Organic and Biological Chemistry

Pathways Leading From Excited-State Reactant to Ground-State Products in Dienone Photochemistry.[1a] Mechanistic Organic Photochemistry. XXVI[1b]

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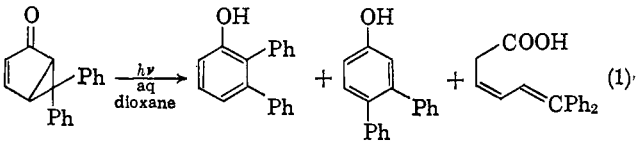
Abstract: 4-Phenyl-4-*p*-cyanophenyl-2,5-cyclohexadienone was synthesized. Irradiation afforded both stereoisomers of 6-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one, whose structures were demonstrated by correlation with the known 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The bicyclic ketone stereoisomers did not interconvert photochemically but afforded 2,3-diaryl- and 3,4-diarylphenol product. As in the case of the diphenylbicyclic ketone, the migration was preferentially to carbon-2 to give the 2,3-diarylphenol. The products obtained were 2-phenyl-3-*p*-cyanophenylphenol and 3-*p*-cyanophenyl-4-phenylphenol, both arising from preferential phenyl migration; no *p*-cyanophenyl migration products were detectable. The rearrangement to give the phenols was *via* the triplet. The migratory behavior supports a mechanism in which electron demotion to afford a zwitterion precedes migration which is then to a positive center. The lack of stereoisomerization shows a slow reclosure of zwitterion to bicyclic ketone. The preference for phenyl migration presently is in sharp contrast with the previously reported preferential *p*-cyanophenyl migration in the rearrangement of 4-phenyl-4-*p*-cyanophenylcyclohexenone and naphthalenone; in these cases it was the excited state which rearranged. In understanding photochemical migratory behavior it is thus important to note the stage at which migration occurs.

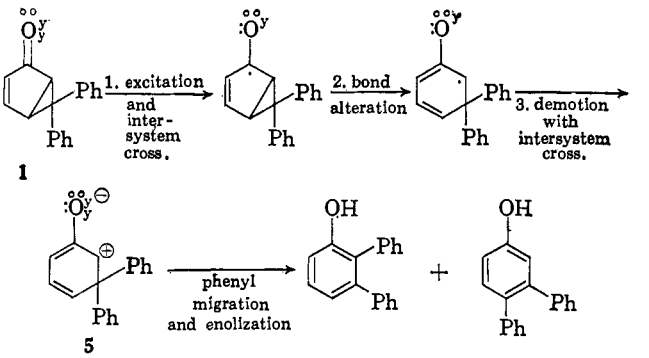
In our studies of the photochemistry of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**) to give 2,3-diphenylphenol (**2**), 3,4-diphenylphenol (**3**), and 6,6-diphenyl-3,5-hexadienoic acid (**4**),[2] we provided evidence[3] that the



1 **2** **3** **4**

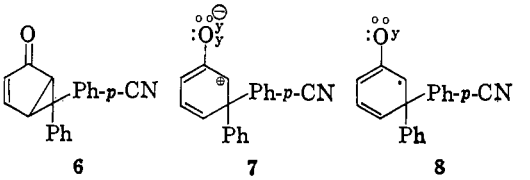
formation of 2,3-diphenylphenol and 3,4-diphenylphenol occurred *via* the triplet state while the 6,6-diphenyl-3,5-hexadienoic acid product derived from both excited singlet and triplet precursors. Additionally, the evidence indicated intervention of a relatively long-lived species subsequent to formation of the initial triplet. We proposed that the mesoionic zwitterion **5** is this species. This accorded with an earlier suggestion[2] that zwitterions such as **5** play an important role in the type B process[4] of bicyclic ketones. This original suggestion[2] included a four-step sequence of (1) excitation, (2) bond alteration (here three-ring bond fission), (3) demotion ($\pi^* \rightarrow n$), and (4) phenyl migration. Our further studies[3,4] showed the necessity of superimposing two intersystem crossing processes since the diphenylphenols arise from the triplet (note Chart I).

Chart I



In pursuing the mechanism further we desired additional evidence bearing on the chronology of events. Thus the question of how the excited state of a reactant molecule transforms itself into the product ground state is of fundamental and broad importance.

One approach which seemed worthwhile required the synthesis and photochemical study of 6-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (**6**). The behavior of this bicyclic ketone promised to help elucidate the chronology. For, if the aryl migration takes place after electron demotion, one would expect preferential phenyl migration; cyanophenyl should not migrate



6 **7** **8**

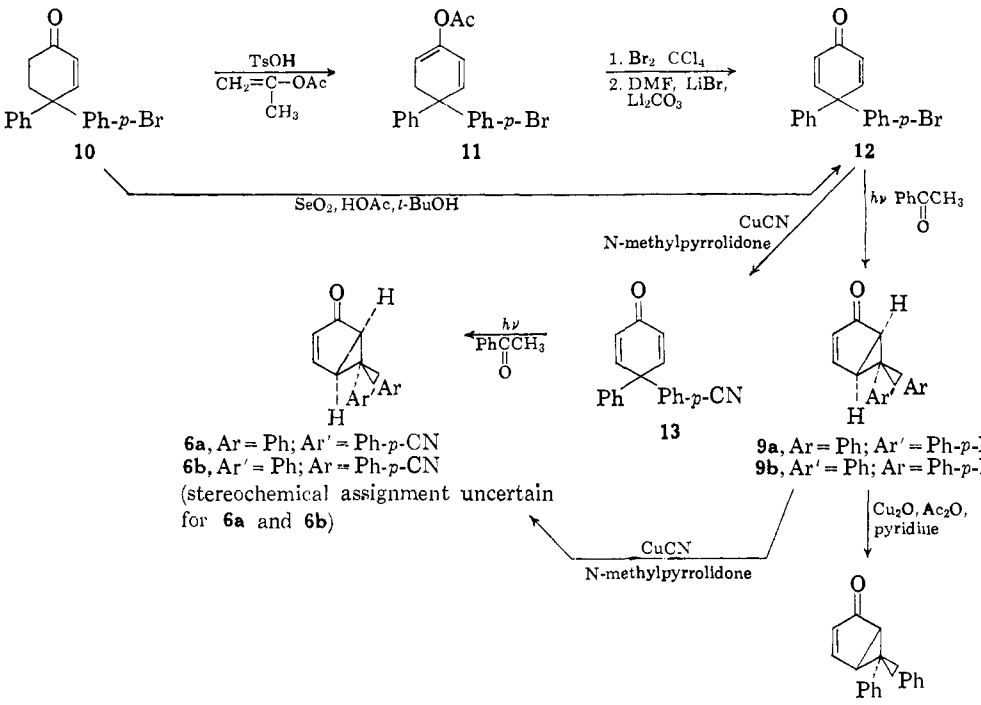
(1) (a) Preliminary communication: H. E. Zimmerman and J. O. Grunewald, *J. Am. Chem. Soc.*, **89**, 3354 (1967). (b) Paper XXIII: H. E. Zimmerman, R. D. Rieke, and J. S. Scheffer, *ibid.*, **89**, 2033 (1967).

(2) (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4486 (1961); (b) *ibid.*, **84**, 4527 (1962)

(3) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

(4) This was defined as a reaction of a bicyclic ketone as **1** in which the internal cyclopropane bond is broken followed by migration of a group from carbon-3 (cyclohexane numbering) to carbon-2 (B-2 process) or to carbon-4 (B-4 process).

Chart II



readily to a positive center as would be required in zwitterion **7**. On the other hand, if migration occurs prior to electron demotion then a different species (*e.g.*, **8**) with an antibonding electron and odd-electron character at C-2 and C-4 is produced. One would anticipate a preferential cyanophenyl migration (*vide infra*) based on excited-state migratory aptitudes and free-radical migration behavior.

Synthetic Aspects. The desired 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one (**6**) was synthesized in two ways as outlined in Chart II. The first method utilized the sensitized photolysis of 4-*p*-cyanophenyl-4-phenyl-2,5-cyclohexadienone (**13**). Two isomeric photoproducts were obtained. Since the *p*-cyano group is known[1b,5] to enhance phenyl migration in cyclohexenone from C-4 to C-3, it was necessary to establish that the two products isolated really resulted from an ordinary type A rearrangement[6] rather than from aryl migration which would instead afford a 5,6-diarylbicyclo-[3.1.0]hex-3-en-2-one, probably the 5-*p*-cyanophenyl-6-phenyl isomer. Therefore, 4-*p*-bromophenyl-4-phenyl-2,5-cyclohexadienone (**12**) was irradiated. Again two photoproducts were obtained. That these were the stereoisomeric *cis*- and *trans*-6-*p*-bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-ones (**9a** and **9b**) was established by their reductive conversion (note Chart II) to the known 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**). Cuprous cyanide in N-methylpyrrolidone converted each of these epimers (**9a** and **9b**) to the corresponding 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one isomer (**6a** and **6b**, respectively). These were identical with the products of photolysis of 4-*p*-cyanophenyl-4-phenylcyclohexadienone (**13**). Hence the dienone irradiation gave only the usual type A rearrangement and no C-4 → C-3 aryl migration.

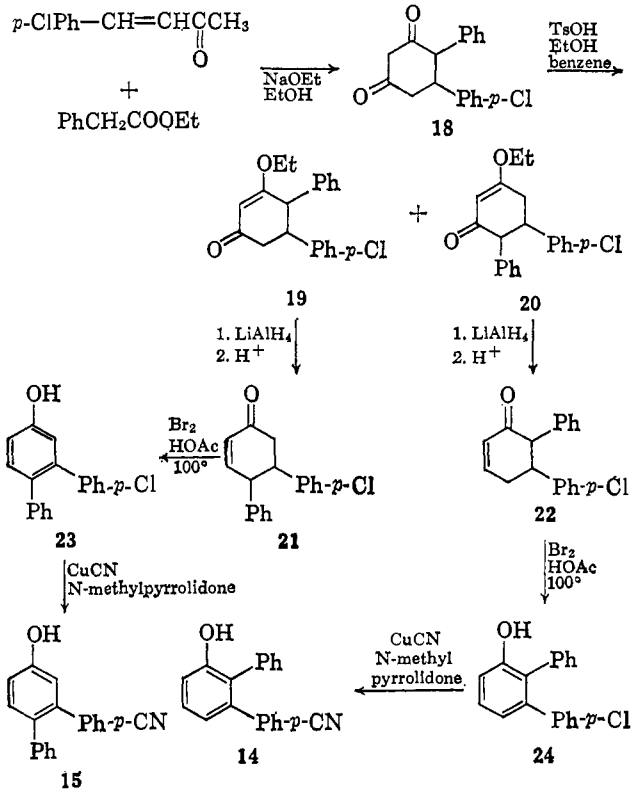
(5) H. E. Zimmerman, R. Hahn, H. Morrison, and M. Wani, *J. Am. Chem. Soc.*, 87, 1138 (1965).

(6) This designation has been used[7] for rearrangements in which C-4 and C-3 exchange places in the cyclohexane framework so that substituents originally at C-4 appear at C-3 (cyclohexane numbering).

