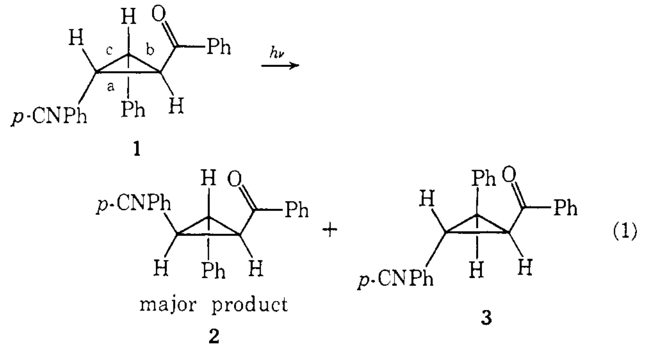
Excited State Electron Distribution in Cyclopropyl Ketone Rearrangements. Mechanistic and Exploratory Organic Photochemistry. LI[1]

Howard E. Zimmerman and Christine M. Moore[2]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received September 19, 1969*

Abstract: The irradiation of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**4**) was found to afford both *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**6**) and *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (**7**). The reaction led preferentially to the *cis,trans* isomer **6** which can be interpreted as arising from bond 1,3 fission in the excited state of the *trans,trans* isomer **4** followed by single rotation about the 2,3 bond and closure. This selectivity corresponded to 78.9 ± 0.4% of the *cis,trans* isomer **6** and 21.1 ± 0.4% of the *trans,cis* isomer **7**. Sensitization, although inefficient, afforded the same distribution of stereoisomers within experimental error. Evidence was obtained that T_1 is the reactant in direct and sensitized photolyses. The reaction could be quenched up to the extent of 42.5% with 1.5 *M* piperylene and a rate of stereoisomerization of 1.5×10^{10} sec^{-1} for the triplet of reactant **4** was estimated from the Stern–Volmer plot. The quantum yield at low conversion determined by isotope dilution assay was 0.76, corresponding to an especially efficient process. The reaction selectivity along with related studies allows the excited state to be depicted as having odd electron density in the three-membered ring.

In our previous study[3] on the substituent effect of the photochemical stereoisomerization of *trans*-3-*p*-cyanophenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**1**), it was found that *cis*-3-*p*-cyanophenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**2**) predominated over the *trans,cis* isomer **3**. This was shown to arise from the preferential fission of bond a relative to bond b (and also c) (eq 1) and could be interpreted as arising from an electronically excited state which had an appreciable odd or excess electron density in the three-membered ring. Thus, an excited state which was electron deficient in the three ring would have led to an open intermediate in which bond b was broken instead.



The present study had as its initial goal the determination of whether the excited state is better pictured as having odd or high electron density delocalized into the three-membered ring and an exploration of the effect of substituents on the efficiency and rates of the reaction. The approach selected was an investigation of the photochemistry of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**4**).

Synthesis of Reactant and Tritium Incorporation. Two routes both beginning with *cis*-1-*p*-methoxyphenyl-2-phenylethylene (**5**) proved useful for the synthesis of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**4**) (Chart I). The reactant **4** was required with a radioactive label for use in quantitative photochemical studies by inverse isotope dilution analysis.[4] The hydrolysis of *p*-bromophenylmagnesium bromide

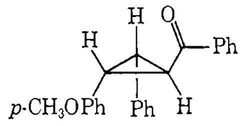


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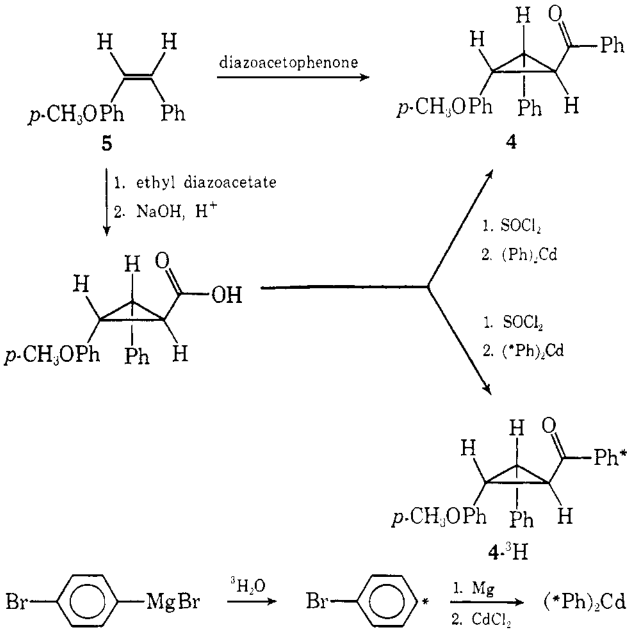
Chart I. Synthesis of *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane and Tritium Incorporation[a]



[a] * represents tritium label.

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[1] Paper XLIX: H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **91**, 7516 (1969); paper L, *ibid.*, in press.

[2] National Institutes of Health Predoctoral Fellow, 1966–1969.

[3] H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *J. Amer. Chem. Soc.*, **92**, 2000 (1970).

[4] (a) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968); (b) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

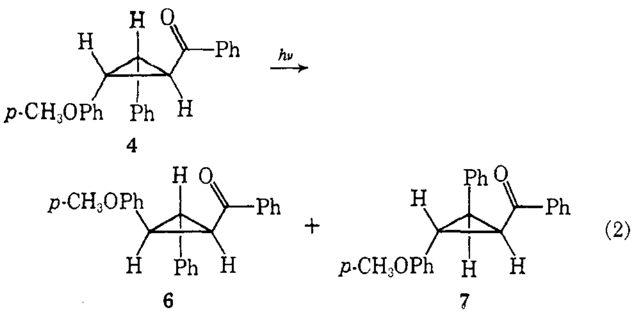


Chart II. Synthesis of *trans*-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane and *cis*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane

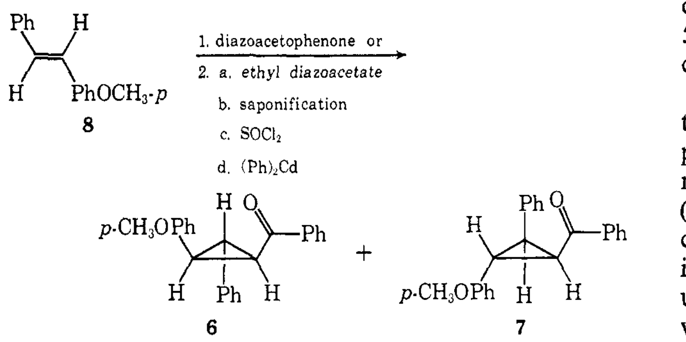
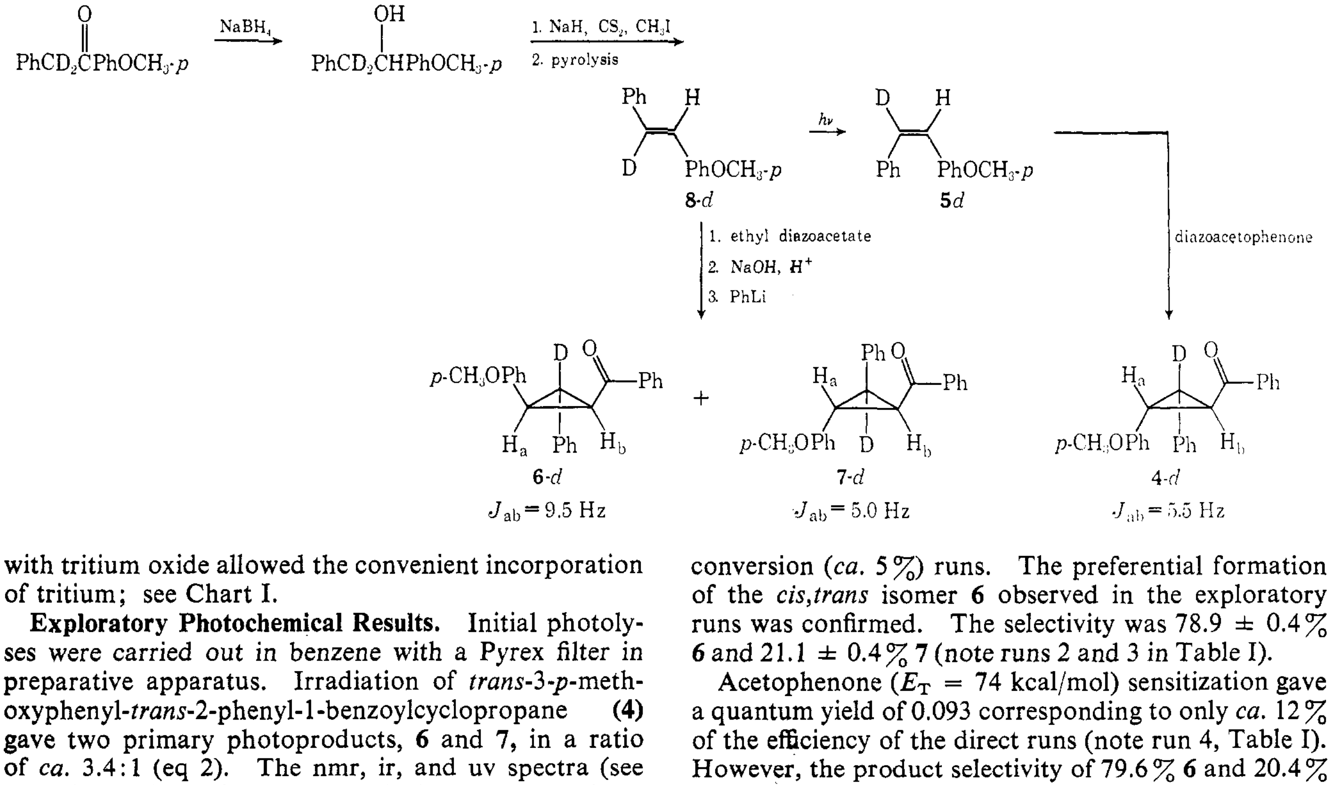


Chart III. Deuterium Labeling and Assignment of Stereochemistry



with tritium oxide allowed the convenient incorporation of tritium; see Chart I.

