Mechanistic and Exploratory Organic Photochemistry.[1] XVIII. Competing Pathways in the Rearrangements of 4,5-Diphenylcyclohexenone

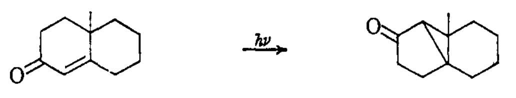
Howard E. Zimmerman and Donnie J. Sam[2]

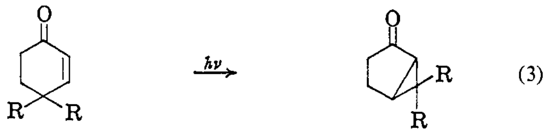
Contribution from the Department of Chemistry of the University of Wisconsin, Madison, Wisconsin 53706. *Received July 5, 1966*

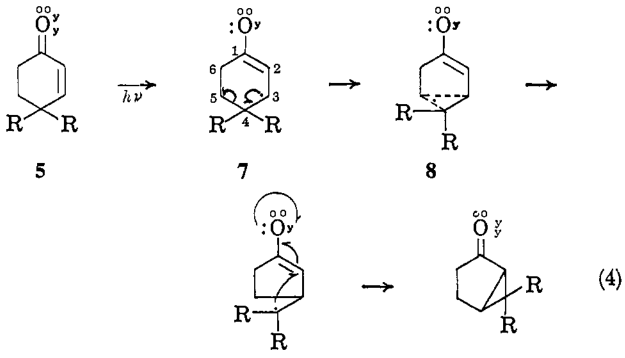
Abstract: Photolysis of 4,5-diphenylcyclohexenone (**16**) in 95% ethanol afforded 4,6-diphenylbicyclo[3.1.0]hexan-2-one (**18**). The mechanism of formation of photoketone **18** was investigated by specific ^{14}C labeling at C-3 of enone **16** and degradation of the photoketone product. Assay of the fragments showed that a (type A) skeletal rearrangement predominated over the alternative phenyl migration by a ratio of 70:1. Irradiation of enone **16** in *t*-butyl alcohol gave the same product and also 2-(*cis*-styryl)-3-phenylcyclobutanone (**19**). The formation of **19** is suggestive of homolytic fission of bond 4–5 of the excited state of enone **16**. Both the acetophenone-sensitized and direct irradiations of enone **16** gave the same product distribution, providing strong evidence that the reactions originated with the triplet.

Recently, we described the photochemical rearrangements of enones **1** and **2** to bicyclo[3.1.0] products **3** and **4**, respectively.[3] Similar skeletal rearrangements, termed "type A," had been previously reported by Chapman[4] for 4,4-dimethylcyclohexenone (**5**), by Gardner[5] for 4-cholestenone, and by Jeger, *et al.*,[6] for testosterone acetate. In our studies[3] it was shown by sensitization and quenching experiments that enones **1** and **2** were rearranging *via* triplet states. A remarkable finding was the dramatic inefficiency of these reactions. The enone triplets rearranged at least 10,000-fold less rapidly and 200-fold less efficiently than in the formally similar rearrangement of the 4,4-diphenylcyclohexadienone triplet.[7] We suggested[3,8d-f] that with the absence of the second double bond the usual pathway utilized by dienones[8a-d] is unavailable to enones and that the mechanism left to these enones is a different and significantly less efficient one.[8] We proposed the mechanism shown in eq 4 for the type A enone rearrangement. This pathway would be expected to be inefficient in light of homolytic fission of the C-4–C-5 σ bond.

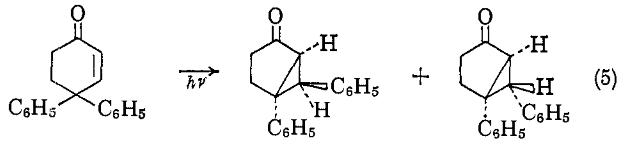

1 **3** (1)


2 **4** (2)


5 (type A enone rearrangement) **6**
(ref 4, R = CH$_3$) (3)


5 **7** **8** **9** **6** (4)

In contrast to the above reactions, 4,4-diphenylcyclohexenone **10** did not yield a type A product on irradiation but rather phenyl migration intervened.[8e] Because such strikingly different enone behavior was observed, depending on substitution, a more thorough investigation of 4-phenyl-substituted enones seemed desirable.


10 **11** **12** (5)

We now describe the photochemical behavior of 4,5-diphenylcyclohex-2-en-1-one (**16**). This compound

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[1] For paper XVI of the series note H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966). Paper XVII, preliminary communication, H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4115 (1966).

[2] Shell Fellow, 1963–1964; National Science Foundation Summer Fellow, 1964.

[3] (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966); (b) *ibid.*, **88**, 159 (1966).

[4] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

[5] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, 84, 2286 (1962).

[6] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

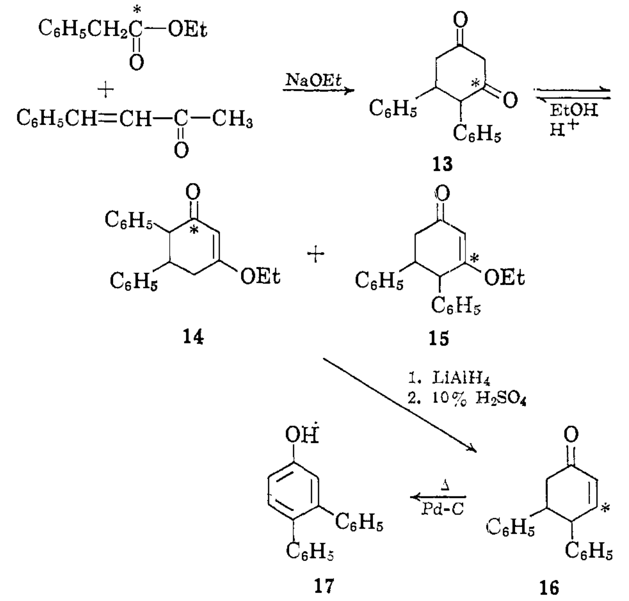
[7] The triplet rearrangement of 4,4-diphenylcyclohexadienone has been described by H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964). The quantum efficiency of this reaction is unpublished research of H. E. Zimmerman and J. S. Swenton.

[8] (a) H. E. Zimmerman, 17th National Organic Chemistry Symposium, June 1961, Abstracts, p 31; (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (d) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (e) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (f) H. E. Zimmerman, "Organic Photochemistry," I.U.P.A.C. Symposium, Butterworth and Co., Ltd., London, 1965, p 493.

seemed of special interest, since *a priori* a 4 → 3 phenyl migration was possible as with enone **10** and yet the likelihood of a type A rearrangement should be enhanced. The 5-phenyl substituent should facilitate breakage of the C-4–C-5 σ bond by odd-electron stabilization at C-5 of species **8** in eq 4.

The three-step synthesis of 4,5-diphenylcyclohexenone (**16**) illustrated in Chart I employs the sequence used by Zimmerman and Schuster for the preparation of 5,6-diphenylcyclohexenone.[8c] The spectral data (infrared, ultraviolet, nmr) and elemental analysis were consistent with structure **16** and are summarized in the Experimental Section. Solid confirmation was obtained by dehydrogenation to 3,4-diphenylphenol (**17**).

Chart I



* represents ^{14}C in labeled compounds

Photolysis of 4,5-diphenylcyclohexenone (**16**) in 95% ethanol through Pyrex, followed by scanning liquid–liquid partition chromatography[8c] of the reaction mixture, yielded 25–30% of a crystalline ketone, mp 90.0–90.5°, designated as "photoketone" **18**. In a typical run, 2.00 g of enone in 500 ml of 95% EtOH was irradiated to the absence of starting material and afforded 0.600 g of photoketone **18**. In runs to shorter conversion, the same products and distribution[9] were obtained.

Interestingly, direct or acetophenone-sensitized irradiation of enone **16** in *t*-butyl alcohol gave not only photoketone **18** but also an additional product with 5.62-μ infrared C=O absorption which was designated "photocyclobutanone" **19**. Silica gel chromatography of the reaction mixture afforded an 8–10% yield of photocyclobutanone **19**, mp 65–66°, in addition to a 40–45% yield of photoketone **18**.

In sensitized runs, in which the acetophenone was calculated to absorb at least 96% of the light, the same products, photoketone **18** and photocyclobutanone **19**, were obtained and in the same distribution as from direct irradiation. The enone concentration, 2.00 × 10^{-3} *M*, was sufficiently low that acetophenone singlet could not survive long enough to collide with enone molecules and excite these to enone singlet species but was sufficiently large to allow acetophenone triplets to collide with enone prior to their spontaneous decay.[3] Thus, these results showed that photoketone **18** and photocyclobutanone **19** were triplet-state photochemical products of enone **16**, for it would be exceedingly fortuitous for two different excited states to give the same product distribution (however, for a special case note ref 1).

Structure Elucidation. Photoketone **18** was shown to be 4,6-diphenylbicyclo[3.1.0]hexan-2-one. From spectral data, elemental analysis, and analogy to other enone photochemical rearrangements,[3–6,8e] it appeared that photoketone **18** was most likely a bicyclo[3.1.0]hexan-2-one. The infrared and ultraviolet spectra were similar to those of the bicyclic products **11** and **12** obtained from enone **10**,[8e] as shown in Table I. The absence of vinyl hydrogens was shown by nmr, and the elemental analysis showed **18** to be isomeric with starting material.

Table I

	Photoketone **18**	Ketone **11**	Ketone **12**
Infrared (CHCl$_3$), μ	5.82 (C=O)	5.83 (C=O)	5.80 (C=O)
Ultraviolet (EtOH),	End absorption	215 (17,160)	215 (17,010)
mμ	225 (9920)	220 (14,820)	220 (15,100)
		230 (7490)	230 (10,810)

The definite presence of the cyclopropane ring and the location of the two phenyl groups were established by the degradative scheme as shown in Chart II. The degradation began with a hypobromite oxidation of photoketone[10] which yielded hydroxy diacid **20**. The infrared spectrum of this material exhibited a hydroxyl absorption at 2.95 μ, typical carboxyl absorption at 3.0–4.4 μ, and a carbonyl band at 5.92 μ. The neutralization equivalent was 156 or 312 per mole which was exactly the same as theory. Lead tetraacetate oxidative cleavage of acid **20** afforded the known[11,12] *cis*-2-benzoyl-*trans*-3-phenylcyclopropane-1-carboxylic acid (**21**). The degradation located the phenyl substituents of photoketone at C-4 and C-6 (bicyclo[3.1.0] numbering), respectively, and thus confirmed the structure assigned. Additionally the stereochemistry at C-4 was defined.