(7) H. E. Zimmerman, *Science*, **153**, 837 (1966).

The bicyclic ketone reactant **6** having been obtained, authentic 2-phenyl-3-*p*-cyanophenylphenol (**14**), 3-*p*-cyanophenyl-4-phenylphenol (**15**), 2-*p*-cyanophenyl-3-phenylphenol (**16**), and 3-phenyl-4-*p*-cyanophenylphenol (**17**) were needed to compare with the products of photolysis of the bicyclic ketone. The first two isomers were synthesized by the sequence shown in Chart III. Of the last two isomers, 2-*p*-cyanophenyl-3-phenylphenol (**16**) was already available[8] for comparison purposes.

Chart III



(8) H. E. Zimmerman and R. Lura, senior honors research, unpublished. Note also Experimental Section.

Table I. Irradiation Runs of 6-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one

Run	Reactant	Type	Recovered bicyclic ketone,[c] %	Product distribution,[a,b] % 2-Phenyl-3-*p*-cyanophenyl-phenol	3-*p*-Cyanophenyl-4-phenylphenol	Photo acids
1	Ketone **6a**	D[d]	86	34 ± 1	12 ± 2	55 ± 4
2	Ketone **6a**	D[d]	35	37 ± 1	12 ± 2	51 ± 4
3	Ketone **6b**	D[d]	71	14 ± 1	6 ± 2	80 ± 5
4	Ketone **6b**	D[d]	45	22 ± 1	7 ± 1	70 ± 4
5	Ketone **6a**	S[e]	89	45 ± 3	23 ± 6	32 ± 4
6	Ketone **6b**	S[e]	86	43 ± 3	21 ± 6	37 ± 4

[a] Per cent of products other than recovered bicyclic ketone. [b] Mass balance 100 ± 2%. [c] Per cent based on total material. [d] Direct runs without sensitizer. [e] Sensitized runs with 0.57 *M* acetophenone; over 97% of the light absorbed by acetophenone.

Although the synthetic sequence leads to both 2,3- and 3,4-diaryl isomers, these are readily distinguished by the occurrence of only a sharp, nonbonded hydroxyl peak at 2.81 μ in the infrared spectra of the 2,3-diarylphenols (*e.g.*, **24**) and broad nonbonded and hydrogen-bonded peaks [2.77 and 2.98 (br)] in the spectra of the 3,4-diarylphenols (*e.g.*, **23**). This has analogy in the spectra of 2,3-diphenylphenol and 3,4-diphenylphenol.[2b]

Photolysis Results. With both stereoisomers **6a** and **6b** of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one and the most likely phenolic products available, the mechanistic investigation was begun. We were particularly interested in the photointerconversion of the two reactant epimers **6a** and **6b**,[9] if the same product distribution resulted from each of the epimers on direct irradiation, the susceptibility of the reaction to sensitization, and, most importantly, which group migrates preferentially in the reaction forming phenolic products.

The irradiation of the epimers of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one (**6a** and **6b**) in 80% aqueous *t*-butyl alcohol at 330–380 mμ proceeded quite similarly to the case of 6,6-diphenylbicyclo[3.10]hex-3-en-2-one (**1**). Two diarylphenols were obtained along with acidic photoproducts. The infrared and nmr spectra of the acidic fraction indicated that this was a mixture of the stereoisomers of 6-*p*-cyanophenyl-6-phenyl-3,5-hexadienoic acid (**25**) analogous to the acid product from 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one; however, attention was focused on the phenolic product, and the acidic material was not investigated further. The phenolic products were separated by deactivated silica gel chromatography. The first phenol eluted melted at 188–190° and was identified as 2-phenyl-3-*p*-cyanophenylphenol (**14**) by infrared, nmr, and mixture melting point comparison with authentic material. The second phenol eluted, mp 222.8–225.4°, was obtained in lesser quantity. This proved by comparison with synthesized material to be 3-*p*-cyanophenyl-4-phenylphenol (**15**). No 2-*p*-cyanophenyl-3-phenylphenol (**16**) could be found and the mass balance was excellent (100 ± 2%) (note Table I). In order to ensure that 2-*p*-cyanophenyl-3-phenylphenol (**16**) was stable under reaction conditions, this isomer was irradiated but no change was observed. This excludes the possibility of this isomer being formed and destroyed.[11]

Additionally, the distribution of phenols appeared to favor 2,3-diarylphenol over 3,4-diarylphenol product as was observed in the earlier studies.[3] The ratio was observed to be *ca.* 3:1; note runs 1, 2, and 4. The accuracy was lower in the other runs due to low weight of minor isomer assayed but similar distributions resulted. Interestingly, the same distribution resulted independent of the stereochemistry of the reactant.

Furthermore, when runs were made starting with **6a** with 15–65% conversion, none of stereoisomer **6b** could be isolated or detected by infrared or nmr. Only recovered isomer **6a** was discernible. Similarly, in runs starting with isomer **6b**, no **6a** was formed. This is important, since the same distribution of phenols resulting from the two stereoisomers **6a** and **6b** could have been attributed to rapid interconversion of these reactants.

Of further interest was the question whether the same migratory behavior would be observed on triplet sensitization since in the case of 6,6-diphenylbicyclo[3.1.0]-hex-3-en-2-one (**1**) evidence has been presented[3] that it is the triplet excited state responsible for the phenolic product. Presently it was observed that the recovered bicyclic ketonic material contained only the original stereoisomer employed, **6a** or **6b** (note runs 5 and 6, Table I), and that the products were the same as in the direct irradiations. Again, 2-phenyl-3-*p*-cyanophenylphenol (**14**) was the preferred product and 3-*p*-cyanophenyl-4-phenylphenol (**15**) was the minor product. No cyanophenyl migration products were detected. The ratio of the two phenols could not be determined with precision due to the low conversion but was within experimental error of that in the unsensitized runs.[12]

Mechanistic Reasoning. The most striking result is the occurrence of only phenyl migration in the rearrangement to give the diaryl phenols. It is quite certain that a species with the internal three-ring bond of **6** already broken is rearranging, since only following such bond breaking is there a free valence at carbons 2 and 4. As noted earlier, reasonable candidates for the rearranging species are the excited state **8** and the zwitterionic species **7** derived from **8**.[13]

(9) This has close precedent in the photochemical interconversion of the *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones; note ref 10.

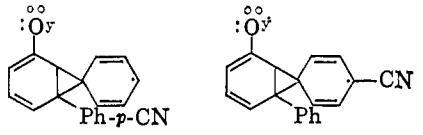
(10) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(11) Although 3-phenyl-4-*p*-cyanophenylphenol was not prepared or available, the 3,4 isomers tend to be the minor products under neutral irradiation conditions (note ref 3 and present discussion), and in any case no trace of an additional isomer was observed in the present work.

(12) (a) The low conversion on sensitization seems to derive from the low concentrations of bicyclic ketone (energy acceptor) utilized, since in the corresponding 6,6-diphenyl analog the sensitized quantum yield was close to the direct one. (b) Table I reveals that on sensitization the ratio of photo acid to phenolic product drops dramatically. This is in agreement with the findings for 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[3] Additionally, however, the partition between phenolic and acid products is dependent on configuration for at least the unsensitized runs.

(13) The n–π^* excited configuration of **8** is shown. The π–π^* configuration is another possibility.

Prior to considering which possibility better accommodates this result, we should note that the preference for phenyl over cyanophenyl migration is strikingly different from the two cases where such competition has been studied earlier. In the case of 4-phenyl-4-*p*-cyanophenyl-1-(4H)naphthalenone (**26**) a 2.2:1 preference for cyanophenyl migration to carbon-3 was observed, to give 3-*p*-cyanophenyl-4-phenyl-1-naphthol.[5] Similarly, the irradiation of 4-phenyl-4-*p*-cyanophenylcyclohexenone was found to show a preference of *ca.* 14:1 for cyanophenyl migration. This behavior is in accord with expectation for migration to an odd-electron-bearing carbon atom. Thus Rüchardt[14] has found a strong preference for cyanophenyl over phenyl migration in free-radical rearrangements. In any case, one cannot generalize about which aryl group will migrate in a new photochemical situation without first considering the nature of the species actually doing the rearranging. In the case of the cyclohexenones, it is the original excited state itself which rearranges. In the present instance it must be a subsequent species, namely **7** or **8**. Actually, the unusual preference for phenyl migrating strongly suggests the zwitterionic species **7**, since here migration is to a positive center. If the migration were prior to electron demotion, then in the rearrangement of **8**, there would be a bridged species as **27** or **28**, and one would anticipate extra stabilization in **28** by the *p*-cyano substituent as in the cyclohexenone and free-radical cases. We can conclude from the present

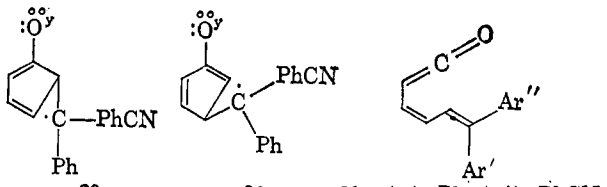


27 **28**

results that of the two processes available to excited species **8**, electron demotion to afford the zwitterion **7** therefore is faster than aryl migration.

Finally, we have the matter of the noninterconversion of the stereoisomeric 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-ones (**6a** and **6b**) under photolysis conditions. This means that neither the zwitterion **7** nor its excited-state precursor **8** revert to bicyclic product at rates competive with the forward processes. Since both **7** and **8** should be relatively planar, the original configurations of **6a** and **6b** have been lost at this point. Reclosure would yield the same mixture of **6a** and **6b** independent of the isomer of **6** photolyzed. Such reversion to reactant had seemed *a priori* reasonable since it would have rationalized the relatively low quantum yield (total reaction, 0.15) observed in the reaction of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**1**).[3] Additionally, other reversible processes leading to loss of configuration are ruled out. This includes a reversible opening of the two peripheral three-ring bonds to give species **29** and **30** with the one reservation that such opening is possible as long as free rotation is slower than reclosure. The reversible opening to ketene **31** is not ruled out since in such an opening the reclosure (thermal or photochemical) could be stereospecific.

(14) C. Rüchardt and S. Eichler, *Chem. Ber.*, **95**, 1921 (1962); C. Rüchardt and R. Hecht, *ibid.*, **98**, 2471 (1965). A preference of between 19:1 and 35:1 was observed.



29 **30** **31a**, Ar' = Ph; Ar'' = PhCN
31b, Ar'' = Ph; Ar' = PhCN

In conclusion, we stress the point that in predicting the course of photochemical rearrangements we do need to delineate the mechanistic details of the reaction and determine at which stage of the process the actual migration takes place. The mechanistic approach presented by us earlier[2,10] is of considerable help in doing this.

