ethanol-*d*, prepared from 1.9 g (0.083 mol) of sodium and 125 mL (100 g, 2.12 mol) of ethanol-*d*,[34] was added 60 g (0.24 mol) of ethyl 3,3-diphenyl-2-propenoate.[35] The mixture was refluxed for 70 h. The ethanol was removed by distillation under reduced pressure and replaced with 140 mL (112 g, 2.38 mol) of fresh ethanol-*d*. After the mixture was refluxed for an additional 70 h, the solvent was removed in vacuo, and the residue was poured into cold water and acidified with 10% hydrochloric acid. Workup A afforded 56 g (93%) of a yellow liquid. Distillation in vacuo gave 48 g (80%) of a colorless liquid, bp 150–160 °C (2–4 mm) [lit.[33] bp 146–148 °C (1.1 mm)]. Analysis by NMR integration using standard additions of ethyl 3,3-diphenylpropenoate indicated 99.8% deuterium incorporation at the α-position of the unsaturated ester. The spectral data were as follows: NMR ($CDCl_3$) δ 7.5–7.2 (m, 10 H, arom), 6.40 (s, <0.005 H, residual vinyl H), 4.06 (q, *J* = 7 Hz, 2 H, CH_2), 1.08 (t, *J* = 7 Hz, 3 H, CH_3); IR (thin film) 3055, 3020, 2980, 1725, 1710, 1694, 1618, 1600, 1578, 1498, 1450, 1372, 1330, 1305, 1242, 1160, 1052, 1035, 780, 738, 708 cm^{-1}; MS *m/e* 253.1231 (calcd for $C_{17}H_{15}O_2D$ *m/e* 253.1209).

2-Deuterio-3,3-diphenyl-2-propenoic Acid. To a solution of sodium deuteroxide in deuterium oxide and ethanol-*d*, prepared from 70 mL (56.5 g, 1.2 mol) of ethanol-*d*,[34] 8 g (0.35 mol) of sodium, and 30 mL (33 g, 1.6 mol) of deuterium oxide, was added 23 g (0.091 mol) of ethyl 2-deuterio-3,3-diphenyl-2-propenoate. The mixture was refluxed for 2 h, cooled, stirred for 10 h at room

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temperature, poured into ice–water, acidified with 10% hydrochloric acid, and ether extracted. The extracts were dried and concentrated in vacuo to afford 20 g of a yellow solid (mp 158–160 °C) which was recrystallized from ethanol to afford 17.2 g (84%) of the α-deuterated acid as colorless needles, mp 161–162 °C [lit.[36] mp (for the undeuterated acid) 162 °C]. The spectral data were as follows: NMR ($CDCl_3$) δ 9.90 (br s, 1 H, CO_2H), 7.48–7.12 (m, 10 H, arom), 6.32 (s, <0.005 H, residual vinyl); IR ($CHCl_3$) 3500–2400 (br, CO_2H), 1685, 1610, 1598, 1575, 1495, 1450, 1425, 1328, 1275, 1220, 1172, 1132, 1080, 1048, 1038, 1026, 935, 882, 868 cm^{-1}; MS *m/e* 225.0901 (calcd for $C_{15}H_{11}O_2D$ *m/e* 225.0897).

2-Deuterio-1,3,3-triphenylprop-2-en-1-one. To a solution of 17 g (0.075 mol) of 2-deuterio-3,3-diphenyl-2-propenoic acid in 500 mL of anhydrous ether at 0 °C was added dropwise 150 mL (0.181 mol) of a 1.21 M solution of phenyllithium in ether. The solution was warmed to room temperature, stirred 2 h, and transferred via cannula to a rapidly stirred solution of ammonium chloride in ice–water. Workup A afforded 23 g of a dark oil which was chromatographed on a 4 × 70 cm silica gel column packed in 2% ether in hexane. Elution with 2–10% ether in hexane in 250-mL fractions gave the following: fractions 3–6 (2% ether), 1.8 g, biphenyl; fractions 7–11 (4% ether), 1.46 g, 2-deuterio-1,1,3,3-tetraphenylprop-2-en-1-ol; fractions 12 and 13 (10% ether), 1.6 g, overlap; fractions 14–20 (10% ether), 15.5 g, 2-deuterio-1,3,3-triphenylprop-2-en-1-one.

Fractions 14–20 were concentrated and dried in vacuo to afford 15.5 g (72%) of the α-deuterio enone as a pale yellow solid, mp 83–85 °C. Recrystallization from dichloromethane in hexane gave 11.2 (52%) of nearly colorless crystals, mp 84–85 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.94 (dd, *J* = 8 Hz, 2 Hz, arom), 7.43 (m, 8 H) arom), 7.24 (m, 5 H, arom); IR ($CHCl_3$) 3050, 2995, 1652, 1598, 1578, 1560, 1490, 1448, 1325, 1295, 1260, 1172, 1078, 1065, 1025, 1002, 968 cm^{-1}; MS *m/e* 285.1247 (calcd for $C_{21}H_{15}OD$ *m/e* 285.1260).

2-Deuterio-3-hydroxy-1,1,3-triphenyl-1-butene. To a solution of 9.8 g (34 mmol) of 2-deuterio-1,3,3-triphenylprop-2-en-1-one in 400 mL of anhydrous ether was added dropwise 45 mL (41 mmol) of a 0.92 M solution of methyllithium in ether. The mixture was stirred for 2 h and quenched by dropwise addition of 4.5 mL of saturated ammonium chloride. Workup B afforded 10.3 g (99%) of the alcohol as a yellow oil, pure by NMR. The spectra data were as follows: NMR ($CDCl_3$) δ 7.50–7.18 (m, 13 H, arom), 7.02 (m, 2 H, arom), 6.60 (s, <0.01 H, residual vinyl), 2.10 (s, 1 H, OH), 1.60 (s, 3 H, CH_3); IR (thin film) 3560, 3440, 3070, 3045, 3015, 2985, 2915, 2855, 1598, 1575, 1492, 1445, 1370, 1325, 1295, 1180, 1168, 1158, 1110, 1095, 1075, 1030, 1018, 918, 785, 768, 725, 700, cm^{-1}; MS *m/e* 301.1578 (calcd for $C_{22}H_{19}OD$ *m/e* 301.1572).

2-Deuterio-1,1,3-triphenyl-1,3-butadiene. To a solution of 10.3 g (34 mmol) of 2-deuterio-3-hydroxy-1,1,3-triphenyl-1-butene in 90 mL of pyridine at 0 °C was added dropwise 16 mL (26 g, 172 mmol) of phosphorus oxychloride. After 15 min the solution was warmed to 50 °C, stirred for 2.5 h, cooled, poured onto ice, diluted with water, and ether extracted. The extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 11 g of an amber oil. Chromatography on a 3.5 × 40 cm silica gel column packed in hexane and eluted with hexane and 0.5% ether in hexane in 200-mL fractions gave, in fractions 3–5, 8.05 g (82%) of the diene as a colorless oil, pure by NMR. The spectral data were as follows: NMR ($CDCl_3$) δ 7.4–6.9 (m, 15 H, arom), 5.30 (s, 1 H, vinyl), 4.95 (s, 1 H, vinyl); IR (thin film) 3075, 3050, 3020, 2950, 2920, 1600, 1572, 1495, 1445, 1325, 1080, 1030, 1020, 910, 895, 795, 780, 772, 748, 705 cm^{-1}; MS *m/e* 283.1471 (calcd for $C_{22}H_{17}D$ *m/e* 283.1467).

1,1-Dibromo-2-phenyl-2-(1-deuterio-2,2-diphenylvinyl)-cyclopropane. To a mechanically stirred slurry of 8.0 g (28 mmol) of 2-deuterio-1,1,3-triphenyl-1,3-butadiene and 6.0 g (53 mmol) of potassium *tert*-butoxide in 10 mL of hexane at 0 °C was added slowly dropwise a solution of 4.8 mL (13.9 g, 55 mmol) of bromoform in 3 mL of hexane. The mixture was stirred for 1 h at 0 °C then 48 h at room temperature. Workup B afforded 14 g of a tan solid, mp 124–132 °C. Recrystallization from hexane gave 9.32 g (73%) of the dibromocyclopropane as light tan needles, mp 130–132 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.20 (m, 13 H, arom), 6.94 (m, 2 H, arom), 6.60 (s, <0.01 H, residual vinyl), 2.04 (d, *J* = 8 Hz, 1 H, CH_2), 1.48 (d, *J* = 8 Hz, 1 H, CH_2); IR ($CHCl_3$) 3070, 3050, 2995, 1600, 1495, 1445, 1428, 1112, 1078, 1068, 1045, 1035, 1005, 998, 920, 840 cm^{-1}; MS *m/e* 452.9840 (calcd for $C_{23}H_{17}Br_2D$ *m/e* 452.9835).