Photocyclobutanone **19** was found to be 2-(*cis*-styryl)-3-phenylcyclobutanone. The elemental analysis and molecular weight (mass spectrum, *m/e* 248) showed the photoproduct to be isomeric with enone **16**, and the infrared spectrum suggested a cyclobutanone from the characteristic 5.62-μ carbonyl band.[13] From the ultraviolet spectrum, 247 mμ (ϵ 11,800) and 292 mμ (ϵ 856), which suggested the presence of a styryl substit-

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(9) In addition to photoketone **18**, hydroxy ketones and a nonhydroxylic ethanol adduct were obtained. The hydroxy ketones seem likely to result by hydrogen abstraction from ethanol followed by addition of HOCH–CH$_3$.

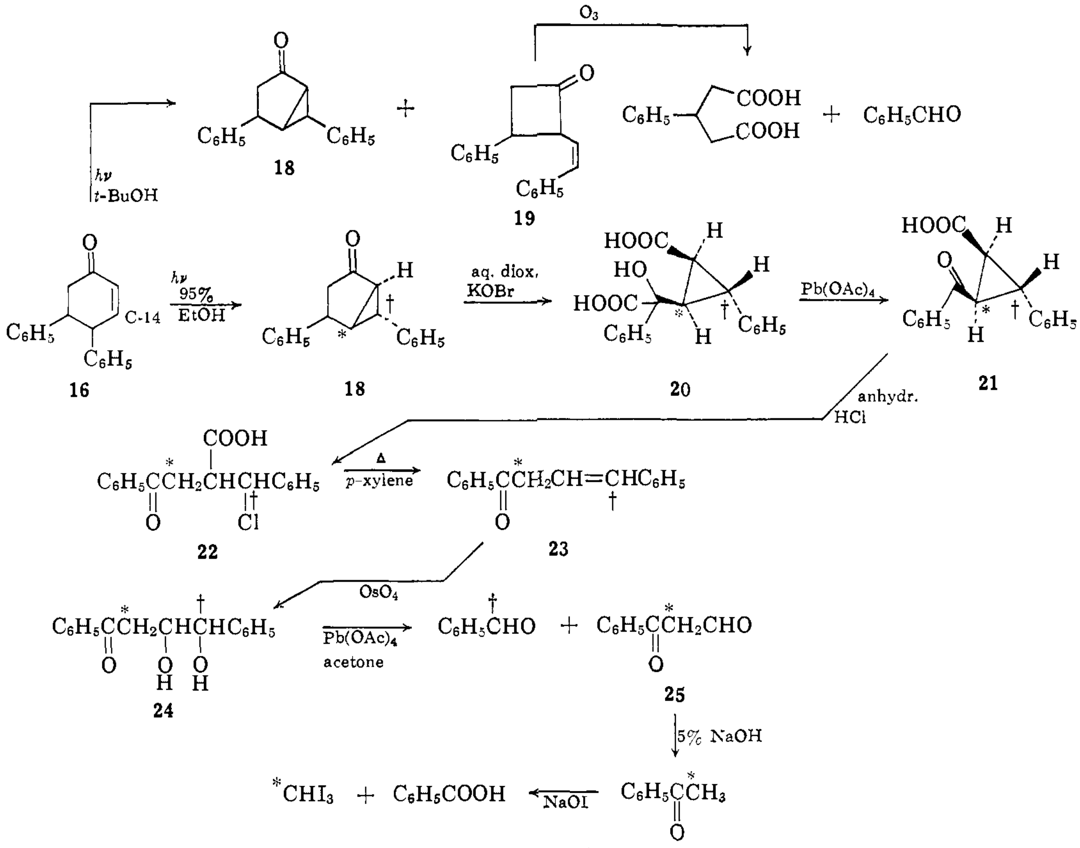
(10) A modification of the experimental method used by Zimmerman and Wilson[8e] for the degradation of ketones **11** and **12**.

(11) E. P. Kohler and L. L. Steele, *J. Am. Chem. Soc.*, **41**, 1093 (1919).

(12) The stereochemistry of the four isomeric 2-benzoyl-3-phenylcyclopropane-1-carboxylic acids was advanced by R. Stoermer and Fr. Schenck, *Ber.*, **60**, 2569 (1927), and was later confirmed by H. I. Bernstein and E. S. Wallis, *J. Org. Chem.*, **7**, 261 (1942).

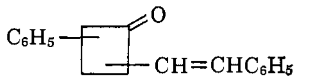
(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

Chart II



* represents ^{14}C if type A rearrangement
† represents ^{14}C if phenyl migration

uent (*cf.* styrene:[14] 244 mμ (ε 12,000), 282 mμ (ε 450)), and the chemical shifts of the two vinyl protons, τ 3.32 and 4.28 (J = 10.5 cps), it seemed certain that photocyclobutanone was a phenylstyrylcyclobutanone. Of the five isomeric phenylstyrylcyclobutanones **27–31**,



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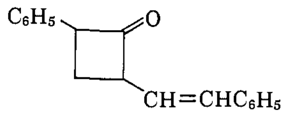
compounds **27** and **28** seemed unlikely in view of the reported chemical shift, τ 8.04, for the C-3 hydrogens of



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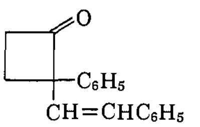

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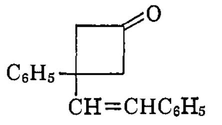

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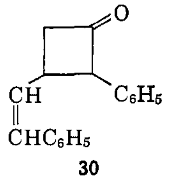

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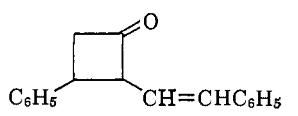

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cyclobutanone[15] and the small increments expected for β-phenyl, τ 0.35, and β-vinyl, τ 0.10, substitution;[16] actually a methylene peak appeared at τ 6.63, the highest field absorption. Structure **29** is inconsistent with the observation of a one-proton peak at τ 5.40, leaving structures **30** and **31** being most consistent with the observed nmr.

Upon ozonolysis of photocyclobutanone, 3-phenylglutaric acid and benzaldehyde were obtained. The isolation of benzaldehyde demonstrated the presence of the styryl substituent in photocyclobutanone. The formation of 3-phenylglutaric acid showed the absence of a carbonyl group adjacent to the phenyl-bearing ring carbon. 2-Styryl-3-phenylcyclobutanone is the only one of the five possible isomers where the phenyl substituent bears a 1,3 relationship to the two potential carboxyl groups in the photoproduct. It is quite clear that ring opening occurred during or following the ozonolysis, however, without introduction of oxygen at C-2 of the 3-phenyl-1-cyclobutanone moiety. Several mechanisms are possible; but the reaction does have precedent.[17]

Finally, the chemical shifts and coupling constants of the two vinyl protons of photocyclobutanone suggested that this was the *cis*-styryl isomer. The chemical shifts of the vinyl protons of *cis*-propenylbenzene are reported to be τ 3.60 and 4.30, while those of *trans*-

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(14) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth and Co., Ltd., London, 1961, p 17.

(15) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, 83, 1226 (1961).

(16) T. Curphey, Ph.D. Thesis, Harvard University.

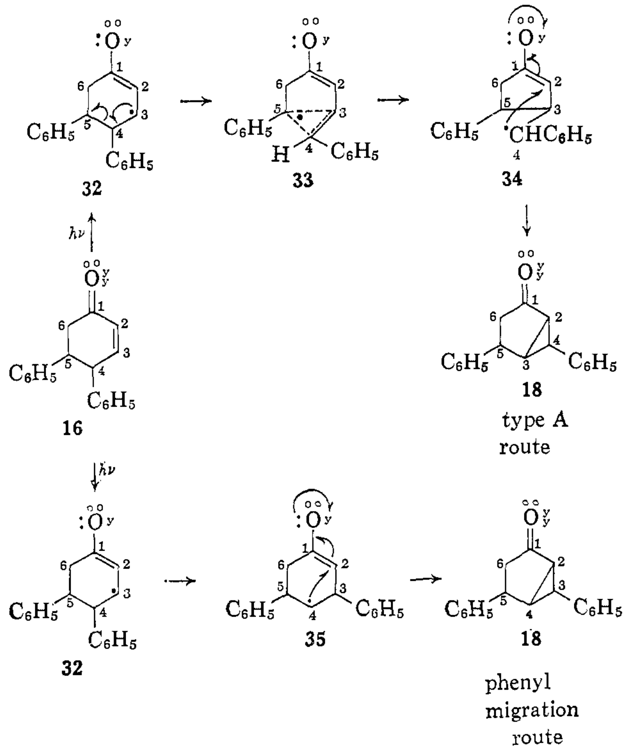
(17) Most simple is a reverse Dieckmann with ring opening of an initially formed 2-formyl-4-phenylcyclobutanone followed by oxidation. 2-Formylcyclohexanone has been reported (ref 18) to give adipic acid on hydrogen peroxide treatment; an oxidative-cleavage mechanism was proposed.

(18) S. I. Zavialov, L. P. Vinogradova, and G. V. Kondratieva, *Tetrahedron*, 20, 2745 (1964).

propenylbenzene are reported to τ 3.80 and 3.90.[19] The coupling constant of 10.5 cps found for photocyclobutanone is close to the 10.6- and 11.4-cps values reported for the *cis* hydrogens of styrene and of *cis*-propenylbenzene;[19] but the observed coupling constant is in poor agreement with the 17.2-cps value found[19] for *trans* hydrogens of styrene. Additionally, the infrared spectrum lacked the 10.4-μ band which is characteristic of a *trans* double bond.[13]

Determination of the Mechanism of Photoketone Formation by Isotopic Labeling. As is apparent from Chart III, both a type A rearrangement and the phenyl migration route lead to the same product, photoketone **18**. However, a skeletal difference exists. The type A reaction interchanges C-3 and C-4 of the six-membered ring while with phenyl migration no such skeletal change occurs.

Chart III



Enone **16** was labeled at C-3 by the synthesis depicted in Chart I. After photolysis of the labeled enone in 95% ethanol, photoketone was degraded as shown in Chart II. The type A rearrangement thus leads to ^{14}C in the benzoylacetaldehyde[20] fragment and the iodoform derived thereform while phenyl migration results in ^{14}C in the benzaldehyde. It remained only to assay these compounds for ^{14}C content to determine the mechanism. The method is outlined in the Experimental Section and the results are summarized in Table II.