Experimental Section[15]

Trimethyloxosulfonium iodide was prepared according to the procedure of Kuhn and Trischmann.[16]

1-*p*-Bromophenyl-1-phenylethylene Oxide.[1b] The procedure of Zimmerman, Rieke, and Scheffer[1b] using the general method of Corey and Chaykovsky[17] for 1,1-diphenylethylene oxide was employed. The product was recrystallized from absolute ethanol to mp 47.0–49.0°. The infrared spectrum ($CHCl_3$) showed a medium band at 11.03 μ, characteristic of epoxides;[18] nmr ($CDCl_3$): τ 2.75 multiplet (9 H, aromatic) and 6.90 doublet (2 H, J = 1.0 cps, methylene).

Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.11; H, 4.03; Br, 29.05. Found: C, 61.23; H, 4.01; Br, 29.10.

1-*p*-Bromophenyl-1-phenylacetaldehyde was prepared by the method of Zimmerman, Rieke, and Scheffer.[1b] The product was obtained as a colorless liquid, bp 152–156° (0.30 mm); infrared ($CHCl_3$): 3.31, 3.53, 3.67, 5.80 (C=O), 6.72, 6.89, 7.12, 9.90 (C–Br), 12.25, and 14.38 μ; nmr (CCl_4): τ 0.25 doublet (1 H, J = 2.2 cps, CHO), 2.82 multiplet (9 H, aromatic), and 5.30 doublet (1 H, J = 2.2 cps, CH). The 2,4-dinitrophenylhydrazone had mp 162–166°.

Anal. Calcd for $C_{20}H_{15}BrN_4O_4$: C, 52.76; H, 3.32; Br, 17.55; N, 12.31. Found: C, 52.58, 52.77; H, 3.55, 3.29; Br, 17.49, 17.72; N, 12.13, 12.33.

4-*p*-Bromophenyl-4-phenylcyclohex-2-en-1-one.[1b] Methyl vinyl ketone (20 g, 0.29 mole) and 78.0 g (0.283 mole) of 1-*p*-bromophenyl-1-phenylacetaldehyde were dissolved in 500 ml of ether and cooled in an ice bath. A solution of 5.30 g (0.094 mole) of potassium hydroxide in 50 ml of 95% ethanol was added dropwise over 0.5 hr. Stirring was continued at 0° for an additional 2 hr. The reaction mixture was then neutralized with dilute hydrochloric acid, washed with water, and dried over sodium sulfate. Removal of the solvent *in vacuo* yielded a viscous yellow oil. This was chromatographed in 30–40-g batches on a 6.5 × 105 cm silica gel column (Davison, 60–200 mesh) slurry packed with 15% ether–hexane. The column was eluted with 20% ether–hexane and 2-l. fractions were collected. Combination of fractions 5–8 from each batch yielded 45.63 g (49%) of 4-*p*-bromophenyl-4-phenylcyclohex-2-en-1-one, mp 120–125°. This was recrystallized from ether to mp 124.0–125.0°; infrared ($CHCl_3$): 5.96 (C=O), 6.73, 6.92, 7.24, 9.92 (C–Br), 11.30, 12.22, and 14.35 μ; nmr (CCl_4): τ 2.83 multiplet (10 H, 9 aromatic, 1 vinyl), 4.00 doublet (1 H, J = 10 cps, vinyl), and 7.59 multiplet (4 H, CH_2CH_2).

Anal. Calcd for $C_{18}H_{15}BrO$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.89; H, 4.63; Br, 24.38.

2-Acetoxy-5-*p*-bromophenyl-5-phenylcyclohexa-1,3-diene.[19] Isopropenyl acetate (100 g, 1.00 mole), 2.91 g (0.015 mole) of *p*-toluenesulfonic acid, and 63.67 g (0.194 mole) of 4-*p*-bromophenyl-4-phenylcyclohex-2-en-1-one were heated at 120–125° for 10 hr, and the acetone produced was distilled off through a 2.0 × 28 cm Vigreux column. The resulting dark mixture was cooled to room

(15) All melting points were taken on a hot-stage apparatus and are corrected. Nmr spectra were run at 60 Mc.

(16) R. Kuhn and H. Trischmann, *Ann.*, **611**, 177 (1958).

(17) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); **87**, 1353 (1965).

(18) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(19) The general procedure of B. Schröder of these laboratories was used.

temperature and benzene was added; the organic solution was washed with sodium bicarbonate and water, then dried over sodium sulfate. After removal of the solvent *in vacuo* there remained 72.0 g of a tan solid, mp 108–113°. The solid was triturated with three portions of ether, leaving 59.5 g of a very light tan solid, mp 109.1–112.2°. An additional 4.99 g, mp 109.0–112.6°, was isolated from the ether washes, giving a total yield of 64.49 g (90%). A small sample was recrystallized to constant mp 112.0–113.6°; infrared ($CHCl_3$): 3.31, 3.40, 3.46, 5.70 (C=O), 6.00, 6.25, 6.72, 6.91, 6.97, 7.16, 7.29, 8.50, 8.73, 9.30, 9.90 (C–Br), 10.42, 10.95–11.12 (broad), 12.23, and 14.35 μ; (CS_2): 8.25 and 13.18–13.33 (broad) μ; nmr ($CDCl_3$): τ 2.76 multiplet (9 H, aromatic), 3.91 quartet (2 H, CH=CH, J_{AB} = 16.5 cps, J_{BC} = 2.0 cps), 4.51 triplet of doublets (1 H, CH=, J_{BC} = 2.0 cps, J_{CX} = 4.5 cps), 7.02 doublet (2 H, CH_2, J_{CX} = 4.5 cps), and 7.92 singlet (3 H, methyl).

Anal. Calcd for $C_{20}H_{17}BrO_2$: C, 65.05; H, 4.64; Br, 21.64. Found: C, 64.94; H, 4.44; Br, 21.65.

4-*p*-Bromophenyl-4-phenylcyclohexadienone. Procedure A. The general procedure of Zimmerman and Schuster[2b] was used. To a solution of 4.70 g (0.0144 mole) of 4-*p*-bromophenyl-4-phenylcyclohex-2-en-1-one in 180 ml of *t*-butyl alcohol and 1.8 ml of glacial acetic acid, 6.80 g (0.061 mole) of selenium dioxide (sublimed from nitric acid) was added; the mixture was stirred and refluxed under nitrogen for 5 hr when an additional 4.0 g of selenium dioxide was added. After 24 hr, the warm reaction mixture was filtered through Celite and the Celite was washed with methanol. The orange solution was concentrated *in vacuo* to approximately 75 ml and 160 ml of benzene was added. The organic solution was washed with water, 5% sodium hydroxide, and again water, dried, and concentrated *in vacuo* to yield 5.04 g of a red oil. This was chromatographed on a 4 × 76 cm liquid–liquid partition column packed with stationary phase formed from 500 g of Celatom and 200 ml of lower phase of a mixture of 1000 ml of cyclohexane, 400 ml of dimethylformamide, and 80 ml of ethyl acetate. The column was saturated with upper phase and the product was placed on the column in a minimum of lower phase. Elution with upper phase and work-up of fractions by addition of benzene, washing with water, and removal of solvent gave fraction 1, 700 ml, void; fraction 2, 200 ml, red semisolid, Se odor; fraction 3, 200 ml, nil; fraction 4, 200 ml, 76 mg of enone; fraction 5, 100 ml, 54 mg, enone and dienone; fractions 6–9, 400 ml, 1.80 g, dienone, mp 117–122°. Recrystallization of fractions 6–9 from ethyl acetate–hexane gave 1.22 g (26%) of 4-*p*-bromophenyl-4-phenylcyclohexadienone, mp 120.5–122.5°; infrared ($CHCl_3$): 6.02 (C=O), 6.17, 6.72, 7.16, 9.28, 9.90 (C–Br), 10.90, 11.75, and 12.20 μ; nmr (CCl_4): τ 2.75 multiplet (11 H, 9 aromatic, 2 vinyl) and 3.79 doublet (2 H, J = 10.5 cps, vinyl).

Anal. Calcd for $C_{18}H_{13}BrO$: C, 66.47; H, 4.04; Br, 24.57. Found: C, 66.38; H, 4.09; Br, 24.72.

Procedure B.[19] Bromine (2.58 g, 0.161 mole) dissolved in 250 ml of carbon tetrachloride was added dropwise with stirring over a 2-hr period to a solution of 59.5 g (0.161 mole) of 2-acetoxy-5-*p*-bromophenyl-5-phenylcyclohexa-1,3-diene in carbon tetrachloride at 25°. The solution was stirred for 15 min after the addition was complete. The solvent was removed *in vacuo* and the viscous brown residue refluxed with 500 ml of 95% ethanol for 0.5 hr. The ethanol was removed *in vacuo* and the residue was taken up in benzene and washed twice with sodium bicarbonate and water; the organic layer was filtered through sodium sulfate and the solvent was removed *in vacuo*, although excessive foaming of the material prevented removal of the last traces of solvent. The tan residue, 68.0 g, showed a strong carbonyl peak at 5.91 μ was and was dehydrobrominated without further purification.

The bromination product above was dissolved in 770 ml of freshly distilled dimethylformamide, lithium carbonate (34.3 g, 0.463 mole) and lithium bromide (40.3 g, 0.463 mole) were added, and the mixture was stirred and refluxed under nitrogen for 12 hr. The cooled reaction mixture was poured into water and extracted with methylene chloride. The organic layer was washed with sodium bicarbonate and water and dried over sodium sulfate. After removal of the solvent there remained *ca.* 63 g of a crystalline light brown solid, the infrared of which was identical with that of 4-phenyl-4-*p*-bromophenylcyclohexadienone prepared by selenium dioxide dehydrogenation of 4-phenyl-4-*p*-bromophenylcyclohex-2-en-1-one (procedure A, *vide supra*). The material was crystallized from ether, then dissolved in methanol, and treated with Norit for 24 hr at 25°. The mixture was filtered and the methanol was removed to leave 37.94 g of a light tan solid, mp 112.5–116.5°. Recrystallization from ethyl acetate–hexane gave 30.76 g (58.5%), mp 118.5–121.5°.

4-*p*-Cyanophenyl-4-phenylcyclohexadienone. Cuprous cyanide (15.61 g, 0.1745 mole) and 28.06 g (0.086 mole) of 4-*p*-bromophenyl-4-phenylcyclohexadienone were dissolved in 150 ml of dimethyl sulfoxide and heated at 150° under nitrogen with stirring for 5 hr. The reaction mixture was taken up in sufficient 30% ammonium hydroxide and benzene for solution, and the aqueous layer was extracted with two additional portions of benzene. The combined organic layers were washed several times with ammonium hydroxide and water, dried, and concentrated *in vacuo* to give 24.6 g of an orange solid. This was decolorized with Norit in cold methanol and the resulting solid crystallized from ethyl acetate–hexane to give 17.8 g of material, mp 140.0–150.5°. Recrystallization from methanol yielded 12.71 g (54%) of 4-*p*-cyanophenyl-4-phenylcyclohexadienone, mp 152.0–153.5°; infrared ($CHCl_3$): 4.48 (C≡N), 6.02 (C=O), 6.17, 6.25, 6.72, 6.92, 7.21, 10.89, 11.76, 12.03, and 14.40 μ; nmr ($CDCl_3$): τ 2.70 multiplet (11 H, 9 aromatic, 2 vinyl) and 3.63 doublet (2 H, J = 10 cps, vinyl).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.15; H, 4.98; N, 5.14.

