Vinylcyclopropene Photochemistry: Photochemistry Applied to Organic Synthesis. Exploratory and Mechanistic Organic Photochemistry[1,2]

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3-Vinylcyclopropenes have been found to rearrange photochemically to afford cyclopentadienes. The reaction is of both synthetic and mechanistic interest. Direct irradiation of 3-vinyl-1,2,3-triphenylcyclopropene led to 1,2,3-triphenylcyclopentadiene, 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene gave 1,2,3,4-tetraphenylcyclopentadiene, and 3-isobutenyl-1,2,3-triphenylcyclopropene yielded 1,2,3-triphenyl-5,5-dimethylcyclopentadiene and 3-isobutenyl-1,2-diphenylindene in a 2.5:1 ratio, while 3-isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene afforded 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene, 1,3-diphenyl-2-*tert*-butyl-5,5-dimethylcyclopentadiene, 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene, and 3-isobutenyl-1-*tert*-butyl-2-phenylindene in a 3:1:4:3 ratio. Similar photolysis of 1,2,3-triphenyl-3-methylcyclopropene gave 3-methyl-1,2-diphenylindene, while irradiation of 1-methyl-2,3,3-triphenylcyclopropene produced 1-methyl-2,3-diphenylindene. Sensitization of the vinylcyclopropenes led to product only in the case of the isobutenyl-substituted cyclopropenes; the vinyl-bearing molecules were unreactive. Quantum yields were determined for direct and sensitized runs, and where triplet reactivity resulted the sensitized efficiencies were slightly more than tenfold greater than the direct run quantum yields. The results revealed a competing vinyl walk reaction in appropriately substituted reactants. This arises from an incipient di-π-methane rearrangement. A trend of quantum efficiencies was observed in which terminal methyl substitution on the vinyl group inhibits reactivity. Similarly, phenyl substitution at the α carbon of the vinyl group was found to enhance reactivity. Finally, phenyl substitution at carbon 1 of the cyclopropene ring enhanced the reaction efficiency. Regioselectivity was encountered when the cyclopropene π bond was unsymmetrically substituted. Here preference is for new carbon to carbon bond formation at the three-ring π-bond position bearing the alkyl rather than the aryl group. The cyclopentadiene-forming reaction proved to be more efficient than indene formation and dominates where both are a priori possibilities. Carbene and diradical mechanisms are considered.

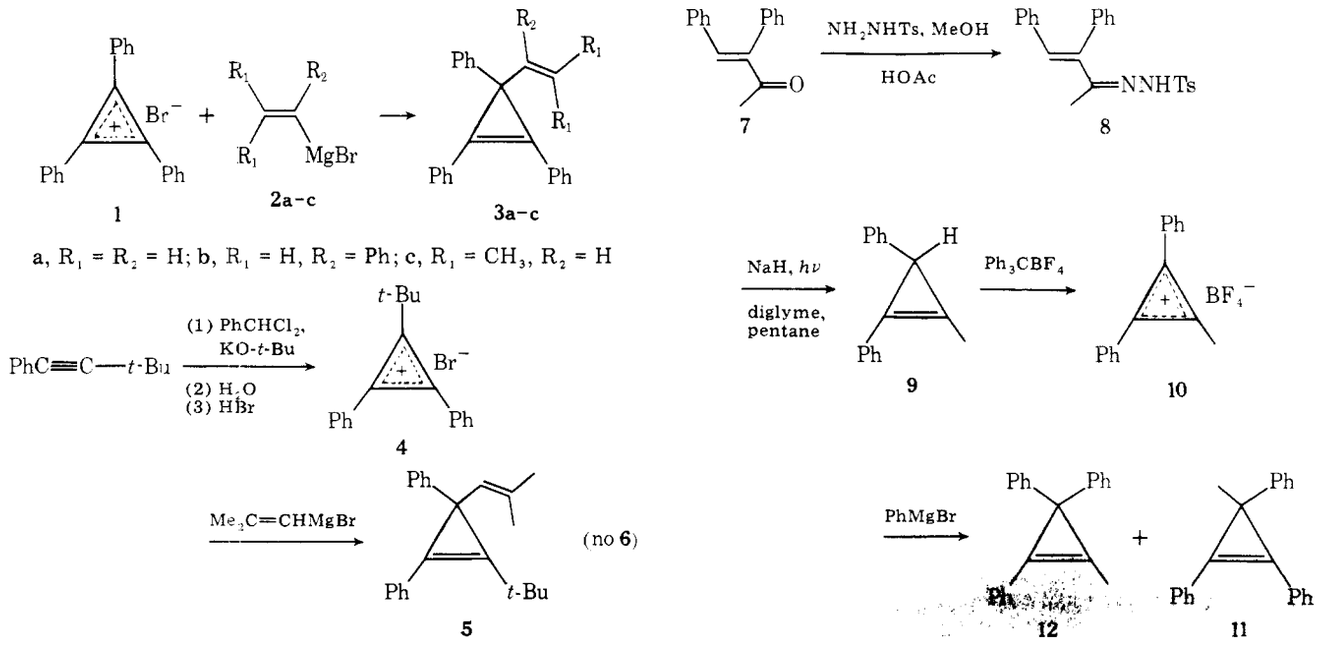
One of the most general of photochemical reactions is the di-π-methane rearrangement.[3] We have been more broadly interested in the photochemistry of molecules containing two π moieties. Our investigations have led us to a study of vinylcyclopropenes. For this study we selected cyclopropenes having some aryl substitution on the three-ring π bond and substitution at the carbon (i.e., C-3) bearing the vinyl group. We were interested in the type of photochemistry observed, in the effect of substitution on the reaction course and reaction efficiency, and in the mechanisms of reactions encountered.

Synthesis of Photochemical Reactants. 3-Vinylcyclopropenes have not been reported previously in the literature.[4] Syntheses are outlined in Chart I, following the known[5,6] reaction of organomagnesium compounds with a cyclopropenium salt. In the preparation of *tert*-butylcyclopropene **5**, no trace of 3-isobutenyl-1,2-diphenyl-3-*tert*-butylcyclopropene (**6**), an a priori product of the reaction, was detectable. Presumably steric hindrance presented a kinetic barrier to formation of this isomer.

Two non-vinyl-substituted cyclopropenes, desired for comparison purposes, 1,2,3-triphenyl-3-methylcyclopropene (**11**)[6] and 1-methyl-2,3,3-triphenylcyclopropene (**12**), also were obtained as outlined in Chart I.[7,8]

Exploratory Photolyses of the Vinylcyclopropenes and Proof of Product Structures. Irradiation of 3-vinyl-1,2,3-triphenylcyclopropene (**3a**) in *tert*-butyl alcohol using a 450-W medium-pressure lamp and a Pyrex filter for 3.25 h

Chart I. Synthesis of Vinylcyclopropenes



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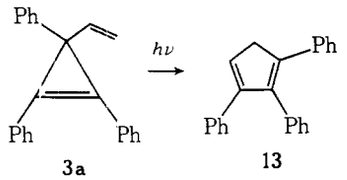
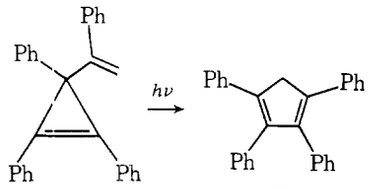
afforded 1,2,3-triphenylcyclopentadiene[9] (13) in 87% yield, identified by the physical data and by independent synthesis. The photoreaction can be depicted as in eq 1a.



(1a)

3a 13

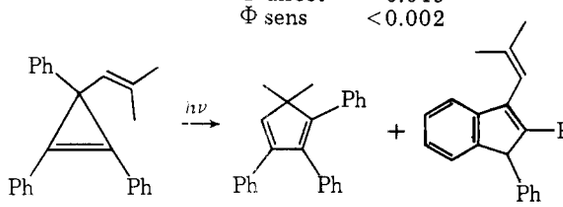
Φ direct 0.027
Φ sens <0.001



(1b)

3b 14

Φ direct 0.049
Φ sens <0.002



(1c)

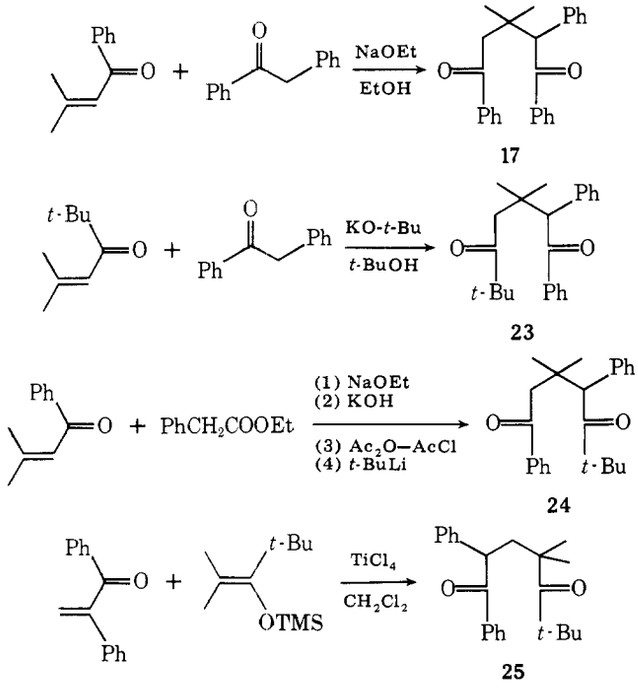
3c 15 16

	15	16
Φ direct	0.010	0.004
Φ sens	0.133	0

Irradiation of the tetraphenylvinylcyclopropene **3b** gave 1,2,3,4-tetraphenylcyclopentadiene (**14**),[10] identified by comparison with an authentic sample. The reaction is shown in eq 1b.

At this juncture it appeared that the reaction involved a formal ring expansion with a [1,3]sigmatropic rearrangement leading from a vinylcyclopropene to a cyclopentadiene. This facilitated structure elucidation in the remaining cases studied.

Chart II. Synthesis of the Diones



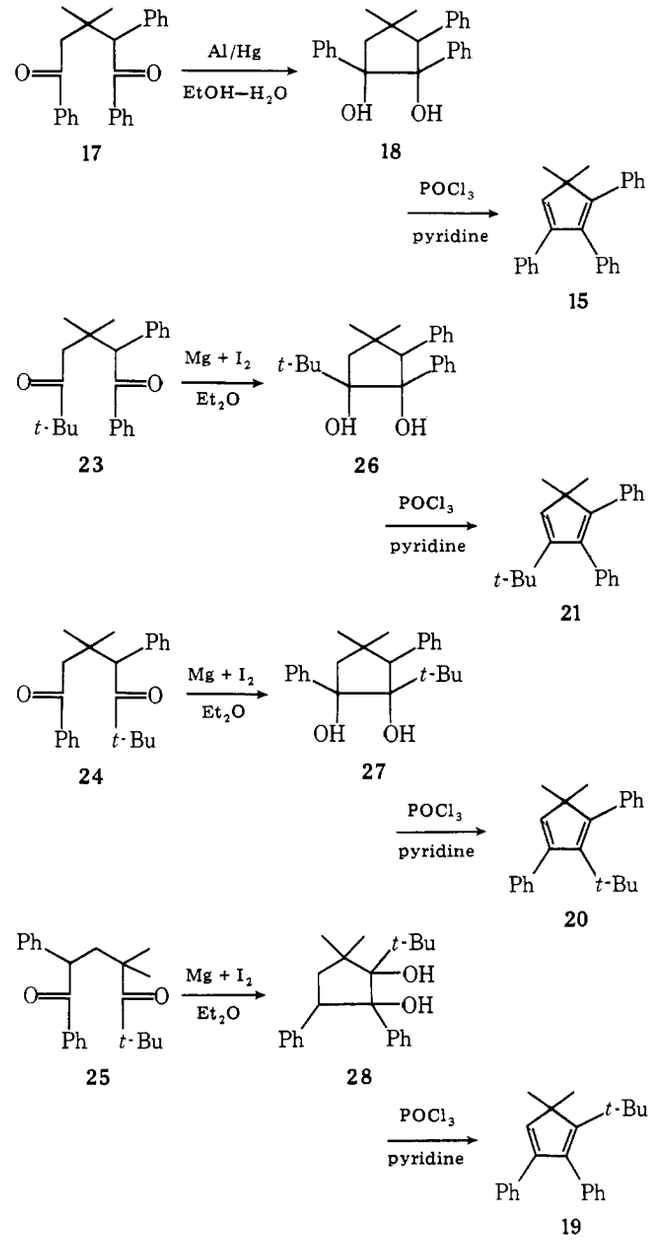
17

23

24

25

Chart III. Synthesis of the Cyclopentadienes



17 18 15

23 26 21

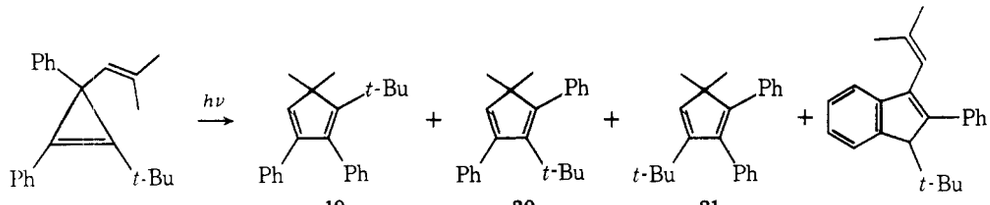
24 27 20

25 28 19

Thus, irradiation of 3-isobutenyl-1,2,3-triphenylcyclopropene (**3c**) gave a cyclopentadiene as the major product (eq 1c). The above formulation of the reaction suggested this to be 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (**15**), which was established by synthesis (see Charts II and III). Additionally, a minor product (**16**) was isolated; however, spectroscopic data indicated that this was not a cyclopentadiene.

The other cyclopentadienes required for structure proofs also were prepared by the general approach of Wislicenus,[10a] and the syntheses are outlined in Charts II and III.