1-Bromo-2-phenyl-2-(1-deuterio-2,2-diphenylvinyl)cyclopropane. To a solution of 3 g (6.6 mmol) of 1,1-dibromo-2-phenyl-2-(1-deuterio-2,2-diphenylvinyl)cyclopropane in 45 mL of tetrahydrofuran at −120 °C[23] was added dropwise 4.5 mL (6.7 mmol) of 1.5 M *n*-butyllithium in hexane. The mixture was stirred for 5 min at −120 °C, and 1.0 mL of concentrated hydrochloric acid was added. The cold bath was removed, the mixture was allowed to warm slowly for 2 min, and 10 mL of water was added. Workup A afforded 2.45 g of an amber oil. Chromatography on a 2.5 × 60 cm silica gel column packed in 1% ether in hexane and eluted with 1–2% ether in hexane in 400-mL fractions gave, in fraction 2 (2% ether), 2.33 g (94%) of a mixture of the epimeric bromocyclopropanes as a yellow oil. The spectral data were as follows: NMR ($CDCl_3$) δ 7.3–6.9 (m, 15 H, arom), 3.12 (m, 1 H, CH), 1.8–1.2 and 0.98 (overlapping m, 2 H total, CH_2); IR (thin film) 3070, 3045, 3015, 2945, 2920, 2860, 1600, 1580, 1495, 1448, 1430, 1325, 1295, 1278, 1215, 1160, 1105, 1080, 1060, 1035, 1020, 920, 786, 775, 762, 730, 700 cm^{-1}; MS *m/e* 375.0732 (calcd for $C_{23}H_{18}BrD$ *m/e* 375.0729).

3-Phenyl-3-(1-deuterio-2,2-diphenylvinyl)cyclopropene. To a solution of 2.23 g (5.9 mmol) of a mixture of epimeric 1-bromo-2-phenyl-2-(1-deuterio-2,2-diphenylvinyl)cyclopropanes in 40 mL of tetrahydrofuran was added 2.7 g (24 mmol) of potassium *tert*-butoxide. The mixture was stirred for 20 h at room temperature and poured into ice–water. Workup B afforded 1.9 g of an orange oil. Chromatography on a 2.5 × 50 cm silica gel column packed in and eluted with hexane in 200-mL fractions gave, in fractions 5–8, 820 mg (47%) of the cyclopropene as a colorless solid, mp 107–116 °C dec. Recrystallization from cold dichloromethane in hexane gave 520 mg (30%) of colorless crystals, mp 118–120 °C dec. The spectral data were as follows: NMR ($CDCl_3$) δ 7.20 (m, 15 H arom), 6.66 (residual vinyl, 0.01 H), 6.42 (s, 2 H, cyclopropenyl); IR ($CHCl_3$) 3075, 3055, 3000, 1645, 1600, 1494, 1448, 1328, 1080, 1035, 995, 964, 920 cm^{-1}; UV (EtOH) λ_{max} 237 nm (ε 18 500), 260 (14 000); MS *m/e* 295.1470 (calcd for $C_{23}H_{17}D$ *m/e* 295.1467).

Expansion of the 270-MHz ^1H NMR spectrum and integration[37] of the cyclopropenyl and residual undeuterated vinyl peaks indicated 1.0 ± 0.5% vinyl proton after correction for relative responses of the individual peaks. The cyclopropene was therefore 99.0 ■ 0.5% deuterated at the α-vinyl position.

5,5-Dideuterio-4,4-diphenylcyclopent-2-en-1-one. To 25 mL of dioxane containing 27 mg (1.1 mmol) of sodium was added carefully 5 mL (5.5 g, 276 mmol) of deuterium oxide. When the reaction of the sodium was complete, a solution of 760 mg (3.24 mmol) of 4,4-diphenylcyclopent-2-en-1-one[27] in 5 mL of dioxane was added. The mixture was stirred for 48 h, poured into dichloromethane, and acidified with 10% hydrochloric acid, and the layers were separated. The organic layer was water washed, dried, and concentrated in vacuo to afford 766 mg (100%) of the dideuterio enone as a colorless oil, pure by NMR. No residual undeuterated methylene protons were visible in the 100-MHz NMR spectrum. The spectral data were as follows: NMR ($CDCl_3$) δ 8.02 (d, *J* = 6 Hz, 1 H, vinyl), 7.24–7.06 (m, 10 H, arom), 6.26 (d, *J* = 6 Hz, 1 H, vinyl); IR (thin film) 3065, 3030, 1720, 1602, 1498, 1455, 1265, 1240, 1200, 1168, 1130, 1092, 1078, 1045, 920, 882, 798, 768, 708 cm^{-1}; MS *m/e* 236.1171 (calcd for $C_{17}H_{12}OD_2$ *m/e* 236.1167).

5,5-Dideuterio-1,4,4-triphenylcyclopent-2-en-1-ol. To a solution of 760 mg (3.2 mmol) of 5,5-dideuterio-4,4-diphenylcyclopent-2-en-1-one in 25 mL of anhydrous ether was added dropwise 5.6 mL (6.8 mmol) of a 1.21 M solution of phenyllithium in ether. The mixture was stirred 14 h, quenched with saturated ammonium chloride, and subjected to workup B. This afforded 1.4 g of an amber oil. Chromatography on a 2.5 × 40 cm silica gel column packed in 5% ether in hexane and eluted with 5–20% ether in hexane in 100-mL fractions gave the following: fractions

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(37) Expanded peaks were digitized and integrated by using a Summagraphics Bitpad interfaced to a DEC PDP11/T55 minicomputer.

2 and 3, 5% ether, 130 mg, biphenyl; fraction 4, 10% ether, 40 mg, overlap; fractions 5–7 (10–20% ether), 1.0 g (99%) of the alcohol as a yellow oil, contaminated with ca. 5% of unreacted enone by NMR. The alcohol was dehydrated without further purification. The spectral data were as follows: NMR ($CDCl_3$) δ 7.4–7.0 (m, 15 H, arom), 6.44 (d, J = 6 Hz, 1 H, vinyl), 5.94 (d, J = 6 Hz, 1 H, vinyl), 2.0 (br s, 1 H, OH); IR (thin film) 3400 (br, OH), 3075, 3050, 3015, 2945, 2920, 2860, 1600, 1492, 1448, 1344, 1335, 1190, 1160, 1125, 1080, 1070, 1040, 1028, 1005, 970, 802, 758, 730, 702 cm^{-1}.

1-Deuterio-2,5,5-triphenylcyclopentadiene. A solution of 1.0 g (3.2 mmol) of 5,5-dideuterio-1,4,4-triphenylcyclopent-2-en-1-ol in 25 mL of pyridine was cooled in an ice bath, and 1.9 mL (3.13 g, 20 mmol) of phosphorus oxychloride was added. The mixture was heated at 60–70 °C for 3 h, cooled, poured onto ice, diluted with water, and ether extracted. The extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 684 mg of a dark oil. Chromatography on a 2.5 × 40 cm silica gel column packed in hexane and eluted with hexane and 1% ether in hexane in 250-mL fractions gave, in fractions 5 and 6, 364 mg (39%) of cyclopentadiene-*1-d* as a yellow oil, pure by NMR. Crystallization from dichloromethane in hexane gave 297 mg (31%) of colorless crystals, mp 97–98 °C. The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.60 (m, 2 H, arom), 7.35–7.20 (m, 13 H, arom), 7.05 (m, 0.027 H, undeuterated 1-H vinyl), 6.94 (d, J = 5.15 Hz, 1 H, vinyl), 6.81 (d, J = 5.15 Hz, 1 H, vinyl); IR ($CHCl_3$) 3050, 2995, 1598, 1490, 1445, 1355, 1150, 1072, 1030, 925, 905, 855, 815 cm^{-1}; UV (EtOH) λ_{max} 235 nm (ϵ 23 500), 270 (4100), 286 (5000); MS m/e 295.1470 (calcd for $C_{23}H_{17}D$ 295.1467).

Expansion of the 270-MHz ^1H NMR spectrum and integration[37] of the vinyl peaks indicated 2.7 ± 0.5% residual protons at the 1-position after correction for relative responses of the individual peaks. The cyclopentadiene was therefore 97.3 ± 0.5% deuterated at C-1.