It was found that 1.39 ± 0.03% of the ^{14}C activity was in the benzaldehyde obtained while 98.48 ± 1.47% of the ^{14}C resided in the benzoylacetaldehyde. Further degradation of the benzoylacetaldehyde by treatment with aqueous base and then hypoiodite gave iodoform with 98.48 ± 1.47% of the original activity. Thus in the photolysis of 4,5-diphenylcyclohexenone the type A skeletal rearrangement predominates to the extent of 98.61 ± 0.03% with the less important phenyl migration route being followed to the small but real extent of 1.39 ± 0.03%.

Table II. Carbon-14 Activities

Synthesis of 4,5-diphenylcyclohexenone-3-^{14}C		
^{14}C compounds		Specific activity, μcuries/mmole
$C_6H_5CH_2CO_2H$		2.52 ± 0.04
Dione **13**		2.47 ± 0.04
Enol ether **14**		2.50 ± 0.04
Enone **16**		2.51 ± 0.04
Photolysis and degradation[a]		
	1st run	2nd run
Photoketone **18**	2.52 ± 0.04	...
Hydroxy diacid **20**	...	2.46 ± 0.04
Acid **21**	...	2.46 ± 0.04
Chloro acid **22**	...	2.57 ± 0.04
Ketone **23**	2.50 ± 0.04	2.56 ± 0.04
Diol **24**	2.50 ± 0.04	...
Formylacetophenone copper chelate[b]	2.46 ± 0.04	2.51 ± 0.04
Benzaldehyde phenylhydrazone[c]	0.0336 ± 0.0004	0.0366 ± 0.0004
Degradation of benzoylacetaldehyde[a]		
Acetophenone	2.46 ± 0.04	
Iodoform	2.45 ± 0.04	
Benzoic acid	Inactive	

[a] Specific activities shown for compounds **22** onward corrected for dilution with inactive material. Absolute values for these compounds are given in the Experimental Section. [b] Formylacetophenone assayed as its copper chelate. [c] Benzaldehyde determined as its phenylhydrazone.

Discussion

Several questions arise as a result of the observations described in the preceding. First, the factors resulting in the preference for the type A skeletal rearrangement of 4,5-diphenylcyclohexenone, in contrast to the preference for phenyl migration in the closely related 4,4-diphenylcyclohexenone,[8e] require inspection. Related to this preference is the second matter of the molecular pathway by which the type A reaction actually occurs. Finally, there is need to consider the mechanism by which the photocyclobutanone is formed and the reasons why this type rearrangement occurs in the present enone.

One can entertain at least four reasons why 4,5-diphenylcyclohexenone (**16**) prefers the type A route over phenyl migration, while the not too dissimilar 4,4-diphenylcyclohexenone chooses phenyl migration. First, inspection of Chart III reveals that the phenyl migration route leads, after migration, to a species **35** in which the odd electron is localized[21] on C-4. In contrast, following phenyl migration in the case of 4,4-diphenylcyclohexenone (**10**) (note eq 6), there is engendered the corresponding species **37** in which the electron at C-4 is delocalized[21] by the phenyl group not

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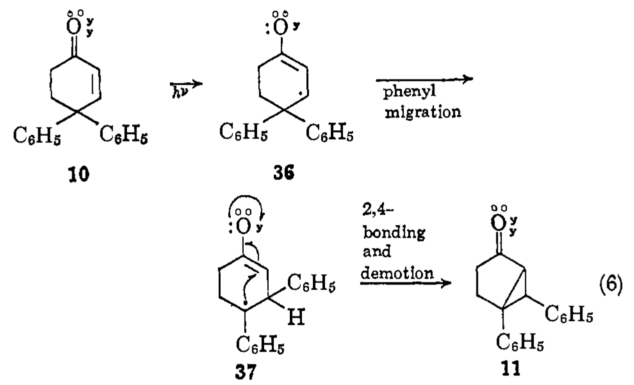
[19] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 238.

[20] This material was purified and assayed as its copper chelate (note Experimental Section).

[21] Evidence is available which suggests that the following step of 2,4 bonding is concerted with migration in the photochemical reactions of cyclohexenone: R. Rieke, J. Scheffer, K. Hancock, and H. E. Zimmerman, unpublished data. The argument here is thus idealized for simplicity.

migrating. Thus the potential energy surface for the n-π^* excited state 32 derived from the 4,5-diphenylcyclohexenone must encounter this poor delocalization at stage 35 and either have a greater barrier than in the case of the 4,4-diphenyl analog or have a less steep descent toward the product.

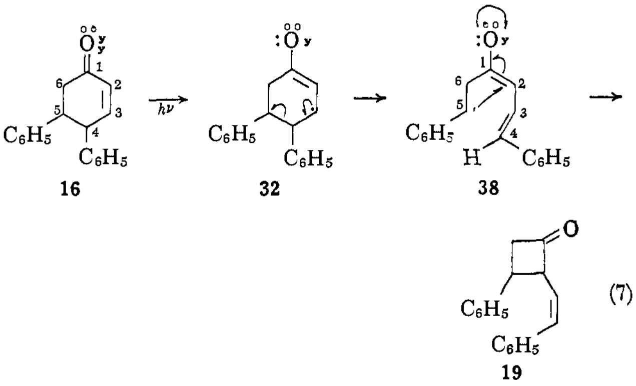


A second factor is the expected greater relief of phenyl–phenyl van der Waals repulsion in the migration of a phenyl group in 4,4-diphenylcyclohexenone (**10**) than in the case of 4,5-diphenylcyclohexenone (**16**). The assumption is that there is more relief of strain beginning with geminal phenyl groups than vicinal ones.

Still another and third consideration is stereochemical. The phenyl groups in 4,5-diphenylcyclohexenone are almost certainly *trans* related. It seems likely that equilibration would take place in the enol ether formation (Chart I) with the *trans* isomer being favored. As a consequence the phenyl group at C-4 will be equatorial in 4,5-diphenylcyclohexenone and in a poor conformation for migration. One might anticipate an axial phenyl group to be better able to bond with the β carbon of the enone excited state. There is no corresponding difficulty in the case of 4,4-diphenylcyclohexenone where one phenyl is necessarily axial.

The previous three factors have had the effect of making the phenyl migration reaction difficult for 4,5-diphenylcyclohexenone. One factor facilitating the type A reaction for the 4,5 isomer relative to the 4,4-diphenylcyclohexenone is phenyldelocalization of the odd-electron center at C-5 of species **33**. The counterpart of species **33** which would have to be formed in a type A rearrangement of the 4,4 isomer would have no similar stabilization. Whether this stabilization is sufficient to allow complete escape of C-5 from the π system is uncertain. We have suggested[3,8e] the possibility in less stabilized cases that the radical fragment may fail to escape from the π system.[22] Nevertheless, some suggestive evidence is afforded by the concurrent formation of the photocyclobutanone **19**.

The photochemical reaction forming 2-(*cis*-styryl)-3-phenylcyclobutanone (**19**) is without precedent in simple cyclohexenone[22b] photochemistry but is a mechanistically reasonable process. This photoproduct has not been observed even in the cases of 4,4-dialkylcyclohexenones where a type A reaction results. It is suggestive of at least a partially ring-opened species. After ring opening, giving rise to species **38**, attack of C-5 on C-2 rather than on C-3 would afford the cyclobutanone photoproduct (note eq 7). Again it is possible that species **38** is never engendered with C-5 free, but rather that C-5 slithers along from C-4 to C-3 to C-2 where it is firmly bound.[23]



In connection with the question of homolytic fission of bond 4–5 it is cogent to question the amount and source of the energy required to break this bond. For β-elimination of C-5 in the excited state of an enone we might use the reaction $CH_3–CH_2–CH_2\cdot \rightarrow CH_3\cdot + CH_2{=}CH_2$ with a heat of reaction of 19 kcal/mole as a very crude guide.[24] Although the enone triplet is 71 kcal/mole above ground state, we must inquire if electronic energy becomes available for reaction. Despite the low quantum efficiency of enone reactions[1] and rates which seem slow compared to dienone rearrangement rates,[1] nevertheless, the triplet rearrangement rates are very rapid (*ca.* 10^5 sec^{-1} for simple type A enone rearrangements[1]) when contrasted with common ground-state transformations. Thus it does seem that electron excitation energy probably is utilized. More specifically this means that electron demotion must occur during the rearrangement process; demotion prior to beginning of skeletal change would merely regenerate reactant ground state. We can conclude that electronic demotion most likely occurs concomitantly with the process leading in Chart III to species **33** and in eq 7 to **38**.

Experimental Section[25]

4,5-Diphenylcyclohexane-1,3-dione. This compound was prepared by the method of Borsche[26] as slightly modified by Zimmerman and Schuster.[8c] Both crystalline modifications, mp 159–160° and mp 191–192°, were obtained in a total yield of 44%.

Enol Ethers of 4,5-Diphenylcyclohexane-1,3-dione. 3-Ethoxy-5,6-diphenycyclohex-2-en-1-one.[27] A solution of 40.2 g (0.152

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(22) (a) Note also O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 161 (1966), for an example where at least 95% of the species do fail to escape. (b) The reaction does have at least formal analogy with the verbenone to chrysanthenone transformation: W. Erman, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, S29; J. J. Hurst and G. Whitam, *J. Chem. Soc.*, 2864 (1960).

(23) One observation arguing in favor of species **38** being formed in the photocyclobutanone formation but the π-bonded species **33** leading to the photoketone **18** is the finding that runs in ethanol no longer gave isolable amounts of photocyclobutanone while still yielding photoketone. In ethanol solvent there were formed a number of products whose composition seemed to suggest hydrogen abstraction from the solvent (note Experimental Section). Thus ethanol may have served as a trap for species **38**. Alternative explanations are possible.

(24) This accords with the high temperature (255–290°) utilized in the pyrolysis of 2-azocamphane which afforded some *isocamphane* by a free radical elimination–readdition mechanism: J. A. Berson, C. J. Olson, and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960).

(25) All melting points were taken on a hot-stage apparatus calibrated with known compounds.

(26) W. Borsche, *Ber.*, **42**, 4496 (1909).

