Excited State Bond Weakening in Photochemical Rearrangements of Cyclopropyl Ketones. Exploratory and Mechanistic Organic Photochemistry. XLVIII[1]

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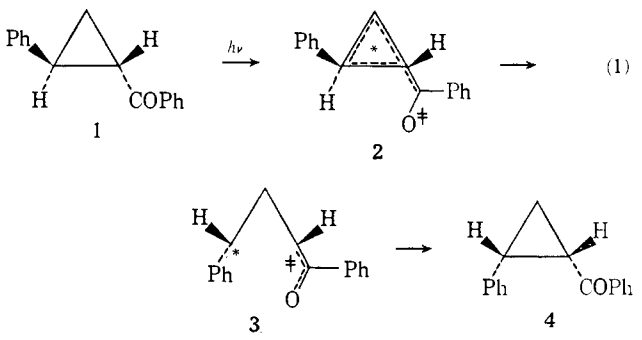
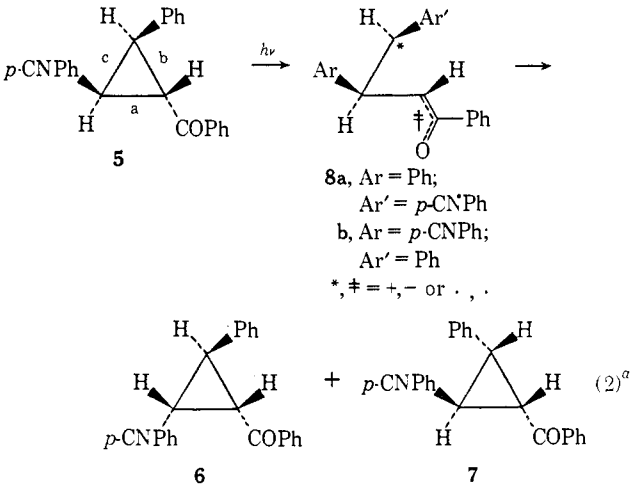
Abstract: An extraordinarily facile photoisomerization of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**) was encountered, affording the two *cis,trans* stereoisomers **6** and **7**. The quantum yield of reaction was 0.81. The reaction was shown to proceed *via* the triplet excited state by sensitization, quenching, and stereochemical studies. The triplet was found to stereoisomerize at a rate of over 10^{11} sec^{-1}. The preferred stereochemistry led to *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**) in a 3.5:1 ratio to *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**). The reaction stereochemistry was studied using optically active **5**. It was shown that the stereochemistry was controlled by an 8:1 preference for fission of bond 1–2 in the excited state followed by rotation about bond 2–3 and reclosure. Scission of bond 1–3 was shown to occur, but less efficiently; rotation of *two* groups in the open biradicals was also found but was minor. The results show that in the reacting excited state electron density is not diminished in the three-membered ring but rather points toward odd electron delocalization.

A large number of photochemical reactions involve fission of a cyclopropyl bond conjugated to a carbonyl group, and therefore delineation of the nature of the excited state of cyclopropyl ketones is basic to an understanding of a large body of photochemical literature. For example, in the *cis–trans* interconversion of 1-benzoyl-2-phenylcyclopropane[3] one might envisage an excited state which is electron deficient in the three ring, one which is electron rich, or one which is neither but possesses odd electron density in the three ring. Very recently results from these laboratories have excluded the possibility that the three-membered ring is appreciably electron rich in the excited state.[4] Equation 1 does not show the nevertheless intriguing alternative that a discrete opened species is not involved in the reaction but rather a concerted conrotatory or disrotatory twisting about two three-ring bonds is involved.



1 2 3 4 (1)

Our approach to the problem utilized the photochemistry of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**). Our reasoning was that in this case two stereoisomeric *cis,trans* products (*i.e.*, **6** and **7**) were *a priori* possibilities, and by studying the distribution of these products one would be able to assess to what extent the different three-ring bonds are broken in the reaction. To the extent that electron density is withdrawn from the three ring in the excited state and during reaction, one would anticipate preferential bond b fission; that is, one would not expect the open species (**8a**, *,‡ = +,−) with a positive charge benzylic to the cyanophenyl group to be favored. On the other hand, to the extent that the excited state has a three ring with odd electron density, one would predict a preferred fission of bond a. The intervention of bond c fission and concerted conrotatory or disrotatory rotations also needed to be assessed in this study. Our approach (*vide infra*) required the synthesis of racemic and optically active cyclopropane stereoisomers **5**, **6**, and **7** and correlation of their configurations as a prelude to the mechanistic aspects.



5 → 8a, Ar = Ph; Ar' = *p*-CNPh; b, Ar = *p*-CNPh; Ar' = Ph; *,‡ = +,− or ·,·

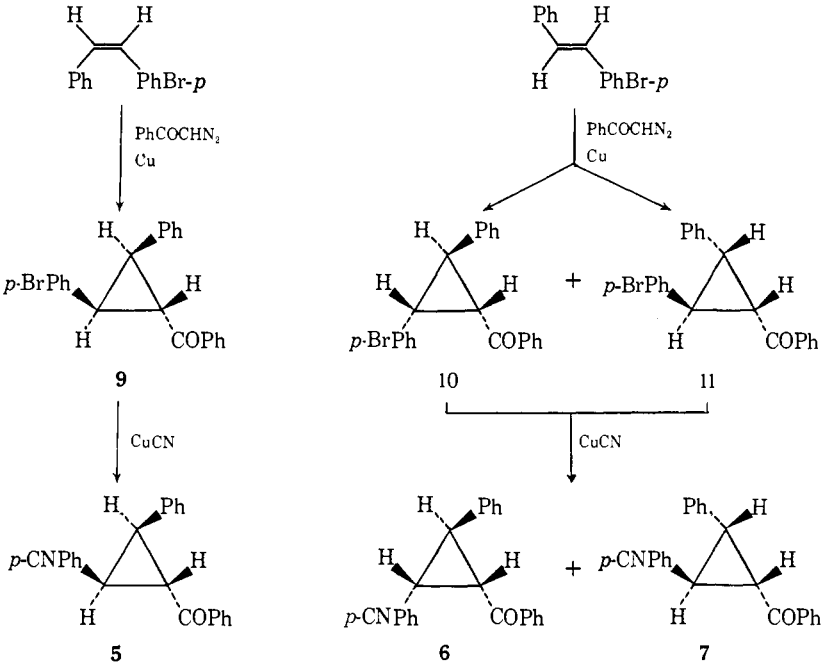
6 + 7 (2)[a]

[a] Relative configurations within each structure are meaningful but are not meant to connote relative configurations between reactant and products.

Synthetic Aspects. Two approaches to the synthesis of the required three stereoisomeric 2-*p*-cyanophenyl-3-phenyl-1-benzoylcyclopropanes (**5**, **6**, and **7**) proved

(1) (a) For paper XLVII, see H. E. Zimmerman and G. Jones, Jr., *J. Amer. Chem. Soc.*, in press; (b) paper XLVI: *ibid.*, **91**, 5678 (1969).
(2) NSF Predoctoral Fellow, 1965–1969.
(3) (a) R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc.*, 144 (1964). (b) Unpublished results on the mechanism of the reaction by H. E. Zimmerman and R. W. Binkley.
(4) H. E. Zimmerman and C. M. Moore, *J. Amer. Chem. Soc.*, **92**, 2023 (1970).

Chart I. Synthesis of Racemic *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**), *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**), and *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**)



useful. These involved the copper-catalyzed stereospecific addition of ethyl diazoacetate and also of diazoacetophenone to *cis*- and *trans*-*p*-bromostilbenes. In the case of diazoacetophenone addition, the *p*-bromo-substituted cyclopropane products **9**, **10**, and **11** were converted to the desired *p*-cyano compounds **5**, **6**, and **7** with cuprous cyanide in N-methylpyrrolidone; compounds **10** and **11** were not readily separated and were thus treated as a mixture. Compounds **6** and **7** were known to be the *cis,trans* and *trans,cis* isomers by their mode of synthesis; however, the actual assignment of geometric configuration derived from deuterium labeling and nmr studies is described below. The diazoacetophenone approach is outlined in Chart I.

For preparation of the resolved *trans,trans*, *cis,trans*, and *trans,cis* isomers (**5**, **6**, and **7**), the ethyl diazoacetate approach proved ideal, since resolution of the three acids—*trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid (**13**), *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid (**16**), and *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid (**17**) could be conveniently effected. Thus, the initial adduct **12**, produced from the addition of ethyl diazoacetate to *cis*-*p*-bromostilbene and saponification, was converted to the desired *trans,trans* acid **13** with cuprous cyanide. In the *trans*-*p*-bromostilbene case, the *p*-bromo-substituted products—the *cis,trans*- and *trans,cis*-cyclopropane acids **14** and **15**—could not be separated, nor could the desired *p*-cyano acids **16** and **17** produced by action of cuprous cyanide on the mixture of **14** and **15**. However, methyl esters **18** and **19** were readily separable by column chromatography; saponification then afforded **16** and **17**.

trans-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid (**13**) was resolved *via* the cinchonidine salt. Treatment of the corresponding acid chloride with diphenylcadmium afforded optically active *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**(+)). *cis*-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid (**16**) and *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid (**17**) were likewise resolved with cinchonidine, and in these cases both enantiomers were obtained. One enantiomer of each of the optically active acids was then converted to the corresponding phenyl ketone to give *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**(−)) and *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**(+)). Throughout these syntheses the compounds were brought to constant rotation; in the cases of the three isomeric cyclopropane ketones **5**(+), **6**(−), and **7**(+), the resolution was followed by ORD analysis as well. Not only the rotations but also the shapes of the ORD curves did not change on repeated crystallization, providing strong evidence for the purity of these ketones and assuring the absence of any highly rotating impurities. The entire sequence is outlined in Chart II.

Assignment of Geometric Configurations. Because the synthesis of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**) and *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**) did not define the configurations of these products, an approach using monodeuterated compounds was employed. Accordingly, *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane (**6**-*d*) and *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-3-*d*-1-benzoylcyclopropane (**7**-*d*) were synthesized photochemically (*vide infra*) from *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane, which, in turn, was prepared by a route similar to that employed for the nondeuterated compound (see Chart III).

The nmr spectra of the monodeuterio derivatives were inspected; the chemical shifts for H_1 and H_2 and the coupling constant J_{12} were calculated[5] from the AB quartet spectra. These values are collected in Table I.

The H_1–H_2 coupling constants of 5.2 and 5.3 Hz in compounds **5**-*d* and **7**-*d*, respectively, are quite typical of those observed for hydrogens situated *trans* on a cyclopropane ring; such values range from 3.9 to 8.0

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 89.

Chart II. Synthesis of Optically Active *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**(+)), *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**(−)), and *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**(+))

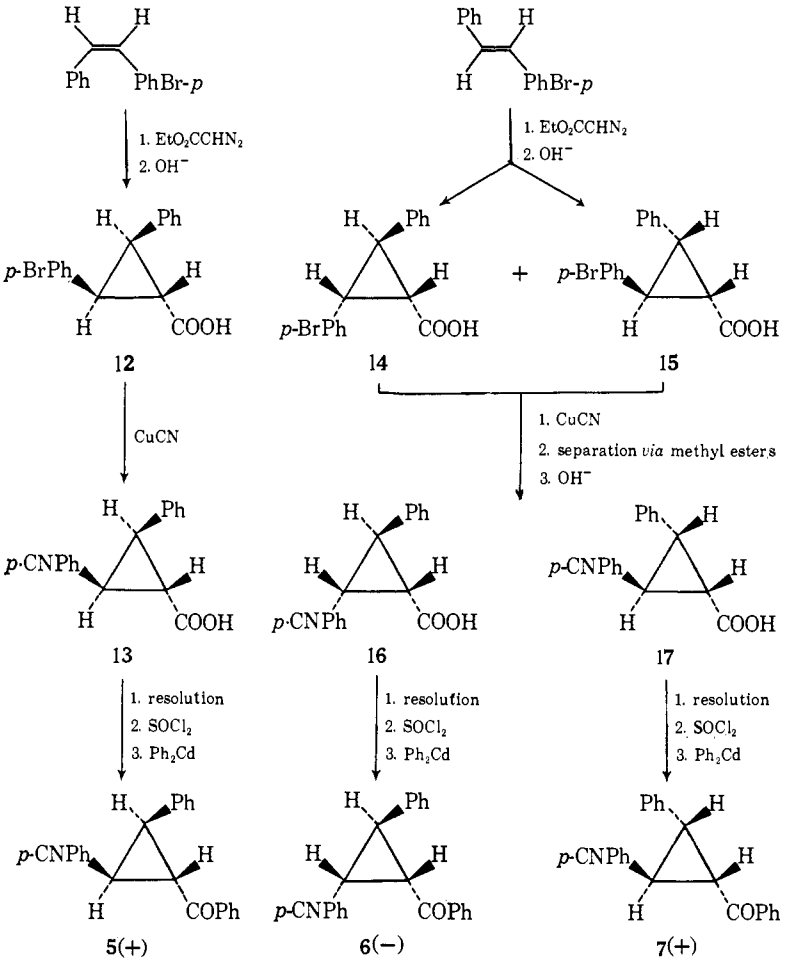
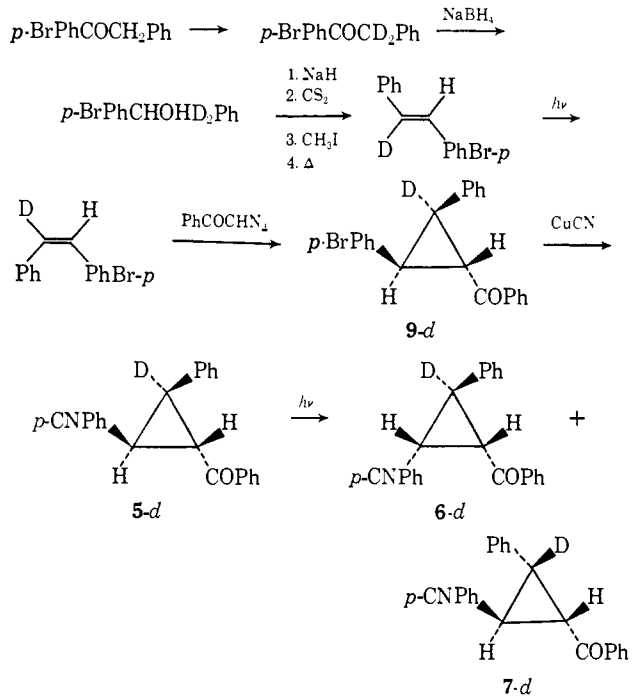


Chart III. Synthesis of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane (**5**-*d*), *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane (**6**-*d*), and *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-3-*d*-1-benzoylcyclopropane (**7**-*d*)



Hz.[6] On the other hand the 9.5-Hz H_1–H_2 coupling constant found in **6**-*d* indicates that the hydrogens are *cis*, since the literature[6] indicates that coupling constants for *cis*-cyclopropyl hydrogens fall within the range of 7.3–11.2 Hz. Thus the nmr confirms the stereochemistry assigned to **5**-*d* based on the mode of synthesis, and of the *cis,trans* and *trans,cis* isomers, **6**-*d* is *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane, and **7**-*d* is *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-3-*d*-1-benzoylcyclopropane.