2,2-Diphenylcyclopentan-1-one. A solution of 8.0 g (34 mmol) of 4,4-diphenylcyclopent-2-en-1-one[27] in 400 mL of glacial acetic acid was catalytically hydrogenated over 500 mg of 10% palladium on carbon at 2–3 atm. After 1.5 h, the catalyst was removed by filtration through Celite. Workup A afforded 7.8 g (97%) of the cyclopentanone as colorless crystals, mp 88–90 °C (lit.[38] mp 87–88 °C). The spectral data were as follows: NMR ($CDCl_3$) δ 7.27 (m, 10 H, arom), 2.72 (t, J = 7 Hz, 2 H, CH_2), 2.44 (t, J = 7 Hz, 2 H, CH_2), 1.92 (pentet, J = 7 Hz, 2 H, CH_2); IR ($CHCl_3$) 3085, 3055, 3000, 2965, 2885, 1740, 1600, 1582, 1495, 1470, 1448, 1408, 1318, 1276, 1235, 1150, 1110, 1092, 1038, 1030, 1004, 900, 834 cm^{-1}.

1-Deuterio-2,2-diphenylcyclopentan-1-ol. To a solution of 7.2 g (30.5 mmol) of 2,2-diphenylcyclopentan-1-one in 100 mL of anhydrous ether at 0 °C was added 700 mg (16.7 mmol) of lithium aluminum deuteride. The suspension was warmed to room temperature, stirred 2 h, cooled, and quenched by careful dropwise addition of 1.0 mL of water and 1.0 mL of 10% sodium hydroxide. The mixture was dried over anhydrous magnesium sulfate and filtered, and the filtrate was concentrated in vacuo to afford 6.37 g (87%) of the alcohol, pure by NMR. No residual methine protons were detectable by NMR. The spectral data were as follows: NMR ($CDCl_3$) δ 7.2 (m, 10 H, arom), 2.18–1.4 (m, 6 H, CH_2) 1.28 (s, 1 H, OH); IR (thin film) 3420, 3075, 3050, 3015, 2950, 2865, 1600, 1580, 1492, 1446, 1300, 1160, 1140, 1095, 1074, 1042, 948, 888, 755, 704 cm^{-1}; MS m/e 239.1419 (calcd for $C_{17}H_{17}OD$ m/e 239.1416).

2-Deuterio-3,3-diphenylcyclopentene. A modification of the procedure of Zimmerman and Little[27] for the preparation of 3,3-diphenylcyclopentene was used. To a solution of 6.5 g (27 mmol) of 1-deuterio-2,2-diphenylcyclopentan-1-ol in 120 mL of anhydrous ether was added 2.0 g (42 mmol) of a 50% dispersion of sodium hydride in mineral oil. The mixture was refluxed 15 h, and 2 mL (2.5 g, 33 mmol) of carbon disulfide was added. The mixture was refluxed for 8 h, and 2.2 mL (5.0 g, 35 mmol) of methyl iodide was added. After being refluxed for 10 h, the mixture was cooled and quenched by careful dropwise addition of water. Workup B afforded 5.66 g (97%) of the yellow crystalline xanthate, pure by NMR. Pyrolysis of the neat xanthate at 210 °C under a stream of nitrogen for 30 min gave 5.5 g of a dark oil which was chromatographed on a 2.5 × 40 cm silica gel column packed in hexane and eluted with 0.5% ether in hexane in 200-mL fractions to afford, in fractions 2 and 3, 4.93 g (82%) of the olefin as a slightly yellow oil, pure by NMR. The spectral data were as follows: NMR ($CDCl_3$) δ 7.1 (m, 10 H, arom), 5.84 (s, 1 H, vinyl), 2.48 (s, 4 H, CH_2); IR (thin film) 3075, 3045, 3015, 2980, 2935, 2840, 1598, 1578, 1490, 1460, 1445, 1062, 1028, 1010, 870, 758, 700, 675 cm^{-1}; MS m/e 221.1315 (calcd for $C_{17}H_{15}D$ m/e 221.1311).

3-Deuterio-4,4-diphenylcyclopent-2-en-1-one. By use of a modification of the general procedure of Ratcliffe and Rodehorst,[39] 45 g (0.45 mol) of chromium trioxide was added to an ice-cooled solution of 73 mL (71 g, 0.9 mol) of dry pyridine in 1.1 L of dichloromethane. After the mixture was stirred for 1 h at room temperature, a solution of 4.4 g (0.02 mol) of 2-deuterio-3,3-diphenylcyclopentene in 30 mL of dichloromethane was added. The mixture was stirred for 40 h and decanted, and the residue was washed with ether. The combined organic portions were diluted with ether, washed several times with 5% sodium hydroxide, 5% hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 7 g of an amber oil. Chromatography on a 3 × 30 cm silica gel column packed in 2% ether in hexane and eluted with 2–16% ether in hexane in 250-mL fractions gave the following: fraction 2 (2% ether), 1.26 g, recovered diphenylcyclopentene; fractions 3–8 (2–8% ether), 300 mg, unidentified yellow oil; fractions 7–11 (16% ether), 2.02 g (61% based on recovered starting material) of the desired enone as a yellow oil, pure by NMR. Recrystallization from ether in hexane gave 1.62 g (49%) of slightly yellow crystals, mp 60–64 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.3–7.0 (m, 10 H, arom), 6.14 (s, 1 H, vinyl), 3.06 (s, 2 H, CH_2); IR (thin film) 3060, 3030, 1715, 1600, 1585, 1570, 1495, 1450, 1415, 1345, 1285, 1260, 1172, 1102, 1040, 1008, 978, 920, 885, 825, 760, 728, 705, 658 cm^{-1}; MS m/e 235.1108 (calcd for $C_{17}H_{13}OD$ m/e 235.1104).

3-Deuterio-1,4,4-triphenylcyclopent-2-en-1-ol. To a solution of 1.6 g (6.8 mmol) of 3-deuterio-4,4-diphenylcyclopent-2-en-1-one in 50 mL of anhydrous ether was added dropwise 14 mL (16.8 mmol) of a 1.2 M solution of phenyllithium in ether. The solution was stirred for 1 h, refluxed for 1.5 h, cooled, and quenched by dropwise addition of 10 mL of saturated ammonium chloride. Workup B afforded 2.25 g of an amber oil. Chromatography on a 3 × 30 cm silica gel column packed in 5% ether in hexane and eluted with 5–15% ether in hexane in 250-mL fractions gave the following: fraction 2 (5% ether), 314 mg, biphenyl; fractions 4–6 (15% ether), 1.71 g (80%) of the alcohol as a colorless oil, contaminated with ca. 20% of the starting enone by NMR. The alcohol was dehydrated without further purification. The spectral data were as follows: NMR ($CDCl_3$) δ 7.2–7.0 (m, 15 H, arom), 6.02 (s, 1 H, vinyl), 3.13 (ν_a, AB q, J_{ab} = 14.5 Hz, 1 H, CH_2), 2.80 (ν_b, AB q, J_{ab} = 14.5 Hz, 1 H, CH_2), 1.90 (s, 1 H, OH); IR (thin film) 3420, 3080, 3060, 3020, 2950, 1600, 1580, 1498, 1450, 1195, 1070, 1055, 1035, 1012, 760, 705 cm^{-1}; MS m/e 313.1578 (calcd for $C_{23}H_{19}OD$ m/e 313.1572).

4-Deuterio-2,5,5-triphenylcyclopentadiene. To an ice-cooled solution of 1.6 g (5.1 mmol) of 3-deuterio-1,4,4-triphenylcyclopent-2-en-1-ol in 35 mL of pyridine was added dropwise 3 mL (4.9 g, 32 mmol) of phosphorus oxychloride. The mixture was heated at 60–65 °C for 3 h, cooled, poured onto ice, diluted with water, and ether extracted. The extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and concentrated in vacuo to afford 1.12 g of an amber oil. Chromatography on a 2.5 × 40 cm silica gel column packed in hexane and eluted with hexane and 1% ether in hexane in 500-mL fractions gave, in fraction 3 (1% ether), 780 mg (52%) of the cyclopentadiene as a nearly colorless solid, mp 92–94 °C. Recrystallization from dichloromethane in methanol gave 655 mg (43%) of colorless crystals, mp 96–97 °C. The spectral data were as follows: 270-MHz NMR ($CDCl_3$) δ 7.60 (m, 2 H, arom), 7.35–7.20 (m, 13 H, arom), 7.05 (d, J = 1.47 Hz, 1 H, vinyl), 6.81 (d, J = 1.47 Hz, 1 H, vinyl); IR ($CHCl_3$) 3050, 2995, 1598, 1490, 1448, 1348, 1185, 1078, 1035, 928, 910 cm^{-1}; UV (EtOH) λ_{max} 232 nm (ϵ 28 000), 269 (4400), 288 (6000); MS m/e 295.1470 (calcd for $C_{23}H_{17}D$ m/e 295.1467).

(38) Legagneur, F. S.; Neuev, C. *Bull. Soc. Chim. Fr.* **1956**, 929–937.

(39) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000–4002.