(27) R. L. Frank and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **72**, 1645 (1950).

mole) of 4,5-diphenylcyclohexane-1,3-dione, 400 ml of dry benzene, 125 ml of absolute ethanol, and 3.0 g of *p*-toluenesulfonic acid was stirred and refluxed for 3.5 hr, and the water produced was collected with a Dean-Stark apparatus. The cooled, yellow reaction mixture was diluted with ether and washed thoroughly with water, 5% aqueous sodium bicarbonate, and again with water. Concentration *in vacuo* of the solvent left 51 g of a viscous, yellow oil. This material was chromatographed on a 5 × 120 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 4% EtOAc–benzene; 1-l. fractions were collected to give: fractions 1-8, 4% EtOAc–benzene, nil; 9–12, 4% EtOAc–benzene, 13.94 g of 3-ethoxy-5,6-diphenylcyclohex-2-en-1-one; 13–15, 4% EtOAc–benzene, 9.55 g of a mixture of both enol ethers; 16–23, 4% EtOAc–benzene, 11.95 g of a mixture of both enol ethers with mainly the undesired 3-ethoxy-4,5-diphenylcyclohex-2-en-1-one; 24–29, 10% EtOAc–benzene, 6.20 g of 3-ethoxy-4,5-diphenylcyclohex-2-en-1-one. Recrystallization of the solid from fractions 9–12 from chloroform–hexane gave 10.0 g of pure 3-ethoxy-5,6-diphenylcyclohex-2-en-1-one, mp 108–109°. Rechromatography of the remaining mixture of enol ethers proved impractical, and the mixture of enol ethers as well as the pure 3-ethoxy-4,5-diphenylcyclohex-2-en-1-one were hydrolyzed back to 4,5-diphenylcyclohexane-1,3-dione. The 22.8 g of β-diketone obtained was recycled to give an additional 4.3 g of the desired 5,6-diphenyl enol ether.

The infrared spectrum ($CHCl_3$) showed: 6.08, 6.22 (characteristic of β-diketone enol ethers[13]), 6.70, 6.90, 7.23, 8.60, 9.00, 9.71, and 11.80 μ.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.44; H, 7.10.

Acid Hydrolysis of 3-Ethoxy-5,6-diphenylcyclohex-2-en-1-one and 3-Ethoxy-4,5-diphenylcyclohex-2-en-1-one. The above mixture of 34.97 g (0.0120 mole) of the two isomeric enol ethers dissolved in 600 ml of ether was added to 1 l. of 6 *N* HCl. The two-phase system was stirred rapidly at 25° for 12 hr. The ether layer was extracted with 5% NaOH and then concentrated *in vacuo* to leave 4.78 g of unhydrolyzed enol ether. The yellow aqueous layer was treated with Norit to give a clear, colorless solution which was acidified with 6 *N* HCl and ether extracted. The extracts were concentrated *in vacuo* to afford 22.84 g of 4,5-diphenylcyclohexane-1,3-dione, mp 159–160° (85%).

4,5-Diphenylcyclohex-2-en-1-one. A solution of 10.73 g (36.8 mmoles) of 3-ethoxy-5,6-diphenylcyclohex-2-en-1-one in 50 ml of anhydrous benzene and 300 ml of anhydrous ether was added dropwise with stirring over a 20-min period to 0.714 g (18.8 mmoles) of lithium aluminum hydride in 100 ml of anhydrous ether. After addition, the solution was stirred at 25° for 2 hr and then cautiously hydrolyzed with 10% sulfuric acid, whereupon vigorous refluxing ensued. The aqueous phase was ether and chloroform extracted. These extracts added to the organic phase were concentrated *in vacuo* leaving 9.63 g of colorless crystals, which on recrystallization from ethanol-water yielded 7.55 g of pure 4,5-diphenylcyclohex-2-en-1-one, mp 97.0–97.5° (83%).

The infrared spectrum ($CHCl_3$) showed: 5.98 (C=O), 6.25, 6.71, 6.90, and 11.90 μ; ultraviolet spectrum (95% EtOH): strong-end absorption with shoulders at 222 mμ (ε 15,100), 235 (10,900), 264 (2600), 269 (1770), and a low intensity n–π* band at λ_{max} 322 (36); nmr (CCl_4): τ 2.78–3.33 (11 H, multiplet, aromatic, one vinyl), 3.90 (1 H, doublet, J = 10 cps, with each peak split into a doublet, J = 2.5 cps, vinyl), 6.12–7.05 (2 H, multiplet, two C_6H_5CH), 7.18–7.46 (2 H, multiplet, CH_2).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.16; H, 6.51.

3,4-Diphenylphenol.[8c] A mixture of 0.407 g (1.65 mmoles) of 4,5-diphenylcyclohex-2-en-1-one in 3.0 ml of *p*-cymene and 0.131 g of 10% palladium on charcoal was stirred and refluxed for 7 hr. The reaction mixture was cooled, and the catalyst was filtered and washed thoroughly with chloroform. The dark, yellow-brown filtrate was concentrated *in vacuo*, and the last traces of *p*-cymene were removed *in vacuo* at 50° and 0.01 mm. An infrared analysis of the residue showed the absence of starting material but the presence of 3,4-diphenylphenol contaminated with a 5.85-μ carbonyl compound. This material was chromatographed on a 2.5 × 75 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 5% ether–hexane; 250-ml fractions were collected to give: fraction 1, 5% ether–hexane; 2–4, 10% ether–hexane; 5–6, 20% ether–hexane, nil; 7–8, 20% ether–hexane, 165 mg of 3,4-diphenylphenol; 9, 20% ether–hexane, 58.6 mg of a mixture of 3,4-diphenylphenol and a 5.85-μ carbonyl compound; 10, 20% ether–hexane, 53.8 mg of a yellow solid, mp 98.5–104.5°, possibly 3,4-diphenylcyclohexanone. The solid obtained from fractions 7–8 was recrystallized from hexane to give 0.147 g of 3,4-diphenylphenol, mp 104–105°. The infrared spectrum was identical with that of an authentic sample of 3,4-diphenylphenol which was available from previous work in this laboratory,[8c] and a mixture melting point with an authentic sample was undepressed.

The infrared spectrum ($CHCl_3$) showed: 2.78 (sharp, nonhydrogen-bonded hydroxyl), 3.00 (broad, hydrogen-bonded hydroxyl), 6.25, 6.40, 6.78, 7.17, 8.54, and 11.23 μ.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.68; H, 5.83.

Photolysis of 4,5-Diphenylcyclohex-2-en-1-one in 95% Ethanol. A solution of 2.010 g (8.47 mmoles) of 4,5-diphenylcyclohex-2-en-1-one in 500 ml of 95% ethanol was stirred and irradiated under nitrogen[28] through a Pyrex filter using a 450-w Hanovia medium-pressure immersion lamp for 18 hr. Concentration *in vacuo* at 40° left 2.422 g of a viscous, yellow oil. This material was subjected to liquid–liquid partition chromatography[8c] using cyclohexane–dimethylformamide–ethyl acetate–water (100:40:25:3, v/v) at 29°, a 150 × 3.5 cm column packed with diatomaceous earth (Celatom FW-80, Eagle Picher Co.) bearing 40% by weight of lower phase. The 40-ml fractions were collected to give: fractions 1–31, nil; 32–41, 0.204 g, yellow oil (mixture of a noncarbonyl compound with a 5.82-μ carbonyl compound); 42–46, 0.148 g, yellow oil (ethanol adduct); 47–53, 0.772 g, yellow oil (photoketone); 54–210, 1.284 g, yellow oil (complex mixture of hydroxy ketones and a small amount of ketonic dimer of starting material).

Characterization of Photoketone. 4,6-Diphenylbicyclo[3.1.0]hexan-2-one. The 0.772 g of yellow oil crystallized on standing and was recrystallized from ether–hexane to give 0.600 g of pure 4,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 90.0–90.5° (30%).

The infrared spectrum ($CHCl_3$) showed: 5.82 (C=O), 6.25, 6.71, 6.90, 7.09, 9.55, 9.72, 9.85, 10.35, and 11.33 μ; ultraviolet spectrum (95% EtOH): end absorption with shoulders at 225 mμ (ε 9920), 266 (827), 273 (620); nmr (CCl_4): τ 2.68–3.15 (10 H, multiplet, aromatic); 6.15 (1 H; triplet, J = 10 cps, split into 3 doublets, J = 4 cps; C_6H_5CH), 7.20–7.96 (5 H, multiplet, three CH, one CH_2).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.08; H, 6.46.

Isolation of Ethanol Adduct. Crystalline adduct was obtained only after silica gel chromatography. A total of 0.266 g of crude adduct from two identical irradiations and liquid–liquid separation was chromatographed on a 70 × 2.5 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 5% ether–hexane; 160-ml fractions were collected to give: fractions 1–6, 5% ether–hexane, 7–16, 10% ether–hexane, nil; 17–25, 15% ether–hexane, 31 mg of a yellow oil; 26–45, 15% ether-hexane, 0.178 g of a pale yellow oil.

A solution of the 0.178 g of oil from fractions 26–45 crystallized to give a colorless solid when cooled with Dry Ice–acetone. Recrystallization from chloroform–hexane yielded 0.134 g of pure ethanol adduct, mp 78–79°.

The infrared spectrum ($CHCl_3$) showed: 5.82 (C=O), 6.25, 6.71, 6.90, 7.29, 9.25 (broad, strong, characteristic[13] of C–O), and 9.74 μ; nmr (CCl_4): τ 3.02 (10 H, singlet, aromatic), 6.7–7.6 (9 H, multiplet), 9.18 (3 H, triplet, J = 7 cps, CH_3).

The C–H analysis corresponds to a 1:1 adduct of ethanol and enone, and since there was no hydroxyl absorption in the infrared, this product is an ethoxylethanol adduct of starting material.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.76; H, 7.57.

Isolation of Dimer and Hydroxy Ketones. From fractions 64–73, 33 mg of solid, mp 215–218°, were obtained which was recrystallized from chloroform–hexane to yield a pure, colorless ketonic dimer, mp 223–224°. The infrared spectrum ($CHCl_3$) showed: no O–H, 5.85 (C=O), 6.25, 6.71, 6.90, and 7.90 μ; mol wt (osmometric in $CHCl_3$): 507, 526 (theory: 496).

From fractions 74–92, an oily solid was obtained which was washed with ether and recrystallized from chloroform–hexane to yield 34 mg of a pure, colorless hydroxy ketone, mp 171–172°. The infrared spectrum ($CHCl_3$) showed: 2.75 (O–H), 2.90 (O–H), 5.85 (C=O), 6.25, 6.71, 6.90, 10.23, 11.05, and 11.30 μ; nmr ($DCCl_3$): τ 2.96 (10 H, singlet, aromatic), 6.3–8.0 (8 H, broad multiplet), 8.58 (1 H, singlet, CH), 8.95 (3 H, doublet, J = 7 cps, CH_3). The C–H analysis is consistent with a 1:1 adduct of ethanol and starting material.

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[28] Purified by vanadous sulfate removal of oxygen by the method of L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.69; H, 7.61.

Infrared spectra of all remaining liquid–liquid chromatography fractions had O–H and C═O absorptions; nmr spectra of these fractions showed no vinyl protons. Silica gel chromatography of the total amount of hydroxy ketones afforded little separation but revealed the complexity of the mixture. These compounds were not further investigated.