Description of Equipment and Apparatus. Light Source. The light source was a General Electric AH6 high-pressure mercury arc centered at the focus of a solid parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter. The light was filtered by a cell of three water-cooled compartments, separated by gasketed quartz disks, 2.4 cm thick and 12 cm in diameter. A 2-mm Corex D glass filter (Corning No. 9700) cutting off below 250 mμ (25% transmittance at 276 mμ) was used preceding the filter cell.

The photolysis cell contained two identical compartments each 12 cm in diameter with a 5-cm optical path and aliphatic epoxy cemented quartz faces. The cells were equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, and nitrogen inlet.

The light output was monitored with an RCA 935 phototube mounted between the filter and irradiation cells, which served as a check for filter decomposition and lamp decay.

Irradiations. All irradiations were carried out at 25.0 ± 0.1° in the two-compartment cell using the appropriate filter solutions. The transmittance curve of the filter solutions was measured before and after each run to insure that no appreciable decomposition had occurred. Before irradiation of the organic solution, oxygen-free nitrogen[20] was bubbled through the solution for 1 hr. During the irradiation a positive pressure of nitrogen was maintained over the solution.

Actinometry. Potassium ferrioxalate was prepared by the procedure of Hatchard and Parker.[21] Four liters of actinometer solution was prepared from 12.0 g of potassium ferrioxalate, 400 ml of 1.0 *N* sulfuric acid, and 3600 ml of distilled water. Analyses were done in duplicate using 2.00 ml of actinometer solution, 3.00 ml of 0.1% 1,10-phenanthroline in water, and 2.00 ml of a buffer solution (600 ml of 1.0 *N* sodium acetate, 360 ml of 1.0 *N* sulfuric acid, diluted to 1 l. with distilled water) diluted to 25 ml. The optical density of the solutions was measured at 510 mμ on a Beckman Model DU spectrometer, and the concentration of the ferrous ion was read from a calibration curve, after correction for the optical density of the blank. The light output was calculated using a quantum yield of 1.23[21] for ferrous ion formation. All operations involving ferrioxalate were protected from light.

Filter Solutions. Transmittance curves for the filter solutions were measured using a cell having three identical 2.4-cm compartments separated by quartz plates and with quartz plates covering the ends. A 7.2-cm quartz cell filled with water served as a reference. The filter solutions of the desired composition were prepared in advance of the irradiations and the transmittance curves were recorded.

For preparation of filters, nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and stannous chloride dihydrate were used. The nickel and cobalt filters were prepared in 10% sulfuric acid; 15% hydrochloric acid (by weight) was used for the tin filters. The filters remained nearly completely stable throughout the irradiations. The filter solutions used were: A, cell I, 130.0 g of nickel salt/liter; cell II, 250.0 g of cobalt salt/liter; cell III, 4.80 g of tin salt/liter. The transmittance curve was as follows: 220–300 mμ, 0%; 310 mμ, 0.10%; 320 mμ, 21.0%; 330 mμ, 40.8%; 340 mμ, 33.5%; 350 mμ, 17.5%; 360 mμ, 3.7%; 370 mμ, 0.10%; 380–440 mμ, 0%. For filter B, the solutions were: cell I, 36.0 g of nickel salt/liter; cell II, 281 g of cobalt salt/liter; cell III, 75.0

(20) Purified with vanadous sulfate by the method of L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

(21) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), 235, 518 (1956).

g of tin salt/liter. The transmittance curve was as follows: 200–330 mμ, 0%; 340 mμ, 18.0%; 352 mμ, 37.0%; 360 mμ, 29.3%; 370 mμ, 10.4%; 380 mμ, 1.8%; 388–440 mμ, 0%. For filter C the solutions were: cell I, 450.0 g of nickel salt/liter; cell II, 281 g of cobalt salt/liter; cell III, 3.50 g of tin salt/liter. The transmittance curve was: 290–305 mμ, 0%; 310 mμ, 1.5%; 320 mμ, 16.0%; 325 mμ, 20.0%; 330 mμ, 18.0%; 340 mμ, 7.0%; 350 mμ, 0.9%; 360 mμ, 0%.

Acetophenone-Sensitized Irradiation of 4-*p*-Cyanophenyl-4-phenylcyclohexadienone to Give the Epimeric 6-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-ones. A solution of 1.005 g (3.70 mmoles) of 4-*p*-cyanophenyl-4-phenylcyclohexadienone and 20.0 g of distilled acetophenone in 700 ml of distilled benzene and 50 ml of methanol was irradiated during 120 min in the apparatus described above using filter A. Light input was 9.20 mEinsteins. An identical irradiation using 9.20 mEinsteins was carried out.

After irradiation, the solvent was removed *in vacuo* and the acetophenone distilled *in vacuo* at <55°. Each photolysis mixture was chromatographed on a 2.5 × 110 cm column of deactivated silica gel, slurry packed with 5% ether–hexane. Fractions of 200 ml were collected: fractions 1–5, 5% ether–hexane, 478.5 mg, acetophenone; 6–10, 7.5% ether–hexane, 131.0 mg, acetophenone; 11–15, 10% ether–hexane, 36.9 mg, photoesters; 16–19, 12.5% ether–hexane, nil; 20–25, 12.5% ether–hexane, 54.1 mg, photophenols; 26–27, 15% ether–hexane, nil; 28–31, 10.1 mg, photophenols; 32–38, 269.3 mg, starting dienone; 39–42, 284.7 mg, dienone and photoketone **6a**; 43, 30.7 mg, photoketone **6a**; 44–48, 197.1 mg, photoketones **6a** and **6b**; 49–53, 15% ether–hexane, 112.8 mg, photoketone **6b**. Ether crystallization of fractions 39–42 and 44–46 yielded 206.0 mg, photoketone **6a**, mp 175.5–182.0°. Crystallization of fraction 48 from methanol yielded 39.3 mg, photoketone **6b**, mp 157.0–159.5°. From chromatography of the second photolysis mixture, there was obtained 241.1 mg of photoketone **6a** and 189.3 mg of photoketone **6b**. Combination of the overlapping fractions from both photolyses and rechromatography gave 36.1 mg of photoketone **6a** and 109.6 mg of photoketone **6b**. Total yields from both photolyses were 513.9 mg of photoketone **6a** (25.5%) and 451.0 mg (22.5%) of photoketone **6b**.

Photoketone **6a** was recrystallized from ethyl acetate–hexane to mp 181.5–183.5° dec; infrared ($CHCl_3$): 3.32, 4.47 (C≡N), 5.92 (C=O), 6.21, 6.36, 6.70, 6.90, 7.45, 8.49, 9.60, 9.76, 9.89, 11.30, 11.58, 12.10, and 14.39 μ; ultraviolet (95% EtOH): λ_{max} 343 mμ (ε 483), shoulder 294 mμ (ε 4780), and shoulder 225 mμ (ε 20,600); nmr ($CDCl_3$): τ 2.62 multiplet (10 H, 9 aromatic, 1 vinyl), 4.41 doublet (1 H, J = 5.3 cps, vinyl), 6.68 quartet (1 H, J_{AB} = 4.8 cps, J_{BX} = 2.5 cps, cyclopropyl CH), and 7.12 doublet (1 H, J = 4.8 cps, cyclopropyl α-CH).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.19; H, 4.86; N, 5.45.

Photoketone **6b** was recrystallized from ethyl acetate–hexane to mp 158.3–160.0°; infrared ($CHCl_3$): 3.32, 4.47 (C≡N), 5.92 (C=O), 6.22, 6.37, 6.70, 6.91, 7.46, 8.49, 9.61, 9.90, 11.45, 11.69, 12.10, and 14.32 μ; ultraviolet (95% EtOH): λ_{max} 344 mμ (ε 638), shoulder 292 mμ (ε 5720), and shoulder 279 mμ (ε 7820), 242 mμ (ε 18,100); nmr ($CDCl_3$): τ 2.58 multiplet (10 H, 9 aromatic, 1 vinyl), 4.41 doublet (1 H, J = 5.8 cps, vinyl), 6.72 quartet (1 H, J_{AB} = 4.8 cps, J_{BX} = 2.3 cps, cyclopropyl CH), and 7.20 doublet (1 H, J = 4.8 cps, cyclopropyl α-CH).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.36; H, 4.67; N, 5.32.

From the spectral data and independent preparation (*vide infra*), photoketones **6a** and **6b** were shown to be epimers with the skeletal structure of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one.

Acetophenone-Sensitized Irradiation of 4-*p*-Bromophenyl-4-phenylcyclohexadienone to Yield the Epimeric 6-*p*-Bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-ones. A solution of 1.001 g (3.08 mmoles) of 4-*p*-bromophenyl-4-phenylcyclohexadienone and 20.0 g of distilled acetophenone in 700 ml of distilled benzene and 50 ml of methanol was irradiated during 60 min in the apparatus described above. Light input was 8.30 mEinsteins. Filter solution A was used. The solvents were removed *in vacuo* and the acetophenone at 50–60° (0.03 mm). The crude photolysis product was subjected to liquid–liquid partition chromatography.[2b]

A two-phase system was obtained from 1000 ml of distilled cyclohexane, 400 ml of reagent dimethylformamide, 250 ml of reagent ethyl acetate, and 30 ml of distilled water, all equilibrated at 28°. The stationary phase, prepared by homogeneous dispersion of 40% by weight of the lower phase on Eagle-Pitcher Celatom FW80, was tamped in a thermostated 4.0 × 150 cm liquid–liquid column and elution with upper (mobile) phase was carried out. The eluent was scanned at 252 mμ through a 0.006-in. cell. Fractions of 40 ml were collected, diluted with benzene, washed three times with water, dried, and concentrated *in vacuo*.

Fractions 38–44 yielded 52.6 mg, photoesters; 47–55, 410.7 mg, starting dienone; 56–59, 339.2 mg, photoketones **9a** and **9b**; 60–63, 145.8 mg, mainly photoketone **9b** plus some **9a**; 64–73, 75.1 mg, photophenols.

Fractions 56–59 from the liquid–liquid partition chromatography were rechromatographed on a 2.5 × 120 cm column of deactivated silica gel, slurry packed with 8% ether–hexane. Elution was with 8% ether–hexane, and 100-ml fractions were collected: fractions 18–21, 8.6 mg. starting dienone; 24–27, 102.5 mg, photoketone **9a**; 28–31, 146.4 mg, photoketones **9a** and **9b**; 32–40, 62.1 mg, photoketone **9b**. Chromatography on deactivated silica gel of fractions 60–63 from the liquid–liquid partition chromatography in a similar manner yielded 11.1 mg of photoketone **9a**, 32.8 mg of photoketones **9a** and **9b**, and 93.5 mg of photoketone **9b**. Rechromatography of the overlapping fractions on two columns of deactivated silica gel gave 56.6 mg of photoketone **9a** and 77.3 mg photoketone **9b**. Total yield of photoketone **9a** was 170.2 mg (17.0%) and of photoketone **9b**, 232.9 mg (23.3%).