The minor photoproduct (**16**) was an isomer of the cyclopropene reactant as judged from mass spectral and elemental analytical data. It exhibited two three-hydrogen peaks at τ 8.02 and 8.41, each split slightly. A one-hydrogen peak at τ 3.79 also was present. This pattern proved to be general and characteristic of isobutenyl groups in the compounds studied in this investigation and related studies.[11] In addition, there was a τ 5.02 one-hydrogen peak. The minor splitting indicated it to be a methine not adjacent to other hydrogen-bearing carbons. The ultraviolet spectrum possessed absorption at 239 nm (ϵ 17 900) and 305 (14 300), which immediately suggested



	19	20	21	22
Φ direct	0.003	0.001	0.004	0.003
Φ sens	0.13	0	0.06	0

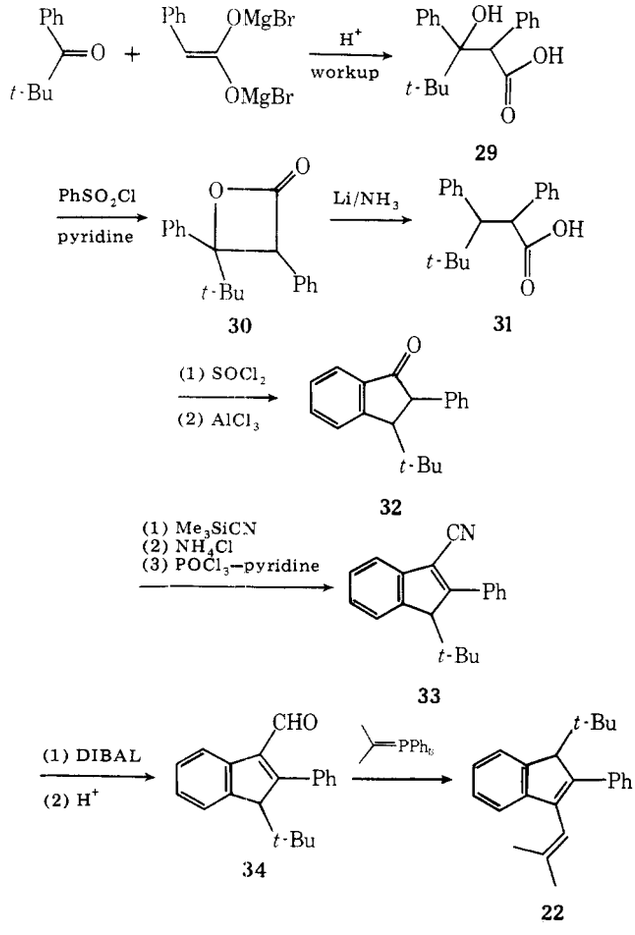
(1d)

a 3-vinyl-3-indene chromophore since this was characteristic of other such indenes studied (vide infra; also note Experimental Section).

This information led to the assignment of the minor photoisomer as 1,2-diphenyl-3-isobutenylindene (**16**). Thus, we may formulate the photochemistry of 3-isobutenyl-1,2,3-triphenylcyclopropene (**3c**) as in eq 1c.

To cast light on the regioselectivity of the photoreaction, 3-isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene (**5**) was examined. Direct irradiation of **5** gave a four-component (**19–22**) product mixture which was separated by silica gel chromatography (eq 1d). The first three products (i.e., **19, 20,** and **21**) proved to be isomeric cyclopentadienes. Their structures were deduced from spectral evidence and were confirmed by independent synthesis as outlined in Charts II and III. The first two of these cyclopentadienes were those expected on the basis of a formal ring expansion as noted above; these were 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (**19**) and 2-*tert*-butyl-1,3-diphenyl-5,5-dimethylcyclopentadiene (**20**). The third photoproduct was established as 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene (**21**); this isomer clearly did not derive from a simple [1,3]sigmatropic ring expansion. The fourth photoproduct, also isomeric with the cyclopropene reactant (high-resolution mass spectrometry), was shown to be 1-*tert*-butyl-2-phenyl-3-isobutenylindene (**22**) by independent synthesis (Chart IV).

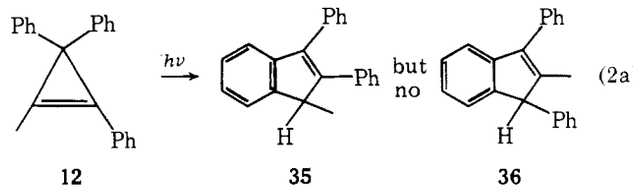
Chart IV. Synthesis of *tert*-Butylindene 22



Comparison Studies Using 3-Arylcyclopropenes. Although the present study is the first dealing with the photochemistry of 3-vinylcyclopropenes, 3-arylcyclopropenes have received some attention. The primary unimolecular photochemistry observed has been indene formation.[12] There has been little mechanistic speculation and no evidence upon which to base a mechanism. However, it has been suggested that the reaction may proceed by fission to give an open biradical of the type $R\dot{C}{=}CR\dot{C}R'_2$.[12a,c,d] Depending on geometry,[13] this may be just a resonance form of one electronic configuration of the corresponding carbene $R\ddot{C}CR{=}CR'_2$.

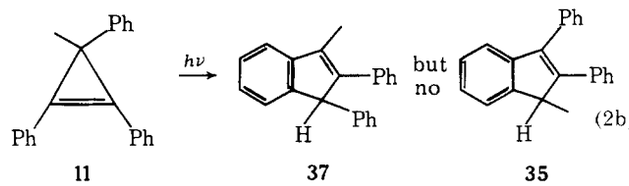
We noted a potential parallel between these 3-phenylcyclopropene systems and the 3-vinylcyclopropenes of our investigation. In particular, the photochemical behavior of 1-methyl-2,3,3-triphenylcyclopropene (**12**) promised to allow a comparison of the reaction regioselectivity with that encountered in the case of *tert*-butyldiphenylisobutenylcyclopropene **5**.

Irradiation of methyltriphenylcyclopropene **12** led to one photoproduct, 1-methyl-2,3-diphenylindene (**35**),[14] an authentic sample of which proved identical to the photoproduct (i.e., **35**). The isomeric indene (**36**) was not detectable (i.e., <5%). Thus, the reaction is regiospecific in forming one of two a priori likely indene products and hence parallels the behavior of the *tert*-butyldiphenylisobutenylcyclopropene **5** (see eq 2a).



(2a)

Another 3-phenylcyclopropene of interest was 3-methyl-1,2,3-triphenylcyclopropene (**11**). Simple extrapolation of the skeletal change observed thus far to this reactant seemed likely to lead to the isomeric indene **37**. This is merely a tautomer of **35** which was formed in the photolysis of the 1-methyl-2,3,3-triphenylcyclopropene (**12**). This photolysis was carried out and did indeed lead to 1,2-diphenyl-3-methylindene (**37**), as noted in eq 2b. The product was known and



(2b)

Table I. Quantum Yields

Reactant	Registry no.	Run[a]	Φ (cyclopentadiene)	Φ (indene)	% conv	Sensitizer
Vinyltriphenylcyclopropene **3a**	62747-62-0	2A	0.028	0	7.0	
		2B	0.027	0	3.9	
		5A	0.001	0	0	Xanthone
Styryltriphenylcyclopropene **3b**	62747-63-1	3A	0.037	0	49	
		3B	0.039	0	34	
		3C	0.047	0	5.5	
		3D	0.049	0	5.1	
		6A	0.016	0	2.1	Xanthone
		6B	0.013	0	2.5	Xanthone
		6C	0.002	0	2.4	4-Dimethylaminobenzophenone
Isobutenyltriphenylcyclopropene (**3c**)	62747-64-2	1A	0.0102	0.004	21.2	
		1B	0.0097	*b*	5.9	
		1C	0.0099	*b*	4.2	
		4A	0.140	0	35.6	4-Dimethylamino-
		4B	0.128	0	61.7	benzophenone
tert-Butylisobutenylcyclopropene **5**	62747-65-3	7A	0.003 (1-*tert*-Bu)			
			0.001 (2-*tert*-Bu)	0.003	20	
			0.004 (3-*tert*-Bu)			
		8B	0.13 (1-*tert*-Bu)			Xanthone
			0 (2-*tert*-Bu)	0	63	
			0.06 (3-*tert*-Bu)			

[a] Run numbers correspond to the Experimental Section. [b] Not determined.

synthesized by the literature procedure[14] for direct comparison. In this instance none (<5%) of the tautomer **35**, an a priori possibility, was formed.

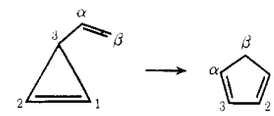
Quantum Yield Determinations and Determination of Multiplicities. We were interested in determining the reaction efficiencies for the various 3-vinylcyclopropene rearrangements in order to correlate these with structure. Also, we were interested in determining efficiencies as a function of direct vs. sensitized conditions with the aim of determining the multiplicity of the excited state undergoing the rearrangement.

All of the quantum yield determinations were carried out with a Wisconsin black box apparatus[15] using solution filters to isolate the wavelength range absorbed by the reactant or sensitizer. An electronic actinometer[16] was employed; this utilized two 1P28 photomultipliers, a multiplexed voltage to frequency converter, and two digital counters. This was calibrated prior to each run and for each wavelength filter used. Low enough conversions were used in each case so that light absorption by products was unimportant; extrapolation to zero time was employed where necessary. Only in the case of 1,3-diphenyl-2-*tert*-butyl-3-isobutenylcyclopropene (**5**) was it not possible to avoid some product light absorption, and up to 20% of the light could have been captured by products, thus diminishing the determined efficiencies by this amount. The reaction efficiency for formation of the unexpected cyclopentadiene **21** is an operational, but not directly theoretically significant number, since this product derives from a two-photon mechanism (vide infra).

The results of the quantum yield determinations are summarized in Table I; note also eq 1a–d. Details of the runs are outlined in the Experimental Section.

Turning now to information bearing on the reaction multiplicity, we note that xanthone (E_T = 71–74 kcal/mol[17a,b]) and *p*-dimethylaminobenzophenone (E_T = 67 kcal/mol[17c]) have energies which should be much higher than any of the triplets of the cyclopropenes studied because of their styrene (E_T = 62 kcal/mol[18]) and *cis*-stilbene (E_t = 57 kcal/mol[19]) chromophores.

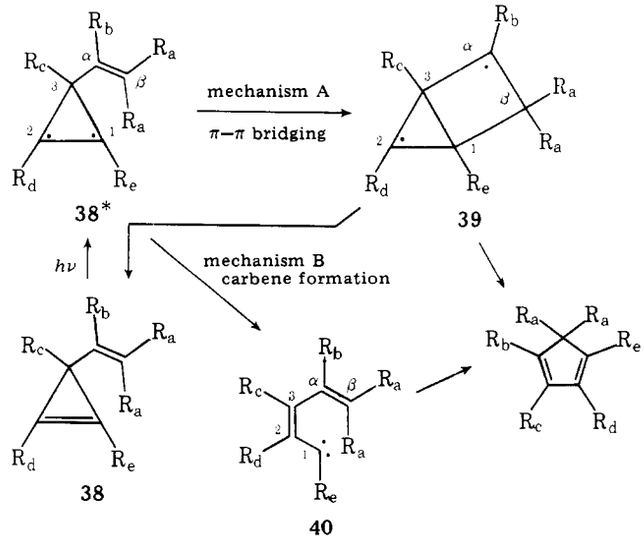
Interpretative Discussion. The first item for discussion is the gross reaction mechanism. Operationally, the skeletal change corresponds to a [1,3]sigmatropic rearrangement in which a three-ring σ bond moves 1,3 and attaches itself to the terminal carbon of the vinyl group (i.e., bond 1–3 breaks and reforms as 1–β, eq 3).



(3)

Two a priori mechanisms seem reasonable. The first of these is termed mechanism A (note Chart V). It begins with π–π bridging in the excited state, with the terminal carbon of the vinyl group bonding to one end of the excited cyclopropene double bond. This leads to housane biradical **39** which may be viewed as a 1,4 diradical in two ways: $\dot{C}_2$–C_1–C_β–$\dot{C}_\alpha$ or $\dot{C}_2$–C_1–C_3–$\dot{C}_\alpha$. Fission of the central bond of such diradicals is common in photochemistry.[20] The first type of fission

Chart V. Possible Mechanisms for the Cyclopropene Rearrangement



merely regenerates the vinylcyclopropene reactant. The second type leads to the observed cyclopentadiene product.

Alternative mechanism B is also shown in Chart V. Here, the excited state undergoes fission of bond 1–3 to give carbene **40**, followed by an electrocyclic closure to give cyclopentadiene product. Indeed, there is evidence for the formation of carbenes and diradical configurations of carbenes from cyclopropenes both thermally[21] and photochemically.[12,22]

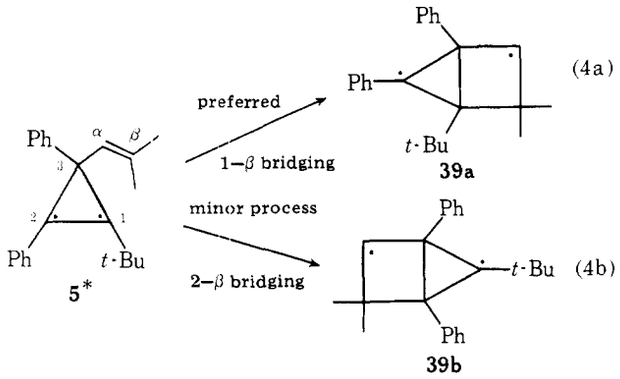
Both mechanisms are skeletally equivalent and lead to the change outlined in Chart V. With regard to the formation of indenes, as encountered in the present study and also as described in the literature,[12] either mechanism will account for the observed products. A diradical variant of the carbene mechanism has already been considered as a possibility in the literature[12a,c,d] (vide supra).

Our evidence accords nicely with the excited-state diradical mechanism A. While mechanism B can not be ruled out, it does not fit the evidence as well.

The first cogent evidence to be considered is the effect of phenyl substitution as group R_b (note Chart V) on the α position of the vinyl group of the 3-vinylcyclopropenes. Reference to eq 1a and 1b (note also Table I) shows that this phenyl substitution enhances the reaction efficiency by nearly a factor of two. This is understood on the basis of mechanism A (note Chart V); here odd-electron density becomes concentrated on the α carbon of housane diradical **39**, where aryl substitution should stabilize. In this argument, we recognize that quantum yields do not invariably parallel excited-state rate constants.[20b] Nevertheless, strongly suggestive evidence is provided.

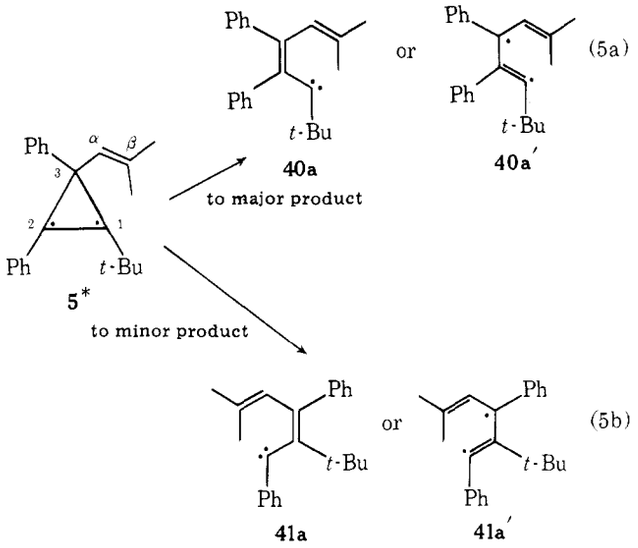
The second point concerns the regioselectivity encountered both in the photorearrangement of *tert*-butyldiphenylisobutenylcyclopropene **5** and in the irradiation of methyltriphenylcyclopropene **12**. Here a consistent pattern is observed.

