Photochemical Migratory Aptitudes in Cyclohexenones. Mechanistic and Exploratory Photochemistry. XXIII[1]

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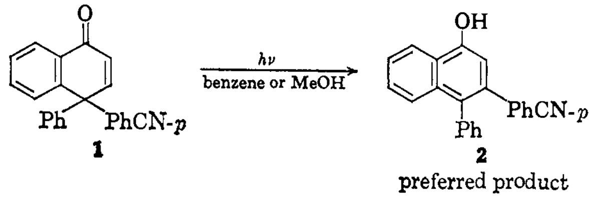
Abstract: The electronic nature of the reactive excited state in 4,4-diarylcyclohex-2-en-1-one photochemical rearrangements has been investigated. The representation $\mathrm{C^+}$—C=C—$\mathrm{O^-}$ was found to provide a poor guide for predicting reactivity; $\dot{\mathrm{C}}$—C=C—$\dot{\mathrm{O}}$ is preferred. Photolysis of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one gave 5,6-diarylbicyclo[3.1.0]hexan-2-one isomers. A preference of *ca.* 14:1 was observed for *p*-cyanophenyl *vs.* phenyl and 10–15:1 for anisyl *vs.* phenyl migration. The migratory aptitudes rule out the rearrangement's being determined by stabilization by the nonmigrating aryl group. Sensitization experiments indicated that these rearrangements are proceeding *via* the triplet excited state. Marked stereochemical selectivity was encountered with the *trans* isomers being kinetically preferred; an explanation of this phenomenon is advanced An intriguing photochemical reaction of the bicyclic ketone isomers was uncovered in which the aryl groups exchanged positions; this proved to be slow.

One of the more challenging and unsettled questions in organic photochemistry concerns the electron distribution and consequent reactivity of the electronically excited enone moiety. Recently, evidence was presented[3] which indicated that $\mathrm{C^+}$—C=C—$\mathrm{O^-}$ is not a good representation of the enone moiety in the reactive excited state of 4-phenyl-4-*p*-cyanophenyl-1(4H)-naphthalenone (**1**). The conclusion was based on the observation that photolysis of **1** (note Chart I) resulted in preferential *p*-cyanophenyl migration from C-4 to C-3 to give as the favored product 3-*p*-cyanophenyl-4-phenyl-1-naphthol (**2**). This is the product expected from an excited state with a β-carbon atom which is either electron rich or odd electron in nature.[4] This behavior contrasted with that anticipated for an excited-state species having an electron-deficient β-carbon; in fact, the nonphotochemical, acid-catalyzed rearrangement gave exclusively phenyl migration.

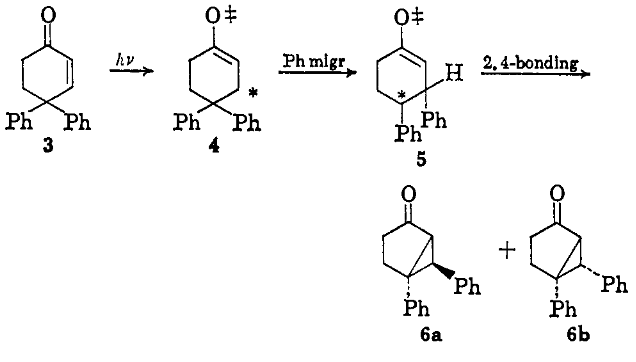
Chart I



Further studies on excited-state migratory aptitudes seemed desirable for several reasons: (1) to determine whether the cyanophenyl migration phenomenon was general, (ii) to explore the behavior of other aryl groups, (iii) to assess the importance of electronic stabilization by groups migrating relative to substituents remaining behind, and (iv) to relate structure to the selectivity of such photochemical rearrangements.

The photochemical rearrangement of 4,4-diphenylcyclohex-2-en-1-one[6] (**3**) seemed ideally suited for such aryl migratory aptitude studies. This rearrangement is outlined in Chart II with the excited state **4** represented generally. The rearrangement has been shown[6] to involve phenyl migration to the valence-deficient, excited-state β-carbon atom with subsequent 2,4 bonding to afford *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6a** and **6b**, respectively). The question is whether $\ddagger$ and * in excited state **4** are best represented by − and +, + and −, or · and ·. The validity of our previously suggested n–π* mechanism is, of course, directly related to this question.[6]

Chart II



The present study utilized a competition between phenyl migration and *p*-cyanophenyl migration in one approach, and considered the relative migratory aptitudes of phenyl and *p*-methoxyphenyl in the second.

Synthesis of 4,4-Diarylcyclohexenones. The synthesis of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) (note Chart III) began with the addition of dimethyloxosulfonium methylide (**7**) to *p*-bromobenzophenone by the method of Corey and Chaykovsky[7] to yield the corresponding epoxide **8**. Acid-catalyzed rearrangement of **8** gave phenyl(*p*-bromophenyl)acetaldehyde (**9**) which was condensed with methyl vinyl ketone to yield 4-phenyl-4-*p*-bromophenylcyclohex-2-

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[1] For paper XXII of the series note H. E. Zimmerman, H. G. C. Dürr, R. S. Givens, and R. G. Lewis, *J. Am. Chem. Soc.*, **89**, 1863 (1967).

[2] (a) National Institutes of Health Predoctoral Fellow, 1962–1965; (b) National Science Foundation Predoctoral Fellow, 1963–1966.

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

[4] This evidence bears on the matter of the excited state and its reactivity. This must be distinguished from subsequent species engendered in many photochemical reactions; these are often electron deficient. Examples are the zwitterions involved in dienone photochemistry.[5]

[5] Note H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961), and subsequent papers.

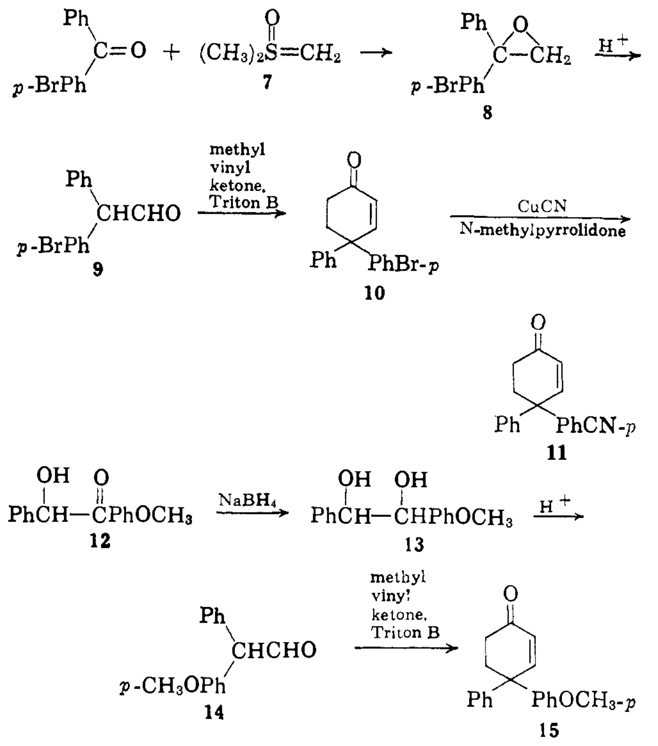
[6] H. E. Zimmerman and J. Wilson, *ibid.*, **86**, 4036 (1964).

[7] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 867 (1962); E. J. Corey, *ibid.*, **87**, 1353 (1965).

en-1-one (**10**). Treatment of **10** with cuprous cyanide in refluxing N-methylpyrrolidone by the method of Newman[8] completed the synthesis of **11**.

4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) was synthesized beginning with *p*-methoxybenzoin (**12**) which was reduced with sodium borohydride to the corresponding hydrobenzoin **13**. Acid-catalyzed rearrangement of **13** gave phenyl(*p*-methoxyphenyl)-acetaldehyde (**14**) which, in turn, was condensed with methyl vinyl ketone to afford the desired enone **15** (see Chart III).

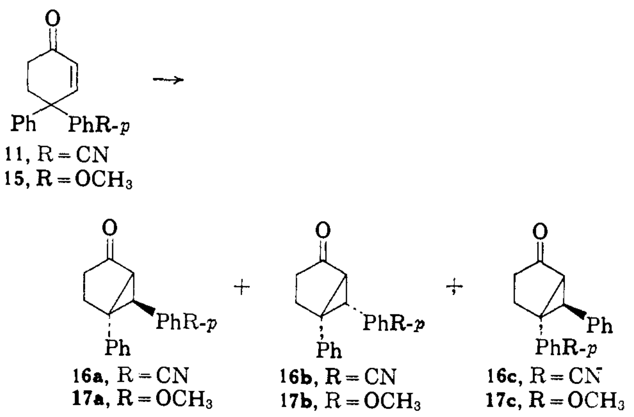
Chart III



Photolysis of 4-Phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (11) and 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (15). Elucidation of Product Structures. Photolysis of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) in benzene through a Pyrex filter afforded the products shown in Chart IV. In typical preparative photolyses, irradiation was continued until the infrared spectra of aliquots showed no further starting enone (3 hr). The resulting mixtures were partially separated by scanning liquid–liquid partition chromatography. Final separation was accomplished by means of silica gel column chromatography in each case. Under these conditions, the yields of the various photoproducts were as follows: **16a**, mp 140–141°, 50%; **16b**, mp 157.5–158.5°, 30%; **16c**, mp 155–157°, 6%; **17a**, mp 105–106°, 71.5%; **17b**, mp 98–99°, 7%; **17c**, mp 91–92°, 0.5%.

Photoketones **16a** and **16b** were shown (*vide infra*) to be *trans*- and *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, respectively, and **16c** was shown to be *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Photoproducts **17a** and **17b** were shown to have the *trans*- and *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one structure, respectively, and isomer **17c** was shown to be *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one.

Chart IV



The structural assignments were based on elemental analysis, spectral data, spectral comparison with the photoproducts from photolysis of 4,4-diphenylcyclohex-2-en-1-one,[6] and degradation.

Elemental analysis showed photoketones **16a–16c** to be isomeric with starting 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**), and showed isomers **17a–17c** to be isomeric with 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**).

Photoproducts **16a–16c** and **17a–17c** had infrared carbonyl absorption very similar to those observed for both stereoisomers of 5,6-diphenylbicyclo[3.1.0]hexan-2-one[6] (**6a** and **6b**, note Chart II). The latter showed carbonyl absorptions at 5.83 and 5.80 μ, respectively, while the following absorptions were exhibited by the former: **16a**, 5.80; **16b**, 5.80; **16c**, 5.80; **17a**, 5.83; **17b**, 5.80; and **17c**, 5.80 μ. All of these values are very close to the carbonyl absorption observed for dihydroumbellulone[9] (5.81 μ), and can be considered characteristic of the bicyclo[3.1.0]hexan-2-one system.

The nmr spectra of photoketones **16a–16c** and **17a–17c** were particularly revealing. The spectra could be divided into two distinct, characteristic types. The first, conveniently referred to as "type a" spectra, were the spectra observed for the photoketones **16a**, **17a**, **16c**, **17c**, and also the known[6] *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6a**). These spectra were all virtually superimposable on each other, with the exception of a sharp singlet near τ 6.2 in **17a** and **17c** due to the methoxyl methyl groups, and with minor differences in the aryl regions. All "type a" spectra displayed AB quartets near τ 7.0 owing to the cyclopropyl methine hydrogens of the bicyclo[3.1.0]hexan-2-one system. The coupling constants are summarized in Table I. These values are seen to agree well with the value of 8.4 cps found by Graham and Rogers[10] for *cis*-cyclopropyl CH–CH coupling.

The second type of nmr spectra ("type b" spectra) were those exhibited by photoketones **16b**, **17b**, and the known[6] *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6b**). Again, these spectra were unique and were nearly superimposable upon one another. The cyclopropyl methine hydrogens of the bicyclo[3.1.0]hexan-2-one system appeared as AB quartets centered near τ 7.3 with the coupling constants summarized in Table I.

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

(9) R. H. Eastman and J. C. Selover, *J. Am. Chem. Soc.*, **76**, 4118 (1954).

(10) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

Table I. Coupling Constants Observed for Photoketones

Compound	Type	J_{AB}, cps
trans-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16a**)	a	10
trans-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**16c**)	a	10
trans-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17a**)	a	10
trans-5-*p*-Methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**17c**)	a	9
trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (**6a**)[a]	a	10
cis-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16b**)	b	3
cis-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17b**)	b	4
cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (**6b**)[a]	b	3

[a] See ref 6.

These values are well in line with the smaller value observed by Graham and Rogers[10] for *trans*-CH–CH cyclopropane coupling.

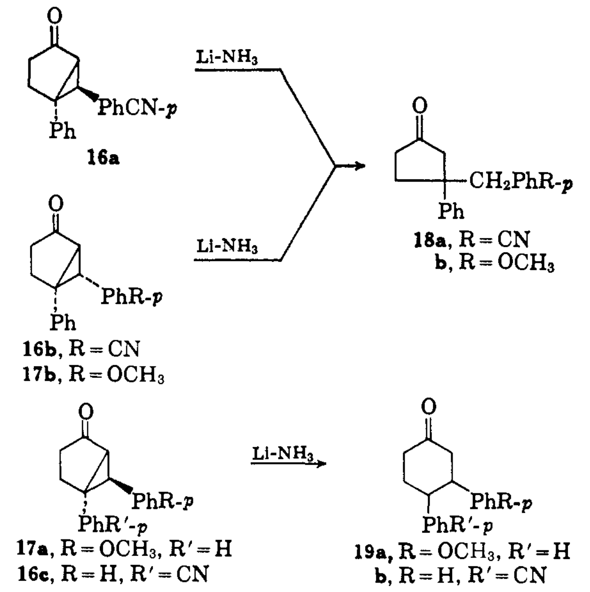
The infrared, nmr, and elemental analysis data thus strongly suggested that compounds **16a**–**16c** and **17a**–**17c** were structurally and stereochemically isomeric 5,6-diarylbicyclo[3.1.0]hexan-2-ones. Analogy with the known reaction of 4,4-diphenylcyclohex-2-en-1-one[6] provides some support. However, firm support for this assumption was derived from degradation of the above photoproducts and synthesis of the resulting degradation products in each case. The degradation delineated the carbon skeleton and furthermore determined which aryl group was located at C-5 and which at C-6 in each of the above photoketones. This latter information was not available from the spectral data.