Table I. Observed Chemical Shifts and Coupling Constants in **5**-*d*, **6**-*d*, and **7**-*d*

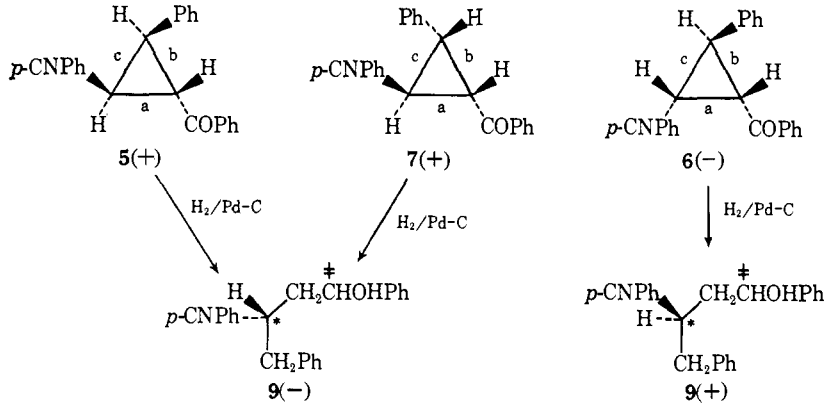
Compd	ν_1[a]	ν_2[a]	J_{12}, Hz
5-*d*	215.7	197.4	5.2
6-*d*	205.8	192.6	9.5
7-*d*	217.8	203.5	5.3

[a] Cycles per second downfield from TMS.

Finally, **6**-*d* and **7**-*d* were shown to be the deuterated analogs of **6** and **7**, respectively, by their undepressed mixture melting points, their identical retention volumes on liquid–liquid partition chromatography (see Experi-

(6) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962); K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963); D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 684 (1963).

Chart IV. Interrelationship of Configurations of Cyclopropyl Ketones[a]



[a] The absolute configurations are not known but are shown to depict the relative configurations. The reduction gave both diastereomers of **9**, but only one was used. The relative configurations in **9**(+) and **9**(−) at the centers marked with an asterisk are opposite although absolute configurations are unknown; the same is true for the centers marked with a dagger. The sign of rotation is for 290 nm for the alcohol and at the ORD maximum for the ketones.

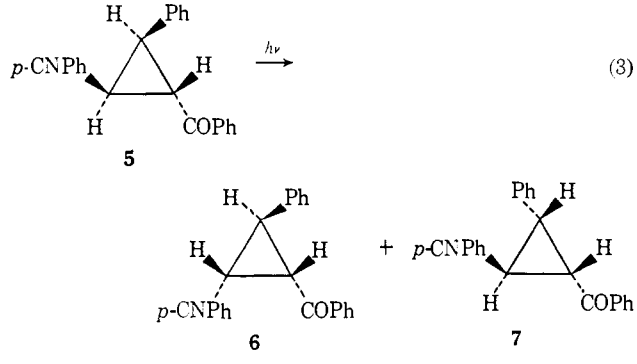
mental Section), the identity of their nmr spectra in the aromatic region, their similar uv spectra, and with the expectation that the ratio of **6**-*d* to **7**-*d* formed in photolysis will be the same as **6** to **7** in the undeuterated system.

Establishment of Relative Configurations of the Optically Active Cyclopropyl Ketones. With the optically active cyclopropyl ketones—**5**(+), **6**(−), and **7**(+)—in hand and knowing that their relative configurations would be needed for the mechanistic studies, we sought a simple scheme for accomplishing this. Such a method was found in the palladium–carbon reduction illustrated in Chart IV. This reaction opened the three ring and reduced the carbonyl group; fission of bond b predominated. From each starting material two diastereomers were obtained, these differing in the relative configurations at the *p*-cyanobenzylic and carbinol positions. For the present proof of only one of these diastereomers was needed.

The reaction had the virtues of (1) destroying all original asymmetric centers except the *p*-cyanobenzylic one and (2) affording the same product **9** from each of the three diastereomeric cyclopropyl ketones **5**, **6**, and **7**. It was found that dextrorotatory **5** (labeled **5**(+) in Chart IV) and dextrorotatory **7** (**7**(+)) in Chart IV afforded the common product **9**(−), with the same specific rotation and ORD curve. This means that **5**(+) and **7**(+) must have the same configuration at the *p*-cyanobenzylic position (*i.e.*, carbon 2); moreover **5**(+) and **7**(+) must be equally optically pure. In contrast, the **6**(−) utilized afforded the other enantiomer of **9** (*i.e.*, **9**(+)); its ORD curve was the mirror image, in shape and magnitude, of the curve of the **9**(−) obtained from **5**(+) and **7**(+). Thus **6**(−) must have the configuration at the *p*-cyanobenzylic position which is the reverse of that of the other two isomers; moreover, it must be of the same optical purity as the other two optically active isomers. This then provides the basis for the relative configurational assignments given in Chart IV.

The independent syntheses and structure proofs for the reduction products **9**, both the diastereomer utilized and also the second one not used, as well as the products resulting from bond a fission, are described in the Experimental Section. It might be added that although strong evidence is available that ketones **5**(+), **6**(−), and **7**(+) were optically pure, this was not necessary for the study. The ketones and their acid precursors were all brought to constant rotation. In the case of **6**(−) and **7**(+) both enantiomers of the acid precursors were obtained with constant rotations which were equal in magnitude but opposite in sign. Finally, when all three optically active ketones were reduced to the optically active alcohol **9**, the **9** obtained was of the same degree of optical purity regardless of the source. It seems highly unlikely that the three ketones would all be resolved to the same extent unless, of course, they were all optically pure. The evidence seems to indicate that this is indeed the case.

Exploratory Photochemical Efforts. Results. Initial photolysis of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**) in benzene did indeed lead to stereoisomerization with formation of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**) and *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**); note eq 3. In these exploratory



(3)

runs the interesting observation was made that the stereoisomer (**6**) with the benzoyl and cyanophenyl groups *cis* to one another predominated in a ratio of 3.5:1 (*i.e.*, 77.6 ± 2.5% of the product stereoisomers). Runs made to successively lower conversion suggested that this distribution is kinetically controlled, and this was confirmed with subsequent very low conversion runs (*vide infra*). The exploratory runs are summarized in Table II.

Table II. Exploratory Irradiations of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**)[a]

Time, min	% Recovered 5	6	7	% convn	[6(100)]/(6 + 7)
6.0	84.8	10.8	3.08	15.2	77.7
10.0	75.2	17.6	4.45	24.8	79.8
20.0	62.3	26.6	7.75	37.8	77.4
15[b]	49.5	40.5	10.9	50.5	78.7
60.0	41.6	38.6	12.7	58.4	75.2

[a] In addition to **5**, **6**, and **7** minor quantities (<6%) of a by-product were observed and are not listed. [b] Irradiation of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane.

Table III. Irradiation of Optically Active *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane

Run	Convn, %	Recovered 5	% optical purity[a,b] 6	7
1	7	99.1 ± 3.5 (+)[c]	99.0 ± 5.0 (−)[d]	5.9 ± 0.7 (+)[c]
2	13	99.7 ± 4.0 (+)[c]	96.4 ± 4.2 (−)[d]	6.8 ± 0.7 (+)[c]
3[e]	17	100.9 ± 3.7 (+)[c]	96.8 ± 3.5 (−)[d]	7.6 ± 0.6 (−)[d]

[a] Assuming synthesized ketones were all brought to optical purity; see test. [b] Rotations taken at maximum of ORD curve; error based on data. [c] Positive enantiomer. [d] Negative enantiomer. [e] Acetophenone-sensitized run.

The findings of the experiments with optically active material may be summarized as follows: (a) direct and sensitized irradiation of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**) gives *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**) with very little or no loss of activity by a process involving inversion at C-2; (b) the *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**) formed is nearly racemic in both the direct and sensitized cases, although retention of configuration at C-3 predominates slightly in the former and inversion at C-3 in the latter; (c) recovered *trans,trans* reactant (**5**) showed no loss of optical activity.

Quantum Yield and Multiplicity Studies. Results. Quantum yield determinations at low conversion were carried out in order to determine the facility of the photoisomerization. Sensitization using acetophenone and propiophenone and quenching with piperylene were also investigated. The results are indicated in Table IV.

Multiplicity and Quantum Yield Studies. Interpretative Discussion. As noted above, the reaction proved to be an especially facile and efficient one with a quantum yield of 0.81 for product appearance and unity for disappearance; 6–19% of by-products were

Table IV. Quantum Yields in Direct, Sensitized, and Quenched Irradiations of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane

Run	Convn, %	Additive concn, *M*	Quantum yields 5	6	7	[6(100)]/(6 + 7)
1[a]	7.0		1.06 ± 0.05	0.64 ± 0.03	0.20 ± 0.05	76.2
2[b]	6.1		1.03 ± 0.03	0.62 ± 0.03	0.15 ± 0.05	80.2
3[a]	10.4	Propiophenone,[c] 0.308	0.29 ± 0.05	0.18 ± 0.03	0.044 ± 0.018	80.0
4[a]	7.2	Acetophenone,[c] 0.958	0.32 ± 0.05	0.21 ± 0.03	0.062 ± 0.018	76.8
5[b]	9.1	Acetophenone,[c] 0.967	0.27 ± 0.05	0.18 ± 0.03	0.049 ± 0.018	78.8
6[a]	5.1	Piperylene,[d] 1.99	0.87 ± 0.05	0.53 ± 0.03	0.18 ± 0.05	75.1
7[a]	8.6	Acetophenone,[c] 1.02 Benzonitrile,[e] 0.0055	0.54 ± 0.05	0.37 ± 0.03	0.092 ± 0.02	80.1

[a] Benzene solvent. [b] *t*-Butyl alcohol solvent. [c] Sensitizers absorbed over 99% of the light. [d] Absorbing less than 3% of the light. [e] Absorbing less than 1% of the light.

Stereochemical Studies. Results. Although eq 2 shows one enantiomer of each of the two products **6** and **7** formed from one enantiomer of reactant **5**, the equation is meant only to designate diastereomers. It was by no means clear which of these enantiomers would result experimentally. Photolysis of optically active *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**(+)) promised to elucidate the reaction stereochemistry, a result needed to understand fully the molecular details of the rearrangement.

Direct irradiation of (+)-*trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**5**(+)) afforded the two products (−)-*cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (**6**(−)) and (+)-*trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane (**7**(+)). ORD curves of the products and recovered starting material were run so that impurities which might conceivably cause errors in analysis could be detected readily from the shape of the curve. The results are listed in Table III.

observed (note Table IV). This seemed reasonable in view of the relief of strain in the triplet three-ring opening and stabilization of the opened species by the aryl groups (*vide infra*).

The near-unit quantum yield further signified that once the three ring opens in the excited state, it does not reclose in its original conformation (note **8**). Rather, free rotation and reclosure to the product ketone stereoisomers must be faster than reclosure back to reactant **5**. This might derive from an unfavorable eclipsed conformation of the opened species as initially formed (note **8**), from this opened species being a triplet, or both.

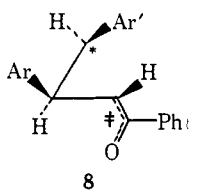


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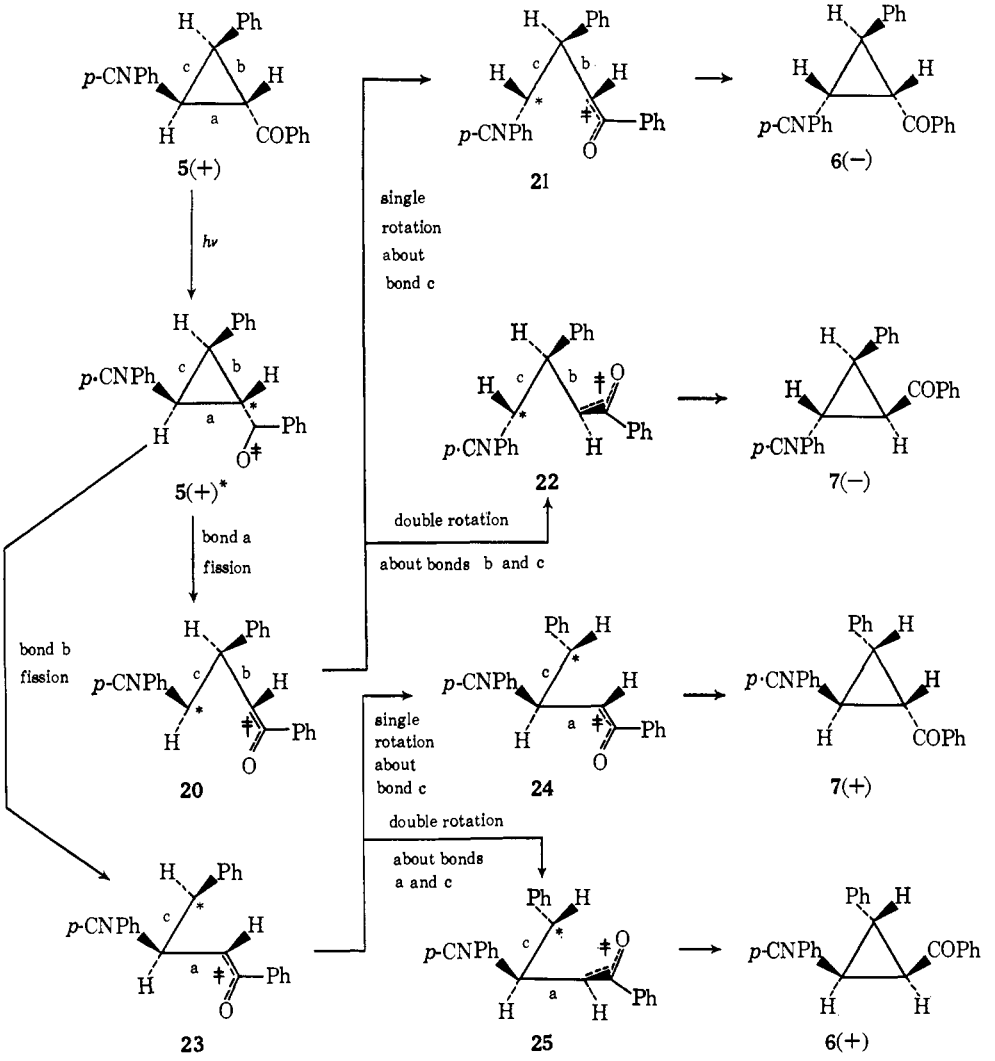
Chart V. Stereochemistry and Pathways for Photoisomerization of the *trans,trans* Isomer (**5**)



That the excited state responsible for this facile reaction is the triplet was suggested by acetophenone and propiophenone sensitization. In experiments (note Table IV) where the sensitizer absorbed more than 99% of the light and concentrations were adjusted to avoid singlet transfer, the same stereoisomerization reaction was observed and the stereochemical course was essentially the same as in direct photolysis. The ratio of *cis,trans* (**6**) to *trans,cis* (**7**) isomers remained the same within experimental error. Solvent change did not affect the product distribution (note Table IV), again suggesting one predominant species in both direct and sensitized reactions. The *cis,trans* product (**6**) still was formed with nearly total inversion of configuration at the cyanobenzylic carbon (*vide supra*, Chart V). However, there was observed a small change in optical composition of the minor product **7**. While in the direct runs the nearly racemic (3% excess (+)-enantiomer) product retained a slightly positive rotation, the sensitized runs revealed nearly racemic product with negative rotation (*ca.* 4% excess (−)-enantiomer). This may correspond to a small extent of intervention of singlet reaction in the direct runs.

