

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

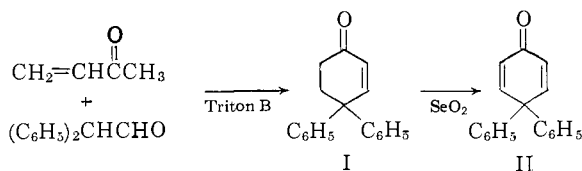
A New Approach to Mechanistic Organic Photochemistry. IV. Photochemical Rearrangements of 4,4-Diphenylcyclohexadienone^{1,2}BY HOWARD E. ZIMMERMAN AND DAVID I. SCHUSTER³

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The photolysis in aqueous dioxane of 4,4-diphenylcyclohexadienone has been found to afford in excellent yield three main products—a ketone, a phenol and an acid. The structures of the first two have been shown to be 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one and 2,3-diphenylphenol. A general mechanistic interpretation of $n-\pi^*$ photochemical transformations is presented. This theory is applied to the known photochemistry of cyclohexadienones and its general applicability indicated.

Of the many known photochemical transformations of organic molecules, those of 4,4-disubstituted-2,5-cyclohexadienones are certainly among the most intriguing. A major portion of the interest associated with those reactions derives from the profound and unusual nature of the rearrangements occurring. Ground state rearrangements of equal complexity would be difficult enough to interpret; in the instance of photochemical transformations even the basic theory allowing one to consider possible mechanisms has been lacking. The present investigation began with two goals—first, the exploration of the photochemistry of 4-aryl substituted 2,5-cyclohexadienones and second, the determination of the extent to which the observed photochemical transformations would be accommodated by a general theoretical treatment developed in this Laboratory.^{4,5,6}

4,4-Diphenyl-2,5-cyclohexadienone (II) was chosen for the present study. This posed a synthetic problem, since 4-aryl-bearing 2,5-cyclohexadienones had not been described in the literature. However, a convenient two-step synthesis was devised, beginning with diphenylacetaldehyde. Triton B-catalyzed Michael addition of this compound to methyl vinyl ketone and concomitant aldolization afforded 4,4-diphenylcyclohex-2-en-1-one (I). Selenium dioxide dehydrogenation of I afforded 4,4-diphenyl-2,5-cyclohexadienone (II).⁷



Photolysis of 4,4-diphenyl-2,5-cyclohexadienone (II) in 75% aqueous dioxane at 25° with ultraviolet light of wave length above 310 $m\mu$ afforded

(1) Presented in part at the 17th National Organic Symposium of the American Chemical Society, June, 1961; *cf.* Abstracts of the Meeting, p. 31.

(2) For a preliminary report of this work note ref. 4; for papers II and III. *cf.* refs. 5 and 6, respectively.

(3) Postdoctoral Fellow, University of Wisconsin 1960-1961; present address: Chemistry Department, New York University, New York 53, N. Y.

(4) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

(5) Paper II, H. E. Zimmerman and V. Sandel, *ibid.*, in press.

(6) Paper III, H. E. Zimmerman and S. Somasekhara, *ibid.*, in press.

(7) The syntheses of diphenylacetaldehyde, 4,4-diphenylcyclohex-2-en-1-one and 4,4-diphenylcyclohexadienone are improved modifications of earlier unpublished preparations by H. E. Zimmerman and K. Wellman.

a mixture of products from which an acid, henceforth designated "photoacid," was separated by mild base extraction. The non-acidic fraction was an oily mixture which was nicely resolved by scanning liquid-liquid partition chromatography.⁸ A typical chromatogram is depicted in Fig. 1.

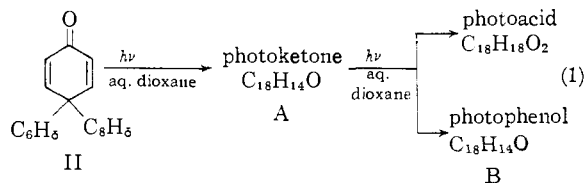
In addition to unreacted 4,4-diphenyl-2,5-cyclohexadienone (II), two new compounds isomeric with dienone reactant (*i.e.*, $C_{18}H_{14}O$) were obtained; these will henceforth be designated "photoketone" (A, m.p. 144°) and "photophenol" (B, m.p. 102.5°). Consideration of the product distribution obtained in a series of photolyses *versus* extent of conversion (Table I) showed an initial

TABLE I
PRODUCT DISTRIBUTION *vs.* EXTENT CONVERSION FROM
THREE REPRESENTATIVE RUNS

Run	1	2	3
Recovered dienone, %	35	14	0
Photoacid, %	27	42	61
Photophenol, %	22	22	32
Photoketone, %	7	10	1
Mass balance, ^a %	91	88	94

^a Peak material obtained from non-overlapping portions of scanning chromatogram; material balance was essentially 100% in all runs including overlapping fractions.

build-up of photoketone followed by a decrease in amount present; this contrasted with a monotonic increase in the yields of photoacid and photophenol. Suspicion that photoketone was an intermediate in the formation of one or both of photoacid and photophenol was confirmed by the finding that the photolysis of photoketone A itself in 75% aqueous dioxane afforded both photoacid and photophenol B in about the same distribution as found in runs beginning with 4,4-diphenyl-2,5-cyclohexadienone (II) itself.⁹



(8) This method was used since the oily photolysis mixture was too high boiling for distillation and vapor phase chromatography and underwent severe decomposition when chromatographed on the common adsorbents. Development of suitable liquid-liquid partition systems resulted from the unpublished efforts of H. E. Zimmerman with S. Somasekhara, B. Cowley and E. Panek; monitoring utilized ultraviolet absorbance.

(9) That there were no dark reactions of 4,4-diphenylcyclohexadienone or photoketone in the presence or absence of typical quantities of

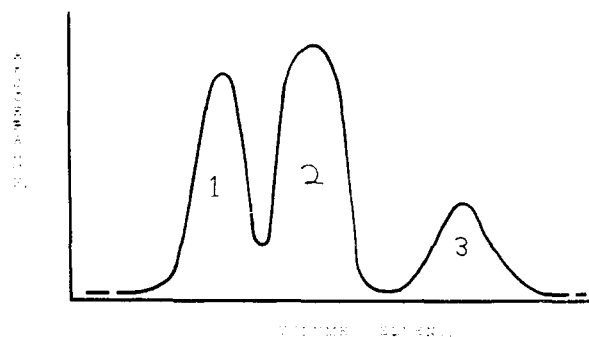


Fig. 1.—Partition chromatogram of non-acidic fraction: peak 1, recovered dienone; peak 2, photoketone; peak 3, photophenol.

Several structure elucidation problems having been posed simultaneously; that of the photophenol was attacked first. At the outset it was apparent that photophenol B was most likely one of the six possible diphenylphenols. Of these all but two were known (*cf.* Table II). While the

TABLE II
KNOWN DIPHENYLPHENOLS

Phenol	M.p., °C.	Ref.
2,4-Diphenyl-	89	10
2,5-Diphenyl-	194	11
2,6-Diphenyl-	101	12
3,5-Diphenyl-	95	13

melting point of 101° of 2,6-diphenylphenol¹² was close to that of photophenol (102.5°), the evidence was against this structural assignment. Most critical, bromination of photophenol in acetic acid under mild conditions afforded a dibromo derivative, m.p. 178°, suggesting the presence of two free *ortho* and *para* positions in the photophenol. 2,6-Diphenylphenol had been reported to afford 2,6-diphenylbenzoquinone under these conditions.¹² Similarly, the ultraviolet spectrum of photophenol (224 $m\mu$ sh.(4.36), 282 $m\mu$ sh. (3.61)) contrasted with that reported¹² for 2,6-diphenylphenol (239 $m\mu$ max. (4.45), 295 $m\mu$ max. (3.75)).

In view of the lack of melting point correspondence with the remaining known isomers and the suggestive evidence provided by dibromination, it seemed likely that the photophenol was one of the unknown diphenylphenols—either 2,3- or 3,4-diphenylphenol. With the 4,4-diphenyl structure of the dienone reactant in mind, it was felt that photophenol was more likely 3,4-diphenylphenol (V) and accordingly syntheses were devised.

The simplest synthesis of 3,4-diphenylphenol involved the hydrochloric acid–aqueous acetic acid catalyzed dienone–phenol rearrangement of 4,4-diphenylcyclohexadienone (II). Also, the corresponding acetate of this phenol was obtained by treatment of 4,4-diphenylcyclohexadienone in acetic anhydride containing a catalytic amount of

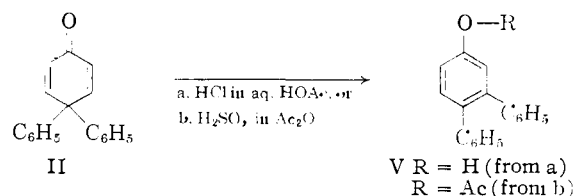
photoacid has been demonstrated in unpublished control experiments by H. E. Zimmerman and R. Keese.

(10) A. Lüttringhaus and G. Wagner—v. Säaf, *Ann.*, **557**, 23 (1945).

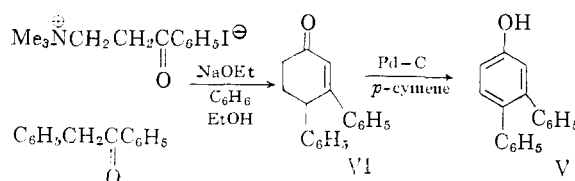
(11) F. Fichter and E. Grether, *Chem. Ber.*, **36**, 1407 (1903).

(12) A. Lüttringhaus and D. Ambros, *ibid.*, **89**, 463 (1956).

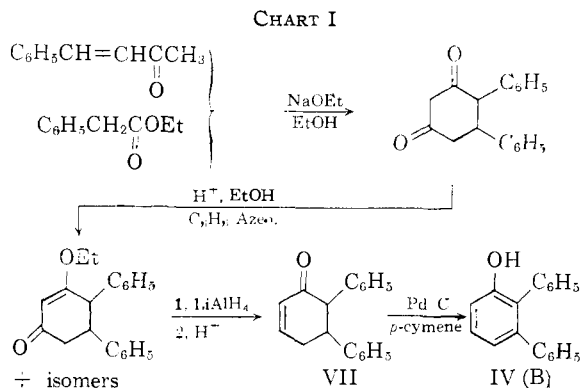
(13) J. Kenner and H. Shaw, *J. Chem. Soc.*, 769 (1931).



sulfuric acid. Although 3,4-diphenylphenol (V) obtained in this fashion melted at 105°, close to the 102.5° m.p. of photophenol, these compounds clearly were not identical. The infrared spectra of the two phenols as well as their acetates showed marked differences; and, additionally, the acetate of 3,4-diphenylphenol melted at 131.5°, contrasting with the 118° m.p. of photophenol acetate. Furthermore, the Pd–C *p*-cymene dehydrogenation of 3,4-diphenylcyclohex-2-en-1-one (VI), a compound reported by Robinson, *et al.*,¹⁴ afforded the same 3,4-diphenylphenol (V) leaving no doubt that photophenol corresponded to another structure.



The remaining and sixth diphenylphenol, namely 2,3-diphenylphenol (IV), was synthesized by the route indicated in Chart I. In this synthesis



4,5-diphenylcyclohexane-1,3-dione¹⁵ was converted to a mixture of enol ethers. Lithium aluminum hydride reduction¹⁶ and chromatographic separation afforded 5,6-diphenylcyclohex-2-en-1-one (VII) which was then dehydrogenated to 2,3-diphenylphenol (IV) with Pd–C *p*-cymene.^{17,18} This

(14) E. D. Dodds, R. L. Huang, W. Lawson and R. Robinson, *Proc. Roy. Soc. (London)*, **140B**, 470 (1953).

(15) W. Borsche, *Chem. Ber.*, **42**, 4496 (1909).

(16) For a recent discussion of the mechanism of this general synthesis *cf.* M. Stiles and A. Longroy, *Tetrahedron Letters*, 337 (1961).

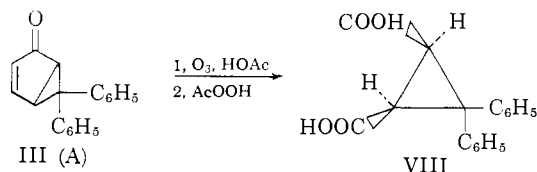
(17) It is to be noted that *a priori* this synthesis could have afforded either 2,3-diphenylphenol (IV) or 3,4-diphenylphenol (V). In actual fact, however, the product obtained proved to be different from 3,4-diphenylphenol as synthesized by the two described routes and is unambiguously assigned the 2,3-diphenyl structure.

(18) Prof. C. F. Koelsch has privately communicated his independent synthesis of the 2,3- and 3,4-diphenylphenols, m.p. 101° and 102°, respectively, and 2,3-diphenylphenyl acetate, m.p. 116°.

product proved to be identical with photophenol in all respects, thus establishing 2,3-diphenylphenol (IV) as the structure of photophenol B.