In the case of the isobutenylcyclopropene **5**, there is a preference for that product arising from bonding between C-1 and the β carbon (note Chart V and eq 1d), although bonding between C-2 and the β carbon was an a priori possibility. This makes sense in terms of mechanism A, where there is a preference for R_d to be phenyl rather than *tert*-butyl as a consequence of the demand for odd-electron delocalization by the phenyl substituent. This can be formulated as shown in eq 4a,b.

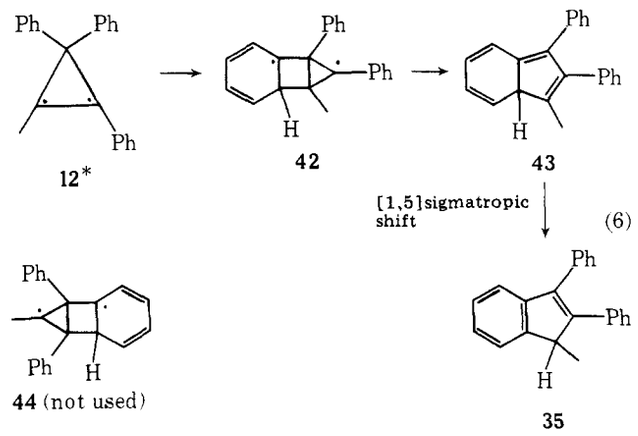


Conversely, mechanism B seems in discord with the reaction regioselectivity since it would require fission of that cyclopropene bond which would afford the less stable *tert*-butyl-substituted carbene (or its diradical configuration **41a'**) rather than the more stable aryl-stabilized carbene **41a** (eq 5a,b).

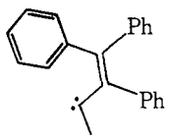
The same logic applies to the preferential formation of one indene (i.e., **35** in eq 2a) in the photolysis of 1-methyl-2,3,3-triphenylcyclopropene (**12**). The diradical mechanism predicts that bridging between the excited cyclopropene double bond



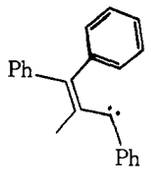
and the ortho position of a phenyl group at C-3 should be preferred since this gives maximum odd-electron delocalization (compare **42** vs. **44**, eq 6).



Again, the carbene mechanism B would require formation of the non-aryl-stabilized carbene **45** in order to account for the regiospecificity.



45 (less stabilized; used in mech B)



46 (more stabilized; not used in mech B)

If there is a weakness in this argument, it derives from our lack of knowledge of the effect of phenyl substitution on the kinetics of opening of the cyclopropenyl σ bond. Thus, for example, on excitation the phenyl group is initially coplanar with the three-ring since it is part of an excited styryl moiety. Hence, it does not overlap initially with the σ bond breaking to form a carbene (or diradical configuration). Still, if more energy were to be gained by overlap with the σ rather than with the π component of the carbene, phenyl rotation should occur.

Another result of interest is the higher reaction efficiency observed in the direct irradiations of the simple vinylcyclopropenes relative to the isobutenyl analogues (note Table I and equations 1a–d). This is logically derived from steric hindrance in the approach of the β carbon of the vinyl group to the electronically excited cyclopropene π bond as pictured in mechanism A. To the extent that there is a trend in carbene reactivity, the present experimental results are the reverse of that which one would expect. Where preferences are shown, it is the more substituted π bond which tends to be more reactive;[23] thus, mechanism B would suggest that the diminished reactivity of the isobutenyl-substituted cyclopropenes is in contrast to expectation.

Additionally, the carbene mechanism could lead to either of two stereoisomers in the case of the reaction of 3-vinylcyclopropenes; for example, note carbenes **40a** and **41a** in eq 5a and 5b. Both carbenes have the divalent carbon pictured cis to the terminal double bond, thus mechanistically allowing electrocyclic closure to the cyclopentadiene product. One might argue that the observed regioselectivity could be accounted for on the basis of a carbene process (i.e., mechanism B) if ring opening of excited state **5*** to give the *tert*-butyl-substituted carbene **40a** afforded the cis isomer required for completion of the reaction while ring opening to give the phenyl-substituted carbene gave the trans stereoisomer of **41a,** which could not cyclize.[24] However, the case of the 3,3-diphenylcyclopropene **12** has no such stereochemical possibilities since carbenes **45** and **46** both have a *cis*-phenyl group; yet, the same regiospecificity was observed.

Another point is that in addition to preferentially obtaining the cyclopentadiene **19,** which would have to be derived from the less stable *tert*-butylcarbene **40a,** the only indene product (**22**) is the one expected from the trans isomer (**40b**) of the same carbene (**40a**). This argues against unfavorable carbene stereochemistry controlling since the stereoisomer of phenylcarbene **41,** which is unfavorable for cyclopentadiene formation, should be favorable for indene generation. Yet, the indene derived from the more stable carbene **41b** (isomer of **41a**) is not observed.

Finally, in connection with the carbene mechanism, one might concern himself that three-ring opening is reversible and that the less stable of the two carbenes preferentially closes to cyclopentadiene while the more stable carbene reverts preferentially to cyclopropene. Indeed, reversion to cyclopropene could be more rapid than five-ring formation for entropy reasons, and formation of cyclopropenes from carbenes is expected. However, the transition state in carbene mechanism B has some residual carbene character, and the transition state derived from the more stable carbene should be favored. This is tantamount to saying that the effect of carbene stabilization by phenyl should be greater on the first step's preequilibrium constant than in slowing five-ring cyclization in the second step by virtue of the more stable carbene being less reactive. The three-ring opening step involves formation of a full carbene center, while the second step only partially dissipates this valence.

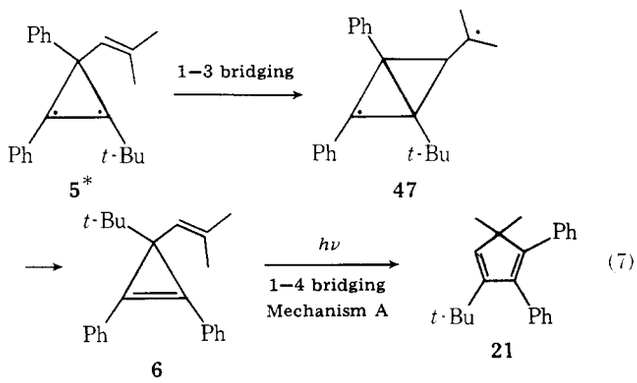
We now turn to the reaction multiplicity. In the nonisobutenyl examples, the evidence points to the excited singlet as the rearranging species. Thus, sensitization of reactants gave no rearrangement.

In the case of the 3-isobutenylcyclopropenes **3c** and **5,** both direct and sensitized irradiations led to reaction. The direct irradiations do indeed represent reactions of the excited singlets rather than mere intersystem crossing to give the triplets with subsequent reaction. This is clear from inspection of eq 1c and 1d, which reveal that the indene products resulting from the direct irradiation are absent in the sensitized runs. Also, the minor cyclopentadiene photoproduct **20** that formed on the direct irradiation of *tert*-butylisobutenylcyclopropene **5** was absent in the sensitized runs. This means that the direct irradiations had product distributions distinctly different from those of the sensitized runs and that the products must derive from an excited state other than the triplet state.

Remarkably, the isobutenyl triplet quantum yields were approximately an order of magnitude greater than the singlet ones. The regioselectivity was enhanced even further in the triplet reaction compared with the singlet process. This marked triplet reactivity though was confined to the isobutenyl-bearing reactants. It is possible that the reactivity difference between the simple vinyl cases and these is derived from steric hindrance of the free rotor energy dissipation,[25] often diminishing the reactivity of triplets having potentially rotating π bonds.

Bearing on the carbene vs. diradical mechanism is Pincock's finding[22d,e] that three-ring opening does not appear to occur in an analogous cyclopropene triplet. Since bimolecular photochemistry intervened, the argument is not entirely conclusive. But the high triplet reactivity of the presently studied vinylcyclopropenes contrasts and thus suggests the lack of carbene involvement in the sensitized examples.

The last aspect requiring discussion is the formation of a product not derived from the mechanisms discussed above. Thus, 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene (**21**) was isolated in both the direct and sensitized reactions of *tert*-butylisobutenylcyclopropene **5.** This is a product which would be expected from an isomeric cyclopropene reactant, namely, 1,2-diphenyl-3-*tert*-butyl-3-isobutenylcyclopropene (**6**). Such a cyclopropene can be seen as arising from an incipient di-π-methane rearrangement to give diradical **47** (note eq 7), which then can revert to reactant or proceed onward to



(7)

the isomeric cyclopropene **6.**[26] This cyclopropene then should proceed onward to give the observed anomalous cyclopentadiene product **21.** NMR monitoring of the reaction did not reveal the cyclopropene intermediate (i.e., **47**), and thus it appears to be consumed as rapidly as it is formed; with a *cis*-stilbenyl chromophore, enhanced absorbtion by **6** is indeed expected.

In summary, the rearrangement of vinylcyclopropenes reveals itself, independent of which mechanism eventually proves to be correct, to be a potentially useful synthetic approach to substituted cyclopentadienes. The reaction promises to be especially general and thus adds to the repertoire of organic photochemical processes. Further efforts on the reaction mechanism and the limits of the reaction are continuing in our laboratories.

Experimental Section[27]

1,2,3-Triphenyl-3-methylcyclopropene. The cyclopropene was prepared by the method of Breslow and Dowd.[6]

1,2-Diphenyl-3-methyl- and 2,3-Diphenyl-1-methylindene. The indenes were prepared by the method of Koelsch and Johnson.[14]

***trans*-3,4-Diphenylbut-3-en-2-one Tosylhydrazone.** A solution

of 29.1 g (131 mmol) of *trans*-3,4-diphenylbut-3-en-2-one[28] and 24.4 g (131 mmol) of *p*-toluenesulfonylhydrazine in 500 mL of anhydrous methanol containing 2 mL of glacial acetic acid was refluxed for 3 h. After cooling, the tosylhydrazone was filtered and washed with methanol. Drying in vacuo gave 44.9 g (88%) of the tosylhydrazone: mp 142–144.5 °C; NMR ($CDCl_3$) τ 8.03 (s, 3 H, CH_3), 7.53 (s, 3 H, CH_3), 2.20–3.33 (m, 16 H, aromatic and vinyl), 1.75 (broad s, 1 H, NH); IR ($CHCl_3$) 2.79, 3.03, 3.11, 3.25, 3.31, 3.42, 3.48, 6.26, 6.70, 6.94, 7.24, 7.50, 7.67, 7.78, 7.90, 8.47, 8.63, 9.20, 9.49, 9.86, 11.03, 11.24, 12.00, 12.38, 14.53 μm.

1,3-Diphenyl-2-methylcyclopropene. The following procedure is based on the general method of Dürr.[7] A degassed suspension of 19.5 g (50.0 mmol) of 3,4-diphenylbut-3-en-2-one tosylhydrazone and 3.00 g (125 mmol) of oil-free sodium hydride in 3 L of 9:1 (v/v) pentane–diglyme was irradiated, with vigorous stirring, through a 2-mm Pyrex filter with a 450-W medium-pressure mercury lamp until TLC analysis indicated complete consumption of the starting material. The suspension was filtered, and the filtrate was thoroughly washed with water. The pentane solution was dried and concentrated in vacuo to give 7.20 g of a light yellow oil. The oil was taken up in ca. 10 mL of pentane and stored in a freezer overnight. The solid impurities were removed by filtration, and the filtrate was concentrated in vacuo. This was repeated to give 6.10 g (59%) of NMR-pure cyclopropene. Attempts to chromatograph the cyclopropene led to extensive decomposition: NMR (CCl_4) τ 7.68 (s, 3 H, CH_3), 7.20 (s, 1 H, CH), 2.54–3.35 (m, 10 H, aromatic); IR (CCl_4) 3.26, 3.29, 3.42, 5.43, 6.26, 6.73, 6.94, 7.42, 8.35, 9.08, 9.35, 9.78, 11.05, 14.53 μm. MS Calcd for $C_{16}H_{14}$: *m/e* 206.10955. Found: *m/e* 206.10986.

1,2-Diphenyl-3-methylcyclopropenium Fluoroborate. The general method of Breslow[8] was used. To a solution of 9.24 g (28.0 mmol) of trityl fluoroborate in 50 mL of dry acetonitrile was added a solution of 6.10 g (29.6 mmol) of 1,3-diphenyl-2-methylcyclopropene in 75 mL of anhydrous ether. After stirring for 30 min the solution was diluted with 800 mL of cold anhydrous ether. The precipitate was filtered and dried to give 3.65 g (45%) of the fluoroborate salt: NMR (CD_3CN) τ 6.79 (s, 3 H, CH_3), 1.48–2.36 (m, 10 H, aromatic); IR (KBr) 3.16, 3.28, 3.35, 3.42, 6.30, 6.71, 7.08, 7.48, 7.67, 7.73, 7.85, 8.54, 9.60, 13.05, 14.67 μm.

The fluoroborate was also prepared from 1,2-diphenyl-3-methylcyclopropene.[29]

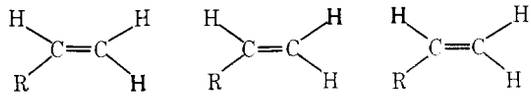
1-Methyl-2,3,3-triphenylcyclopropene. Method A. To a stirred suspension of 4.39 g (16.8 mmol) of 1,2-diphenyl-3-methylcyclopropenium fluoroborate in 200 mL of anhydrous ether was added 20 mL of 1 M phenylmagnesium bromide in ether. After 1 h the mixture was poured into water and extracted with ether. The ether extract was dried and concentrated in vacuo to give a 2:1 mixture of 1,2,3-triphenyl-3-methylcyclopropene and 1-methyl-2,3,3-triphenylcyclopropene. The cyclopropenes were separated by column chromatography on silica gel.

Method B. A mixture of 45.0 g (388 mmol) of diphenyldiazomethane and 10.0 g (51.6 mmol) of 1-phenylpropyne was stirred at room temperature until the purple color disappeared. The excess 1-phenylpropyne was removed in vacuo. Ether was added and the benzophenone azine was removed by filtration. The azine was washed with ether, and the combined filtrates were concentrated in vacuo. From the residue 437 mg (3.3%) of 1-methyl-2,3,3-triphenylcyclopropene, mp 94–95.5 °C, was obtained after chromatography on a 2.5 × 7.5 cm silica gel column and recrystallization from ethanol: NMR (CCl_4) τ 7.60 (s, 3 H, CH_3), 2.33–3.17 (m, 15 H, aromatic); IR ($CHCl_3$) 3.25, 3.27, 3.32, 3.44, 3.52, 5.40, 6.23, 6.72, 6.94, 7.12, 8.70, 8.95, 9.36, 9.77, 10.03, 10.20, 10.97, 11.29, 14.51 μm; UV (EtOH) λ_{max} 261 nm (ϵ 15 900). MS Calcd for $C_{22}H_{18}$: *m/e* 282.14085. Found: *m/e* 282.14034.