Since it is known that quantum yields alone do not give a quantitative estimate of the facility with which excited states react it was of interest to get a measure of the excited triplet reactant rate. Quenching studies were attempted (note Table VI) using piperylene. However, only at *ca.* 2 *M* piperylene were the beginnings of quenching noted, and this quenching was minor. Using the rate of diffusion in benzene of 10^{10} l. mol^{-1} sec^{-1} as an approximation[7] to the rate of quenching, k_q, one can calculate the rate, k_r, of triplet reaction. Thus, in eq 4, we know that

$$\phi_0/\phi = 1 + k_q Q/(k_r + k_d) \qquad (4)$$

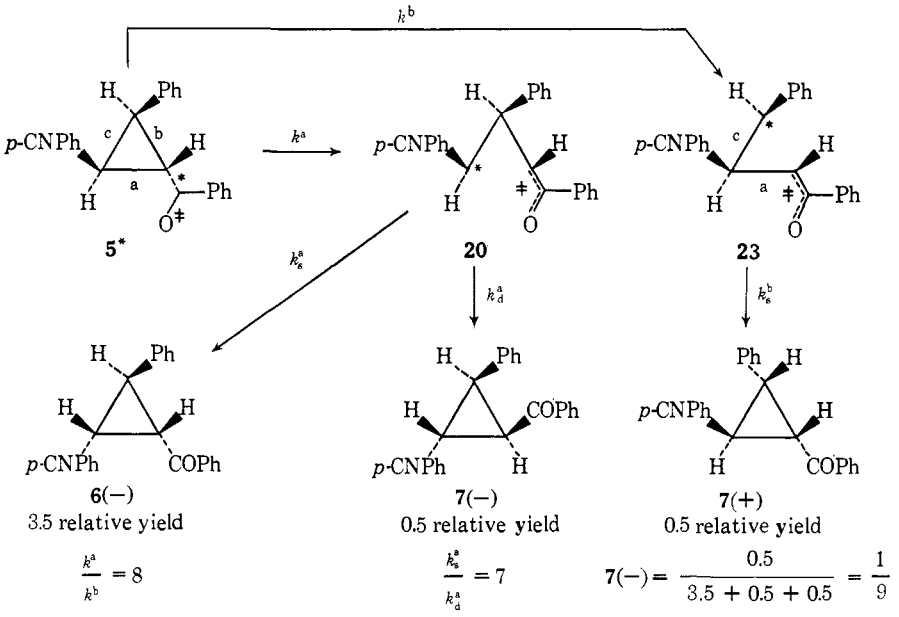
$\phi_0/\phi = 1/0.9$, $k_q = 10^{10}$ l. mol^{-1} sec^{-1}, the quencher concentration $Q = 1.99$ *M*, and the rate of decay $k_d \ll k_r$. This allows us to solve for k_r which is evaluated as 2×10^{11} sec^{-1}.

A final comment should be made, this regarding the inefficient sensitization of the reaction. This might not seem unreasonable in view of the nearly isoenergetic nature of the sensitization. However, the remarkable observation was made that introduction of benzonitrile,

(7) Justification has been given earlier [H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **99**, 3749 (1968)] for use of rates of diffusion as approximations to quenching rates despite the knowledge that quenching efficiency is known to be less than unity. The argument is based on an asymptotic approach to diffusion control. The rate of quenching may be less than the rate of collision especially for very fast reactions as has been noted by Schuster.[8] However, the error due to the approximation is generally less than threefold, while here we are dealing with orders of magnitude.

(8) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *J. Amer. Chem. Soc.*, **90**, 5027 (1968).

Chart VI. Summary of Observed Bond Openings and Rotations



under the conditions where this additive itself did not absorb light but where these molecules should encounter excited sensitizer molecules four times as frequently as reactant molecules do, led to a dramatic increase in the quantum efficiency. The nature of this phenomenon is being investigated further, but independent of its rationale, it is clear that triplet sensitization is occurring.

Molecular and Stereochemical Aspects. Interpretative Discussion. Inspection of Chart V reveals that if one excludes the possibility of bond c cleavage for the moment, there are two pathways by which both cyclopropane photoproducts **6** and **7** may be formed from the reactive excited state of the *trans,trans* ketone (**5**). Thus, the major product **6** may be formed by breaking bond a followed by a single rotation about bond c and reclosure or, alternatively, by cleaving bond b and rotating about both bonds a and c (*i.e.*, a double rotation). The minor photoproduct **7** may arise from bond b opening followed by a rotation about bond c or from bond a breaking and a double rotation about bonds b and c.

However, while it is indeed true that the two cyclopropane photoproducts **6** and **7** may arise by the different pathways indicated, the stereochemical results of the various pathways are not identical as may be seen from Chart V. Thus if one starts with optically active *trans,trans* ketone **5**(+), the *cis,trans* ketone (**6**) arising from a "bond a fission–single rotation" process, **6**(−), is the mirror image of enantiomer **6**(+) coming from the "bond b fission–double rotation" pathway. Likewise, the *trans,cis* ketone (**7**) which would come from breaking bond b and rotating once, **7**(+), is the mirror image of enantiomer **7**(−) which would arise *via* a "bond a cleavage–double rotation" process. By irradiating optically active **5** and observing which enantiomers of **6** and **7** are formed one can determine not only which routes are preferred but also to what extents.

Indeed, the results of irradiation of optically active *trans,trans* ketone (**5**) do delineate quite nicely the preferred mode of reaction of the excited ketone (Table III). We note (*vide supra*) that in both the direct and sensitized irradiations the major photoproduct, *cis,trans* ketone (**6**), was formed with virtually no loss of optical activity by a process affording enantiomer **6**(−) from **5**(+), thus involving inversion of configuration at C-2. One can conclude, therefore, by reference to Chart V that this isomer is formed from excited **5** by bond a cleavage followed by a single rotation and reclosure. A small amount (<4%) of the alternative process—"bond b fission and double rotation"—cannot be ruled out.

On the other hand, the minor photoproduct (**7**) isolated is nearly racemic in both the direct and sensitized runs, indicating that both pathways shown in Chart V operate to approximately the same extent. In the direct runs there is a slight preference (6–7%) for the "bond b cleavage–single rotation" sequence, while in the acetophenone-sensitized run, the "bond a cleavage–double rotation" mode predominates to the same small extent.

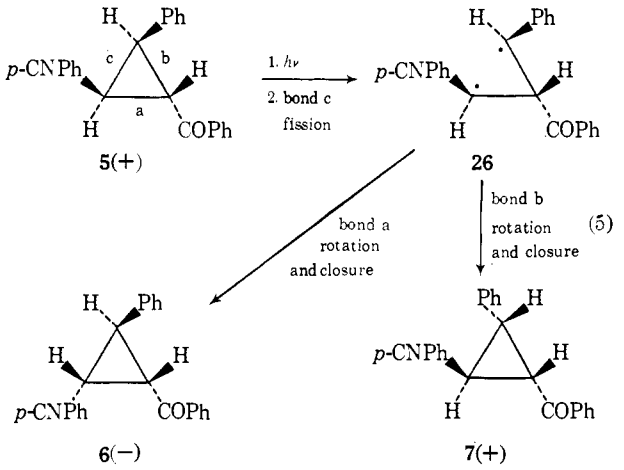
The 3.5/1 ratio of **6** to **7**, coupled with the knowledge that the 3.5 parts of **6** derive exclusively from bond a fission while the 1 part of **7** comes 0.5 from bond a fission and 0.5 from bond b fission, allows us to derive the overall ratio of bond a to bond b cleavage as (3.5 + 0.5)/0.5 = 8.0. The source of this eightfold preference for bond a fission is discussed below.

Moreover, it is seen that single rotations are heavily favored over double rotations in the ring-opened species; and one can actually calculate the relative rates of the single and double rotation pathways leading to product from the initial ring-opened species arising from cleavage of bond a. This is equivalent to determining the relative rate of closure of a single rotated species (*i.e.*, **21** in Chart V) compared to further free rotation. Using reasoning similar to that immediately above one sees that in Chart VI, $k_s^a/k_d^a = 3.5/0.5$ or $k_s^a = 7k_d^a$, where the k's represent effective rate constants for the single and double rotation mechanisms beginning with the bond a opened species **20**.

In our discussion thus far the possibility of bond c cleavage has been neglected for simplicity. Inspection of eq 5 shows that a process involving bond c fission followed by rotation about bond b and reclosure is

stereochemically equivalent to bond b fission followed by a single rotation. Likewise, bond c cleavage and rotation about bond a in the open species is equivalent to the previously discussed "bond a cleavage–single rotation" mechanism.

However, several factors argue against bond c fission as a major route. First, the triplet excitation energy should be most heavily localized in the benzoyl moiety,[9] with the expectation of a normal cyclopropyl ketone ring fission.[3] Moreover, direct experimental evidence is available on the extent of bond c fission; this derives from the results with optically active reactant and enables one to put an upper limit on this process.



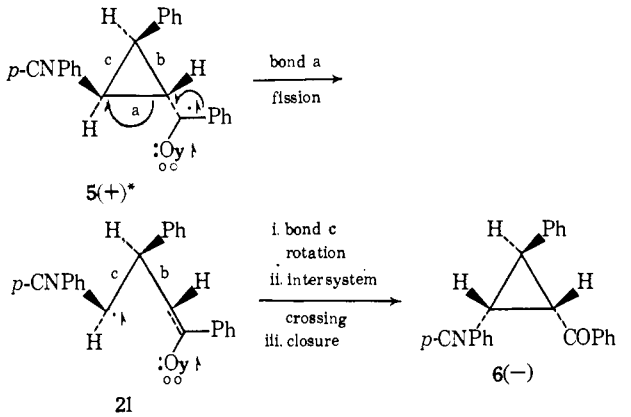
To begin with, no process initiated with bond c opening is equivalent stereochemically to the observed "bond a fission–double rotation" mode involved in the formation of 7(−) which constitutes one-ninth of the product. Thus, not all of the reaction could proceed *via* bond c cleavage.

Furthermore, to the extent that bond c does break, this portion of the reaction should lead to equal amounts of the *cis,trans* isomer (**6**) and the *trans,cis* isomer (**7**), since sterically the transition states leading to these two products from the bond c opened biradical **26** (eq 5) are essentially identical. The unequal amounts of products **6** and **7** then reveal major processes other than bond c fission.

The maximum amount of bond c cleavage permitted by the experimental results derives from the following line of reasoning. (1) The product 7(−), as noted, cannot arise from bond c fission but only from bond a fission and double rotation, a process occurring one-ninth of the time (*i.e.*, 11% of the isomerization processes). (2) The *trans,cis* isomer **7** as actually obtained was essentially racemic, meaning that processes leading to 7(+) must also constitute 11% of the pathways. (3) There are only two processes (note Chart V and eq 5) which can lead to 7(+), namely, bond b fission and single rotation or bond c fission and rotation about bond b, and these must total the 11%. (4) Even if the former process, involving bond b fission, were nonexistent, the bond c pathway is limited to the observed maximum of 11% of all bond fissions. The same limit is established by symmetry for rotation about bond a, leading to the major product 6(−), after any bond c fission. These are naturally high upper limits, since bond b fission involving phenacyl–benzylic cleavage, a known process,[3] must be occurring and is to be subtracted from the 11%.

The preferred mode of reaction of excited *trans,trans* ketone **5** is cleavage of bond a; a concerted conrotatory or disrotatory process can be ruled out since these are equivalent to double rotations which have been excluded as major processes. Bond c fission is at most a minor process. It is clear, then, from our initial reasoning (*vide supra*) that in the reactive excited state of **5**, electron density is not withdrawn from the ring. With electron donation having been excluded,[1a,4] the results are compatible only with an excited state which is diradical-like and which has odd electron density delocalized into the three ring.

Chart VII. Mechanism of Major Product Formation[a]



[a] Minor products are electronically analogous, differing in the bond broken or the number of rotations.

Experimental Section[11]

4′-Bromo-2-phenylacetophenone. This was prepared by the method of Speer and Hill[12] to give product, mp 115.5–116.2° (lit.[12] 114–115°).

trans-p-**Bromostilbene.** This was obtained by the sodium borohydride reduction of 4′-bromo-2-phenylacetophenone followed by dehydration with *p*-toluenesulfonic acid to give product, mp 139.5–140.5° (lit.[13] mp 139.5–140.0°).

cis-p-**Bromostilbene.** A solution of 10.00 g (0.0386 mol) of *trans-p*-bromostilbene in 5 l. of hexane was irradiated for 10 hr with a Hanovia 450-W medium-pressure mercury lamp under oxygen-free nitrogen[14] using a Corex filter. The mixture was concentrated *in vacuo* and the residue chromatographed on a 4.5 × 65 cm silica gel column (Davison, Grade 950, 60–200 mesh) slurry packed in hexane. Elution was with 1 l. of hexane, 1 l. of 1% benzene–hexane, 1 l. of 2%, 5 l. of 4%, 1 l. of 10%, 1 l. of 30%, 2 l. of 60%, and 1 l. of 100% benzene. Fraction size was 250 ml. Fractions 17–22 contained 5.821 g (58%) of *cis-p*-bromostilbene, a clear, viscous liquid. Fractions 23–32 contained 2.680 g (26.8%) of *trans-p*-bromostilbene, and fractions 41–45 contained 0.822 g of an unknown compound, mp 170.0–171.5°.

The spectral data of *cis-p*-bromostilbene were: ir (CS_2) 3.24, 3.27, 3.31, 7.10, 7.19, 9.04, 9.33, 9.71, 9.89, 10.60, 10.89, 11.49, 12.20,

(9) To a first approximation one can decide which portion of a molecule is most perturbed in the excitation process by considering the hypothetically isolated moieties. Presently, the triplet energy of the cyanophenyl group is 77 kcal/mol, the phenyl 83 kcal/mol, and the benzoyl 74 kcal/mol (using cyclopropyl phenyl ketone as a model[10]). Hence the excitation must be most heavily localized in the benzoyl group.

(10) L. M. Stephenson and G. S. Hammond, *Angew. Chem. Intern. Ed. Engl.*, 8, 261 (1969).

(11) Melting points were observed on a hot-stage apparatus and are corrected. Nmr spectra were recorded on either a Varian A-60 or A-60-A spectrometer.

(12) J. A. Speer and A. J. Hill, *J. Org. Chem.*, 2, 139 (1938).

(13) J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 4164 (1962).

(14) L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

12.87, 13.12, 13.83, and 14.37 μ; $n^{25}D$ 1.6451; uv (EtOH) 227 nm max (ϵ 21,760), 280 (ϵ 12,460); nmr (CCl_4) τ 2.63–3.05 (m, 9 H, arom), 3.27, 3.47, 3.51, 3.72 (AB q, 2 H, vinyl, J_{AB} = 12 Hz, σ_A 3.42, σ_B 3.56).

Anal. Calcd for $C_{14}H_{11}Br$: C, 64.88; H, 4.28. Found: C, 65.02; H, 4.13.