The degradation consisted of treating the appropriate photoketone with lithium and liquid ammonia, a little-known reaction apparently first investigated by Volkenburgh.[11] The net effect of the reaction was to open the three-membered ring of the bicyclic system with concomitant reduction. Since the work described below was completed, Norin[12] and Nickon[13] have reported similar transformations.

Thus, treatment of the *trans*- and *cis*-*p*-cyanophenyl-substituted photoketones **16a** and **b** with lithium in liquid ammonia gave 3-phenyl-3-*p*-cyanobenzylcyclopentan-1-one (**18a**, see Chart V) in each case. Similar treatment of the *cis*-*p*-methoxyphenyl-substituted photoketone **17b** gave 3-phenyl-3-*p*-methoxybenzylcyclopentan-1-one (**18b**). Degradation of the minor *trans*-*p*-cyanophenyl photoisomer **16c** afforded 3-phenyl-4-*p*-cyanophenylcyclohexanone (**19b**), while degradation of the major *trans*-*p*-methoxyphenyl-substituted photoketone **17a** gave 3-*p*-methoxyphenyl-4-phenylcyclohexanone (**19a**).[14]

The structures of the above degradation products were established by elemental analysis, spectral data, mass spectral data [in the case of 3-phenyl-3-*p*-cyanobenzylcyclopentan-1-one (**18a**)], and by independent synthesis.

Chart V



Analyses of degradation products **18a**, **18b**, **19a**, and **19b**, showed their respective starting materials plus two hydrogen atoms. The infrared spectra of products **18a** and **b** exhibited carbonyl absorptions at 5.75 and 5.74 μ, respectively, typical of cyclopentanones.[15] Products **19a** and **b** each showed carbonyl absorptions at 5.85 μ, typical of cyclohexanones.[15] The mass spectrum of degradation product **18a** showed a strong peak (mass 116) for the *p*-cyanobenzyl cation. A strong peak for the benzyl (as tropylium) cation would have been expected if the structure of **18a** had been 3-*p*-cyanophenyl-3-benzylcyclopentan-1-one.

Ultimate proof of structure for the degradation products was found in an independent synthesis of each as outlined in Chart VI.[16]

All of the above degradative evidence thus proves that photoketones **16a** and **b** possess the 5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one structure, and that **17a** and **b** have the 5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one structure. This evidence, coupled with the nmr evidence presented earlier, unequivocally establishes the original structural assignments (*vide supra*).

Similarly, photoketone **16c** is shown to be *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Photoketone **17c**, which was never isolated in large enough amounts to permit degradation, is shown by virtue of its elemental analysis, its nmr and infrared spectra, and exclusion (two *p*-methoxyphenyl migrated products already being known), to possess the *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one structure.

The Question of Interconversion of Photoketones. The evidence obtained thus far shows a preference for

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(11) R. Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, 71, 3595 (1949).

(12) T. Norin, *Acta Chem. Scand.*, 19, 1289 (1965).

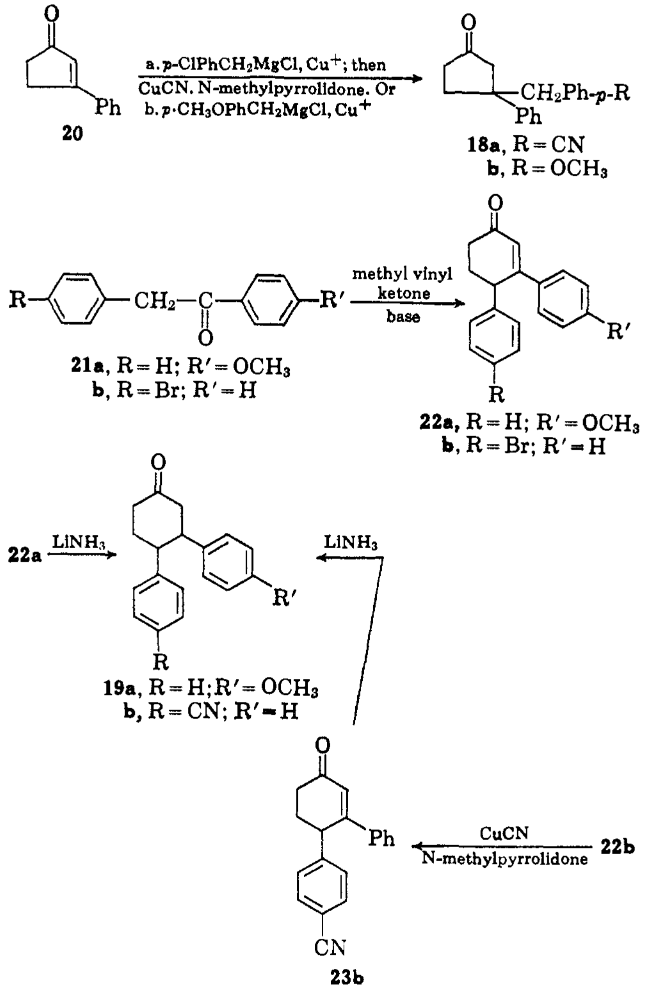
(13) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, 87, 1615 (1965).

(14) The reaction appears to proceed by formation of the radical anion or dianion of the carbonyl compound followed by fission of either the internal (1–5) or external (1–6) three-ring bond and protonation of the carbanionic center γ to the carbonyl carbon in the product. Ketonization must occur during work-up. Mechanistic details are under investigation.

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

(16) Although the final reductive step in the synthesis of 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one and 3-phenyl-4-*p*-cyanophenylcyclohexan-1-one could have given either the *cis* or the *trans* stereoisomer in each case, it gave the same stereoisomers as obtained from degradation. Both the degradative and synthetic processes involve carbanion protonation in determining stereochemistry, and thus the product identity is not totally surprising.[14]

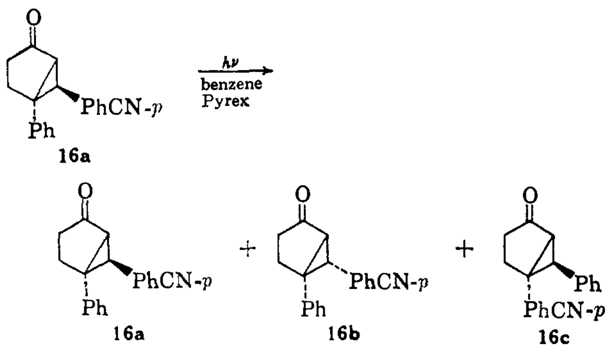
Chart VI



certain of the bicyclic ketone products. However, before the importance of this could be assessed, it was necessary to determine (a) the stability of these products on further irradiation, and (b) the kinetic ratio, as extrapolated back toward zero time; only if the photoketones did react further would this be necessary. We turn our attention to the first matter now.

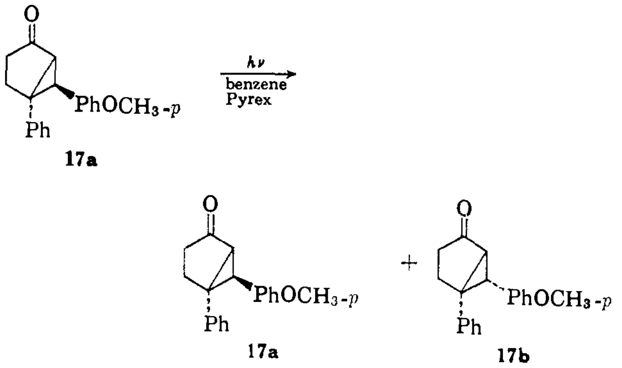
Photolysis of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16a**) was found to give a mixture of this starting material **16a** and the product of epimerization, *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16b**). Strikingly, this photolysis was also found to produce small amounts of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**16c**), a rearrangement that involves interchange of the aryl groups. This rearrangement is outlined in Chart VIIA.

Chart VIIA. Rearrangement of *trans*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one



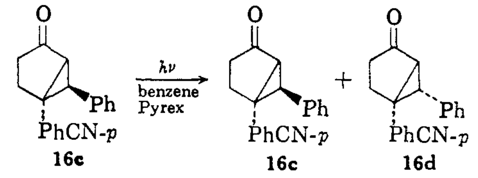
Photolysis of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17a**) afforded *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17b**), the product of epimerization at C-6 (see Chart VIIB). No products which had resulted from aryl interchange were found in this reaction.

Chart VIIB. Rearrangement of *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one



Similarly, *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**16c**) was converted upon photolysis to a mixture of starting material and the fourth possible photoisomer in this series, *cis*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**16d**) (see Chart VIIC). The proof of structure for photoproduct **16d** rests on elemental analysis, spectral data, and analogy with the previously mentioned photoepimerization reactions. Besides exhibiting an infrared carbonyl absorption of 5.80 μ, shown earlier (*vide supra*) to be typical of bicyclo[3.1.0]hexan-2-ones, isomer **16d** had an nmr spectrum which was of the "b type" ($J_{AB} = 3$ cps) and virtually identical with the nmr spectra of the *cis*-5,6-diphenyl, *cis*-5-phenyl-6-*p*-cyanophenyl, and *cis*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketones **6b**, **16b**, and **17b**, respectively (note Table I).

Chart VIIC. Rearrangement of *trans*-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one



The above photoepimerization reactions parallel the behavior observed by Zimmerman and Wilson[6] for the photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**6a**) which also underwent stereoisomerization. The results of the above stereochemical and structural isomerization reactions are collected in Table II.

Table II. Yields Observed in Photolysis of Photoketones

Compd photolyzed	Photolysis, hr	%						
		16a	16b	16c	16d	17a	17b	17c
16a	2.5	33.4	47.8	1–2	...	...	...	...
16a	24.0	21.2	54.0	5.6	...	...	...	...
16a	92.0	18.0	58.0	8.0	...	...	...	...
16c	20.0	...	...	47.5	36.8	...	...	...
17a	20.0	...	...	...	...	48.7	35.3	...

Photolysis of 4-Phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (11) and 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (15) for Varying Times. The original goal of the present study was elucidation of migratory aptitudes in 4-phenyl-4-arylcyclohexenone photolyses. However, since both a facile stereoisomerization reaction and a slow rearrangement involving scrambling of aryl groups was found to occur in the photoproducts it was necessary to extrapolate the product distribution back to near zero time in order to determine the kinetic photoisomer preference. The results of time dependence studies in the photolysis of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) are summarized in Tables IIIA and IIIB, respectively.

Table IIIA. Photolysis of 4-Phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) for Varying Times[a,b]

	%					
Photolysis, hr	Recovered enone	**16a**	**16b**	**16c**	**16a**/**16b**	(**16a** + **16b**)/**16c**
0.25	59	30	2	2.4	15.0	13 ± 2.5
0.5	29	49	5.4	3.6	9.1	15 ± 2.5
1.0	7	60	18	5.4	3.3	14 ± 2.5
3.0	0	50	30	6.0	1.7	13 ± 2.5

[a] **16a** is *trans*-5-phenyl-6-*p*-cyanophenyl bicyclic ketone; **16b** is *cis*-5-phenyl-6-*p*-cyanophenyl bicyclic ketone, and **16c** is *trans*-5-*p*-cyanophenyl-6-phenyl bicyclic ketone. [b] Analysis by isolation.

Table IIIB. Photolysis of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) for Varying Times[a,b]

	%					
Photolysis time	Recovered enone	**17a**	**17b**	**17c**	**17a**/**17b**	(**17a** + **17b**)/**17c**
6 min	87.4	11.6	None[c]	1	. . .	12 ± 2.5
15 min	71.2	25.9	0.9	2	28.4	13 ± 2.5
25 min	59.7	35.4	1.9	3	18.3	12 ± 2.5
3.0 hr	None	71.5	7.0	0.5	10.2	. . .

[a] Analysis by chromatography and quantitative infrared and nmr. [b] **17a** is *trans*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, **17b** is *cis*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, and **17c** is *trans*-5-*p*-methoxyphenyl-6-phenyl bicyclic ketone. [c] <0.2%.

A number of conclusions can be drawn from the data in Tables IIIA and IIIB. First, with respect to the stereochemistry, the ratios of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one to *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16a**/**16b**) are seen to be quite large in low conversion runs. Similarly, the results in Table IIIB show that *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17b**) is not an appreciable direct photoproduct of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. Thus the *trans* stereoisomers in each case are formed initially in preference followed by equilibration to a *cis–trans* mixture. Secondly, the ratio (**16a** + **16b**)/**16c** (total yield of *p*-cyanophenyl migrated product to yield of phenyl-migrated product) remains constant within experimental error with changing irradiation time. This indicates that this ratio does represent the migratory aptitude of *p*-cyanophenyl relative to phenyl and rules out the possibility of a rapid scrambling of aryl groups. A rapid interconversion of this sort is additionally unlikely since photolysis of the *trans*-5-phenyl-6-*p*-cyanophenyl and *trans*-5-*p*-cyanophenyl-6-phenyl bicyclic ketones showed no appreciable interconversion during a period of time equal to that of the original enone photolysis.

The same argument applies in the case of the *p*-methoxyphenyl-substituted photoketones, in which the ratio of *p*-methoxyphenyl-migrated material (**17a** + **17b**) to phenyl-migrated material (**17c**) was found to be constant at 12.5 ± 2.5.

Sensitization Experiments. In order to gain some evidence on the multiplicity of the rearranging species, experiments were carried out to determine if enones **11** and **15** could be sensitized with acetophenone.

Photolysis of a benzene solution of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) for 10.0 min in the presence of acetophenone as a sensitizer afforded the products and yields shown in Table IVA. The concentration of acetophenone was such that it absorbed 98% of the light passing through a filter solution[17] having a window from 310 to 370 mμ.

Table IVA. Sensitization of 4-Phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one

Compound	%
Recovered enone	34.5
trans-5-Phenyl-6-*p*-cyanophenyl bicyclic ketone (**16a**)	42
cis-5-Phenyl-5-*p*-cyanophenyl bicyclic ketone (**16b**)	15
trans-5-*p*-Cyanophenyl-6-phenyl bicyclic ketone (**16c**)	4
(**16a** + **16b**)/**16c**	14 ± 2

Similarly, a benzene solution of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) was irradiated in the presence of acetophenone as a sensitizer. The same filter solution[17] as above was used, and the acetophenone concentration was such that it absorbed 97.5% of the transmitted light. Two runs were made for 4.0 and 11.0 min, respectively. The results are shown in Table IVB.