Expansion of the vinyl region of the 270-MHz ^1H NMR spectrum revealed the complete absence of any residual vinyl proton absorption at δ 6.94. It is estimated that <0.5% of undeuterated material would have been detectable under these conditions. The cyclopentadiene was therefore >99.5% deuterated at C-4.

(*E*)-3,5,5-Triphenyl-2,4-pentadienal. By use of a modification of the procedure of Lorenz and Wizigner[40] for the formylation of 1,1-diphenylethylene, a mixture of 4.6 mL (7.6 g, 50 mmol) of phosphorus oxychloride and 3.1 mL (3.4 g, 25 mmol) of *N*-methylformanilide in 4 mL of trichloroethylene was mechanically stirred for 1 h. The resultant orange slurry was cooled in an ice bath, and a solution of 7.0 g (25 mmol) of 1,1,3-triphenyl-1,3-butadiene in 10 mL of trichloroethylene was added dropwise. The resultant deep red solution was then stirred for 14 h at room temperature, poured onto ice, neutralized with 10% sodium hydroxide, and steam distilled. The pot residue was ether extracted, and the extracts were brine washed, dried, and concentrated in vacuo to afford 7.5 g (96%) of a yellow oil, identified as a 5:1 mixture of the isomeric dienals by NMR. Chromatography of the crude product on a 3.5 × 25 cm silica gel column packed in and eluted with 10% ether in hexane in 150-mL fractions gave, in fractions 4–7, 5.61 g (72%) of a partially crystalline yellow oil. Crystallization from dichloromethane in hexane gave 3.96 g (51%) of the major isomer of the aldehyde, mp 91–95 °C. Recrystallization from hexane gave 3.0 g (39%) of the major isomer, mp 94–95 °C.

The spectral data for the major isomer were as follows: NMR ($CDCl_3$) δ 9.94 (d, J = 8 Hz, 1 H, CHO), 7.64–7.04 (m, 15 H, arom), 6.92 (s, 1 H, vinyl), 6.22 (d, J = 8 Hz, 1 H, vinyl); IR ($CHCl_3$) 3055, 3010, 2840, 1710, 1600, 1575, 1500, 1450, 1390, 1364, 1330, 1225, 1190, 1148, 1082, 1038, 870 cm^{-1}; UV (EtOH) λ_{sh} 229 nm (ϵ 7600), 242 (7300), λ_{max} 331 (5300); MS m/e 310.1348 (calcd for $C_{23}H_{18}O$ m/e 310.1358).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.12; H, 6.00.

The spectral data for the minor isomer were as follows: NMR ($CDCl_3$) δ 9.44 (d, J = 7 Hz, 1 H, CHO), 7.6–7.0 (m, 15 H, arom), 6.86 (s, 1 H, vinyl), 6.12 (d, J = 7 Hz, vinyl).

The assignment of *E* stereochemistry to the major isomer derived from its oxidation with argentine oxide[41] to the known[42] (*E*)-3,5,5-triphenyl-2,4-pentadienoic acid [mp 164–166 °C (lit.[25] mp 165–166 °C)] under nonisomerizing conditions by the method of Corey and co-workers.[43] The spectral data for the *E* acid were as follows: NMR ($CDCl_3$) δ 7.48 (br s, 1 H, vinyl), 7.3–6.8 (m, 15 H, arom), 5.96 (br s, 1 H, vinyl); IR ($CHCl_3$) 3500–2400 (br, COOH), 1608, 1602, 1585, 1572, 1492, 1448, 1408, 1285, 1250, 1198, 1182, 1080, 878 cm^{-1}.

(*E*)-3,5,5-Triphenyl-2,4-pentadienal Tosylhydrazone. To a solution of 1.6 g (5.2 mmol) of (*E*)-3,5,5-triphenyl-2,4-pentadienal and 960 mg (5.2 mmol) of *p*-toluenesulfonhydrazide in 7 mL of absolute ethanol was added 0.25 mL of glacial acetic acid. The mixture was heated on a steam bath for 30 min and cooled to −20 °C. The precipitate was removed by filtration, washed with cold ethanol, and dried in vacuo to afford 2.1 g (85%) of the tosylhydrazone as an orange solid, mp 183–187 °C dec. The spectral data were as follows: NMR ($CDCl_3$) δ 7.8–7.0 (m, 21 H, arom, HC=NNHTs), 6.64 (s, 1 H, vinyl), 6.36 (d, J = 8 Hz, 1 H, vinyl), 2.46 (s, 3 H, $ArCH_3$); IR ($CHCl_3$) 3020, 1600, 1496, 1448, 1420, 1365, 1335, 1308, 1220, 1190, 1170, 1065 cm^{-1}; UV (EtOH) λ_{sh} 220 nm (ϵ 26 600), 238 (21 700), λ_{max} 278 (19 600), 330 (17 600); MS, no parent at low electron volt values.

Anal. Calcd for $C_{30}H_{26}N_2O_2S$: C, 75.78; H, 5.48. Found: C, 75.12; H, 5.69.

1,2,4-Triphenylcyclopentadiene. Method A. Treatment of 1,1-Dibromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane with *n*-Butyllithium at −100 °C. To a stirred solution of 2.0 g (4.4 mmol) of 1,1-dibromo-2-phenyl-2-(2,2-diphenylvinyl)-cyclopropane in 25 mL of tetrahydrofuran cooled to −100 °C (ether/CO_2) was added 2.9 mL (4.4 mmol) of 1.5 M *n*-butyllithium in hexane. The mixture was stirred for 5 min at −100 °C, and 2.0 mL of concentrated hydrochloric acid was added. The mixture was stirred for 15 additional min at −100 °C and then warmed slowly to room temperature. Workup A afforded 1.53 g of an oily tan solid. Trituration with hexane and filtration gave 853 mg of a tan solid which was fractionally crystallized from hexane to afford 155 mg (12%) of slightly yellow needles (mp 150–151 °C) identified from spectral data as 1,2,4-triphenylcyclopentadiene.

The mother liquors were combined and concentrated in vacuo to afford 1.3 g of an oily yellow solid which was chromatographed on a 2.5 × 150 cm silica gel column packed in hexane. Elution with hexane in 500 mL fractions gave the following: fractions 7–9, 676 mg of 1-bromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane, mp 126–129 °C; fractions 10 and 11, 249 mg of 1,2,4-triphenylcyclopentadiene, mp 144–148 °C.

Recrystallization of fractions 7–9 from hexane gave 521 mg (32%) of 1-bromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropane (epimer A), mp 130–131 °C. The spectral data were identical with those reported for epimer A above.

Recrystallization of fractions 10 and 11 from hexane gave an additional 180 mg (14%, 26% total) of 1,2,4-triphenylcyclopentadiene, mp 150–151 °C. The spectral data were as follows: NMR ($CDCl_3$) δ 7.60–7.05 (m, 15 H, arom), 6.98 (s, 1 H, vinyl), 3.84 (s, 2 H, CH_2); IR ($CHCl_3$) 3060, 3010, 1600, 1580, 1498, 1450, 1380, 1080, 1040, 925, 900, 878 cm^{-1}; MS m/e 294.1408 (calcd for $C_{23}H_{18}$ m/e 294.1408).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.66; H, 6.28.

Method B. Acid-Catalyzed Dehydration of 1,4,4-Triphenylcyclopent-2-en-1-ol. A solution of 150 mg (0.48 mmol) of 1,4,4-triphenylcyclopent-2-en-1-ol and 50 mg (0.26 mmol) of *p*-toluenesulfonic acid monohydrate in 20 mL of benzene was refluxed for 2 h, cooled, diluted with 80 mL of benzene, and filtered with suction through a 3 × 4 cm pad of silica gel. The silica gel was washed with 100 mL of hexane, and the combined filtrates were concentrated in vacuo to afford 143 mg (100%) of 1,2,4-triphenylcyclopentadiene as an amber oil, pure by NMR. Crystallization from hexane gave 73 mg (52%) of amber needles, mp 150–152 °C. The spectral data were identical with those reported above.

General Procedure for Exploratory Photolyses. All direct and sensitized exploratory irradiations were performed by using a 450-W medium-pressure mercury lamp immersion apparatus or the "black box"[44] apparatus as specified for each run. All runs were purged with purified nitrogen[45] for 1 h before and during photolysis. Base-washed glassware was employed throughout.