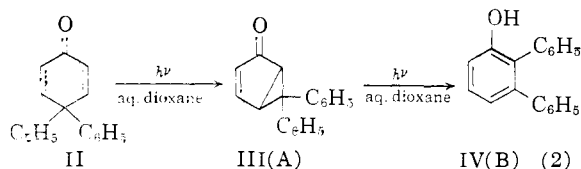
An understanding of the remarkable photochemical transformation of a 4,4-diphenylcyclohexane derivative (*i.e.*, II) to a 2,3-diphenyl product (*i.e.*, IV) required elucidation of the structure of the photoketone reaction intermediate III. The ultraviolet spectrum of photoketone was suggestive of an umbellulone-like moiety together with non-conjugated phenyl groups (note Fig. 2) and tended to rule out conjugation between phenyl and olefinic moieties. Similarly, the 5.90 μ carbonyl band of photoketone in the infrared was consistent with the presence of the cyclopentenone chromophore of an umbellulone-like structure (*cf.* 5.88 μ for umbellulone itself¹⁹).

However, most enlightening was the ozonolysis of photoketone with peracetic acid workup to give the known^{20,21} *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid (VIII); the ozonolysis product, its anhydride and its dimethyl ester were compared with independently synthesized authentic compounds. This degradation of photoketone A reveals the presence of a cyclopropane ring, locates the two phenyl groups on this ring and defines the points of attachment of the *cis*-fused five-membered ring which was destructively oxidized—all allowing unambiguous assignment of a 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one structure (III) to A. Additional confirmation was



found in the n.m.r. spectrum of III (A) which showed the presence of two relatively high field hydrogen atoms centering at 6.82 and 7.50 τ ²² as well as one of the two olefinic hydrogen atoms. The second olefinic hydrogen band appeared to merge with the aromatic absorption.

The photochemical transformations of equation 1 may now be reformulated as²³



where there is a sequential conversion of the 4,4-diphenyl reactant II to 3,3-diphenyl compound III to 2,3-diphenyl final product IV.

Hitherto, the discussion of a photochemical rearrangement would have had to conclude at this

(19) H. E. Smith and R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 5500 (1957).

(20) J. Van Alphen, *Rec. trav. chim.*, **62**, 210 (1943).

(21) W. M. Jones, *J. Am. Chem. Soc.*, **81**, 3776 (1959).

(22) Compare the 7.25 τ absorption (Experimental section) of the cyclopropane hydrogen atoms of dimethyl *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylate.

(23) The structure of photoacid has now been elucidated as 6,6-diphenyl-3,5-hexadienoic acid (unpublished results by H. E. Zimmerman and R. Keese) and will be the subject of a future publication.

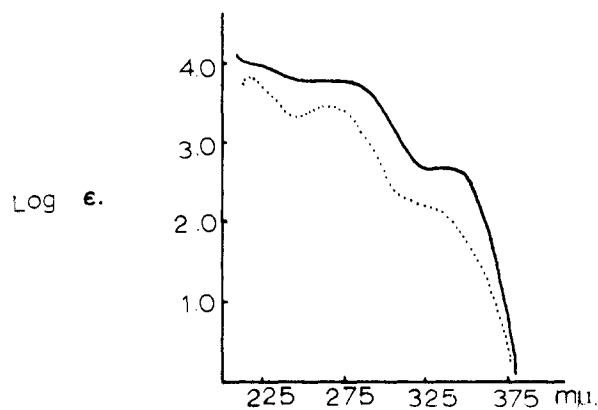


Fig. 2.—Spectra: —, photoketone; ·····, umbellulone (footnote 19).

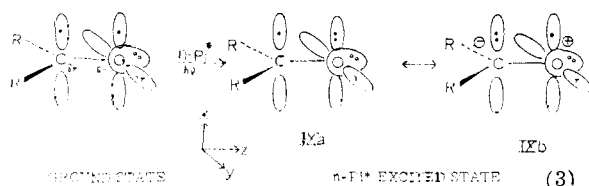
point. At best, either a series of arrows could be drawn indicating which bonds are broken and which are formed, or "unpairing" of two bonding electrons might be envisaged followed by reaction of the species so formed. This is a far from intellectually and practically satisfying situation, for such treatments do not indicate, except *a posteriori*, which electrons are to be "unpaired" or how the arrows are to be drawn; these are more formalisms than mechanistic descriptions. Thus the electron redistribution process and concomitant molecular reorganization occurring in a given photochemical reaction have not been subject to detailed description; this is in contrast to the situation in ordinary ground state organic reactions where a detailed mechanistic picture of molecular change in reactions is commonplace. The result of this limiting situation in organic photochemistry is an undesired aura of mystery and, more important, a barrier to discussion and investigation of mechanistic possibilities. With such a limitation, each photochemical reaction becomes a unique and isolated problem.

Especially in $n-\pi^*$ transformations of carbonyl compounds, where reaction is effected by absorption of light in the 300 $m\mu$ region of the ultraviolet, this distressing situation need not be the case. It is the purpose of the second half of this paper to introduce a theoretical treatment of $n-\pi^*$ reactions,²⁴ to apply this treatment to the photochemical rearrangements described in this paper, and to explore the general applicability of the concepts.

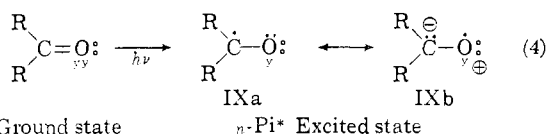
The beginning point is the precise nature of the $n-\pi^*$ excitation process of carbonyl groups. It was long ago suggested²⁵ that the weak absorption band of ketones and aldehydes occurring in the 280–360 $m\mu$ region arises from excitation of a non-bonding 2p-electron to the antibonding π -orbital, and this has been designated the $n-\pi^*$ transition. An atomic orbital representation is equivalent to the molecular orbital picture and is more convenient for the present purposes

(24) This treatment has been discussed by us in preliminary form; *cf.* refs. 1 and 4, also *Chem. Eng. News*, July 17, 48 (1961).

(25) This was first pointed out by R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935). *Cf.* also papers by H. L. McMurry, *ibid.*, **9**, 231, 241 (1941) and M. Kasua, *Disc. Far. Soc.*, **9**, 14 (1950); J. Sidman, *Chem. Rev.*, **58**, 689 (1958) has reviewed the subject.



Two of the four unshared oxygen electrons are placed in a spheroidal, heavily 2S-weighted orbital²⁶ at oxygen. The other two are in the 2P_x-oxygen orbital parallel to the *y*-axis of a three-coordinate system. The π -electrons appear in 2P_x-orbitals on carbon and oxygen, these orbitals being parallel to the *x*-axis of the coordinate system.^{26,27} A convention is used in which π -electrons are depicted as solid dots, heavily S-weighted electrons as circular dots and P_{*y*}-electrons as small *y*'s.²⁸ This "circle-dot-*y*" notation is useful since it allows two dimensional representation of three dimensional species. Thus eq. 4 has the same connotation as 3.



Given the structure of an excited state, one is faced with the question whether ground state concepts of reactivity are applicable. Inspection of the known organic photochemical transformations strongly suggests that photochemically excited species, despite their high energy, do not react indiscriminately and that bonds are not randomly broken and formed. It is presently postulated that the ground state requirement for continuous electron redistribution²⁹ has parallel in excited state transformations.

The photochemical transformations of 4,4-disubstituted 2,5-cyclohexadienones serve to introduce the present treatment. In the photochemistry of these compounds one aspect is especially puzzling. On one hand, there is evidence that these rearrangements result from $n-\pi^*$ excitation. The intense $\pi-\pi^*$ (often termed K) bands appear

(26) In our preliminary Communications for simplicity we had pictured the oxygen atom as having a spherical 2S-orbital containing the "circle" electrons. Due to hybridization with the P_{*x*}-orbital this picture is imperfect; it is nevertheless qualitatively not misleading.

Similarly the *y*-electron containing orbital pictured as P_{*y*} may contain some S-character. Excitation from a pure P_{*y*}-orbital to the π system would be symmetry forbidden; in point of fact the $n-\pi^*$ bands are very weak but finite. Interestingly, S-character could account for lack of complete forbiddenness, since an S- π^* excitation is not symmetry forbidden. Despite this possibility, the present picture is adequate for our purposes; thus this does convey the point that the *y*-electron being promoted is excited from the *v-z* plane to the *x-z* plane.

(27) The *z*-axis is taken along the C-O bond single bond to conform to the convention for the C_{*v*} symmetry group. In our previous papers the X- and Z-axes were reversed. Either convention is internally consistent.

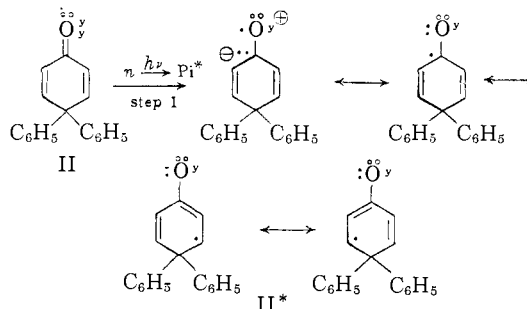
(28) This is a modification of the two dimensional suggestion of G. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p. 282, that different type electrons be labeled. Planar analogs of IXa and IXb were proposed as contributors to the excited state.

(29) This criterion is implicit in ordinary ground state mechanistic reasoning (*e.g.*, arrow notation for electron redistribution). It assumes that successful reactions are likely when there is continued orbital overlap and minimum electron localization in the reaction process. Although rarely stated explicitly, this recognized requirement has had a profound effect on ground state organic chemistry.

only at much shorter wave length, and dienone rearrangements have been reported to occur in sunlight and in Pyrex where little if any light below 300 m μ is available. Similarly, in the present research a filter excluding light below 300 m μ was used.³⁰ Also, it is known that in these $n-\pi^*$ excited states of ketones the electron density of the π -system, and at the carbonyl carbon itself, is enhanced relative to that in the ground state.³¹ Thus the $n-\pi^*$ excited state has the π -system of a metal ketyl, having one excess (anti-bonding) electron. Unlike the ketyl, however, the $n-\pi^*$ state lacks a P_{*y*}-electron.

On the other hand, and in striking contrast to this picture of involvement of an electron-rich π -system in the cyclohexadienone excited state, are the rearrangements themselves—rearrangements in which alkyl and (in the present study) aryl carbon to carbon migrations have been observed. Such migrations are especially characteristic of electron-deficient (*e.g.*, carbonium ion) species.³² A reasonable mechanistic interpretation must accommodate this dichotomy.

In the case of the 4,4-diphenylcyclohexadienone (II) rearrangement the proposed mechanism may be presented in four steps. $n-\pi^*$ excitation (step 1) can be depicted as



where a total of six valence bond contributors (four are drawn) may be used to represent the excited state II*. For reasons to be outlined, specification is not made whether II* is the initially formed and short lived singlet, in which the electrons occur in pairs with opposite spins, or whether it is instead the longer lived and subsequently formed triplet resulting from change of spin of one electron. Consideration of the continuous electron redistribution processes available to II* includes³⁴ a gradually increasing overlap

(30) Even where shorter wave length light is used and $\pi-\pi^*$ excitation is observed, degradation of the higher energy $\pi-\pi^*$ state to the $n-\pi^*$ state is expected to be rapid.

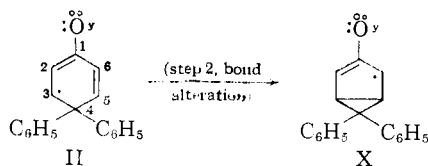
(31) Cf. J. Sidman (ref. 25) and M. Kasha (ref. 25).

(32) Alkyl and aryl 1,2-migrations of carbonium ions are commonplace and free radical and carbanion migration of aryl groups are known but few in number. In contrast, no *bona fide* free radical or carbanion alkyl migrations are known. Also, molecular orbital theory (ref. 33) suggests a decreasing ease of 1,2-carbon to carbon shifts in the sequence carbonium ion > free radical > carbanion with the energy barrier being higher for alkyl than phenyl. This comment does not apply to apparent migration by dissociation recombination processes which are clearly not involved in the present case.

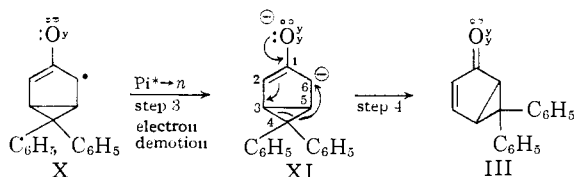
(33) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

(34) Also available to II* are radiationless transitions leading to the ground state dienone, and transitions to the ground state with radiation. If radiation is from the singlet state, this is fluorescence; if from the triplet state, it is phosphorescence. These processes generally detract from the photochemical conversion to product.

between carbons 3 and 5 with covalent bond formation³⁵; this step is termed "bond alteration."