Table IVB. Sensitization of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one[a,b]

	%				
Photolysis min	Recovered enone	**17a**	**17b**	**17c**	(**17a** + **17b**)/**17c**
4.0	91.8	7.7	None[c]	0.5	14 ± 2.5
11.0	65.5	32.5	None[c]	2	16 ± 2.5

[a] Analysis by chromatography and quantitative infrared and nmr. [b] **17a** is *trans*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, **17b** is *cis*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, and **17c** is *trans*-5-*p*-methoxyphenyl-6-phenyl bicyclic ketone. [c] <0.2%.

The preceding sensitization experiments indicate that energy transfer from acetophenone to 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**) and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) has definitely taken place. With a bimolecular diffusion rate in benzene[18] of 10^{10} l./mole sec and a concentration of

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(17) H. E. Zimmerman and R. S. Givens, unpublished results.

(18) As given by F. Wilkenson, *Advan. Photochem.*, 3, 248 (1964), as calculated from Debye's equation [P. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942)].

enone in both cases of 0.0018 *M*, the pseudo-unimolecular rate of collision becomes 1.8×10^7 sec^{-1}. The rate of singlet acetophenone decay[19] is $>10^{10}$ sec^{-1}, and the rate of triplet acetophenone decay[20] is 10^5 sec^{-1}. Thus, singlet energy transfer is too slow and is ruled out, and the sensitized reaction must be taking place *via* the triplet excited state.

The above sensitization experiments provide strong evidence that it is the triplet excited state which is undergoing rearrangement in the direct photolyses of enones **11** and **15**. First of all, the sensitization experiments gave the same products as observed in the direct runs, showing that the triplet is capable of giving the ordinary, unsensitized reaction. Secondly, the migratory aptitudes observed in the sensitized photolyses were the same, within experimental error, as those found in the direct irradiations, with *p*-cyanophenyl and *p*-methoxyphenyl migration being favored in each case.[21]

Discussion

The fact that *p*-cyanophenyl was found to migrate in preference to phenyl by a ratio of 14 ± 2.5 to 1 suggests that $^{+}$C—C═C—O^{-} is not a helpful representation of the enone moiety in the reactive excited state of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one (**11**). This is in complete accord with the findings in the 4-phenyl-4-*p*-cyanophenylnaphthalenone study.[3] Similarly, the fact that *p*-methoxyphenyl migrated in preference to phenyl by a factor of 12.5 ± 2.5 indicates that $^{-}$C—C═C—O^{+} is not a useful representation for the reactive excited state of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**).

The assumption is made that migratory behavior of *p*-methoxyphenyl and *p*-cyanophenyl serves as a useful probe of excited-state electron distribution in the same way as in ground-state systems.[22]

Also, the possibility, in the case of 4-phenyl-4-*p*-cyanophenylcyclohex-2-en-1-one, that the excited state may be electron deficient at the β-carbon atom, and that migratory preference might then be controlled by stabilization by the group remaining behind (*i.e.*, phenyl), is ruled out by the present results. If this were the case, photolysis of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one (**15**) would be expected to result in phenyl migration, leaving the *p*-methoxyphenyl group behind to stabilize the positive charge. This, however, is not the experimental case. Further evidence that excited-state migratory aptitudes are not controlled by stabilization by the nonmigrating group is found in the observations that phenyl migrates in preference to methyl in the photolysis of 4-phenyl-4-methylnaphthalenone,[3] and that 4,4-diarylcyclohex-2-en-1-one photorearrangements are found to involve 1,2-aryl shifts rather than C-5 (type A)[24] migration, even though C-5 migration would leave behind a highly resonance-stabilized, benzhydryl-type moiety.

Thus, the results of the present study indicate that $\dot{\text{C}}$—C═C—$\dot{\text{O}}$ best represents the product determining excited state in 4,4-diarylcyclohex-2-en-1-one photorearrangements.[25] This conclusion assumes that the basic mechanism is the same for the *p*-cyanophenyl and *p*-methoxyphenyl examples, and that one can judge the excited-state makeup from its reactivity.[22]

The present photochemical results are thus in accord with the mechanism postulated by us earlier for the rearrangements of α,β-unsaturated ketones and cross-conjugated dienones.[6,24,29] This mechanism involved initial n-π* triplet formation to give excited-state species which were radical like at the β-carbon atom of the enone moiety. The present results are also in agreement with the recent suggestion of Schuster, *et al.*[30]

Still unanswered, however, is the question of the reason for the striking stereoselectivity observed in the rearrangements of 4,4-diarylcyclohex-2-en-1-ones. In the present study, and in the case of 4,4-diphenylcyclohex-2-en-1-one,[6] *trans*-bicyclic ketone formation was greatly favored over *cis*-bicyclic ketone formation. The 4,4-diphenylcyclohex-2-en-1-one mechanism[6] accounts very nicely for this stereoselectivity if one assumes that aryl migration and 2,4 bonding are concerted processes as shown in Chart VIII. If one considers the half-migrated species **25** shown in Chart VIII, it is apparent that atomic orbitals χ_3 and χ_5 are in favorable position to engage in overlap, back lobe with back lobe (*i.e.*, to undergo 2,4 bonding). This overlap does lead to the σ bond found between these carbon atoms in the products. As the overlap between the bottom lobes of orbitals χ_3 and χ_5 becomes greater, and as the migrating aryl group moves from its half-migrated position more toward product, the β-carbon atom of the cyclohexane ring is forced upward along with the aryl

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(19) F. Wilkenson and J. T. DuBois, *J. Chem. Phys.*, **39**, 377 (1963).

(20) S. G. Cohen, D. A. Laufer, and W. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).

(21) It should be noted that the ratios of *trans*- to *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one and the ratios of *trans*- to *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one observed in the direct and sensitized runs should not necessarily be expected to be the same because of differing steady-state ratios being approached in the *cis–trans* photoepimerization reactions.

(22) (a) The excited-state electron distribution of the diarylcyclohexenones presently studied should be similar to that of unsubstituted enones, since the excitation should be heavily localized in the enone moiety, whose triplet energy[23a] should be low relative to *p*-cyanophenyl[23b] and *p*-methoxyphenyl.[23c] The localization of excitation should diminish only gradually as aryl to β-carbon bonding ensues. (b) Ground-state rearrangement examples, for the most part, are highly exothermic with an early transition state. Approximate calculations (J. Scheffer, Ph.D. thesis) indicate the present reaction to be quite exothermic if the 2,4 bond of the product is considered developing during the reaction. (c) The present reasoning takes the 4,4-diphenylcyclohexenone excited state and rearranging species derived therefrom and considers the introduction of a *p*-methoxy or *p*-cyano group to provide only a mild perturbation of the system. This reasoning is consistent with the available facts.

(23) (a) Cyclohexenones have been reported (ref 24, footnote 29) to have triplet energies ranging from 68 to 71 kcal/mole. (b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944), have reported benzonitrile to have a triplet energy of 77 kcal/mole. (c) Phenol, a reasonable model for anisole, has been reported (ref 23b) to have a triplet energy of 82 kcal/mole.

(24) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, 88, 1965 (1966).

(25) In an *inter*molecular comparison of rates of ground-state, free-radical aryl migration, Rüchardt[26] has presented data on *p*-methoxyphenyl. In two cases, anisyl migrates less readily than phenyl, and in another, slightly more efficiently. Triphenylmethyl *is* stabilized by *p*-methoxy substitution.[27] Similarly, anisole *does* undergo homolytic phenylation at a greater rate than benzene,[28] but, for the most part, polar effects seem to be important in determining the effect of anisyl in ground-state radical reactions, and thus ground-state literature analogy is not too helpful.

(26) C. Rüchardt and R. Hecht, *Ber.*, **98**, 2471 (1965), and references cited therein.

(27) S. T. Bowden, *J. Chem. Soc.*, 4235 (1957), and references cited therein.

(28) For a recent review on substituent effects in homolytic aromatic substitution reactions, see G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960.

(29) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(30) D. I. Schuster and C. J. Polowczyk, *ibid.*, 88, 1722 (1966); D. I. Schuster and D. J. Patel, *ibid.*, **88**, 1825 (1966).

Chart VIII

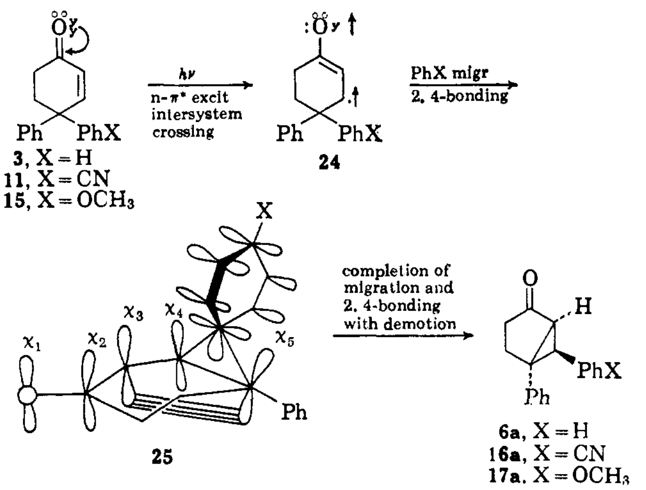
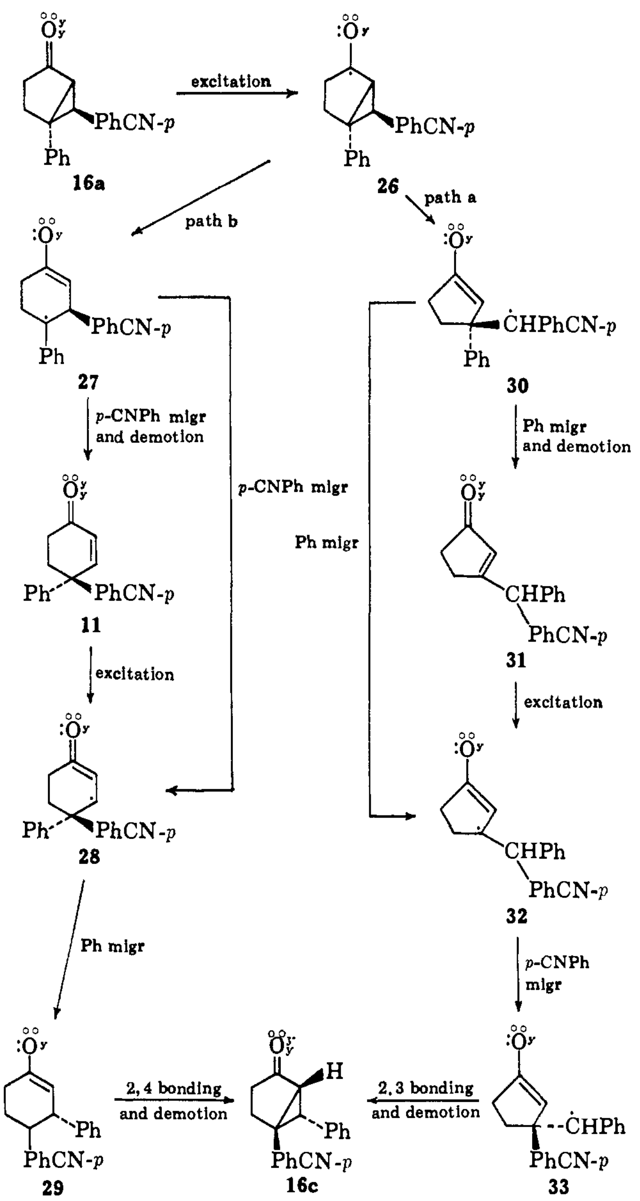


Chart IX



group attached to it, and inversion at C-4 ensues. Completion of 2,4 bonding and aryl migration thus leads to bicyclic ketones with the *trans* stereochemistry. *cis*-Photoisomer formation requires a top-top overlap of orbitals χ_3 and χ_5, which would require a nonconcerted or noninversion mechanism involving a higher energy transition state than in the converted process.[31]

An intriguing aspect of this rearrangement is the possibility of internal conversion during formation of the bridged species **25**. Available evidence indicates that the n–π* triplet is the lowest energy initial excited state, but elongation of the π system as the aryl group begins to undergo migration may allow internal conversion to occur to a resulting, low-energy π–π* triplet.

A mechanistic scheme for the photoepimerization reaction (*i.e.*, *trans*-photoketone → *cis*-photoketone) has previously been presented,[6] but the finding that photolysis of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**16a**) gives small yields of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**16c**) presents an entirely different problem. Two possible mechanisms can explain the observed results (see Chart IX). Further studies are needed to provide evidence on this point.

Experimental Section[32]

1-*p*-Bromophenyl-1-phenylethylene Oxide. The preparation was similar to that described by Corey and Chaykovsky.[7] Trimethyloxosulfonium iodide (45.0 g, 0.204 mole) prepared by the method of Kuhn and Trischmann[33] was dissolved in 400 ml of dimethyl sulfoxide under nitrogen. A 5.33-g (0.222 mole) portion of sodium hydride, obtained from 10.25 g of a 52% suspension in mineral oil, washed free of oil, was added slowly to the trimethyloxosulfonium iodide during 30 min. *p*-Bromobenzophenone (50 g, 0.1915 mole) dissolved in 150 ml of dimethyl sulfoxide was then added to the dimethyloxosulfonium methylide during 10 min. Ten minutes after the addition, the light yellow mixture became gray black. The dark solution was stirred at room temperature for 1 hr and then heated to 50–55° for 2 hr. The hot reaction mixture was then poured into ice water and quickly ether extracted. The ether extracts were washed, dried, and concentrated *in vacuo*, leaving a light yellow oil weighing 53 g. The infrared spectrum showed no trace of starting material and showed a strong band at 11.0 μ, characteristic of epoxides.[16] The nmr spectrum (CCl_4) showed: τ 2.75 multiplet (9 H, aromatic) and 6.90 doublet (2 H, J = 1 cps, HCH). This material was used directly without further purification in the next step.

2-*p*-Bromophenyl-2-phenylacetaldehyde. *p*-Toluenesulfonic acid (1.6 g) was refluxed in 300 ml of benzene for 12 hr under nitrogen; water was removed with a Dean–Stark tube. Freshly prepared crude 1-*p*-bromophenyl-1-phenylethylene oxide (53 g) dissolved in 50 ml of benzene was rapidly added to the refluxing solution. The resulting mixture was refluxed for 2 hr. The reaction mixture was then allowed to cool to room temperature, and the benzene solution was washed with aqueous sodium bicarbonate and water, dried, and concentrated *in vacuo*, leaving a brown oil weighing 53.0 g. The crude aldehyde was distilled to give 29.5 g (0.1072 mole, 55% from *p*-bromobenzophenone) of 1-*p*-bromophenyl-1-phenylacetaldehyde, bp 139–141° (0.25 mm).