Filter Solutions. For black box photolyses, the band-pass was controlled by one of a series of filter solution combinations held in a 750-mL total volume three-compartment quartz-faced filter solution cell.[44] The filter solution employed was filter A (cell 1, 2.0 M nickel sulfate hexahydrate in 5% sulfuric acid; cell 2, 1.0 M cobalt sulfate heptahydrate in 5% sulfuric acid; cell 3, 6.85 × 10^{-5} M bismuth trichloride in 40% hydrochloric acid; transmission was 0% below 254 nm, 22% at 284 nm, and 0% above 306 nm). Where specified, a filter solution was circulated through the cooling jacket of the immersion apparatus. The filter solution employed was filter B (2.5 × 10^{-2} M sodium metavanadate in 5 × 10^{-2} M sodium hydroxide; transmission was 0% below 330 nm and 80% at 376 nm and above). The filter solutions remained unchanged after photolysis.

Exploratory Direct Photolytis of 3-Phenyl-3-(2,2-diphenylvinyl)cyclopropene. Product Isolation and Identification. Run A. A solution of 147 mg (0.50 mmol) of 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene in 240 mL of cyclohexane was irradiated through filter A on the black box apparatus for 7.25 h (0.88 mEinsteins, 56% conversion). Concentration in vacuo without heat gave 150 mg of a yellow oil. Chromatography on a 1.5 × 100 cm silica gel column packed in and eluted with hexane in 40-mL fractions and monitored at 254 nm by UV scanner gave the following: fractions 6–12, 108 mg, identified by NMR as a mixture of recovered cyclopropene, 2,5,5-triphenylcyclopentadiene, and 3-(2,2-diphenylvinyl)indene; fractions 13–16,

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(42) Anghelova, Y. *Synthesis* **1974**, 343–344.
(43) Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616–5617.
(44) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.
(45) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

9 mg, 1,4,5-triphenylcyclopentadiene, identified (vide infra) from spectral characteristics, derivitization, and degradation; fractions 17–24, 11 mg, a mixture of 1,4,5-triphenylcyclopentadiene and decomposed material due to prolonged irradiation. Analysis of the photolysis mixture by HPLC indicated a 26:9:1 ratio of cyclopropene/2,5,5-triphenylcyclopentadiene/indene.

Run B. Similar irradiation of 200 mg (0.68 mmol) of the cyclopropene as above (3 h, 2.25 mEinsteins, 63% conversion) gave 206 mg of a yellow oil. Separation on a 20 × 20 cm thick-layer plate eluted three times with pentane gave four bands. Band 1 contained 74 mg (37%) of starting cyclopropene containing a small amount of indene by NMR. Band 2 gave 60 mg (30%) of 2,5,5-triphenylcyclopentadiene. Band 3 contained 37 mg (18%) of 1,4,5-triphenylcyclopentadiene. Band 4 contained 15 mg (8%) of decomposed material.

Crystallization of the material from band 1 from dichloromethane–methanol gave 35 mg of recovered cyclopropene as yellow crystals (mp 104–108 °C dec), identical with starting material.

Crystallization of the material from band 2 from dichloromethane–methanol gave 25 mg of 2,5,5-triphenylcyclopentadiene as nearly colorless crystals (mp 95–96 °C), identical with the independently synthesized material.

Crystallization of the material from band 3 gave 20 mg of 1,4,5-triphenylcyclopentadiene as slightly yellow needles, mp 132–134 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$) δ 7.4–6.8 (m, 15 H, arom), 6.76 (s, 2 H, vinyl), 4.83 (s, 1 H, CH); ^{13}C NMR (acetone-d_6) 154.0, 139.7, 137.6, 136.1, 129.2, 129.0, 128.6, 127.5, 127.1, 126.8, 58.2 ppm; IR ($CHCl_3$) 3055, 3000, 1602, 1590, 1492, 1445, 1185, 1110, 1078, 1034, 1022, 914, 858 cm^{-1}; UV (EtOH) λ_{max} 235 nm (ϵ 13 500), 349 (13 000); MS m/e 294.1400 (calcd for $C_{23}H_{18}$ m/e 294.1408).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.70; H, 6.05.

The 1,4,5-triphenylcyclopentadiene obtained from photolysis of the cyclopropene gave the same adduct with 4-phenyl-1,2,4-triazoline-3,5-dione[46] as the cyclopentadiene obtained from irradiation of 2,5,5-triphenylcyclopentadiene (vide infra).

Exploratory Direct Photolysis of 2,5,5-Triphenylcyclopentadiene. Product Isolation and Identification. A solution of 203 mg (0.69 mmol) of 2,5,5-triphenylcyclopentadiene in 230 mL of benzene was irradiated for 15 min through Pyrex on the immersion apparatus. Concentration in vacuo gave 213 mg of an oily yellow solid. Chromatography on a 2.5 × 140 cm silica gel column packed in and eluted with hexane in 40-mL fractions and monitored by UV scanner at 254 nm gave the following: fractions 32–36, 5 mg, 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene, identical (NMR, IR) with the independently synthesized material; fractions 37–54, 75 mg, recovered 2,5,5-triphenylcyclopentadiene; fractions 56–76, 100 mg, 1,4,5-triphenylcyclopentadiene, identical with that obtained from irradition of the (diphenylvinyl)cyclopropene; fractions 77–86, 10 mg, a mixture of 1,4,5-triphenylcyclopentadiene and decomposed material.

Fractions 56–76 were combined, concentrated, and crystallized from dichloromethane in hexane to afford 66 mg of 1,4,5-triphenylcyclopentadiene as pale yellow needles, mp 134–136 °C. The spectral data were identical with those of the 1,4,5-triphenylcyclopentadiene obtained from photolysis of the (diphenylvinyl)cyclopropene.

Structure Proof. Formation of 1,4,7,10-Tetraphenyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione from 1,4,5-Triphenylcyclopentadiene. To an ice-cooled solution of 50 mg (0.17 mmol) of 1,4,5-triphenylcyclopentadiene in 5 mL of chloroform was added dropwise a solution of 30 mg (0.17 mmol) of 4-phenyl-1,2,4-trazoline-3,5-dione[46] in 2 mL of chloroform. The mixture was stirred for 5 min and concentrated in vacuo to afford 80 mg of a pink oil. Trituration with ether in pentane and filtration gave 57 mg (71%) of a nearly colorless solid, mp 148–152 °C dec. Recrystallization from dichloromethane in hexane gave 50 mg (63%) of the adduct as colorless crystals, mp 148–152 °C dec. The spectral data were as follows: NMR ($CDCl_3$) δ 7.7–7.2 (m, 16 H, arom), 6.94 (m, 2 H, arom), 6.88 (s, 2 H, vinyl), 6.56 (m, 2 H, arom), 4.14 (s, 1 H, CH); IR ($CHCl_3$) 3040, 1780, 1725, 1508, 1458, 1405, 1240, 1152, 1040, 1025, 984, 850 cm^{-1}; MS m/e 469.1789 (calcd for $C_{31}H_{23}N_3O_2$, m/e 469.1785).

Structure Proof. Base Treatment of 1,4,5-Triphenylcyclopentadiene. Method A. To a solution of 14 mg (0.048 mmol) of 1,4,5-triphenylcyclopentadiene in 4 mL of tetrahydrofuran was added 0.04 mL (0.06 mmol) of 1.5 M n-butyllithium in hexane. The yellow solution was stirred for 5 min and poured onto ice. Workup B afforded 14 mg (100%) of a yellow oil, identical with independently synthesized[3] 1,2,3-triphenylcyclopentadiene.

Method B. To a solution of 55 mg (0.19 mmol) of 1,4,5-triphenylcyclopentadiene in 15 mL of 30% methanol in benzene was added 2 mg (0.037 mmol) of sodium methoxide. The solution was stirred for 48 h at room temperature. Workup B afforded 50 mg (90%) of a 2.8:1 mixture of 1,2,3- and 1,4,5-triphenylcyclopentadiene by NMR.

Exploratory Direct Photolysis of 3-Phenyl-(1-phenylvinyl)cyclopropene. Product Isolation and Identification. Run A. A solution of 130 mg (0.60 mmol) of 3-phenyl-3-(1-phenylvinyl)cyclopropene in 150 mL of purified cyclohexane was irradiated through Corex on the immersion apparatus for 0.5 h. Concentration in vacuo gave 137 mg of a yellow oil which was separated on a 20 × 20 cm thick-layer plate eluted with pentane to afford three distinct bands. Band 1 gave 46 mg (35%) of a 1:2:1 mixture by NMR of 1,2-diphenylcyclopentadiene and 3-(1-phenylvinyl)indene, identified by comparison of the NMR spectrum to those of the independently synthesized materials, and 3,4-diphenyl-1,2,4-pentatriene, identified (vide infra) from its characteristic NMR and IR spectral data. Band 2 gave 47 mg (36%) of recovered starting material. Band 3 gave 22 mg (17%) of decomposed material. The overall mass balance was 88%.