Photolysis of 4,5-Diphenylcyclohex-2-en-1-one in *t*-Butyl Alcohol. A solution of 1.497 g (6.05 mmoles) of 4,5-diphenylcyclohex-2-en-1-one in 1 l. of distilled *t*-butyl alcohol was stirred and irradiated under nitrogen[28] through a Pyrex filter using a 450-w Hanovia medium-pressure immersion lamp for 12 hr at 36°. The optical density of the photolysis solution at 322 mμ, the λ_{max} of the n–π^* band of starting material, at 0, 1, 3.5, 6.5, 9.5, and 12.5 hr was in the ratio of 1:3.3:6.6:10.0:11.6:11.6, respectively. Concentration *in vacuo* at 40° left 1.550 g of a viscous, yellow oil. This material combined with 1.277 g of oil from a similar irradiation of 1.268 g (5.11 mmoles) of enone was chromatographed on a 100 × 2 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 5% ether–hexane. The eluate was scanned at 256 mμ and collected in 40-ml fractions. Fractions 1–5, 5% ether–hexane, nil; 6–39, 5% ether–hexane, 0.247 g of a mixture of a nonhydroxyl, noncarbonyl compound and a 5.82-μ carbonyl compound; 40–65, 5% ether–hexane, 0.234 g of 2-(*cis*-styryl)-3-phenylcyclobutanone; 66–115, 5% ether–hexane, 0.229 g of a 5.62-μ carbonyl compound contaminated with 5.82- and 5.90-μ carbonyl compounds; 116–135, 5% ether–hexane, nil; 135–147, 20% ether–hexane, 0.114 g of a yellow oil; 148–180, 20% ether–hexane, 1.647 g of a mixture of 4,6-diphenylbicyclo[3.1.0]hexan-2-one and unreacted enone contaminated with a trace of a 5.62-μ carbonyl compound.

Isolation and Characterization of 2-(*cis*-Styryl)-3-phenylcyclobutanone. The solid from fractions 40–65 was recrystallized from ether–hexane to yield 0.170 g (9%) of pure 2-(*cis*-styryl)-3-phenylcyclobutanone, mp 65–66°.

The infrared spectrum ($CHCl_3$) showed: no O–H, 5.62 (characteristic[13] of cyclobutanone C═O), 6.25, 6.71, 6.90, 7.18, 8.98, and 9.30 μ; ultraviolet spectrum (cyclohexane): λ_{max} 247 mμ (ϵ 11,800) with shoulders at 292 (856) and 310 (527); ultraviolet spectrum of styrene (EtOH): λ_{max} 244 (12,000) and 282 (450);[14] nmr ($CHCl_3$): τ 2.78 (10 H, multiplet, aromatic), 3.32 (1 H, doublet, J = 10.5 cps, $C_6H_5CH{=}C$), 4.28 (1 H, triplet, J = 10.5 cps, $C_6H_5C{=}CH{-}$), 5.40 (1 H, triplet, CH), 6.63 (3 H, broad singlet, CH_2, C_6H_5CH). The chemical shifts of the ethylenic protons of *cis*-propenylbenzene are reported[19] to be τ 3.60 and 4.30.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.84; H, 6.27.

Isolation of 4,6-Diphenylbicyclo[3.1.0]hexan-2-one. Recrystallization of the 1.647 g of material from fractions 148–180 from ether–hexane afforded 0.298 g of pure reactant enone, mp 97.0–97.5°, and 0.457 g of pure photoketone, mp 90.0–90.5°. The remaining 0.900 g of viscous, yellow oil in the filtrates was subjected to liquid–liquid partition chromatography on a 100 × 3.5 cm column; 40-ml fractions were collected: fractions 1–14, nil; 15–21, 57 mg of a yellow oil with 5.62- and 5.82-μ C═O bands; 22–28, 0.711 g of enone and photoketone A; 29–44, 28 mg of a yellow oil with 5.62- and 5.8–6.0-μ C═O bands. The 0.711 g from fractions 22–28 was recrystallized from ether–hexane to yield 0.221 g of enone, mp 97.0–97.5°, and 76 mg of photoketone, mp 90.0–90.5°, leaving 0.410 g as an oily mixture of the two components. In other runs, the separation of photoketone from enone was considerably better, and an average yield of 43% of pure 4,6-diphenylbicyclo[3.1.0]hexan-2-one was obtained. In a total of six runs, 7.844 g of enone was irradiated similarly and yielded a 4.990-g mixture of enone and photoketone. Upon liquid–liquid separation and recrystallization from ether–hexane, 2.05 g of unreacted enone and 2.50 g of pure photoketone were obtained.

Photolysis of 2-(*cis*-Styryl)-3-phenylcyclobutanone in 95% EtOH. In order to determine the stability of 2-(*cis*-styryl)-3-phenylcyclobutanone under ethanol irradiation conditions, a 0.050-g (0.20 mmole) sample of the pure cyclobutanone in 125 ml of 95% EtOH was stirred and irradiated under nitrogen[29] through a Pyrex filter using a 450-w Hanovia medium-pressure immersion lamp. The infrared of the photolysis solution after 1 hr was unchanged except for the formation of a weak band at 10.35 μ. After 3 hr, the solution was concentrated *in vacuo* to yield 40 mg of a pale yellow oil. The infrared was the same as that of starting cyclobutanone except for intensification of the new band at 10.35 μ and broadening of the 9.30-μ band initially present in the 2-(*cis*-styryl)-3-phenylcyclobutanone.

This control experiment showed that the absence of the cyclobutanone photoproduct in the irradiation of 4,5-diphenylcyclohex-2-en-1-one in 95% EtOH cannot be attributed to formation and subsequent photochemical conversion to one of the products of the ethanol irradiation.

Acetophenone-Sensitized Irradiation of 4,5-Diphenylcyclohex-2-en-1-one in *t*-Butyl Alcohol. A solution of 0.495 g (2.00 mmoles) of 4,5-diphenylcyclohex-2-en-1-one and 23.3 g (0.195 mole) of acetophenone, calculated to absorb at least 96% of the light, in 1 l. of distilled *t*-butyl alcohol, was stirred and irradiated at 36° under nitrogen[28] through a solution filter with a 450-w Hanovia medium-pressure immersion lamp for 3 hr. The filter solution, prepared from 40 g of $CuSO_4$, 315 g of $NiSO_4$, 600 g of $CoSO_4$, and 47 g of KNO_3 in 1 l. of water, transmitted light between 313 and 373 mμ with 7.3, 26.0, 34.3, 28.0, 14.0, and 2.4% transmittance at 320, 330, 340, 350, 360, and 370 mμ, respectively. This was circulated through the cooling jacket of the immersion well. The infrared of the photolysis solution corresponded to that of a 6.5-hr direct irradiation, and the optical density had increased slightly, 3% at 310 mμ and 4% at 340 mμ. The filter solution was unchanged. Concentration *in vacuo* removed the *t*-butyl alcohol, and the acetophenone was removed by short-path distillation *in vacuo*, leaving 0.658 g of yellow oil. This material was chromatographed on a 90 × 2.5 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 5% ether–hexane; 40-ml fractions were collected as follows: fractions 1–5, 5% ether–hexane, nil; 6–53, 5% ether–hexane, 32 mg of a mixture of a nonhydroxyl, noncarbonyl compound with a 5.82-μ C═O compound; 54–71, 5% ether–hexane, 30 mg of 2-(*cis*-styryl)-3-phenylcyclobutanone; 72–130, 5% ether–hexane, 48 mg of a 5.62-μ C═O compound contaminated with 5.82- and 5.90-μ C═O compounds; 131–137, 15% ether–hexane, nil; 138–219, 15% ether–hexane, 0.332 g of a mixture of starting material and 4,6-diphenylbicyclo[3.1.0]hexan-2-one. The products and scan of the chromatography were the same as for direct irradiation, and the material obtained from chromatography was less colored in this sensitized run such that the products were obtained easily without further chromatography. Recrystallization of the solid from fractions 54–71 yielded 21 mg (8%) of pure 2-(*cis*-styryl)-3-phenylcyclobutanone, mp 65–66°. Photoketone and enone were fractionally crystallized to yield 0.107 g (37%) of pure 4,6-diphenylbicyclo[3.1.0]hexan-2-one and 0.203 g of pure 4,5-diphenylcyclohex-2-en-1-one.

2-(α-Carboxy-α-hydroxybenzyl)-3-phenylcyclopropane-1-carboxylic Acid. The general method of Zimmerman and Wilson[8e] was used. Potassium hypobromite, prepared from 1.28 g (8.0 mmoles) of bromine and 1.71 g (26.0 mmoles) of potassium hydroxide in 160 ml of water, was added to a solution of 0.455 g (1.83 mmoles) of 4,6-diphenylbicyclo[3.1.0]hexan-2-one in 120 ml of *p*-dioxane. The mixture was stirred under nitrogen at 25° for 16 hr. Then 2.0 g of sodium bisulfite in 10 ml of water was added to decompose excess hypobromite, and the resulting solution was made basic with potassium hydroxide. The solvent was concentrated *in vacuo* to about 100 ml and ether extracted. The ether extracts contained only 2.4 mg of neutral material. The basic, aqueous phase was acidified in the cold with 6 *N* HCl and then ether extracted. The extracts were dried and concentrated *in vacuo* leaving 0.498 g of a yellow, gummy solid. The solid was washed with hexane and recrystallized from acetone–water to yield 0.246 g (45%) of 2-(α-carboxy-α-hydroxybenzyl)-3-phenylcyclopropane-1-carboxylic acid, mp 198–199°.

The infrared spectrum (KBr) showed: 2.95 (broad, O–H), 3.0–4.4 (broad), and 5.92 μ (C═O); neut equiv: 156 (*i.e.*, 312 per mole); theory: $C_{18}H_{16}O_5$: 312.

Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.12. Found: C, 69.05; H, 5.31.

2-Benzoyl-3-phenylcyclopropane-1-carboxylic Acid. The general procedure of Hardtmann was employed.[29] A solution of 85 mg (0.27 mmole) of 2-(α-carboxy-α-hydroxybenzyl)-3-phenylcyclopropane-1-carboxylic acid in 7.0 ml of dry acetone was stirred at 25° for 50 min with 0.177 g (0.40 mmole) of acetic acid free lead tetraacetate. The yellow reaction mixture was diluted with 20 ml of ether, and 20 ml of hexane was added, precipitating lead salts. The organic phase was washed with water and concentrated *in vacuo*, leaving 63 mg of a colorless solid. Recrystallization from chloroform–hexane left 53 mg (74%) of 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid, mp 176–177°. The infrared of this material was identical in all respects with an authentic sample of *cis*-2-benzoyl-

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(29) The general method of G. Hardtmann, Ph.D. Thesis, Technische Hochschule, Braunschweig, 1961.

trans-3-phenylcyclopropane-1-carboxylic acid, and a mixture melting point with an authentic sample was undepressed.