***trans*-2-*p*-Bromophenyl-*trans*-3-phenyl-1-benzoylcyclopropane.** A mixture of 19.26 g (0.0744 mol) of *cis*-*p*-bromostilbene, 10 ml of xylene, and 1.00 g of copper bronze (Luco No. 16, Leo Uhlfelder Co., New York, analyzed for 99.5+% copper) was stirred at 130° under nitrogen, and 23.61 g (0.1617 mol) of diazoacetophenone[15] in 35 ml of xylene was added at 130° over 3 hr; 3910 cc (96%) of nitrogen was evolved. After filtration and concentration *in vacuo* the residue was chromatographed on a 7 × 80 cm silica gel column slurry packed with 3% ether–hexane. Elution was with 2 l. of 3%, 3 l. of 5%, 7 l. of 10%, 1 l. of 15%, 2 l. of 20%, 2 l. of 25%, and 2 l. of 50% ether–hexane; 500-ml fractions were collected. Fractions 6–11 contained 13.53 g of *cis*-*p*-bromostilbene, while fractions 14–25 contained 3.844 g of *trans*-2-*p*-bromophenyl-*trans*-3-phenyl-1-benzoylcyclopropane product, mp 104–106°. The filtrates from fractions 12–25 were rechromatographed on a 4 × 25 cm silica gel column slurry packed with 5% ether–hexane and eluted with 500 ml of 5% ether–hexane and 1500 ml of 10% ether–hexane. Fraction size was 40 ml. Fractions 21–38 contained 1.486 g of product, mp 103–105°, giving a total of 5.330 g. This was recrystallized from 90° ligroin to a mp of 106.0–107.0°; yield, 64% based on reacted *cis*-*p*-bromostilbene.

The spectral data were: ir (KBr) 6.04, 6.27, 6.33, 6.70, 6.91, 7.06, 7.16, 7.55, 7.66, 7.73, 8.19, 9.31, 9.60, 9.92, 10.77, 11.60, 12.24, 12.88, 13.16, 13.51, 13.99, 14.2–14.3, 14.52, and 15.12 μ; (CS_2) 3.26, 3.28, 3.31, and 5.98 μ; uv (isooctane) 237 nm max (ϵ 25,100); nmr (CCl_4) τ 1.90–2.10 (m, 2 H, *o*-benzoyl), 2.50–3.28 (m, 12 H, arom), 6.52–6.89 (m, 3 H, cyclopropyl).

Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.04; H, 4.54; Br, 21.18. Found: C, 70.01; H, 4.49; Br, 21.45.

***trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane.** A mixture of 2.190 g (5.80 mmol) of *trans*-2-*p*-bromophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 0.832 g (4.65 mmol) of cuprous cyanide, and 12 ml of distilled N-methyl-2-pyrrolidone was heated at 178° for 3 hr. The cooled mixture was shaken vigorously with a solution of 2.00 g of sodium cyanide in 50 ml of water; 250 ml of benzene was added and the mixture shaken. The mixture was filtered and the benzene layer separated and washed thoroughly with 10% aqueous sodium cyanide and then water. The benzene solution was dried and concentrated *in vacuo*, and the residue was chromatographed on a 3.5 × 90 cm silica gel column slurry packed in 5% ether–hexane. Elution was with 4 l. of 5%, 1 l. of 10%, 3 l. of 15%, 1 l. of 20%, and 1 l. of 25% ether–hexane; fraction size was 40 ml. Fractions 56–109 contained 0.509 g (23%) of starting material, while fractions 180–235 contained 0.965 g (67% based on reacted bromo compound) of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, mp 97–98°. Recrystallization from ether–hexane gave a constant melting point of 97.5–98.5°. Another crystalline modification, mp 113.5–115.5°, with the same CS_2 ir and $CDCl_3$ nmr spectra was obtained on crystallization from 90° ligroin–methylene chloride.

The spectral data were: ir (KBr) 4.48, 6.04, 6.22, 6.33, 6.68, 6.91, 7.03, 7.12, 7.54, 7.68, 7.79, 8.20, 8.49, 9.6, 9.8, 9.91, 11.42, 11.63, 12.12, 12.83, 13.5, 14.3–14.45, and 15.17 μ; ir (CS_2) 4.47 and 5.98 μ; uv (95% EtOH) 246 nm max (ϵ 30,480); n→π^* band (cyclohexane) 356 nm sh (ϵ 13), 341 nm sh (71), 327 sh (136), 316 max (175), 305 max (182); nmr ($CDCl_3$) τ 1.80–1.98 (m, 2 H, *o*-benzoyl), 2.37–3.10 (m, 12 H, arom), 6.30–6.72 (m, 3 H, cyclopropyl).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.25; H, 5.52; N, 4.30.

4′-Bromo-2-phenylacetophenone-2,2-d_2. A solution of 14% sodium deuterioxide, prepared from 40 ml (2.20 mol) of 99.5% deuterium oxide and 6.145 g (0.268 g-atom) of sodium, was stirred for 12 hr under nitrogen with 80 ml of dry dioxane and 30.19 g (0.110 mol) of 4′-bromo-2-phenylacetophenone at room temperature. The mixture was extracted with anhydrous ether and dried over sodium sulfate. Concentration afforded 27.72 g (92%) of 84% deuterated product (nmr analysis). A second exchange utilized 30 ml of deuterium oxide (1.66 mol), 80 ml of dry *p*-dioxane, and 3.75 g (0.163 g-atom) of sodium metal. The mixture was stirred 16 hr at room temperature, dry benzene extracted, dried over magnesium sulfate, and concentrated *in vacuo* to give 25.29 g (92%) of 4′-bromo-2-phenylacetophenone-2,2-d_2, mp 112.5–114°. Recrystallization from 90° ligroin gave mp 113.5–115.0°. A mixture melting point with undeuterated material, mp 115.5–116.2°, showed no depression.

The spectral data were: nmr (CCl_4) no trace of methylene hydrogen at τ 5.89, aromatic region identical with undeuterated ketone; ir (KBr) 5.94, 6.31, 6.69, 6.90, 7.18, 7.80, 8.20, 8.51, 9.33, 9.91, 10.72, 11.10, 12.51, 13.5, and 14.20 μ; absorption at 10.72 and 11.10 μ proved characteristic of the deuterated ketone and 7.48, 8.34, and 10.10 μ characteristic of the undeuterated ketone; ir (CS_2) 5.93, 7.17, 7.68, 7.93, 8.22, 8.50, 9.33, 9.89, 10.19, 10.80, 11.21, 13.74, 14.01, and 14.33 μ, of which the peaks at 10.80 and 11.21 μ are characteristic of the deuterated ketone, while peaks at 8.36 and 13.86 μ are characteristic of the undeuterated ketone.

1-*p*-Bromophenyl-2-phenylethanol-2,2-d_2. To 24.82 g (0.0895 mol) of 4′-bromo-2-phenylacetophenone-2,2-d_2, 500 ml of anhydrous 1,2-dimethoxyethane (freshly distilled from $LiAlH_4$), and 8.20 ml (9.45 mol) of deuterium oxide was added 3.40 g (0.09 mol) of sodium borohydride at 25°. After stirring for 2.5 hr, 200 ml of water was added and the aqueous layer was benzene extracted. The extracts were washed, dried, and concentrated *in vacuo* to give 23.08 g (92.5%) of the alcohol, mp 52–54°. This was recrystallized from hexane to give 22.79 g of 1-*p*-bromophenyl-2-phenylethanol-2,2-d_2, mp 54.0–55.0°. A mixture melting point with undeuterated alcohol, mp 54.0–55.0°, showed no depression.

The nmr (CCl_4) showed τ 2.61–3.09 (m, 9 H, arom), 5.43 (s, 1 H, CH), 7.72 (s, 1H, OH). The aromatic region was very similar to that of the undeuterated compound. No trace of methylene hydrogen at τ 7.17 was found.

Methyl Xanthate of 1-*p*-Bromophenyl-2-phenylethanol-2,2-d_2. The general procedure of Roberts and Sauer[16] was used. A mixture of 12.50 g (0.0448 mol) of 1-*p*-bromophenyl-2-phenylethanol-2,2-d_2, 350 ml of dry benzene, and 1.62 g (0.0675 mol) of sodium hydride was stirred under nitrogen 1 hr at room temperature and then refluxed 3 hr. After cooling, 27 ml (0.448 mol) of carbon disulfide was added followed by 0.5 hr of stirring and 3 hr of refluxing. A heavy orange precipitate formed; 28 ml (0.448 mol) of methyl iodide was added and the stirring continued for 0.5 hr followed by refluxing for 3 hr. Water was added slowly to the cooled mixture to decompose excess sodium hydride. Ether was added, and the solution was washed, dried, and concentrated. The residue crystallized to give 9.043 g of product, mp 66–70°. Recrystallization from hexane gave 6.268 g (38%) of pale yellow xanthate, mp 73.5–75.5°.

The spectral data were: ir (KBr) 6.73, 6.92, 7.13, 7.73, 7.88, 8.3–8.4 (br, s), 9.3–9.5 (br, s), 9.88, 10.30, 10.53, 10.71, 12.2, 13.6–13.7, and 14.36 μ; nmr (CCl_4) τ 2.55–3.08 (m, 9 H, arom), 3.42 (s, 1 H, CH), 7.52 (s, 3 H, CH_3). No trace of methylene hydrogen was found.

***trans*-1-Phenyl-1-*d*-2-*p*-bromophenylethylene.** The methyl xanthate of 1-*p*-bromophenyl-2-phenylethanol-2,2-d_2, 6.171 g (0.167 mol), was heated at 160° for 20 min under nitrogen. The residue was cooled and recrystallized from hexane, affording 1.392 g of product, mp 140.5–141.5°. The mother liquors were concentrated and passed through a 4 × 20 cm silica gel column packed and eluted with hexane to give an additional 1.993 g of *trans*-1-phenyl-1-*d*-2-*p*-bromophenylethylene, mp 140.5–141.5° (78% total yield). A mixture melting point with *trans*-*p*-bromostilbene, mp 139.5–140.5°, showed no depression.

The spectral data were: ir (KBr) 6.69, 7.15, 9.29, 9.93, 11.07, 12.16, 12.88, 14.36, and 14.54 μ. Absorption at 11.07 and 12.88 μ proved characteristic of deuterated *trans*-*p*-bromostilbene, while 10.38 and 13.35 μ peaks were characteristic of undeuterated *trans*-*p*-bromostilbene; ir (CS_2) 4.48, 9.31, 9.93, 11.15, 12.23, 12.93, and 14.41 μ; peaks at 11.15 and 12.93 μ are characteristic of the deuterated compound and peaks at 10.42 and 13.40 μ are characteristic of undeuterated *trans*-*p*-bromostilbene; nmr ($CDCl_3$) τ 2.50–2.85 (m, 9 H, arom), 3.08 (t, 1 H, vinyl, J = 2.1 Hz). The aromatic region is identical with that of the undeuterated compound; however, it is concentration dependent.

***cis*-1-Phenyl-1-*d*-2-*p*-bromophenylethylene.** *cis*-1-Phenyl-1-*d*-2-*p*-bromophenylethylene was prepared from the *trans* isomer *via* the same procedure used for the production of the nondeuterated *cis* material (*vide supra*). From 5.074 g (0.0196 mol) of *trans* isomer, 3.01 g (59.5%) of the *cis* product was obtained.

The spectral data were: ir (CS_2) 3.24, 3.26, 3.30, 4.48, 7.16, 9.33, 9.89, 10.90, 11.90, 12.32, 13.03, 13.26, 13.82 and 14.36 μ; absorp-

(15) M. S. Newman and P. Beal, *J. Amer. Chem. Soc.*, 71, 1506 (1949).

(16) J. D. Roberts and C. W. Sauer, *ibid.*, 71, 3925 (1949).

tion characteristic of the deuterated compound was at 11.90 μ, while a 12.87-μ peak was characteristic of the undeuterated compound; nmr (CCl_4) τ 2.63–3.05 (m, 9 H, arom), 3.55 (br s, 1 H, vinyl). The aromatic region was identical with that of the undeuterated *cis*-*p*-bromostilbene.

***trans*-2-*p*-Bromophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane.** *trans*-2-*p*-Bromophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane was prepared from *cis*-1-phenyl-1-*d*-2-*p*-bromophenylethylene and diazoacetophenone[15] *via* a procedure similar to that used for the production of nondeuterated ketone (*vide supra*). From 7.284 g (0.0280 mol) of deuterated stilbene, 1.86 g (0.0049 mol) of ketone, mp 106.5–107.0°, was obtained. A mixture melting point with undeuterated compound, mp 106.0–107.0°, was undepressed.

The spectral data were: ir (KBr) 6.04, 6.26, 6.69, 6.90, 7.07, 7.16, 7.71, 8.16, 9.29, 9.64, 9.80, 9.89, 10.98, 12.28, 12.74, 12.93, 13.50, 14.3, and 15.34 μ; absorption at 10.98, 12.74, and 15.34 μ is characteristic of the deuterated compound, while that at 13.16 and 15.12 μ is characteristic of the undeuterated compound; ir (CS_2) 5.99, 7.18, 7.76, 8.24, 8.48, 9.31, 9.89, 11.94, 12.33, 12.78, 14.4, and 15.35 μ; peaks at 11.94 and 12.78 μ are characteristic of the deuterated compound and those at 13.20 and 15.10 μ are characteristic of the undeuterated compound; nmr (CCl_4) τ 1.9–2.1 (m, 2 H, *o*-benzoyl), 2.50–3.28 (m, 12 H, arom), 6.57, 6.66, 6.84, 6.93 (AB q, 2 H, cyclopropyl, σ_A τ 6.619, σ_B 6.872, J_{AB} = 5.2 Hz). The aromatic region was identical with that of the undeuterated compound.

***trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane.** *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane was prepared from *trans*-2-*p*-bromophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane and cuprous cyanide *via* a procedure similar to that used for the synthesis of the undeuterated ketone. From 1.532 g (4.05 mmol) of the *trans,trans* reactant, 0.468 g (36%) of deuterated product, mp 113.0–114.5°, was obtained. A mixture melting point with undeuterated ketone, mp 113.5–115.5°, was undepressed.

The spectral data were: ir (KBr) 4.47, 6.03, 7.12, 7.42, 7.70, 8.15, 8.47, 9.67, 9.79, 10.70, 10.85, 11.02, 11.79, 12.20, 13.6–13.7, 14.3, 14.45, and 15.23 μ; absorption at 7.70, 11.02, and 11.79 μ is characteristic of the deuterated compound, while that at 7.51, 9.91, and 12.00 μ is characteristic of the undeuterated compound; ir (CS_2) 4.48, 5.98, 7.74, 8.20, 8.49, 9.84, 11.85, 12.24, 13.70, 14.4, 14.57, and 15.31 μ; peaks at 11.85, 12.24, and 13.70 μ are characteristic of the deuterated compound and peaks at 12.12 and 13.56 μ are characteristic of the undeuterated compound; uv (95% EtOH) 245 nm max (ϵ 30,150); nmr ($CDCl_3$) τ 1.80–1.98 (m, 2 H, *o*-benzoyl), 2.37–3.10 (m, 12 H, arom), 6.35, 6.44, 6.67, 6.76 (AB q, 2 H, cyclopropyl, σ_A τ 6.405, σ_B 6.710, J_{AB} = 5.2 Hz). The aromatic region was identical with that of the undeuterated compound, with peaks at 420, 421, 426, 428, 441, 449, 454, and 455 Hz downfield from TMS.