Run B. In a similar run, irradiation of 124 mg (0.57 mmol) of the cyclopropene for 0.5 h under the above conditions gave 125 mg of a yellow oil containing, by NMR, starting cyclopropene, 1,2-diphenylcyclopentadiene, 3-(1-phenylvinyl)indene, and 3,4-diphenyl-1,2,4-pentatriene. Treatment of the mixture with 10 mg (0.068 mmol) of dimethyl azodicarboxylate[47] effected immediate reaction with the cyclopentadiene, as evidence by the disappearance in the NMR of the cyclopentadiene peaks and the appearance of peaks corresponding to the adduct, 2,3-bis(carbomethoxy)-1,6-diphenyl-2,3-diazabicyclo[2.2.1]hept-5-ene, which were identical with those of independently synthesized adduct (vide infra). Chromatography of the resultant mixture on a 20 × 20 cm thick-layer plate eluted once with pentane gave, in two rapidly eluting bands, 25 mg (20%) of a mixture of the allene and indene (band 1) and 83 mg (67%) of recovered cyclopropene (band 2), identical with starting material.

Fractional crystallization of the mixture from band 1 from ether–methanol gave 15 mg (12%) of pure indene as colorless crystals (mp 76–79 °C), identical with the independently synthesized material. The mother liquor contained a mixture of indene and allene.

Run C. Irradiation of 206 mg (0.94 mmol) of the cyclopropene as above for 45 min gave 215 mg of a yellow oil, again containing starting cyclopropene and the indene, cyclopentadiene, and allene photoproducts by NMR. Treatment as above with 80 mg (0.55 mmol) of the dimethyl azodicarboxylate[47] gave, as before, immediate reaction with the cyclopentadiene and formation of the bicyclo[2.2.1] adduct. Concentration of the sample in vacuo gave, on allowing the mixture to stand for 1.5 h, further reaction of the excess azo compound with the indene. Chromatography on a 20 × 20 cm thick-layer plate eluted once with pentane gave, in two rapidly moving bands, 20 mg (10%) of 3,4-diphenyl-1,2,4-pentatriene as a nearly colorless oil, identified from characteristic NMR and IR spectral data (band 1) and 55 mg (27%) of recovered cyclopropene (band 2), identical with starting material.

The spectral data for the allene were as follows: NMR ($CDCl_3$) δ 7.5–7.0 (m, 10 H, arom), 5.58 (s, 1 H, styryl vinyl), 5.30 (s, 1 H, styryl vinyl), 5.05 (s, 2 H, allenic vinyls); IR (thin film) 3080, 3050, 3010, 1935 (C=C=C), 1602, 1500, 1450, 1080, 1035, 918, 860 (C=C=CH_2), 785, 775, 762, 740, 700 cm^{-1}; MS m/e 218.1095 (calcd for $C_{17}H_{14}$ m/e 218.1092).

2,3-Bis(carbomethoxy)-1,6-diphenyl-2,3-diazabicyclo[2.2.1]hept-5-ene. To a solution of 25 mg (0.11 mmol) of 1,2-

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diphenylcyclopentadiene[10] in 0.45 mL of deuterated chloroform was added a solution of 13.5 mg (0.09 mmol) of dimethyl azodicarboxylate[47] in 0.17 mL of deuterated chloroform. Concentration in vacuo gave 35 mg of the adduct as a slightly yellow oil. The spectral data were as follows: NMR ($CDCl_3$) δ 7.1–7.5 (m, 10 H, arom), 6.66 (d, J = 3 Hz, 1 H, vinyl), 5.34 (m, 1 H, CH), 3.82 (s, 3 H, CO_2CH_3), 3.52 (s, 3 H, CO_2CH_3), 2.24 (d, J = 9 Hz, 1 H, CH_2), 1.96 (d, J = 9 Hz, 1 H, CH_2); IR (thin film) 3045, 3015, 2940, 1715, 1595, 1488, 1438, 1340, 1315, 1250, 1192, 1160, 1134, 1110, 1060, 1025, 932, 910, 760, 730, 696, 645 cm^{-1}; MS m/e 364.1424 (calcd for $C_{21}H_{20}N_2O_4$ m/e 364.1428).

Exploratory Sensitized Photolysis of 3-Phenyl-3-(1-phenylvinyl)cyclopropene. Product Isolation. A solution of 150 mg (0.69 mmol) of 3-phenyl-3-(1-phenylvinyl)cyclopropene and 500 mg (2.55 mmol) of xanthone in 160 mL of benzene was photolyzed for 70 min on the immersion apparatus through filter B. The crude photolysate was concentrated in vacuo, dissolved in 10 mL of benzene, and suction filtered through a 3 × 4 cm pad of silica gel. The silica gel was washed with hexane, and the combined filtrates were concentrated in vacuo to afford 152 mg (101%) of a yellow oil. Separation on a 20 × 20 cm thick-layer plate eluted once with pentane gave the following: band 1, 40 mg (26%) of 1,2-diphenylcyclopentadiene, identical with the independently synthesized[10] material; band 2, 85 mg (56%) of recovered cyclopropene, identical with starting material.

Exploratory Sensitized Photolysis of 2,5,5-Triphenylcyclopentadiene. Product Isolation. A solution of 167 mg (0.57 mmol) of 2,5,5-triphenylcyclopentadiene and 600 mg (2.66 mmol) of 4-(dimethylamino)benzophenone in 150 mL of benzene was irradiated for 1.5 h on the immersion apparatus through filter B. Concentration in vacuo gave 900 mg of a yellow oil. Chromatography on a 2.5 × 40 cm silica gel column packed in and eluted with 0.5% ether in hexane gave, in fractions 4 and 5, the entire hydrocarbon fractions eluting as a single band. Concentration in vacuo gave 142 mg (85%) of a mixture of the 2,5,5- and 1,4,5-cyclopentadienes by NMR. Separation on a 20 × 20 cm thick-layer plate eluted twice with pentane gave three distinct bands. The workup of the fastest moving band gave 86 mg (51%) of recovered 2,5,5-triphenylcyclopentadiene as a colorless oil, identical with the starting material. Crystallization from dichloromethane in hexane gave 30 mg of colorless crystals, mp 97–98 °C. The workup of band 2 gave 36 mg (22%) of 1,4,5-triphenylcyclopentadiene as a pale yellow solid (mp 122–127 °C), pure by NMR. Recrystallization from dichloromethane in hexane gave 25 mg of pale yellow needles (mp 135–138 °C), identical with the product obtained from the direct irradiation. The workup of the noneluting band gave 18 mg of decomposed material.

Exploratory Photolysis of 3-Phenyl-3-(1-deuterio-2,2-diphenylvinyl)cyclopropene. A solution of 200 mg (0.68 mmol) of 3-phenyl-3-(1-deuterio-2,2-diphenylvinyl)cyclopropene in 250 mL of cyclohexane was irradiated for 3 h on the black box apparatus through filter A (2.03 mEinsteins, 52% conversion). Concentration in vacuo gave 210 mg of a yellow oiil which was chromatographed on a 20 × 20 cm thick-layer plate eluted three times with pentane to give four distinct bands. The workup of the fast-moving band gave 96 mg (48%) of recovered starting cyclopropene, mp 106–110 °C dec. Band 2 gave 53 mg (27%) of 1-deuterio-2,5,5-triphenylcyclopentadiene. Band 3 gave 16 mg (8%) of 5-deuterio-1,4,5-triphenylcyclopentadiene. The slow-moving band contained 26 mg (13%) of decomposed material. The overall mass balance was 96%.

Recrystallization of the material from band 1 from dichloromethane in hexane gave 50 mg of colorless crystals (mp 113–116 °C dec), identical with starting cyclopropene. No scrambling of the deuterium label was observed by NMR.

Expansion of the vinyl region of the 270-MHz NMR spectrum of the deuterated 1,5,5-triphenylcyclopentadiene from band 2 and integration[37] of the residual proton absorption at δ 7.03 gave 0.9 ± 0.5% residual H at C-1 after correction for relative response of the individual peaks. The 2,5,5-triphenylcyclopentadiene formed in the irradiation of the 1-deuterated cyclopropene was therefore 99.1 ± 0.5% deuterated at C-1.

Crystallization of the material from band 2 from dichloromethane in hexane gave 36 mg of the 1-deuterio-2,5,5-triphenylcyclopentadiene as colorless crystals (mp 94–96 °C), identical with the independently synthesized material.