Spectral data were: infrared ($CHCl_3$), 3.67 (CHO), 5.80 (C=O), 6.72, 6.89, 7.12, 9.90 (C–Br), 12.25, and 14.38 μ; nmr (CCl_4), τ 0.24 doublet (1 H, J = 2.0 cps, OCH), 2.82 multiplet (9 H, aromatic), 5.30 doublet (1 H, J = 2.0 cps, CH).

4-*p*-Bromophenyl-4-phenylcyclohex-2-en-1-one. An approximately 40% aqueous solution of Triton B was prepared by adding water to a 40% solution of Triton B (benzyltrimethylammonium methoxide) in methanol and distilling an equal volume of alcohol from the mixture. 1-*p*-Bromophenyl-1-phenylacetaldehyde (5.0 g, 0.0182 mole) and 1.35 g (0.0193 mole) of methyl vinyl ketone were dissolved in 11.5 ml of *t*-butyl alcohol under nitrogen. The mixture was cooled to 0° and 2.90 ml of the aqueous Triton B was added dropwise over 2 hr. The reaction mixture was then poured

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[31] More quantitative evidence on the stereochemistry of this type of reaction derives from studies of H. E. Zimmerman and K. G. Hancock (to be published) on the photochemistry of 4,4-diphenylcyclohexenone.

[32] All melting points were taken on a hot-stage apparatus and were corrected.

[33] R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

into ice water and ether extracted; the extracts were dried and concentrated *in vacuo*, leaving 5.4 g of a dark yellow-brown oil. Infrared analysis showed the mixture to consist mainly of the desired product, however, containing some intermediate aldol. To complete the elimination, 5.40 g of the crude mixture was dissolved in 300 ml of absolute ethanol containing 50 ml of concentrated hydrochloric acid and was refluxed for 30 min. The reaction mixture was then poured into ice water and ether extracted. The extract was washed, dried, and concentrated *in vacuo*, leaving a dark brown oil which crystallized on standing. Recrystallization from ether–hexane yielded 2.337 g (39%) of 4-*p*-bromophenyl-4-phenylcyclohex-2-en-1-one, mp 124–125°.

Spectral data were: infrared ($CHCl_3$), 5.95 (C=O), 6.72, 6.92, 7.24, 9.90 (C–Br), 11.28, 12.20, and 14.32 μ; nmr ($CDCl_3$), τ 2.63 multiplet (10 H, 9 aryl and CH=), 3.80 doublet (1 H, J = 11.0 cps, CH=), 7.46 multiplet (4 H, CH_2CH_2).

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.05; H, 4.61; Br, 24.68.

4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one. The following procedure is essentially that used by Newman and Boden.[8] 4-*p*-Bromophenyl-4-phenylcyclohex-2-en-1-one (7.50 g, 23.0 mmoles) and 3.83 g (21.0 mmoles) of cuprous cyanide were refluxed in 22 ml of N-methylpyrrolidone for 2 hr. The reaction mixture was cooled and poured into 6.1 g of sodium cyanide in 150 ml of water. The resulting mixture was shaken thoroughly, 500 ml of benzene added, and the mixture shaken again. The organic and aqueous layers were then filtered. The benzene layer was washed with 10% sodium cyanide and water, then dried, and concentrated *in vacuo* leaving 6.6 g of a dark brown oil. This was chromatographed on a 6 × 90 cm silica gel (Davison silica gel, grade 950, 60–200 mesh) column slurry packed in 15% ether–hexane. The column was eluted with 4 l. of 25% ether–hexane, 5 l. of 35% ether–hexane, 4 l. of 40% ether–hexane, and 25 l. of 45% ether–hexane; 1-l. fractions were collected. Fractions 17–29 afforded 5.55 g of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one. Recrystallization from ether gave 4.90 g (78%) which melted at 78–79°. Further recrystallization raised the melting point to 81.0–81.5°. Physical data on the compound were the following: infrared ($CHCl_3$), 4.48 (C≡N), 5.95 (C=O), 6.22, 6.70, 6.92, 11.25, 12.00, and 14.32 μ; nmr (CCl_4), τ 2.17–2.92 multiplet (10 H, 9 aromatic and CH=), 3.76 half of AB quartet (1 H, J = 10 cps, =CH), 7.43 A_2B_2 multiplet (4 H, CH_2CH_2); ultraviolet, λ_{max} (benzene) 340 mμ (n–π^*, ϵ 30.2).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.17; H, 5.48; N, 5.16.

***p*-Methoxyhydrobenzoin.** To a solution of 42.0 g (0.17 mole) of *p*-methoxybenzoin (prepared by the method of Kinney[34]) in 1 l. of 95% ethanol was added with stirring a suspension of 3.15 g (0.085 mole) of sodium borohydride in 100 ml of cold 95% ethanol during 15 min. The resulting solution was stirred for 1 hr at room temperature, an additional 1.0 g (0.027 mole) of solid sodium borohydride added, and stirring continued for 2 hr more. The solution was then diluted to a volume of 4 l. with water, and the resulting *p*-methoxyhydrobenzoin was filtered and dried. The crude yield was 32.3 g (76.9%), mp 130–133°. Recrystallization from benzene furnished 29.4 g of colorless needles, mp 133–134° (lit.[35,36] 134–135 and 133–134°).

Phenyl(*p*-methoxyphenyl)acetaldehyde. A solution of 100 g (0.41 mole) of *p*-methoxyhydrobenzoin and 5.0 g of *p*-toluenesulfonic acid in 1 l. of dry benzene was refluxed and stirred under nitrogen for 5 min. Then 200 ml of benzene was distilled during 40 min and the cooled residue extracted with sodium bicarbonate and water and dried. Benzene was removed *in vacuo* yielding 93 g of yellow oil which was shaken vigorously with 300 ml of a solution prepared by dissolving 160 g of sodium bisulfite in 240 ml of water, adding 60 ml of ethanol, and decanting from the precipitated sodium bisulfite.[37] Filtration and washing successively with absolute ethanol, chloroform, and absolute ether afforded 15.0 g of the bisulfite addition compound of phenyl(*p*-methoxyphenyl)acetaldehyde.

To a solution of 7.11 g of the above sodium bisulfite addition compound in 150 ml of water was added 10.0 g of solid sodium carbonate. The resulting solution was stirred at 40° for 15 min under nitrogen, the cooled solution ether extracted, and the ether extract washed and dried. Concentration *in vacuo* yielded 3.67 g of light yellow oil. The oil was distilled to give 2.69 g (6% yield based on *p*-methoxyhydrobenzoin) of phenyl(*p*-methoxyphenyl)acetaldehyde, bp 130–132° (0.40 mm), $n^{25}D$ 1.5853 (lit.[38] $n^{25}D$ 1.5886).

A 2,4-dinitrophenylhydrazone derivative (needles from 95% ethanol) melted at 146–147°.

Anal. Calcd for $C_{21}H_{18}O_5N_4$: C, 62.06; H, 4.46; N, 13.79. Found: C, 62.15; H, 4.61; N, 12.55.

4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. A 40% aqueous solution of Triton B was prepared by adding 5.0 ml of water to 12.0 ml of a 40% solution of Triton B methoxide (benzyltrimethylammonium methoxide) in methanol and distillation of the methanol. To a solution of 7.00 g (0.031 mole) of phenyl(*p*-methoxyphenyl)acetaldehyde plus 2.49 g (0.034 mole) of methyl vinyl ketone in 25 ml of *t*-butyl alcohol was added, with stirring under nitrogen, 5.0 ml of the aqueous Triton B solution over 2 hr at 0–5°. Then the reaction mixture was stirred for 4 hr at room temperature. The dark reaction mixture was poured into 100 ml of ice water; the resulting suspension was ether extracted, washed, and dried. Distillation of the ether *in vacuo* yielded 9.40 g of viscous yellow oil. This material was placed on a 5 × 100 cm silica gel chromatography column, slurry packed with 5% ether–hexane; 500-ml fractions were collected. Fractions 1–4, hexane, fractions 5 and 6, 5% ether–hexane, fractions 7 and 8, 10% ether–hexane, fractions 9 and 10, 15% ether–hexane, and fractions 11 and 12, 20% ether–hexane, were empty; fractions 13 and 14, 20% ether–hexane, fractions 15–20, 22.5% ether–hexane, and fractions 21–23, 25% ether–hexane, contained 1.36 g of oily uneliminated aldol, which was discarded. Fractions 24–32, 25% ether–hexane, gave 5.34 g (62.5%) of crystalline material, mp 79–82°. Recrystallization from ether–hexane afforded colorless cubes, mp 81–82°.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.08; H, 6.55.

Physical data were the following: infrared (CS_2), 5.95 (C=O), 8.00, 8.48, 9.61, 12.10, 14.32 μ; nmr (CCl_4), τ 2.82–3.34 multiplet (10 H, aryl and α-vinyl), 3.97 doublet (1 H, J = 10 cps, β-vinyl), 6.27 singlet (3 H, OCH_3), 7.56 multiplet (4 H, ring CH_2); ultraviolet λ_{max} (cyclohexane), 284 mμ (ϵ 2250), 278 (2750), and 200 (26,400), λ_{max} (benzene) 340 mμ (n–π^*, ϵ 31.3).

Preparative Photolyses and Photoproduct Characterization. Photolysis of 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one. The photolysis was carried out by dissolving 0.500 g (1.83 mmoles) of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one in 1 l. of freshly distilled benzene. Purified nitrogen was passed through the solution for 1 hr before and then during photolysis. The light source was a 450-w Hanovia medium pressure mercury lamp with a Pyrex filter, all in an immersion well. The photolysis was monitored by removing aliquots and checking the infrared spectrum. The 5.95-μ carbonyl band characteristic of the starting material disappeared and was replaced by a new band at 5.80 μ. The photolysis was at least 90% completed in 2 hr; however, the photolysis was allowed to go a total of 3 hr. The slightly yellow solution was concentrated *in vacuo*, yielding 0.520 g of a light yellow oil which was chromatographed on a liquid–liquid partition chromatography column. The two-phase solvent system was prepared from 1000 ml of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water at 29.0°. The 5 × 150 cm column was packed with a mixture of 700 g of Celatom FW-80 (Eagle-Picher Co.) bearing 305 ml of lower phase. Elution was with upper phase, and the ultraviolet of the eluent was scanned at 260 mμ; 40-ml fractions were collected. From fractions 60–62 there was obtained 0.171 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one which, upon recrystallization from ether, afforded 0.150 g, mp 139–140.5°. Fractions 63–70 contained 0.165 g of a mixture containing *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and a second photoproduct, *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Fractions 75–85 contained 0.184 g of a third photoproduct, *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, which, upon recrystallization from ether, afforded 0.140 g, mp 156.5–158.5°. Fractions 47–55 contained a fourth photoproduct in small yield, approximately 1%, and no further work was done on this photoproduct. The fractions were worked up by washing with water, drying, and concentrating *in vacuo*. Fractions 63–70 were chromatographed on a 1.2 × 100 cm silica gel column slurry packed with 20% ether–hexane. The column was eluted with 25% ether–hexane, and the ultraviolet of the eluent was scanned at 260 mμ; 20-ml fractions were collected. Fractions 40–60 contained 0.127 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one which, upon re-

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(34) C. R. Kinney, *J. Am. Chem. Soc.*, **51**, 1592 (1929).

(35) A. Orekhoff and M. Tiffeneau, *Bull. Soc. Chim.*, **37**, 1410 (1925).

(36) S. S. Jenkins, *J. Am. Chem. Soc.*, **54**, 1157 (1932).

(37) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 149.

(38) D. Y. Curtin and A. Bradley, *J. Am. Chem. Soc.*, **76**, 5777 (1954).

crystallization, gave 0.090 g, mp 139–140°. Fractions 63–100 gave 0.039 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one which, upon recrystallization, gave 0.025 g, mp 154–157°.

Characterization of *trans*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]-hexan-2-one. This material was further recrystallized from ether to give a colorless solid, mp 140–141°. The physical data were as follows: infrared (CS_2), 4.49 ($C{\equiv}N$), 5.79 ($C{=}O$), 12.02, 13.25, 14.3 μ, (KBr), 4.49 ($C{\equiv}N$), 5.80 ($C{=}O$), 6.22, 6.67, 6.90, 7.10, 12.0, 12.58, 13.18, and 14.30 μ; nmr ($CDCl_3$), τ 2.23–2.67 multiplet (9 H, aromatic), 7.08 AB quartet (2 H, J = 10 cps, CHCH), 7.48–9.33 multiplet (4 H, CH_2CH_2); ultraviolet (benzene), 290 mμ (ϵ 181) 300 (111), 310 (61), and 320 (23).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.35; H, 5.61; N, 5.09.

Characterization of *cis*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]-hexan-2-one. Further recrystallization from ether yielded colorless crystals, mp 157.5–158.5°. The physical data were as follows: infrared (CS_2), 4.49 (CN), 5.78 ($C{=}O$), 11.25 (broad), 11.95 (broad), 13.20, and 14.35 μ, (KBr), 4.48 (CN), 5.80 ($C{=}O$), 6.23, 7.08, 8.11, 8.57, 11.05, 11.78, 13.05, and 14.21 μ; nmr ($CDCl_3$), τ 2.54–3.25 multiplet (9 H, aromatic), 7.23 AB quartet (2 H, J = 3.0 cps, CH-CH), 7.38–7.83 multiplet (4 H, CH_2CH_2), ultraviolet (benzene), 290 mμ (ϵ 604), 300 (254), 310 (107), and 320 (30).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.41; H, 5.36; N, 5.19.

Characterization of *trans*-5-*p*-Cyanophenyl-6-phenylbicyclo-[3.1.0]hexan-2-one. Recrystallization from ether yielded a colorless solid, mp 155–157°. The physical data were as follows: infrared (KBr), 4.49 (CN), 5.80 ($C{=}O$), 6.21, 6.69, 7.21, 11.89, 12.00, 12.82, 13.74, and 14.20 μ; nmr ($CDCl_3$), τ 2.20–2.69 multiplet (9 H, aromatic), 7.08 AB quartet (2 H, J = 10.0 cps, CHCH), 7.38–9.22 multiplet (4 H, CH_2CH_2); ultraviolet (benzene), 290 mμ (ϵ 467), 300 (255), 310 (122), and 320 (47).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.46; H, 5.55; N, 5.11.