Photoketone **9a** was recrystallized from ethyl acetate–hexane to mp 112.5–113.5° (second crystalline form with identical solution infrared, mp 123.0–124.0°); infrared ($CHCl_3$): 3.32, 5.92 (C=O), 6.28, 6.36, 6.73, 6.91, 7.18, 7.46, 8.48. 9.31, 9.64, 9.85, 9.91, 11.33, 11.61, 12.23, and 14.39 μ; (CS_2): 12.43, 13.46, and 13.95 μ; nmr (CCl_4): τ 2.81 multiplet (10 H, 9 aromatic, 1 vinyl), 4.42 doublet (1 H, J = 5.7 cps, vinyl), 6.78 quartet (1 H, J_{AB} = 5.2 cps, J_{BX} = 2.3 cps, cyclopropyl CH), and 7.19 doublet (1 H, J = 5.2 cps, cyclopropyl α-CH).

Anal. Calcd for $C_{18}H_{13}BrO$: C, 66.47; H, 4.04; Br, 24.57. Found: C, 66.56; H, 4.09; Br, 24.70.

Photoketone **9b** was recrystallized from ethyl acetate–hexane to mp 110.1–111.6°; infrared ($CHCl_3$): 3.32, 5.93 (C=O), 6.38, 6.72, 6.91, 7.18, 7.48, 8.49, 9.33, 9.61, 9.97, 11.52 (shoulder), 11.73, 12.19, and 14.39 μ; (CS_2); 8.31, 12.75, 13.20, 13.65, 14.00, and 14.23 μ; nmr (CCl_4): τ 2.79 multiplet (10 H, 9 aromatic, 1 vinyl), 4.46 doublet (1 H, J = 5.5 cps, vinyl), 6.82 quartet (1 H, J_{AB} = 4.8 cps, J_{BX} = 2.5 cps, cyclopropyl CH), and 7.25 doublet (1 H, J = 4.8 cps, cyclopropyl α-CH).

Anal. Calcd for $C_{18}H_{13}BrO$: C, 66.47; H, 4.04; Br, 24.57. Found: C, 66.49; H, 4.02; Br, 24.60.

From the spectral data and conversion to 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one (*vide infra*), photoketones **9a** and **9b** were shown to be epimers with the skeletal structure of 6-*p*-bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one.

6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one from Photoketone 9a. The general procedure of Bacon and Hill[22] was used. To a solution of 65.0 mg (0.20 mmole) of photoketone **9a** and 20.0 mg (0.20 mmole) of acetic anhydride in 1.0 ml of distilled pyridine was added 30.0 mg (0.20 mmole) of dry cuprous oxide and the mixture was stirred and refluxed under nitrogen for 2.5 hr. Benzene (50 ml) was added to the cooled mixture and the solution was extracted twice with 15% hydrochloric acid and twice with saturated sodium bicarbonate solution. The organic layer was dried and the solvent was removed *in vacuo* to yield 63 mg of a dark tarry material. This was chromatographed on a 2.5 × 90 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. Fractions of 40 ml were collected: fractions 1–24, 10% ether–hexane, nil; 25–49, 15% ether–hexane, nil; 50–59, 20% ether–hexane, nil; 60–68, 20% ether–hexane, 14.5-mg product; 69–88, 20% ether–hexane, 27.8 mg, starting photoketone **9a**. Fractions 60–68 were crystallized from ethyl acetate–hexane to give 7.0 mg of material, mp 139.5–141.0°, with an infrared identical with that of authentic[2] 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and mmp 139.0–141.0°.

6,6-Diphenylbicyclo[3.1.0]hex-3-ene-2-one from Photoketone 9b. The procedure and amounts of reagents used for photoketone **9b** were the same as those above for photoketone **9a**, but the mixture was refluxed for 4 hr. Chromatography on a 2.5 × 90 cm column of deactivated silica gel, collecting 40-ml fractions, yielded the following: fractions 1–26, 10% ether–hexane, nil; 27–32, 15% ether–hexane, nil; 33–42, 15% ether–hexane, 23.6-mg product; 43–47, 15% ether–hexane, 5.2 mg starting photoketone **9b**. Fractions 33–42 were crystallized from ether to give 11.5 mg of material mp 139.0–141.0°, with an infrared identical with that of authentic[2] 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and mmp 139.0–140.5°.

(22) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1112 (1964).

Table II. Irradiation of 6-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one

Run	Starting photoketone, mg (mmole)[c]	Light, mEinsteins (min)	Recovered photoketone, mg (mmole)	2,3-Diaryl-phenol,[a] mg (mmole)	3,4-Diaryl-phenol,[b] mg (mmole)	Photo acids, mg (mmole)	% Recov
1	416.0 (1.54)A	1.40 (16.6)	359.8 (1.33)A	22.4 (0.083)	7.9 (0.029)	38.6 (0.134)	101
2	202.1 (0.745)A	4.53 (55.5)	71.2 (0.263)A	48.6 (0.179)	16.1 (0.059)	70.4 (0.244)	100
3	205.6 (0.758)B	1.42 (13.0)	145.0 (0.535)B	8.5 (0.031)	3.4 (0.013)	51.5 (0.178)	101
4	206.7 (0.763)B	2.81 (32.0)	92.4 (0.341)B	24.7 (0.091)	8.2 (0.030)	82.4 (0.285)	98
5	204.8 (0.755)A[d]	3.02 (71.0)	182.0 (0.671)A	11.3 (0.042)	5.7 (0.021)	8.7 (0.030)	101
6	200.9 (0.741)B[d]	2.96 (79.0)	172.6 (0.637)B	9.4 (0.035)	4.6 (0.017)	8.7 (0.030)	98

[a] 2-Phenyl-3-*p*-cyanophenylphenol. [b] 3-*p*-Cyanophenyl-4-phenylphenol. [c] Solvent 80% aqueous *t*-butyl alcohol. [d] Acetophenone concentration 0.57 *M*.

Photoketone 6a from 6-*p*-Bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one, Epimer 9a. A solution of 57.0 mg (0.18 mmole) of 6-*p*-bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one and 74.0 mg (0.80 mmole) of dry cuprous cyanide in 0.2 ml of dimethyl sulfoxide was stirred and heated at 105° for 3 hr under nitrogen. The mixture was taken up in sufficient 15% ammonium hydroxide and benzene for solution, and the aqueous layer was extracted with two additional portions of benzene. The combined organic layers were washed with three portions of ammonium hydroxide and two portions of water and dried, and the solvent was removed *in vacuo* to yield 58 mg of a brown residue. This was chromatographed on a 1.5 × 38 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. The column was eluted with 700 ml of 10% ether–hexane, 200 ml of 12.5% ether–hexane, 100 ml of 15% ether–hexane, 100 ml of 20% ether–hexane, and 500 ml of 25% ether–hexane. From elution with 10% ether–hexane, 37.3 mg of starting photoketone **9a** was obtained, and from the 20–25% ether–hexane fractions, 8.1 mg of a crystalline solid was obtained. This material was crystallized from methylene chloride–hexane to give 3.5 mg of a compound with mp 182.7–183.7° and an infrared identical with that of photoketone **6a** from photolysis of 4-*p*-cyanophenyl-4-phenylcyclohexadienone, mmp 181.5–183.5°.

Photoketone 6b from 6-*p*-Bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one, Epimer 9b. A solution of 65.0 mg (0.20 mmole) of 6-*p*-bromophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one and 74.0 mg (0.80 mmole) of cuprous cyanide in 0.20 ml of dimethyl sulfoxide was stirred and heated at 101° for 4 hr under nitrogen. The reaction mixture was worked up as described above for photoketone **6a** and chromatographed on a 1.5 × 38 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. The column was eluted with 500 ml of 10% ether–hexane, 200 ml of 12.5% ether–hexane, 200 ml of 15% ether–hexane, 200 ml of 20% ether–hexane, and 500 ml of 25% ether–hexane. From elution with 10% ether–hexane, 37.5 mg of starting photoketone **9b** was obtained, and from 25% ether–hexane, 7.4 mg of a crystalline solid, the infrared of which was identical with that of photoketone **6b** from photolysis of 4-*p*-cyanophenyl-4-phenylcyclohexadienone.

Irradiation of Epimer 6a, 0.91 mEinstein/mmole. A solution of 208.0 mg (0.770 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]-hex-3-en-2-one, epimer **6a**, in 750 ml of 80% aqueous *t*-butyl alcohol was irradiated for 8.25 min, using filter B (*vide supra*). Light input was 0.70 mEinstein. An identical irradiation of 208.0 mg of epimer **6a** was carried out under the same conditions with light input of 0.70 mEinstein. The two photolysis solutions were combined, and the solvent was removed *in vacuo* at <35°. The residue was dissolved in chloroform and extracted with 5% sodium hydroxide. The organic layer was dried and concentrated *in vacuo* to give 406.0 mg of a nearly white solid, the infrared and nmr spectra of which showed no bands attributable to epimer **6b**. This material was chromatographed on deactivated silica gel (*vide infra*) (see Table II).

The sodium hydroxide extracts were acidified with dilute sulfuric acid to *ca.* pH 3, and the cloudy aqueous solution was extracted with chloroform. The chloroform solution was dried and concentrated *in vacuo* to give 38.6 mg of a mixture of stereoisomers of 6-*p*-cyanophenyl-6-phenyl-3,5-hexadienoic acid, as a slightly yellow semisolid; infrared ($CHCl_3$): 2.80–4.40 (broad), 4.47 (C≡N), 5.85 (C=O), 6.22, 6.71, 6.91, 7.12, 7.80, 9.00, 9.31, 11.90, 14.37 μ; nmr ($CDCl_3$): τ 0.26 broad singlet (1 H, acid proton), 2.25–4.50 complex multiplet (12 H, aryl and vinyl), 6.60, 6.85 pair of doublets (2 H, CH_2). The structural assignment is based on analogy and infrared and nmr similarity with *cis*- and *trans*-6,6-diphenyl-3,5-hexadienoic acid;[3] however, the material was not further characterized.

Chromatography of the nonacidic product was carried out on a 2.5 × 110 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. The eluent was scanned at 290 mμ through a 2.0-mm flow cell. Fractions were 40 ml. The column was eluted with 2 l. of 10% ether–hexane, 2 l. of 12.5% ether–hexane, 1 l. of 15% tener–hexane, 1 l. of 17.5% ether–hexane, and 4 l. of 20% ether–hexane. Fractions 10–15 and fractions 16–24 yielded 4.0 and 2.6 mg, respectively, of unidentified products, which showed cyano and carbonyl absorption in the infrared at 4.47 and 5.82 μ, respectively, but no phenolic band. Fractions 82–116 contained 22.4 mg of a yellowish solid, mp 180.3–186.6°; infrared (CH_2Cl_2): 2.81, 3.27, 4.48, 6.22, 6.32, 6.93, 7.70, 8.40, 8.60, 9.80, 9.91, 11.21, 11.88, and 12.54 μ; (KBr): 2.96 (broad), 4.47, 6.25, 6.33, 6.85, 6.98, 7.50, 7.70, 7.91, 8.53, 9.11, 9.21, 9.37, 9.81, 9.95, 10.05, 11.15, 11.80, 11.96, 12.08, 12.55, 13.06, 13.57, 13.70, 14.20, and 14.36 μ. This compound was subsequently shown to be 2-phenyl-3-*p*-cyanophenylphenol (*vide infra*). Fractions 132–151 gave 7.9 mg of material later shown to be 3-*p*-cyanophenyl-4-phenylphenol; infrared (CH_2Cl_2): 2.78 (sharp), 2.95 (weak, broad), 3.26, 4.47, 6.22, 6.32, 6.37, 6.85, 7.69, 8.48, 8.62, 9.32, 9.95, 11.22, and 11.91 μ. Fractions 161–213 gave 359.8 mg (86.6%) of recovered starting epimer **6a**. No indication of epimer **6b** was found in the infrared spectra of these fractions.