Exploratory Photolysis of 4-Deuterio-2,5,5-triphenylcyclopentadiene. A solution of 220 mg (0.75 mmol) of 4-deuterio-2,5,5-triphenylcyclopentadiene in 185 mL of benzene was irradiated through Pyrex on the immersion apparatus for 0.5 h. Concentration in vacuo gave 228 mg of an oily yellow solid. Chromatography on a 20 × 20 cm thick-layer plate eluted twice with pentane gave the following: band 1, 5 mg (2%) of 1-deuterio-3-phenyl-3-(2,2-diphenylvinyl)cyclopropene, mp 106–108 °C dec; band 2, 92 mg of recovered 4-deuterio-2,5,5-triphenylcyclopentadiene, mp 94–96 °C; band 3, 100 mg (45%) of 2-deuterio-1,4,5-triphenylcyclopentadiene, mp 122–132 °C; band 4, 20 mg of decomposed material. The overall mass balance was 98%.

Expansion and integration[37] of the vinyl and cyclopropenyl absorptions in the 270-MHz NMR spectrum of the deuterated cyclopropene from band 1 gave a relative integration of 1.005:1.00, respectively, after correction for relative responses of the individual peaks. The cyclopropene was therefore 100 ± 0.5% deuterated at one of the positions on the three-membered-ring double bond (i.e., C-1).

The material from band 1 crystallized to afford 5 mg (mp 106–108 °C dec) of 1-deuterio-3-phenyl-3-(2,2-diphenylvinyl)-cyclopropene.

Recrystallization of the material from band 2 gave 81 mg of recovered 4-deuterio-2,5,5-triphenylcyclopentadiene, mp 95–97 °C. No deuterium scrambling was observed by NMR.

Recrystallization of the material from band 3 gave 47 mg of pale yellow needles (mp 138–140 °C), identified as 2-deuterio-1,4,5-triphenylcyclopentadiene from comparison of the spectral data with those of the nondeuterated material. The spectral data were as follows: NMR ($CDCl_3$) δ 7.4–6.8 (m, 15 H, arom), 6.76 (s, 1 H, vinyl), 4.64 (s, 1 H, CH); IR ($CHCl_3$) 3060, 3000, 1600, 1495, 1448, 1180, 1078, 1038, 915, 880, 860, 840 cm^{-1}; UV (EtOH) λ_{max} 237 nm (ϵ 12 500), 350 (21 000); MS m/e 295.1470 (calcd for $C_{23}H_{17}D$ m/e 295.1467).

Exploratory Photolysis of 1-Deuterio-2,5,5-triphenylcyclopentadiene. A solution of 185 mg (0.63 mmol) of 1-deuterio-2,5,5-triphenylcyclopentadiene was irradiated through Pyrex on the immersion apparatus for 0.5 h. Concentration in vacuo gave 190 mg of a yellow oil which was chromatographed on a 20 × 20 cm thick-layer plate eluted twice with pentane to afford the following: band 1, 7 mg (4%) of 3-phenyl-3-(1-deuterio-2,2-diphenylvinyl)cyclopropene, contaminated with a small amount of starting cyclopentadiene; band 2, 75 mg (41%) of recovered 1-deuterio-4,5,5-triphenylcyclopentadiene as a yellow oil; band 3, 63 mg (34%) of 5-deuterio-1,4,5-triphenylcyclopentadiene, mp 124–134 °C; band 4, 14 mg (8%) of decomposed material. The overall mass balance was 87%.

The 3-phenyl-3-(1-deuterio-2,2-diphenylvinyl)cyclopropene from band 1 was identified by comparison with the independently synthesized material. Expansion and integration[37] of the vinyl region revealed 2.8 ± 0.5% of residual vinyl proton absorption at δ 6.66. The cyclopropene formed during the irradiation was therefore 97.2 ± 0.5% deuterated at the α-vinyl position.

No scrambling of the deuterium was observed by NMR in the recovered 1-deuterio-2,5,5-triphenylcyclopentadiene from band 2.

The spectral data for the 5-deuterio-1,4,5-triphenylcyclopentadiene isolated from band 3 were as follows: NMR ($CDCl_3$) δ 7.5–7.0 (m, 15 H, arom), 6.76 (s, 2 H, vinyls); IR ($CHCl_3$) 3060, 3000, 1600, 1492, 1450, 1180, 1030, 915, 860 cm^{-1}.

Independent Carbene Generation. Direct Photolysis of the (*E*)-3,5,5-Triphenyl-2,4-pentadienal Tosylhydrazone Sodium Salt. The sodium salt of 300 mg (0.63 mmol) of (*E*)-3,5,5-triphenyl-2,4-pentadienal tosylhydrazone was prepared by addition of 113 mg (2.46 mmol) of sodium methoxide in 200 mL of anhydrous tetrahydrofuran. The solution was irradiated for 10 min on the immersion apparatus through filter B. Concentration in vacuo gave 560 mg of an oily solid. The hydrocarbon products were dissolved in 20 mL of hexane and suction filtered through a 1 × 2.5 cm pad of alumina. The residue was rinsed with hexane and filtered through alumina, and the combined filtrates were concentrated in vacuo to afford 100 mg (54%) of a slightly yellow solid containing, by NMR, a mixture of 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene, 2,5,5-triphenylcyclopentadiene, and 3-(2,2-diphenylvinyl)indene. Analysis by HPLC

Table II. Direct Quantum Yields for 3-Phenyl-3-(2,2-diphenylvinyl)cyclopropene (1)

run	mmol of reactant	light absd, mEinsteins	% conv	photoproduct (mmol)	ϕ
1[a]	0.21	0.20	13.3	**12** (0.028)	0.14
2[a]	0.19	0.099	8.1	**12** (0.015)	0.15
3[b]	0.19	0.086	6.9	**12** (0.013)	0.16
4[b]	0.23	0.78	2.6	**13** (0.0060)	0.0077
5[b]	0.24	0.34	1.6	**13** (0.0040)	0.012
6[b]	0.24	0.53	2.1	**13** (0.0050)	0.0093

[a] Cyclohexane, 250 mL, analysis by HPLC. [b] Pentane, 250 mL, analysis by 270-MHz NMR.

Table III. Direct Quantum Yields for 2,5,5-Triphenylcyclopentadiene (12)

run	mmol of reactant	light absd, mEinsteins	% conv	photoproduct (mmol)	ϕ
1[a]	0.20	0.065	3.0	**16** (0.0061)	0.094
2[b]	0.20	0.12	5.3	**16** (0.011)	0.090
3[b]	0.20	0.082	3.7	**16** (0.0076)	0.092
4[b]	0.21	0.32	10.3	**1** (0.0011)	0.0034
5[b]	0.21	0.49	17.3	**16** (0.036)	0.072
				1 (0.001)	0.0029
6[b]	0.22	0.76	22.8	**16** (0.052)	0.068
				1 (0.002)	0.0028

[a] Cyclohexane, 250 mL, analyses by 270-MHz NMR. [b] Pentane, 250 mL, analyses by 270-MHz NMR.

Table IV. Direct Quantum Yields for 3-Phenyl-3-(1-phenylvinyl)cyclopropene (2)

run[a]	mmol of reactant	light absd, mEinsteins	% conv	photoproduct (mmol)	ϕ
1	0.50	0.64	15.5	**15** (0.03)	0.046
				17 (0.023)	0.035
				18 (0.025)	0.040
2	0.52	0.44	12.6	**15** (0.026)	0.060
				17 (0.020)	0.046
				18 (0.019)	0.043
3	0.52	0.19	6.9	**15** (0.014)	0.074
				17 (0.012)	0.066

[a] Pentane, 250 mL, analysis by 270-MHz NMR.

Table V. Sensitized Quantum Yields for 3-Phenyl-3-(1-phenylvinyl)cyclopropene (2) and 2,5,5-Triphenylcyclopentadiene (12)

run	reactant (mmol)	light absd, mEinsteins	% conv	photoproduct (mmol)	ϕ
1[a]	**2** (0.19)	0.096	1.2	**17** (0.0021)	0.022
2[a]	**2** (0.20)	0.083	0.6	**17** (0.0012)	0.015
3[b]	**12** (0.21)	0.20	1.6	**16** (0.0034)	0.018
4[b]	**12** (0.17)	0.21	2.3	**16** (0.0041)	0.019

[a] Benzene, 40 mL, 334 nm, xanthone (1.27 mmol). [b] Benzene, 40 mL, 366 nm, 4-(dimethylamino)benzophenone (1.11 mmol).

under the analytical conditions described for the quantum yield determinations (vide infra) indicated a cyclopropene/cyclopentadiene/indene ratio of 6:1:1.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were performed by using the black box apparatus[44] or a semimicrooptical bench.[44] Light output for each run was measured by using a digital actinometer[48] calibrated by ferrioxolate actinometry.[49] Microoptical bench photolyses employed an Osram HBO 200-W high-pressure mercury lamp and Bausch and Lomb Model 33-86-79 monochrometer with a 5.4-mm entrance slit and a 3.0-mm exit slit, giving a band-pass of 22 nm at half-peak height. The band-pass for black box photolyses was controlled by the filter solutions described above.