Exploratory Photochemical Results. Initial photolyses were carried out in benzene with a Pyrex filter in preparative apparatus. Irradiation of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**4**) gave two primary photoproducts, **6** and **7**, in a ratio of *ca.* 3.4:1 (eq 2). The nmr, ir, and uv spectra (see Experimental Section) suggested that these products were stereoisomers of reactant **4**. This assignment was confirmed by synthesis of isomers **6** and **7** from *trans*-1-*p*-methoxyphenyl-2-phenylethylene (**8**) as shown in Chart II. The reaction appeared to be facile and the mass balance was excellent (*ca.* 95%).

Assignment of Stereochemistry. In order to assign the configurations of isomers **6** and **7** and confirm the stereochemistry of **4**, the cyclopropyl rings were labeled with one deuterium atom at carbon 2 (*i.e.*, the benzylic position) and the nmr spectrum of each isomer was examined. A modification of the original synthesis was employed, as is described in Chart III, to give the three cyclopropane stereoisomers **4**-*d*, **6**-*d*, and **7**-*d*.

The nmr spectrum for each of the monodeuterated compounds contained an AB quartet in the cyclopropyl CH–CH region from which the coupling constant was readily obtained for comparison with known *cis* and *trans* values. Reported coupling constants[5] for *cis*-cyclopropyl hydrogens range from 8 to 11 Hz and for *trans* hydrogens range from 5 to 7 Hz. For **6**-*d* the coupling constant of 9.5 Hz indicated that the two three-ring hydrogens are *cis*. For **7**-*d* the coupling constant was 5.0 Hz; therefore the hydrogens are *trans*. The remote possibility that reactant **4** might have the all-*cis* configuration was excluded by the coupling constant of 5.5 Hz observed for **4**-*d* which confirmed that the hydrogens were *trans*.

Quantum Yield Runs. Quantum yields for the photoisomerization of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**4**), affording *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (**6**) and *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (**7**), were determined by the method of inverse isotope dilution analysis. Direct runs (*i.e.*, unsensitized) showed the reaction to be very efficient with a total quantum yield averaging 0.76 for low-conversion (*ca.* 5%) runs. The preferential formation of the *cis,trans* isomer **6** observed in the exploratory runs was confirmed. The selectivity was 78.9 ± 0.4% **6** and 21.1 ± 0.4% **7** (note runs 2 and 3 in Table I).

Acetophenone (E_T = 74 kcal/mol) sensitization gave a quantum yield of 0.093 corresponding to only *ca.* 12% of the efficiency of the direct runs (note run 4, Table I). However, the product selectivity of 79.6% **6** and 20.4% **7** was the same as that obtained in the direct runs.

The results of the quenching experiments are listed in Table II. The reciprocal of each quantum yield was observed to vary linearly, within experimental error, with the quencher concentration (see Figures 1–3) in accordance with the Stern–Volmer expression (eq 3).[6]

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(5) (a) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962); (b) K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963); (c) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(6) The intersystem crossing efficiency *f* in eq 3 is taken to be unity in view of the very rapid rates of intersystem crossing of benzoyl-type

Table I. Direct and Sensitized Quantum Yields of *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane Stereoisomerization

Run[a,b]	Reactant **4** used, mmol	Light, mEinstein	Quantum yields[c] **6**[d]	**7**[e]	$[\phi_6/(\phi_6 + \phi_7)] \times 100$, %
1	0.359	0.101	0.548 (±0.027)	0.130 (±0.007)	80.8
2	0.289	0.0207	0.590 (±0.030)	0.154 (±0.008)	79.3
3	0.165	0.00836	0.607 (±0.031)	0.165 (±0.009)	78.6
4[f]	0.154	0.0483	0.0742 (±0.0040)	0.0188 (±0.0010)	79.6

[a] Runs 1 and 2 at 313 nm in benzene at 24.0°; run 3 at 340 nm in benzene at 24.0°. [b] All runs to *ca.* 5% conversion except for run 1, which was 20%. [c] In mmol/mEinstein. Errors estimated from experimental data. [d] Appearance of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane. [e] Appearance of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane. [f] In 4.0 *M* acetophenone in benzene at 313 nm and 24.0°.

$$\frac{1}{\Phi} = \frac{k_r^{\text{tot}} + k_d}{fk_r} + \frac{k_q}{fk_r}[Q] \tag{3}$$

Multiplicity. Interpretative Discussion. It is clear from the acetophenone sensitization that the triplet excited state of the *trans,trans* isomer **4**, when independently generated, does lead to the same stereoisomerization process. Since the sensitization is relatively inefficient and the chromophores of the donor (acetophenone) and the acceptor (the reactant **4**) are not grossly different, it is reasonably safe to conclude that it is the lowest triplet T_1 which is generated in the acetophenone-sensitized runs.

Next, quenching studies were initiated. The two quenchers employed, naphthalene (E_T = 61 kcal/mol) and piperylene (E_T = 59 kcal/mol), were found to quench the stereoisomerization with different efficiencies (note Figures 1–3). Making the assumption that triplet quenching with piperylene occurs with a rate which approaches diffusion control[7] a rate of rearrangement of the triplet excited state of *trans,trans* isomer **4** can be estimated (*i.e.*, k_r *ca.* 1.5 × 10^{10} sec^{-1}), taking 1.0 × 10^{10} sec^{-1} as the rate of diffusion in benzene.

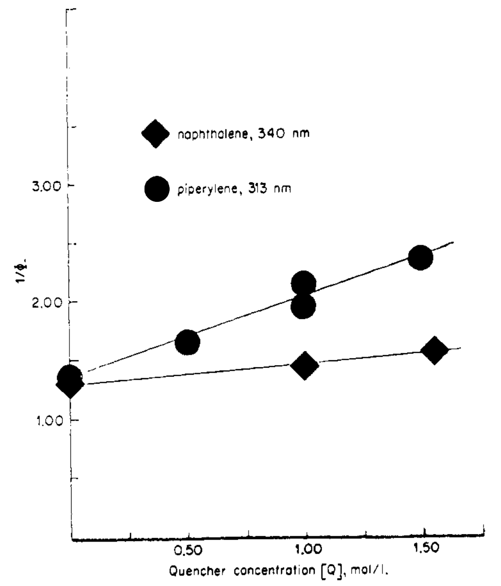

Figure 1. Stern–Volmer plot; disappearance of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane.

It is seen from Tables I and II that the composition of the product mixture varied from 78.9% *cis,trans* isomer **6** in the direct runs to 86.5% isomer **6** in the 1.54 *M* naphthalene run. This change in product composition is small (*i.e.*, a spread of *ca.* 7%) but does seem real. In considering the possibility of intervention of two different excited state species, one often looks for curvature in the Stern–Volmer plots and such curvature is not detectible presently (note Figures 1–3). However, with minor intervention and the usual experimental accuracy such curvature may not be expected to be discerned. Further support for involvement of a second excited species is found in the $\phi_0 S$ values[8] (note Table III) which are known[8] to be characteristic of individual excited states and which are unequal for appearance of products **6** and **7**.