The infrared spectrum (KBr) showed: 3.0–4.3 (broad), 5.95 (C=O), 6.90, 9.40, 9.60, 9.80, 10.00, and 10.50 μ; nmr (DCCl$_3$): τ 1.85–2.20 (2 H, multiplet, *ortho* in benzoyl), 2.38–3.00 (8 H, multiplet, aromatic), -0.78 (1 H, singlet, COOH), and 6.58–7.60 (3 H, multiplet, three C–H).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.43; H, 5.39.

1-Phenacyl-2-chloro-2-phenylpropionic Acid.[11] Anhydrous HCl was bubbled through a solution of 0.144 g (0.54 mmole) of 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid in 60 ml of glacial acetic acid for 80 min. The yellow, HCl-saturated solution was kept at 25° for 3 hr. Concentration *in vacuo* below 40° yielded 0.200 g of a yellow oil which crystallized on standing. Recrystallization from ether–hexane gave 0.151 g (92%) of pure 1-phenacyl-2-chloro-2-phenylpropionic acid, mp 118–119° dec (with gas evolution) (lit.[11] 131–132° dec (with gas evolution)).

The infrared spectrum (CHCl$_3$) showed: 3.0–4.0 (broad), 5.82 (C=O), 5.94 (C=O), 6.25, 6.34, 6.71, 6.90, and 10.00 μ.

Another crystalline modification of this β-chloro acid was obtained, mp 125–126° dec (and gas evolution). Recrystallization of this material in the presence of a seed of the lower melting crystalline form only gave material which melted at 118–119°. Similarly, when the lower melting crystals were seeded with the 125–126° crystalline form, the resulting solid material melted at 125–126°.

Anal. Calcd for $C_{17}H_{15}O_3Cl$: C, 67.44; H, 4.99; Cl, 11.71. Found: C, 67.39; H, 4.96; Cl, 12.05.

1,4-Diphenylbut-3-en-1-one.[11] A 1.984-g (8.944 mmoles) sample of 1-phenacyl-2-chloro-2-phenylpropionic acid was suspended in 12.5 ml of *p*-xylene. The mixture was heated at 150° under nitrogen. Within 5 min the β-chloro acid dissolved, the solution had become a pale yellow, and HCl and carbon dioxide were evolved. After 4 hr an aliquot was free of starting material. Concentration *in vacuo* gave a yellow oil which crystallized on standing. Recrystallization from ether–hexane yielded 0.663 g of 1,4-diphenylbut-3-en-1-one, mp 93.5–94.0° (lit.[11] 93–94°). Microdistillation of the remaining yellow oil gave an additional 50 mg of solid, mp 93.5–94.0°. The total yield was 0.713 g (49%).

The infrared spectrum (CHCl$_3$) showed: 5.94 (C=O), 6.25, 6.34, 6.71, 6.90, 10.00, 10.15, and 10.38 μ (characteristic[13] of a *trans* C=C); ultraviolet (cyclohexane): λ_{max} 247.5 mμ (ϵ 27,100) with shoulders at 285 (3460) and 292 (1660) and a low intensity n–π^* band at 327 (267); ultraviolet spectrum of acetophenone (heptane): λ_{max} 240 mμ (ϵ 13,000), 278, (1100), and an n–π^* band at 325 mμ.

The ultraviolet spectrum of styrene (EtOH) showed: λ_{max} 244 mμ (ϵ 12,000) and 282 mμ (ϵ 450);[14] nmr (DCCl$_3$): τ 1.85–2.18 (2 H, multiplet, *ortho* in benzoyl), 2.38–2.95 (8 H, multiplet, aromatic), 3.72 (2 H, broad singlet, CH=CH), and 6.12 (2 H, broad singlet, CH$_2$). The ethylenic protons in *trans*-propenylbenzene are reported[19] to be at τ 3.80 and 3.90.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.36; H, 6.38.

3,4-Dihydroxy-1,4-diphenylbutan-1-one. Addition of 0.892 g (4.02 mmoles) of 1,4-diphenylbut-3-en-1-one in 40 ml of THF, freshly distilled from potassium hydroxide and then lithium aluminum hydride, to 0.077 g (0.303 mmole) of osmium tetroxide and 1.18 g (9.57 mmoles) of potassium chlorate in 28 ml of water produced a two-phase system with the upper layer being a dark brown indicative of osmate ester formation. The mixture was stirred at 50–55°, and after 19 hr the upper layer was a pale yellow. Upon cooling, one phase resulted, and the solution was diluted with ether and washed with 3% sodium hydroxide and water. The organic layer was dried and concentrated *in vacuo* to give 0.750 g of an oily, yellow solid, mp 115–125°. Recrystallization from chloroform–hexane gave 0.343 g (34%) of pure 3,4-dihydroxy-1,4-diphenylbutan-2-one, mp 138–139°.

The infrared spectrum (KBr) showed: 3.0 (broad, O–H), 5.98 (C=O), 6.71, 6.90, 7.30, 7.70, 8.30, 8.55, 9.37, and 9.80 μ.

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.90; H, 6.09.

Lead Tetraacetate Oxidation of 3,4-Dihydroxy-1,4-diphenylbutan-2-one to Benzoylacetaldehyde and Benzaldehyde. A solution of 0.137 g (0.533 mmole) of 3,4-dihydroxy-1,4-diphenylbutan-2-one in 9.0 ml of dry acetone was stirred with 0.307 g (0.694 mmole) of lead tetraacetate (acetic acid free) at 25° for 45 min. The yellow reaction mixture was diluted with 20 ml of ether, and 20 ml of hexane was added, precipitating lead salts. The organic phase was extracted with water, 5% sodium hydroxide, and again with water. The ether layer was concentrated *in vacuo* to *ca.* 5 ml, and 0.155 g of phenylhydrazine and 0.05 ml of acetic acid were added. The ether was removed, and the solution was heated on a steam bath for 10 min. Water was added producing a yellow solid. Recrystallization from ethanol–water yielded 25 mg of pure benzaldehyde phenylhydrazone, mp 155–156°, whose infrared spectrum was identical with that of authentic material; a mixture melting point with an authentic sample was undepressed. In an earlier run, benzaldehyde was isolated before derivatization, and its infrared spectrum was identical with that of authentic material.

The aqueous phase containing the β-keto aldehyde was acidified with 6 *N* HCl and ether extracted. The extracts were concentrated *in vacuo* to *ca.* 2 ml, and 3.0 ml of ethanol followed by 1.0 ml of saturated aqueous cupric acetate were added to give a dark green solution. Concentration *in vacuo*, dilution with benzene, drying over sodium sulfate, and concentration *in vacuo* left 78 mg of a dark green solid. Recrystallization from benzene–hexane yielded 45 mg of pure copper chelate of benzoylacetaldehyde,[30,31] mp 199–200°. The infrared spectrum was identical with that of authentic material,[30] and a mixture melting point with an authentic sample was undepressed.

Base Degradation of Benzoylacetaldehyde to Acetophenone. A 0.311-g (0.869 mmole) sample of the copper chelate of benzoylacetaldehyde in 50 ml of ether was shaken with 25 ml of 5% HCl until all of the green solid had been hydrolyzed (5 min). The ether layer was washed with water, dried, and concentrated *in vacuo* to leave benzoylacetaldehyde as a yellow oil. The β-keto aldehyde was dissolved in 15 ml of 5% sodium hydroxide and heated on a stream bath for 10 min, whereupon the solution became opaque and an oil separated. The cooled solution was ether extracted, and the extracts were dried and concentrated *in vacuo* to yield 0.181 g of acetophenone (87%). The infrared spectrum was identical in all respects with that of acetophenone, and the semicarbazone, mp 198–200°, was identical with authentic material.

Hypoiodite Oxidation of Acetophenone. Iodoform and Benzoic Acid. A 10% solution of iodine in 20% aqueous potassium iodide (5.0 g of iodine and 10 g of potassium iodide in 40 ml of water) was added dropwise to a 0.108-g (0.90 mmole) sample of acetophenone in 2.0 ml of *p*-dioxane and 3.0 ml of 10% sodium hydroxide until the iodine color persisted; iodoform precipitated. The reaction mixture was heated at 60° to coagulate the iodoform, and 10 ml of 10% sodium hydroxide was added which dissipated the brown iodine color. The cooled solution was filtered, and the 0.172 g of solid obtained was recrystallized from methanol–water to yield 0.154 g of iodoform, mp 121–122° (49%).

The yellow filtrate containing benzoic acid was treated with Norit, acidified with 6 *N* HCl, and then ether extracted. Concentration *in vacuo* yielded a colorless solid which was recrystallized from water to give 0.101 g of pure benzoic acid, mp 121–122° (92%).

Since this reaction was used in the ^{14}C scheme, it was necessary to demonstrate that the *p*-dioxane did not contain impurities affording iodoform. A control run without acetophenone yielded no iodoform.

Synthesis of Benzoylacetaldehyde. This compound was prepared by the method of von Auwers and Schmidt[30] from 40 g (0.54 mole) of ethyl formate and 60 g (0.50 mole) of acetophenone to give 69.5 g (82%) of sodium salt of benzoylacetaldehyde. The copper chelate was used for purification. A 12.0-g (0.071 mole) portion of the sodium salt was dissolved in water, and a saturated, aqueous solution of cupric acetate was added until a light blue coloration was observed, indicative of excess reagent. The green solid which precipitated was filtered, washed thoroughly with water, and dried *in vacuo* over P$_2$O$_5$. Recrystallization from benzene–hexane yielded 9.1 g of dark green crystals, mp 199–200° (lit.[31] 212–213° from Et$_2$O–pentane).

A solution of 5.92 g (16.5 mmoles) of the copper chelate in ether was shaken with 200 ml of 5% HCl for 15 min. The ether layer was dried and concentrated *in vacuo* to yield 4.63 g of benzoylacetaldehyde, a yellow liquid (95%).

The infrared spectrum (CHCl$_3$) showed: 6.25 (broad), characteristic of β-keto aldehydes which exist as monoenols,[13] 6.90 and 9.81 μ; infrared spectrum of copper chelate (KBr) showed: 6.28, 6.40, 6.65, 6.77, 6.90, 7.09, 7.40, 8.00, 8.45, 9.37, 9.80, and 10.73 μ.