All quantum yield photolyses were run in purified solvents purged with deoxygenated nitrogen for 1 h prior to and during photolysis. Base-washed glassware was employed throughout to minimize complications due to acid-catalyzed reactions of cyclopropenes.

Direct Quantum Yield Results. All direct runs were performed by using the black box apparatus and filter A. Analyses were performed either by integration[37] of expanded peaks in the 270-MHz FT NMR spectrum, calibrated for responses relative to an added internal standard, or by HPLC with a 4 × 250 mm column packed with 5–10-μm silica beads[50] and eluted with 1–2% dichloromethane in hexane, employing an added standard and integrating as above. The standards employed were as follows: for HPLC analyses, *p*-terphenyl; for NMR analyses of 3-phenyl-3-(1-phenylvinyl)cyclopropene runs, 1,2,3-triphenylcyclopentadiene; for NMR analyses of 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene and 2,5,5-triphenylcyclopentadiene runs, 1,1-dibromo-2-phenyl-2-(1-phenylvinyl)cyclopropane. The data are reported in Tables II–IV.

Sensitized Quantum Yield Results. All sensitized runs were performed by using a semimicrooptical bench at 366 nm for

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4-(dimethylamino)benzophenone-sensitized irradiations or at 334 nm for xanthone-sensitized irradiations. Concentrations of the sensitizers were such that greater than 98% of the incident light was absorbed by the sensitizer. Analyses were performed by 270-MHz NMR with added standards as described for the direct runs. The data are reported in Table V.

Control Experiment. Direct Irradiation of 3-(2,2-Diphenylvinyl)indene. A solution of 101 mg (0.34 mmol) of 3-(2,2-diphenylvinyl)indene in benzene was irradiated for 3 h on the immersion apparatus through Pyrex. Concentration in vacuo gave 98 mg (97%) of recovered indene, identical with starting material by NMR.

Control Experiment. Direct Irradiation of 1,4,5-Triphenylcyclopentadiene. A solution of 10 mg (0.034 mmol) of 1,4,5-triphenylcyclopentadiene in 10 mL of benzene was irradiated for 35 min on the immersion apparatus through Pyrex. Concentration in vacuo gave 8 mg (80%) of recovered 1,4,5-triphenylcyclopentadiene as nearly colorless needles (mp 129–131 °C), identical with starting material.

Control Experiment. Direct Irradiation of 1,2-Diphenylcyclopentadiene. A solution of 15 mg of 1,2-diphenylcyclopentadiene in 15 mL of cyclohexane was irradiated for 30 min on the immersion apparatus through Corex. Concentration in vacuo gave 14 mg (93%) of recovered cyclopentadiene. The spectral data were identical with those of starting material.

Control Experiment. Direct Irradiation of 3-(1-Phenylvinyl)indene. A solution of 20 mg (0.092 mmol) of 3-(1-phenylvinyl)indene in 15 mL of cyclohexane was irradiated for 0.5 h on the immersion apparatus through Corex. Concentration in vacuo gave 20 mg (100%) of recovered indene, identical with starting material by NMR.

Control Experiment. Test for Singlet Energy Transfer from Xanthone to 3-Phenyl-3-(1-phenylvinyl)cyclopropene. The fluorescence of a degassed 3.18×10^{-2} M solution of xanthone in benzene was unquenched by addition of 5.0×10^{-3} M 3-phenyl-3-(1-phenylvinyl)cyclopropene, indicating that no singlet energy transfer was occurring.

Control Experiment. Direct Irradiation of 3-Phenyl-3-(2,2-diphenylvinyl)cyclopropene in Tetrahydrofuran. A solution of 100 mg (0.34 mmol) of 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene in 250 mL of tetrahydrofuran was irradiated for 2.5 h on the black box apparatus through filter A (1.7 mEinsteins). Concentration in vacuo gave 112 mg of a yellow oil containing, in addition to recovered starting material, 2,5,5- and 1,4,5-triphenylcyclopentadiene and a trace of 3-(2,2-diphenylvinyl)indene by NMR. No increase in the amount of indene relative to cyclopentadiene photoproducts was apparent by NMR, when compared with amounts of products from similar runs carried out in cyclohexane.

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Registry No. 1, 81245-47-8; 1(1'd), 81245-48-9; 2, 81245-49-0; 3, 81245-50-3; 3(2d), 81245-51-4; 4, 81245-52-5; 4(1d), 81245-53-6; *cis*-5(1'd), 81255-40-5; *trans*-5(1'd), 81245-54-7; 6, 5074-28-2; 12, 81245-55-8; 12(1d), 81245-56-9; 12(4d), 81245-57-0; 13, 81245-58-1; 15, 81245-59-2; 16, 81245-60-5; 16(2d), 81245-61-6; 16(5d), 81245-62-7; 17, 24102-68-9; 18, 81245-63-8; 19, 17792-17-5; 19(2d), 78522-52-8; 20, 81245-64-9; 21, 81245-65-0; 22, 81245-66-1; (*E*)-27, 81245-67-2; (*Z*)-27, 81245-68-3; (E)-28, 81245-69-4; (E)-29, 81245-70-7; 1-bromo-2-phenyl-2-(2,2-diphenylvinyl)cyclopropene (isomer 1), 81245-71-8; 1-bromo-2-phenyl-2(2,2-diphenylvinyl)cyclopropene (isomer 2), 81245-72-9; 1,1-dibromo-2-phenyl-2(1-phenylvinyl)cyclopropane, 81245-73-0; 2,3-diphenyl-1,3-butadiene, 2548-47-2; 1-bromo-2-phenyl-2-(1-phenylvinyl)cyclopropane, 81245-74-1; 1,4,4-triphenylcyclopent-2-en-1-ol, 81245-75-2; 4,4-diphenylcyclopent-2-en-1-one, 38464-75-4; 1-bromo-2,2-diphenylethylene, 13249-58-6; 1-indanone, 83-33-0; 1-bromostyrene, 98-81-7; 2-deuterio-1,1,3,3-tetraphenylprop-2-en-1-ol, 81245-76-3; 5,5-dideuterio-4,4-diphenylcyclopent-2-en-1-one, 81245-77-4; 5,5-dideuterio-1,4,4-triphenylcyclopent-2-en-1-ol, 81255-41-6; 2,2-diphenylcyclopentan-1-one, 15324-42-2; 1-deuterio-2,2-diphenylcyclopentan-1-ol, 81245-78-5; 2-deuterio-3,3-diphenylcyclopentene, 81245-79-6; 3-deuterio-4,4-diphenylcyclopent-2-en-1-one, 81245-80-9; 3-deuterio-1,4,4-triphenylcyclopent-2-en-1-ol, 81245-81-0; 1,4,7,10-tetraphenyl-2,4,6-triazatricyclo-[5.2.1.$3^{2,6}$]dec-8-en-3,5-dione, 81245-82-1; 2,3-bis(carbomethoxy)-1,6-diphenyl-2,3-diazabicyclo[2.2.1]hept-5-ene, 81245-83-2.

Effect of Neighboring Alkyl Groups on the Rate of Proton Loss in Methylpyrimidine Derivatives

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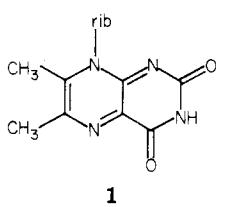
A number of alkyl-substituted 2-iminopyrimidines, 2-pyrimidones, and 2-pyridonium quaternary salts have been prepared and measurements made of the rates of proton loss from an activated methyl group in these compounds (aqueous solution, acetate ion as base). In all cases the presence of a methyl group at next-but-one position of the ring (in most cases the 4-position) causes a decrease in the rate of reaction of the reactive methyl group (in most cases located at the 6-position), the deactivating effect being in the range 4–40. With only one exception an alkyl group at an *adjacent* position (position 5) to the reactive methyl group produces an increase in the rate of reaction, the effects being in the range 2–4. The size of the adjacent alkyl group does not seem to be significant, at least in the iminopyrimidine series. This effect could not be evaluated in the other two series because of spontaneous dealkylation of groups larger than methyl during synthesis. These results duplicate those recently reported in other heterocyclic systems, though the cause of the activating effect of an adjacent alkyl group remains obscure.

Proton loss from the 7-methyl group in 6,7-dimethyl-8-ribityllumazine (1) is a key step in its conversion to riboflavin in nature.[1] We have observed that proton loss from the 7-position in the 8-methyl analogue of 1 is slower in the absence of the 6-methyl group, and this effect is duplicated in the series of 5-deazalumazines (2) which we have also examined.[2] In this series the rate constants for



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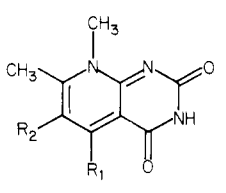

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