Table II. Quantum Yields of Piperylene and Naphthalene Quenching of *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane Stereoisomerization

Run[a]	Reactant **4** used, mmol	Quencher[b] concn, *M*	Light, mEinstein	Quantum yields[c] **4**[d]	**6**[e]	**7**[f]	$[\phi_6/(\phi_6 + \phi_7)] \times 100$, %
Q-1	0.297	0.50	0.0204	0.603 (±0.028)	0.487 (±0.024)	0.116 (±0.006)	80.8
Q-2	0.287	1.00	0.0191	0.516 (±0.026)	0.424 (±0.022)	0.0921 (±0.0060)	82.1
Q-3	0.150	1.00	0.0178	0.467 (±0.023)	0.382 (±0.020)	0.0848 (±0.0043)	81.8
Q-4	0.283	1.50	0.0204	0.428 (±0.021)	0.355 (±0.019)	0.0734 (±0.0037)	82.9
Q-5	0.424	1.00	0.0175	0.685 (±0.033)	0.574 (±0.028)	0.111 (±0.006)	83.9
Q-6	0.715	1.54	0.0173	0.642 (±0.030)	0.554 (±0.026)	0.0875 (±0.0043	86.5

[a] Runs 1–4 in benzene at 313 nm and 24.0°; 5–6 at 340 nm. [b] Runs 1–4, piperylene quenching with reactant absorbing over 98.8% of the available light; runs 5–6, naphthalene quenching with reactant absorbing over 96.0% of the available light. [c] Error estimated from scatter of the data. [d] Disappearance of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, taken as the sum of product appearance. [e] Appearance of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane. [f] Appearance of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane.

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ketones and the known unity crossing efficiency of acetophenone and benzophenone.

(7) This is reasonable since previous studies[4a] have shown that a 8 kcal/mol decrease in quencher triplet energy changed the quenching efficiency only about sixfold. Hence, less than an order of magnitude error should be involved in this estimation of rate of rearrangement.

(8) Here *S* is the slope. The $\phi_0 S$ values obtained from Stern–Volmer plots of $1/\phi$ *vs.* quencher concentration are equal to the $k_q\tau$ values of ϕ/ϕ_0 treatments. Note H. E. Zimmerman and N. Lewin, *J. Amer. Chem. Soc.*, **91**, 879 (1969).

Table III. Slopes and $\phi_0 S$ Values from Stern–Volmer Plots

	Piperylene		Naphthalene	
	S (slope)[a]	$\phi_0 S$ ($k_q\tau$)	S (slope)	$\phi_0 S$ ($k_q\tau$)
Disappearance of *trans,trans*-**4**	0.676 ± 0.067	0.495 ± 0.071	0.168 ± 0.004	0.129 ± 0.010
Appearance of *cis,trans*-**6**	0.759 ± 0.085	0.453 ± 0.083	0.102 ± 0.006	0.062 ± 0.008
Appearance of *trans,cis*-**7**	4.82 ± 0.28	0.743 ± 0.073	3.42 ± 0.25	0.564 ± 0.083

[a] Errors for slopes are standard deviations.

Several explanations are *a priori* possibilities. First, two totally different electronically excited state reactant species may be involved, one to a lesser extent. However, Table I reveals that the same product distribution is formed in the direct photolyses as in sensitization where T_1 is known to be the reactant; thus one can conclude that the direct runs also utilize only T_1. This leaves only the quenched runs showing evidence of two excited species. One possibility is that quencher reveals the ordinarily very minor participation of a second excited state (T_2 or S_1) by selectively quenching T_1. More interesting is the possibility that an exiplex is formed in the quenching process and that this exiplex may either decay or react. Such an exiplex would not be expected to have the same selectivity as the uncomplexed excited triplet T_1. A related rationale is that quenching occurs far enough along the reaction coordinate that the identity of the product is already determined and that quenching does not occur with equal efficiency in the pathways leading to the two different products **6** and **7** (note Chart IV). This interesting effect is being pursued further. However in conclusion it should be noted that the effect is a minor one, and in the ordinary and sensitized photolyses the conclusion that T_1 is primarily responsible is unaffected and the triplet rate calculation is valid to the accuracy usually obtained in such treatments.

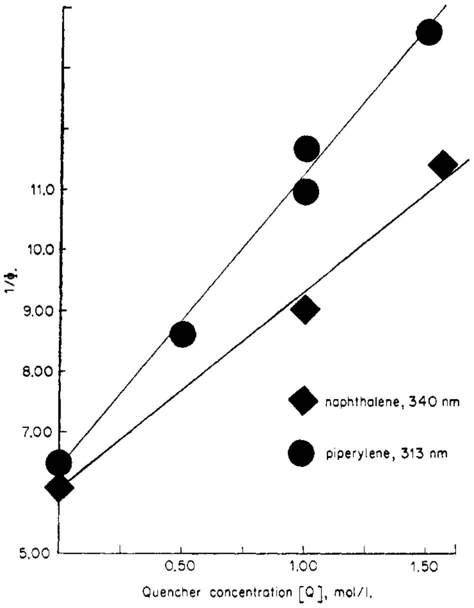

Figure 2. Stern–Volmer plot; appearance of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane.

Excited State Reactivity. Interpretative Discussion. The preferential formation of the *cis,trans* isomer **6** in all runs, direct, sensitized, and quenched, has mechanistic significance. The overall nature of the process is known from the photolysis of optically active *trans*-3-*p*-cyanophenyl-*trans*-2-phenyl-1-benzoylcyclopropane, a structurally similar molecule.[3] The reaction in that case was shown to proceed by way of an excited state which was either electron rich or odd electron in character in the three-membered ring. The present results make it clear that the excited state and the reacting molecule are not electron rich but rather have odd electron density in the three ring. The reaction may be interpreted as proceeding with selective fission of bond a followed by a single rotation about the benzylic–benzylic bond c and closure to give the *cis,trans* isomer **6** in the major pathway. For the minor pathway in analogy to the cyanophenyl study, the *trans,cis* isomer **7** probably arises from two processes, *i.e.*, from double rotation of the bond a opened species **10** and single rotation of the bond b opened species **9**. This mechanism is summarized in Chart IV.

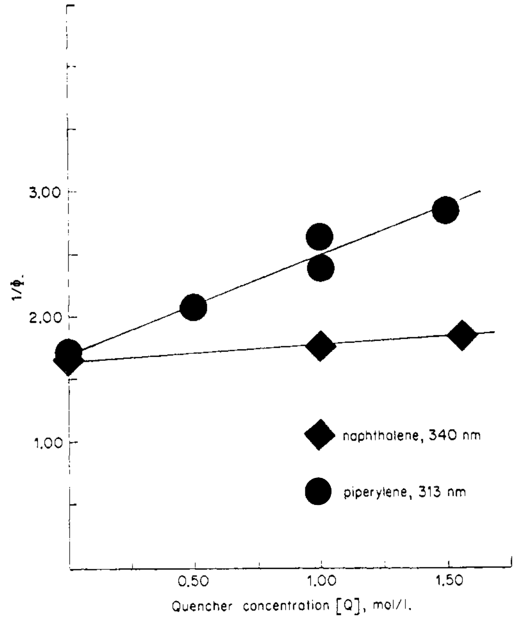

Figure 3. Stern–Volmer plot; appearance of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane.

Experimental Section[9]

Benzyl *p*-Methoxyphenyl Ketone. This was prepared in 77% yield by the method of Buck and Ide. The melting point after crystallization from hexane was 76–77° (lit.[10] mp 74–75°).

1-*p*-Methoxyphenyl-2-phenylethanol. Sodium borohydride (5.50 g, 0.145 mol) reduction of 100.0 g (0.443 mol) of benzyl *p*-methoxyphenyl ketone in 1.5 l. of ethanol afforded 1-*p*-methoxyphenyl-2-

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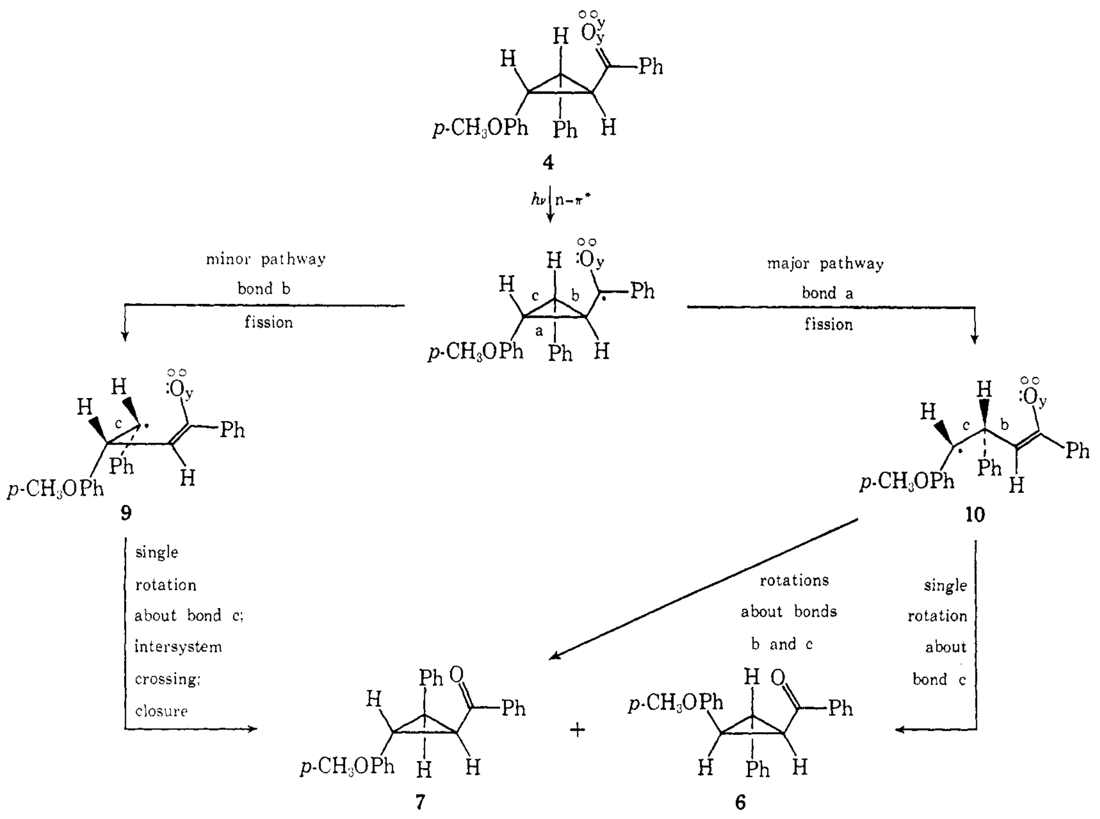
(9) Melting points were obtained on a hot-stage apparatus calibrated with known compounds.