1,2,3-Triphenyl-3-isobutenylcyclopropene. To a stirred ether suspension (200 mL) of 6.94 g (20.0 mmol) of triphenylcyclopropenium bromide[30] was added 50.0 mmol of isobutenylmagnesium bromide[31] in 50 mL of tetrahydrofuran. The suspension was stirred for 30 min before quenching with water. The aqueous phase was extracted with ether, and the extract was washed with water, dried, filtered, and concentrated in vacuo. The residue, a yellow oil which crystallized on standing, was purified by percolating through a 2.5 × 15 cm column of silica gel, eluting with 2.5 L of hexane. The colorless solid product was recrystallized from ethanol to give 4.06 g (63%) of the pure cyclopropene: mp 133–135 °C; NMR (CCl_4) τ 8.42 (broad s, 3 H, CH_3), 8.23 (broad s, 3 H, CH_3), 4.33 (broad s, 1 H, vinyl), 2.29–3.07 (m, 15 H, aromatic); IR (CCl_4) 3.24, 3.26, 3.31, 3.37, 3.43, 5.52, 6.24, 6.72, 6.93, 7.28, 7.70, 8.05, 8.55, 8.68, 10.78, 11.01, 11.41, 14.01, 14.35, 14.55 μm; UV (EtOH) λ_{max} 331 nm (ϵ 20 500), 313 (25 500), 228 (26 600).

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.09; H, 6.98.

1,2,3-Triphenyl-3-vinylcyclopropene. To a stirred ether (200 mL) suspension of 6.94 g (20.0 mmol) of triphenylcyclopropenium bromide[30] was added 40.0 mmol of vinylmagnesium bromide[31] in 50 mL of tetrahydrofuran. The reaction mixture was stirred at room temperature for 30 min before quenching with water. The aqueous solution was extracted with ether, and the extract was washed with water, dried, and concentrated in vacuo. The product was percolated through a 2.5 × 90 cm column of silica gel. Elution with 4 L of hexane and recrystallization from ethanol gave 3.54 g (60.2%) of a pure colorless solid: mp 88.5–90.0 °C; NMR (CCl_4) τ 4.90 (d, 1 H, see i below), 4.96 (d, 1 H, see ii below), 3.45 (dd, 1 H, see iii below), 2.00–3.04 (m,



i ii iii

15 H, aromatic); IR (CCl_4) 3.22, 3.26, 3.29, 3.43, 3.46, 5.50, 6.18, 6.25, 6.37, 6.72, 6.92, 7.13, 7.25, 7.55, 7.67, 7.78, 8.12, 8.55, 8.67, 9.13, 9.35, 9.78, 10.11, 10.38, 10.79, 11.06, 13.93, 14.60, 15.00 μm; UV (EtOH) λ_{max} 328 nm (ϵ 20 500), 313 (22 700), 227 (20 500).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.93; H, 5.97.

1,2,3-Triphenylcyclopentadiene. A sample of 1,2,5-triphenyl-1,5-pentanedione was prepared according to the procedure of Allen and Barker.[32] To a solution of 5.00 g (15.5 mmol) of the dione in 120 mL of 2:1 ethanol–water (v/v) was added a large excess of freshly prepared aluminum amalgam, prepared from 1.44 g of aluminum foil and 2% aqueous mercuric chloride followed by rinsing. The mixture was refluxed for 3 h, cooled, and filtered. The solid materials were washed with ether and the combined filtrates concentrated in vacuo. From the colorless oil 1.00 g of the desired diol, mp 132.5–133.5 °C (lit. 132.5–133.5 °C), was obtained by trituration from methanol. The residue obtained from concentration of the filtrate was chromatographed on a 2.5 × 90 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in 5% ether–hexane). The elution was with 500-mL fractions; fractions 5–7 contained 1.98 g of the desired diol, making the total yield 2.98 g (59.6%). Dehydration of the diol as described by Pauson[9] gave the cyclopentadiene: NMR (CCl_4) τ 6.47 (d, 2 H, J = 1.5 Hz, CH_2), 3.60 (t, 1 H, J = 1.5 Hz, vinyl), 2.70–3.21 (m, 15 H, aromatic); IR (CS_2) 3.23, 3.25, 3.28, 3.47, 5.16, 5.38, 5.58, 6.25, 7.31, 7.42, 7.74, 8.05, 8.24, 8.50, 9.35, 9.44, 9.75, 10.24, 10.87, 11.02, 11.33, 11.48, 14.45 μm; UV (EtOH) λ_{max} 239 nm (ϵ 24 200), 310 (8080). MS Calcd for $C_{23}H_{18}$: *m/e* 294.14085. Found: *m/e* 294.14061.

1,2,3-Triphenyl-3-(1-phenylvinyl)cyclopropene. To a stirred ether (200 mL) suspension of 5.10 g (15.0 mmol) of triphenylcyclopropenium bromide[30] was added 20.0 mmol of 1-phenylethenylmagnesium bromide[31] in 30 mL of tetrahydrofuran. The reaction mixture, after stirring for 45 min, was hydrolyzed by pouring it into water. The aqueous solution was extracted with ether, and the extract was washed with water, dried, and concentrated in vacuo. The resulting yellow oil, which crystallized on standing, was recrystallized from ethanol to give 2.55 g (48%) of the pure cyclopropene: mp 121.5–122.5 °C; NMR (CCl_4) τ 4.63 (s, 2 H, vinyl), 2.00–3.10 (m, 20 H, aromatic); IR (CCl_4) 3.24, 3.26, 3.31, 3.48, 5.52, 6.24, 6.37, 6.71, 6.92, 7.15, 7.24, 7.78, 8.15, 8.55, 8.68, 9.33, 9.84, 10.44, 10.72, 11.12, 14.35, 14.55, 14.95 μm; UV (EtOH) λ_{max} 332 nm (ϵ 17 700), 318 (20 800), 228 (28 100).

Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.87; H, 5.98.

1,2-Diphenyl-3-*tert*-butylcyclopropenium Bromide. The following is patterned after the general procedure of Breslow.[30] To a mixture of 7.14 g (50.0 mmol) of *tert*-butylphenylacetylene and 13.46 g (120 mmol) of potassium *tert*-butoxide in 250 mL of dry benzene was added 9.66 g (60.0 mmol) of benzal chloride. The stirred mixture was refluxed under nitrogen for 1.5 h. After cooling the mixture was poured into water and extracted with ether. The ether extract was washed with water, and the ether–benzene solution was dried over anhydrous magnesium sulfate. The cyclopropenium salt was precipitated by bubbling dry hydrogen bromide through the solution. The product was filtered off and dried in vacuo to give 6.20 g (38%) of the bromide: NMR (Me_2SO-d_6) τ 8.33 (s, 9 H, *t*-Bu), 1.33–2.27 (m, 10 H, aromatic); IR (KBr) 3.25, 3.36, 6.27, 6.67, 6.76, 6.92, 7.29, 7.58, 8.24, 11.76, 12.72, 12.90, 14.66 μm.

1,3-Diphenyl-2-*tert*-butyl-3-isobutenylcyclopropene. To a stirred ether (200 mL) suspension of 1,2-diphenyl-3-*tert*-butylcyclopropenium bromide was added 50.0 mmol of isobutenylmagnesium bromide in 50 mL of tetrahydrofuran. The reaction mixture was

stirred at room temperature for 2 h, poured into water, and extracted with ether. The combined ether extract was washed with water and saturated aqueous sodium chloride. The dried ether solution was concentrated in vacuo to give a light yellow oil. The oil was percolated through a 2.5 × 20 cm column of silica gel. Elution with 3 L of hexane gave a colorless oil which was triturated from methanol at −78 °C and recrystallized from methanol to give 2.80 g (46.3%) of the pure cyclopropene: mp 61–63 °C; NMR (CCl_4) τ 8.72 (s, 9 H, *t*-Bu), 8.48 (broad s, 3 H, CH_3), 8.24 (broad s, 3 H, CH_3), 4.56 (broad s, 1 H, vinyl), 2.56–3.10 (m, 10 H, aromatic); IR (CCl_4) 3.23, 3.26, 3.29, 3.33, 3.37, 3.41, 3.43, 3.48, 5.45, 6.27, 6.72, 6.79, 6.93, 7.19, 7.27, 7.35, 7.84, 8.38, 8.53, 8.71, 9.33, 9.42, 9.74, 10.38, 11.01, 11.85, 13.94, 14.33, 14.50, 15.10, 15.70 μm; UV (EtOH) λ_{max} 263 nm (ϵ 19 900), 204 (43 000).

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.33; H, 8.69.

3,3-Dimethyl-1,2,5-triphenyl-1,5-pentanedione. To 8.00 g (50.0 mmol) of 3,3-dimethylacrylophenone[33] and 9.60 g (49.0 mmol) of deoxybenzoin in 150 mL of anhydrous methanol was added 50 mL of a solution of sodium methoxide in anhydrous methanol (prepared by dissolving 1.20 g of sodium in 50 mL of anhydrous methanol). The solution was refluxed for 3 h. The cooled reaction mixture was acidified with glacial acetic acid. The methanol was removed in vacuo, and the residue was taken up in ether–water. The aqueous solution was extracted with ether. The combined extract was washed with water and saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether was concentrated in vacuo, leaving an oil which was chromatographed on a 2.5 × 200 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane): fractions 1–6, 6 L of hexane, 2.32 g of unidentified material; 7–9, 1.75 L of 0.5% ether–hexane, 3.32 g of 3,3-dimethylacrylophenone; 10–22, 1.9 L of 0.5% ether–hexane, 3.84 g of deoxybenzoin; 23–29, 1.75 L of 1% ether–hexane, 2.13 g of deoxybenzoin; 30–40, 2.75 L of 2.5–7.5% ether–hexane, 3.02 g (17.3%) of the desired diketone as a colorless oil. The dione was sufficiently pure enough for further transformations. A portion of the dione was rechromatographed and molecularly distilled to give a material with an unchanged NMR spectrum: NMR (CCl_4) τ 8.80 (s, 3 H, CH_3), 8.75 (s, 3 H, CH_3), 6.52–7.40 (AB q, 2 H, J = 16 Hz, CH_2), 4.67 (s, 1 H, CH), 1.97–3.03 (m, 15 H, aromatic); IR (NaCl) 3.23, 3.26, 3.30, 3.37, 3.42, 3.48, 5.97, 6.25, 6.32, 6.70, 6.90, 7.12, 7.20, 7.34, 7.70, 8.03, 8.22, 8.50, 8.63, 9.30, 9.68, 9.93, 10.00, 10.35, 10.78, 11.10, 11.80, 12.75, 13.10, 13.31, 13.52, 14.30, 14.53, 15.18 μm.

Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.14; H, 6.83.

4,4-Dimethyl-1,2,3-triphenyl-1,2-cyclopentanediol. To a solution of 921 mg (2.59 mmol) of 3,3-dimethyl-1,2,5-triphenyl-1,5-pentanedione in 30 mL of 2:1 (v/v) ethanol–water was added a tenfold excess of aluminum amalgam prepared from 240 mg of aluminum foil by dipping in 2% aqueous mercuric chloride followed by rinsing with ethanol and ether. The mixture was refluxed for 4.5 h, cooled, and filtered. The solid material was washed with ether, and the filtrate was concentrated in vacuo to give 778 mg (83.6%) of a mixture of diastereomeric diols. The major stereoisomer was separated by fractional recrystallization from hexane, giving 368 mg (39.5%), and the minor isomer was isolated in a less pure state. For further transformation either isomer or a mixture of the isomers was successfully used. Major isomer: mp 186.5–188 °C; NMR ($CDCl_3$) τ 8.85 (s, 3 H, CH_3), 8.60 (s, 3 H, CH_3), 6.90–8.05 (AB q, 2 H, J = 14 Hz, CH_2), 5.73 (s, 1 H, CH), 8.17 (broad s, 1 H, OH), 7.90 (broad s, 1 H, OH), 2.30–3.05 (m, 15 H, aromatic); IR ($CHCl_3$) 2.86, 2.89, 3.22, 3.26, 3.32, 3.37, 3.47, 6.26, 6.73, 6.94, 7.35, 7.60, 7.85, 8.78, 9.08, 9.28, 9.47, 9.70, 10.08, 14.40 μm.

Minor isomer: mp 129–135 °C; NMR (CCl_4) τ 8.73 (s, 3 H, CH_3), 8.67 (s, 3 H, CH_3), 7.03–7.73 (AB q, 2 H, J = 15 Hz, CH_2), 6.47 (s, 1 H, CH), 6.80 (broad s, 1 H, OH), 6.07 (broad s, 1 H, OH), 2.40–3.20 (m, 15 H, aromatic).

Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.64; H, 7.36.

5,5-Dimethyl-1,2,3-triphenylcyclopentadiene. A mixture of the above diols was prepared from 712 mg (2.00 mmol) of 1,2,5-triphenyl-3,3-dimethyl-1,5-pentanedione as described above. The diols (531 mg, 1.48 mmol) were dissolved in 12 mL of dry pyridine containing 0.80 mL (8.73 mmol) of phosphorous oxychloride and refluxed for 23 h. After cooling, the solution was partitioned between ether and water. The aqueous solution was extracted with ether, and the combined extract was washed with saturated aqueous ammonium chloride, water, and saturated aqueous sodium chloride. The ether solution was dried and concentrated in vacuo. The crude product was chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). After three developments with hexane, the fastest moving band was collected and the residue recrystallized from ethanol to give 411 mg (84%) of the cyclopentadiene as a colorless solid: mp 137.5–138.5 °C; NMR (CCl_4) τ 8.67 (s, 6 H, CH_3's), 3.67 (s, 1 H, vinyl), 2.20–3.33 (m, 15 H, aromatic); IR (CCl_4) 3.27, 3.30, 3.37, 3.42, 3.48, 6.30, 6.72, 6.81, 6.92, 7.41, 8.32, 8.61, 9.32, 9.77, 11.09, 12.15, 12.64, 12.91, 13.10, 13.50, 13.95, 14.32 μm; UV (EtOH) λ_{max} 300 nm (ϵ 3200), 242 (32 900).

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.08; H, 6.93.