Step three is postulated to be a $\pi^* \rightarrow n$ electron demotion process in which a π -system electron is returned to the low energy non-bonding P_y -orbital from whence the electron was originally excited.³⁶



Most interestingly, the species XI formed as a result of the electron demotion process of step 3 is a mesoionic zwitterion with an electron-deficient carbon π -system. Species XI has one less covalent bond than maximum and suffers energetically from unlike charge separation; it is coerced to undergo further molecular change. Inspection of this species, however, reveals that it contains a cyclopropylcarbinyl carbonium moiety conjugated with an enolate system in a way that there is an especially low energy rearrangement process available (step 4), this being a migration of the benzhydryl group (*i.e.*, carbon 4 and its phenyl groups) from carbon 3 to carbon 6. Rearrangements of cyclopropylcarbinyl carbonium ions to isomeric cyclopropylcarbinyl systems have precedent in the studies of Roberts and co-workers.^{37,38} In contrast to the examples investigated by Roberts, where rearrangement leads (*inter alia*) to an isomeric carbonium ion, rearrangement of XI leads directly to a neutral and stable product (III).

Several comments are pertinent to this proposed four-step³⁹ photochemical mechanism. Step 1 involving $n \rightarrow \pi^*$ excitation is non-controversial. The $\pi^* \rightarrow n$ electron demotion step is inevitable; however, whether this occurs in the sequence as

(35) (a) Consideration of the alternative bridging processes shows that the one in step 2 involves the least electron localization. (b) Species X will differ somewhat in geometry from II* and therefore these two species are not taken to be resonance contributors to the same state.

(36) It is to be noted that this process is an electronic transition rather than a mesomeric effect. Thus X and XI are written as entities connected by a single headed arrow. Also, despite the misleading distance between the oxygen atom and the odd π -electron in the one contributor X above, it should be noted that the π system includes the oxygen atom and demotion of an electron from this π system to the P_y -orbital poses no special problem. The most interesting possibility exists for observing a demotion process accompanied by fluorescence or phosphorescence.

(37) E. F. Cox, M. C. Caserio, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961); M. S. Silver, M. C. Caserio, H. E. Rice and J. D. Roberts, *ibid.*, **83**, 3671 (1961), and earlier papers cited therein.

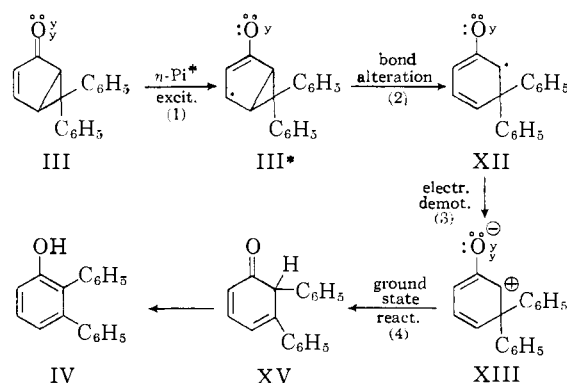
(38) In the present instance the arrow in structure XI indicating benzhydryl migration may be considered to be a formalism indicating the net result of the over-all process, which may actually proceed by a mechanism more closely resembling two 1,2-shifts *via* a bicyclobutonium species rather than a direct 1,3-rearrangement.

(39) Although the four steps are formulated as discrete processes, some of these steps could be concerted.

suggested is subject to argument. Electron demotion prior to any change in gross structure and bonding of the $n \rightarrow \pi^*$ excited state (II) should detract from the efficiency of the photochemical rearrangement with the regeneration of ground state reactant.⁴⁰ Accepting that a change in molecular structure (*i.e.*, bond alteration) is the second step, one is confronted with the question whether electron demotion (here step 3) actually precedes a final rearrangement process (formulated as step 4). However, not only the present rearrangement but, as noted above, much of cyclohexadienone photochemistry is suggestive of electron-deficient intermediates rather than odd electron or electron-rich species. Thus, while the possibility cannot presently be excluded that species X undergoes the final skeletal rearrangement prior to rather than after electron demotion, the preceding formulation is especially attractive in resolving the enigma of carbonium ion type reactions occurring from an $n \rightarrow \pi^*$ excited state.

An important aspect concerns the lack of specification of whether II* and X are singlet or triplet species. Although initial excitation is almost certainly to the singlet $n \rightarrow \pi^*$ excited state (*i.e.*, ¹II*), it is entirely possible that prior to the bond alteration step 2 there is a change in spin of one electron (intersystem crossing) to give a triplet (*i.e.*, ³II*); in such an event species X would also most likely be a triplet (*i.e.*, ³X).⁴¹ While an answer to the triplet-singlet question is of real intrinsic interest and while the spin multiplicity would affect the lifetime of the species involved, it is nevertheless true that the electron distribution of the π -systems of II* and X will be relatively independent of the spin of the odd electron left behind in the orthogonal P_y (non-bonding) orbital. Singlet-triplet identification can be postponed for a future communication.

In considering now the photochemical rearrangement of photoketone III to 2,3-diphenylphenol (IV), we find that virtually the same mechanistic sequence can be applied as illustrated in Chart II—(1) $n \rightarrow \pi^*$ excitation, (2) bond alteration

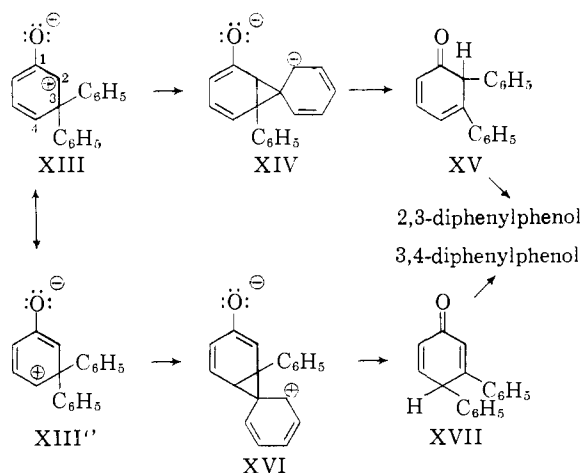


(40) The possibility that the rearrangement results from vibrationally excited but electronically unexcited 4,4-diphenylcyclohexadienone molecules, resulting from electron demotion of the $n \rightarrow \pi^*$ species, seems unlikely. Dissipation of kinetic energy should be rapid. It is to be noted that $n \rightarrow \pi^*$ photochemical transformations do not in general parallel the thermal transformations.

(41) Also in this event there would have to be a spin reversal in the electron demotion process so that the final electron-deficient species would in any case be a singlet.

of the $n-\pi^*$ excited state, (3) electron demotion, and (4) transformations having ground state analogy.

One interesting aspect of the rearrangement is the virtually exclusive phenyl migration from carbon 3 to carbon 2 with formation of 2,3-diphenylphenol (IV). It is noted that another resonance structure for XIII (XIII'') may be written in which the positive charge is at carbon-4 rather than carbon-2 and that there is an *a priori* possibility of phenyl migration to carbon-4 with formation of 3,4-diphenylphenol.⁴² This selectivity is best understood by use of the phenonium intermediates XIV and XVI as approximate models for the two alternative migration transition states.⁴³ It is seen that intermediate XIV, leading to 2,3-diphenylphenol, has greater electron delocalization in the enolate system than intermediate XVI; thus, neglecting distribution of the positive charge which is equivalent in the two species, one finds three contributing structures for XIV *versus* two for XVI.



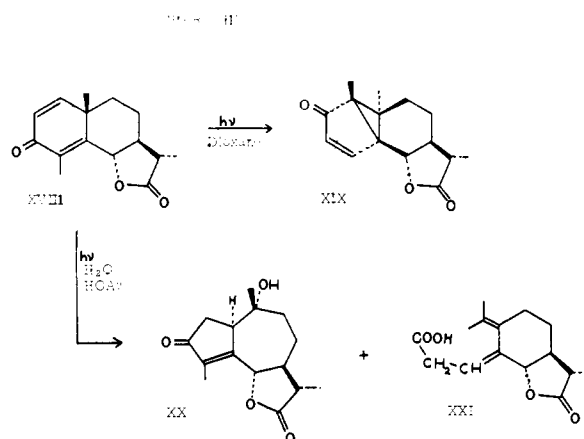
A mechanistic pattern capable of rationalizing the photochemistry of 4,4-diphenylcyclohexadienone having been advanced,⁴⁴ it is now of more than minor interest to apply this reasoning to the literature of 4,4-disubstituted cyclohexadienone photolyses. Of special concern is the applicability to the intriguing case of santonin (XVIII), much of whose chemistry derives from the elegant and

(42) No chromatographic peak corresponding to 3,4-diphenylphenol and no infrared indication of the presence of this compound was found under the present photolysis conditions. However, a small quantity of 3,4-diphenylphenol has been isolated from the 2,3-phenol peak tailings in more recent work by H. E. Z. and R. Keese. Additionally, a striking solvent dependence of the presence or absence of the 3,4-isomer will be described in a forthcoming publication by H. E. Zimmerman and R. Keese.

(43) Due to the exothermic nature of the rearrangement step, in which a zwitterion is converted to a cyclohexadienone intermediate, the barrier preceding the phenonium intermediates will be of higher energy than that following these intermediates. Hence it is the former barrier which constitutes the reaction transition state. Similarly, due to the expectation that the phenonium intermediates (having lost the stabilization of a phenyl group) will be of higher energy than their zwitterionic precursors, the choice of transition state models is reasonable. Hammond's postulate (G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955)) is implicit in this reasoning.

(44) This approach nicely rationalizes the now elucidated (ref. 23) structure of the photoacid. Prior to our forthcoming publication on the subject the reader might test the efficacy of this mechanistic approach in this case.

thorough researches of Barton and co-workers.⁴⁵ There are three main photochemical transformations of santonin (XVIII) (Chart III). Lumisantonin^{46,47} (XIX) is obtained from the photolysis of santonin in dioxane. Isophotosantonin lactone⁴⁶ (XX) results from irradiation in aqueous acetic acid; this product does not arise *via* a lumisantonin (XIX), since the latter is unaffected by cold aqueous acetic acid in the dark while converted to photosantonin acid⁴⁸ (XXI) on irradiation in this medium. Photosantonin acid (XXI) results as an additional product in the aqueous acetic acid irradiation of santonin and (as the ethyl ester photosantonin) in the ethanolic photolysis. Knowledge of the stereochemistry of lumisantonin is available through chemical elucidation by Barton⁵⁰ while the stereochemistry of isophotosantonin lactone has recently been derived by X-ray analysis.^{51,52}



It is found that application of the exactly parallel mechanism presented (*vide supra*) for the 4,4-diphenylcyclohexadienone (II) rearrangement to the case of santonin leads to the correct structure and stereochemistry of lumisantonin; this is pictured in three dimensions in Chart IV.

In this mechanism the assumption is made in step 2 that bonding to form the three-membered ring of XXII will occur as shown to engender only *cis* fusions of this small ring with the five- and six-membered rings. The nature of the cyclopropylcarbinyl rearrangement of step 4 also demands inspection. One *a priori* mechanistic possibility existing in stereochemically simpler systems can be ruled out in the present instance; this is the direct 1,3-shift of carbon-10 from carbon-1 to carbon-4 with retention of C-10 configuration and bond 5-10 remaining intact. In such a rearrangement, as a result of pivoting of groups about the

(45) Cf. D. H. R. Barton, J. McGhie and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), for a survey and leading references.

(46) (a) D. H. R. Barton, P. DeMayo and M. Shafiq, *ibid.*, 140 (1958); (b) *Proc. Chem. Soc.*, 205 (1957).

(47) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

(48) E. F. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky and P. Aldrich, *J. Am. Chem. Soc.*, **80**, 501 (1958); cf. also ref. 49.

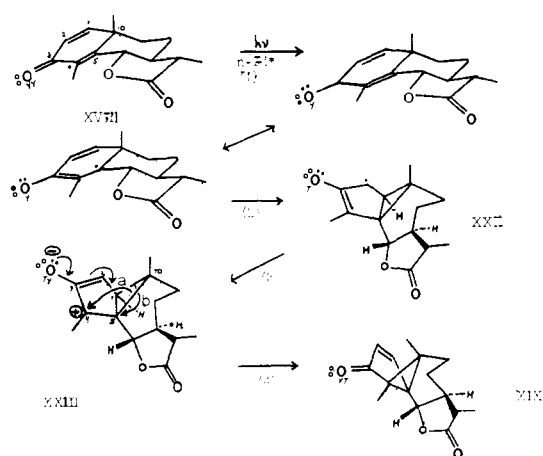
(49) D. H. R. Barton, P. deMayo and M. Shafiq, *J. Chem. Soc.*, 3314 (1958).