Addition of Diazoacetophenone to *trans*-*p*-Bromostilbene. To a mixture of 15.00 g (0.058 mol) of *trans*-*p*-bromostilbene, 60 ml of xylene, and 1.00 g of copper bronze at 130° under nitrogen was added with stirring 18.73 g (0.128 mol) of diazoacetophenone[15] in 55 ml of xylene over 3.75 hr. After filtration and concentration *in vacuo*, the dark residue was chromatographed on a 7 × 60 cm silica gel column slurry packed with 3% ether–hexane. Elution was with 3 l. of 3%, 5 l. of 5%, and 7 l. of 10% ether–hexane. Fraction size was 500 ml. Fractions 3–6 contained 10.74 g of *trans*-*p*-bromostilbene, while fractions 13–16 contained 0.602 g of a solid, mp 142–145°, along with considerable impure oily material. Residues from fractions 3–24 were rechromatographed on a 4 × 30 cm silica gel column slurry packed with 3% ether–hexane. Elution was with 5 l. of 3% ether–hexane using 40-ml fractions. Fractions 38–65 contained 1.537 g of *trans*-*p*-bromostilbene giving a total of 12.272 g, while fractions 95–155 contained 3.762 g of impure oily material which had a 5.97 μ carbonyl (CS_2). This 3.762 g of material was treated with cuprous cyanide as described in the next preparation to give two readily separable cyano compounds.

The 0.602 g of solid, which proved to be *cis*-2-*p*-bromophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, was recrystallized from methylene chloride–hexane to mp 145.0–146.5°. The ir (KBr) had peaks at 6.01, 6.71, 7.31, 8.20, 9.56, 9.89, 10.30, 11.48, 12.31, 12.77, 13.22, 13.55, 13.86, 14.35, 15.38, and 15.70 μ.

***cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane and *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane.** A mixture of 3.762 g of impure bromo compounds from the preceding reaction, 1.00 g of cuprous cyanide, and 10 ml of N-methyl-2-pyrrolidone was heated at 185° for 4 hr. The cooled mixture was shaken well with 5% aqueous sodium cyanide and benzene extracted. The benzene layers were washed with 10% sodium cyanide and then water, dried, and concentrated *in vacuo* to give 3.48 g of residue which was chromatographed on a 4.5 × 150 cm liquid–liquid partition chromatography column;[19] 40-ml fractions were collected. The material was placed on the column in two batches; the fractions listed are for the first scan, but combined weights are given. Fractions 82–93 contained 0.340 g of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, while fractions 94–108 contained 0.333 g of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane. The *cis,trans* isomer was recrystallized from ether–hexane to mp 134.5–135.5°; the *trans,cis* isomer was recrystallized from methylene chloride–ligroin (bp 90°) to mp 132.0–133.5°. A second crystalline form of the latter isomer, mp 128–131°, was obtained in some ether–hexane crystallizations.

The spectral data for *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane were: ir (KBr) 4.48, 6.01, 6.23, 6.31, 6.67, 6.90, 7.1, 7.31, 7.64, 7.72, 7.89, 8.21, 8.45, 9.56, 9.74, 10.24, 11.39, 12.16, 13.09, 13.34, 14.26, 14.49, and 15.20 μ; uv (95% EtOH) 242.5 nm max (ϵ 31,440); n → π^* band (cyclohexane) 360 nm sh (ϵ 55), 345 sh (164), 331 max (255), 319 max (275); nmr ($CDCl_3$) τ 1.97–2.13 (m, 2 H, *o*-benzoyl), 2.41–2.76 (m, 12 H, arom), 6.26–6.93 (m, 3 H, cyclopropyl).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.21; H, 5.26; N, 4.50.

The spectral data for *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane were: ir (KBr) 4.48, 6.01, 6.21, 6.68, 6.92, 7.10, 7.29, 7.56, 7.71, 7.88, 8.19, 8.48, 9.53, 9.77, 10.15, 10.69, 11.89, 12.20, 12.66, 13.09, 13.74, 13.91, 14.29, 14.53, 15.21, and 15.52 μ; uv (95% EtOH) 246.5 nm max (ϵ 35,480); n → π^* band (cyclohexane) 360 nm sh (ϵ 51), 345 sh (131), 331 max (196), 319 max (211), 309 max (196); nmr ($CDCl_3$) τ 1.95–2.10 (m, 2 H, *o*-benzoyl), 2.29–2.76 (m, 12 H, arom), 6.23–6.91 (m, 3 H, cyclopropyl); the 128–131° crystalline form had an ir (KBr) which had new peaks at 7.67, 8.07, 8.43, 11.5, 12.97, and 14.17 μ and lacked peaks at 7.56, 10.69, and 13.09 μ.

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.67; H, 5.26; N, 4.31.

***cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane.** A mixture of 0.6025 g (1.60 mmol) of *cis*-2-*p*-bromophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 0.215 g (1.20 mmol) of cuprous cyanide, and 4.0 ml of N-methyl-2-pyrrolidone was heated at 185° for 3.5 hr. Work-up similar to that of the preceding experiment afforded 0.124 g (20.6%) of starting material and 0.299 g (73% based on reacted bromo compound) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane.

***trans*-2-*p*-Bromophenyl-*trans*-3-phenylcyclopropanecarboxylic Acid.** The general method of Blatchford and Orchin[17] was used. To a mixture of 30.00 g (0.116 mol) of *cis*-*p*-bromostilbene, 45 ml of *n*-octane, and 2.00 g of copper bronze under nitrogen at 122° was added 25.76 g (0.23 mol) of ethyl diazoacetate in 90 ml of *n*-octane with stirring over 9.75 hr. The mixture was filtered, added to 14.0 g (0.35 mol) of sodium hydroxide in 200 ml of methanol, and stirred overnight at room temperature. The two-phase mixture was then refluxed 1 hr. Methanol and octane were removed *in vacuo* followed by addition of water and hexane extraction. The hexane extracts gave 12.51 g (42%) of unreacted *cis*-*p*-bromostilbene after washing with water, drying, and concentrating *in vacuo*. The above aqueous phase was acidified to Congo red (6 *N* HCl), ether extracted, washed, dried, and concentrated under vacuum to give 18.04 g of crude *trans*-2-*p*-bromophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, mp 168–170°. Crystallization from methanol–water gave 15.56 g (72.5% based on reacted *cis*-*p*-bromostilbene) of acid, mp 171.0–172.0°. Further recrystallization gave mp 171.0–172.0°.

The spectral data were: ir (KBr) 6.69, 7.73, 8.28, 9.32, 9.90, 12.23, 13.03, 13.34, 13.98, and 14.34 μ; carbonyl (CS_2) 5.93 μ; nmr ($CDCl_3$) τ −1.65 (s, 1 H, COOH), 2.69–3.29 (m, 9 H, arom), 6.90 (double doublet, 2 H, H's β to COOH), 7.49 (double doublet or t, 1 H, H α to COOH).

Anal. Calcd for $C_{16}H_{13}BrO_2$: C, 60.59; H, 4.13; Br, 25.19. Found: C, 60.83; H, 4.33; Br, 25.23.

***trans*-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic Acid.** A mixture of 30.0 g (0.0945 mol) of *trans*-2-*p*-bromophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, 12.67 g (0.0708 mol) of cuprous cyanide, and 90 ml of N-methyl-2-pyrrolidone was heated at 184° for 5 hr under nitrogen. Work-up with 300 ml of 6 *N* HCl containing 20.0 g of ferric chloride, ether–benzene ex-

(17) J. Blatchford and M. Orchin, *J. Org. Chem.*, **29**, 839 (1964).

traction (1:1), washing with water, drying, and concentration *in vacuo* gave 26.54 g of solid, which was eluted through a 7.5 × 14 cm silica gel column slurry packed with 50% ether–hexane. Elution with 5.5 l. of 50% ether–hexane gave 22.50 g (90%) of product. One crystallization from methanol–water gave 20.04 g (81%) of *trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid of constant mp 181.5–182.5°.

The spectral data were: ir (KBr) 4.47, 5.90, 6.21, 7.01, 7.71, 8.00, 9.18, 9.81, 10.70, 11.88, 12.14, 13.21, 13.61, 14.35, and 14.58 μ; nmr ($CDCl_3$) τ −0.73 (s, 1 H, COOH), 2.55–3.10 (m, 9 H, arom), 6.85 (double doublet, 2 H, hydrogens β to COOH), 7.42 (double doublet, or t, 1 H, hydrogen α to COOH).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.64; H, 4.87; N, 5.38.

Resolution of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic Acid. To 13.27 g (0.0504 mol) of racemic *trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid was added 14.85 g (0.0504 mol) of (−)-cinchonidine alkaloid and 133 ml of ethyl acetate. The mixture was heated until solution occurred and then filtered and let stand overnight at room temperature, yielding 12.61 g of cinchonidine salt, mp 155–160°, $[\alpha]^{25}_{436}$ −192° (*c* 0.00240, $CHCl_3$). This salt was recrystallized three times from hot ethyl acetate to give 4.121 g of salt, $[\alpha]^{25}_{436}$ −63° (*c* 0.00350, $CHCl_3$). A total of 73.59 g (0.279 mol) of acid and 84.32 g (0.286 mol) of cinchonidine was carried through this procedure to give a total of 25.31 g of salt with a constant $[\alpha]^{25}_{436}$ −53 ± 10°, mp 202° dec.

The 25.31 g of resolved salt thus obtained was hydrolyzed with 10% HCl to give 11.59 g of the resolved acid, mp 154–156°, $[\alpha]^{25}_{436}$ +215 ± 2° (*c* 0.00300, $CHCl_3$). Recrystallization of the acid from methylene chloride–hexane yielded 9.901 g (13% based on racemic acid used) of optically active *trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, mp 154–156°, $[\alpha]^{25}_{436}$ +217 ± 2° (*c* 0.00300, $CHCl_3$). The nmr ($CDCl_3$) and ir ($CHCl_3$) spectra of the optically active acid were identical with those of the racemic material.

Optically Active *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. To a solution of phenylmagnesium bromide, prepared from 0.464 g (0.0190 g-atom) of magnesium turnings and 2.980 g (0.0190 mol) of bromobenzene in 30 ml of anhydrous ether, was added 1.832 g (0.0100 mol) of anhydrous cadmium chloride in two batches while stirring at 0° under nitrogen. The mixture was stirred 10 min at 0° and refluxed for 2.25 hr. A subsequent Gilman test was negative. The ether was rapidly distilled and 180 ml of dry benzene added; 50 ml of benzene was then distilled and 20 ml more added.

To 1.000 g (0.00380 mol) of *trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, $[\alpha]^{25}_{436}$ +217 ± 2°, under nitrogen was added 10 ml of thionyl chloride dropwise with stirring. The resulting yellow solution was heated to reflux and the excess thionyl chloride was distilled carefully, avoiding heating the residue. Then 10 ml of dry benzene was added and distilled, ensuring thionyl chloride removal.

The oily acid chloride, dissolved in 20 ml of dry benzene, was added to the stirred diphenylcadmium mixture at 0° under nitrogen. The reaction mixture was stirred 10 min at 0° and 2 hr at 25–28°, after which time 100 ml of 4% ammonium chloride solution was added. The organic layer was extracted with 5% sodium carbonate solution, washed with water, and then dried and concentrated to give 1.790 g of a yellow oil. The basic extract was acidified (Congo red) with 6 *N* HCl and ether extracted to give 0.045 g of the starting acid. The 1.790 g of oily ketone was chromatographed on a 3 × 96 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 1 l. of 10% followed by 4 l. of 20% ether–hexane; 40-ml fractions were collected and scanned at 280 nm. Fractions 60–67 contained 0.025 g of an unknown compound; 68–70, 0.035 g of a mixture of an unknown and the desired ketone; 71–108, 0.876 g of the ketone.

In several runs a total of 7.208 g of the same crude ketone was produced from 7.000 g (0.0256 mol) of the optically active acid. This ketone was recrystallized from benzene–hexane, giving a 3.176-g crop of colorless crystals, mp 126–127.5°, and a second crop of 1.822 g, mp 126–127.5°. Further recrystallization from benzene–hexane to constant melting point and ORD curve gave 5.469 g (66%) of trans-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, mp 126–127.5°; ORD max at 325 nm; $[\alpha]^{25}_{325}$ +912 ± 19° (*c* 0.000118, $CHCl_3$). The nmr ($CDCl_3$) and ir (CS_2) were identical with those of the racemic material.

This procedure was also used to prepare 1.792 g (55%) of racemic ketone, mp 113–114°, from racemic *trans*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid.

Addition of Ethyl Diazoacetate to *trans*-*p*-Bromostilbene and Saponification. A 54.31-g (0.210 mol) portion of *trans*-*p*-bromostilbene and 4.00 g of copper bronze were heated to 140° under nitrogen. When the stilbene had melted, the temperature was brought to 120–130°; 40 g (0.35 mol) of ethyl diazoacetate in 50 ml of xylene was added under nitrogen over 12 hr with vigorous Trubore stirring. The copper bronze was then filtered, and 25 g (0.62 mol) of sodium hydroxide in 500 ml of methanol was added. The basic mixture was refluxed 1 hr and stirred 2 hr at room temperature. The methanol was then removed *in vacuo*, 500 ml of water was added, and the unreacted *p*-bromostilbene was ether extracted. Washing, drying, and concentrating the ether extracts gave 38.42 g (0.148 mol) of unreacted *p*-bromostilbene. The basic fraction was acidified to Congo red with 6 *N* HCl and ether extracted. The ether extracts were washed, dried, and concentrated to give 42.24 g of a dark oil, which was chromatographed on a 6.5 × 45 cm silica gel column slurry packed in 5% ether–hexane and eluted with 15 l. of 10% ether–hexane; 1-l. fractions were collected. Fractions 2–15 contained 17.13 g of a yellow solid–oil mixture which, upon crystallization from benzene–hexane, gave 14.12 g (73% based on unrecovered *p*-bromostilbene) of a mixture of *cis*-2-*p*-bromophenyl-*trans*-3-phenylcyclopropanecarboxylic acid and *trans*-2-*p*-bromophenyl-*cis*-3-phenylcyclopropanecarboxylic acid. The mixture of stereoisomers was used directly in the next step.

Methyl *cis*-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylate and Methyl *trans*-2-*p*-Cyanophenyl-*cis*-3-phenylcyclopropanecarboxylate. The mixture of *cis*-2-*p*-bromophenyl-*trans*-3-phenylcyclopropanecarboxylic acid and *trans*-2-*p*-bromophenyl-*cis*-3-phenylcyclopropanecarboxylic acid (14.14 g, 0.0446 mol) was heated with 5.994 g (0.0669 mol) of cuprous cyanide in 40 ml of N-methylpyrrolidone at 180–185° for 5 hr under nitrogen. The reaction mixture was cooled, poured onto a solution of 20 g of ferric chloride in 300 ml of 6 *N* HCl, and extracted with 50% benzene–ether. The organic layer was washed well with water, dried, and concentrated *in vacuo* to give 15.02 g of a dark oil, which was chromatographed on a 6.5 × 40 cm silica gel column slurry packed with 15% ether–hexane and eluted with 1 l. of 15% followed by 9 l. of 30% ether–hexane; 1-l. fractions were collected. Fractions 6–10 contained 10.73 g of a yellow solid which, upon recrystallization from benzene–hexane, gave 9.832 g (0.0378 mol, 84%) of a pale yellow solid mixture of *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid and *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid.

The acid mixture was refluxed with stirring under nitrogen with 25 ml of thionyl chloride, 5 g of potassium carbonate was added, and the excess thionyl chloride was distilled. The reaction was then cooled to 5° and 50 ml of anhydrous methanol added dropwise. The reaction was stirred at 5° for 30 min and then brought to room temperature. The potassium carbonate was filtered and the methanol removed *in vacuo* leaving an oil which was taken up in 300 ml of 50% ether–benzene. This was washed with water, dried, and concentrated to give 10.75 g of a yellow oil. Crystallization from ether–hexane yielded 2.508 g of a colorless solid, mp 100–101.5°. The remainder was chromatographed on a 4.5 × 190 cm silicic acid column slurry packed with 12% ether–hexane and eluted with 16.5 l. of 15% ether–hexane; 40-ml fractions were collected and scanned at 260 nm. Two peaks overlapping slightly were observed. The first, fractions 36–149, contained 2.489 g of a colorless solid, mp 99.5–101.5°, the ir of which was identical with that of the ester crystallized from the original mixture. The 4.997 g of combined material was recrystallized from benzene–hexane to give 4.943 g of methyl *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylate, mp 100.5–101.5° (47%).