Ethyl 3,3-Dimethyl-2,5-diphenyl-5-oxopentanoate. A solution of sodium ethoxide in ethanol was prepared by dissolving 1.95 g of sodium in 40 mL of absolute ethanol. To the solution was added 12.3 g (75.0 mmol) of ethyl phenylacetate and 14.0 g (87.5 mmol) of 3,3-dimethylacrylophenone. The solution was stirred at room temperature for 26 h and poured into dilute aqueous acetic acid. The aqueous solution was extracted with ether, and the combined ether extract was washed with saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The ether solution was dried over anhydrous magnesium sulfate and concentrated in vacuo. The yellow oil was subjected to chromatography on a 2.5 × 140 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane): fractions 1–4, 3 L of 0.5% ether–hexane, nil; 5–9, 2.5 L of 1% ether–hexane, 9.22 g of a mixture of ethyl phenylacetate and an unidentified product; 10–17, 4 L of 1% ether–hexane, 9.56 g (39.5%) of the desired keto ester as a yellow oil. The spectral properties were as follows: NMR ($CDCl_3$) τ 8.87 (t, 3 H, J = 7 Hz, $-OCH_2CH_3$), 8.67 (s, 3 H, CH_3), 8.63 (s, 3 H, CH_3), 6.53–7.42 (AB q, 2 H, J = 16 Hz, CH_2), 4.07 (d of q, 2 H, J = 1.5, 7.0 Hz, $-OCH_2CH_3$), 5.97 (s, 1 H, CH), 1.92–2.80 (m, 10 H, aromatic); IR ($CHCl_3$) 3.18–3.50 broad, 5.80, 5.95, 6.25, 6.32, 6.70, 6.82, 6.91, 7.30, 7.39, 7.53, 7.69, 7.87, 7.97, 8.05, 8.20, 8.51, 8.58, 8.70, 8.91, 8.97, 9.15, 9.26, 9.62, 9.71, 9.96, 10.10, 10.36, 10.85, 12.42, 14.56 μm. MS Calcd for $C_{21}H_{24}O_3$: *m/e* 324.17254. Found: *m/e* 324.17192.

3,3-Dimethyl-2,5-diphenyl-5-oxopentanoic Acid. To a solution of 29.0 g (518 mmol) of potassium hydroxide in 200 mL of 95% ethanol was added 17.2 g (53.1 mmol) of ethyl 3,3-dimethyl-2,5-diphenyl-5-oxopentanoate. The solution was refluxed for 45 min. After cooling, water was added and the mixture was extracted with ether. The ether extract was discarded. The aqueous solution was acidified with glacial acetic acid, and the mixture was extracted with ether. The ether extract was washed with saturated sodium bicarbonate, water, and saturated sodium chloride. The dried solution was concentrated in vacuo to give 11.2 g (75%) of the crude acid. Recrystallization from ether–pentane gave the pure acid, mp 111–113 °C, in slightly diminished yield: NMR ($CDCl_3$) τ 8.84 (s, 3 H, CH_3), 8.76 (s, 3 H, CH_3), 6.62–7.26 (AB q, 2 H, J = 15 Hz, CH_2), 5.88 (s, 1 H, CH), 1.90–2.81 (m, 10 H, aromatic), 0.52 (broad s, 1 H, COOH); IR ($CHCl_3$) 2.70–4.10, 5.08, 5.29, 5.83–5.97, 6.25, 6.32, 6.70, 6.90, 7.07, 7.22, 7.35, 7.55, 7.70, 8.13, 8.30, 8.48, 8.60, 9.00, 9.27, 9.68, 9.90, 11.08, 14.55, 15.05 μm.

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.14; H, 6.50.

4,4-Dimethyl-3,5-diphenyl-3,4-dihydro-2-pyrone. A mixture of 1.50 g (5.06 mmol) of 3,3-dimethyl-2,5-diphenyl-5-oxopentanoic acid, 25 mL of acetic anhydride, and 10 mL of acetyl chloride was refluxed for 46 h. After removal of the solvent in vacuo, the residue was taken up in ether and washed with aqueous sodium carbonate, water, and saturated aqueous sodium chloride. The ether solution was dried and concentrated in vacuo to give the crude enol lactone in almost quantitative yield. Recrystallization from ether–pentane gave the pure product (1.13 g, 80.1%) as a colorless solid: mp 96.5–98 °C; NMR ($CDCl_3$) τ 9.00 (s, 3 H, CH_3), 8.88 (s, 3 H, CH_3), 6.32 (s, 1 H, CH), 4.30 (s, 1 H, vinyl), 2.21–3.00 (m, 10 H, aromatic); IR ($CHCl_3$) 3.26, 3.32, 3.35, 3.40, 5.67, 6.00, 6.24, 6.69, 6.91, 7.19, 7.30, 7.40, 7.58, 7.65, 7.84, 8.24, 8.47, 8.60, 8.82, 8.93, 9.30, 9.57, 9.75, 10.68, 10.81, 11.17, 11.49, 11.81, 14.71 μm.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.02; H, 6.53.

2,2,5,5-Tetramethyl-4,7-diphenyl-3,7-heptanedione. To 1.20 g (4.31 mmol) of 4,4-dimethyl-3,5-diphenyl-3,4-dihydro-2-pyrone in 15 mL of anhydrous ether under nitrogen was added 8.0 mL of 1.1 M *tert*-butyllithium in pentane. After 10 min the reaction mixture was poured into saturated aqueous ammonium chloride. The aqueous solution was extracted with ether, and the combined ether extract was washed with water and saturated aqueous sodium chloride. The solvent was removed in vacuo to yield an oil which was chromatographed on a 2.5 × 90 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane): fractions 1–9, 4.5 L of hexane, 129 mg of unidentified material; 10–14, 1.25 L of 1% ether–hexane, 141 mg of unidentified material; 15–18, 1 L of 1% ether–hexane, 742 mg of the desired dione; 20–23, 1 L of 1% ether–hexane, 125 mg of starting enol lactone. The crude yield of dione was 55.1%

based on unrecovered enol lactone. The dione, a colorless oil, was triturated from hexane at −78 °C. Recrystallization from hexane gave the pure dione as white needles: mp 76–78 °C; NMR ($CDCl_3$) τ 8.97 (s, 9 H, *t*-Bu), 8.86 (s, 3 H, CH_3), 8.84 (s, 3 H, CH_3), 6.59–7.37 (AB q, 2 H, J = 16 Hz, CH_2), 5.23 (s, 1 H, CH), 1.90–2.72 (m, 10 H, aromatic); IR ($CHCl_3$) 3.22, 3.26, 3.31, 3.35, 3.42, 3.47, 5.92, 6.23, 6.32, 6.69, 6.75, 6.88, 7.19, 7.32, 8.14, 8.28, 8.47, 9.35, 9.90, 10.25, 10.83, 11.12, 11.47, 14.33, 14.50 μm.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.08; H, 8.28.

4,4-Dimethyl-1,3-diphenyl-2-*tert*-butyl-1,2-cyclopentanediol. A solution of magnesium and iodine in 50 mL of ether was prepared by adding 6.75 g (26.6 mmol) of iodine in small portions to a suspension of 1.31 g (53.9 mg-atom) of magnesium powder in refluxing ether. To this solution under nitrogen was added an ether solution containing 3.07 g (9.14 mmol) of 2,2,5,5-tetramethyl-4,7-diphenyl-3,7-heptanedione. The mixture was refluxed overnight, cooled, and poured into saturated ammonium chloride. The aqueous solution was extracted with ether, and the combined ether extract was washed with water and saturated aqueous sodium chloride. The solution was dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give the crude product as a yellow oil which was chromatographed on a 2.5 × 90 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in 2% ether–hexane): fraction 1, 5 L of 2% ether–hexane, 0.420 g of unidentified material; 2–5, 1 L of 2% ether–hexane, 0.850 g of starting diketone; 6–16, 2.5 L of 2% ether–hexane, 1.24 g of diol; 17 and 18, 0.5 L of 50% ether–hexane, 0.600 g of unidentified material. The yield based on unrecovered starting material was 68%. The pure diol was obtained in slightly diminished yield by recrystallization from ether–hexane: mp 113.5–115.5 °C; NMR ($CDCl_3$) τ 9.48 (s, 9 H, *t*-Bu), 8.88 (s, 3 H, CH_3), 8.84 (s, 3 H, CH_3), 7.34–7.96 (AB q, 2 H, J = 14 Hz, CH_2), 6.72 (s, 1 H, OH), 6.54 (s, 1 H, CH), 6.48 (s, 1 H, OH), 2.24–2.80 (m, 10 H, aromatic); IR ($CHCl_3$) 2.76, 2.83, 3.31, 3.46, 3.48, 6.24, 6.70, 6.79, 6.92, 7.15, 7.22, 7.32, 7.83, 8.00–8.50, 9.04, 9.50–9.70, 9.90, 10.15, 10.75, 14.30 μm.

Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.83; H, 8.92.

5,5-Dimethyl-1,3-diphenyl-2-*tert*-butylcyclopentadiene. A solution of 86 mg (0.25 mmol) of 4,4-dimethyl-1,3-diphenyl-2-*tert*-butyl-1,2-cyclopentanediol and 0.140 mL (1.53 mmol) of phosphorous oxychloride in 2 mL of dry pyridine under nitrogen was refluxed for 17 h. The solution was cooled and partitioned between ether and water. The ether was washed with saturated ammonium chloride, water, and saturated sodium chloride. The solution was dried over anhydrous magnesium sulfate and concentrated in vacuo to give 70 mg (93%) of the cyclopentadiene. The crude product was recrystallized from ethanol to yield 61 mg (81%) of the pure cyclopentadiene: mp 148.5–151.5 °C; NMR ($CDCl_3$) τ 9.08 (s, 9 H, *t*-Bu), 8.92 (s, 6 H, CH_3's), 3.92 (s, 1 H, vinyl), 2.60–3.01 (m, 10 H, aromatic); IR (CCl_4) 3.24, 3.26, 3.29, 3.31, 3.35, 3.41, 3.44, 3.48, 6.24, 6.75, 6.83, 6.95, 7.20, 7.35, 7.38, 7.75, 7.95, 9.18, 9.37, 9.74, 13.70, 14.28 μm; UV (EtOH) λ_{max} 235 nm (ϵ 6800).

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.06; H, 8.90.

2,2,4,4-Tetramethyl-6,7-diphenyl-3,7-heptanedione. Following the general procedure of Mukaiyama,[34] a solution of 4.00 g (20.2 mmol) of 1,1-dimethyl-2-*tert*-butyl-2-trimethylsilyloxyethylene[35] in 25 mL of methylene chloride was added to a stirred solution of 4.20 g (20.2 mmol) of 2-phenylacrylophenone and 4.00 g (20.5 mmol) of titanium tetrachloride at −78 °C and under nitrogen. Stirring at −78 °C was continued for 30 min. The solution was poured into dilute aqueous sodium carbonate, and the aqueous phase was extracted with methylene chloride. The combined extract was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give an oil which was chromatographed on a 2.5 × 90 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane): fractions 1–9, 2.25 L of 0.5% ether–hexane, 2.96 g of unidentified material; 10–14, 1.25 L of 0.5% ether–hexane, 0.500 g of impure dione. The dione (fractions 10–14) was sufficiently pure enough for further transformation. A portion of the dione was recrystallized from hexane to give a colorless solid: mp 66–68 °C; NMR ($CDCl_3$) τ 8.77 (s, 12 H, t-Bu and CH_3), 8.74 (s, 3 H, CH_3), 8.02 (dd, 1 H, J = 3, 14 Hz, CH_2), 7.14 (dd, 1 H, J = 8, 14 Hz, CH_2), 5.42 (dd, 1 H, J = 3, 8 Hz, CH), 1.96–2.92 (m, 10 H, aromatic); IR ($CHCl_3$) 3.23, 3.30, 3.38, 3.47, 5.94, 6.25, 6.33, 6.70, 6.77, 6.90, 7.20, 7.42, 7.85, 8.13, 8.27, 8.51, 9.30, 9.52, 9.75, 10.00, 10.28, 10.67, 14.40 μm.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.11; H, 8.36.

1,2-Diphenyl-3-*tert*-butyl-4,4-dimethyl-2,3-cyclopentanediol. To a stirred ether (20 mL) suspension under nitrogen of 300 mg (12.5 mg-atom) of magnesium powder was added 1.52 g (6.00 mmol) of iodine in small portions. When the iodine color had disappeared, an ether solution containing 336 mg (1.00 mmol) of 2,2,4,4-tetramethyl-6,7-diphenyl-3,7-heptanedione was added. The reaction mixture was stirred at reflux for 9 h. The mixture was hydrolyzed by the addition of saturated aqueous ammonium chloride. The aqueous solution was extracted with ether, and the combined ether extract was washed with saturated aqueous sodium chloride. The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude diol was purified by chromatography on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). The diol band was collected after elution with 5% ether–hexane. The solid was recrystallized from ether–hexane to give 261 mg (77.2%) of pure diol: mp 128.5–131.5 °C; NMR ($CDCl_3$) τ 9.20 (s, 9 H, *t*-Bu), 8.62 (s, 3 H, CH_3), 8.48 (s, 3 H, CH_3), 7.83 (broad s, 1 H, OH), 7.15 (AB of ABX, 2 H, CH_2), 5.84 (X of ABX, 1 H, CH), 5.60 (s, 1 H, OH), 2.01–3.25 (m, 10 H, aromatic); IR ($CHCl_3$) 2.82, 2.87, 3.24, 3.27, 3.33, 3.37, 3.41, 6.23, 6.33, 6.69, 6.88, 6.92, 7.15, 7.23, 7.29, 7.39, 7.81, 8.55, 9.41, 9.70, 9.76, 9.95, 10.15, 10.69, 10.87, 11.30, 11.51, 14.22 μm.

Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.68; H, 8.96.

1-*tert*-Butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene. To a solution of 88 mg (0.26 mmol) of 1,2-diphenyl-3-*tert*-butyl-4,4-dimethyl-2,3-cyclopentanediol in 2 mL of dry pyridine was added 1.07 g (1.68 mmol) of phosphorous oxychloride. The solution was refluxed for 18 h. After cooling, the reaction mixture was poured into aqueous ammonium chloride. The aqueous solution was extracted with ether, and the combined ether extract was washed with aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The dried solution was concentrated in vacuo and the residue chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). After two developments with hexane, the plate was divided into two bands. The first band (largest R_f) contained 25 mg (32.6%) of the desired cyclopentadiene. The second band contained 54 mg (61.3%) of unreacted starting material. Recrystallization from methanol gave the diene as a colorless solid: mp 73–76.5 °C; NMR (CCl_4) τ 8.84 (s, 9 H, *t*-Bu), 8.54 (s, 6 H, CH_3's), 4.06 (s, 1 H, vinyl), 2.60–3.32 (m, 10 H, aromatic); IR ($CHCl_3$) 3.26, 3.32, 3.37, 3.41, 3.43, 3.45, 3.48, 6.25, 6.77, 6.94, 7.10, 7.19, 7.25, 7.34, 7.50, 7.63, 8.15, 8.33, 9.71, 10.47, 10.79, 13.97, 14.99 μm; UV λ_{max} 282 nm (ϵ 5200). MS Calcd for $C_{23}H_{26}$: m/e 302.20345. Found: m/e 302.20379.