(50) D. H. R. Barton and P. T. Gilham, *ibid.*, 4596 (1960).

(51) J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 111 (1962).

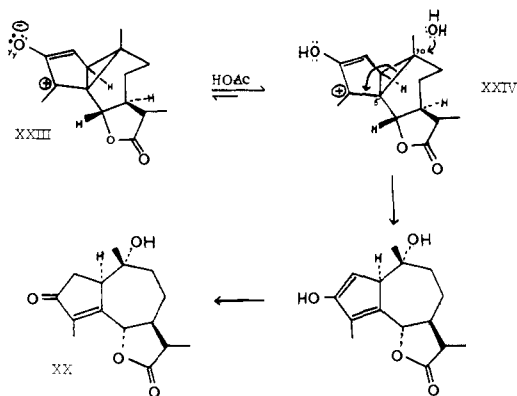
(52) D. H. R. Barton, T. Miki, J. T. Pinhey and R. J. Wells, *ibid.*, 112 (1962).

CHART IV



5-10 bond, a *trans* fusion of the three- and six-membered rings would result. The simplest remaining alternative is the sequence of two 1,2-shifts indicated by arrows a and b in step 4.

In the case of the aqueous acetic acid photolysis of santonin to afford isophotosantonin lactone (XX), the reaction may be formulated in three dimensions beginning with the conjugate acid XXIV of intermediate XXIII in the santonin to lumisantonin reaction. Thus XXIII possesses a potentially basic zwitterionic moiety and is envisaged to be heavily protonated in the acidic photolysis solvent. In XXIII the electron deficiency of carbon-4 is satisfied by electron transmission from the negative oxygen *via* the three ring by means of the cyclopropylcarbonyl rearrangement. In the conjugate acid XXIV the oxygen electrons are less available:

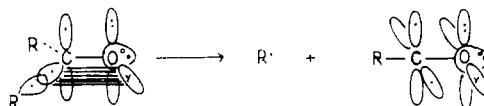


the 5-10 bond becomes the next best electron source and β -fission of carbon-10 as a cationic species ensues⁵³ and a solvent water molecule is picked up. Both the formation of alcoholic product and the effect of acetic acid on the reaction course provide

(53) The formation of photosantonin acid from irradiation of lumisantonin may be envisioned as involving a transformation exactly parallel to that described for the formation of 2,3-diphenylphenol (IV) from photoketone (III). Thus $n-\pi^*$ excitation, bond alteration with breaking of the 1-5 bond of lumisantonin and electron demotion leaves an electron deficiency at C-4 with the possibility of migration of the methyl group from C-10 to C-4. There results a 2,2-disubstituted cyclohexadienone which would be expected to cleave to photosantonin acid in analogy to the work of D. H. R. Barton and G. Quinkert, (*J. Chem. Soc.*, **1** (1960)).

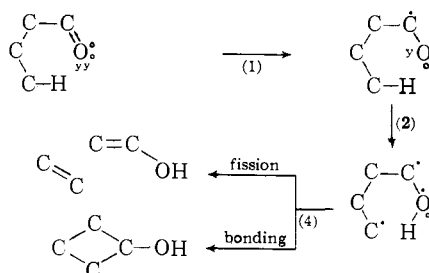
strong support for the postulated ionic intermediates (*e.g.*, XXIII).

A discussion of applications of the present photochemical approach to cyclohexadienone chemistry having been presented, it should be noted that the same type of mechanistic reasoning based on the electronic structure of the excited state can be applied to $n-\pi^*$ reactions in general. However, it is important to note that the four-step sequence proposed above is not necessarily common to all photochemical reactions. Thus, in a number of photochemical reactions a group attached to the carbonyl group is cleaved. Here the odd electron containing P_y orbital is envisaged as beginning to overlap with the coplanar σ -orbital bonding the group (R) to the carbonyl carbon atom. As overlap increases, an acyl radical is generated with



fission of the R radical. In this case steps three and four are not involved.

Similarly, a number of ketone reactions seem to involve initial abstraction of a γ -hydrogen atom followed either by cleavage of the α - β -carbon-to-carbon bond⁵⁴ or instead by collapse of the divalent intermediate to a cyclobutanol.⁵⁵ In these examples it seems likely to be the odd electron containing P_y oxygen orbital which abstracts the hydrogen atom.



The present discussion cannot be exhaustive.⁵⁶ It does present representative examples of the present approach allowing one to discuss the electronic aspects of photochemical reactions. While some of the details of the present hypothesis may eventually have to be modified, and while some details still need to be filled in, the presently presented approach does nevertheless provide a basis for beginning discussion and planning further experimentation.

(54) W. Davis, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **69**, 2153 (1947); T. W. Martin and J. N. Pitts, Jr., *ibid.*, **77**, 5465 (1955); J. N. Pitts, Jr., *J. Chem. Ed.*, **34**, 112 (1957); *cf.* R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 5061 (1959), for a recent discussion and listing of references. It is to be noted that the timing of hydrogen abstraction relative to α - β -carbon-to-carbon bond breaking may vary from case to case.

(55) N. C. Yang and D. H. Yang, *ibid.*, **80**, 2913 (1958).

(56) A large number of the known photochemical transformations of the literature can be accommodated by the present treatment. Some examples to be cited are the rearrangements of eucarvone reported by J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 116 (1961), and G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); rearrangements in the tropolone system as for example, reported by W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, *ibid.*, **83**, 1768 (1961).

Experimental⁵⁷

Diphenylacetaldehyde.—Hydrobenzoin was prepared by the reduction of benzil with sodium borohydride in 95% ethanol. In a large scale run, 867 g. of hydrobenzoin (85% yield), m.p. 137.5–141.0°, was prepared in two batches from 1 kg. of benzil and 122 g. of sodium borohydride in 5.5 l. of ethanol. The hydrobenzoin above was dissolved in 3 l. of benzene to which was added 76 g. of *p*-toluenesulfonic acid. The mixture was heated to reflux and 167 ml. of water was collected in an azeotropic distillation apparatus over 2.5 hours. The mixture was heated at reflux for an additional 3 days. The organic solution was extracted with water and sodium bicarbonate solution and was dried over sodium sulfate. Benzene was removed *in vacuo* and the residue was distilled to give 447 g. (50%) of diphenylacetaldehyde, b.p. 143–155° (0.65 mm.), n_D^{25} 1.5873–1.5884 (reported⁵⁸ n_D^{25} 1.5876). When the reflux time in the reaction was decreased to only a few hours, a crystalline compound, m.p. 124–126°, was isolated which could be quantitatively converted to diphenylacetaldehyde on further reflux in benzene with *p*-toluenesulfonic acid. The infrared spectrum of the crystalline compound had no hydroxyl or carbonyl band and indicated the compound could be the acetal formed from one molecule each of diphenylacetaldehyde and hydrobenzoin. The compound was not investigated further.

4,4-Diphenylcyclohex-2-en-1-one.—An approximately 40% aqueous solution of Triton B was prepared by adding sufficient water to a 40% solution of Triton B methoxide (benzyltrimethylammonium methoxide) in methanol (Matheson, Coleman and Bell) and distillation of the bulk of the methanol. In a typical run, the reagents were: 37.0 g. (0.19 mole) of diphenylacetaldehyde, 15.1 g. (0.21 mole) of methyl vinyl ketone (Pfizer), 31 ml. of aqueous Triton B solution (see above) and 125 ml. of *t*-butyl alcohol. The aldehyde and ketone were dissolved in the alcohol and the solution was cooled in ice. The base was added in small portions with shaking. If the mixture was not kept cool or if the base was added too rapidly, the mixture was found to darken considerably. With care, only slight darkening occurred. After 2 hr., ice was added and then ether. The layers were separated and the aqueous solution was extracted with ether. The ether extracts were extracted several times with water and were dried over sodium sulfate. The ether was removed *in vacuo* and the residue was taken up in sufficient hot ethanol and set aside to crystallize at room temperature. Rapid cooling inevitably led to separation of an oil. The first crop of slightly yellow crystals, after drying *in vacuo*, amounted to 18.87 g., m.p. 88.0–90.5°. Concentration of the mother liquors afforded a second crop, 4.10 g., m.p. 88.0–91.0°. The total yield was 49.1% of theory.

Anal. Calcd. for C₁₈H₁₆O: C, 87.06; H, 6.50. Found: C, 86.59, 86.65; H, 6.46; 6.61.

4,4-Diphenylcyclohex-2-en-1-one has intense infrared absorption bands at 6.00, 6.30, 6.75, 6.95 and 11.25 μ . The ultraviolet spectrum (cyclohexane) had λ_{max} 217 (ϵ 20,800), shoulders at 259, 264 and 271 (ϵ 1220), and λ_{max} 318 m μ (ϵ 218).

When this preparation was carried out on a large scale, starting with 447 g. (2.34 moles) of diphenylacetaldehyde, purification of the product by recrystallization from ethanol did not succeed; only colored, gummy solids were obtained in addition to 88 g. of crystalline solid, m.p. 89.0–90.5°. The impure material, dissolved in chloroform, was put on an 8 × 80 cm. silica gel chromatography column (Davison silica gel, grade 950, 60–200 mesh), slurry packed in 5% ether-hexane. The column was eluted with 5 l. of hexane, 1 l. of 5% ether-hexane, 5 l. of 10% ether-hexane, 1 l. of 15% ether-hexane, 6 l. of 20% ether-hexane, 4 l. of 25% ether-

hexane and 3 l. of 40% ether-hexane. The eluent, in 1-l. fractions, was concentrated and dried *in vacuo*. The crystalline solid from elution with 5–15% ether-hexane had m.p. 85–90°; that from elution with 20–25% ether-hexane had m.p. 85–89°. These fractions totaled 228 g. and had infrared spectra identical with 4,4-diphenylcyclohex-2-ene-1-one obtained previously. Later fractions from the column gave only dark oils from which crystalline solids could not be obtained. The total yield of crystalline 4,4-diphenylcyclohex-2-en-1-one was 316 g. (54.4%).

4,4-Diphenylcyclohexadienone.—Many runs were made of which the following is typical. In a 2-l. 3-neck flask equipped with an efficient mechanical stirrer and a reflux condenser were placed 25.0 g. (0.10 mole) of 4,4-diphenylcyclohex-2-en-1-one, 1250 ml. of *t*-butyl alcohol, 12.5 ml. of glacial acetic acid and 75 g. of selenium dioxide freshly sublimed from nitric acid. Much lower yields of the desired product were obtained in runs in which selenium dioxide powder (Matheson, Coleman and Bell) was used without further purification. The mixture was stirred and heated at reflux for 24 hr. The warm mixture was filtered through Celite and the reaction flask was washed with methanol. The red filtrate was concentrated to about 200 ml. *in vacuo* on a steam-bath. The residue was diluted with chloroform and extracted several times with water and then with 5% sodium hydroxide solution. Initial base extractions resulted in the formation of bad emulsions which were broken up by addition of some saturated sodium chloride solution. The color of the base extracts went from orange to pale yellow in the later extracts. The organic solution was then washed with water and dried over sodium sulfate. Removal of the solvent *in vacuo* left 33 g. of a residue, the infrared spectrum of which indicated a mixture of the desired 4,4-diphenylcyclohexadienone (the strong band at 11.65 μ is useful in this analysis) and selenium compounds (band at 12.0 μ). The residue was heated with 250 ml. of ether for 10 min. The solution was decanted and a fresh ether portion added to the undissolved residue; the process was repeated three times. The undissolved residue was shown by its infrared spectrum to contain only traces, at most, of the desired dienone. The ethereal extracts were concentrated until bumping started as a precipitate settled. The mixture was cooled in the refrigerator for several hours. The solution was decanted from the fine orange precipitate and again concentrated until the next batch of solid separated. Infrared spectra showed the solid to be the undesired selenium compounds. The mother liquors were decanted and the solvent removed *in vacuo* to give 20.8 g. of dark solid which had an infrared spectrum indicating that the proportion of desired dienone had been increased by the above operations.