Photolysis of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. In a typical preparative run, a solution of 1.00 g (3.6 mmoles) of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one in 1 l. of anhydrous benzene was irradiated 3 hr with a 450-w medium pressure Hanovia immersion well apparatus using a Pyrex filter. The solution was purged with nitrogen for 1 hr prior to photolysis and positive pressure maintained during the run. The reaction was followed from the infrared of aliquots which showed development of a 5.83-μ carbonyl absorption at the expense of the 5.95-μ carbonyl band of the starting 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. By the end of the photolysis, the 5.95-μ carbonyl had completely disappeared. Removal of benzene *in vacuo* left a light yellow oil which was subjected to liquid–liquid partition chromatography. The scans varied from run to run, but invariably showed only two peaks with good to fair separation. Using the liquid–liquid partition system given above and a 4.5 × 150 cm thermostated column, a 1.86-g portion of crude photolysate from several runs afforded 1.67 g of material in the first peak appearing at 1.84 l. of upper phase eluent, and 185 mg in the second appearing at 2.24 l. retention volume. The peaks were worked up by diluting with ether, washing, drying, and concentrating *in vacuo*. Crystallization from ether of the oil from the first peak afforded 1.19 g of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 104–106°. Crystallization from ether–hexane of the material in peak 2 gave 85 mg of *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 94–98°.

The filtrate material from peak 1 was chromatographed on a 3 × 67 cm column slurry packed with 5% ether–hexane and deactivated silica gel; 100-ml fractions were taken. Deactivated silica gel was prepared by swirling 300 g of activated silica gel with 500 ml of water, cooling, filtering, and drying at 90° for 8 hr, stirring periodically to let steam escape. Fractions 1–5, 5% ether–hexane, 6–10, 10% ether–hexane, and 11–15, 15% ether–hexane, were empty. Fractions 16–20, 20% ether–hexane, gave 125 mg of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 95–101°. Fractions 21–26, 30% ether–hexane, gave 305 mg of an oily mixture of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Repeated crystallization of this mixture invariably gave material having a melting point range of about 20° (70–90°).

A portion (160 mg) of this mixture was chromatographed on a 2 × 60 cm deactivated silica gel column, slurry packed with 5% ether–hexane; 50-ml fractions were collected. Fractions 1–4, 5% ether–hexane, 5–8, 10% ether–hexane, and 9–12, 15% ether–hexane, were empty. Fractions 13–18, 30% ether–hexane, contained 125 mg of a mixture of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo-[3.1.0]hexan-2-one and *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo-[3.1.0]hexan-2-one. Fractions 19–22, 30% ether–hexane, contained 22 mg of nearly pure *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo-[3.1.0]hexan-2-one as indicated by infrared. Crystallization of this material from hexane gave 10.0 mg, mp 85–91°.

The filtrate material from peak 2 (100 mg) was chromatographed on a 2 × 50 cm deactivated silica gel column slurry packed with 5% ether–hexane; 50 ml fractions were taken. Fractions 1 and 2, 5% ether–hexane, 3–6, 10% ether–hexane, 7–10, 15% ether–hexane, 11–16, 20% ether–hexane, and 17 and 18, 25% ether–hexane, were empty. Fractions 19–24, 25% ether–hexane, and 25 and 26, 30% ether–hexane, contained 5.4 mg of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 103–105°. Fractions 27–35, 30% ether–hexane, contained 41.5 mg of *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 66–84°.

The total yields were as follows: *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, 1.32 g (71.5%); *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one, 127 mg (7%); *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one, 10 mg (0.5%); and 295 mg (16%) of a mixture of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one, the infrared of which indicated that it could not contain more than 20–30% of the latter.

Characterization of *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo-[3.1.0]hexan-2-one. This material was crystallized to a constant melting point of 105–106° from ether. The physical data were as follows: infrared (CS_2), 5.82 ($C{=}O$), 8.02, 8.53, 9.63, 12.08, 13.21, 14.35 μ; nmr (CCl_4), τ 2.78–3.33 multiplet (9 H, aryl), 6.27 singlet (3 H, OCH_3), 7.02–9.28 complex multiplet (6 H, ring CH_2 and cyclopropyl methines). An AB quartet (J_{AB} = 10 cps) can be discerned (τ 7.02, 7.18, 7.43, and 7.59) and the following chemical shifts were calculated: A, τ 7.17; B, τ 7.50. This quartet was assigned to the *cis*-cyclopropyl methine hydrogens. The value of 10 cps for the coupling constant above agrees well with the value of 8.4 cps for *cis*-cyclopropane CH–CH coupling observed by Graham and Rogers.[10] The ultraviolet spectrum showed λ_{max} (cyclohexane) 286 mμ (ϵ 1350), 230 (18,150), (benzene) sh 313 (n–π^*, 55), and sh 302 (n–π^*, 115).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.71; H, 6.50.

Characterization of *cis*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one. This material was recrystallized from ether–hexane to a constant melting point of 98–99°.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.85; H, 6.49.

The physical data were as follows: infrared (CS_2), 5.80 ($C{=}O$), 8.01, 8.48, 9.62, 11.21, 12.09, 13.33, and 14.33 μ; nmr (CCl_4), τ 2.96–3.46 multiplet (9 H, aromatic), 6.28 singlet (3 H, OCH_3), 7.29–7.78 complex multiplet (6 H, CH_2 and methines). An AB quartet with J_{AB} = 4 cps can be picked out at τ 7.28, 7.34, 7.53, and 7.59, and the following chemical shifts calculated: A, τ 7.33, B, τ 7.57. This quartet was assigned to the *trans*-cyclopropyl methine hydrogens. The value of 6 cps for *trans*-cyclopropane CH–CH coupling is reported in the literature.[10] The ultraviolet spectrum showed λ_{max} (cyclohexane) 291 mμ (ϵ 1360), 236 mμ (ϵ 13,900), and (benzene) sh 301 mμ (n–π^*, ϵ 85).

Characterization of *trans*-5-*p*-Methoxyphenyl-6-phenylbicyclo-[3.1.0]hexan-2-one. An analytical sample of this material had a constant melting point of 91–92°.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.87; H, 6.38.

The physical data were as follows: infrared (CS_2), 5.80 ($C{=}O$), 8.01, 8.55, 9.63, 12.09, 13.00, and 14.28 μ; nmr (CCl_4), τ 2.67–3.20 multiplet (9 H, aryl), 6.19 singlet (3 H, OCH_3), 6.82–9.23 complex multiplet (6 H, CH_2 and methine). An AB quartet (J_{AB} = 9 cps) can be picked out at τ 6.82, 6.97, 7.36, and 7.51. The chemical shifts are calculated to be A, τ 6.92, and B, τ 7.41, and can be attributed to the *cis*-cyclopropyl methine hydrogens.[10]

Degradation of *trans*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]-hexan-2-one. To 80 ml of liquid ammonia in an apparatus equipped with a Dry Ice condenser and sodium hydroxide drying tube was added 0.300 g (1.1 mmoles) of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one dissolved in 50 ml of diethyl ether; 0.020 g (2.7 g-atoms) of lithium was then added with stirring. While the metal was dissolving, the solution turned a light yellow-green and a white precipitate formed. The metal dissolved in 30 min and, after stirring for 1 hr, 200 mg of ammonium chloride was added to neutralize the medium. The liquid ammonia was allowed to evaporate and 300 ml of ether was added to the reaction flask. The ether solution was washed, dried, and concentrated *in vacuo*, leaving 0.295 g of a light yellow oil. This was chromatographed on a 3 × 90 cm silical gel column slurry packed in 20% ether–hexane. The column was eluted with 1.5 l. of 20% ether–hexane, 2.5 l. of 25% ether–hexane, 2 l. of 30% ether–hexane, 3 l. of 35% ether–hexane, and 4 l. of 50% ether–hexane; 250-ml fractions were collected. Fractions 23–32 contained 0.047 g of starting material. Fractions 37–46 contained 0.105 g of solid. Recrystallization from ether–hexane yielded 0.070 g (28% based on unrecovered starting material) of solid,mp 106–108°.

The physical data were: infrared of reduction product (CS_2): 4.49 (C≡N), 5.75 (C=O), 6.23, 7.14, 8.69, 11.90, 12.17, 13.05, 13.45, and 14.32 μ. The nmr spectrum ($CDCl_3$) showed: τ 2.57–3.42 multiplet (9 H, aromatic) 7.02 singlet (2 H), 7.41 singlet (2 H), 7.74 singlet (4 H). The ultraviolet spectrum (95% EtOH) showed: λ_{max} 236 mμ (log ϵ 4.24) and 281 mμ (log ϵ 2.91).

Anal. Calcd for $C_{19}H_{17}ON$: 82.88; H, 6.22; N, 5.09. Found: C, 82.72; H, 6.19; N, 5.11.

The product proved identical with authentic 3-*p*-cyanobenzyl-3-phenylcyclopentanone. Infrared, nmr and mixture melting point comparisons were used.

Degradation of *cis*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. To 60 ml of liquid ammonia was added 0.300 g (1.1 mmoles) of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one dissolved in 70 ml of diethyl ether; 0.020 g (2.7 g-atoms) of lithium was then added with stirring. As the metal dissolved, the solution turned a light yellow-green. The metal was completely dissolved in 40 min. After 1.5 hr, 200 mg of ammonium chloride was added, and the liquid ammonia was allowed to evaporate. The remaining ether solution was diluted with 300 ml of ether, washed, dried, and concentrated *in vacuo*, leaving 0.280 g of a light yellow oil. The oil was chromatographed on a 3 × 90 cm silica gel column packed in 20% ether–hexane. The column was eluted with 1.5 l of 20% ether–hexane, 1.5 l. of 25% ether–hexane, 1 l. of 30% ether–hexane, 3 l. of 35% ether–hexane, 1 l. of 45% ether–hexane, 2.5 l. of 50% ether–hexane, and 4 l. of 60% ether–hexane; 250-ml fractions were collected. Fractions 41–54 contained 0.085 g of starting material. Fractions 33–38 contained 0.055 g of solid. Recrystallization from ether–hexane gave 0.045 g (21% based on unrecovered starting material) of solid, mp 106–108°.

The infrared and nmr spectra and melting point of the reduction product of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one were identical with those of the reduction product of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and the independently synthesized 3-*p*-cyanobenzyl-3-phenylcyclopentanone. The mixture melting points were undepressed.

A second reduction product weighing 0.040 g was found in fractions 20–25. The infrared indicated that it was also a cyclopentanone. The material is being further characterized.

Degradation of *trans*-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. To 60 ml of liquid ammonia was added 0.088 g (0.032 mmole) of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one dissolved in 40 ml of diethyl ether; 0.006 g (0.81 g-atom) of lithium was added to the mixture with stirring. The metal dissolved in 15 min, during which time the colorless solution became light yellow at first and finally a dark yellow brown. The solution was deeply colored for 5–10 min, after which it gradually lessened in intensity. Ammonium chloride (150 mg) was added after 45 min to neutralize the medium. The liquid ammonia was allowed to evaporate and 300 ml more ether was added. The ether solution was washed, dried, and concentrated *in vacuo*, leaving a light yellow oil weighing 0.080 g. Thin layer chromatography of the crude material showed it was composed of two compounds. The crude oil was chromatographed on a 3 × 65 cm silica gel column slurry packed in 15% ether–hexane. The column was eluted with 600 ml of 15% ether–hexane, 1 l. of 20% ether–hexane, 1 l. of 25% ether–hexane, 2 l. of 30% ether–hexane, 1 l. of 35% ether–hexane, 1 l. of 40% ether–hexane, 1 l. of 50% ether–hexane, and 3.5 l. of 60% ether–hexane; 200-ml fractions were collected. Fractions 26–39 contained 0.012 g of starting material. Fractions 44–58 contained 0.042 g of solid. Recrystallization from ether–hexane yielded 0.015 g (21% based on unrecovered starting material) of solid, mp 148–149°.

The infrared spectrum of the reduction product (KBr) showed: 4.48 (C≡N), 5.85 (C=O), 11.85, 12.00, 12.27, 12.91, 13.33, and 14.25 μ. The nmr spectrum ($CDCl_3$) showed: τ 2.48–3.60 multiplet (9 H, aromatic), 6.42 singlet (2 H), 6.25–7.50 multiplet (4 H), 7.50–8.2 multiplet (2 H).

Anal. Calcd for $C_{19}H_{17}ON$: C, 82.88; H, 6.22. Found: C, 82.58; H, 6.40.

Infrared, nmrs and mixture melting point comparisons with authentic 4-*p*-cyanophenyl-3-phenylcyclohexanone showed these to be identical.

Degradation of *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one. A dry, one-necked flask fitted with a Dry Ice condenser, dropping funnel, and ammonia inlet was immersed in a Dry Ice–acetone (−78°) bath and 100 ml of ammonia distilled into it. A solution of 400 mg (1.42 mmoles) of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one in 50 ml of anhydrous ether was added to the liquid ammonia solution, and lithium wire (30 mg, 4.28 g-atoms) added immediately thereafter. The mixture was stirred at −78° for 1 hr and then quenched by the addition of excess solid ammonium chloride. The ammonia was allowed to evaporate, and the resulting ethereal solution washed and dried. Concentration of half of the ether solution *in vacuo* gave 202 mg of yellow oil. This oil was subjected to liquid–liquid partition chromatography on a 2.5 × 150 cm column using the usual 100:40:25:3 cyclohexane–DMF–ethyl acetate–water system, and gave a scan showing two main peaks. The first peak appeared at 800 ml upper phase retention volume and contained 150 mg of 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one, mp 99–101°. The second peak contained 19.0 mg of oily starting *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one appearing at 920 ml of upper phase eluent. Crystallization from ether gave 10.1 mg, mp 101–102°. The total yield based on unrecovered starting material was 79%.

Recrystallization from ether–hexane of the 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one obtained above afforded 132 mg, mp 100–102°, and one more recrystallization gave 69.0 mg of an analytical sample, mp 102–103° which did not depress the melting point of an authentic sample of 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one prepared by an independent route (*vide infra*). In addition, the infrared and nmr spectra of the degradation product were exactly the same as the corresponding spectra of the synthetic material.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.41; H, 7.29.