Irradiation of Epimer 6a, 6.04 mEinsteins/mmole. A solution of 202.1 mg (0.750 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo-[3.1.0]hex-3-en-2-one, epimer **6a**, in 750 ml of 80% *t*-butyl alcohol was irradiated for 55.5 min, using filter B (*vide supra*). Light input was 4.53 mEinsteins. The photolysis solution was worked up as described above, giving 70.4 mg of photo acids and 182.1 mg of nonacidic product. The infrared and nmr spectra of the nonacidic portion showed no bands attributable to epimer **6b**.

Chromatography of the noncarboxylic portion of the photo product on deactivated silica gel under the conditions given above gave five peaks: peak 1 (fractions 8–14) and peak 2 (fractions 15–25) gave 12.1 and 5.6 mg, respectively, of unidentified oils, which had no phenolic infrared bands; peak 3 (fractions 73–107) contained 48.6 mg of 2-phenyl-3-*p*-cyanophenylphenol, identified by infrared, while peak 4 (fractions 113–149) yield 16.1 mg of 3-*p*-cyanophenyl-4-phenylphenol, identified by infrared. From peak 5 there was obtained 71.2 mg (35.1%) of starting epimer **6a**, with no indication of the presence of epimer **6b** in either the chromatogram or the infrared spectra.

Irradiation of Epimer 6b, 1.89 mEinsteins/mmole. A solution of 205.6 mg (0.758 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo-[3.1.0]hex-3-en-2-one, epimer **6b**, in 750 ml of 80% aqueous *t*-butyl alcohol was irradiated for 13.0 min using filter B (*vide supra*). Light input was 1.42 mEinsteins. The photolysis solution was concentrated *in vacuo* at <35° to leave a residue which was taken up in chloroform and extracted with 5% sodium hydroxide. The organic layer was dried and concentrated *in vacuo* to give 186.9 mg of a yellowish semisolid, which was chromatographed on deactivated silica gel (*vide infra*).

The sodium hydroxide extracts were acidified to *ca.* pH 3 with dilute sulfuric acid, and the cloudy aqueous solution was extracted with chloroform; the organic extracts were dried and concentrated *in vacuo* to yield 51.5 mg of a yellowish oil; infrared ($CHCl_3$): 2.77–4.40, 4.48, 5.85, 6.23, 6.70, 6.93, 7.10, 7.81, 8.99, 9.31, 11.91, and 14.33 μ; nmr ($CDCl_3$): τ −0.55 broad singlet (1 H, acidic proton), 2.20–4.60 complex multiplet (12 H, 9 aryl and 3 vinyl), 6.58, 6.92 pair of doublets (2 H, CH_2). This appeared to be a mixture of acids similar to that from irradiation of epimer **6a**, but it was not further characterized (*vide supra*).

The nonacidic photoproduct was chromatographed on a 2.5 × 110 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. The eluent was scanned at 280 mμ through a 2.5-mm cell, and fractions of 40 ml were collected. The column was eluted with 2 l. of 10% ether–hexane, 2 l. of 12.5% ether–hexane, 1 l. of 15% ether–hexane, 1 l. of 20% ether–hexane, and 2 l. of 25% ether–hexane. Peak 1 (fractions 9–13) and peak 2 (fractions 15–24) contained 2.3 and 5.4 mg, respectively, of unidentified oils, which had no phenolic infrared bands. Peak 3 (fractions 72–99) contained 8.5 mg of 2-phenyl-3-*p*-cyanophenylphenol as a yellow solid, mp 179.5–185.0°; infrared (CH_2Cl_2): 2.81, 3.27, 4.47, 6.22, 6.31, 6.93, 7.70, 8.40, 8.60, 9.80, 9.91, 11.22, 11.88, and 12.52 μ; (KBr): 3.05 (broad), 4.48, 6.25, 6.33, 6.87, 6.98, 7.50, 7.70, 7.97, 9.23, 9.33, 9.83, 9.95, 10.07, 11.15, 11.80, 11.93, 12.08, 12.55, 13.05, 13.55, 13.70, 14.20, and 14.35 μ. From peak 4 (fractions 113–143) there was obtained 3.4 mg of 3-*p*-cyanophenyl-4-phenylphenol; infrared (CH_2Cl_2): 2.79, 2.94 (weak, broad), 3.26, 4.47, 6.22, 6.32, 6.85, 7.68, 8.48, 8.60, 9.31, 9.94, 11.22, and 11.90 μ. Peak 5 (fractions 161–200) yielded 145.0 mg (70.2%) of starting epimer **6b**, with no indication of epimer **6a** either from the scan or the infrared spectra.

Irradiation of Epimer 6b, 3.65 mEinsteins/mmole. A solution of 206.7 mg (0.763 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo-[3.1.0]hex-3-en-2-one, epimer **6b**, in 750 ml of 80% aqueous *t*-butyl alcohol was irradiated for 32.0 min using filter B (*vide supra*). Light input was 2.81 mEinsteins. The photolysis solution was worked up as described above, yielding 82.4 mg of photoacids and 172.1 mg of nonacidic products. The infrared and nmr of the latter showed no indication of epimer **6a**.

Chromatography of the noncarboxylic products on deactivated silica gel as described above gave five peaks. Peak 1 (fractions 9–14) and peak 2 (fractions 16–25) contained 5.4 and 5.6 mg, respectively, of unidentified oils which had no phenolic infrared bands. Peak 3 (fractions 78–105) gave 24.7 mg of 2-phenyl-3-*p*-cyanophenylphenol, identified by infrared, and peak 4 (fractions 116–157) yielded 8.2 mg of 3-*p*-cyanophenyl-4-phenylphenol, identified by infrared. From peak 5 (fractions 183–221) there was obtained 92.4 mg (44.8%) of starting epimer **6b**, with no indication of epimer **6a** either from the chromatogram or the infrared spectra of these fractions.

Acetophenone-Sensitized Irradiation of Epimer 6a. A solution of 204.8 mg (0.755 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo-[3.1.0]hex-3-en-2-one, epimer **6a**, and 51.1919 g (0.426 mole, 50 ml) of distilled acetophenone in 700 ml of 80% aqueous *t*-butyl alcohol was irradiated for 71.0 min using filter C (*vide supra*). Light input was 3.02 mEinsteins. The photolysis solution was concentrated at <35° *in vacuo* to remove the solvent and acetophenone. The semisolid residue was dissolved in chloroform and extracted with three portions of 5% sodium hydroxide, then the basic extracts were made acidic with dilute sulfuric acid. The cloudy aqueous solution was extracted with chloroform and the organic solution was dried and concentrated to yield 8.7 mg of photoacids.

The chloroform solution of nonacidic products was dried and concentrated *in vacuo* to give 257.6 mg of material, which contained some acetophenone and had no indication of epimer **6b** in its infrared spectrum. This was chromatographed on a 2.5 × 110 cm column of deactivated silica gel, slurry packed with 10% ether–hexane. The column was eluted with 2 l. of 10% ether–hexane, 2 l. of 12.5% ether–hexane, 1 l. of 15% ether–hexane, 1 l. of 17.5% ether–hexane, and 2 l. of 20% ether–hexane. Fractions of 40 ml were collected, and the eluent was scanned at 280 mμ through a 2.5-mm quartz cell. Peak 1 (fractions 12–21) contained 3.3 mg of an unidentified oil. Peak 2 (fractions 67–97) yielded 11.3 mg of 2-phenyl-3-*p*-cyanophenylphenol, identified by infrared. Fractions 109–134 (peak 3) gave 5.7 mg of 3-*p*-cyanophenyl-4-phenylphenol, identified by infrared. Starting epimer **6a** was recovered from peak 4 (fractions 135–153) in the amount of 182.0 mg (89.0%), with no indication of the presence of epimer **6b**.

Acetophenone-Sensitized Irradiation of Epimer 6b. A solution of 200.9 mg (0.741 mmole) of 6-*p*-cyanophenyl-6-phenylbicyclo-[3.1.0]hex-3-en-2-one, epimer **6b**, and 50.9407 g (0.424 mole, 50 ml) of distilled acetophenone in 700 ml of 80% aqueous *t*-butyl alcohol was irradiated for 79.0 min using filter C (*vide supra*). Light input was 2.96 mEinsteins. The solvent and acetophenone were removed *in vacuo* at <35°, and the residue was dissolved in chloroform and extracted with three portions of 5% sodium hydroxide. The basic solution was acidified to *ca.* pH 3 with dilute sulfuric acid and the cloudy aqueous solution was extracted with chloroform. The chloroform solution was dried and concentrated to yield 8.7 mg of photoacids.

The chloroform solution of the nonacidic products was dried and concentrated *in vacuo* to give 301.7 mg of material still containing acetophenone, which was chromatographed on deactivated silica gel as described above. The column was eluted with 2 l. of 10% either–hexane, 2 l. of 12.5% ether–hexane, 1 l. of 15% ether–hexane, 1 l. of 20% ether–hexane, and 2 l. of 25% ether–hexane. Peak 1 (fractions 11–19) and peak 2 (fractions 22–35) contained 2.6 and 3.0 mg, respectively, of unidentified oils. Peak 3 (fractions 69–99) yielded 9.4 mg of 2-phenyl-3-*p*-cyanophenylphenol, identified by infrared, and peak 4 (fractions 107–144) contained 4.6 mg of 3-*p*-cyanophenyl-4-phenylphenol, identified by infrared. From peak 5 (fractions 160–195) there was obtained 172.6 mg (85.8%) of starting epimer **6b**, with no indication of the presence of epimer **6a** either from the scan or the infrared spectra of these fractions.

Identification of Phenolic Photoproducts. The 2-phenyl-3-*p*-cyanophenylphenol isolated from the irradiations of epimer **6a** and that isolated from the irradiations of epimer **6b** of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one were found to be identical with each other, having the same infrared spectra in KBr and similar crude melting points. Additionally the infrared spectra were identical with that of authentic 2-phenyl-3-*p*-cyanophenylphenol but different from those of the other authentic isomers (*vide infra*). The phenols from the six runs were combined and crystallized from methanol to give 53.5 mg of white needles of 2-phenyl-3-*p*-cyanophenylphenol, mp 188.0–190.0°; nmr (CD_3COCD_3): τ 1.97 singlet (1 H, phenolic), 2.79 complex multiplet (12 H, aryl). The melting point and spectra of this phenol were identical with those (*vide infra*) of authentic 2-phenyl-3-*p*-cyanophenylphenol, mp 188.5–190.0°, mmp 187.5–190.0°, and not to those (*vide infra*) of authentic 2-*p*-cyanophenyl-3-phenylphenol,[23] mp 206.0–209.0°, mmp 161.5–172.2°.