A two-phase liquid system was prepared from 1000 ml. of cyclohexane (Phillips), 400 ml. of reagent-grade dimethylformamide (Baker) and 80 ml. of ethyl acetate. To 500 g. of Celite (Johns-Mansville 545) in a large reagent bottle was added 200 g. of the lower phase of the two-phase system above and the mixture was shaken until homogeneous on a mechanical shaker (*ca.* 1 hr.). The material was then dry-packed using a tamper to give a column 78 × 8 cm. The column was then saturated with the upper (mobile) phase of the two-phase system by allowing the liquid to pass through the column. Once the column was saturated, the mixture of dienone and selenium compound, obtained above, was put on the column dissolved in the minimum amount of lower (stationary) phase. The fractions collected from the column were diluted with chloroform and were washed three times with water and filtered through sodium sulfate. Concentration of the solvent *in vacuo* and drying gave the following fractions: fraction 1, 2 l., nil; fraction 2, 0.5 l., 0.109 g., red, odorous liquid; fraction 3, 0.5 l., 0.207 g., red, odorous liquid; fraction 4, 0.5 l., 1.505 g., yellow-orange solid; fraction 5, 0.4 l., 5.380 g., yellow-orange solid; fraction 6, 0.3 l., 2.054 g., yellow-orange solid; fraction 7, 0.3 l., 0.148 g., gummy orange solid; fraction 8, 0.3 l., 0.343 g., gummy orange solid. Infrared analysis indicated that fractions 4–6 were almost pure product; 7 contained little dienone and was mostly selenium compound. Fractions 4–6 were dissolved in excess chloroform and treated with Norite to remove most of the residual color. The clear filtrate was partially concentrated, hexane was added and the solution was again partially concentrated. Hexane was added until the solution became cloudy. The product crystallized in long colorless needles (6.10 g.) which were recrystallized from chloroform-hexane to give beautiful needles, 4.63 g., m.p. 123–124.5°.

(57) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Illini Microanalytical Laboratory, Urbana, Ill. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, model 137, a Beckman IR-5 infrared spectrophotometer and a Baird infrared spectrophotometer. The nuclear magnetic resonance spectra were determined at 60 Mc. with the Varian Associates high resolution spectrometer (V-4300 B) with 12-inch magnet and equipped with a flux stabilizer. Tetramethylsilane was used as an internal standard. We acknowledge with pleasure the assistance of Mr. Gary A. Zimmerman in obtaining the n.m.r. spectra.

(58) D. J. Reif and H. O. House, *Org. Syntheses*, **38**, 26 (1958).

Concentration of mother liquors gave additional crops of product, 1.91 g., m.p. 121–123°. The yield of pure 4,4-diphenylcyclohexadienone was 6.54 g. (26%).

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.97, 88.04; H, 5.86, 6.02.

The infrared spectrum of 4,4-diphenylcyclohexadienone has a series of sharp bands at 6.05, 6.15, 6.25 (decreasing intensity), 6.70, 6.90 and 7.15 μ and a series of sharp intense bands at 10.75, 10.95 and 11.65 μ . The ultraviolet spectrum in ethanol has λ_{max} 223 m μ (ϵ 23,500) with shoulders at 260 (ϵ 4500) and 268 m μ (ϵ 3950). The absorption above 300 m μ falls off only gradually with no new maxima in the spectrum. Typical extinction values are: 320 (ϵ 74.5), 330 (ϵ 50.0), 350 (ϵ 29.3), 366 m μ (ϵ 15.2).

In an early run, the yellow-orange solid which had separated during ethereal treatments of the crude reaction mixture (see above) was recrystallized from acetic acid–water to give a yellow powdery solid, m.p. 208–210°. The infrared spectrum of this material is similar to that of 4,4-diphenylcyclohexadienone (bands at 6.05, 6.15, 6.25, 6.72, 6.96 μ). The band at 11.65 μ characteristic of the dienone is absent and there is a new band at 12.00 μ . This selenium compound was not further investigated.

Photolysis of 4,4-Diphenylcyclohexadienone.—The photolysis apparatus used in these experiments has been described in detail elsewhere.⁵⁹ The 4,4-diphenylcyclohexadienone was dissolved in 550 ml. of spectroquality dioxane (Matheson, Coleman and Bell) and 200 ml. of water in a 5-cm. thick cell. Benzophenone–ketyl purified nitrogen was passed through the solution for at least 45 min. before irradiation commenced and a positive pressure of nitrogen was maintained throughout. The solution was stirred mechanically and the temperature was maintained at $25 \pm 0.1^\circ$ by internal heat exchanger coils and thermistor monitoring. A General Electric AH-6 1000 watt high pressure mercury lamp in a parabolic reflector was used as the source. The light was first passed through a three-compartment filter cell consisting, in the first compartment, of 2.4 cm. of a solution of 11.0 g. of potassium acid phthalate in 500 ml. of water; the other two 2.4 cm. compartments were filled with water. The ultraviolet spectrum of the filter solution shows a very sharp cutoff at 310–320 m μ , being opaque below 310 m μ and completely transparent above 320 m μ . The amounts of dienone used in the various runs, the length of time of the photolyses and the yields of the various products are summarized in Table III.

After the irradiation was completed, the colorless solution and cell washings (acetone) were concentrated *in vacuo* (water aspirator) heating gently on a steam-bath, until the mixture became quite turbid. Water was added and the mixture was extracted three times with ether–chloroform. The etheral solution was extracted with three portions of 3% sodium hydroxide solution and was then dried over sodium sulfate. The ether was removed *in vacuo* and the residual “neutral” fraction was treated as described below. The basic extracts were made strongly acidic with 10% sulfuric acid and the acidic solution was extracted three times with ether. These extracts were dried over sodium sulfate, the ether was removed *in vacuo* and the orange residue was dried to give the “acidic” fraction.

The “neutral” fraction was subjected to liquid–liquid partition chromatography. All the following operations were carried out in water-jacketed apparatus kept at a constant temperature of $25.0 \pm 0.5^\circ$, except in run 7 where the temperature was $29.0 \pm 0.5^\circ$. The two-phase liquid system was prepared from 1000 ml. of cyclohexane (Phillips), 400 ml. of reagent-grade dimethylformamide (Baker), 350 ml. of ethyl acetate and 30 ml. of water. In run 7, the amount of ethyl acetate was changed to 300 ml. The two-phase mixture was allowed to equilibrate for at least 30 min. before use. A homogeneous distribution of 40% by weight of the lower phase of this system on 545 Celite (Johns–Mansville) was prepared by mechanically shaking the mixture in a large reagent bottle. The material was dry-packed, using a tampo, into a thermostated column 100 \times 3.5 cm. which was then saturated with the upper (mobile) phase of the system. When the mobile phase reached the bottom of the column, the “neutral” fraction was then put on the column dissolved in the minimum amount of the mobile phase. The material coming off the column was passed by means of thin polyethylene tubing through the cell of a Beckman DU

quartz spectrophotometer, set at 280 m μ , to an automatic variable fraction collector. The spectrophotometer was connected to a 10 millivolt recorder. The change in fractions was noted automatically on the recorded chromatogram so that the various components could be easily located in the appropriate fractions. There were three peaks in the chromatogram, although in some cases (see below) there were only two. Fractions were processed as follows: the solution was diluted with ether and chloroform, washed three times with water, filtered through sodium sulfate and evaporated to dryness. The infrared spectra of the residues indicated that the three components, in order of their elution from the column, were recovered 4,4-diphenylcyclohexadienone, a new ketone produced by the photolysis (“photoketone”) and a phenol produced by the photolysis (“photophenol”). There was no indication of any other component in the “neutral” fraction. The data reported in Table III also indicate that the material balance is nearly 100% in some runs in terms of only these products. By means of infrared analysis, it was possible in cases of overlapping of the peaks in the chromatogram to determine the composition of the various fractions. The infrared characteristics of greatest use in this analysis were the dienone bands at 6.05, 6.15 and 11.55 μ ; the photoketone carbonyl band at 5.90 μ with a shoulder at 5.75 μ ; the sharp hydroxyl band of the photophenol at 2.80 μ and another sharp band at 11.15 μ and, of course, the absence of bands in the carbonyl region. Fractions containing the same pure component were combined and processed together. In cases in which the components, particularly dienone and photoketone, were not well separated the mixed fractions were combined and subjected to a second separation by liquid–liquid chromatography, performed as described above. The amounts of the pure components isolated are reported in Table III.

In runs 6 and 7 in which the degree of conversion of 4,4-diphenylcyclohexadienone was small, the procedure was slightly amended. The neutral fraction was isolated as described above, but this fraction was then dissolved in chloroform–hexane, concentrated, hexane added, etc., until a first crop of crystalline solid separated. Infrared analysis showed this crop to be pure dienone. The mother liquors were then concentrated *in vacuo* and the residual mixture of dienone, photoketone and photophenol was separated into its pure components by liquid–liquid partition chromatography as described above.

Photolytically Derived Acid (Photoacid).—This material was not investigated in detail, but was simply isolated in each run. The red-orange oil partially solidified after standing for several months. In an early run recrystallization of this material was attempted. It came out of methanol–water as a slightly yellow powdery solid with successive melting points of 114–116°, 116–117 and 116–117°. The elemental analysis indicated that the assumed composition (dienone plus water) is probably correct, but the solid was not analytically pure.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 80.55; 80.63; H, 5.79, 5.87.

The infrared spectrum of the material in chloroform shows broad absorption from 2.8–4.5 μ , characteristic of carboxylic acids. The carbonyl band is at 5.85 μ and there are other sharp bands at 6.25 and 6.70 μ in addition to the usual aromatic bands. The ultraviolet spectrum in cyclohexane has λ_{max} 230 (ϵ 12,700), λ_{max} 236 (ϵ 12,900), λ_{min} 254 and λ_{max} 291 m μ (ϵ 21,800). Further purification and structure elucidation was not pursued in the present investigation.²⁸

Photolytically Derived Phenol (Photophenol).—The phenol isolated by liquid–liquid partition chromatography of the neutral fraction from photolysis of 4,4-diphenylcyclohexadienone was characterized as follows. The material judged from infrared analysis (*vide supra*) to contain only phenol and no carbonyl-containing compounds was taken up in ether and treated with Norite to remove the yellow-orange color. The colorless solution was concentrated, hexane was added to the point of cloudiness and the material was set aside to crystallize at room temperature. The colorless prisms had m.p. 100.0–100.5°. Further recrystallizations from hexane gave material of m.p. 101.5–102.0° after drying *in vacuo*. The infrared spectrum of this material was the same as that of the chromatographic fraction before crystallization.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.90, 87.99; H, 6.11, 6.01.

(59) V. Sandel, Ph.D. Thesis, Northwestern University, 1961.

The infrared spectrum of the photophenol in chloroform shows a strong sharp non-bonded hydroxyl band at 2.80μ with only an indication of a very weak accompanying broader bonded hydroxyl band. There is a characteristic series of sharp medium intensity peaks at 6.30 , 6.38 and 6.45μ and another group at 6.80 (shoulder), 6.82 and 6.95μ . The strong sharp band at 11.15μ is especially useful in analysis for this compound. In carbon disulfide, one can see other strong bands at 12.40 , 13.0 (broad), 13.45 , 14.2 (broad) and 14.60μ . The ultraviolet spectrum (methanol) shows no discrete maxima. There is a shoulder at $224 m\mu$ (ϵ 23,000) and another shoulder at $282 m\mu$ (ϵ 4030). In ethanolic sodium hydroxide solution, there is a broad maximum at $320 m\mu$ (ϵ 9150) with no other maxima or shoulders. The absorption is very intense, however, as ϵ at $250 m\mu$ is 31,600.

The structure of the photophenol was determined to be 2,3-diphenylphenol by the reactions of the phenol and its independent synthesis described below.

Photolytically Derived Ketone (Photoketone).—The second component of the neutral fraction from photolysis of 4,4-diphenyl-cyclohexadienone eluted by liquid-liquid partition chromatography appeared from its infrared spectrum to be a ketone. This material could be recrystallized from hexane containing a little chloroform, after initial treatment with Norite to remove some residual yellow color. The recrystallized material had successive melting points of 140.0 – 142.5° , 141.5 – 144.0° and 142.0 – 144.0° , but did not give a completely acceptable elemental analysis. Vacuum sublimation of a portion of this material at 0.1 mm. in a micro-sublimation apparatus gave crystals of m.p. 138.5 – 140.5° which gave a satisfactory elemental analysis.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.83, 88.05; H, 5.70, 5.92.

The infrared spectrum of the photoketone is chiefly characterized by a sharp intense carbonyl band at 5.90μ with a shoulder at 5.75μ and a series of sharp medium-intensity bands at 6.25 , 6.35 , 6.65 and 6.88μ . In contrast to dienone and the other photolysis products, the photoketone does not possess a sharp absorption band in the 11 – 12μ region but shows only weak absorption at 11.3 and 11.6μ . The ultraviolet spectrum in methanol has a shoulder at $216 m\mu$ (ϵ 16,000), a plateau at 252 – 256 (ϵ 4800) shoulders at 274 (ϵ 4530) and 282 (ϵ 4330) and λ_{max} $334 m\mu$ (ϵ 533). The u.m.r. spectrum in carbon tetrachloride has a sharp doublet for the phenyl protons at 2.83 and 2.88τ ; a doublet at 4.40 and 4.57τ (each peak is split into a doublet with a peak separation of 1.5 c.p.s.); a series of four resonances at 6.73 , 6.79 , 6.83 and 6.90τ in which the first two peaks are of equal intensity while the latter two peaks are of equal but somewhat greater intensity; two resonances at 7.43 and 7.56τ , each of which appears to be a closely spaced triplet with a separation of 1.5 c.p.s.