The physical data on 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one were as follows: infrared (CS_2), 5.85 (C=O), 7.99, 8.48, 9.57, 9.67, 12.00, 12.24, and 14.36 μ; nmr (CCl_4), τ 2.85–3.72 multiplet (9 H, aryl), 6.33 (singlet (3 H, OCH_3), 6.4–8.5 poorly resolved multiplet (8 H, CH_2 and methine).

Degradation of *cis*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one. To a Dry Ice-acetone cooled (−78°) solution of 100 mg (0.36 mmole) of *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one in 40 ml of liquid ammonia and 15 ml of anhydrous ether was added with stirring 8.5 mg (1.22 g-atoms) of freshly cut lithium. The reaction was stirred for 1 hr at −78° and then quenched by the addition of excess ammonium chloride. The ammonia was allowed to evaporate, the residue diluted with ether, and the ether solution washed and dried. Ether was removed *in vacuo* yielding 105 mg of yellow oil. This material was subjected to liquid–liquid partition chromatography on a 2.5 × 150 cm column using the 100:40:25:3 cyclohexane–DMF–ethyl acetate–water system, and dry packed with 40% by weight of lower phase on Celite. A scan was obtained containing two major peaks appearing at 760 and 920 ml of upper phase eluent, respectively. Work-up of the first peak afforded 76.5 mg of a new ketone which was shown to be (*vide infra*) 3-phenyl-3-*p*-methoxybenzylcyclopentan-1-one. The second peak contained 8 mg of starting *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, mp 88–98°. The yield, based on unrecovered starting material, was 84%. All attempts to crystallize 3-phenyl-3-*p*-methoxybenzylcyclopentan-1-one were unsuccessful, and an analytical sample was prepared by gradient temperature molecular distillation in an 8 × 100 mm tube.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.33; H, 7.35.

The physical data were as follows: $n^{25}\text{D}$ 1.5765; infrared (CS_2), 5.74 (C=O), 8.02, 8.50, 9.62, 12.17, 13.02, 13.43, 14.33 μ; nmr (CCl_4), τ 2.77–3.52 multiplet (9 H, aromatic), 6.33 singlet (3 H, OCH_3), 7.22 singlet (2 H), 7.55 singlet (2 H), and 7.80 slightly broadened singlet (4 H).

3-Phenylcyclopent-2-en-1-one. This compound was prepared by the method of Borsche and Menz.[39]

3-*p*-Chlorobenzyl-3-phenylcyclopentanone. A. Preparation of *p*-Chlorobenzylmagnesium Chloride. Magnesium (3.06 g, 0.15 g-atom) was placed in a dry flask under nitrogen and 2.2 g (0.015 mole) of freshly distilled *p*-chlorobenzyl chloride was added; the resulting mixture was stirred for 3 min, and 40 ml of ether was added to the

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(39) W. Borsche and W. Menz, *Chem. Ber.*, 41, 190 (1908).

reaction. The remaining 20.0 g (0.135 mole) of *p*-chlorobenzyl chloride, making a total of 22.2 g (0.15 mole), in 70 ml of ether was added dropwise over 1.5 hr. The mixture was refluxed throughout the addition by slight external heating. As the metal reacted, the solution turned dark green; after all the chloride had been added, the mixture was refluxed 1 hr and 15 min. The amount of Grignard reagent present was determined by titration by adding 5.0 ml of the Grignard solution to 75 ml of 0.1 *N* hydrochloric acid and back titrating with 0.1 *N* sodium hydroxide.

B. Addition of *p*-Chlorobenzylmagnesium Chloride to 3-Phenylcyclopentenone. *p*-Chlorobenzylmagnesium chloride solution (0.014 mole as determined by titration) was transferred with a syringe to a second flask which had also been dried under nitrogen and contained 0.040 g of cuprous bromide. The resulting mixture was stirred at room temperature for 45 min and cooled in ice; 1.58 g (0.01 mole) of 3-phenylcyclopent-2-en-1-one dissolved in 50 ml of ether was added dropwise during 1 hr. The dark green solution was stirred at 0° for 1 hr, room temperature for 2 hr, refluxed for 2.5 hr, allowed to stand at room temperature overnight, and then poured onto 100 g of ice, 100 ml of water, and 5 ml of concentrated hydrochloric acid. The mixture was ether extracted, washed, dried, and concentrated *in vacuo*, leaving a light yellow oil weighing 4.0 g. An infrared spectrum indicated that the oil was a mixture of 1,2- (85–90%) and 1,4- (10–15%) addition products. The oil was chromatographed on a 3 × 90 cm silica gel column slurry packed in 5% ether–hexane. The column was eluted with 2 l. of 5% ether–hexane, 3 l. of 10% ether–hexane, 2 l. of 20% ether–hexane, 3 l. of 30% ether–hexane, and 3 l. of 50% ether–hexane; 250-ml fractions were collected. Fractions 5–14 contained 1.7 g of what appeared to be *p,p'*-dichlorobiphenyl from its infrared spectrum and was discarded. Fractions 27–42 contained 0.682 g of the 1,4-addition product. Fractions 45–60 contained 0.534 of the 1,2-addition product which was discarded. The 1,4-addition product could not be crystallized and was chromatographed on a 2.5 × 82 cm alumina (Fisher, 80–200 mesh) column slurry packed in 10% ether–hexane. The column was eluted with 20% ether–hexane. The first 3.5 l. yielded a small amount of oil. The next 3 l. yielded 0.170 g of 3-*p*-chlorobenzyl-3-phenylcyclopentanone as a light yellow solid; recrystallization from ether–hexane yielded 0.075 g of 3-*p*-chlorobenzyl-3-phenylcyclopentanone (2.5%), mp 61–62°.

Spectral data showed: infrared (CS_2), 5.73 (C=O), 7.11, 8.68, 9.16, 9.84, 11.96, 12.43, 13.40, 13.41, and 14.30 μ; nmr ($CDCl_3$), τ 2.50–3.55 multiplet (9 H, aromatic), 7.1 singlet (2 H), 7.4 singlet (2 H), and 7.67 singlet (4 H).

Anal. Calcd for $C_{18}H_{17}OCl$: C, 75.91; H, 6.02; Cl, 12.45. Found: C, 75.99; H, 6.19; Cl, 12.60.

3-*p*-Cyanobenzyl-3-phenylcyclopentanone. The following procedure is patterned after that of Newman and Boden.[8] 3-*p*-Chlorobenzyl-3-phenylcyclopentanone (0.200 g, 0.703 mmole, mp 60.5–62.0°), 0.111 g (0.625 mmole) of cuprous cyanide, and 0.25 ml of N-methylpyrrolidone were refluxed under nitrogen for 21 hr. To the cooled reaction mixture 0.200 g of sodium cyanide in 6 ml of water was added, and the resulting solution was thoroughly mixed. Benzene (50 ml) was then added, and the combined layers were filtered. The benzene layer was washed once with 10% aqueous sodium cyanide and with water and dried and concentrated *in vacuo*, leaving 0.200 g of black solid. The crude material was subjected to chromatography on a 3 × 90 cm silica gel column slurry packed in 10% ether–hexane. The column was eluted with 1 l. of 10% ether–hexane, 3 l. of 20% ether–hexane, and 4 l. of 45% ether–hexane, collecting 500-ml fractions. Fractions 4–10 contained 0.050 g of 3-*p*-chlorobenzyl-3-phenylcyclopentanone. Fractions 21–26 contained 0.045 g of 3-*p*-cyanobenzyl-3-phenylcyclopentanone which on recrystallization from ether gave 0.030 g (21% based on unrecovered starting material), mp 106–108°. The compound had an infrared spectrum in KBr identical with the spectrum of the degradation product from *trans*- and *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. The nmr of the reduction products and that of 3-*p*-cyanobenzyl-3-phenylcyclopentanone were identical. The mixture melting points were undepressed.

***p*-Bromophenylacetonitrile.** This compound was prepared by the method of Misra and Shukla.[40]

***p*-Bromophenylacetic Acid.** A modification of the procedure of Misra and Shukla[40] was used to prepare the acid. *p*-Bromophenylacetonitrile (7.30 g, 0.037 mole) was refluxed with a mixture of 8 ml of concentrated sulfuric acid, 8 ml of glacial acetic acid, and 8 ml of water for 1 hr. The solution was poured onto ice yielding a white solid which was collected, washed with water, dissolved in 5% aqueous sodium hydroxide solution, ether extracted, and acidified with hydrochloric acid, yielding 6.50 g (89%) of a white solid, mp 114–116° (lit.[40] 113–114°).

The infrared spectrum (CS_2) showed bands at 5.83 (C=O), 9.33, 9.87, and 12.51 μ.

***p*-Bromobenzyl Phenyl Ketone.** This material was prepared by the Friedel–Crafts reaction of *p*-bromophenylacetyl chloride and benzene according to the procedure of Huttel, Franke, Martin, and Riedl.[41]

4-*p*-Bromophenyl-3-phenylcyclohex-2-en-1-one. *p*-Bromobenzyl phenyl ketone (2.00 g, 0.0073 mole), mp 151–152°, 0.51 g (0.0073 mole) of methyl vinyl ketone, and 50 ml of ether were placed in a flask cooled in an ice bath. Ethanolic potassium hydroxide (0.200 g of potassium in 2.0 ml of 95% ethanol) was added to the reaction mixture dropwise over 30 min. During the last few minutes a heavy white solid precipitated. The mixture was stirred at 0° for another 30 min; 25 ml of benzene was added to the reaction flask and the resulting mixture was refluxed for 21 hr, during which time the solid dissolved. The reaction was then poured into 100 ml of water, acidified with 1 *N* hydrochloric acid, and ether extracted. The ether layer was washed, dried, and concentrated *in vacuo*, leaving 2.54 g of light yellow solid. The crude solid was chromatographed on a 3 × 90 cm silica gel column slurry packed in 15% ether–hexane. The column was eluted with 2.5 l. of 15% ether–hexane, 1 l. of 20% ether–hexane, 2.5 l. of 30% ether–hexane, and 2.5 l. of 40% ether–hexane; 250-ml fractions were collected. Fractions 5–10 contained 0.170 g of starting material, *p*-bromobenzyl phenyl ketone. Fractions 23–27 contained 1.48 g of 4-*p*-bromophenyl-3-phenylcyclohex-2-en-1-one which on recrystallization from ether gave 1.165 g (49%), mp 108.5–109.5°.

Spectral data showed: infrared (CS_2), 5.98 (C=O), 11.30, 12.14, 12.52, 13.27, and 14.50 μ; nmr ($CDCl_3$), τ 2.42–2.95 multiplet (9 H, aromatic), 3.33 singlet (1 H, CH=), 5.73 singlet (1 H, PhCH), 7.25–8.05 multiplet (4 H, CH_2CH_2).

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.08; H, 4.62; Br, 24.42. Found: C, 66.19; H, 4.50; Br, 24.50.

4-*p*-Cyanophenyl-3-phenylcyclohex-2-en-1-one. The method used was essentially that of Newman and Boden.[8] 4-*p*-Bromophenyl-3-phenylcyclohex-2-en-1-one (1.01 g, 0.0031 mole, mp 108.5–109.5°), 0.456 g (0.0025 mole) of cuprous cyanide, and 2.7 ml of N-methylpyrrolidone were refluxed for 2 hr under nitrogen. The reaction was allowed to cool and then was poured into 0.82 g of sodium cyanide in 20 ml of water. The resulting mixture was shaken thoroughly, 200 ml of benzene was added, and the combined organic and aqueous layers were filtered. The organic layer was washed with 10% sodium cyanide solution, and with water, dried, and concentrated *in vacuo*, leaving 0.91 g of dark brown oil. The oil was chromatographed on a 3 × 90 cm silica gel column slurry packed in 15% ether–hexane. The column was eluted with 1 l. of 15% ether–hexane, 1 l. of 20% ether–hexane, 1 l. of 25% ether–hexane, 1 l. of 30% ether–hexane, 1 l. of 40% ether–hexane, 1 l. of 45% ether–hexane, 1 l. of 55% ether–hexane, 1 l. of 65% ether–hexane, and 3 l. of 75% ether–hexane, collecting 250-ml fractions. Fractions 35–39 contained 0.546 g of 4-*p*-cyanophenyl-3-phenylcyclohex-2-en-1-one which on recrystallization from ether gave 0.360 g (43%), mp 137.5–139.0°.

Spectral data showed: infrared ($CHCl_3$), 4.48 (C≡N), 6.00 (C=O), 6.25, 6.68, 6.93, 7.46, 7.51, 11.30, and 11.95 μ; nmr ($CDCl_3$), τ 2.27–2.88 multiplet (9 H, aromatic), 3.27 singlet (1 H, CH=), 5.58 multiplet (1 H, *p*-N≡CPhCH), 7.17–8.00 multiplet (4 H, CH_2-CH_2).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.27; H, 5.44; N, 5.06.

4-*p*-Cyanophenyl-3-phenylcyclohexanone. 4-*p*-Cyanophenyl-3-phenylcyclohex-2-en-1-one (0.180 g, 0.66 mmole), mp 138–140°, dissolved in 50 ml of ether was added to 50 ml of liquid ammonia. Lithium (0.014 g, 1.98 g-atoms) was added to the reaction flask, and the solution turned bright red. After stirring the solution for 30 min, all the metal had dissolved; during an additional hour of stirring the solution changed from bright red to orange. Ammonium chloride (200 mg) was added to neutralize the medium and caused the solution to turn colorless. The liquid ammonia was then allowed to evaporate. The resulting solution was diluted with 200 ml of ether, washed, dried, and concentrated *in vacuo*, leaving 0.18 g of light yellow oil. This was chromatographed on a 3 × 90

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(40) G. Misra and J. Shukla, *J. Indian Chem. Soc.*, **28**, 480 (1951).

(41) R. Huttel, K. Franke, H. Martin, and J. Riedl, *Chem. Ber.*, **93**, 1433 (1960).

cm silica gel column slurry packed in 20% ether–hexane. The column was eluted with 1.5 l. of 20% ether–hexane, 1 l. of 30% ether–hexane, 1 l. of 40% ether–hexane, 1 l. of 50% ether–hexane, 2 l. of 60% ether–hexane, and 3 l. of 70% ether–hexane; 250-ml fractions were collected. Fractions 28–33 contained 0.070 g of 4-*p*-cyanophenyl-3-phenylcyclohexanone which on recrystallization from ether gave 0.038 g (21%), mp 144–147°. Recrystallization raised the melting point to 148–149°.