(10) J. S. Buck and W. S. Ide, *J. Amer. Chem. Soc.*, **54**, 3013 (1932).

Chart IV. Formal Mechanism for the Stereoisomerization of *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane



phenylethanol (71.4 g, 0.312 mol) in 71% yield after crystallization from hexane, mp 57–58° (lit.[11] mp 58–59.5°).

***trans*-1-*p*-Methoxyphenyl-2-phenylethylene.** This was prepared by the dehydration of 40.0 g (0.175 mol) of 1-*p*-methoxyphenyl-2-phenylethanol with 0.50 g of *p*-toluenesulfonic acid in refluxing toluene. After recrystallization from ether–hexane, the yield of *trans* olefin was 30.7 g (83%), mp 135–136° (lit.[12] mp 136°).

Solvent Benzene. The benzene used for photolysis was purified by stirring with concentrated sulfuric acid and distilling from phosphorus pentoxide.

***cis*-1-*p*-Methoxyphenyl-2-phenylethylene.** In five runs of 6.5 hr each a total of 41.36 g (0.196 mol) of *trans*-1-*p*-methoxyphenyl-2-phenylethylene in a total of 8.75 l. of purified benzene was irradiated under deoxygenated nitrogen[13] through a Corex filter ($\lambda > 250$ nm) with a Hanovia 450-W medium-pressure immersion mercury lamp. Recrystallization of the combined photolysates from ether–hexane afforded 18.71 g of *trans* olefin. The residues were chromatographed on a 4.5 × 70 cm column of alumina (Fisher, adsorption grade) slurry-packed in 2% ether in hexane. Elution in 225-ml fractions gave: fractions 1–5, 3% ether in hexane, nil; 6–21, 5%, 19.5 g of *cis*-1-*p*-methoxyphenyl-2-phenylethylene; 22, 8%, nil; 23–33, 20%, 1.30 g of *trans* olefin. The yield of *cis* olefin, a clear, viscous liquid,[12] was 47%. The spectral data were ir (neat) 3.25–3.5, 6.2, 6.6, 8.5, 9.68, 12.0, 13.45, and 14.35 μ; nmr ($CDCl_3$) τ 2.7–3.6 (m, 11 H, arom, CH=CH), 6.4 (s, 3 H, $-OCH_3$) (lit.[12] nmr τ 6.5 ± 0.1).

***trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-cyclopropanecarboxylic Acid.** Ethyl diazoacetate (40.0 g, 0.351 mol) was added dropwise with stirring over 5 hr to 23.56 g (0.112 mol) of *cis*-1-(*p*-methoxyphenyl)-2-phenylethylene and 4.00 g of copper–bronze (Luco No. 16, Leo Uhlfelder Co., N. Y., analyzed for 99.5+% copper) maintained at 120° under nitrogen. The cooled reaction mixture was filtered and refluxed with 10.0 g of sodium hydroxide in 200 ml of ethanol. After concentration under reduced pressure the mixture was diluted with water and ether extracted; the ether extracts were dried and concentrated to give 6.56 g of *cis* olefin. The aqueous layer from the saponification was acidified and ether extracted. Concentration afforded a brown oil which was eluted with 40% ether in hexane through a 4 × 50 cm column of silica gel (Davison 950, 60–200 mesh). The recovered orange oil, 16.8 g, was rechromatographed on a similar column. The fraction volume was 200 ml and fractions 4–16, 35% ether in hexane, contained 14.6 g of the cyclopropanecarboxylic acid. Recrystallization from chloroform–hexane gave 8.69 g (40% yield based on consumed olefin) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-cyclopropanecarboxylic acid, mp 121–123°. The spectral data were ir (CS_2) 3.0–4.35, 5.9, 7.75, 8.0, 8.25, 8.6, 9.6, 12.15, 13.2, and 14.4 μ; nmr ($CDCl_3$) τ −2.1 (br s, 1 H, –COOH), 2.8–3.4 (m, 9 H, arom), 6.3 (s, 3 H, $-OCH_3$), 6.9 (d, 2 H, cyclopropyl ring CH–CH), 7.5 (t, 1 H, cyclopropyl CHCOOH).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.01; H, 6.03.

Reaction of Diazoacetophenone with *cis*-1-*p*-Methoxyphenyl-2-phenylethylene. Diazoacetophenone[14] (13.0 g, 88.6 mmol) in 25 ml of xylene was added dropwise with stirring over 2.5 hr to 22.3 g (0.109 mol) of *cis*-1-*p*-methoxyphenyl-2-phenylethylene and 0.60 g of copper–bronze maintained at 130° under nitrogen. The cooled reaction mixture was filtered and concentrated *in vacuo*. The residue was chromatographed on a 4 × 70 cm silica gel column slurry-packed in 3% ether in hexane. Elution in 200-ml fractions gave: fractions 6–9, 8% ether in hexane, 18.2 g of *cis* olefin; 14–23, 18%, 11.4 g of cyclopropyl ketone in yellow oil. Extensive crystallization from hexane–ether and from methanol gave 3.69 g (57% yield based on consumed olefin) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, mp 83–85°.

The spectral data were uv (EtOH) λ_{max} 233 nm (ϵ 22,100), 275 sh (6500); ir (CS_2) 3.2–3.5, 6.0, 7.8, 8.0, 8.23, 8.5, 9.65, 12.15, 13.5, and 14.9 μ; nmr ($CDCl_3$) τ 1.8–2.0 (m, 2 H, arom *ortho* to C=O), 2.4–2.5 (m, 2 H, arom *meta* to C=O), 2.8–3.5 (m, 10 H, arom), 6.34 (s, 3 H, $-OCH_3$), 6.35–6.8 (m, 3 H, cyclopropyl ring CHCH).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.89; H, 6.01.

***trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane.** *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-cyclopropanecarboxylic acid chloride was formed from 2.683 g (10.0 mmol) of the corresponding acid (*vide supra*) by refluxing for 15 min with 10 ml of thionyl chloride, followed by concentration.

A solution of the acid chloride in 20 ml of benzene was added dropwise to a vigorously stirred solution of diphenylcadmium at 0° in 250 ml of benzene. The diphenylcadmium was prepared from

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[11] M. A. Orekhoff and M. Tiffeneau, *Bull. Soc. Chim. Fr.*, **37**, 1414 (1925).

[12] O. W. Wheeler and H. N. Batlle de Pabon, *J. Org. Chem.*, **30**, 1473 (1965).

[13] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

[14] M. Newman and P. Beal, *J. Amer. Chem. Soc.*, **71**, 1506 (1949).

5.01 g (27.4 mmol) of anhydrous cadmium chloride added to the Grignard reagent formed from 1.49 g (61.5 mg-atoms) of magnesium and 3.0 ml (28.7 mmol) of bromobenzene. The reaction was stirred for 1 hr at 25°, then hydrolyzed with saturated aqueous ammonium chloride, ether extracted, and concentrated to give 3.26 g of oily ketone. This was chromatographed on a 4 × 50 cm silica gel column slurry-packed in 4% ether in hexane. Elution was in 200-ml fractions with fractions 13–21, 18% ether in hexane, affording 2.60 g of cyclopropyl ketone. This was rechromatographed on a 2.5 × 100 cm silica gel column, similarly packed. Fractions 7–14, 18% ether in hexane, contained 2.54 g of ketone. Crystallization from hexane–ether afforded 1.89 g (58% yield) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, mp 83–85°. The nmr and ir spectra were superimposable with those of this compound prepared by the alternative synthetic method above and a mixture melting point showed no depression.