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(30) Authentic material was prepared by the method of K. von Auwers and W. Schmidt, *Ber.*, **58**, 528 (1925).

(31) H. O. House, D. J. Reif, and R. L. Wasson, *J. Am. Chem. Soc.*, 79, 2490 (1957).

3-Carbethoxy-4-phenyl-5-benzoyl-2-pyrazoline. This compound was prepared by the method of Kohler and Steele.[11] A 20-g (0.175 mole) sample of ethyl diazoacetate was added to a solution of 36.5 g (0.177 mole) of benzalacetophenone in 500 ml of 90–100° petroleum ether. The resulting yellow solution was stirred and refluxed for 4.75 hr, whereupon crystalline pyrazoline separated. The cooled reaction mixture was filtered, and the colorless crystals obtained were recrystallized from absolute ethanol to give 31.2 g (55%) of pure 3-carbethoxy-4-phenyl-5-benzoyl-2-pyrazoline, mp 159–160.5° (lit.[11] 156–158°).

The infrared spectrum ($CHCl_3$) showed: 2.96 (N–H), 5.85 (C=O), 5.93 (C=O), 6.26, 6.34, 6.71, 6.90, 7.08, 7.45, and 8.93 μ.

Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.69; H, 5.74; N, 8.67.

Pyrolysis of 3-Carbethoxy-4-phenyl-5-benzoyl-2-pyrazoline. Ethyl *cis*-2-Benzoyl-*trans*-3-phenylcyclopropane-1-carboxylate.[11] A total of 70 g (0.217 mole) of 3-carbethoxy-4-phenyl-5-benzoyl-2-pyrazoline was pyrolyzed in five portions. In a typical run, 13.9 g of pyrazoline and 3.0 g of small pieces of sheet platinum was heated at 225–240° for 15 min. Nitrogen was evolved vigorously and 12.6 g of red, viscous oil remained. Hexane was added to the product of five runs, and 23.95 g of yellow solid crystallized. The infrared spectrum revealed the presence of the desired ester contaminated with 4,6-diphenylpyrone, a by-product reported by Kohler.[11] This material was chromatographed on a 6 × 120 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 5% ether–hexane; 1-l. fractions were collected to give: fractions 1–3, 5% ether–hexane, 4–7, 10% ether–hexane, nil; 8–14, 15% ether–hexane, 0.088 g of a red oil; 15–28, 15% ether–hexane, 15.93 g of the desired ester. Further fractions of 25% ether–hexane gave only 4,6-diphenylpyrone. The solid from fractions 15–28 was recrystallized from chloroform–hexane to yield 15.25 g (24%) of pure ethyl *cis*-2-benzoyl-*trans*-3-phenylcyclopropane-1-carboxylate, mp 103.5–104.0° (lit.[11] 102–103°)

The infrared spectrum ($CHCl_3$) showed: 5.79 (C=O), 5.95 (C=O), 6.25, 6.34, 6.90, 7.30, 7.43, and 7.80 μ.

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.65; H, 6.20.

Saponification of Ethyl *cis*-2-Benzoyl-*trans*-3-phenylcyclopropane-1-carboxylate. Authentic *cis*-2-benzoyl-*trans*-3-phenylcyclopropane-1-carboxylic Acid. A solution of 0.204 g (0.694 mmole) of ethyl *cis*-2-benzoyl-*trans*-3-phenylcyclopropane-1-carboxylate in 25 ml of absolute ethanol was swirled with 25 ml of 2% aqueous potassium hydroxide at 25° for 6 min. The reaction mixture was ether extracted, and the extracts were dried and concentrated *in vacuo* to give 32 mg of unreacted ester. The aqueous phase was acidified with 5% HCl and then ether extracted. The extracts were dried and concentrated *in vacuo* to yield 0.149 g of a colorless solid, mp 140–168°. Recrystallization from acetone-water yielded 0.109 g of pure *cis*-2-benzoyl-*trans*-3-phenylcyclopropane-1-carboxylic acid, mp 176–177° (lit.[11] 175–176°).

The infrared spectrum (KBr) showed: 3.0–4.3 (broad), 5.95 (C=O), 6.90, 9.40, 9.60, 9.80, 10.00, and 10.50 μ.

Ozonolysis of 2-(*cis*-Styryl)-3-phenylcyclobutanone. 3-Phenylglutaric Acid and Benzaldehyde. Ozone (0.437 mmole) was bubbled through a solution of 100 mg (4.03 mmoles) of 2-(*cis*-styryl)-3-phenylcyclobutanone in 10 ml of acetic acid and 10 ml of ethyl acetate at −10° for 17.5 min. The reaction mixture was purged with nitrogen for 2 min and then warmed to room temperature. Addition of 5.0 ml of water caused a slight gas evolution, and then 2.0 ml of 40% peracetic acid (Becco; *d* 1.15) was added. The colorless solution was kept at 25° for 12 hr, then was diluted with ether and extracted with 5% sodium bicarbonate. The ether layer was dried and concentrated *in vacuo* to yield 55 mg of a colorless liquid which was mainly benzaldehyde. The infrared spectrum showed no starting material, a minor 5.80-μ C=O band, and strong intensities of all benzaldehyde peaks. Conversion to its phenylhydrazone yielded 30 mg of benzaldehyde phenylhydrazone, mp 155–156°. The infrared spectrum was identical in all respects with authentic material, and a mixture melting point with an authentic sample was undepressed.

The bicarbonate extracts were acidified with 6 *N* HCl and ether extracted, and the ether extracts dried over sodium sulfate and concentrated *in vacuo* leaving 82 mg of a pale yellow oil which crystallized on standing. Recrystallization from chloroform–hexane yielded 44 mg of a colorless solid, mp 141–142°, shown to be 3-phenylglutaric acid. The infrared spectrum was identical with that of authentic material, and a mixture melting point with an authentic sample showed no depression; neut equiv, 103 (*i.e.*, 206 per mole); theory, $C_{11}H_{12}O_4$, 208 per mole. In addition, esterification with diazomethane (procedure identical with that described for the synthesis of dimethyl 3-phenylglutarate) of 15 mg (0.072 mmole) of the acid yielded 17 mg of a solid ester, mp 86.5–87.0°. The infrared spectrum in either chloroform or carbon disulfide was identical with dimethyl 3-phenylglutarate, and a mixture melting point with authentic dimethyl 3-phenylglutarate was undepressed. Subsequent determination of the oxidation power of the peracetic acid used showed it to have no oxidant left; consequently, peracid is not a necessary reagent for the formation of the ozonolysis products.

5-Phenylcyclohexane-1,3-dione. This compound was prepared by the method of Crossly and Renouf[32] in 84% yield. The product melted at 183–185° dec (lit.[32] 184° dec).

3-Phenylglutaric Acid. A modification of the method of Vorlander and Kohlmann[33] was used. Sodium hypobromite, prepared from 9.60 g (60 mmoles) of bromine and 10.0 g (250 mmoles) of sodium hydroxide in 35 ml of water, was added to a solution of 1.88 g (10.0 mmoles) of 5-phenylcyclohexane-1,3-dione in 40 ml of 10% sodium hydroxide. The reaction mixture was stirred and refluxed for 12 hr. The colorless solution was acidified with 6 *N* HCl and ether extracted. The extracts were dried over sodium sulfate and concentrated *in vacuo* leaving a colorless solid, mp 135–137°. Recrystallization from chloroform–hexane yielded 1.85 g of pure 3-phenylglutaric acid, mp 141–142° (89%).

The infrared spectrum (KBr) showed: 3.0–4.5 (broad), 5.90 (C=O), 6.98, 7.10, 7.58, 7.70, 8.00, 8.22, 13.00, and 14.22 μ; nmr (acetone-d_6): τ 1.97 (2 H, singlet, two COOH), 2.72 (5 H, singlet, aromatic), 6.37 (1 H, quintet, C–H), and 7.28 (4 H, doublet, two CH_2).

Carbon tetrabromide, mp 89–90°, was also formed during the reaction and sublimed into the reflux condenser. The infrared spectrum showed no C–H, C=O, or phenyl absorption.

Dimethyl 3-Phenylglutarate. A solution of 0.417 g (2.0 mmoles) of 3-phenylglutaric acid in 50 ml of anhydrous ether was treated with an ethereal solution of excess diazomethane. The solution was allowed to stand for 15 min, and the excess diazomethane was then codistilled with ether. Concentration *in vacuo* of the solvent left 0.471 g of a colorless solid, mp 82–85°. Recrystallization from methanol–water yielded 0.440 g (93%) of pure dimethyl 3-phenylglutarate, mp 86.5–87.0° (lit.[33] 86–87°).

The infrared spectrum ($CHCl_3$) showed: 5.80 (C=O), 6.24, 6.71, 6.90, 7.33, 9.25, 10.00, 10.40, and 11.22 μ; nmr ($DCCl_3$): τ 2.78 (5 H, singlet, aromatic), 6.43 (7 H, singlet masking weak quintet, two OCH_3, CH), and 7.43 (4 H, doublet, two CH_2).

Syntheses of ^{14}C Compounds. The apparatus and experimental conditions were identical with those described previously for the corresponding inactive compounds.

Phenylacetic Acid-Carboxyl-^{14}C by Carbonation of Benzylmagnesium Chloride. A total of 136.3 g (1.08 moles) of benzyl chloride, 26.3 g (1.08 g-atoms) of magnesium turnings, 204 g (1.04 moles) of inactive barium carbonate, and 0.074 g of barium carbonate-^{14}C (8 mcuries/mmole; 3.0 mcuries) was used in three runs to give 105 g (75%) of phenylacetic acid-carboxyl-^{14}C, mp 79–80°, with a specific activity (three independent analyses) of 2.52 ± 0.04 μcuries/mmole.

Ethyl Phenylacetate-Carboxyl-^{14}C. From the Fischer esterification of 104 g (0.765 mole) of phenylacetic acid-carboxyl-^{14}C, 109 g (88%) of distilled ethyl phenylacetate-carboxyl-^{14}C, bp 68–70° (1.0 mm), was obtained. This material was not assayed for ^{14}C content.

4,5-Diphenylcyclohexane-1,3-dione-3-^{14}C. A total of 108 g (0.658 mole) of ethyl phenylacetate-carboxyl-^{14}C and 105.6 g (0.724 mole) of benzalacetone were used in two identical runs. The pure 4,5-diphenylcyclohexane-1,3-dione-3-^{14}C obtained was 73.3 g (42%). The specific activity of this material was 2.47 ± 0.004 μcuries/mmole.