The infrared spectrum (KBr) showed bands at 4.48 ($C{\equiv}N$), 5.85 ($C{=}O$), 6.69, 6.90, 7.06, 11.85, 12.00, 12.27, 12.91, 13.33, and 14.25 μ. In $CHCl_3$, bands were at 4.48 ($C{\equiv}N$), 5.85 ($C{=}O$), 6.42, 6.70, 6.91, 7.10, and 12.00 μ. The nmr spectrum ($CDCl_3$) showed peaks at τ 2.48–3.60 multiplet (9 H, aromatic), 6.42 singlet (2 H, PhCH and N=CPhCH), 6.25–7.50 multiplet (4 H), and 7.50–8.20 multiplet (2 H).

Anal. Calcd for $C_{19}H_{17}ON$: C, 82.88; H, 6.22. Found: C, 83.15; H, 6.47.

The compound exhibited the same nmr and infrared spectra as the lithium reduction product of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. The mixture melting point was undepressed.

Benzyl *p*-methoxyphenyl ketone was prepared by the method of Buck and Ide.[42]

3-*p*-Methoxyphenyl-4-phenylcyclohex-2-en-1-one. A solution of 2.0 g (8.84 mmoles) of freshly crystallized benzyl *p*-methoxyphenyl ketone and 0.68 g (9.72 mmoles) of methyl vinyl ketone in 25 ml of anhydrous benzene was cooled to 0° and 1.40 ml of a 40% solution of Triton B methoxide in methanol added with stirring under nitrogen during 3 hr. The ice bath was then removed and the golden red solution stirred for 1 hr at room temperature. The solution was diluted with ether and extracted with water and saturated sodium chloride solution, and the organic layer dried. Evaporation of ether *in vacuo* gave 3.05 g of yellow oil which was chromatographed on a 3.5 × 87 cm silica gel column, slurry packed with 5% ether–hexane; 250-ml fractions were collected. Fractions 1 and 2, 5% ether–hexane, 3–6, 10% ether–hexane, 7–10, 15% ether–hexane, and 11–29, 20% ether–hexane, were essentially empty and were discarded. Fractions 30–38, 20% ether–hexane, gave 1.93 g of oil which crystallized upon trituration with hexane, mp 90–100°. Recrystallization from ether gave 1.06 g (43%), mp 113–115°, and recrystallization from chloroform–hexane gave a constant melting compound, mp 115–116.5°.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.63; H, 6.62.

Spectral data were as follows: infrared (CCl_4), 6.03 ($C{=}O$), 6.25, 8.05, 8.49, 9.63, 12.00, and 14.30 μ; nmr (CCl_4), τ 2.58–3.48 multiplet (10 H, aryl and vinyl), 5.78 broad (1 H, methine), 6.28 singlet (3 H, OCH_3), and 7.17–8.20 broad multiplet (4 H, ring CH_2).

3-*p*-Methoxyphenyl-4-phenylcyclohexan-1-one. 3-*p*-Methoxyphenyl-4-phenylcyclohex-2-en-1-one (100 mg, 0.36 mmole) in 20 ml of anhydrous ether was added dropwise during 15 min to a Dry Ice–acetone cooled (−78°) solution of 7.5 mg (1.08 g-atoms) of lithium in 30 ml of liquid ammonia. The solution was then stirred for an additional hr at −78°. Excess ammonium chloride was added, the ammonia allowed to evaporate, and the residual ether solution washed and dried. Removal of the ether *in vacuo* afforded 88 mg (87%) of oily 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one which crystallized upon trituration with hexane, mp 91–99°. Recrystallization from absolute ethanol gave 40.2 mg, mp 101–103°, which, after recrystallization from hexane (mp 102–103°), proved to be identical in every respect with the 3-*p*-methoxyphenyl-4-phenylcyclohexan-1-one obtained from lithium–ammonia degradation of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one.

3-Phenylcyclopent-2-en-1-one was prepared by the method of Borsche and Menz.[39]

***p*-Methoxybenzyl Chloride.** The method used was a modification of the method of Quelet and Allard.[43] *p*-Methoxybenzyl alcohol (100 g, 0.725 mole) and 181 ml (2.18 moles) of concentrated HCl were stirred together for 1 hr at room temperature. This solution was benzene extracted; the benzene solution was quickly washed with water, sodium bicarbonate solution and again with water, and dried. Removal of benzene *in vacuo* and distillation of the residue gave 47.3 g (42%) of *p*-methoxybenzyl chloride, bp 120° (10 mm) [lit.[43] 113–114° (15 mm)].

3-Phenyl-3-*p*-methoxybenzylcyclopentan-1-one. A suspension of 30 mg of cuprous bromide and 15.0 ml of *p*-methoxybenzylmagnesium chloride solution, prepared from 6.20 g (39.5 mmoles) of *p*-methoxybenzyl chloride, 0.95 g (39.5 g-atoms) of magnesium, and 100 ml of ether, was cooled to 0° by means of an external ice bath, and 1.00 g (6.30 mmoles) of 3-phenylcyclopent-2-en-1-one in 100 ml of anhydrous ether added dropwise during 30 min with stirring under nitrogen. The solution was stirred for 1 hr at 0°; 25.0 ml of Grignard reagent was added, stirring for 30 min at 0°; 20.0 ml of Grignard reagent was added, stirring for 30 min at 0° and for 3.5 hr at room temperature, and finally refluxing for 2.5 hr. After standing overnight, the mixture was hydrolyzed with ice and HCl, and the ether layer washed and dried. Removal of ether *in vacuo* afforded 3.37 g of oily yellow solid, the infrared of which indicated a trace of 5.75-μ carbonyl absorption (cyclopentanone carbonyl).[15] This material was crystallized twice from ether–hexane yielding 1.98 g of yellow solid and 1.39 g of orange oil. The solid appeared from its infrared to be a mixture of starting 3-phenylcyclopent-2-en-1-one and *p*-methoxybibenzyl. The infrared of the solid material contained no 5.75-μ carbonyl, whereas the infrared of the oily material showed that it contained an enhanced proportion of 5.75-μ material. This oily material was placed on a 3.5 × 93 cm silica gel chromatography column slurry packed with 5% ether–hexane, and 500-ml fractions were taken. After elution with 2 l. of 5% ether–hexane, 4 l. of 10% ether–hexane, 4 l. of 15% ether–hexane, 2 l. of 20% ether–hexane, and 1.5 l. of 25% ether–hexane, 102 mg of colorless oil was eluted with 25% ether–hexane. The infrared showed this to be a mixture composed mainly of the desired 5.75-μ compound with varying lesser amounts of starting material.

The 102 mg was chromatographed on a 2.5 × 50 cm alumina column, slurry packed with 10% ether–hexane; 250-ml fractions were collected. After elution with 2 l. of 10% ether–hexane, 2 l. of 15% ether–hexane, 2 l. of 20% ether–hexane, 2 l. of 25% ether–hexane, 2 l. of 30% ether–hexane, 2 l. of 40% ether–hexane, 2 l. of 50% ether–hexane, and 2 l. of 65% ether–hexane, 40 mg of pure 3-phenyl-3-*p*-methoxybenzylcyclopentan-1-one, $n^{25}D$ 1.5759, was obtained upon elution with 4 l. of 80% ether–hexane. The infrared of this material was exactly identical with the infrared of the material obtained from the lithium–ammonia treatment of *cis*-5-phenyl-6-anisylbicyclo[3.1.0]hexan-2-one. The nmr spectra of both compounds were also exactly the same.

Photolysis of *trans*-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Using the standard procedure described above, 0.500 g (1.83 mmoles) of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one was photolyzed in 1 l. of benzene for 24 hr with a Pyrex filter. The benzene was removed *in vacuo* leaving 0.500 g of colorless oil. The crude oil was subjected to liquid–liquid partition chromatography on a 5 × 150 cm column packed with a mixture of 700 g of Celite and 305 ml of lower phase. The eluate was scanned at 260 mμ and collected in 40-ml fractions. Fractions 43–72 contained 0.068 g of starting material. Fractions 73–78 contained 0.066 g of a mixture of starting material and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Fractions 79–130 contained 0.260 g of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. The separation of the mixture consisting of *trans*-5-phenyl-6-*p*-cyanophenyl- and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one was carried out by chromatographing the mixture on a 1.2 × 85 cm silica gel column, slurry packed in 20% ether–hexane. The column was eluted with 25% ether–hexane, and the eluate was scanned at 270 mμ and collected in 20-ml fractions. Fractions 30–58 contained 0.038 g of starting *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, and fractions 63–100 contained 0.028 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one.

The yields of photoketones obtained from the irradiation of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one for varying lengths of time are shown in Table V.

Table V

Photolysis, hr	Photoketone **16a**, g (%)	Photoketone **16b**, g (%)	Photoketone **16c**, g (%)
2.5	0.167 (33.4)	0.239 (47.8)	(1–2, estimated by infrared)
24	0.106 (21.2)	0.260 (52.0)	0.028 (5.6)
92	0.090 (18.0)	0.290 (58.0)	0.040 (8)

Photolysis of *trans*-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Using the standard procedure described above, 0.095 g

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[42] J. S. Buck and W. S. Ide, *J. Am. Chem. Soc.*, **54**, 3012 (1932).

[43] R. Quelet and J. Allard, *Bull. Soc. Chim. France*, **4**, 1468 (1937)

(0.349 mmole) of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]-hexan-2-one, dissolved in 300 ml of benzene, was irradiated for 20 hr using a Pyrex filter. The course of the photolysis was followed by determining the infrared of aliquots removed during the photolysis; little change was indicated after 8 hr. Concentration *in vacuo* left 0.095 g of colorless oil which was subjected to liquid-liquid partition chromatography. The 2.5 × 150 cm column was packed with a mixture of 700 g of Celite and 305 ml of lower phase. The column was eluted with upper phase, and the eluate was scanned at 256 mμ and collected in 20-ml fractions. Fractions 45-58 contained 0.045 g of starting material, and fractions 68-85 contained 0.035 g of a new photoproduct which was shown (*vide infra*) to be *cis*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one, mp 96-99°; continued recrystallization raised the melting point to 103-104°. Fractions 59-67 contained 0.013 g of material which was not characterized; however it was neither *cis*- nor *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one.

Characterization of *cis*-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]-hexan-2-one. Infrared spectral data (KBr) showed: 4.47 (CN), 5.80 (C=O), 6.22, 8.35, 8.56, 11.97; 12.40, and 14.32 μ. Nmr spectral data ($CDCl_3$) showed: τ 2.43-3.33 multiplet (9 H, aromatic), 7.18 AB quartet (2 H, *J* = 3 cps, CHCH), and 7.37-7.92 multiplet (4 H, CH_2CH_2).

Anal. Calcd for $C_{19}H_{15}ON$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.43; H, 5.47; N, 5.14.

Photolysis of *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one. A solution of this material (415 mg, 1.49 mmoles) in 500 ml of benzene was photolyzed as above for 20.0 hr. Aliquots were removed periodically for ultraviolet analysis and showed a buildup of opacity in the 300-350-mμ region which diminished somewhat toward the end of the photolysis. Removal of benzene *in vacuo* afforded 434 mg of yellow oil which was chromatographed on a 2.5 × 87 cm silica gel column, slurry packed with 5% ether-hexane; 125-ml fractions were collected. After elution with 500 ml of 5% ether-hexane, 750 ml of 10% ether-hexane, 1 l. of 15% ether-hexane, and 1 l. of 20% ether-hexane, elution with 2 l. of 22.5% ether-hexane yielded 191.3 mg (48.7%), mp 100-102°, of crystalline material identical in every respect with starting material, *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one. Further elution with 2.125 l. of 27% ether-hexane gave 139 mg, mp 94-96° (35.3%), of *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo-[3.1.0]hexan-2-one, exactly identical (infrared, melting point) with the material isolated from the photolysis of 4-*p*-methoxyphenyl-4-phenylcyclohex-2-en-1-one. No other products were isolated or indicated. The total yield of crystalline product, based on unrecovered starting material, was 84%.

Photolysis of 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one for Varying Lengths of Time. 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one (0.500 g, 1.83 mmoles) dissolved in 1 l. of benzene was irradiated with a 450-w, medium pressure, Hanovia immersion well apparatus in the same manner as previously described. Three identical runs were carried out: one for 15 min, one for 30 min, and one for 1 hr. The three irradiation runs were worked up in the same manner; the following is a typical example. The benzene was removed *in vacuo* leaving 0.510 g of colorless oil which was first subjected to liquid-liquid partition chromatography. The 5 × 150 cm column was packed with 700 g of Celite and 305 ml of lower phase. The eluate was scanned at 260 mμ and collected in 40-ml fractions. Fractions 62-67 contained 0.122 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Fractions 68-79 contained 0.265 g of a mixture containing *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one and 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one. Fractions 80-94 contained 0.080 g of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Fractions 68-79 were then chromatographed on a 2.5 × 90 cm silica gel column, slurry packed in 20% ether-hexane. The column was eluted with 3 l. of 20% ether-hexane, 6 l. of 25% ether-hexane, 1 l. of 30% ether-hexane, and 2 l. of 30% ether-hexane; 250-ml fractions were collected. Fractions 15-24 contained 0.178 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Fractions 26-34 contained 0.027 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Fractions 35-43 contained 0.033 g of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one. Table VI summarizes the results of these three photolyses.

Table VI[a]

Photolysis, hr	%			
	Recovered enone	**16a**	**16b**	**16c**
0.25	59	30	2	2.4
0.5	29	49	5.4	3.6
1.0	7	60	18	5.4

[a] **16a** is *trans*-5-phenyl-6-*p*-cyanophenyl bicyclic ketone, **16b** is *cis*-5-phenyl-6-*p*-cyanophenyl bicyclic ketone, and **16c** is *trans*-5-*p*-cyanophenyl-6-phenyl bicyclic ketone.

Photolysis of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one for Varying Times. Three solutions, each composed of 500 mg (1.80 mmoles) of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one in 700 ml of dry, distilled benzene, were photolyzed through a Pyrex filter for 25, 15, and 6 min, respectively. Each photolysis was carried out under the same conditions, that is, same lamp (Hanovia, 450-w, medium pressure), same purging conditions (nitrogen, 1 hr prior to photolysis), same container, and same temperature. The photolyses were monitored by ultraviolet and showed no buildup of opacity. Each solution was concentrated *in vacuo* and subjected to scanning liquid-liquid partition chromatography on a 4.5 × 150 cm column packed in the usual manner. Since neither *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one nor *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one can be separated from starting 4-*p*-methoxyphenyl-4-phenylcyclohex-2-en-1-one by liquid-liquid chromatography, only *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one was separated by this procedure. All three photolyses were chromatographed on the same column, and the products were eluted at the following upper-phase retention volumes (length of photolysis, weight of mixture of starting enone and *trans*-photoketones, retention volume of mixture, weight of *cis*-photoketone, retention volume of *cis*-photoketone, melting point of *cis*-photoketone): 15 min, 469 mg, 0.94 l., 4.4 mg, 1.28 l., 95-98°; 6 min, 468 mg, 2.32 l., 0 mg; 25 min, 470 mg, 5.14 l., 9.7 mg, 5.50 l., 93-98°.