The spectral data for the ester were as follows: ir ($CHCl_3$) 3.22–3.31, 3.38, 4.47, 5.80, 6.22, 6.68, 6.93, 7.09, 7.31, 7.78, 7.89, 8.52, 11.87, and 14.40 μ; nmr ($CDCl_3$) τ 2.35–2.90 (m, 9 H, arom), 6.49 (s, 3 H, OCH_3), 6.66–7.25 (m, 2 H, cyclopropyl), and 7.41–7.66 (double doublet, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.99; H, 5.40; N, 5.04.

Fractions 150–181 of the column contained 0.695 g of an oily mixture of two esters as shown by nmr and tlc. The second peak, fractions 182–324, contained 4.092 g (39%) of an oily ester which was extremely difficult to crystallize and was used as such. Low-temperature crystallization of a small portion of the oil from ether–hexane produced colorless crystals of methyl *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylate, mp 53.5–55.5°.

Spectral data for the ester were as follows: ir ($CHCl_3$) 3.22–

3.33, 3.38, 4.47, 5.80, 6.22, 6.68, 6.92, 8.52, 12.11, and 14.40 μ; nmr ($CDCl_3$) τ 2.33–2.77 (m, 9 H, arom), 6.50 (s, 1 H, OCH_3), 6.65–7.20 (m, 2 H, cyclopropyl), and 7.42–7.67 (double doublet, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.10; H, 5.54; N, 4.85.

cis-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic Acid. To 500 ml of methanol containing 25 g (0.62 mol) of sodium hydroxide was added 10.64 g (0.0385 mol) of methyl *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylate. The reaction mixture was stirred for 18 hr after which time tlc (15% ether–hexane on silica gel) showed that no more ester remained. The methanol was removed *in vacuo*, 500 ml of water was added, and the reaction mixture was acidified (Congo red) with 6 *N* HCl and extracted with 50% ether–benzene. The organic extracts were washed with water, dried, and concentrated to give 10.93 g of an oil, which was crystallized from benzene–hexane–ether to give a first crop of 9.431 g, mp 137–139°, and a second crop of 0.459 g of *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, mp 137–139° (97%). Further recrystallization afforded a melting point of 137.5–139°.

Spectral data for the acid were as follows: ir ($CHCl_3$) 2.78–4.18, 4.47, 5.90, 6.22, 6.68, 6.92, 8.10–8.50, 11.95, and 14.37 μ; nmr ($CDCl_3$) τ −0.04 (s, 1 H, COOH), 2.46–2.96 (m, 9 H, arom), 6.74–7.23 (m, 2 H, cyclopropyl), 7.48–7.73 (double doublet, 1 H, cyclopropyl).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.32; H, 5.04; N, 5.23.

trans-2-*p*-Cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic Acid. To 500 ml of methanol containing 25 g (0.62 mol) of sodium hydroxide was added 11.10 g (0.0395 mol) of methyl *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylate; the mixture was stirred 18 hr. The methanol was removed *in vacuo*, 500 ml of water was added, and the reaction mixture was chloroform extracted. The aqueous layer was then acidified (Congo red) with 6 *N* HCl and extracted with chloroform. The latter chloroform extracts were then washed, dried, and concentrated to give 10.03 g of an oil which formed a colorless solid on standing. Recrystallization from methanol–benzene produced 0.538 g of a very high melting compound which was not further characterized. Concentration of the mother liquors and addition of hexane produced a first crop of 7.294 g, mp 175.5–178°, and a second crop of 0.585 g, mp 175.5–178°, Further recrystallization of the combined crops from benzene gave 6.953 g (67%) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid, mp 178–179°.

Spectral data for the acid were: ir ($CHCl_3$) 2.78–4.14, 4.47, 5.89, 6.21, 6.67, 6.90, 7.89, 8.10–8.50, 12.14, and 14.40 μ; nmr ($CDCl_3$) τ −1.00 (s, 1 H, COOH), 2.36–2.74 (m, 9 H, arom), 6.70–7.18 (m, 2 H, cyclopropyl), 7.50–7.75 (double doublet, 1 H, cyclopropyl).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.34; H, 4.79; N, 5.24.

Resolution of *cis*-2-*p*-Cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic Acid. A mixture of 15.98 g (0.0607 mol) of racemic *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, 17.90 g (0.0607 mol) of (−)-cinchonidine, and 3.5 l. of 50% ethyl acetate–chloroform was heated until solution occurred, then filtered and let stand 18 hr at room temperature, yielding 12.79 g of white crystalline salt, mp 191° dec. A portion of the salt on hydrolysis (10% HCl) gave acid with $[\alpha]^{25}_{436}$ +142° (*c* 0.00228, $CHCl_3$). Two more crystallizations of the salt produced 9.493 g, hydrolyzed to 4.445 g of acid, mp 103–106°, $[\alpha]^{25}_{436}$ +158° (*c* 0.00236, $CHCl_3$). Four crystallizations of the acid from ether–hexane yielded 1.837 g (11%) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, $[\alpha]^{25}_{436}$ +165 ± 1° (*c* 0.00317, $CHCl_3$), mp 103–105°, with no further change in rotation on crystallization.

Concentration of the mother liquor of the first crop of the salt followed by cooling at 0° gave 11.10 g of the salt of acid, $[\alpha]^{25}_{436}$ −123° (*c* 0.00856, $CHCl_3$). Three more crystallizations of the salt from ethyl acetate–chloroform yielded 5.246 g which gave acid with $[\alpha]^{25}_{436}$ −141 ± 1° (*c* 0.00584, $CHCl_3$). This solvent system would not resolve the salt further. Recrystallization from 50% methanol–acetone gave 4.477 g of salt with acid $[\alpha]^{25}_{436}$ −145° (*c* 0.00378, $CHCl_3$). The acid, regenerated from the salt with 10% HCl and recrystallized four times from ether–hexane, gave 0.981 g of *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid with constant $[\alpha]^{25}_{436}$ −164° (*c* 0.00532, $CHCl_3$), mp 101.5–104.5° (6%). The nmr ($CDCl_3$) and ir ($CHCl_3$) spectra of both enantiomers were identical with those of the racemic acid.

Resolution of *trans*-2-*p*-Cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic Acid. To 15.78 g (0.0595 mol) of racemic *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid was added 17.53 g (0.0595 mol) of (−)-cinchonidine and 3.6 l. of ethyl acetate; solution occurred upon refluxing. After filtration and standing 18 hr at room temperature, 9.829 g of salt, mp 189° dec, crystallized, corresponding to acid with $[\alpha]^{25}_{436}$ −47° (*c* 0.00253, $CHCl_3$). Two recrystallizations from ethyl acetate yielded 4.173 g of salt with acid $[\alpha]^{25}_{436}$ −70° (*c* 0.00257, $CHCl_3$). Hydrolysis with 10% HCl gave an oil which crystallized (4 weeks) from benzene, yielding 1.921 g of acid, $[\alpha]^{25}_{436}$ −78° (*c* 0.00310, $CHCl_3$). This was recrystallized three times from benzene to give 1.063 g of acid with a constant $[\alpha]^{25}_{436}$ −85 ± 1° (*c* 0.00291, $CHCl_3$), mp 155.5–158.5°. The mother liquor of the salt of the −70° acid, after concentration, gave on standing 1.210 g of salt, acid $[\alpha]^{25}_{436}$ −86° (*c* 0.00151, $CHCl_3$). Recrystallization from ethyl acetate provided 0.824 g of salt which gave 0.379 g more *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid with a constant $[\alpha]^{25}_{436}$ −85 ± 1° (*c* 0.00254, $CHCl_3$) on hydrolysis; total 9% of this enantiomer.

The mother liquor of the original salt of the −47° acid, after standing at 0° for 2 days, gave 7.240 g of salt, mp 190° dec, acid $[\alpha]^{25}_{436}$ +57° (*c* 0.00258). This salt was crystallized four times from ethyl acetate to give 1.376 g of salt corresponding to acid of constant $[\alpha]^{25}_{436}$ +85 ± 2° (*c* 0.00304, $CHCl_3$). Hydrolysis gave 0.637 g (4%) of this enantiomer of *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid, mp 155.5–158.5°. The nmr ($CDCl_3$) and ir ($CHCl_3$) spectra of both enantiomers were identical with those of the racemic acid.

Optically Active *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. A 1.003-g (0.00381 mol) portion of *cis*-2-*p*-cyanophenyl-*trans*-3-phenylcyclopropanecarboxylic acid, $[\alpha]^{25}_{436}$ +165°, and 10 ml of thionyl chloride were refluxed under nitrogen and the excess thionyl chloride was distilled, avoiding excessive heating of the residue; 10 ml of dry benzene was added and distilled, ensuring removal of thionyl chloride.

The acid chloride in 20 ml of dry benzene was added dropwise to a benzene solution of diphenylcadmium, prepared from 0.464 g (0.0191 g-atom) of magnesium turnings, 2.980 g (0.0190 mol) of bromobenzene, and 1.832 g (0.0100 mol) of anhydrous cadmium chloride (*vide supra*), at 0° with stirring under nitrogen. The mixture was stirred at 0° for 10 min and at room temperature for 2 hr. Then 100 ml of 4% ammonium chloride solution was added. The organic layer was washed with 5% sodium carbonate and with water, dried, and concentrated to give 1.932 g of a yellow oil which was chromatographed on a 2.5 × 98 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 240 ml of 10% followed by 3.5 l. of 20% ether–hexane; 40-ml fractions were collected and scanned at 280 nm. Fractions 35–78 contained 0.611 g of the desired ketone. Crystallization of the material from benzene–hexane to constant melting point and ORD curve yielded 0.513 g (42%) of optically active *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, mp 152.5–157.5°. Two crystalline forms of the ketone, one melting at 152.5° with rearrangement to the other, mp *ca.* 155.5–157.5°, were observed. The nmr ($CDCl_3$) and ir ($CHCl_3$) spectra of the ketone were identical with those of the racemic ketone; ORD max at 343 nm, intercept at 313.8 nm, $[\alpha]^{25}_{343}$ −3080 ± 30° (*c* 0.000130, $CHCl_3$).

Optically Active *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane. Optically active *trans*-2-*p*-cyanophenyl-*cis*-3-phenylcyclopropanecarboxylic acid (1.002 g, 0.00381 mol), $[\alpha]^{25}_{436}$ −86°, was converted to the corresponding phenyl ketone by the method (*vide supra*) used on the *cis,trans* isomer.

The crude product, 2.258 g, was chromatographed on a 3.5 × 30 cm silica gel column slurry packed in 10% ether–hexane and eluted with 500 ml of 10% followed by 6 l. of 20% ether–hexane; 1-l. fractions were collected. Fractions 3–7 contained 1.259 g of impure ketone which was crystallized from methylene chloride–hexane to give a first crop of 0.904 g, mp 137–141°, and a second crop of 0.221 g, mp 141.5–145°. The ORD curves of the two crops were identical, so they were combined and recrystallized from benzene–hexane to constant melting point and ORD curve, yielding 0.666 g (54%) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, mp 139–141°. The nmr ($CDCl_3$) and ir ($CHCl_3$) spectra of the active ketone were identical with those of the racemic material; ORD max at 345 nm, intercept at 313.8 nm, $[\alpha]^{25}_{345}$ +1480 ± 20° (*c* 0.000120, $CHCl_3$).

4-Phenyl-3-*p*-chlorophenylbutyrophenone. To benzylmagnesium chloride formed from 1.210 g (0.0498 g-atom) of magnesium turnings and 6.334 g (0.050 mol) of benzyl chloride in 50 ml of anhydrous ether was added 0.075 g of cuprous bromide. The mixture was stirred 10 min and then 10.20 g (0.042 mol) of 4-chlorochalcone[18]

in 40 ml of dry benzene was added during 30 min with refluxing followed by refluxing for an additional 30 min. Work-up with ice–HCl, ether extraction, washing with water, drying, and concentration gave a white solid. Recrystallization from hexane–ligroin (bp 90°) gave 9.605 g (68.5%) of 4-phenyl-3-*p*-chlorophenylbutyrophenone, mp 119.0–120.0°.

The spectral data were: ir (KBr) 5.97 (5.92 in CS_2), 6.80, 8.15, 9.13, 9.87, 12.27, 13.25, 14.17, and 14.52 μ; nmr ($CDCl_3$) τ 2.06–2.23 (m, 2 H, *o*-benzoyl), 2.47–3.02 (m, 12 H, arom), 6.18–7.15 (m, 5 H, CH and CH_2).

Anal. Calcd for $C_{22}H_{19}ClO$: C, 78.91; H, 5.72; Cl, 10.59. Found: C, 78.67; H, 5.59; Cl, 10.82.

4-Phenyl-3-*p*-cyanophenylbutyrophenone. A mixture of 3.00 g (9.0 mmol) of 4-phenyl-3-*p*-chlorophenylbutyrophenone, 1.20 g (6.70 mmol) of cuprous cyanide, and 5.0 ml of N-methyl-2-pyrrolidone was heated under nitrogen at 220° for 24 hr. The cooled mixture was diluted with ether, washed repeatedly with ammonium hydroxide solution (1:1) until the aqueous layer was clear, washed with water, dried, and concentrated *in vacuo*. The residue was chromatographed on a 4 × 45 cm silica gel column slurry packed with 5% ether–hexane. Elution was with 1 l. of 5%, 2 l. of 10%, 4 l. of 20%, 2 l. of 30%, and 2 l. of 50% ether–hexane. Fraction size was 40 ml. Fractions 36–67 contained 0.748 g (25%) of starting material, while fractions 100–217 contained 1.890 g (86.5% based on reacted chloro compound) of 4-phenyl-3-*p*-cyanophenylbutyrophenone, mp 125.5–127.0°. This was recrystallized from methylene chloride–hexane to mp 127.0–128.0°.

The spectral data were: ir (KBr) 4.49, 5.97 (5.93 in CS_2), 7.48, 8.15, 9.01, 9.39, 9.70, 9.81, 10.45, 10.98, 11.86, 12.14, 13.19, 13.42, 13.68, 14.2–14.5, and 15.19 μ; nmr ($CDCl_3$) τ 2.04–2.20 (m, 2 H, *o*-benzoyl), 2.41–3.05 (m, 12 H, arom), 6.10–7.11 (m, 5 H, CH and CH_2).

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.55; H, 5.74; N, 4.44.