1,2-Diphenyl-3,3,6,6-tetramethyl-1,5-heptanedione. To 10 mL of freshly distilled *tert*-butyl alcohol containing 1.40 g (12.5 mmol) of potassium *tert*-butoxide was added 3.92 g (20.0 mmol) of deoxybenzoin and 2.80 g (20.0 mmol) of 2,2,5-trimethylhex-4-en-3-one.[36] The stoppered flask was shaken vigorously to dissolve the solid materials. The solution was stirred under nitrogen at room temperature for 96 h. The reaction mixture was neutralized and partitioned between ether and water. The combined ether extract was washed with saturated aqueous sodium bicarbonate and water. The solution was dried and concentrated in vacuo to give an oil which was chromatographed on a 2.5 × 90 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane): fractions 1–3, 1 L of hexane, 243 mg of unidentified material; 4–7, 0.8 L of 0.5% ether–hexane, 2.68 g (40%) of pure dione; 8–11, 0.8 L of 1% ether–hexane, 1.88 g of a mixture of dione and deoxybenzoin. The dione was recrystallized from hexane to give 2.47 g (36.8%) of a colorless solid: mp 90.5–93 °C; NMR ($CDCl_3$) τ 8.93 (s, 9 H, *t*-Bu), 8.86 (s, 3 H, CH_3), 8.84 (s, 3 H, CH_3), 6.25–6.98 (AB q, 2 H, J = 18 Hz, CH_2), 4.48 (s, 1 H, CH), 1.93–2.90 (m, 10 H, aromatic); IR ($CHCl_3$) 3.24, 3.26, 3.29, 3.36, 3.40, 3.45, 5.10, 5.18, 5.51, 5.88, 5.96, 6.25, 6.32, 6.69, 6.75, 6.77, 6.87, 6.90, 7.15, 7.20, 7.29, 7.38, 7.60, 7.65, 7.92, 8.08, 8.33, 8.45, 8.59, 8.89, 9.33, 9.63, 9.71, 9.85, 9.95, 10.44, 10.71, 10.80, 11.01, 11.64, 11.79, 14.16 μm.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.10; H, 8.40.

1-*tert*-Butyl-2,3-diphenyl-4,4-dimethyl-1,2-cyclopentanediol. An ether (5 mL) solution of 500 mg (1.49 mmol) of 1,2-diphenyl-3,3,6,6-tetramethyl-1,5-heptanedione was added to an ether solution of the magnesium–iodine reagent (a tenfold excess) prepared as described above. The solution was refluxed for 16 h. After cooling, the reaction mixture was poured into saturated aqueous ammonium chloride. The aqueous solution was extracted with ether, and the combined extract was washed with saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The dried solution was concentrated in vacuo, and the residue was chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). The diol band was collected eluting with 5% ether–hexane and recrystallized from ethanol to give 411 mg (82%) of the pure diol: mp 163–164 °C; NMR ($CDCl_3$) τ 9.29 (s, 9 H, *t*-Bu),

8.85 (broad s, 6 H, CH_3), 7.47–8.19 (AB q, 2 H, J = 14 Hz, CH_2), 7.00 (broad s, 1 H, OH), 6.35 (s, 1 H, CH), 6.05 (broad s, 1 H, OH), 2.32–3.16 (m, 10 H, aromatic); IR ($CHCl_3$) 2.71–3.18, 3.23, 3.25, 3.32, 3.47, 6.24, 6.32, 6.69, 6.74, 6.81, 6.91, 7.16, 7.22, 7.29, 7.56, 7.73, 8.03, 8.45, 8.88, 8.98, 9.23, 9.42, 9.55, 9.71, 9.97, 10.20, 10.47, 10.98, 11.20, 11.29, 11.90, 14.16 μm.

Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.39; H, 8.83.

1,2-Diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene. A solution of 390 mg (1.15 mmol) of 1-*tert*-butyl-2,3-diphenyl-4,4-dimethyl-1,2-cyclopentanediol and 1.80 mL (19.5 mmol) of phosphorous oxychloride in 10 mL of dry pyridine was refluxed for 18 h. After cooling, the reaction mixture was poured into saturated aqueous ammonium chloride, and the aqueous phase was extracted with ether. The combined extract was washed with saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. The ether solution was dried and concentrated in vacuo. The residue was chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). The fastest moving band was collected and recrystallized from ethanol to give 276 mg (73.9%) of the cyclopentadiene: mp 119–122.5 °C; NMR ($CDCl_3$) τ 8.93 (s, 9 H, *t*-Bu), 8.80 (s, 6 H, CH_3's), 3.97 (s, 1 H, vinyl), 2.44–3.08 (m, 10 H, aromatic); IR (CCl_4) 3.23, 3.25, 3.29, 3.36, 3.40, 3.43, 3.48, 6.25, 6.69, 6.73, 6.76, 6.83, 6.93, 7.18, 7.33, 7.37, 7.49, 7.79, 8.08, 8.31, 8.53, 9.06, 9.30, 9.71, 10.42, 10.68, 10.94, 13.76, 14.12, 14.20 μm; UV (EtOH) λ_{max} 271 nm (ε 7400).

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.05; H, 8.67.

2,3-Diphenyl-4,4-dimethyl-3-hydroxypentanoic Acid. Under Ivanov conditions,[37] an ether (150 mL) solution of 375 mmol of isopropylmagnesium bromide was added dropwise with stirring under nitrogen to a solution of 20.4 g (150 mmol) of phenylacetic acid in 150 mL of anhydrous ether. The solution was stirred at room temperature overnight. To this was added a solution of 22.1 g (136 mmol) of pivalophenone in 150 mL of anhydrous ether over 75 min. The mixture was stirred at reflux for 4 h and then for 18 h at room temperature. The reaction mixture was hydrolyzed by the addition of 250 mL of 5% hydrochloric acid followed by the addition of 200 mL of water. The aqueous solution was extracted with ether, and the extract was washed with water and saturated sodium chloride. The ether solution was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was recrystallized from ether–hexane to give 33.3 g (82%) of the hydroxy acid as a 4:1 mixture of diastereomers. The diastereomers were partially separated by fractional recrystallization from ether–hexane: NMR major isomer ($CDCl_3$) τ 9.32 (s, 9 H, *t*-Bu), 5.40 (s, 1 H, CH), 2.21–3.20 (m, 12 H, aromatic, OH, and COOH); NMR minor isomer ($CDCl_3$) τ 9.04 (s, 9 H, t-Bu), 5.41 (s, 1 H, CH), 2.21–3.20 (m, 12 H, aromatic, OH, and COOH); IR mixture ($CHCl_3$) 2.70–3.13, 3.23, 3.26, 3.31, 3.34, 3.37, 3.42, 3.47, 5.83, 6.25, 6.69, 6.74, 6.87, 7.16, 7.31, 7.55, 7.78, 7.89, 8.39, 8.52, 8.81, 9.24, 9.33, 9.64, 9.82, 9.97, 10.45, 10.89, 11.20, 14.06, 14.22 μm.

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.47; H, 7.44. Found: C, 76.27; H, 7.39.

3,4-Diphenyl-4-*tert*-butyloxetan-2-one. The general procedure of Adam[38] was used. A solution of 11.9 g (40.0 mmol) of 2,3-diphenyl-4,4-dimethyl-3-hydroxypentanoic acid (the mixture of diastereomers) and 10 mL (78.5 mmol) of benzenesulfonyl chloride in 200 mL of dry pyridine was stirred for 4 h at room temperature under nitrogen. The reaction mixture was poured into 400 mL of cold 5% hydrochloric acid and extracted with ether. The combined extract was washed with cold 5% hydrochloric acid, water, and saturated aqueous sodium chloride. The solution was dried over anhydrous magnesium sulfate and concentrated in vacuo to give 9.54 g (84.8%) of a mixture of diastereomeric lactones. The mixture of diastereomers was used in subsequent transformations. The major isomer was separated by fractional recrystallization from ether–hexane: mp 107–110 °C; NMR ($CDCl_3$) τ 9.12 (s, 9 H, *t*-Bu), 4.81 (s, 1 H, CH), 2.21–3.02 (m, 10 H, aromatic); IR ($CHCl_3$) 3.23, 3.25, 3.32, 3.34, 3.43, 3.47, 5.46, 6.23, 6.68, 6.83, 6.86, 6.90, 7.15, 7.30, 7.91, 8.22, 8.51, 8.64, 8.70, 9.40, 9.66, 9.74, 9.90, 9.95, 10.18, 10.42, 10.53, 10.91, 11.33, 11.60, 11.76, 13.79, 14.18, 14.93, 16.10 μm.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.20. Found: C, 81.35; H, 7.26.

2,3-Diphenyl-4,4-dimethylpentanoic Acid. To a solution of 360 mg (51.0 mg-atom) of lithium in 150 mL of dry liquid ammonia under nitrogen was added 5.20 g (17.9 mmol) of 3,4-diphenyl-4-*tert*-butyloxetan-2-one (a mixture of diastereomers) in 25 mL of anhydrous ether.[39] After stirring for 1.5 h at reflux, the reaction was quenched by the addition of 3.50 g (65.4 mmol) of solid ammonium chloride. The ammonia was evaporated, and the residue was partitioned between ether and water. The aqueous phase was extracted with ether, and the ether extract was washed with water and saturated aqueous sodium chloride. The dried ether solution was concentrated in vacuo, and the residue was recrystallized from hexane. The product (4.68 g, 90%) was a 1:1 mixture of diastereomers. In subsequent reactions the mixture or either isomer was used successfully. The isomers were separated by fractional recrystallization from hexane. Isomer with mp 184–185 °C: NMR ($CDCl_3$) τ 9.00 (s, 9 H, *t*-Bu), 6.40 (d, 1 H, J = 11 Hz, CH α to carboxyl), 5.89 (d, 1 H, J = 11 Hz, CH β to carboxyl), 2.72–3.24 (m, 10 H, aromatic), 2.02 (broad s, 1 H, COOH); IR ($CHCl_3$) 2.68–3.18, 3.23, 3.25, 3.29, 3.31, 3.34, 3.37, 3.42, 3.46, 5.83, 6.25, 6.33, 6.69, 6.74, 6.87, 7.16, 7.30, 7.55, 7.78, 7.90, 8.38, 8.51, 8.81, 9.01, 9.23, 9.32, 9.64, 9.83, 9.96, 10.44, 10.87, 11.17, 11.49, 11.90, 12.35, 14.06, 14.22 μm.

Isomer with mp 200–202 °C: NMR ($CDCl_3$) τ 9.38 (s, 9 H, *t*-Bu), 6.81 (d, 1 H, J = 11 Hz, CH α to carboxyl), 5.88 (d, 1 H, J = 11 Hz, CH β to carboxyl), 2.36–3.12 (m, 10 H, aromatic), 1.60 (broad s, 1 H, COOH).

Anal. (mp 184–185 °C isomer) Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.86. Found: C, 80.56; H, 7.72.

2-Phenyl-3-*tert*-butyl-1-indanone. A solution of 6.10 g (21.6 mmol) of the mixture of 2,3-diphenyl-4,4-dimethylpentanoic acid isomers and 2 mL of thionyl chloride in 150 mL of dry benzene was refluxed for 1 h. After cooling, 2.93 g (22.0 mmol) of anhydrous aluminum chloride was added in small portions. The resulting solution was refluxed for 1 h. The solution was cooled and poured into cold 5% hydrochloric acid. The aqueous phase was extracted with ether, and the extract was washed with water and saturated aqueous sodium chloride. The ether–benzene solution was dried over anhydrous magnesium sulfate and concentrated in vacuo to give an oil which crystallized on standing. Recrystallization from hexane gave the pure indanone (3.80 g, 66.7%) as a colorless solid: mp 115–117.5 °C; NMR ($CDCl_3$) τ 9.00 (s, 9 H, *t*-Bu), 6.68 (d, 1 H, J = 1.5 Hz, CH), 6.21 (d, 1 H, J = 1.5 Hz, CH), 2.08–3.00 (m, 9 H, aromatic); IR ($CHCl_3$) 3.24, 3.26, 3.30, 3.33, 3.38, 3.40, 3.44, 3.49, 5.88, 6.25, 6.33, 6.71, 6.78, 6.82, 6.85, 6.90, 7.18, 7.32, 7.46, 7.55, 7.62, 7.75, 7.86, 8.16–8.26, 8.54, 8.71, 9.10, 9.18, 9.32, 9.66, 9.86, 10.10, 10.47, 10.70, 11.04, 11.31, 11.60, 11.75, 14.39 μm.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.31; H, 7.63. Found: C, 86.36; H, 7.60.

1-*tert*-Butyl-2-phenyl-3-cyanoindene. Following the general procedure of Evans,[40] a mixture of 2.30 g (8.39 mmol) of 2-phenyl-3-*tert*-butyl-1-indanone, 3 mg of anhydrous zinc iodide, and 3 mL of trimethylsilyl cyanide under nitrogen was stirred at room temperature overnight. The reaction mixture was diluted with ether and washed with water. The ether solution was dried and concentrated in vacuo to give an oil which was analyzed (NMR) as a 1:1 mixture of the desired cyanohydrin trimethylsilyl ethers.

Without further purification, the product was dissolved in 25 mL of 3:1 (v/v) methanol–water containing 300 mg (5.56 mmol) of ammonium chloride. The solution was stirred at room temperature for 4 h before diluting with water and extracting with ether. The combined ether extract was washed with water and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated in vacuo to give the cyanohydrins as a light yellow oil.

The crude cyanohydrins were dissolved in 12 mL of dry pyridine containing 2.34 g (15.2 mmol) of phosphorous oxychloride. The solution was refluxed for 1 h. Upon cooling to room temperature, the solution was poured into cold 5% aqueous hydrochloric acid. The aqueous phase was extracted with ether, and the extract was washed with water and saturated aqueous sodium chloride. The solution was dried and concentrated in vacuo to give 1.92 g of the crude cyanoindene. The crude product was percolated through a 2.5 × 25 cm silica gel column eluting with hexane. Recrystallization of the product from pentane gave 1.34 g (56.5%, based on starting indanone) of pure colorless solid: mp 72–75 °C; NMR ($CDCl_3$) τ 9.18 (s, 9 H, *t*-Bu), 6.04 (s, 1 H, CH), 2.41–3.03 (m, 9 H, *t*-Bu); IR ($CHCl_3$) 3.26, 3.34, 3.35, 3.36, 3.38, 3.40, 4.48, 6.76, 6.83, 6.92, 7.15, 7.30, 7.55, 7.87, 8.68, 8.78, 9.05, 9.22, 9.61, 9.71, 10.15, 10.64, 10.99, 11.49, 11.88, 12.66–13.79, 14.33 μm.

Anal. Calcd for $C_{20}H_{19}N$: C, 87.86; H, 7.01. Found: C, 87.99; H, 7.14.