This evidence taken together with the degradation of the photoketone by ozonolysis described below establishes that the photoketone is 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.

Acetylation of the Photophenol (2,3-Diphenylphenol).—A 60.0-mg. sample of the phenolic irradiation product (2,3-diphenylphenol) was heated with 0.5 ml. of acetic anhydride for 1 hr. at gentle reflux. The mixture was cooled and diluted with water. The oil which separated quickly crystallized. Enough sodium carbonate solution was added to make the solution slightly basic. The white crystalline solid was separated and dried to give 58.6 mg., m.p. 114 – 116° . Recrystallization from hexane afforded long colorless needles, m.p. 117.5 – 118.0° , which analyzed for a diphenylphenyl acetate.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.11; H, 5.83.

This acetate, which on the basis of later experiments must be 2,3-diphenylphenyl acetate, had an infrared spectrum similar but not identical with that of 3,4-diphenylphenyl acetate (*vide infra*). 2,3-Diphenylphenyl acetate has bands at 5.70 , 6.90 , 7.05 , 7.35 , 8.3 , 8.54 , 9.09 , 9.9 , 10.75 , 10.95 , 11.50 , 12.50 , 13.0 , 13.3 and 14.3μ . Comparison of this spectrum with that of the isomeric 3,4-diphenylphenyl acetate indicates that the band at 8.54μ (1170 cm^{-1}) in 2,3-diphenylphenyl acetate is shifted to 8.48μ (1180 cm^{-1}) and is intensified in the 3,4-compound. Also, the bands at 9.09 (1100 cm^{-1}) and 12.50μ (800 cm^{-1}) in the 2,3-diphenylphenyl acetate are absent in the 3,4-compound and,

similarly, bands at 11.25 (890 cm^{-1}) and 12.20μ (820 cm^{-1}) in the spectrum of 3,4-diphenylphenyl acetate are absent in the spectrum of the 2,3-compound. These spectra were obtained with a Baird double beam spectrometer.

Bromination of the Photophenol (2,3-Diphenylphenol).—The conditions by which Lüttringhaus and Ambros¹² converted 2,6-diphenylphenol (m.p. 101°) to 2,6-diphenylbenzoquinone (m.p. 138°) were applied to the photophenol. In 15 ml. of glacial acetic acid was dissolved 97.6 mg. (0.40 mmole) of the photophenol, m.p. 101 – 102° . The solution was cooled below 20° and to it was added dropwise a solution of 0.16 g. (1 mmole) of bromine in 1 ml. of acetic acid. The bromine color disappeared initially but then persisted with later additions. The mixture was allowed to stand for 10 min. and water was then added until an off-white crystalline solid precipitated. This material was separated and dried and had a m.p. of 168 – 175° . Recrystallization from hexane and drying gave solid which melted successively at 177 – 178° , 177.5 – 178.0° and 177.5 – 178.0° . The material analyzed for a dibromo derivative of a diphenylphenol and, from subsequent results, must be 2,3-diphenyl-4,6-dibromophenol.

Anal. Calcd. for $C_{18}H_{12}OBr_2$: C, 53.50; H, 2.99; Br, 39.55. Found: C, 53.40, 53.28; H, 3.34, 3.20; Br, 40.55, 40.58. A second sample gave the analysis: C, 53.37; H, 3.57; Br, 39.40, 39.51.

Acid-catalyzed Rearrangement of 4,4-Diphenylcyclohexadienone. (a) In Acetic Anhydride.—The procedure of Arnold and Buckley⁶⁰ was used. In 5 ml. of acetic anhydride was dissolved 207 mg. of 4,4-diphenylcyclohexadienone. To the mixture was added 0.2 ml. of concentrated sulfuric acid. The slightly orange mixture was allowed to stand at room temperature for 5 hr. and was then poured onto ice. The white solid which precipitated was filtered and dried to give 221 mg. (97.5%) of 3,4-diphenylphenyl acetate, m.p. 128 – 130° . Recrystallization from hexane gave colorless prisms, m.p. 130.0 – 131.5° .

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.11, 83.26; H, 5.85, 5.79.

(b) In Acetic Acid, Concentrated Hydrochloric Acid and Water.—The procedure of Dreiding, Pummer and Tomaszewski⁶¹ was adapted to the present case. To 500 mg. of 4,4-diphenylcyclohexadienone was added 7.5 ml. of glacial acetic acid, 1 ml. of water and 2.5 ml. of concentrated hydrochloric acid; the mixture was heated at reflux for 5 hr. Darkening occurred immediately. After being cooled, the mixture was diluted with water. The dark oil which separated was extracted with chloroform and the extracts were dried over sodium sulfate. Evaporation of the solvent *in vacuo* left 556 mg. of a dark oil. The infrared spectrum of this oil, with the exception of a few bands due to traces of residual acetic acid, proved to be identical with that of 3,4-diphenylphenol prepared independently by hydrolysis of the acetate prepared above and by dehydrogenation of 3,4-diphenylcyclohex-2-en-1-one (*vide infra*).

The oil was chromatographed on a 72×3.5 cm. silica gel column. After elution of small amounts of material with 1 l. of hexane, 1 l. of 5% ether-hexane and 2 l. of 10% ether-hexane, 489 mg. of a yellow viscous oil was eluted with 1700 ml. of 20% ether-hexane. The infrared spectrum of this residue indicated that it was the phenol still contaminated by traces of a carbonyl-containing compound absorbing at 5.85μ . Initial attempts at recrystallization from hexane-chloroform gave oils, but when concentrations were adjusted so that crystallization was very slow, a solid was obtained. The crude solid had m.p. 41 – 51° and subsequent recrystallizations gave material of m.p. 99 – 101° , 101 – 102° and 104 – 105° .

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.33, 87.21; H, 5.69, 5.67.

The infrared spectrum of 3,4-diphenylphenol in chloroform is chiefly characterized by a sharp medium-intensity non-bonded hydroxyl band at 2.70μ and a broad band of similar intensity at 2.9μ due to hydrogen-bonded hydroxyl groups. This latter band does not appear in the spectrum of 2,3-diphenylphenol (see above). There are other sharp bands at 6.15 , 6.3 , 6.7 , 6.95 , 7.6 , 7.9 , 8.5 and 11.15μ .

(60) R. T. Arnold and J. S. Buckley, *J. Am. Chem. Soc.*, **71**, 1781 (1949).

(61) A. S. Dreiding, W. J. Pummer and A. J. Tomaszewski, *ibid.*, **75**, 3159 (1953).

TABLE III
 PHOTOLYSIS OF 4,4-DIPHENYLCYCLOHEXADIENONE

Run	Amount of dienone photolyzed, g.	Time of photolysis, hr.	Products, g., %			
			Photoacid ^a	Photophenol	Photoketone	Dienone
1	0.52	2.0	0.29, 55	0.13, 25	. . ^{b,c}	None ^b
2	0.93	1.0	.36, 36	.31, ^d 33	. . ^c	0.34, ^d 36
3 ^e	1.08	1.25	.48, 42	.24, 22	0.11, 10	0.15, 14
4 ^e	3.04	6.0	1.99, 61	.97, 32	.04, 1.3	None
5 ^e	2.40	0.5	0.70, 27	.52, 22	.17, 7.1 ^f	0.84, 35
6 ^e	5.60 ^g	.33	.62, 11	.45, 8.1	.47, 8.4	4.02, 72
7 ^e	6.72 ^g	.5	.84, 12	.34, 5.1	.19, 2.8 ^h	4.82, 72

^a Weight of crude acid fraction. ^b Material partially separated by silica-gel chromatography. Infrared spectra indicated that there was no recovered dienone while photoketone was not a recognized product at this time. There are also indications that photoketone isomerizes on silica gel. ^c Infrared of the crude neutral fraction indicated the presence of some photoketone which was not isolated. ^d Material separated partially by silica gel chromatography; figures represent approximate yields. ^e Liquid partition chromatography used; yields given are chromatographic yields of pure components; mixed fractions are not included. ^f Mixed fractions of photoketone and dienone amounted to 0.32 g. ^g Material photolyzed and processed in two portions; results combined and reported as one run. ^h 0.33 g. (4.9%) of photoketone-containing fractions were not processed.

In carbon disulfide there are strong bands at 12.6, 13.0 and 14.2 μ . The ultraviolet spectrum of 3,4-diphenylphenol in methanol has λ_{\max} 234 $m\mu$ (ϵ 25,400) with a broad shoulder centered at about 260 $m\mu$ (ϵ 12,650).

Hydrolysis of 3,4-Diphenylphenyl Acetate.—The acetate obtained above from acidic rearrangement of 4,4-diphenylcyclohexadienone in acetic anhydride was hydrolyzed as follows. In 5 ml. of 5% methanolic potassium hydroxide was heated 167 mg. of the acetate at reflux for 1.5 hr. The mixture, after being cooled, was acidified with dilute hydrochloric acid. The cloudy solution was extracted with 2 \times 20 ml. of ether and the extracts were dried over sodium sulfate. Evaporation of the ether and drying afforded 161 mg. of a viscous yellow material which smelled of acetic acid. The material was taken up in ether and extracted twice with 40 ml. of 1% sodium hydroxide solution and washed with water. Drying and evaporation of the ether gave 150 mg. of an oily material whose infrared spectrum showed a very weak carbonyl band (at 5.85 μ) but which otherwise was identical to that of 3,4-diphenylphenol prepared directly by acidic rearrangement of 4,4-diphenylcyclohexadienone (see above) and by an independent method now to be described. This material was not purified further.

3,4-Diphenylcyclohex-2-en-1-one was prepared by the procedure of Robinson and co-workers¹⁴ using 4-diethylamino-2-butanone methiodide prepared⁶² from 18.4 g. (0.13 mole) of freshly prepared⁶³ aminoketone and 20 g. (0.10 mole) of desoxybenzoin in 150 ml. of benzene. The crude product (26.2 g.) was dissolved in benzene and passed through an alumina column 20 \times 4.5 cm. The first fraction, 250 ml., gave 16.1 g. of an orange residue, m.p. 55–87°; the second fraction, 500 ml., gave 3.9 g. of a yellow residue, m.p. 90–96°. These fractions were recrystallized separately from hexane-chloroform, after treatment with Norite, to give material of m.p. 97–102°. A second recrystallization gave, in three crops, 8.7 g., m.p. 101.5–103.0°, which was again recrystallized to give colorless prisms, m.p. 101.5–103.0° (reported¹⁴ m.p. 99.0–99.5° from methanol). The infrared spectrum has sharp peaks at 6.00, 6.20, 6.30, 6.67 and 6.85 μ and, at higher wave length, 11.05 and 11.25 μ .

Anal. Calcd. for C₁₈H₁₆O: C, 87.06; H, 6.50. Found: C, 87.03, 87.10; H, 6.61, 6.64.

The 2,4-dinitrophenylhydrazone of 3,4-diphenylcyclohex-2-en-1-one formed brilliant dark red needles, m.p. 215–217° (with slight earlier softening) after several recrystallizations from hexane-chloroform (reported¹⁴ m.p. 205–206°).

Anal. Calcd. for C₂₄H₂₀N₂O₄: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.09, 66.93; H, 4.79, 4.81; N, 12.59, 12.61.

Dehydrogenation of 3,4-Diphenylcyclohex-2-en-1-one. **3,4-Diphenylphenol.**—Following the general procedure of Horning and Horning,⁶⁴ 575 mg. of 3,4-diphenylcyclohex-2-en-1-one was dissolved in 3 ml. of *p*-cymene to which was added

105 mg. of 10% palladium-on-charcoal diluted with 100 mg. of charcoal. The mixture was stirred magnetically and heated at reflux for 4 hr. After being cooled to about 50°, the mixture was filtered; the reaction flask and catalyst were washed with four portions of hot ethyl acetate. The bulk of the solvents was removed using a concentrator and water aspirator; the last traces were removed using a vacuum pump operating at 0.1 mm., heating with a water-bath. The residue amounted to 562 mg. and had an infrared spectrum identical in all respects with that of 3,4-diphenylphenol prepared above by treatment of 4,4-diphenylcyclohexadienone with acid. Recrystallization of the residue from hexane-chloroform gave white crystalline material which melted successively at 96.5–101°, 100–104.5°, 104.0–105.5°, 104.0–105.0°.

Anal. Calcd. for C₁₈H₁₄O: C, 87.77; H, 5.73. Found: C, 87.58, 87.43; H, 5.84, 5.85.

The mixed melting point of this material (m.p. 104–105°) with that of 3,4-diphenylphenol prepared independently above (m.p. 104–105°) was undepressed at 102.5–104.5°.