The combined 3-*p*-cyanophenyl-4-phenylphenol from six runs was crystallized from methanol to give material with mp 220.5–224.0°, mixture melting point with authentic 3-*p*-cyanophenyl-4-phenylphenol 220.5–224.5°; infrared (KBr): 2.95, 3.00, 3.30, 4.47, 6.24, 6.31, 6.42, 6.65, 6.75, 6.98, 7.11, 7.52, 7.63, 7.87, 8.36, 11.20, 11.90, 12.10, 13.03, 13.43, 13.70, 14.05, and 14.29 μ. This infrared was identical with that of authentic 3-*p*-cyanophenyl-4-phenylphenol (*vide infra*).

Stability of 2-*p*-Cyanophenyl-3-phenylphenol under Photolysis Conditions. To determine whether 2-*p*-cyanophenyl-3-phenylphenol was stable to light, a control irradiation of this compound was carried out using conditions identical with those used for the direct irradiations of epimers **6a** and **6b** (*vide supra*). A solution of 30.3 mg (0.112 mmole) of 2-*p*-cyanophenyl-3-phenylphenol in 750 ml of 80% aqueous *t*-butyl alcohol was irradiated for 15.7 min, using filter B (*vide supra*). Light input was 1.40 mEinsteins, but the photolysis solution absorbed only 0.51 mEinstein, the remainder of the light passing through to the actinometer solution in the second cell. The ultraviolet of the solution was the same before and after photolysis. Removal of the solvent *in vacuo* at <35° left 38.7 mg of a white solid, mp 200.8–208.5°, and the infrared in KBr was identical with that of the starting material.

***p*-Chlorobenzalacetone.**[24] The method of Lutz and co-workers[24] was used.

4-Phenyl-5-*p*-chlorophenylcyclohexane-1,3-dione. The general procedure of Borsche[25] for 4,5-diphenylcyclohexane-1,3-dione was employed. Sodium (4.24 g, 0.184 g-atom) was dissolved in 75 ml of absolute ethanol under nitrogen and then 28.70 g (0.175 mole) of ethyl phenylacetate and 31.60 g (0.175 mole) of *p*-chlorobenzalacetone in 75 ml of absolute ethanol were added. The mixture was stirred at reflux for 12 hr. Water was then added, and the thick brown precipitate was filtered. The filtrate was concentrated,

(23) This compound was synthesized by Mr. Richard Lura in these laboratories; *cf.* Richard Lura, Senior Thesis, University of Wisconsin, 1967.

(24) R. E. Lutz, *et al.*, *J. Org. Chem.*, **14**, 993 (1949).

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

acetic acid was added to give a yellow gum, which was ether extracted, and the ether solution was dried and concentrated *in vacuo*. The residual orange oil which still contained some acetic acid was crystallized by treating with methanol–water. A slightly yellow solid, 20.75 g, mp 133–160°, was obtained. This was recrystallized from ether to give 8.35 g, mp 155.5–160.9°, 5.03 g, mp 154.0–159.5°, and 3.32 g, mp 151.0–157.5°, totalling 16.70 g (32%). A sample was recrystallized from ether to mp 156.5–160.0°; infrared ($CHCl_3$): 2.85–4.50 (broad), 5.83, 6.26 (broad), 6.70, 9.15, and 9.84 μ; nmr ($CDCl_3$): τ 0.08 singlet (1 H, enolic), 3.00 multiplet (9 H, aryl), 4.31 singlet (1 H, vinyl), 6.15–7.48 multiplet (4 H, CH_2 and 2CH).

Anal. Calcd for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06; Cl, 11.87. Found: C, 72.34; H, 5.33; Cl, 12.04.

Enol Ethers of 4-Phenyl-5-*p*-chlorophenylcyclohexane-1,3-dione. A solution of 5.986 g (0.020 mole) of 4-phenyl-5-*p*-chlorophenylcyclohexane-1,3-dione and 0.504 g of *p*-toluenesulfonic acid in 50 ml of dry benzene and 15 ml of absolute ethanol was stirred at reflux for 3 hr and the water collected in a Dean–Stark tube. The cooled mixture was diluted with ether, washed with water, 5% sodium bicarbonate, and water, then dried and concentrated *in vacuo*, leaving 6.73 g of a colorless oil. This was subjected to liquid–liquid partition chromatography (*vide supra*) in four batches on a 4.0 × 150 cm column. The eluent was scanned at 270 mμ through a 0.006-in. quartz cell; 40-ml fractions were collected and three peaks were obtained.

Peak 1 (fractions 53–58) contained 1.345 g (20.7%) of a white solid, mp 106.6–132.1°; infrared ($CHCl_3$): 3.33, 6.10, 6.27, 6.70, 7.25, 7.37, 7.49, 8.40, 8.67, 9.00, 9.15, 9.73, 9.85, 11.50, 11.90, 12.10, and 14.30 μ; nmr (CCl_4): τ 3.12 doublet of multiplets (9 H, aryl), 4.44 singlet (0.73 H, vinyl), 4.57 singlet (0.27 H, vinyl), 6.17 multiplet (4 H, CH_2 and 2 benzylic), 7.50 multiplet (2 H, α-methylene), 8.78 triplet with shoulders (3 H, methyl). The nmr spectrum indicated a mixture of two isomers in *ca.* 3:1 ratio. This material was not used in subsequent steps.

The material from peak 2 (fractions 60–65, 2.227 g, 34%) was crystallized from ether–hexane to give successive crops of 1.738 g, mp 88.0–90.0°, and 0.189 g, mp 86.0–90.5°, of 3-ethoxy-4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one. A sample was recrystallized to a constant mp 88.8–89.8°; infrared ($CHCl_3$): 3.33, 6.09, 6.25, 6.70, 7.25, 7.41, 7.46, 8.40, 8.67, 9.00, 9.15, 9.62, 9.95, 11.90, 12.05, 12.25, and 14.32 μ; nmr (CCl_4): τ 2.90 multiplet (9 H, aryl), 4.47 singlet (1 H, vinyl), 5.97–6.82 complex pattern (4 H, CH_2CH_3 and 2 benzylic), 7.46 doublet (2 H, α-methylene, J = 6.5 cps), 8.85 triplet (3 H, methyl); ultraviolet (95% EtOH): λ_{max} 253 mμ (ϵ 18,500).

Anal. Calcd for $C_{20}H_{19}ClO_2$: C, 73.50; H, 5.86; Cl, 10.85. Found: C, 73.57; H, 5.86; Cl, 10.92.

The compound in peak 3 (fractions 66–73, 2.415 g, 37%) was crystallized from chloroform–hexane to give successive crops of 0.828 g, mp 111.0–112.6°, and 1.317 g, mp 110.6–113.1°, of 3-ethoxy-5-*p*-chlorophenyl-6-phenylcyclohex-2-en-1-one. A sample was recrystallized to constant mp 111.5–112.7°; infrared ($CHCl_3$): 3.33, 6.11, 6.24, 6.72, 7.12, 7.24, 7.35, 8.45, 8.62, 9.11, 9.16, 9.73, 9.85, 10.48, 10.78, 11.43, 11.80, 12.02, 12.15, and 14.35 μ; nmr (CCl_4): τ 3.00 multiplet (9 H, aryl), 4.58 singlet (1 H, vinyl), 6.13 quartet (2 H, CH_2CH_3, J = 7.0 cps), 6.37–6.62 multiplet (2 H, benzylic), 7.22–7.47 multiplet (2 H, allylic), 8.71 triplet (3 H, methyl, J = 7.0 cps); ultraviolet (95% EtOH): λ_{max} 252 mμ (ϵ 15,800).

Anal. Calcd for $C_{20}H_{19}ClO_2$: C, 73.50; H, 5.86; Cl, 10.85. Found: C, 73.70; H, 6.00; Cl, 11.02.

5-*p*-Chlorophenyl-6-phenylcyclohex-2-en-1-one. A solution of 0.426 g (1.30 mmoles) of 3-ethoxy-4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one in 20 ml of anhydrous ether and 2.0 ml of dry benzene was added dropwise to a slurry of 31.0 mg (0.83 mmole) of lithium aluminum hydride in 10 ml of ether.[26] The mixture was stirred for 2 hr under nitrogen at room temperature and then 15 ml of 10% sulfuric acid was slowly added and the two-phase system stirred rapidly for 1 hr. The layers were separated, and the aqueous layer was ether extracted several times. The combined ether extracts were washed with water, dried, and concentrated *in vacuo* to give 420 mg of an oil which was crystallized from ether–hexane to give successive crops of 239.1 mg, mp 93.0–96.9°, 84.2 mg, mp 90.1–94.0°, and 9.8 mg, mp 92.0–95.0°, a yield of 353 mg (96%) of 5-*p*-chlorophenyl-6-phenylcyclohex-2-en-1-one. A sample was recrystallized from ether to mp 96.0–98.4°; infrared (CS_2): 3.25, 3.29, 3.42, 3.45, 5.95 (C=O), 7.21, 7.82, 8.22, 8.70, 9.15, 9.67, 9.85, 10.76, 11.75, 12.00, 12.22, 13.32, 13.42, 13.83, 14.05, 14.38, and 15.05 μ; nmr ($CDCl_3$): τ 3.10 multiplet (10 H, 9 aryl, 1 vinyl), 3.92 doublet of triplets (1 H, vinyl, J_{AB} = 10 cps, J_{BX} = 1.8 cps), 6.49 complex pattern (2 H, benzylic), 7.24 unresolved multiplet (2 H, allylic).

Anal. Calcd for $C_{18}H_{13}ClO$: C, 76.45; H, 5.35; Cl, 12.54. Found: C, 76.53; H, 5.51; Cl, 12.71.