Reaction of Diazoacetophenone with *trans*-2-*p*-Methoxyphenyl-1-phenylethylene. Diazoacetophenone (14.3 g, 97.3 mmol) in 30 ml of xylene was added dropwise with stirring over 3 hr to a mixture of 15.1 g (71.8 mmol) of *trans*-2-*p*-methoxyphenyl-1-phenylethylene, 0.50 g of copper–bronze, and 30 ml of xylene maintained at 125° under nitrogen. A benzene solution of the reaction mixture was filtered to remove the copper and concentrated *in vacuo*. The residue was chromatographed on a 3.5 × 60 cm silica gel column slurry-packed in 4% ether in hexane. Elution in 400-ml fractions gave: fractions 4–14, 8% ether in hexane, 10.1 g of *trans* olefin; 27–44, 14%, 5.53 g of isomeric ketones in yellow oils. This mixture was rechromatographed on a similar column. The fraction volume was 500 ml and fractions 17–24, 8% ether in hexane, contained 4.76 g (61% yield based on consumed olefin) of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane and *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzocyclopropane.

This mixture was separated by preparative tlc on 25 × 25 cm plates coated with a slurry of 50 g of silica gel (Brinkman GF_{254}) in 90 ml of water and activated for 3 hr at 100°. Mixtures were applied and alternatively eluted and dried (multidevelopment) with benzene until separation was observed under ultraviolet light.[15] The zone containing each component was ether extracted.

The first zone, R_f *ca.* 0.16, was ether extracted. Concentration and crystallization from hexane–ether gave *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane, mp 111–112°. The spectral data were uv (EtOH) λ_{max} 231 nm (ϵ 23,000), 275 sh (7000); ir (CS_2) 3.25–3.53, 6.0, 7.9, 8.0, 8.28, 8.5, 9.65, 9.80, 12.25, 13.8, and 14.45 μ; nmr ($CDCl_3$) τ 2.0–2.2 (m, 2 H, arom *ortho* to C═O), 2.4–3.2 (m, 12 H, arom), 6.22 (s, 3 H, -OCH_3), 6.3–6.8 (m, 3 H, cyclopropyl ring CHCH).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6 14. Found: C, 84.36; H, 6.31.

Similar work-up of the second zone, R_f *ca.* 0.14, gave *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, mp 132–133° after crystallization from hexane–ether. The spectral data were uv (EtOH) λ_{max} 230 nm (ϵ 24,500), 275 sh (6050); ir (CS_2) 3.25–3.53, 6.0, 8.0, 8.25, 8.5, 9.6, 12.23, 13.45, and 14.4 μ; nmr ($CDCl_3$) τ 1.9–2.1 (m, 2 H, arom *ortho* to C═O), 2.4–3.3 (m, 12 H, arom), 6.29 (s, 3 H, -OCH_3), 6.3–6.8 (m, 3 H, cyclopropyl ring CHCH).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.00; H, 5.93.

Reaction of Ethyl Diazoacetate with *trans*-1-*p*-Methoxyphenyl-2-phenylethylene and Saponification. Ethyl diazoacetate (40.0 g, 0.351 mol) in 10 ml of xylene was added dropwise with stirring over 8 hr to 45.8 g (0.217 mol) of *trans*-1-*p*-methoxyphenyl-2-phenylethylene and 4.5 g of copper–bronze maintained at 145° under nitrogen. A benzene solution of the cooled reaction mixture was filtered and concentrated *in vacuo*. The residue was refluxed for 1.5 hr with 10.0 g of sodium hydroxide in 200 ml of ethanol. After concentration under reduced pressure, the mixture was diluted with water and ether extracted. *trans* olefin, 24.1 g after crystallization from methanol, mp 133–134°, was obtained from the ether layer. The aqueous layer from the saponification was acidified and ether extracted. Concentration afforded a brown oil which was eluted with 35% ether in hexane through a 4 × 50 cm silica gel column slurry-packed in 20% ether in hexane to give a white solid in yellow oil. Recrystallization from methanol gave 11.4 g (41% yield based on consumed olefin) of a not readily separable mixture of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-cyclopropanecarboxylic acid and *cis*-3-*p*-methoxyphenyl-*trans*-2-phenylcyclopropanecarboxylic acid, mp 135–165°. The spectral data were ir (CS_2) 3.2–4.0, 5.9, 7.0, 8.0, 9.65, 12.2, and 14.45 μ; nmr ($CDCl_3$) τ −0.8 (br s, 1 H, COOH), 2.8–3.4 (m, 9 H, arom), 6.29 (s, 3 H, -OCH_3), 6.68–8.0 (m, 3 H, cyclopropyl ring CHCH).

***trans*-3-*p*-Methoxylphenyl-*cis*-2-phenyl-1-benzoylcyclopropane and *cis*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane.** The acid chlorides were formed from 2.00 g (7.50 mmol) of a mixture of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-cyclopropanecarboxylic acid by refluxing for 15 min with 10 ml of thionyl chloride, followed by concentration.

A solution of the acid chlorides in 20 ml of benzene was added dropwise to a vigorously stirred solution of diphenylcadmium at 0° in 250 ml of benzene. The diphenylcadmium was prepared from 6.90 g (37.5 mmol) of anhydrous cadmium chloride added to the Grignard reagent formed from 0.950 g (37.5 mg-atoms) of magnesium and 4.0 ml (37.5 mmol) of bromobenzene. The reaction was stirred for 1 hr at 25°, then hydrolyzed with saturated aqueous ammonium chloride, ether extracted, and concentrated to give 3.08 g of oily ketone mixture. This was chromatographed on a 4 × 50 cm silica gel column slurry-packed in 4% ether in hexane. Elution was in 200-ml fractions with fractions 15–27, 16% ether in hexane, affording 1.39 g of ketone mixture. This mixture, 1.27 g, was separated by preparative tlc (*vide supra* for method). The first zone, R_f *ca.* 0.16, afforded 0.432 g of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane, mp 110–111° after crystallization from hexane–ether. The nmr and ir spectra were identical with those of this compound obtained by the alternative synthetic method above and a mixture melting point showed no depression. The second zone, R_f *ca.* 0.14, gave 0.755 g of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, mp 132–133° after crystallization from hexane–ether. The nmr and ir spectra were identical with those of this compound obtained by the alternative synthetic method above and a mixture melting point showed no depression. The yield was 48%.

***p*-^{3}H-Bromobenzene.** A modification of the procedure of Weldon and Wilson[16] for the preparation of *p*-*d*-bromobenzene was used. *p*-Bromophenylmagnesium bromide formed from 1.214 g (50.0 mg-atoms) of magnesium and 11.80 g (50.0 mmol) of *p*-dibromobenzene in 100 ml of anhydrous ether was hydrolyzed with 0.380 ml (22.1 mmol) of tritium oxide (84.4 mCi, Volk Radiochemicals). The hydrolysis was completed with excess saturated aqueous ammonium chloride, followed by ether extraction. After drying with sodium sulfate and concentration, *p*-^{3}H-bromobenzene, bp 150–152°, was isolated by short-path distillation. The labeled product was diluted and removed from the distillation apparatus by three successive distillations of 1.0-ml portions of unlabeled bromobenzene to give a total of 6.65 g.

***trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-(*p*-^{3}H-benzoyl)cyclopropane.** The acid chloride was formed from 2.683 g (10.0 mmol) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-cyclopropanecarboxylic acid by refluxing for 15 min with 10 ml of thionyl chloride, followed by concentration.

A solution of the acid chloride in 20 ml of benzene was added dropwise to a vigorously stirred solution of di-*p*-^{3}H-phenylcadmium, at 0° in 250 ml of benzene. The diphenylcadmium had been prepared from 5.21 g (30.0 mmol) of anhydrous cadmium chloride added to the Grignard reagent formed from 1.49 g (59.0 mg-atoms) of magnesium and 6.65 g (40.0 mmol) of *p*-^{3}H-bromobenzene. The reaction was stirred for 1 hr at 25° and was hydrolyzed with ammonium chloride. The washed, dried, and concentrated ether extracts gave 3.42 g of clear oil which was chromatographed on a 4 × 50 cm silica gel column slurry-packed in 4% ether in hexane. Elution was in 200-ml fractions; fractions 14–22, 18% ether in hexane, gave 2.87 g of oily ketone which was purified by preparative tlc (*vide supra* for method). The first zone, R_f *ca.* 0.22, gave 2.369 g of clear oil which was recrystallized from hexane–ether to afford 2.01 g (60%) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-(*p*-^{3}H-benzoyl)cyclopropane, mp 82–84°, specific activity 559 nCi/mg. The nmr spectrum ($CDCl_3$) was superimposable with that of the unlabeled compound and a mixture melting point showed no depression. The second zone, R_f *ca.* 0.13, gave 0.284 g of white solid which was recrystallized from hexane–ether to give 0.204 g (6%) of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-(*p*-^{3}H-benzoyl)cyclopropane (identified by nmr), mp 131–132°.