4,5-Diphenylcyclohexane-1,3-dione was prepared by the method of Borsche.¹⁵ To a solution of 6.9 g. (0.3 g. atom) of sodium in 135 ml. of absolute alcohol was added 51 g. (0.307 mole) of ethyl phenylacetate and then 45 g. (0.309 mole) of benzalacetone in 45 ml. of ethanol. The mixture was cooled in an ice-bath during the addition. The mixture turned blood-red and was heated at reflux overnight. Addition of water produced a copious red-brown precipitate which was removed. The filtrate was concentrated *in vacuo* to remove the ethanol and the residue was filtered through Celite. Addition of acetic acid to the red solution did not result in precipitation of a crystalline solid, as reported by Borsche,¹⁵ but rather to separation of a red oil. The mixture was extracted with chloroform. Removal of the chloroform *in vacuo* left 56.5 g. of a red oil. Attempted crystallization of this material from ethanol¹⁶ did not afford a nice crystalline material but only an oil which, on standing, solidified to an amorphous solid. This solid was taken up in 150 ml. of chloroform to give an orange solution. Dilution to 500 ml. with hexane led to separation of a yellow-white crystalline solid which, after drying, softened at 155–160° and melted at 160–163°. Borsche¹⁵ reported m.p. 159–160° for 4,5-diphenylcyclohexane-1,3-dione. The infrared spectrum of this material in chloroform shows broad absorption in the region 3–4.5 μ characteristic of hydrogen-bonded hydroxyl groups (carboxylic acids and enols), a sharp weak doublet at 6.75 and 6.85 μ and an intense broad band centered at 6.25 μ (1600 cm^{-1}), very characteristic of β -diketones which exist as mono enols.⁶⁵ The ultraviolet spectrum in ethanol has λ_{\max} 258 $m\mu$ (ϵ 17,000). The spectrum of cyclohexane-1,3-dione mono enol is reported to have λ_{\max} 255 $m\mu$ (ϵ 16,000).⁶⁶

The total amount of crystalline 4,5-diphenylcyclohexane-1,3-dione, m.p. 160–165°, obtained after one recrystalliza-

(62) A. L. Wilds and C. H. Shunk, *J. Am. Chem. Soc.*, **65**, 469 (1943).

(63) M. S. Newman and A. B. Mekler, *ibid.*, **82**, 4039 (1960).

(64) E. C. Horning and M. G. Horning, *ibid.*, **69**, 1359 (1947).

(65) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 142.

(66) E. A. Braude, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 177.

tion was 22.2 g. (28%). Later crops of solid were obtained which melted partially at 160–165° and finished melting at 187–190°, but whose infrared spectra were identical in all respects with that of material of m.p. 160–165° obtained initially.

Attempted Reduction of 4,5-Diphenylcyclohexane-1,3-dione.—Treatment of 4,5-diphenylcyclohexane-1,3-dione with either one or two equivalents of sodium borohydride in methanol at 0° and with 2.5 equivalents of lithium aluminum hydride in ether or 3.9 equivalents of lithium aluminum hydride in tetrahydrofuran gave, as the only isolated product, 65–95% yields of recovered starting material. In all cases, gas evolution occurred when the hydride was initially added.

Enol Ether of 4,5-Diphenylcyclohexane-1,3-dione.—According to the general procedure of Frank and Hall,⁶⁷ 5.0 g. of 4,5-diphenylcyclohexane-1,3-dione, m.p. 160–163°, was heated at reflux with 10 ml. of absolute ethanol, 50 ml. of benzene and 0.5 g. of *p*-toluenesulfonic acid and water was collected by azeotropic distillation. After 2.5 hr. the mixture was cooled, diluted with chloroform and ether and washed with water, aqueous sodium bicarbonate solution and again with water and was dried over sodium sulfate. Evaporation of the solvent left 6.53 g. of a viscous yellow liquid. The infrared spectrum of this material was quite sharp; there was a sharp, weak band at 5.85 μ and intense bands at 6.05 and 6.20 μ , characteristic of β -diketone enol ethers,⁶⁸ followed by sharp bands at 6.65, 6.75 and 6.85 μ .

When the reaction was carried out with a sample of 4,5-diphenylcyclohexane-1,3-dione that was a mixture of material of m.p. 160–163° and 183–187° (see above), the infrared spectrum of the product was identical with that obtained using material which exhibited only m.p. 160–163°. In both runs, no attempt was made to purify further the product, which did not crystallize after standing for several months. This material was used directly in the next step.

Lithium Aluminum Hydride Reduction of Enol Ether Derived from 4,5-Diphenylcyclohexane-1,3-dione.—To 75 mg. (0.002 mole) of fresh lithium aluminum hydride in 10 ml. of ether, stirred magnetically, was added a solution of 1.92 g. (0.0066 mole) of the enol ether above in 30 ml. of ether. There was slight warming on addition. The mixture was stirred for 1 hr. at room temperature and was then hydrolyzed with 10% sulfuric acid. The aqueous layer was extracted with a mixture of chloroform and ether and the organic extracts were dried over sodium sulfate. Evaporation of the solvent left 1.81 g. of residue. The mixture, dissolved in the minimum amount of chloroform, was chromatographed on a 3 × 84 cm. silica gel column, slurry packed in 5% ether-hexane. Fractions 1–4 were eluted with 2050 ml. of hexane and contained 0.0212 g. of material; fraction 5, 1 l. of 5% ether-in-hexane, 0.0449 g.; 6–10 eluted with 1 l. of 7% ether-hexane, 1 l. of 10% ether-hexane and 500 ml. of 20% ether-hexane, 0.0435 g.; 11–13, 500 ml. of 20% ether-hexane, 500 ml. of 30%, 0.3616 g.; 14, 250 ml. of 30% ether-hexane, 0.0666 g.; 15–18, 1 l. of 30% ether-hexane, 0.4787 g.; 19–23, 250 ml. of 30% ether-hexane, 1 l. of 40% ether-hexane, 500 ml. of ether, 1.5 l. of chloroform, 0.3251 g. The infrared spectra of fractions 11–13 were identical, as were those of fractions 15–18. Fraction 14 was a mixture of the two components. Fractions 19–23 had an infrared spectrum identical with that of starting material. The only fractions which immediately solidified were 15–18 which crystallized on standing to give a solid, m.p. 80–85°. Successive recrystallizations from hexane gave white crystals of m.p. 81.5–83°, 87–88°, 89–90°, 90.0–90.5°, 93.0–94.5°. The material analyzed for a diphenylcyclohexenone.

Anal. Calcd. for C₁₈H₁₆O: C, 87.06; H, 6.50. Found: C, 86.99, 87.04; H, 6.55, 6.71.

The infrared spectrum of the crystalline compound is in accord with its assignment as a diphenylcyclohexenone. The carbonyl band is at 5.95 μ , and there follow sharp bands at 6.15 and 6.20 μ (both weak) and strong bands at 6.65 and 6.75 μ . The ultraviolet spectrum in methanol has very strong end absorption, a shoulder at 226 $m\mu$ (ϵ 12,500); a series of shoulders at 258 (ϵ 1220), 264 (ϵ 846) and 270 $m\mu$ (ϵ 533); λ_{max} 324 $m\mu$ (ϵ 47). Based on the method of synthesis and the subsequent dehydrogenation reported below, this compound must be 5,6-diphenylcyclohex-2-en-1-one.

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

(68) Reference 65, p. 144.

The material in fraction 13 solidified on standing for a period of several months. The resultant solid had m.p. 86–91° with some initial softening. Recrystallization from hexane-chloroform gave a somewhat gummy solid with successive melting points of 86–95° and 94–97°. The material separated initially as an oil which later solidified. The infrared spectrum of this material is very similar to that of fractions 15–18 indicating that it may be an isomeric diphenylcyclohexenone. Except for a dehydrogenation experiment reported below, this material was not investigated further.

Dehydrogenation of 5,6-Diphenylcyclohex-2-en-1-one. 2,3-Diphenylphenol.—The procedure described above for the dehydrogenation of 3,4-diphenylcyclohex-2-en-1-one was used here employing 71 mg. of 5,6-diphenylcyclohex-2-en-1-one (from fractions 15–18 above) and 34 mg. of 5% palladium-on-charcoal in 2 ml. of *p*-cymene. There was obtained by this procedure 60 mg. of a residue which solidified on standing. Recrystallization from hexane gave crystals of m.p. 99.0–99.5° which had an infrared spectrum identical in every detail with the photophenol—that is, 2,3-diphenylphenol—produced on irradiation of 4,4-diphenylcyclohexadienone.

An attempt was made to dehydrogenate the solid, m.p. 86–95°, obtained from fraction 13 above. When 48 mg. of the ketone was heated at reflux with 50 mg. of 5% palladium-on-charcoal in 3 ml. of *p*-cymene for 4 hr. there was obtained by the usual procedure 41 mg. of material whose infrared spectrum was virtually identical with that of the starting material and which gave no indication of the presence of any phenol. When the heating period was extended to 2 days, the material isolated was very dark and had a complicated infrared spectrum indicating the presence of several materials. This mixture was not investigated further.

***cis*-3,3-Diphenylcyclopropane-1,2-dicarboxylic acid anhydride** was prepared by the method of Van Alphen.⁶⁹ To 8.3 g. (0.085 mole) of maleic anhydride in 250 ml. of ether, cooled in an ice-bath, was added a solution of 16.5 g. (0.085 mole) of diphenyldiazomethane⁶⁹ in 80 ml. of ether. Van Alphen²⁰ reported the separation of a white solid in 10 min. accompanied by the evolution of heat. In our hands, slow gas evolution began after about 15 min. The ice-bath was removed. After 40 min. some white precipitate settled out and more separated as the red-violet color of the solution gradually faded. After 3 hr. the color of the solution was light orange and there was steady gas evolution. The supernatant liquid was separated and the crystalline residue was washed twice with ether; the washings were combined with the supernatant solution and treated separately (see below). A 200-ml. portion of benzene was added to the solid residue and the mixture was heated to reflux as gas evolution proceeded at a moderate pace. After 12 hr. the benzene was removed *in vacuo* leaving a residue of 4.98 g. This solid was washed with ether and filtered to give 2.05 g. of colorless *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid anhydride, m.p. 163–165°. Van Alphen²⁰ reported m.p. 162°.

To the supernatant ethereal solution (see above) was added 200 ml. of benzene. The ether was removed by distillation and the resulting benzene solution was heated at reflux for 12 hr. Removal of benzene *in vacuo* left 18.14 g. of an orange mushy semi-solid. This material was taken up in ether to give an orange solution and some undissolved white solids which were separated. This second crop of anhydride, recrystallized from hexane-chloroform, amounted to 3.62 g. of white needles, m.p. 164–167°.

The infrared spectrum of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid anhydride is chiefly characterized by a pair of intense peaks in the carbonyl region at 5.40 and 5.63 μ and other sharp peaks at 8.03, 9.07, 10.08 and 10.80 μ . The ultraviolet spectrum in ethanol has a plateau at 220–224 (ϵ 9860), a shoulder at 248 (ϵ 2590), a shoulder at 268 (ϵ 1230) and λ_{max} 275 $m\mu$ (ϵ 730). The very simple nuclear magnetic resonance spectrum in deuteriochloroform shows a complex doublet for the phenyl protons at 2.86 τ and a sharp singlet for the cyclopropane hydrogens at 6.60 τ .

***cis*-3,3-Diphenylcyclopropane-1,2-dicarboxylic Acid.**—Following the procedure of Van Alphen,²⁰ 2.00 g. of the anhydride above was dissolved in a solution of 2 g. of sodium hydroxide in 100 ml. of water by heating for a few minutes on a steam-bath. The hot solution was cooled, 10% sulfuric acid was added until the mixture was strongly acidic and a

(69) L. I. Smith and K. L. Howard, *Org. Syntheses*, **24**, 53 (1944).

white solid precipitated. The solid was separated and washed with water and hexane. After being dried at 75° and 1 mm., the solid weighed 1.99 g. and had m.p. 183–190° dec. Successive recrystallizations from acetone–water gave white needles, m.p. 183–193° dec. and 179–189° dec. Water was given off during the melting process and the melt solidified on cooling to give anhydride, m.p. 164–166.5°.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 71.99; H, 4.99.

Van Alphen²⁰ reported m.p. 204° dec. for *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid. Our samples never melted this high. The melting point apparently depends strongly on crystalline form and recrystallization solvent. For instance, a sample recrystallized from hexane–chloroform had m.p. 170–178° dec. and the melt remelted, after solidification, at 162–166.5°. The infrared spectrum of this latter sample was exactly the same as of the material recrystallized from acetone–water.