The amount of *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]-hexan-2-one in the above mixtures was impossible to determine quantitatively. The liquid-liquid chromatography achieved partial separation of these three component mixtures, with the order of elution being (1) *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]-hexan-2-one, (2) *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]-hexan-2-one, and (3) 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. Qualitative infrared analysis of fractions where *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one was expected gave the results shown in Table VI. The limit of infrared detection was assumed to be 10%.

The composition of the mixture remaining after removal of the *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one was determined by means of both quantitative infrared and nmr spectroscopy. In the spectral analysis, *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo[3.1.0]hexan-2-one was ignored, since it was formed in very minor amounts.

The infrared analysis[44] was carried out using the formula

$$Q = (D_{\mathrm{mixt}}{}^{\lambda_E} D_A{}^{\lambda_A} - D_{\mathrm{mixt}}{}^{\lambda_A} D_A{}^{\lambda_E})/(D_{\mathrm{mixt}}{}^{\lambda_A} D_E{}^{\lambda_E} - D_{\mathrm{mixt}}{}^{\lambda_E} D_E{}^{\lambda_A})$$

in which *D* is optical density and subscripts *A* and *E* refer to *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one, respectively. Samples consisted of 43 ± 1 mg of material in 0.20 ml of carbon disulfide. Three spectra were made of each sample, and the results averaged. The result of analysis of a series of known mixtures is shown in Table VII.

Table VIII outlines the results obtained from analysis of the unknown mixtures.

Peak height analysis of the nmr spectra was also carried out on the same unknown mixtures. The method used was essentially the same as for the infrared analysis, but, instead of optical densities, the peak heights were measured in centimeters. The peaks chosen were the main aryl peaks of *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one and 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one occurring at τ 2.78 and 2.82, respectively. Each sample consisted of 50 ± 1 mg of material dissolved in 0.50 ml of carbon tetrachloride. Four spectra were made of each sample, and the results averaged. The data in Table IX show the results obtained with known mixtures, and Table X gives the values obtained with the unknown mixtures.

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(44) H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956); H. E. Zimmerman and H. J. Giallombardo, *ibid.*, **78**, 6259 (1956).

Table VII. Analysis of Known Mixtures of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one Plus *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17a**)

% **17a**$_{act}$	R_{act}	Q^a	F	F_{used}	R_{calcd}	% **17a**$_{calcd}$
19.5	4.12	5.42	0.76	0.82	4.44	18.4
28.0	2.57	3.38	0.76		2.77	26.5
39.5	1.54	1.88	0.82		1.54	39.5
51.8	0.93	1.09	0.85		0.90	52.8
75.6	0.32	0.36	0.89		0.30	77.1

[a] Determined at the following wavelengths: *A*, 12.65 μ; *E*, 12.94 μ.

Table VIII. Analysis of Unknown Mixtures of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one Plus *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (**17a**)

Photolysis, min	Q	F_{used}	R_{calcd}	% **17a**$_{calcd}$
6.0	8.40	0.82	6.89	12.7
15.0	3.28		2.69	27.1
25.0	2.01		1.65	37.7

Table IX. Nmr Analysis of Known Mixtures of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one Plus *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one (17a)

% **17a**$_{act}$	R_{act}	Q	F	F_{used}	R_{calcd}	% **17a**$_{calcd}$
9.0	10.10	8.01	1.26	1.13	9.05	9.9
13.1	6.62	5.42	1.22		6.13	14.0
20.6	3.86	2.44	1.12		3.89	20.4
26.4	2.79	2.41	1.16		2.73	26.8
33.3	2.00	1.78	1.12		2.01	33.2
40.5	1.47	1.30	1.13		1.47	40.5
48.9	1.05	0.98	1.07		1.10	47.5

Table X. Nmr Analysis of Unknown Mixtures of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one Plus *trans*-5-Phenyl-6-*p*-methoxyphenylbicyclo[2.1.0]hexan-2-one

Photolysis, min	Q	F_{used}	R_{calcd}	% **17a**$_{calcd}$
6.0	7.41	1.13	8.37	10.7
15.0	2.52		2.85	26.0
25.0	1.52		1.72	36.8

Table XI gives the over-all results obtained from these three photolyses.

Table XI. Over-all Results of Photolysis of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one for Varying Times (Corrected for Per Cent of **17b** and **17c** Present)[a]

Photolysis, min	%					
	Recovered enone		**17a**			
	Infrared	Nmr	Infrared	Nmr	**17b**	**17c**
6	86.4	88.4	12.6	10.6	None[b]	1
15	70.7	71.8	26.4	25.3	0.9	2
25	59.2	60.1	35.9	35.0	1.9	3

[a] **17a** is *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, **17b** is *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one, and **17c** is *trans*-5-*p*-methoxyphenyl-6-phenylbicyclo-[3.1.0]-hexan-2-one. [b] <0.2%.

Filter Solution Used for Photosensitization of 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one and 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. The following filter solution is that described by Zimmerman and Givens.[17] The solution was prepared by dissolving 40.0 g of copper sulfate·5H_2O, 315 g of nickel sulfate·6H_2O, 600 g of cobalt sulfate·7H_2O, and 47.0 g of potassium nitrate in 1 l. of water. The per cent transmission of this solution at various wavelengths is as follows [wavelength, mμ (per cent transmission)]: 300 (0.00), 310 (0.50), 320 (7.00), 330 (27.50), 340 (37.20), 350 (30.50), 360 (14.20), 370 (2.50), 380 (0.20), 390 (0.00), 400 (0.00).

Actinometry. Potassium ferrioxalate[45] (3.00 g) was dissolved in 900 ml of water and 100 ml of 1.0 *N* sulfuric acid. The resulting solution was irradiated for 5 min with the same mercury lamp and filter solution as was used for the standard photolysis and for the sensitized photolysis. A 1.00-ml aliquot of the ferrioxalate solution was then added to a 25-ml volumetric flask. To this was added 3.00 ml of a 0.1% solution of 9,10-phenanthroline prepared by dissolving 1.0009 g of the hydrochloride salt in 1000 ml of water. Next 2.00 ml of a buffer solution prepared by adding 600 ml of 1 *N* sodium acetate to 360 ml of 1 *N* sulfuric acid and adding enough water to yield a total volume of 1000 ml was added to the volumetric flask. Finally, distilled water was added to bring the total volume to 25 ml. The resulting mixture was shaken thoroughly and was allowed to stand in the dark for 30 min. The optical density of the mixture at 510 mμ was determined. From the optical density, the concentration of ferrous ion was determined from a standard curve of optical density *vs.* ferrous ion concentration. The above procedure was also followed to determine the light output of the lamp after the standard and sensitized photolysis.

Photosensitization of 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one. Potassium ferrioxalate solution was first irradiated to check the light output of the lamp. A standard photolysis of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one was then carried out; next, the sensitized photolysis of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one was run. Finally, the light output of the lamp was checked again by irradiating ferrioxalate solution once more.

Standard Photolysis. 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one (0.350 g, 1.285 mmoles), mp 81–82°, dissolved in 700 ml of benzene was irradiated for 10 min with a 450-w, medium pressure, Hanovia immersion well apparatus. The filter solution allowed only light from 320 to 370 mμ to enter the photolysis cell. An approximate Beer's law calculation showed 17% of the light to be absorbed by enone reactant. The benzene was then removed *in vacuo*, leaving 0.350 g of a light oil. The oil was chromatographed on a 2.5 × 90 cm silica gel column, slurry packed in 20% ether–hexane. The column was eluted with 7 l. of 25% ether–hexane, 4 l. of 30% ether–hexane, and 2 l. of 40% ether–hexane, collecting 500-ml fractions. Fractions 6–13 contained 0.042 g (12%) of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Fractions 16–24 contained 0.300 g (86%) of starting material, 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one. Traces of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one were found. However, they were present in such small amounts that they could not be isolated.

Sensitized Photolysis Run. 4-*p*-Cyanophenyl-4-phenylcyclohex-2-en-1-one (0.350 g, 1.285 mmoles), mp 81–82°, and 14.0 g (0.167 mole) of acetophenone dissolved in 700 ml of benzene were irradiated for 10 min. The amount of acetophenone added was such that it absorbed 98% of the light transmitted by the filter solution. The filter solution was the same one used for the standard run. The benzene was then removed *in vacuo*, leaving the mixture of acetophenone and photoketones. The acetophenone was removed by placing the mixture under a vacuum of 0.025 mm and heating it in a water bath to 38°. The remaining oil was subjected to chromatography on a 2.5 × 90 cm silica gel column, slurry packed with 20% ether–hexane. The column was eluted with 3 l. of 20% ether–hexane, 8 l. of 25% ether–hexane, 4 l. of 30% ether–hexane, and 4 l. of 40% ether–hexane; 500-ml fractions were collected. Fractions 7–16 contained 0.147 g (42%) of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one. Fractions 18–19 contained 0.010 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]-hexan-2-one. Fractions 20–21 contained 0.004 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one and 0.025 g of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one as determined by infrared analysis. Fractions 22–27 contained 0.095 g of 4-*p*-cyanophenyl-4-phenylcyclohex-2-en-1-one. Fractions 29–36 contained 0.052 g (15%) of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one.

Photosensitization of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one. A solution (1 l.) of 500 mg (1.80 mmoles, 0.0018 *M*) of 4-

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

phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one plus 30.16 g (0.251 mole, 0.251 *M*) of acetophenone in anhydrous benzene was photolyzed for 11.0 min through the filter solution previously described.[17]

Next, a control photolysis was carried out in which 500 mg (1.80 mmoles) of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one in 1 l. of anhydrous distilled benzene was photolyzed for 11.0 min using the filter solution previously described,[17] but with no acetophenone present. Both the control and the sensitized runs were purged with nitrogen 1 hr prior to photolysis.

Before and after these photolyses, the light output of the lamp (Hanovia medium pressure mercury lamp, 450 w) was determined by ferrioxalate actinometry as previously described. These actinometry runs indicated that the light output of the lamp had not changed during the course of the experiment. Ultraviolet spectra of the reaction solution taken before and after the sensitized run were virtually identical. Additionally, the ultraviolet of the filter solution before and after the experiment showed that it had not changed appreciably during the course of photolysis.

The control and sensitized runs were freed of benzene by concentration *in vacuo*. In addition, the acetophenone was removed from the sensitized run at 35–40° (0.05 mm) with stirring. Each run was then chromatographed on a 2.5 × 95 cm silica gel column, slurry packed with 5% ether–hexane; 250-ml fractions were taken in each case. After elution with 250 ml of 5% ether–hexane, 1 l. of 10% ether–hexane, 1 l. of 15% ether–hexane, and 1 l. of 20% ether–hexane, the crude photolysate from the control run (521 mg) afforded 490 mg of a mixture of 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one and *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one upon elution with 3 l. of 22.5% ether–hexane. The composition of this mixture was determined directly by infrared and nmr analysis as previously described, and gave the results shown in Table XII. No *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one was isolated or indicated.

Table XII. Over-all Results of Sensitized Photolyses of 4-Phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one for Varying Times[a]

Type of photolysis	Photolysis time, min	% Recovered enone Infrared	Recovered enone Nmr	17a Infrared	17a Nmr	17b	17c
Sensitized	4.0	. . .	91.8	. . .	7.7	None[b]	0.5
Control	11.0	89.6	85.5	9.4	13.5	None[b]	1
Sensitized	11.0	66	64.9	32.0	33.1	None[b]	2

[a] **17a** is *trans*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, **17b** is *cis*-5-phenyl-6-*p*-methoxyphenyl bicyclic ketone, and **17c** is *trans*-5-*p*-methoxyphenyl-6-phenyl bicyclic ketone. [b] <0.2%.

The column containing the crude material (591 mg) from the sensitized photolysis was eluted with 500 ml of 5% ether–hexane, 750 ml of 10% ether–hexane, 750 ml of 15% ether–hexane, and 1 l. of 20% ether–hexane; 479 mg of a mixture of starting 4-phenyl-4-*p*-methoxyphenylcyclohex-2-en-1-one and *trans*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one was obtained by elution with 3 l. of 22.5% ether–hexane. This mixture was analyzed by infrared and nmr; the results are shown in Table XII. Again, no *cis*-5-phenyl-6-*p*-methoxyphenylbicyclo[3.1.0]hexan-2-one could be detected.

A second sensitized photolysis was carried out exactly as above, but for 4.0 min. The results of this run are summarized in Table XII.

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A Reinterpretation of the Nuclear Magnetic Resonance Spectrum of Cyclobutene

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Abstract: A reinvestigation of the nmr spectrum of cyclobutene has led to a revised set of coupling constants which is consistent both with the ^{13}C proton satellite spectra of cyclobutene and with the spectra of partially deuterated cyclobutene isomers. The present treatment differs from that reported previously by inclusion of long-range ^{13}C–C–H and ^{13}C–C–C–H couplings which in effect make the two methylene groups and the two vinyl hydrogens nonequivalent.

The nmr spectrum of cyclobutene consists of two rather sharp lines without obvious indication of spin–spin coupling.[2–4] Several explanations have been put forth for the intriguing simplicity of this spectrum.[3,5,6] Most recently, Borčić and Roberts[6] have examined the ^{13}C satellites in the proton resonance spectra of cyclobutene and cyclobutene-1,2-d_2. These exhibit coupling patterns of considerable complexity. A complete set of proton–proton coupling constants was derived by matching observed and calculated ^{13}C satellite spectra. It now appears, on the basis of results presented below, that an oversimplification in the calculations resulted in a substantial error in the derived values for J_{13} ($=J_{25}$) and J_{15} ($=J_{23}$). In addition, higher quality satellite spectra have now been obtained, which require slightly revised values for some of the other coupling constants. In the discussion to follow, the numbering (I) of Borčić and Roberts[6] is retained.

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