Benzyl *p*-Methoxyphenyl Ketone-d_2. Benzyl *p*-methoxyphenyl ketone (30.0 g, 0.13 mol), in 80 ml of anhydrous, purified *p*-diox-

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(15) Uv fluorescence employed a technique avoiding light impinging directly on compound zones. Only zone edges were inspected briefly.

(16) L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).

ane[17] was added to sodium deuterioxide prepared from 3.5 g (0.15 g-atom) of sodium and 25 ml of deuterium oxide. After stirring for 24 hr under nitrogen, the solution was diluted with anhydrous ether and the aqueous layer was decanted. The (sodium sulfate) dried, concentrated ether layer afforded 29.3 g of ketone with *ca.* 90% deuterium incorporation (nmr analysis). Recycling under identical conditions gave 29.1 g of benzyl *p*-methoxyphenyl ketone-d_2 (100% deuterium incorporation by nmr), mp 74.5–76°. The spectral data were ir (CS$_2$) 3.2–3.5, 6.0, 7.6, 8.0, 8.55, 9.7, 12.0, 12.45, and 13.7–14.5 μ; nmr (CDCl$_3$) τ AB quartet centered at 2.58 (J_{AB} = 9 Hz, 4 H, arom), 2.75 (s, 5 H, arom), and 6.2 (s, 3 H, -OCH$_3$).

1-*p*-Methoxyphenyl-2-phenyl-2,2-d_2-ethanol. To a solution of 29.07 g (0.13 mol) of benzyl *p*-methoxyphenyl ketone-d_2 in 350 ml of anhydrous *p*-dioxane and 10 ml of deuterium oxide at 0° was added 4.5 g (0.12 mol) of sodium borohydride. After stirring for 10 hr at 25°, the reaction was hydrolyzed and ether extracted. The clear oil obtained from the dried, concentrated ether layer was crystallized from hexane–ether to give 22.8 g (78%) of 1-*p*-methoxyphenyl-2-phenyl-2,2-d_2-ethanol, mp 56.5–5–58°. The spectral data were ir (CS$_2$) 2.75–3.05, 3.2–3.55, 6.20, 7.65, 8.0, 8.5, 9.6, 12.0, 13.75, and 14.3 μ; nmr (CDCl$_3$) τ 2.8–3.3 (m, 9 H, arom), 5.3 (s, 1 H, -CHO), 6.3 (s, 3 H, -OCH$_3$), and 7.75 (s, 1 H, -OH).

***trans*-1-*p*-Methoxyphenyl-2-phenyl-2-*d*-ethylene.** The methyl xanthate of 1-*p*-methoxyphenyl-2-phenyl-2,2-d_2-ethanol (46.8 g, 0.205 mol) was prepared by the method of Roberts and Sauer[18] from 6.0 g (0.205 mol) of sodium hydride, 20.0 ml (0.205 mol) of carbon disulfide, and 20.0 ml (0.205 mol) of methyl iodide in anhydrous benzene. The crude xanthate was pyrolyzed at 160° for 1 hr. Crystallization of the pyrolysate from hexane–ether afforded 15.4 g of *trans*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene. The filtrate material was chromatographed on a 4 × 50 cm alumina column slurry-packed in 3% ether in hexane. The fraction volume was 200 ml and fractions 9–19, 15% ether in hexane, contained 2.1 g of olefin. After recrystallization from hexane–ether, the yield of *trans*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene was 17.5 g (40.7%), mp 134–136°. The spectral data were ir (CS$_2$) 3.2–3.55, 6.25, 8.0, 8.5, 9.6, 11.13, 12.1, 12.93, 14.35, and 14.5 μ; nmr (CDCl$_3$) τ 2.5–3.2 (m, 10 H, arom, =CH), 6.25 (s, 3 H, -OCH$_3$).

***cis*-1-*p*-Methoxyphenyl-2-phenyl-2-*d*-ethylene.** In three runs of 6 hr each a total of 10.67 g (50.2 mmol) of *trans*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene in a total of 4.5 l. of benzene was irradiated under deoxygenated nitrogen[13] through a Corex filter (λ >250 nm) with a Hanovia 450-W medium-pressure immersion mercury lamp. The combined photolysates were crystallized from hexane–ether to give 2.85 g of *trans* olefin. The filtrate material was chromatographed on a 4 × 40 cm alumina column slurry-packed in 5% ether in hexane. Elution in 200-ml fractions gave: fractions 4–12, 12% ether in hexane, 4.86 g of *cis*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene (45.5% yield); 13–25, 22% 1.41 g of *trans* olefin.

The spectral data for the *cis* olefin were ir (neat) 3.25–3.52, 6.25, 6.65, 7.75, 8.05, 8.55, 9.7, 11.75–12.55, 13.3, 13.6, and 14.4 μ; nmr (CDCl$_3$) τ 2.70–3.60 (m, 10 H, arom, C=CH), 6.35 (s, 3 H, -OCH$_3$).

Reaction of Diazoacetophenone with *cis*-1-*p*-Methoxyphenyl-2-phenyl-2-*d*-ethylene. Diazoacetophenone (13.3 g, 90.4 mmol) in 25 ml of xylene was added dropwise with stirring over 4 hr to a mixture of 4.70 g (22.4 mmol) of *cis*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene, 0.47 g of copper–bronze, and 5.0 ml of xylene maintained at 130° under nitrogen. The cooled reaction mixture was filtered and concentrated *in vacuo*. The residue was chromatographed on a 4.5 × 50 cm silica gel column slurry-packed in 3% ether in hexane. The fraction volume was 200 ml and fractions 11–21, 16% ether in hexane, contained 5.04 g of oily ketone. After rechromatography on a similar column, 2.72 g of ketone was recovered. Crystallization three times from hexane–ether afforded 0.960 g (17%) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-2-*d*-1-benzoylcyclopropane, mp 83–84°. The spectral data were uv (EtOH) λ_{max} 230 nm (ϵ 22,900), 275 sh (6900); ir (CS$_2$) 3.25–3.55, 6.0, 7.15, 7.80, 8.0, 8.25, 9.7, 9.85, 12.25, 13.1, 13.7, 14.4, and 15.4 μ; nmr (CDCl$_3$) τ 1.78–3.42 (m, 14 H, arom), 6.32 (s, 3 H, -OCH$_3$), AB quartet centered at 6.63 (J_{AB} = 5.5 Hz, 2 H, cyclopropyl ring CHCH).

The aryl and methoxyl portions of the nmr spectrum were superimposable in all respects with that of the unlabeled compound and a mixture melting point showed no depression.

Reaction of Ethyl Diazoacetate with *trans*-1-*p*-Methoxyphenyl-2-phenyl-2-*d*-ethylene and Saponification. Ethyl diazoacetate (36.7 g, 0.322 mol) in 10 ml of xylene was added dropwise with stirring over 7 hr to a mixture of 20.0 g (95.3 mmol) of *trans*-1-*p*-methoxyphenyl-2-phenyl-2-*d*-ethylene and 0.50 g of copper–bronze maintained at 145° under nitrogen. After filtration and concentration of a benzene solution of the reaction mixture, the residue was refluxed for 2.5 hr with a solution of 18.2 g of sodium hydroxide in 225 ml of ethanol. Ether extraction and concentration gave 7.59 g of *trans* olefin, mp after crystallization 135–137°. The aqueous layer from the saponification was acidified and ether extracted. Concentration afforded a brown oil which was chromatographed on a 4 × 50 cm silica gel column slurry-packed in 5% ether in hexane. The fraction volume was 200 ml and fractions 17–29, 35% ether in hexane, contained 7.68 g of cyclopropane acids in yellow oil. Recrystallization from methanol afforded 4.64 g (25% yield based on consumed olefin) of a not readily separable mixture of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-2-*d*-1-cyclopropanecarboxylic acid and *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-2-*d*-1-cyclopropanecarboxylic acid, mp 135–165°. The spectral data were ir (CHCl$_3$) 3.0–4.8, 5.9, 6.95, 7.9–8.3, 9.7, 12.1 and 14.4 μ; nmr (CDCl$_3$) τ −0.8 (br s, 1 H, -COOH), 2.7–3.2 (m, 9 H, arom), 6.2 (s, 3 H, -OCH$_3$), 6.7–7.8 (m, 2 H, cyclopropyl CHCH).