The other properties of this compound support the structural assignment. The crystals are only slightly soluble at room temperature in chloroform and ether. The lack of solubility in common n.m.r. solvents precluded obtaining a satisfactory n.m.r. spectrum. The ultraviolet spectrum in ethanol has several sharp maxima: 225 (ϵ 12,700), 254 (ϵ 596), 260 (ϵ 663), 267 (ϵ 602), 274 μ (ϵ 320). The spectrum is very much like that of *trans*-2-phenylcyclopropanecarboxylic acid which is reported²⁰ to have maxima at 222 (ϵ 11,000) and 267 μ (ϵ 380). The infrared spectrum of the acid in potassium bromide is characterized by broad absorption in the region 3–5 μ a sharp carbonyl band at 5.85 μ , two broader more intense bands at 6.25 and 6.85 μ and other sharp bands at 7.95(s), 8.20(m), 10.40(m), 12.15(w), 12.85(m), 12.95(m), 13.30(m), 14.10(s) and 14.40(m) μ . The spectrum, with the exception of some variation in the dependable region in potassium bromide spectra of 3–5 μ , is the same for all samples of the diacid, despite the wide variation in melting point described above.

Dimethyl *cis*-3,3-Diphenylcyclopropane-1,2-dicarboxylate.—Diazomethane was prepared from an excess of *N*-nitroso-*N*-methylurea by standard procedures. The yellow ethereal solution of diazomethane was added to a solution of 255 mg. of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid in 75 ml. of ether cooled in an ice-bath. When the yellow color persisted, addition was stopped and the mixture was allowed to stand for 10 min. The bulk of the ether and excess diazomethane were distilled off on a steam-bath. Hexane was added, the rest of the ether was boiled off and the solution concentrated to about 5 ml. A crystalline precipitate soon settled. This first crop, 9.0 mg., evolved gas on melting at 100–125° and was discarded. Further concentration of the mother liquors led to the separation of another crop of crystals, m.p. 62–74° (no decomposition). Recrystallization from hexane containing a few drops of chloroform gave 167 mg. of material, m.p. 70–75°, after drying. Further recrystallizations gave material, m.p. 73.5–76.0°. Van Alphen²⁰ reported for dimethyl *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylate m.p. 72° while Jones²¹ reported m.p. 71–72°.

The n.m.r. spectrum of the ester in deuteriochloroform is in excellent agreement with the proposed structure. There is a complex resonance for the phenyl protons centered at 2.81 τ , a sharp singlet at 6.35 τ in the region characteristic of the protons of the methoxy group of methyl esters,⁷¹ and a less intense sharp singlet at 7.25 τ for the two cyclopropane hydrogens. The infrared spectrum of the ester in carbon tetrachloride has a split carbonyl band at 5.72 and 5.80 μ , followed by a series of sharp bands at 6.25, 6.70, 6.95, 7.10, 7.35 and 7.76 μ .

Ozonolysis of the Photolytically Derived Ketone (Photoketone).—A Welsbach ozonizer was used, operating at an oxygen pressure of 8 lb./in.², 70 volts and a flowmeter reading of 0.01. The sampling outlet valve was barely opened so that the rate of exist flow of ozone through the sampling outlet was very low. The gas from the sampling outlet was bubbled through excess 5% aqueous potassium iodide solution for 5.0 min. and the iodine produced, after acidification with 10% sulfuric acid, was titrated with standard thio-

sulfate solution. The amount of ozone passing out of the sampling valve per 5.0 min. period was thus found to be, in successive analyses, 0.131, 0.130 and 0.130 mmole.

The general ozonolysis procedure of Turner⁷² was used and was found to be the best of several tried. In 5 ml. of acetic acid and 5 ml. of ethyl acetate was dissolved 119 mg. (0.48 mmole) of the photoketone. The solution was cooled in an ice–salt-bath at 0 to –10° and ozone was passed through the solution for 45 min., corresponding to 1.17 mmoles of ozone, according to the flow rate determined above. Titration after the reaction was over indicated the flow had slightly changed to a value of 0.156 mmole of ozone per 5.0-min. period. To the yellow ozonized mixture was added 5 ml. of water and then 2 ml. of a 40% solution of peracetic acid in acetic acid (Becco) to which enough sodium acetate had been added to neutralize the small amount of sulfuric acid in the reagent. There was immediate gentle gas evolution and decolorization. The mixture was allowed to stand at room temperature for 20 hr. The mixture was then diluted with 175 ml. of ether and extracted with 3 \times 50 ml. of water and then with 150 ml. of 3% sodium hydroxide solution in three portions. The basic aqueous solution was extracted once with ether and was then made strongly acidic with 10% sulfuric acid. There was no cloudiness or separation of a precipitate on acidification. The aqueous solution was extracted with 300 ml. of ether and was then saturated with sodium chloride and extracted with 2 \times 300 ml. of ether. The ethereal solution was dried over sodium sulfate. Evaporation of the ether and drying left 112 mg. of acidic residue which was taken up in chloroform and concentrated to 10 ml. Hexane was added to the warm solution to the point of cloudiness, whereupon a crystalline solid precipitated. The solid was separated after the mixture had been cooled for 3 hr. and, after drying, amounted to 70 mg., m.p. 175–183° dec. Concentration of the mother liquors gave two additional crops of solid: crop II, 7.5 mg., m.p. 167–168°; and crop III, 11.3 mg. Recrystallization of crop I from hexane–chloroform gave, after drying, 63 mg., m.p. 168–173° dec.; the melt resolidified on cooling and remelted at 161.5–163.0°. The infrared spectrum of this acidic substance in a potassium bromide pellet was identical in every detail with that of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid prepared independently (see above). While the elemental analysis of this material was not completely satisfactory, it was the same as a sample of the "authentic" diacid submitted at the same time. It is suspected that the material is somewhat hygroscopic.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found for ozonolysis product: C, 71.55; H, 5.07. Found for sample of authentic *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid: C, 71.52; H, 5.10.

The identity of the ozonolysis product as *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid was further confirmed by the following transformations. The acid was esterified with diazomethane by the same procedure described above for the preparation of authentic dimethyl *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylate. From 43 mg. of ozonolysis product there was obtained 27 mg. of crystalline diester, m.p. 68–76°, which was recrystallized from hexane to give 15 mg. of solid m.p. 73–76°, whose infrared spectrum was identical in every detail with that of the authentic diester.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 73.53; H, 5.85. Found: C, 74.00; H, 5.80.

The infrared spectrum of the uncrystallized residue, 21.5 mg., from the mother liquors in the preparation of the above ester was identical with that of the crystalline material.

The ozonolysis product was also converted to *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid anhydride as follows. A 3.4-mg. sample of the ozonolysis product was heated in a centrifuge tube in an oil-bath at 190–200° for 15 min. The white solid melted to give a yellow liquid which crystallized on cooling to give a solid, m.p. 154–163° (m.p. of pure anhydride is 163–165°; see above), whose infrared spectrum was identical in all details with that of the authentic anhydride.

Infrared spectra of crops II and III of the ozonolysis-derived acids indicated that II was additional *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid (slightly impure) while III had a totally different spectrum indicating it was a different substance. The latter material was not investi-

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gated further. The total yield of crystalline *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid from ozonolysis of the photoketone was 77.5 mg. (56.5% of theory). This establishes that the photoketone must be 6,6-bicyclo[3.1.0]hex-3-en-2-one.

Ozonolysis Run II.—The ozonolysis procedure above was repeated as exactly as possible on a sample of 77 mg. of the photoketone. The acidic residue was 76 mg. from which 26 mg. of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid, m.p. 168–174° dec. could be obtained. Again, the acid had an infrared spectrum identical with that of the authentic diacid. The diacid was converted to the corresponding diester, 5.8 mg., m.p. 69–73°, which also had an infrared spectrum identical with that of the authentic diester.

Hydrogenation of the Photoketone (6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one).—The photoketone was hydrogenated using a standard micro hydrogenation apparatus, employing 5.9 mg. of the ketone in 8 ml. of ethanol containing 17 mg. of 10% palladium-on-charcoal catalyst at 21.8° and 738.2 mm. Hydrogen uptake was rapid as 1.125 ml. was absorbed in 10 min. and 1.270 ml. after 3.5 hr. One equivalent of hydrogen, under these conditions, was 0.639 ml.; thus, 2.0 equivalents of hydrogen was absorbed. Separation of the catalyst and evaporation of the solvent left 4 mg. of a residue whose infrared spectrum possessed an intense carbonyl band at 5.70 μ (1755 cm^{-1}), characteristic of a cyclopentanone.

Photolysis of Bicyclo[3.1.0]hex-3-en-2-one (Photoketone).—In the customary photolysis solvent used in the photolysis of 4,4-diphenylcyclohexadienone, 550 ml. of spectroquality dioxane and 200 ml. of water was dissolved 120 mg. of the photoketone. The solution was photolyzed for 2.0 hr. exactly as described above in the dienone photolyses, using the same potassium acid phthalate filter solution. The mixture after photolysis was concentrated until turbid, extracted three times with ether, dried over sodium sulfate and concentrated *in vacuo* to give 170 mg. of residue. This material was dissolved in ether and extracted with three 30-ml. portions of 3% sodium hydroxide. The ethereal solution was dried over sodium sulfate and concentrated to give 80 mg. of a "neutral fraction" described below. The base extracts were acidified with 10% sulfuric acid and the cloudy solution was extracted with ether. The ethereal solution was dried and concentrated leaving 56 mg. of a residue whose infrared spectrum was virtually the same as that of the photoacid obtained from photolysis of 4,4-diphenylcyclohexadienone (see above).

The "neutral" fraction obtained above had an infrared spectrum with a sharp hydroxyl band at 2.80 μ and a sharp

band at 11.15 μ , both strongly indicative of the presence of 2,3-diphenylphenol. There were also two carbonyl bands at 5.65 and 5.8 μ . Attempts to obtain crystalline material from this mixture in hexane-chloroform were completely unsuccessful. A 68-mg. portion of the mixture was subjected to liquid-liquid partition chromatography as described above for the neutral fraction from the dienone photolysis. Passage through a column 3.5 \times 30 cm. with ultraviolet scanning resulted in the elution of a symmetrical peak and processing gave a residue of 55 mg. This material was not pure, according to infrared analysis, as the spectrum contained a strong carbonyl band at 5.80 μ and a few other weaker bands in addition to all the bands present in the spectrum of 2,3-diphenylphenol. A second passage through a column 3.5 \times 100 cm. again led to the elution of material which gave a symmetrical peak, but whose infrared spectrum was unchanged from that of the material put on the column. It was suspected from earlier work that small traces of impurities, suspected to be benzoate esters, in the dimethylformamide used in the chromatography were contaminating the phenolic product. Therefore this residue, 46 mg., was chromatographed on a 2 \times 30 cm. silica gel column. After elution of trace quantities of material with 250 ml. of hexane and 250 ml. of 5% ether-hexane, 9.7 mg. of a carbonyl compound was eluted with the next 125 ml. of 5% ether-hexane. This material contained no phenol and possessed the infrared spectrum of the solvent impurity. Fraction 5, 5.9 mg., eluted with 125 ml. of 5% ether-hexane was a mixture of the carbonyl component and the phenol while fractions 6–8, totaling 18.7 mg., eluted with 250 ml. of 10% ether-hexane and 125 ml. of 20% ether-hexane, were pure phenol. The infrared spectra of fractions 6–8 were identical with that of 2,3-diphenylphenol obtained earlier from several different sources. Fractions 6–8 were taken up in chloroform hexane and the solution was concentrated and more hexane added until the volume of the solution was about 0.3 ml. The solution was cooled and crystallization took place. The solid was separated and dried. It weighed 10.0 mg., m.p. 101.5–103.5° (2,3-diphenylphenol obtained above had m.p. 101.5–102.0°). The infrared spectrum of the solid was superimposable on that of 2,3-diphenylphenol obtained earlier.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Nucleophilic Displacement Reactions of Hexachlorocyclopentadiene. II.^{1,2} Reactions with Secondary Amines³

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In a continued study of reactions undergone by hexachlorocyclopentadiene with nucleophiles, the halide was treated with secondary aliphatic amines to give 5,5-diamino-1,2,3,4-tetrachlorocyclopentadienes. Allyl alcohol reacted with 5,5-dimorpholinyl-1,2,3,4-tetrachlorocyclopentadiene to give 5,7-methyleneoxy-7-morpholinyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene, an intramolecular Diels-Alder adduct, which on hydrolysis produced *exo*-5-hydroxymethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one.

Hexachlorocyclopentadiene (I) reacts with alcoholic or thiolic bases to yield ketals⁴ (II) or thio-

ketals⁵ of 2,3,4,5-tetrachlorocyclopentadienone. This remarkable reactivity of I and octachlorocyclopentene (III), the latter producing ketals of the type IV in alcoholic base, and of derivatives of the two unsaturates, was discussed more fully in the first paper of this series.¹ As a continuation of this line of study, reaction of I and III with amines deserved attention.

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