1-*tert*-Butyl-2-phenyl-3-formylindene. The general procedure of Marshall[41] was employed. To a solution of 590 mg (2.16 mmol) of 1-*tert*-butyl-2-phenyl-3-cyanoindene in 50 mL of dry hexane under nitrogen at −60 °C was added 1.8 mL of a 1.40 M hexane solution of diisobutylaluminum hydride. After stirring for 15 min, the solution was allowed to warm to room temperature and stirring was continued for 2 h. The reaction was quenched by adding 15 mL of saturated aqueous ammonium chloride followed by 10 mL of 5% aqueous hy-

drochloric acid. The two-phase mixture was stirred for 15 min. The aqueous phase was extracted with ether, and the ether–hexane solution was washed with water and saturated aqueous sodium chloride. The dried solution was concentrated in vacuo. The residue was dissolved in 10 mL of 1:1 (v/v) ether–methanol and treated with 10 mL of 5% aqueous hydrochloric acid. After stirring for 2 h, the solution was diluted with water and extracted with ether. The ether solution was dried and concentrated in vacuo to give a red oil. The aldehyde was triturated at −78 °C from hexane. Attempts to chromatograph the product led to complete decomposition of the aldehyde. Recrystallization from hexane–ether gave 310 mg (52.3%) of aldehyde, mp 104–106 °C, sufficiently pure enough for further transformation: NMR ($CDCl_3$) τ 9.29 (s, 9 H, *t*-Bu), 6.16 (s, 1 H, CH), 2.36–3.12 (m, 9 H, aromatic), 0.19 (s, 1 H, CHO); IR ($CHCl_3$) 3.28, 3.29, 3.37, 3.40, 3.42, 3.46, 3.51, 3.52, 6.00, 6.27, 6.43, 6.73, 6.79, 6.88, 6.97, 7.20, 7.35, 7.58, 7.75, 7.87, 9.01, 9.17, 9.30, 9.37, 9.77, 10.05, 10.24, 10.63, 11.07, 11.63, 12.66–13.99 μm. MS Calcd for $C_{20}H_{20}O$: *m/e* 276.15141. Found: *m/e* 276.15156.

1-*tert*-Butyl-2-phenyl-3-isobutenylindene. To a stirred suspension of 720 mg (1.74 mmol) of isopropyltriphenylphosphonium iodide in 5 mL of dry tetrahydrofuran at 0 °C under nitrogen was added 1.2 mL of 1.45 M *n*-butyllithium in hexane. The solution was stirred for 45 min at 0 °C. The above aldehyde (311 mg, 1.08 mmol) in 8 mL of dry tetrahydrofuran was added dropwise with stirring to the Wittig reagent. After stirring for 1 h, the reaction mixture was poured into ether–water. The dried ether solution was filtered through Celite and concentrated in vacuo. The residue was chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). After elution with hexane, the fastest moving band was collected to give 151 mg (46.3%) of the indene as a colorless oil: NMR ($CDCl_3$) τ 9.16 (s, 9 H, *t*-Bu), 8.46 (s, 3 H, CH_3), 8.14 (s, 3 H, CH_3), 6.20 (broad s, 1 H, CH), 4.20 (broad s, 1 H, vinyl), 2.41–3.02 (m, 9 H, aromatic); IR (KBr) 3.26, 3.30, 3.34, 3.37, 3.41, 3.45, 3.48, 6.25, 6.70, 6.76, 6.83, 6.93, 7.18, 7.27, 7.34, 7.92, 8.21, 8.37, 8.63, 8.30, 9.72, 10.75, 11.35, 11.82, 12.08, 12.42, 13.07, 13.33, 13.70, 14.31 μm; UV (EtOH) λ_{max} 236 nm (ϵ 19 100), 299 (14 600). MS Calcd for $C_{23}H_{26}$: *m/e* 302.20345. Found: *m/e* 302.20379.

Exploratory Photolysis of 1,2,3-Triphenyl-3-methylcyclopropene. A solution of 483 mg (1.71 mmol) of 1,2,3-triphenyl-3-methylcyclopropene in 500 mL of *tert*-butyl alcohol was purged with vanadous purified nitrogen for 2 h prior to and during the photolysis. The solution was irradiated through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Removal of the solvent in vacuo left 452 mg (93.6%) of a yellow oil which crystallized on standing. The crude photolysate was a 15:1 mixture of 1,2-diphenyl-3-methylindene and starting cyclopropene. The pure indene, mp 91–93 °C (lit. mp 91 °C), was isolated by recrystallization from ethanol. The spectral data were previously unreported: NMR (CCl_4) τ 7.80 (broad s, 3 H, CH_3), 5.32 (broad s, 1 H, CH), 2.53–3.33 (m, 14 H, aromatic); UV (EtOH) λ_{max} 294 nm (ϵ 17 400).

Exploratory Photolysis of 1-Methyl-2,3,3-triphenylcyclopropene. A solution of 173 mg (0.613 mmol) of 1-methyl-2,3,3-triphenylcyclopropene in 250 mL of *tert*-butyl alcohol, distilled from calcium hydride, was purged with purified nitrogen[42] for 1 h prior to and during the photolysis. The solution was irradiated for 2 h through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Removal of the solvent in vacuo left a yellow oil which was analyzed (NMR) as a 70:30 mixture of 1-methyl-2,3-diphenylindene and starting cyclopropene. Attempts to increase the conversion led to secondary photolysis of the indene. The indene was isolated by column chromatography on silica gel. Recrystallization from ethanol gave the pure indene, mp 105–106 °C (lit. mp 105–106 °C). The isomeric unreported spectral data were as follows: NMR (CCl_4) τ 8.70 (d, 3 H, J = 8 Hz, CH_3), 5.98 (q, 1 H, J = 8 Hz, CH), 2.43–2.90 (m, 14 H, aromatic); UV (EtOH) λ_{max} 303 nm (ϵ 13 300), 234 (17 300).

Exploratory Photolysis of 1,2,3-Triphenyl-3-isobutenylcyclopropene. A solution of 450 mg (1.40 mmol) of 1,2,3-triphenyl-3-isobutenylcyclopropene in 500 mL of anhydrous methanol was purged with purified nitrogen[42] for 1 h prior to and during the photolysis. The solution was irradiated for 4 h through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to give a 2.5:1 mixture of two photoproducts (100% conversion) as a light yellow oil. The product ratio was independent of the percent conversion. The oil was dissolved in 5 mL of hot methanol and allowed to stand for 2 h. The solid material was filtered off to give 268 mg (60%) of NMR-pure 1,2,3-triphenyl-5,5-dimethylcyclopentadiene. The filtrate was concentrated in vacuo, and the residue was chromatographed on a 20 × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt; GF-254). After one development with hexane, the fastest moving band was collected. The material was triturated at −78 °C (MeOH) to give, after recrystallization from methanol, 106 mg (26%) of 1,2-diphenyl-3-isobutenylindene. The second band contained nonhydrocarbon material (<5%), presumably methanol incorporation products. This "impurity" was not formed when the photolysis was performed in benzene or *tert*-butyl alcohol. The cyclopentadiene was identical with a sample prepared by an independent method. The structure of the indene rests on its spectral, physical, and microanalytical data: mp 102–104 °C; NMR ($CDCl_3$) τ 8.41 (s, 3 H, CH_3), 8.02 (s, 3 H, CH_3), 5.02 (broad s, 1 H, CH), 3.79 (broad s, 1 H, vinyl), 2.44–3.41 (m, 14 H, aromatic); IR ($CHCl_3$) 3.27, 3.33, 3.37, 3.41, 3.43, 3.50, 5.14, 5.33, 5.55, 5.71, 6.26, 6.70, 6.89, 7.26, 7.45, 8.42, 8.70, 9.32, 9.74, 9.85, 9.98, 10.66, 10.98, 11.49, 11.71, 12.08, 14.47 μm; UV (EtOH) λ_{max} 305 nm (ϵ 14 300). MS Calcd for $C_{25}H_{22}$: *m/e* 322.17215. Found: *m/e* 322.17218.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 92.86; H, 6.90.

Exploratory Photolysis of 1,2,3-Triphenyl-3-vinylcyclopropene. A solution of 500 mg (1.70 mmol) of 1,2,3-triphenyl-3-vinylcyclopropene in 500 mL of *tert*-butyl alcohol was purged with purified nitrogen[42] for 1 h and then irradiated with continued purging for 3.25 h through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to give a light yellow oil which crystallized on standing. The recrystallized (ethanol) product (436 mg, 87%) was identical in all respects with an authentic sample of 1,2,3-triphenylcyclopentadiene prepared by the method of Pauson. In runs of varying percent conversion there was no evidence for any indene formation.

Exploratory Photolysis of 3-(1-Phenylvinyl)-1,2,3-triphenylcyclopropene. A solution of 313 mg (0.846 mmol) of 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene in 200 mL of *tert*-butyl alcohol was purged with purified nitrogen[42] for 1 h prior to and during the photolysis. The solution was irradiated for 35 min through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Removal of the solvent in vacuo left a light yellow oil. The oil was a mixture (3:1) of starting cyclopropene and 1,2,3,4-tetraphenylcyclopentadiene. The oil was taken up in 2 mL of anhydrous ether and allowed to stand overnight. The crystals were filtered to give 62 mg (21%) of pure 1,2,3,4-tetraphenylcyclopentadiene, mp 177–179 °C. This material was identical in all respects with an authentic sample; the mixture melting point was undepressed. The filtrate was concentrated in vacuo, and the residue was recrystallized from ethanol to give 226 mg (70%) of starting cyclopropene. Occasionally the filtrate contained some cyclopentadiene, and in this case the residue was redissolved in ether and the cyclopentadiene was allowed to crystallize out. Filtration removed the cyclopentadiene. The starting material could then be recovered as described above. Again there was no indene product observed.

Exploratory Photolysis of 3-Isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene. A solution of 1.40 g (4.63 mmol) of 3-isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene in 700 mL of *tert*-butyl alcohol, distilled from calcium hydride, was purged with purified nitrogen[42] for 1 h prior to and during the irradiation. The solution was irradiated for 7.5 h through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo, and the yellow oil was chromatographed on a 2.5 × 140 cm silica gel column (Matheson, Coleman and Bell; grade 62, 60–200 mesh, slurry packed in hexane). Elution with 1 L of hexane gave nil, and 50-mL aliquots were used for fractions 2–38: fractions 2–15, 87 mg of 1,3-diphenyl-2-*tert*-butyl-5,5-dimethylcyclopentadiene; 16–21, 246 mg of a mixture of 1,3-diphenyl-2-*tert*-butyl-3-isobutenylcyclopropene and 1-*tert*-butyl-2-phenyl-3-isobutenylindene; 22–30, 399 mg of a mixture of 1,3-diphenyl-2-*tert*-butyl-3-isobutenylcyclopropene, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene, and 1-*tert*-butyl-2-phenyl-3-isobutenylindene; 31–36, 125 mg of a mixture of 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene and 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene; 37 and 38, 63 mg of 1,3-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene.

Fractions 16–28 were combined, and 391 mg of the mixture was chromatographed on a 2.5 × 90 cm silica gel column packed as described above. Elution with hexane in 50-mL fractions gave the following results: fractions 1–5, nil; 6–8, 70 mg of 1-*tert*-butyl-2-phenyl-3-isobutenylindene; 9–12, 126 mg of a mixture of 1-*tert*-butyl-2-phenyl-3-isobutenylindene, 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene, and 1,3-diphenyl-2-*tert*-butyl-3-isobutenylcyclopropene; and 13–18, 87 mg of 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene. 1-*tert*-Butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene could not be obtained completely free from

the other products. These compounds were identical with samples prepared by independent syntheses.

Photolysis Equipment and Quantum Yield Determinations. Quantum yield irradiations were performed on the black box apparatus previously described.[15] Light output was monitored by ferrioxalate actinometry,[43] and the light absorbed in the reaction cell was determined by the splitting ratio technique.[15]

For the direct irradiations the solution filters employed were as follows: filter A, (a) 2 M nickel sulfate in 5% sulfuric acid, (b) 0.80 M cobalt sulfate in 5% sulfuric acid, and (c) 0.10 M copper sulfate in 5% sulfuric acid (combination (2.5 cm thickness for each of three cells) gave a 38% transmission maximum at 314 nm and was opaque above 353 nm and below 283 nm); filter B, (a) 2 M nickel sulfate in 10% sulfuric acid, (b) 2 M cobalt sulfate in 10% sulfuric acid, and (c) 0.0002 M bismuth trichloride in 10% hydrochloric acid (combination gave an 18% transmission maximum at 280 nm and was opaque above 305 nm and below 255 nm); filter C, (a) 0.19 M nickel sulfate in 10% sulfuric acid, (b) 1 M cobalt sulfate in 10% sulfuric acid, and (c) 0.01 M sodium metavanadate in 0.10 M aqueous sodium hydroxide (combination gave a 16% transmission maximum at 356 nm and was opaque above 388 nm and below 328 nm); filter D, (a) 1 M cobalt sulfate in 5% sulfuric acid, (b) 1 M copper sulfate in 5% sulfuric acid, and (c) 0.10 M sodium metavanadate in 0.10 M aqueous sodium hydroxide (combination gave a maximum transmission of 29% at 370 nm and was opaque above 430 nm and below 345 nm). All filter solutions were stable during the irradiations.

The quantum yields for product formation were determined by high-pressure liquid chromatography (LC) and, where noted, NMR spectroscopy. The columns used for the LC analysis were as follows: column A, a 4 ft × ⅛ in column packed with high-speed, Woelm alumina (particle size 18–30 μm); column B, a 15-¾ × ⅛ in column packed with high-speed, Woelm alumina (particle size, 18–30 μm). For calibration (column A) of the high-pressure liquid chromatographic system with respect to 1,2,3-triphenyl-3-isobutenylcyclopropene and 1,2,3-triphenyl-5,5-dimethylcyclopentadiene, the internal standard employed was 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene. For calibration of column B with respect to 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene, 1,2,3-triphenyl-3-vinylcyclopropene, 1,2,3,4-tetraphenylcyclopentadiene, and 1,2,3-triphenylcyclopentadiene, the internal standard used was 1,1-bis(*p*-methoxyphenyl)-2-methyl-1-propene.

The retention times[44] for column A were the following: 1,2,3-triphenyl-5,5-dimethylcyclopentadiene, 7.5 min; 1,2,3-triphenyl-3-isobutenylcyclopropene, 11 min; 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene, 28 min. The retention times for column B were as follows: 3-(1-phenylvinyl)-1,2,3-triphenylcyclopropene, 3.1 min; 1,2,3,4-tetraphenylcyclopentadiene, 7.5 min; 3-vinyl-1,2,3-triphenylcyclopropene, 1.9 min; 1,2,3-triphenylcyclopentadiene, 5 min; 1,1-bis(*p*-methoxyphenyl)-2-methyl-1-propene, 28.8 min.

Summary of the Quantum Yield Results for the Direct Irradiation of 1,2,3-Triphenyl-3-isobutenylcyclopropene. For each of the runs filter A was used, and 750 mL of purified benzene was used as solvent. The results are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, and percent conversion.

Run 1A: Starting cyclopropene, 145 mg (0.451 mmol), 9.40 mEinstein, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (0.096 mmol), Φ = 0.0102, 21.2%. Note: analysis by NMR spectroscopy confirmed the above quantum yield; additionally the quantum yield for the formation of 1,2-diphenyl-3-isobutenylindene was estimated to be 0.004.

Run 1B: Starting cyclopropene, 139 mg (0.431 mmol), 2.63 mEinstein, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (0.026 mmol), Φ = 0.0097, 5.9%.