3-Phenyl-4-*p*-chlorophenylbutyrophenone. To *p*-chlorobenzylmagnesium chloride formed from 4.86 g (0.20 g-atom) of magnesium turnings and 32.2 g (0.20 mol) of *p*-chlorobenzyl chloride in 150 ml of anhydrous ether was added 0.230 g of cuprous bromide. The mixture was stirred 1 hr under nitrogen followed by addition of 33.1 g (0.16 mol) of benzalacetophenone in 100 ml of ether during 1 hr at 0°. It was stirred 15 min at room temperature and refluxed 1 hr. Hydrolysis with ice–HCl, ether extraction, washing, drying, and concentration *in vacuo* gave a yellow oil. Addition of hexane gave 12.98 g of a solid, mp 108–112°, which was recrystallized from hexane–petroleum ether (90°) to mp 113.0–114.5° The filtrates were chromatographed on a 6.5 × 60 cm silica gel column slurry packed with 3% ether–hexane. Elution was with 4 l. of 3%, 8 l. of 5%, 5 l. of 10%, 6 l. of 20%, 4 l. of 50%, and 3 l. of 100% ether–hexane. Fraction size was 1 l. Fractions 7–10 contained 6.694 g of product giving a total of 19.67 g (37%) of 3-phenyl-4-*p*-chlorophenylbutyrophenone, mp 113.0–114.5°.

The spectral data were: ir (KBr) 5.96, 7.89, 8.23, 9.15, 9.83, 10.17, 12.26, 13.10, 13.22, 13.43, 13.95, 14.27, 14.60, and 15.00 μ; nmr ($CDCl_3$) τ 2.05–2.21 (m, 2 H, *o*-benzoyl), 2.44–3.14 (m, 12 H, arom), 6.23–7.15 (m, 5 H, CH and CH_2).

Anal. Calcd for $C_{22}H_{19}ClO$: C, 78.91; H, 5.72; Cl, 10.59. Found: C, 79.05; H, 5.89; Cl, 10.22.

3-Phenyl-4-*p*-cyanophenylbutyrophenone. A mixture of 3.00 g (9.00 mmol) of 3-phenyl-4-*p*-chlorophenylbutyrophenone, 1.20 g (6.70 mmol) of cuprous cyanide, and 5.0 ml of N-methyl-2-pyrrolidone was heated under nitrogen at 220° for 23 hr. The cooled mixture was diluted with 400 ml of ether and washed with 1:1 ammonium hydroxide until the aqueous extracts were clear. The ether layer was then washed, dried, and concentrated *in vacuo* to give 2.816 g which was chromatographed on a 4 × 40 cm silica gel column slurry packed with 5% ether–hexane. Elution was with 1 l. of 5%, 3 l. of 10%, 4 l. of 20%, and 2 l. of 30% ether–hexane. Fraction size was 40 ml. Fractions 25–49 contained 0.552 g (18.4%) of starting material, while fractions 85–134 contained 1.521 g (64% based on reacted chloro compound) of 3-phenyl-4-*p*-cyanophenylbutyrophenone, mp 111–112.5°. This was recrystallized from hexane–ethyl acetate to mp 112.5–113.5°.

The spectral data were: ir (KBr) 4.49, 5.99, 7.41, 8.13, 8.49, 9.25, 9.76, 9.94, 11.41, 12.13, 13.43, and 14.60 μ; nmr ($CDCl_3$) τ 2.02–2.18 (m, 2 H, *o*-benzoyl), 2.49–2.98 (m, 12 H, arom), 6.30–7.17 (m, 5 H, CH and CH_2).

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.73; H, 5.91; N, 4.45.

1,3-Diphenyl-4-*p*-cyanophenylbutan-1-ol. A solution of 2.000 g (0.00618 mol) of 3-phenyl-4-*p*-cyanophenylbutyrophenone in 500 ml of 95% ethanol was reduced with 160 cc (0.0065 mol) of hydrogen at room temperature and 1 atm for 5 hr using 0.900 g of 10% Pd–C (preequilibrated), the uptake finally stopping sharply. Filtration, concentration, and drying gave 1.880 g of oil, which was chromatographed on a 3.5 × 94 cm silicic acid column slurry packed in 5% ether–hexane and eluted with 1 l. of 10%, 3 l. of 20%, and 7 l. of 30% ether–hexane; 40-ml fractions were collected and scanned at 260 nm. Fractions 171–192 (first peak, 0.300 g) and 193–281 (second peak plus overlap region, 1.075 g) were worked up separately. The latter fractions were rechromatographed on a similar column, yielding 0.135 g in the first peak and 0.895 g in the second. The first peaks from each column were combined and crystallized from methylene chloride–hexane to give 0.356 g of colorless crystals, mp 98–103°. Four more crystallizations from methylene chloride–hexane gave 0.153 g (8%) of one diastereomer of 1,3-diphenyl-4-*p*-cyanophenylbutan-1-ol, mp 102.5–104°.

Spectral data for the alcohol were: ir (KBr) 2.85, 3.32, 3.42–3.45 (d), 3.52, 4.50, 6.22, 6.71, 6.91, 6.95, 9.29, 9.42, 9.90, 12.16, 13.08, and 14.22 μ; nmr ($CDCl_3$) τ 2.47–3.10 (m, 14 H, arom), 5.50–5.78 (double doublet, 1 H, HCO), 6.53–7.18 (m, 3 H).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.49; H, 6.46; N, 4.26.

The second peak of the second column contained 0.521 g of a white solid, mp 100–106°, and 0.374 g of an oil. These were recrystallized from methylene chloride–hexane to give 0.436 g of the second diastereomer of 1,3-diphenyl-4-*p*-cyanophenylbutan-1-ol, mp 106–108° (22%).

Spectral data for the alcohol were: ir (KBr) 2.85, 3.31, 3.41, 3.45, 4.49, 6.22, 6.71, 6.89, 9.42, 11.93, 12.12, 13.01, 13.31, and 14.32 μ; nmr ($CDCl_3$) τ 2.48–3.13 (m, 14 H, arom), 5.35–5.68 (double doublet, 1 H, HCO), 6.87–7.65 (m, 3 H), and 7.67–8.07 (m, 3 H).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.12; H, 6.30; N, 4.26.

1,4-Diphenyl-3-*p*-cyanophenylbutan-1-ol. The hydrogenation of 2.000 g (0.00614 mol) of 4-phenyl-3-*p*-cyanophenylbutyrophenone was carried out precisely as with 3-phenyl-4-*p*-cyanophenylbutyrophenone (*vide supra*) (175 cc, 0.0072 mol uptake). The product was chromatographed in two batches after reduction. The first batch (0.948 g) was chromatographed on a 3.5 × 94 cm silicic acid column slurry packed with 5% ether–hexane and eluted with 400 ml of 5%, 1 l. of 10%, 5 l. of 25%, and 2 l. of 35% ether–hexane; 40-ml fractions were collected and scanned at 260 nm. Two main peaks were observed: fractions 135–176 contained 0.195 g of a white solid; 197–288, 0.452 g of a clear oil. The second batch (0.935 g) on similar chromatography gave 0.194 g of a white solid and 0.415 g of a pale yellow oil. The first peaks from each column were combined and crystallized from methylene chloride–hexane twice and then from ethanol–water and from ether–hexane to give 0.144 g (7%) of diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol, mp 120.5–122°. Another crystalline form melting at 135° was sometimes observed.

Spectral data for the alcohol were: ir (KBr) 2.87, 3.31, 3.44, 3.52, 4.49, 6.22, 6.70, 6.89, 7.13, 7.69, 9.22, 9.39, 9.99, 12.02, 13.25, 13.60, and 14.30 μ; nmr ($CDCl_3$) τ 2.38–3.20 (m, 14 H, arom), 5.58–5.90 (double doublet, 1 H, HCO), 6.46–6.92 (m, 1 H), 7.00–7.31 (m, 2 H), and 7.55–8.15 (m, 3 H).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.36; H, 6.51; N, 4.22.

The combined second peaks of the two columns (0.903 g, 45%) were very difficult to crystallize; storing the oil in ethanol–water for an extended period of time produced 0.413 g of the crystalline diastereomer B of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol, mp 86.5–88.5° (20%), after recrystallization from ethanol–water.

Spectral data for the alcohol were: ir (KBr) 2.77, 4.48, 6.23, 6.70, 6.90, 9.26, 9.52, 9.77, 10.59–10.67, 11.49, 11.74, 12.11, 12.16, 13.14, 13.47, 13.63, and 14.32 μ: nmr ($CDCl_3$) τ 2.50–3.25 (m, 14 H, arom), 5.47–5.51 (t, 1 H, HCO), and 6.89–8.15 (m, 7 H).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.58; H, 6.36; N, 4.16.

Catalytic Reduction of *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. A solution of 0.206 g (0.683 mmol) of racemic *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane in 75 ml of 95% ethanol was reduced with 40 cc (1.64 mmol) of hydrogen at room temperature and 1 atm for 2 hr using 0.158 g of 10% Pd–C (preequilibrated), the uptake having stopped. Filtration and concentration *in vacuo* gave 0.211 g of a colorless oil

(18) E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 78.

which was chromatographed on a 2.5 × 200 cm silicic acid column slurry packed and eluted with 25% ether–hexane. The 40-ml fractions were scanned at 260 nm: fractions 148–153, 0.009 g (4%) of a colorless solid, mp 117.5–137.5°; 247–283, 0.112 g (50%) of pale yellow oil identified as diastereomer B of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol by inspection of the nmr spectrum. Fractions 148–153 were crystallized from ether–hexane to give 7.0 mg of colorless crystals with melting point, nmr, and KBr ir identical with those of the independently synthesized diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol. Nmr evidence was obtained for the occurrence of the diastereomeric 1,3-diphenyl-4-*p*-cyanophenylbutan-1-ols in the ends of the two peaks.

Catalytic Reduction of *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane. A solution of 0.400 g (1.23 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane in 125 ml of 95% ethanol was reduced with 70 ml (2.87 mmol) of hydrogen at room temperature and 1 atm for 15 min using 0.350 g of 10% Pd–C (preequilibrated), the uptake having stopped sharply. The usual work-up yielded 0.402 g of a colorless oil which was chromatographed on a 2.0 × 117 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 480 ml of 10% followed by 4 l. of 25% ether–hexane. The 40-ml fractions were scanned at 260 nm. Nmr spectra indicated that fractions 47–48, 0.014 g, and 49–50, 0.031 g (11%), contained only the first diastereomer of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol, whereas fractions 66–90 contained 0.275 g of diastereomer B of this alcohol (68%). Recrystallization of fractions 47–50 from ether–hexane gave 0.030 g of colorless crystalline alcohol, the melting point and KBr ir of which were identical with those of the independently synthesized material.

Catalytic Reduction of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. A solution of 0.497 g (1.54 mmol) of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane in 125 ml of 95% ethanol was reduced with 80 cc (3.28 mmol) of hydrogen at room temperature and 1 atm for 20 min using 0.250 g of 10% Pd–C (preequilibrated), the uptake having stopped sharply. The usual work-up and chromatography gave the following: first major peak, 0.066 g (13%) of a colorless solid, mp 117–132.5°, the nmr spectrum of which was identical with that of diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol; second major peak, 0.220 g (44%) of the diastereomer B of this alcohol (nmr). Recrystallization of the diastereomer A from ether–hexane gave 0.054 g of material with a melting point and KBr ir identical with those of the known sample.

Catalytic Reduction of Optically Active *trans*-2-*p*-Cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane. A solution of 0.250 g (0.774 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{345}$ +1480 ± 20°, in 150 ml of 95% ethanol was reduced with 45 cc (1.84 mmol) of hydrogen at room temperature and 1 atm for 20 min using 0.250 g of 10% Pd–C (preequilibrated), the uptake having stopped sharply. The usual work-up gave 0.249 g of an oil which was chromatographed on a 2.0 × 117 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 640 ml of 10% followed by 3.5 l. of 25% ether–hexane. The 40-ml fractions were scanned at 260 nm: fractions 53–54, 0.0078 g, 55, 0.0081 g, 56, 0.0098 g, and 57, 0.0014 g, were identified as the diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol by their position on the uv scan of the column fractions and by their combined nmr spectrum. The ORD curves of all four cuts were found to be identical in shape; despite difficulties due to high absorption below 250 nm, the maximum and intercept for all fractions were determined as 244.5 ± 1.5 and 235.5 ± 1.5 nm, respectively. For each fraction $[\alpha]^{25}_{290}$ was determined: 53–54, −1730 ± 50°; 55, −1820 ± 60°; 56, −1840 ± 40°; 57, −1760 ± 30°; average, −1790 ± 40° (*c* 0.00040, methanol).

Catalytic Reduction of Optically Active *cis*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. A solution of 0.250 g (0.774 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{343}$ −3080 ± 30°, in 150 ml of 95% ethanol was reduced with 40 cc (1.64 mmol) of hydrogen at room temperature and 1 atm for 20 min using 0.250 g of 10% Pd–C (preequilibrated), the uptake having stopped sharply. The usual work-up gave 0.247 g of an oil which was chromatographed on a 2.0 × 117 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 320 ml of 10% followed by 3 l. of 25% ether–hexane. The 20-ml fractions were scanned at 260 nm: fractions 98–99, 0.0088 g, 100, 0.0056 g, 101, 0.0060 g, 102, 0.0052 g, and 103, 0.0052 g, were identified as diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol by their position on the uv scan of the column fractions and by their combined nmr spectrum. The ORD curves were identical in shape: all had a max and intercept at 244.5 ± 1.5 and 235.5 ± 1.5 nm, respectively. For each fraction $[\alpha]^{25}_{290}$ was determined: (98–99, +1560 ± 60°); 100, +1870 ± 80°; 101, 1830 ± 70°; 102, +1780 ± 80°; 103, +1840 ± 90°; average (omitting 98–99), +1830 ± 80° (*c* 0.00025, methanol).

Catalytic Reduction of Optically Active *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. The reduction of 0.250 g (0.774 mmol) of optically active *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{325}$ +912 ± 19°, was carried out exactly as for the optically active *cis,trans* isomer. The crude product, 0.252 g, was chromatographed on a 2.0 × 117 cm silicic acid column slurry packed in 10% ether–hexane and eluted with 100 ml of 10% followed by 4.5 l. of 25% ether–hexane. The 20-ml fractions were scanned at 260 nm: fractions 90–91, 0.0071 g; 92, 0.0053 g; 93, 0.0053 g; 94, 0.0056 g; 95, 0.0053 g; and 96–97, 0.0088 g, were identified as diastereomer A of 1,4-diphenyl-3-*p*-cyanophenylbutan-1-ol by their position on the uv scan of the column fractions and by their combined nmr spectrum. The ORD curves of the fractions were identical in shape with each other and with those of the alcohols isolated from the optically active *cis,trans*- and *trans,cis*-ketone isomers, showing the same maximum and intercept. For each fraction $[\alpha]^{25}_{290}$ was determined: (90–91, −1560 ± 50°); 92, −1730 ± 80°; 93, −1810 ± 70°; 94, −1760 ± 70°; 95, −1710 ± 80°; 96–97, −1810 ± 50°; average (omitting 90–91) −1760 ± 70° (*c* 0.00025, methanol).

Photolysis of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. A solution of 500.0 mg of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane in 700 ml of dry benzene was irradiated under purified nitrogen[14] for 10.0 min with a 450-W Hanovia medium-pressure mercury lamp. A Pyrex filter and a circulating filter solution composed of 40.0 g of cupric sulfate pentahydrate, 315.0 g of nickelous sulfate hexahydrate, 600.0 of cobalt sulfate heptahydrate, and 47.0 g of potassium nitrate dissolved in 1 l. of water were used. The solution was opaque below 300 nm; 310 nm, 1% transmittance (T); 320 nm, 5% T; 330 nm, 20% T; 340 nm, 35% T; 350 nm, 35% T; 360 nm, 20% T; 370 nm, 5% T; and opaque from 380 to 500 nm.