Enol Ether of 4,5-Diphenylcyclohexane-1,3-dione-3-^{14}C. 3-Ethoxy-5,6-diphenylcyclohex-2-en-1-one-1-^{14}C. A 40.2-g (0.152 mole) sample of 4,5-diphenylcyclohexane-1,3-dione-3-^{14}C yielded 14.3 g (32%) of pure 3-ethoxy-5,6-diphenylcyclohex-2-en-1-one-1-^{14}C, mp 108–109°. The specific activity of this material was 2.50 ± 0.04 μcuries/mmole.

4,5-Diphenylcyclohex-2-en-1-one-3-^{14}C. A solution of 14.2 g (48.6 mmoles) of 3-ethoxy-5,6-diphenylcyclohex-2-en-1-one-1-^{14}C in 100 ml of anhydrous ether and 50 ml of dry benzene was reduced with 0.924 g (25.9 mmoles) of lithium aluminum hydride. The crude yield was 12.11 g, and after recrystallization from ethanol–

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[32] A. W. Crossly and N. Renouf, *J. Chem. Soc.*, 602 (1915).

[33] D. Vorlander and M. Kohlmann, *Ber.*, **32**, 1879 (1899).

water, 10.39 g (86%) of pure 4,5-diphenylcyclohex-2-en-1-one-3-^{14}C, mp 97.0–97.5°, was obtained. The mean value of the specific activity of this material from two independent analyses was 2.51 ± 0.04 μcuries/mmole.

Photolysis of 4,5-Diphenylcyclohex-2-en-1-one-3-^{14}C in 95% Ethanol. A solution of 2,33 g (9.40 mmoles) of 4,5-diphenylcyclohex-2-en-1-one-3-^{14}C in 1050 ml of 95% ethanol was irradiated under nitrogen for 22 hr. Liquid–liquid partition chromatography afforded 0.501 g (22%) of 4,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C, mp 90.0–90.5°. The specific activity of this material was 2.51 ± 0.04 μcuries/mmole.

In a second run, 3.01 g (12.1 mmoles) of active enone in 1050 ml of 95% ethanol was irradiated for 22 hr. Liquid–liquid partition chromatography yielded 0.670 g of photoketone (23%).

Hypobromite Oxidation of 4,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C. 2-(α-Carboxy-α-hydroxybenzyl)-3-phenylcyclopropane-1-carboxylic Acid-2-^{14}C. A solution of 0.410 g (1.66 mmoles) of 4,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C in 120 ml of *p*-dioxane was oxidized with an aqueous solution of potassium hypobromite prepared from 1.28 g (8.0 mmoles) of bromine and 1.69 g (30.0 mmoles) of potassium hydroxide in 160 ml of water. A 0.265-g (51%) yield of 2-(α-carboxy-α-hydroxybenzyl)-3-phenylcyclopropane-1-carboxylic acid-2-^{14}C was obtained. This material was not assayed for ^{14}C content.

In another run, 0.535 g (2.16 mmoles) of photoketone was used. A yield of 0.157 g (24%) of the desired hydroxy diacid, mp 199–200°, was obtained. The specific activity of this material was 2.46 ± 0.04 μcuries/mmole.

2-Benzoyl-3-phenylcyclopropane-1-carboxylic Acid-2-^{14}C. A solution of 0.265 g (0.849 mmole) of the above hydroxy diacid in 30 ml of anhydrous acetone was oxidized with 0.530 g (1.20 mmoles) of lead tetraacetate. The crude yield was 0.126 g, and after recrystallization from chloroform–hexane, 97 mg (43%) of pure 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid-2-^{14}C, mp 176–177°, was obtained. This material was not assayed for ^{14}C content.

In another run, 0.150 g (0.481 mmole) of hydroxy diacid was treated with 300 mg (0.680 mmole) of lead tetraacetate to yield 62 mg (48%) of 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid-2-^{14}C, mp 176–177°. The specific activity of this material was 2.46 ± 0.04 μcuries/mmole.

1-Phenacyl-2-chloro-2-phenylpropionic Acid-^{14}C. Hydrogen chloride addition to 85 mg (0.319 mmole) of 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid-2-^{14}C yielded 86 mg (90%) of the desired β-chloro acid, mp 118–119°. The ^{14}C assay was erratic and not reproducible. It was subsequently found that satisfactory results of halogen compounds were obtained only when a column of silver was used in the combustion train of the assay apparatus.

In a second run, 52.0 mg (0.196 mmole) of 2-benzoyl-3-phenylcyclopropane-1-carboxylic acid-2-^{14}C and 1.858 g (6.98 mmoles) of inactive cyclopropane acid yielded 1.70 g (78%) of the β-chloro acid. The mean value of the specific activity of this material from two independent analyses was $7.02 \pm 0.20 \times 10^{-2}$ μcurie/mmole (theory: based on a 35.7:1 dilution, 6.81×10^{-2} μcurie/mmole).

1,4-Diphenylbut-3-en-1-one-2-^{14}C. Pyrolysis of 70.5 mg (0.233 mmole) of the above active β-chloro acid and 1.864 g (6.172 mmoles) of the inactive acid gave 0.614 g (44%) of pure 1,4-diphenylbut-3-ene-1-one-2-^{14}C, mp 93.5–94.0°. The mean value of the specific activity of this material from two independent analyses was 9.08 $\pm 0.20 \times 10^{-2}$ μcurie/mmole (theory: based on a 26.5:1 dilution, 9.09×10^{-2} μcurie/mmole).

In a second run, 1.558 g (5.16 mmoles) of the β-chloro acid (specific activity = 7.02×10^{-2} μcurie/mmole) yielded 0.359 g (31%) of 1,4-diphenylbut-3-en-1-one-2-^{14}C, mp 93.5–94.0°. The specific activity of this material was $6.98 \pm 0.12 \times 10^{-2}$ μcurie/mmole.

3,4-Dihydroxy-1,4-diphenylbutan-1-one-2-^{14}C. The reaction of 0.561 g (2.53 mmoles) of 1,4-diphenylbut-3-en-1-one-2-^{14}C with 31.8 mg (0.12 mmole) of osmium tetroxide and 0.615 g (5.0 mmoles) of potassium chlorate yielded 0.245 g (38%) of pure 3,4-dihydroxy-1,4-diphenylbutan-1-one-2-^{14}C, mp 138–139°. The mean value of the specific activity of this material from two independent analyses was $9.10 \pm 0.15 \times 10^{-2}$ μcurie/mmole.

In a second run, 0.3555 g (1.60 mmoles) of 1,4-diphenylbut-3-en-1-one yielded 0.146 g of the desired diol (35%). This material was not assayed for ^{14}C content.

Lead Tetraacetate Oxidation of 3,4-Dihydroxy-1,4-diphenylbutan-1-one-2-^{14}C. A 0.220-g (0.86 mmole) sample of 3,4-dihydroxy-1,4-diphenylbutan-1-one-2-^{14}C was treated with 0.496 g (1.12 mmoles) of lead tetraacetate. Benzaldehyde was isolated as its phenylhydrazone, 46 mg, mp 155–156° (28%), and benzoylacetaldehyde was isolated as its copper chelate, 80 mg, mp 199–200° (52%). From two independent analyses, the mean value of the specific activity of the benzaldehyde phenylhydrazone was $1.22 \pm 0.03 \times 10^{-4}$ μcurie/mmole, which is 1.34% of theoretical (9.09×10^{-2} μcurie/mmole). The mean value of the specific activity of the copper chelate of benzoylacetaldehyde from two independent analyses was 0.179 ± 0.003 μcurie/mmole which was 98.56% of theoretical (0.181 μcurie/mmole).

In a second run, 96 mg (0.36 mmole) of diol yielded 28 mg of the copper chelate and 10 mg of benzaldehyde phenylhydrazone. From two independent analyses, the mean value of the specific activity of the benzaldehyde phenylhydrazone was $9.97 \pm 0.15 \times 10^{-4}$ μcurie/mole, which was 1.43% of theoretical (6.98×10^{-2} μcurie/mmole). The mean value of the specific activity of the copper chelate of benzoylacetaldehyde from two independent analyses was 0.137 ± 0.002 μcurie/mmole which is 98.40% of theoretical (0.139 μcurie/mmole).

Dilution of Benzoylacetaldehyde-2-^{14}C with Inactive Benzoylacetaldehyde. A 42.1-mg (0.118 mmole) sample of the copper chelate of benzoylacetaldehyde-2-^{14}C (specific activity = 0.179 μcurie/mmole) was diluted with 0.3444 g (0.962 mmole) of inactive material. To homogenize the mixture, the green solid was dissolved in benzene and then concentrated *in vacuo*. The mean value of the specific activity of the resulting copper complex, mp 199–200°, from two independent analyses was $1.96 \pm 0.03 \times 10^{-2}$ μcurie/mmole (theory: based on a 8.18:1 dilution, 1.95×10^{-2} μcurie/mmole).

Base Degradation of Benzoylacetaldehyde-2-^{14}C. Acetophenone-Methyl-^{14}C. A 0.334-g (0.933 mmole) sample of the copper chelate of benzoylacetaldehyde-2-^{14}C was hydrolyzed to the free β-keto aldehyde, and the resulting yellow liquid was treated with 15 ml of 5% sodium hydroxide to yield 0.203 g of acetophenone-methyl-^{14}C (91%). A sample of the acetophenone was converted to its semicarbazone, mp 198–200°. The mean value of the specific activity of this material from two independent analyses was $9.83 \pm 0.15 \times 10^{-3}$ μcurie/mmole (theory: 9.80×10^{-3} μcurie/mmole).

Hypoiodite Oxidation of Acetophenone-Methyl-^{14}C. Iodoform-^{14}C and Benzoic Acid. A 0.136-g (1.13 mmoles) sample of acetophenone-methyl-^{14}C was oxidized with sodium hypoiodite and yielded 0.120 g (27%) of iodoform-^{14}C, mp 121–122°, and 0.116 g (84%) of benzoic acid, mp 121–122°. The benzoic acid was assayed for ^{14}C content and was found to be inactive. The mean value of the specific activity of the iodoform from two independent analyses was $9.74 \pm 0.15 \times 10^{-3}$ μcurie/mmole (theory: 9.80×10^{-3} μcurie/mmole).

Assay of ^{14}C Compounds. The ^{14}C compounds were combusted by Van Slyke solution[34] to carbon dioxide which was transferred by vacuum line techniques to a 100-cc Bernstein–Ballentine ionization tube. Propane was used as the ionizing gas and the ionization rate was determined with a proportional counter and scaler. The apparatus was calibrated with benzoic acid of known activity.

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(34) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); D. D. Van Slyke, J. Plarin, and T. R. Weisiger, *ibid.*, **191**, 299 (1951).