***trans*-3-*p*-Methoxyphenyl-*cis*-2-phenyl-2-*d*-1-benzoylcyclopropane and *cis*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-2-*d*-1-benzoylcyclopropane.** Phenyllithium (21.0 ml of 2.0 *M* in ether, 42.0 mmol) was added dropwise with vigorous stirring to a 4.63-g (17.3 mmol) mixture of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-2-*d*-1-cyclopropanecarboxylic acid and *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-2-*d*-1-cyclopropanecarboxylic acid in 100 ml of anhydrous ether at 0° under nitrogen. The reaction was hydrolyzed and ether extracted; the extracts were concentrated to give 7.95 g of oil prior to chromatography. The remaining aqueous layer was acidified, ether extracted, and concentrated to give 0.333 g (1.24 mmol) of cyclopropane acids. The oily ketone mixture was chromatographed on a 4 × 50 cm silica gel column slurry-packed in 3% ether in hexane. Elution in 200-ml fractions gave: fractions 16–22, 15% ether in hexane, 2.99 g (56% yield based on consumed acid) of a *ca.* 1:1 (by nmr analysis) mixture of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-2-*d*-1-benzoylcyclopropane and *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-2-*d*-1-benzoylcyclopropane. These isomers were separated by preparative tlc (*vide supra* for method).

The first zone, R_f *ca.* 0.16, gave *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-2-*d*-1-benzoylcyclopropane, mp 110–111° after crystallization from hexane–ether. The spectra data were uv (EtOH) λ_{max} 231 nm (ϵ 23,300), 275 sh (7200); ir (CS$_2$) 3.2–3.6, 6.0, 8.0, 8.25, 8.6, 9.65, 9.8, 12.15, 13.7, and 14.45 μ; nmr (CDCl$_3$) τ 1.95–2.15 (m, 2 H, arom, *ortho* to C=O), 2.5–3.2 (m, 12 H, arom), 6.24 (s, 3 H, -OCH$_3$), AB quartet centered at 6.57 (J_{AB} = 5.0 Hz, 2 H, cyclopropyl ring CHCH).

The second zone, R_f *ca.* 0.14, gave *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-2-*d*-1-benzoylcyclopropane, mp 131–133° after crystallization from hexane–ether. The spectral data were uv (EtOH) λ_{max} 229 nm (ϵ 24,500), 275 sh (6030); ir (CS$_2$) 3.25–3.55, 6.0, 8.0, 8.3, 8.5, 9.65, 9.9, 12.1, 13.6, and 14.4 μ; nmr (CDCl$_3$) τ 1.85–2.03 (m, 2 H, arom *ortho* to C=O), 2.35–3.20 (m, 12 H, arom), 6.25 (s, 3 H, -OCH$_3$), AB quartet centered at 6.70 (J_{AB} = 9.5 Hz, 2 H, cyclopropyl ring CHCH).

Exploratory Photolysis of *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane. A solution of 0.461 g (1.41 mmol) of *trans*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane in 700 ml of purified benzene was irradiated for 20 min under deoxygenated nitrogen[13] through Pyrex with a Hanovia 450-W medium-pressure immersion mercury lamp. The solvent was removed *in vacuo* and the residue was subjected to liquid–liquid partition chromatography[19] using a 4.5 × 150 cm column and a two-phase system of cyclohexane–dimethylformamide–ethyl acetate–water (100:40:25:3, v:v). The fraction volume was 20 ml and fractions 61–72 contained 17.8 mg of an unidentified yellow oil; 77–94, 133.3 mg of reactant ketone; 85–114, 305.8 mg of a *ca.* 3:1 mixture of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane and *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane. Analysis of the stereoisomers was by nmr integration of the methoxyl resonances at τ 6.29 and 6.22. This mixture was separated by preparative tlc (*vide supra* for method). After 5 elutions with benzene, two bands were observed, R_f *ca.* 0.16 and

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(17) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 1955, p 285, method A.

(18) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949).

(19) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

R$_f$ *ca.* 0.14. Ether extraction and concentration of the first gave 68.1 mg of clear oil, identified by nmr as *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane, melting point after crystallization from hexane–ether, 110–112°. The second band, after similar work-up, gave 228.3 mg of white solid, identified by nmr as *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane, melting point after crystallization from hexane–ether, 132–133°.

Quantum Yield Equipment. The basic apparatus employed by Zimmerman and Hancock[4a] was used. Irradiations were carried out on an L-shaped optical bench in quartz-faced,[20] thermostated cells under deoxygenated nitrogen, and with stirring. One actinometer cell was situated perpendicularly to the main beam path in order to receive the light deflected from a beam splitter consisting of a 2 × 2 × $^1/_{16}$ in. quartz plate mounted at 45°. The light source was an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator.

Quantum Yield Irradiations. The basic procedure for each determination consisted of three runs. In the first and third, actinometer solution was contained in two consecutive, identical cells and in the side cell. In the second run, the reactant solution was contained in the first cell and actinometer in the second and side cells. The transmission to reflection ratio of the beam splitter (*ca.* 10:1) was calculated for runs 1 and 3. The light incident to the sample cell was calculated from this ratio and the light deflected to the side cell. Available light was corrected for light transmitted to the second cell (less than 5%) and, when necessary, for direct absorption of light by reactant in sensitized runs or for direct absorption by quencher in quenched runs.

Ca. 0.003–005 *M* solutions of radioactive reactant in benzene were irradiated at 24.0°. Ultraviolet spectra recorded before and after photolysis agreed with calculated spectra assuming Beer's law. Weighed aliquots of the ^{3}H-photolysate were withdrawn for isotopic dilution with weighed excesses of unlabeled photoisomers and reactant ketone. After dilution, each mixture was concentrated *in vacuo* to remove solvent (and quencher or sensitizer when present). The diluted photoisomers were recrystallized to constant activity using hexane–ether. The diluted reactant was purified by preparative tlc (*vide supra* for method) prior to determination of specific activity.

A control dilution indicated that 0.06% of *cis*-3-*p*-methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane and 0.02% of *trans*-3-*p*-methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane were present in radioactive reactant. Final specific activities of diluted photoisomers were corrected for these readings and for blanks determined on the unlabeled compounds.

Potassium Ferrioxalate Actinometry.[21] Potassium ferrioxalate actinometry was employed. Absorbance of the ferrous phenanthroline complex was measured at 510 nm on a Beckman Model DU spectrometer with absorbance readout. The apparatus was calibrated[4a] at 366 nm with uranyl oxalate actinometry.

Specific Activity of ^{3}H Compounds. Determinations were made by liquid scintillation counting using a Nuclear-Chicago Mark I scintillation system.

Sensitizers and Quenchers. Piperylene (Aldrich) was distilled at atmospheric pressure with a 25:1 reflux ratio. Naphthalene (Allied Chemicals) was recrystallized from methanol and sublimed at 0.1 mm and 50°, mp 80–80.5°. Acetophenone (Matheson) was distilled, bp 42° (0.1 mm).

Quantum Yield Summaries. Data for individual runs are listed as follows: first, conditions for irradiation of ^{3}H-labeled reactant (weight, solvent (including sensitizer or quencher, where present), wavelength, and amount of light), followed by isotope dilution data. The weight of each unlabeled isomer used to dilute an aliquot of the labeled photolysate is followed by the number of the final recrystallization, recovered weight, melting point, asymptotic specific activity with error obtained from scatter of data; calculated amount of product or reactant recovered; quantum yield. The quantum yield for disappearance of reactant was obtained only as the quantum yield for the appearance of products, since the low conversions made the absolute errors in amounts of reactant recovered and consumed comparable in magnitude to their difference.

Run 1. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (117.9 mg, 0.359 mmol) had specific activity 194 ± 1 μCi/mmol, in 39.0 ml of benzene, irradiated at 313 nm (band width 22 nm), 0.101 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (174.7 mg, 0.532 mmol) added to ^{3}H-photolysate (28.206 mg, 0.0859 mmol): 2 (after tlc); 0.121 mg, 83–85°, 21.1 ± 0.1 μCi/mmol; 0.228 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (41.9 mg, 0.432 mmol) added to ^{3}H-photolysate (16.884 mg, 0.0514 mmol): 7.35 mg, 132–133°, 328 ± 3 nCi/mmol; 0.0553 mmol; ϕ = 0.548 ± 0.027.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (116.1 mg, 0.354 mmol) added to ^{3}H-photolysate (8.0877 mg, 0.0246 mmol): 7, 29 mg, 110–112°, 470 ± 7 nCi/mmol; 0.0131 mmol; ϕ = 0.130 ± 0.007.

Run 2. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (94.9 mg, 0.289 mmol) had specific activity 182 ± 1 μCi/mmol, in 39.0 ml of benzene, irradiated at 313 nm (band width 22 nm), 0.0207 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (129.3 mg, 0.394 mmol) added to ^{3}H-photolysate (16.563 mg, 0.0504 mmol): 2 after tlc, 88 mg, 83–85°, 19.6 ± 0.1 μCi/mmol; 0.272 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (129.1 mg, 0.393 mmol) added to ^{3}H-photolysate (13.132 mg, 0.0400 mmol): 7, 33 mg, 132–133.5°, 791 ± 6 nCi/mmol; 0.122 mmol; ϕ = 0.590 ± 0.030.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (146.4 mg, 0.446 mmol) added to ^{3}H-photolysate (9.281 mg, 0.0283 mmol): 7, 21 mg, 110–112°, 129 ± 1 nCi/mmol; 0.00318 mmol; ϕ = 0.154 ± 0.008.