2-Phenyl-3-*p*-chlorophenylphenol. The general method of Polaczkowa and Porowska[27] was used. A solution of 282.6 mg (1.00 mmole) of 5-*p*-chlorophenyl-6-phenylcyclohex-2-en-1-one in 1.00 ml of 97% acetic acid was heated to 75° and then 1.00 ml of a solution of 0.55 ml (1.65 g, 10.3 mmoles) of bromine in 10.0 ml of 97% acetic acid was added. The resulting yellow solution was heated at 102° for 2 hr, allowed to cool, and then made basic by addition of saturated sodium bicarbonate solution. The aqueous solution was extracted with chloroform and the combined chloroform extracts were washed with water, dried, and concentrated *in vacuo* to yield 318.4 mg of an oil. This was chromatographed on a 2.5 × 108 cm column of activated silica gel, slurry packed with 5% ether–hexane. The column was eluted with 2 l. of 5% ether–hexane, 1.5 l. of 8% ether–hexane, 1 l. of 20% ether–hexane, and 1 l. of 40% ether–hexane; fractions were 200 ml. Fractions 12–15 (8% ether–hexane) yielded 195 mg of 2-phenyl-3-*p*-chlorophenylphenol, which was recrystallized from hexane to give 157.3 mg (56%). This compound existed in two crystalline forms, which were interconvertible on melting or crystallization; they had melting points of 102.2–103.5 and 110.0–110.9°; infrared ($CHCl_3$): 2.81, 3.31, 6.21, 6.32, 6.39, 6.70, 6.80, 6.89, 6.93, 7.16, 7.52, 7.72, 7.88, 8.42, 8.60, 9.11, 9.21, 9.33, 9.85, 9.91, 11.19, 12.03, and 14.27 μ; (CS_2): 3.25, 12.60, 13.10, 13.55, 13.87, and 14.05 μ; nmr ($CDCl_3$): τ 2.85 multiplet (12 H, aryl) and 4.91 singlet (1 H, hydroxyl).

Anal. Calcd for $C_{18}H_{13}ClO$: C, 77.00; H, 4.67; Cl, 12.63. Found: C, 77.37; H, 4.27; Cl, 12.70.

2-Phenyl-3-*p*-cyanophenylphenol. A modified procedure based on the method of Newman and Boden was used.[28] A solution of 338.0 mg (3.8 mmoles) of cuprous cyanide and 266.8 mg (0.95 mmole) of 2-phenyl-3-*p*-chlorophenylphenol in 1.50 ml of N-methyl-2-pyrrolidone was stirred at reflux for 14 hr. The cooled reaction mixture was taken up in sufficient benzene and 30% ammonium hydroxide for solution and the aqueous layer was extracted with three portions of benzene. The combined organic extracts were washed with ammonium hydroxide and then water, filtered, and concentrated *in vacuo* to give 260.6 mg of a brown solid. This was extracted with boiling hexane, and the hexane-insoluble portion was chromatographed on a 1.5 × 15 cm column of silica gel, slurry packed with 5% ether–hexane. Elution with 150 ml of 5% ether–hexane and 100 ml of 15% ether–hexane gave 16.6 mg of starting material; then elution with 500 ml of 25% ether–hexane gave 125.7 mg of 2-phenyl-3-*p*-cyanophenylphenol. Chromatography of the hexane-soluble material under similar conditions gave 49.0 mg of starting material and 30.5 mg of the cyanophenol. Combination of the product from both columns and crystallization from ethyl acetate–hexane gave 133.1 mg (52%) of 2-phenyl-3-*p*-cyanophenylphenol, mp 186.5–191.3°. A sample was recrystallized from methanol to mp 189.5–190.5°; infrared (CH_2Cl_2): 2.81, 3.27, 4.47 (C≡N), 6.22, 6.31, 6.93, 7.70, 8.39, 8.60, 9.80, 9.90, 11.19, 11.88, and 12.53 μ; (KBr): 3.00 (broad, OH), 4.47 (C≡N), 6.25, 6.33, 6.85, 6.97, 7.50, 7.70, 7.90, 8.52, 9.11, 9.20, 9.35, 9.81, 9.93, 10.05, 11.15, 11.80, 11.95, 12.08, 12.55, 13.05, 13.56, 13.70, 14.20, and 14.35 μ; nmr (CD_3COCD_3): τ 1.97 singlet (1 H, hydroxyl), and 2.80 multiplet (12 H, aryl).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.55; H, 5.12; N, 5.27.

4-Phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one. A solution of 589 mg (1.80 mmoles) of 3-ethoxy-5-*p*-chlorophenyl-6-phenylcyclohex-2-en-1-one in 20 ml of anhydrous ether and 2.0 ml of dry benzene was added dropwise to a slurry of 43 mg (1.13 mmoles) of lithium aluminum hydride in 10 ml of ether.[26] The mixture was stirred at 25° for 2 hr under nitrogen and then 15 ml of 10% sulfuric acid slowly added, and the two-phase system stirred rapidly for 1 hr. The layers were separated, and the aqueous layer was ether extracted several times. The combined ether extracts were washed with water, dried, and concentrated *in vacuo* to leave 508.4

(26) See M. Stiles and A. Longray, *Tetrahedron Letters*, 337 (1961), for discussion of mechanism.

(27) W. Polaczkowa and N. Porowska, *Roczniki Chem.*, **34**, 1659 (1960); *cf. Chem. Abstr.*, **56**, 5865g (1962).

(28) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).

mg of a slightly yellow oil. This was crystallized from ether–hexane to give 387.9 mg (76%), mp 92.0–120.0°. Slow crystallization from ether–hexane gave three crops: 119.4 mg, mp 124.5–126.0°; 78.0 mg, mp 109.2–124.0°; and 115.7 mg, mp 90.4–122.2°. The nmr ($CDCl_3$) and infrared (CS_2) spectra of crops 1 and 3 were identical in all respects, indicating that the wide melting range is due to two crystalline forms of 4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one. Extensive recrystallization did not narrow the melting point range; infrared (CS_2): 3.29, 3.38, 3.45, 5.96 (C=O), 7.23, 7.68, 7.91, 8.09, 8.72, 9.15, 9.29, 9.72, 9.85, 11.87, 12.11, 13.20, 13.44, and 14.32 μ; nmr ($CDCl_3$): τ 2.92 multiplet (10 H, 9 aryl, 1 vinyl), 3.75 doublet of doublets (1 H, vinyl, J_{AB} = 10.2 cps, J_{BX} = 2.5 cps), 6.05–7.52, complex multiplet (4 H, benzylic and α-methylene).

Anal. Calcd for $C_{18}H_{15}ClO$: C, 76.45; H, 5.35; Cl, 12.54. Found: C, 76.29; H, 5.55; Cl, 12.81.

3-*p*-Chlorophenyl-4-phenylphenol. The general method of Polaczkowa and Porowska[27] was used. A solution of 422.0 mg (1.50 mmoles) of 4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one in 1.50 ml of 97% acetic acid was heated to 75°, and then a solution of 240 mg (1.50 mmoles) of bromine in 1.50 ml of 97% acetic acid was added. The mixture was heated at 102° for 2 hr, allowed to cool, and made basic by addition of saturated sodium bicarbonate solution. The aqueous solution was extracted with chloroform; the organic extracts were washed with water and concentrated *in vacuo* to yield 446.0 mg of an oil. This was crystallized from carbon tetrachloride–hexane to yield successive crops of 219.5 mg, mp 127.2–130.0°; 16.8 mg, mp 127.2–129.2°; and 26.4 mg, mp 120.0–126.0°, giving a total of 262.7 mg (62%). A sample was recrystallized from hexane to mp 129.1–131.1°; infrared ($CHCl_3$): 2.77, 2.98 (broad), 3.31, 6.23, 6.31, 6.41, 6.78, 6.90, 7.01, 7.27, 7.65, 8.54, 9.17, 9.85, 9.92, 11.21, 12.05, and 14.33 μ; (CS_2): 13.05, 13.56, 13.82, and 14.13 μ; nmr ($CDCl_3$): τ 2.92 multiplet (12 H, aryl) and 4.68 broad singlet (1 H, hydroxyl).

Anal. Calcd for $C_{18}H_{13}ClO$: C, 77.00; H, 4.67; Cl, 12.63. Found: C, 77.02; H, 4.67; Cl, 12.56.

3-*p*-Cyanophenyl-4-phenylphenol. A modified procedure based on the method of Newman and Boden was used.[28] A mixture of 246.8 mg (2.75 mmoles) of cuprous cyanide and 196.2 mg (0.70 mmole) of 3-*p*-chlorophenyl-4-phenylphenol in 1.0 ml of N-methyl-2-pyrrolidone was stirred at reflux for 14 hr. The cooled reaction mixture was taken up in sufficient benzene and 30% ammonium hydroxide for solution. A black solid, possibly elemental copper, remained undissolved between the layers and was discarded. The aqueous solution was extracted with benzene, and the combined organic extracts were washed with ammonium hydroxide, then with water, dried, and concentrated *in vacuo* to give 166 mg of a brown solid. This was chromatographed on a 1.6 × 43 cm silica gel column, slurry packed with 15% ether–hexane. The crude product was placed on the column in a minimum of ethyl acetate. The column was eluted with 15% ether–hexane and 100-ml fractions were collected. Fractions 4–15 yielded 118.8 mg (62%) of 3-*p*-cyanophenyl-4-phenylphenol, mp 220.5–224.5°. This was recrystallized from ethyl acetate–hexane and then methanol to mp 222.8–225.4°; infrared (KBr): 2.95, 4.47 (C≡N), 6.25, 6.32, 6.44, 6.66, 6.77, 6.99, 7.12, 7.53, 7.64, 7.88, 8.38, 11.22, 11.91, 12.11, 13.05, 13.45, 13.71, 14.06, and 14.30 μ; nmr (CD_3COCD_3): τ 1.38 singlet (1 H, hydroxyl) and 2.72 complex multiplet (12 H, aryl).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.35; H, 5.03; N, 5.29.

2-*p*-Cyanophenyl-3-phenylphenol.[23] An authentic sample of this compound[23] had mp 206–209° and spectra as follows; infrared (KBr): 2.94, 4.45, 6.22, 6.32, 6.37, 6.88, 7.14, 7.52, 7.68, 7.85, 7.97, 8.13, 8.49, 8.57, 8.67, 9.02, 9.12, 9.34, 9.77, 9.95, 10.38, 10.47, 11.10, 11.74, 11.96, 12.46, 13.12, 13.29, and 14.21 μ; nmr (CD_3COCD_3): τ 1.65 singlet (1 H, phenolic) and 2.77 complex multiplet (12 H, aryl).

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Substituent Effects on the Hyperfine Splitting Constants of N,N-Dimethylaniline Cation Radicals[1]

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Abstract: The effects of *meta* and *para* substituents on the hyperfine splitting constants of the CH_3 protons, nitrogen, and the ring protons of N,N-dimethylaniline cation radicals in acetonitrile solution have been determined. The effects of *para* −R substituents are well correlated by σ^+ parameters and those of *para* +R substituents by σ_I parameters, both on a single regression line. The effects of *meta* −R substituents are found to be unique, with enhancement exceeding that expected for even *para* σ^+ parameters. A bisectional analysis of the observed substituent effects to polar effects (σ_I dependence) and π-delocalization effects (σ_R^+ dependence) has been carried out. This analysis indicates for strong −R substituents that the ratio of corresponding *para* to *meta* π-delocalization effects is (uniquely) less than one. Model HMO calculations give spin density distributions in accord with these findings. In further accord with the theoretical calculations, it is concluded that the correlations of the experimental splitting constants with σ values indicate that a close correspondence exists between the effects of substituents on spin and charge density distributions.

The relationship between nuclear hyperfine splitting constants (hfsc) from electron spin resonance (esr) spectrometry and substituent constants provides an approach to the understanding of the relationship of spin density to electron pair density distributions. This conclusion follows from the known relationships between hfsc and spin density[2] and between σ_R values and electron-pair densities.[3]

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