Run 1C: Starting cyclopropene, 156 mg (0.485 mmol), 2.02 mEinstein, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (0.020 mmol), Φ = 0.0099, 4.2%.

Summary of the Quantum Yield Results for the Direct Irradiation of 3-Vinyl-1,2,3-triphenylcyclopropene. For each of the runs filter A was used, and 750 mL of purified benzene was used as solvent. The data are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3-triphenylcyclopentadiene (mmol), quantum yield, and percent conversion.

Run 2A: Starting cyclopropene, 178 mg (0.604 mmol), 1.54 mEinstein, 1,2,3-triphenylcyclopentadiene (0.042 mmol), Φ = 0.028, 7%.

Run 2B: Starting cyclopropene, 206 mg (0.702 mmol), 1.01 mEinstein, 1,2,3-triphenylcyclopentadiene (0.027 mmol), Φ = 0.027, 3.9%.

Summary of the Quantum Yield Results for the Direct Irradiation of 3-(1-Phenylvinyl)-1,2,3-triphenylcyclopropene. For each of the runs filter A was used, and 750 mL of purified benzene was used as solvent. The data are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3,4-tetraphenylcyclopentadiene (mmol), quantum yield, and percent conversion.

Run 3A: Starting cyclopropene, 171 mg (0.462 mmol), 6.22 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.227 mmol), Φ = 0.0365, 49%.

Run 3B: Starting cyclopropene, 151 mg (0.409 mmol), 3.47 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.138 mmol), Φ = 0.0395, 34%.

Run 3C: Starting cyclopropene, 316 mg (0.853 mmol), 1.02 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.048 mmol), Φ = 0.0469, 5.5%.

Run 3D: Starting cyclopropene, 351 mg (0.948 mmol), 1.01 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.049 mmol), Φ = 0.049, 5.1%.

Summary of the Quantum Yield Results for the Sensitized Irradiation of 3-Isobutenyl-1,2,3-triphenylcyclopropene. For run 4A filter C was used, and for run 4B filter D was used. Each run used 750 mL of purified benzene as solvent. The sensitizer used was 4-dimethylaminobenzophenone (enough to absorb 98% of the light). Note: xanthone also was an efficient sensitizer. Run 4A was analyzed by LC and NMR spectroscopy. Run 4B was analyzed by NMR spectroscopy. The data are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, percent conversion, and sensitizer mass.

Run 4A: Starting cyclopropene, 156 mg (0.486 mmol), 1.23 mEinstein, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (0.173 mmol), Φ = 0.140 (by NMR, Φ = 0.133), 35.6%, 1.99 g.

Run 4B: Starting cyclopropene, 149 mg (0.462 mmol), 2.22 mEinstein, 1,2,3-triphenyl-5,5-dimethylcyclopentadiene (0.285 mmol), Φ = 0.128 (by NMR), 61.7%, 1.59 g.

Note: the 3-isobutenyl-1,2-diphenylindene observed in the direct irradiation was not observed in either run. Chromatography (run 4A) on a 20 × 20 cm × 2 mm silica gel plate after three developments with hexane gave a quantitative mass balance of hydrocarbon material. NMR spectroscopy confirmed the photoproduct to be 1,2,3-triphenyl-5,5-dimethylcyclopentadiene; the absence of the indene was also confirmed.

Summary of the Quantum Yield Results for the Sensitized Irradiation of 3-Vinyl-1,2,3-triphenylcyclopropene. For the sensitized run filter C was used, and 750 mL of purified benzene was used as solvent. Enough xanthone was used to absorb 95% of the light. The data are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3-triphenylcyclopentadiene (mmol), quantum yield, percent conversion, and sensitizer mass.

Run 5A: Starting cyclopropene, 178 mg (0.607 mmol), 0.933 mEinstein, 1,2,3-triphenylcyclopentadiene (no significant product formation), Φ < 0.001, ~0%, 2.12 g.

Summary of the Quantum Yield Results for the Sensitized Irradiation of 3-(1-Phenylvinyl)-1,2,3-triphenylcyclopropene. For runs 6A and 6B filter C was used, and xanthone was used as a sensitizer (the xanthone absorbed 70–80% of the incident light). For run 6C filter D was used, and 4-dimethylaminobenzophenone, which absorbed 95% of the incident light, was used as a sensitizer. All runs employed 750 mL of purified benzene as solvent. The data are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1,2,3,4-tetraphenylcyclopentadiene (mmol), quantum yield, percent conversion, and sensitizer mass.

Run 6A: Starting cyclopropene, 298 mg (0.805 mmol), 1.02 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.017 mmol), Φ = 0.016, 2.1%, 2.07 g of xanthone.

Run 6B: Starting cyclopropene, 223 mg (0.602 mmol), 1.11 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.015 mmol), Φ = 0.013, 2.5%, 2.06 g of xanthone.

Run 6C: Starting cyclopropene, 169 mg (0.457 mmol), 5.01 mEinstein, 1,2,3,4-tetraphenylcyclopentadiene (0.011 mmol), Φ = 0.002, 2.4%, 1.51 g of 4-dimethylaminobenzophenone. Analysis was by NMR spectroscopy.

Summary of the Quantum Yield Results for the Direct Irradiation of 3-Isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene. For run 7A filter B was used, and 750 mL of *tert*-butyl alcohol, distilled from calcium hydride, was used as solvent. The analysis was by NMR integration. The results are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, 2-*tert*-butyl-1,3-diphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, 3-*tert*-butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, 1-*tert*-butyl-2-phenyl-3-isobutenylindene (mmol), quantum yield, and percent conversion.

Run 7A: Starting cyclopropene, 188 mg (0.623 mmol), 14.2 mEin-

stein, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (0.043 mmol), $\Phi = 0.003$, 2-*tert*-butyl-1,3-diphenyl-5,5-dimethylcyclopentadiene (0.014 mmol), $\Phi = 0.001$, 3-*tert*-butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene (0.056 mmol), $\Phi = 0.004$, 3-isobutenyl-1-*tert*-butyl-2-phenylindene (0.042 mmol), $\Phi = 0.003$, 20%. The percent conversion was obtained by taking the ratio of the integration of vinyl protons of the products to the integration of the vinyl protons of starting material. The integration of the aliphatic region roughly confirmed this.

Summary of the Quantum Yield Results for the Sensitized Irradiation of 3-Isobutenyl-1,3-diphenyl-2-*tert*-butylcyclopropene. For run 8A filter D was used, and for run 8B filter C was used. Each run employed 750 mL of *tert*-butyl alcohol, distilled from calcium hydride, as solvent. The analysis was by NMR integration. The results are listed as follows: starting cyclopropene, mass (mmol), light absorbed, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, 3-*tert*-butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene (mmol), quantum yield, percent conversion, and sensitizer mass.

Run 8A: Starting cyclopropane, 233 mg (0.772 mmol), 2.20 mEinstein, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (0.0097 mmol), $\Phi = 0.004$, 3-*tert*-butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene (0.029 mmol), $\Phi = 0.013$, 5%, 719 mg of 4-dimethylaminobenzophenone.

Run 8B: Starting cyclopropene, 225 mg (0.745 mmol), 2.45 mEinstein, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (0.15 mmol), $\Phi = 0.13$, 3-*tert*-butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene (0.32 mmol), $\Phi = 0.06$, 63%, 424 mg of xanthone.

In both runs 8A and 8B, 2-*tert*-butyl-1,3-diphenyl-5,5-dimethylcyclopentadiene and 3-isobutenyl-1-*tert*-butyl-2-phenylindene were *not* detected.

Photolysis of 3-*tert*-Butyl-1,2-diphenyl-5,5-dimethylcyclopentadiene. The photolysis was performed on the Wisconsin black box apparatus previously described. Filter B was used, and 750 mL of *tert*-butyl alcohol, distilled from calcium hydride, was used as solvent. The light output was monitored by ferrioxalate actinometry.

A solution containing 256 mg (0.848 mmol) of the cyclopentadiene absorbed 3.30 mEinstein of light. Upon concentration of the solution, no isomeric cyclopentadiene was detectable by NMR spectroscopy. It is estimated that 1% conversion ($\Phi = 0.003$) could have been detected.

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Registry No.—**1**, 12190-18-0; **4**, 65102-01-4; **7**, 38661-88-0; **8**, 56005-69-7; **9**, 65102-39-8; **10**, 65102-02-5; **11**, 58310-19-3; **12**, 62747-66-4; **13**, 4982-35-8; **14**, 15570-45-3; **15**, 62747-67-5; **16**, 62747-68-6; **17**, 65102-40-1; **18**, 65102-41-2; **19**, 62747-69-7; **20**, 62747-70-0; **21**, 62747-71-1; **22**, 62747-72-2; **23**, 65102-18-3; **24**, 65102-42-3; **25**, 65102-23-0; **26**, 65102-24-1; **27**, 65102-25-2; **28**, 65102-26-3; **29** (isomer I), 65102-27-4; **29** (isomer II), 65102-28-5; *cis*-**30**, 65102-29-6; *trans*-**30**, 65102-30-9; **31** (isomer I), 65102-31-0; **31** (isomer II), 65102-32-1; **32**, 65102-33-2; **32** (cyanohydrin TMS ether deriv), 65102-34-3; **32** (cyanohydrin deriv), 65102-35-4; **33**, 65102-36-5; **34**, 65102-37-6; **35**, 51310-25-9; **37**, 62747-73-3; *p*-toluenesulfonylhydrazine, 1576-35-8; trityl fluoroborate, 341-02-6; phenyl bromide, 108-86-1; diphenyldiazomethane, 17421-82-8; 1-phenylpropyne, 673-32-5; isobutenyl bromide, 3017-69-4; vinyl bromide, 593-60-2; 1,2,5-triphenyl-1,5-pentanedione, 58337-98-7; 1,2,3-triphenyl-1,2-cyclopentanediol, 65102-38-7; 1-phenylethenyl bromide, 98-81-7; *tert*-butylphenylacetylene, 4250-82-2; benzal chloride, 98-87-3; 3,3-dimethylacrylophenone, 5650-07-7; deoxybenzoin, 451-40-1; ethyl 3,3-dimethyl-2,5-diphenyl-5-oxopentanoate, 65102-14-9; ethyl phenylacetate, 101-97-3; 3,3-dimethyl-2,5-diphenyl-5-oxopentanoic acid, 65102-15-0; 4,4-dimethyl-3,5-diphenyl-3,4-dihydro-2-pyrone, 65102-16-1; 1,1-dimethyl-2-*tert*-butyl-2-trimethylsilyloxyethylene, 65102-17-2; 2-phenylacrylophenone, 4452-11-3; 2,2,5-trimethylhex-4-en-3-one, 14705-30-7; isopropyl bromide, 75-26-3; phenylacetic acid, 103-82-2; pivalophenone, 938-16-9; trimethylsilyl cyanide, 7677-24-9; isopropyltriphenylphosphonium, bromide, 1530-33-2.

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Photodecomposition of Diethyl Mercurybis(diazoacetate) in Several Heterocyclic Systems[1a]

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The products from the photolysis of diethyl mercurybis(diazoacetate) (1) in the solvent–reactant systems of tetrahydrofuran, tetrahydrothiophene, and pyrrolidine were studied for the determination of the relative importance of the various competing photodecomposition modes. Regioselective insertion reactions into carbon–hydrogen bonds α to the heteroatom were observed, whereas carbon–heteroatom insertion reactions were not observed. Analysis of the organic products, mercury, and nitrogen indicated that carboethoxycarbyne (:$\dot{C}CO_2Et$(A)) could account for 10–30% of the yields of α carbon–hydrogen insertion products. Mercury-containing products from the photodecomposition of 1 in pyrrolidine solution gave evidence for major participation of a mercury carbene (B) intermediate. The evidence also showed that other reaction paths were of little importance.

Monovalent carbon atoms, carbynes, represent an intriguing and little studied class of chemical intermediates. Diethyl mercurybis(diazoacetate) (1),[2] Buchner's compound, has been studied by Strausz et al. and was observed to furnish carboethoxymethyne (A) in low but usable yield under proper photolytic conditions.[3]

$Hg(N_2CCO_2C_2H_5)_2$ (1) $\qquad$ $:\dot{C}CO_2C_2H_5$ (A)

We previously reported that photolysis of 1 in chlorocarbon solvents gave products that could arise from association between A and the chlorine atoms; however, the reactions were very complex.[4]

We initiated the study reported here with the objective of finding less complicated reactions that would permit better definition of the photodecomposition paths followed by 1 and allow a better description of the chemistry of the intermediates involved. The heterocyclic solvent–reaction systems of tetrahydrofuran (THF), tetrahydrothiophene (THT), and pyrrolidine were chosen for study because their geometries are well defined and the heteroatom electronic effects are predictable.[5] Thus, meaningful rationalization of the photodecomposition routes and intermediates involved could be obtained from the study of their reaction products.

Results

Photolysis of 1 in THF and THT. Photolysis of 1 in THF gave N_2, Hg, and ethyl α-(tetrahydrofuranyl)acetate (2). Compound 2 was formed in good yield but was not isolated in a good state of purity. Direct hydrolysis of the reaction mixture containing 2 furnished α-(2-tetrahydrofuranyl)acetic acid in 41% yield. Comparison of the acid with a sample prepared unambiguously (see the Experimental Section) served to establish the correct α insertion structure. Products from insertion into either the β carbon–hydrogen bond or the carbon–oxygen bond were not observed.[6]

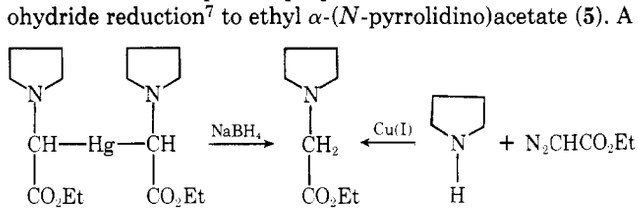
Photodecomposition of 1 in THT solution gave ethyl α-(2-tetrahydrothienyl)acetate (3) in 54% yield. This product

2 (>41%) $\qquad$ 3 (54%)

from α-carbon–hydrogen insertion was identified through its spectral characteristics which were similar to those of 2 and through conversion of the crude reaction product to the corresponding acid in 30% yield. The structure of the acid was confirmed by spectral analysis. The THT system, similar to the THF system, did not yield products resulting from insertion into either the β-carbon–hydrogen bonds or the carbon–sulfur bond.[6]

Olefinic products were observed in small amounts by NMR spectroscopy, but their structures were not determined. Product analysis was performed after nitrogen evolution had ceased even though mercury formation was not complete at that time (Table I).

Photolysis of 1 in Pyrrolidine. Three products were isolated from the photolysis of 1 in pyrrolidine. The major product, 4, was isolated in 48% yield. The structure of 4 was determined from spectral properties and from sodium borohydride reduction[7] to ethyl α-(*N*-pyrrolidino)acetate (5). A



4 $\qquad$ 5

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