Run 3. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (54.0 mg, 0.165 mmol) had specific activity 180 ± 2 μCi/mmol, in 39.0 ml of benzene, irradiated at 340 nm (band width 7 nm), 0.00836 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (95.5 mg, 0.291 mmol) added to ^{3}H-photolysate (19.623 mg, 0.0598 mmol): 2 after tlc, 76.5 mg, 83.5–86°, 29.1 ± 0.1 μCi/mmol; 0.159 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (217.5 mg, 0.662 mmol) added to ^{3}H-photolysate (20.435 mg, 0.0622 mmol): 7, 60 mg, 132–133°, 522 ± 6 nCi/mmol; 0.00508 mmol; ϕ = 0.607 ± 0.031.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (125.6 mg, 0.383 mmol) added to ^{3}H-photolysate (13.943 mg, 0.045 mmol): 7, 23 mg, 110–111°, 169 ± 1 nCi/mmol; 0.00138 mmol; ϕ = 0.165 ± 0.009.

Run S. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (50.4 mg, 0.154 mmol) had specific activity 180 ± 2 μCi/mmol, in 39.0 ml of 4.0 *M* acetophenone in benzene, irradiated at 313 nm (band width 22 nm) with the sensitizer absorbing 98.7% of the light, 0.0483 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (90.9 mg, 0.277 mmol) added to ^{3}H-photolysate (24.984 mg, 0.0761 mmol): 2 after tlc, 92.1 mg, 82–85°, 32.8 ± 0.1 μCi/mmol; 0.127 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (135.1 mg, 0.411 mmol) added to ^{3}H-photolysate (15.981 mg, 0.0487 mmol): 7, 60 mg, 131–132°, 555 ± 3 nCi/mmol; 0.00358 mmol; ϕ = 0.0742 ± 0.0040.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (138.2 mg, 0.420 mmol) was added to ^{3}H-photolysate (9.435 mg, 0.0287 mmol): 7, 10 mg, 110–111°, 82.1 ± 0.3 nCi/mmol; 0.000907 mmol; ϕ = 0.0188 ± 0.0010.

Run Q-1. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (97.4 mg, 0.297 mmol) had specific activity 182 ± 1 μCi/mmol, in 39.0 ml of 0.50 *M* piperylene in benzene, irradiated at 313 nm (band width 22 nm) with the reactant absorbing 99.7% of the light, 0.0204 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (97.2 mg, 0.296 mmol) added to ^{3}H-photolysate (30.104 mg, 0.0917 mmol): 2 after tlc, 67.2 mg, 83–85°, 41.7 ± 0.6 μCi/mmol; 0.284 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (136.2 mg, 0.415 mmol) added to ^{3}H-photolysate (17.756 mg, 0.0541 mmol): 7, 33 mg, 131–132°, 811 ± 1 nCi/mmol; 0.00993 mmol; ϕ = 0.487 ± 0.024.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (130.9 mg, 0.399 mmol) added to ^{3}H-photolysate (11.948 mg, 0.0363 mmol): 7, 39 mg, 110–111°, 136 ± 0.3 nCi/mmol; 0.00236 mmol; ϕ = 0.116 ± 0.006.

Run Q-2. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (94.0 mg, 0.287 mmol) had specific activity 182 ±

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(20) An epoxy adhesive not containing aromatic or other low-energy chromophores was used to cement quartz faces to Pyrex.

(21) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1965).

1 μCi/mmol, in 39.0 ml of 1.00 *M* piperylene in benzene, irradiated at 313 nm (band width 22 nm) with the reactant absorbing 99.4% of the light, 0.0191 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (101.8 mg, 0.310 mmol) added to ^{3}H-photolysate (36.143 mg, 0.110 mmol): 2 after tlc, 74 mg, 84–85°, 45.7 ± 0.4 μCi/mmol; 0.274 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (142.7 mg, 0.435 mmol) added to ^{3}H-photolysate (18.234 mg, 0.0555 mmol): 7, 29 mg, 130.5–132°, 659–65 nCi/mmol; 0.0809 mmol; $\phi = 0.424 \pm 0.022$.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (141.0 mg, 0.429 mmol) added to ^{3}H-photolysate (14.601 mg, 0.0445 mmol): 7, 22 mg, 110–111°, 118 ± 1 nCi/mmol; 0.0176 mmol; $\phi = 0.0921 \pm 0.0050$.

Run Q-3. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (49.1 mg, 0.150 mmol) had specific activity 180 ± 2 μCi/mmol, in 39.0 ml of 1.00 *M* piperylene in benzene, irradiated at 313 nm (band width 22 nm) with the reactant absorbing 98.8% of the light, 0.0178 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (103.9 mg, 0.316 mmol) added to ^{3}H-photolysate (22.316 mg, 0.0689 mmol): 2 after tlc, 80 mg, 84–86°, 29.4 ± 3 μCi/mmol; 0.132 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (118.6 mg, 0.361 mmol) added to ^{3}H-photolysate (15.614 mg, 0.0475 mmol): 7, 42 mg, 131–132°, 1.08 ± 0.01 μCi/mmol; 0.00680 mmol; $\phi = 0.382 \pm 0.020$.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (132.4 mg, 0.403 mmol) added to ^{3}H-photolysate (11.169 mg, 0.0340 mmol): 7, 20 mg, 110–111°, 156 ± 1 μCi/mmol; 0.00151 mmol; $\phi = 0.0848 \pm 0.0043$.

Run Q-4. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (92.6 mg, 0.283 mmol) had specific activity 182 ± 1 μCi/mmol, in 39.0 ml of 1.50 *M* piperylene in benzene, irradiated at 313 nm (band width 22 nm) with the reactant absorbing 99.0% of the light, 0.0204 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (123.0 mg, 0.375 mmol) added to ^{3}H-photolysate (17.096 mg, 0.0521 mmol): 2 after tlc, 83–85°, 21.0 ± 0.3 μCi/mmol, 0.270 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (129.3 mg, 0.394 mmol) added to ^{3}H-photolysate (14.618 mg, 0.0445 mmol): 8, 50 mg, 131–132°, 538 ± 1 nCi/mmol; 0.00721 mmol; $\phi = 0.355 \pm 0.01$.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (131.8 mg, 0.401 mmol) added to ^{3}H-photolysate (9.4726 mg, 0.0289 mmol): 9, 11 mg, 110–111°, 72.2 ± 0.2 nCi/mmol; 0.00149 mmol; $\phi = 0.0734 \pm 0.0037$.

Run Q-5. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (139.1 mg, 0.424 mmol) had specific activity 180 ± 2 μCi/mmol, in 39.0 ml of 1.00 naphthalene in benzene, irradiated at 340 nm (band width 7.4 nm) with the reactant absorbing 96.0% of the light, 0.0175 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (97.9 mg, 0.298 mmol) added to ^{3}H-photolysate (17.574 mg, 0.0535 mmol): 2 after tlc, 64.2 mg, 83–85°, 27.0 ± 0.5 μCi/mmol; 0.417 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (124.5 mg, 0.379 mmol) added to ^{3}H-photolysate (26.332 mg, 0.0802 mmol): 7, 54 mg, 132–133°, 900 ± 6 nCi/mmol; 0.01004 mmol; $\phi = 0.574 \pm 0.028$.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (125.1 mg, 0.381 mmol) added to ^{3}H-photolysate (23.166 mg, 0.0705 mmol): 7, 37 mg, 110–111°, 154 ± 1 nCi/mmol; 1.942 mmol; $\phi = 0.111 \pm 0.006$.

Run Q-6. *trans*-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane-^{3}H (235.0 mg, 0.715 mmol) had specific activity 180 ± 2 μCi/mmol, in 39.0 ml of 1.54 *M* naphthalene in benzene, irradiated at 340 nm (band width 7.4 nm) with the reactant absorbing 96.0% of the light, 0.0173 mEinstein.

trans-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (142.9 mg, 0.435 mmol) added to ^{3}H-photolysate (25.001 mg, 0.0761 mmol): 2 after tlc, 114.3 mg, 83–85°, 25.9 ± 0.5 μCi/mmol; 0.690 mmol recovered.

cis-3-*p*-Methoxyphenyl-*trans*-2-phenyl-1-benzoylcyclopropane (167.1 mg, 0.509 mmol) added to ^{3}H-photolysate (54.191 mg, 0.165 mmol): 8, 59.2 mg, 132–133°, 782 ± 3 nCi/mmol; 0.009644 mmol; $\phi = 0.554 \pm 0.027$.

trans-3-*p*-Methoxyphenyl-*cis*-2-phenyl-1-benzoylcyclopropane (146.7 mg, 0.434 mmol) added to ^{3}H-photolysate (38.409 mg, 0.117 mmol): 7, 67.4 mg, 110–111°, 102 ± 1 nCi/mmol; 0.00151 mmol; $\phi = 0.0875 \pm 0.0043$.

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