The benzene was removed *in vacuo* to give 538.6 mg of an oil which was chromatographed on a 2.5 × 150 cm liquid–liquid partition chromatography column[19] with monitoring by uv at 280 nm and 20-ml fractions. The material was placed on the column in two batches and the corresponding fractions were combined to give total yields as follows: fractions 38–43, 14.2 mg (2.7%) of an unknown oil; 54–63, 390.3 mg (75.2%) of starting material; 66–74, 91.4 mg (17.6%) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane; 75–83, 23.1 mg (4.4%) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane. The fractions were recrystallized from ether–hexane to give 355.0 mg of starting material, mp 112–115°; 70.7 mg of the *cis,trans* isomer, mp 132–134°; and 15.0 mg of the *trans,cis* isomer, mp 127.5–129.0°.

In each of the three further runs, 500.0 mg of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane was photolyzed exactly as above for 6.0, 20.0, and 60.0 min. The 6.0-min irradiation gave chromatography fractions of 6.9 mg (1.3%) of an unknown oil, 438.1 mg (84.8%) of starting material, 55.5 mg (10.8%) of *cis,trans* isomer, and 15.9 mg (3.1%) of *trans,cis* isomer. The 20.0-min irradiation gave 17.9 mg (3.4%) of an unknown oil, 323.8 mg (62.3%) of starting material, 138.2 mg (26.6%) of *cis,trans* isomer, and 40.3 mg (7.8%) of *trans,cis* isomer. The 60.0-min irradiation gave 27.0 mg (5.4%) of an unknown oil, 209.6 mg (41.7%) of starting material, 194.0 mg (38.6%) of *cis,trans* isomer, and 64.1 mg (12.7%) of *trans,cis* isomer.

Photolysis of *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane. A solution of 0.3000 g of *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane in 700 ml of dry benzene was irradiated under purified nitrogen[14] for 15 min with a Hanovia 450-W medium-pressure mercury lamp. The same Pyrex and solution filter combination (*vide supra*) was employed (310–375 nm). The usual liquid–liquid partition chromatography gave 0.1487 g (49.5%) of starting material, 0.1211 g (40.5%) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-3-*d*-1-benzoylcyclopropane, and 0.0327 g (10.9%) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-3-*d*-1-benzoylcyclopropane. Recrystallization from methylene chloride–hexane gave 0.1353 g (45.0%) of starting material, mp 111–113°, 0.0832 g (27.8%) of deuterio-*cis,trans* isomer, mp 134.5–136.0°, and 0.0187 g (6.2%) of deuterio-*trans,cis* isomer, mp 130.5–132.0°. A mixture melting point between deuterio-*cis,trans* isomer and nondeuterated

(19) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Amer. Chem. Soc.*, 89, 2033 (1967).

cis,trans isomer, mp 134.5–136.0°, showed no depression, whereas mixture melting points between this deuterio isomer and both nondeuterated and deuterio-*trans,cis* isomer were depressed to 105–120°. The deuterio-*trans,cis* isomer gave an undepressed mixture melting point with undeuterated *trans,cis* isomer, mp 132.0–133.5°, whereas a mixture melting point with *cis,trans* isomer was depressed to 105–120°.

The spectral data of the deuterio-*cis,trans* isomer were: ir (KBr) 4.48, 6.02, 6.22, 6.31, 6.68, 6.90, 7.12, 7.36, 7.93, 8.14, 8.25, 8.45, 9.51, 9.65, 9.86, 10.94, 11.98, 12.39, 13.5, 14.26, 14.50, 15.38, and 15.52 μ; uv (95% EtOH) 242.5 nm max (ϵ 31,230); nmr ($CDCl_3$) τ 1.97–2.13 (m, 2 H, *o*-benzoyl), 2.41–2.76 (m, 12 H, arom), 6.46, 6.62, 6.74, 6.89 (AB q, 2 H, cyclopropyl, σ_A τ 6.57, σ_B 6.79, J_{AB} = 9.5 Hz). The aromatic region was identical with that of the undeuterated compound and was characteristic for each of the three isomers: 439, 445, 447, 449, 541 Hz downfield from TMS.

The spectral data of the deuterio-*trans,cis* isomer were: ir (KBr) 4.47, 6.02, 6.21, 6.31, 6.67, 6.90, 7.11, 7.33, 7.92, 8.17, 8.41, 8.48, 9.46, 9.62, 9.89, 10.48, 11.02, 12.09, 12.56, 12.72, 13.5, 13.68, 13.89, 14.33, 15.29, and 15.57 μ; uv (95% EtOH) 246 nm max (ϵ 35,695); nmr ($CDCl_3$) τ 1.95–2.10 (m, 2 H, *o*-benzoyl), 2.29–2.76 (m, 12 H, arom), 6.32, 6.41, 6.57, 6.66 (AB q, 2 H, cyclopropyl, σ_A τ 6.37, σ_B 6.61, J_{AB} = 5.3 Hz). The aromatic region was identical with that of the undeuterated compound with peaks at 434, 448, 450, 451, 454, and 462 Hz downfield from TMS.

Quantitative Photochemical Procedures. Reactant solutions were irradiated under oxygen-free nitrogen[14] using a GE AH-6 high-pressure mercury arc centered at the focus of a parabolic reflector 13.7 cm long and 14.0 cm in diameter. Light was filtered through three 2.4-cm path length water-cooled compartments containing one of two filter combinations: filter A, cell 1, 0.76 *M* cobalt sulfate and 0.08 *M* cupric sulfate in 10% sulfuric acid; cell 2, 0.89 *M* nickelous sulfate in 10% sulfuric acid; cell 3, 1.29×10^{-3} *M* potassium chromate in 5% potassium carbonate solution; transmission 0% below 300 nm, 12% at 313 nm, and 0% above 330 nm; filter B, cell 1, 0.96 *M* cobalt sulfate in 10% sulfuric acid; cell 2, 0.74 *M* nickelous sulfate in 10% sulfuric acid; cell 3, 0.155 *M* stannous chloride in 40% hydrochloric acid; transmission 0% below 320 nm, 12% at 337 nm, and 0% above 362 nm. Incident light was measured by ferrioxalate actinometry[20] before and after the sample run and was monitored for transmission through the reactant solution with a backup cell. The solvent was then removed *in vacuo*. Sensitizer, when present, was removed by short path distillation (40°, 0.1 mm). The residue was then subjected to chromatography on one of two chromatographic systems: system A, a 2.5 × 150 cm liquid–liquid column (*vida supra*); the retention volumes of the various materials were unknown oil, 780 ml, *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 1080 ml, *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 1300 ml, *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, 1500 ml, propiophenone, 780 ml; system B, a 2.5 × 115 cm silicic acid column slurry packed in 15% ether–hexane and eluted with the same; retention volumes were unknown oil, 340 ml, *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 1200 ml, *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, 1840 ml, *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, 2600 ml, acetophenone, 480 ml. The eluents were scanned at 280 nm; the contents of each fraction were identified by ir spectra and by their characteristic retention volumes. In runs with optically active material, center cuts of the appropriate fractions from the original column were separately rechromatographed on column A. Then center cuts of the eluted material were taken and the ORD curves determined without further purification. In all cases the curves were found to be quantitatively identical in shape with those of the independently synthesized optically active material.

Specific data for individual irradiations are given as follows: weight of ketone and additive (if any), solution volume, temperature, filter system, amount of light absorbed, and column system used. Then, for each product isolated, the weight, quantum yield, and specific rotations are listed as determined.

Run QY-OA-1. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (1.0102 g, 3.13 mmol), $[\alpha]^{25}_{325}$ +912 ± 19°, 730-ml benzene solution, 25.0°, filter A, 0.202 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (941.3 mg, 2.91 mmol), ϕ = 1.06, $[\alpha]^{25}_{325}$ +903 ± 14°; 41.5 mg (0.132 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.64, $[\alpha]^{25}_{343}$ −3050 ± 130°; 12.9 mg (0.040 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.20, $[\alpha]^{25}_{345}$ +87 ± 9°; 12.2 mg of unknown oil.

Run OA-2. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (500.2 mg, 1.55 mmol), $[\alpha]^{25}_{325}$ +912 ± 19°, 730-ml benzene solution, 25.0°, filter A, 0.156 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (433.4 mg, 1.34 mmol), $[\alpha]^{25}_{325}$ +909 ± 17°; 26.6 mg (0.0824 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{343}$ −2970 ± 100°; 7.4 mg (0.023 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{345}$ +100 ± 10°; 3.6 mg of unknown oil.

Run QY-3. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (1.0026 g, 3.10 mmol), in 730 ml of a *t*-butyl alcohol solution, 27.0°, filter A, 0.183 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (941.8 mg, 2.92 mmol), ϕ = 1.03); 36.6 mg (0.113 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.62; 9.1 mg (0.028 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.15; 2.6 mg of unknown oil.

Run QY-S-4. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (199.9 mg, 0.620 mmol) and 30.149 g (0.225 mol) of propiophenone (capturing 99% of light), in 725 ml of a benzene solution, 25.0°, filter B, 0.226 mEinstein, column A.

The products recovered were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (179.0 mg, 0.554 mmol), ϕ = 0.29; 12.8 mg (0.0397 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.18; 3.2 mg (0.0099 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.044; the unknown oil was eluted with the propiophenone and was not determined.

Run QY-S-5. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (324.2 mg, 1.00 mmol) and 84.08 g (0.700 mol) of acetophenone (capturing 99% of light), in a 730-ml benzene solution, 25.0°, filter B, 0.229 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (300.7 mg, 0.932 mmol), ϕ = 0.32; 15.2 mg (0.471 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.21; 4.6 mg (0.014 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.062; 2.9 mg of unknown oil.

Run QY-S-6. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (324.7 mg, 1.01 mmol) and 84.74 g (0.706 mol) of acetophenone (capturing 99% of light), in a 730-ml *t*-butyl alcohol solution, 27.0°, filter A, 0.335 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (295.1 mg, 0.913 mmol), ϕ = 0.27; 20.0 mg (0.0619 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.18; 5.4 mg (0.016 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.049; 2.4 mg of unknown oil.

Run QY-Q-7. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (2.0183 g, 6.25 mmol) and 99.00 g (1.45 mol) of piperylene (capturing not over 3% of light), in a 730-ml benzene solution, 25.0°, filter A, 0.371 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (1.9138 g, 5.92 mmol), ϕ = 0.87; 63.8 mg (0.197 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.53; 21.1 mg (0.0653 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.18; the amount of unknown oil could not be determined because it eluted with piperylene polymer.

Run QY-S-8. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (323.9 mg, 1.00 mmol), in 412 mg (4.0 mmol) of benzonitrile, and 89.29 g (0.734 mol) of acetophenone (capturing 99% of light), 730-ml benzene solution, 25°, filter A, 0.266 mEinstein, column B.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (277.6 mg, 0.859 mmol), ϕ = 0.54; 31.8 mg (0.0984 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.37; 7.9 mg (0.0244 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, ϕ = 0.092; the amount of unknown oil could not be determined.

Run OA-S-9. *trans*-2-*p*-Cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane (323.2 mg, 1.00 mmol), $[\alpha]^{25}_{325}$ +912 ± 19°, 84.20 g (0.700 mol) of acetophenone (capturing 99% of light), 730-ml benzene solution, 25°, filter B, 0.452 mEinstein, column A.

The recovered products were *trans*-2-*p*-cyanophenyl-*trans*-3-

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

phenyl-1-benzoylcyclopropane (258.0 mg, 0.800 mmol), $[\alpha]^{25}_{325}$ 920 ± 15°; 43.1 mg (0.133 mmol) of *cis*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{343}$ −2980 ± 80°; 6.8 mg (0.021 mmol) of *trans*-2-*p*-cyanophenyl-*cis*-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}_{345}$ −104 ± 8°.

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Thermal and Photochemical Interconversions of Cyclooctatetraenes and Semibullvalenes. Exploratory Organic Photochemistry. LII[1,2]

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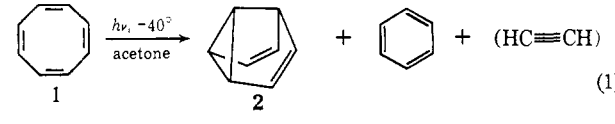
Abstract: Irradiation of cyclooctatetraene at −60° in isopentane with an acetone sensitizer afforded semibullvalene and benzene as the major volatile products. Nmr and vpc assay indicated *ca.* 42% of semibullvalene based on reacted cyclooctatetraene; despite vpc overlap with cyclooctatetraene, semibullvalene could be isolated by silver nitrate liquid partition chromatography with 26% recovery. Bicyclo[4.2.0]octa-2,4,7-triene, independently prepared, was irradiated under typical conditions and found to afford only benzene, thus establishing that this compound was not an intermediate in the semibullvalene formation. Low-temperature irradiations were monitored by low-temperature infrared analysis, and evidence was obtained for the direct formation of semibullvalene. In related efforts 1,3,5,7-tetramethylcyclooctatetraene was found to be only slightly reactive on irradiation under similar conditions and the tetramethylsemibullvalenes were not among the products. Contrariwise, pyrolysis of 1,3,5,7-tetramethylcyclooctatetraene afforded $\beta,\beta',\gamma,\gamma'$-tetramethylsemibullvalene and presumably $\alpha,\alpha',\alpha'',\alpha'''$-tetramethylsemibullvalene. Photolysis of the former semibullvalene was investigated and found to give 1,3,5,7-tetramethylcyclooctatetraene.

In an attempt to delineate both the excited and ground state pathways interrelating the $(CH)_8$ hydrocarbons, we have investigated the photochemistry of cyclooctatetraene (**1**). Although cyclooctatetraene has been obtained[2,3] on irradiation of two of its $(CH)_8$ isomers, namely barrelene[2] and semibullvalene (**2**),[3] and similar behavior has been found for the benzo[4] and naphtho[5] derivatives of barrelene and semibullvalene, the photochemistry of cyclooctatetraene has not been extensively studied. There are reports of the formation of benzene and acetylene,[6] and also, the valence tautomer bicyclo[4.2.0]octa-2,4,7-triene (**3**)[7] from the photolysis of cyclooctatetraene.

Low-Temperature Photolysis of Cyclooctatetraene. Results. In pursuing our study of the low-temperature photochemistry of cyclooctatetraene, we began with exploratory irradiation of small samples (*ca.* 100 mg) under different conditions in sealed quartz tubes kept at temperatures ranging from −65 to −30°. Nmr analysis used to follow the direct irradiation of cyclooctatetraene (*i.e.*, without sensitizer) strikingly revealed approximately equal amounts of semibullvalene and benzene. Above −30°, the formation of benzene predominated and the inside wall of the tube was badly coated with opaque polymeric material. In the presence of acetone sensitizer the conversion was somewhat accelerated, suggesting that triplet sensitization is occurring. With large concentrations of acetone, the



1 2 (1)

efficiency diminished slightly perhaps due to self-quenching. Acetophenone and benzophenone, however, were found ineffective in sensitizing the reaction. The results are summarized in Table I.

Preparative Low-Temperature Photolysis of Cyclooctatetraene. Results. Hitherto semibullvalene had been obtained by laborious multistep syntheses with limited overall yield.[3] In view of the single step formation of semibullvalene from easily available cyclooctatetraene, our attention was turned toward the matter of preparative utility. A low-temperature photolysis assembly (note Figure 1) utilizing a vacuum chamber between a Hanovia immersion well and the surrounding flask was found convenient. In a typical run irradiation of 11.4 g (0.109 mol) of cyclooctatetraene and 16.6 g of acetone in 500 ml of isopentane at −60° with a 450-W medium-pressure lamp with a

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