t_f	Duration of the forward generation step	sec
t_r	Elapsed time into the second generation step, measured from its beginning	sec
A	Working electrode area	cm^2
D	Diffusion coefficient of the reaction participants	cm^2/sec
C	Concentration of the parent substance	mol/cm^3
F	Faraday	coul/equiv
Q_f	Total charge given to reactant ion production in the forward step	coul
i_f	Faradaic current attributable to reactant generation at $t = t_f$	amp
r	Intercept of the working curve relating α to a_i	none
s	Intercept of the working curve relating β and a_i	none

The important dimensionless aggregate parameters have been defined as follows.

Coulombic efficiency

$$\phi_{\text{coul}} = (F/Q_f)\int_{t_f}^{\infty} I\mathrm{d}t$$

Intensity parameter (accessible experimentally)

$$\omega_i = It_f^{1/2}/AD^{1/2}C$$

Redox reaction rate parameter (accessible theoretically)

$$\omega_n = Nt_f^{1/2}/AD^{1/2}C$$

T-route efficiency parameter

$$\alpha = \phi_t\phi_{tt}\phi_f/(1 - g)$$

T-route quenching parameter

$$\beta = f(t)t_f\phi_{tt}\phi_f/8k_a\tau^2C(1 - g)^2$$

Data are plotted according to $\log \omega_y = a_y + b_y(t_r/t_f)^{1/2}$. When y = i, a and b refer to values obtained from experimental intensity–time data, and when y = n, the plots refer to simulated reaction rate data.

Photochemistry of Phenylcyclopropanes

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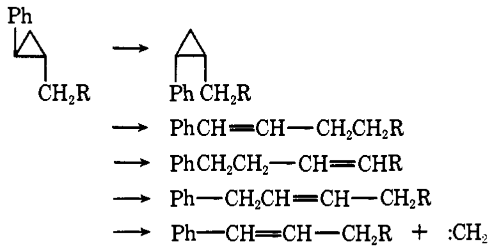
Received July 14, 1971

Abstract: The gas-phase fluorescence yields of two phenylcyclopropanes show a dramatic increase as compared to monoalkylbenzenes. This increase has been explained by a decrease in the intersystem crossing rate constants. The gas-phase photolysis of *trans*-methylphenylcyclopropane gives the cis isomer as the major product and, by a different route, *trans*-1-phenylbut-1-ene and 1-phenyl-2-methylprop-2-ene in much lower quantum yields. The same products, in the same ratio, are obtained on benzene photosensitization. Evidence for and against triplet and singlet mechanisms in the direct photolysis is presented.

There have been several reports of the liquid-phase photolysis of phenylcyclopropanes[1–7] and in general there seem to be five major reaction paths (Scheme I).

Scheme I



On the other hand, sensitization in solution results in clean geometric isomerization with little contribution from any of the other processes.[1,7] The gas-phase photochemistry of phenylcyclopropanes has received very limited attention. The available data indicate rather similar behavior to the solution photochemistry, but with olefin formation becoming much more important.[8a] Since almost all the available data on the photochemistry of these molecules are rather qualitative, and the nature of the excited states, from which reactions occur on direct excitation, in many cases remains in doubt, it was decided to make a quantitative study of the gas-phase photochemistry of *trans*-1-phenyl-2-methylcyclopropane (I). This molecule represents the simplest phenylcyclopropane structurally capable of undergoing all the known photochemical reactions of this class. Furthermore, it was felt that a knowledge of the fluorescence of phenylcyclopropanes was necessary to obtain a better understanding of these molecules.

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Table I. Fluorescence Quantum Yields[a] of Phenylcyclopropanes Compared to Related Alkylbenzenes

	λ, nm						τ_{rad},[c]
	248	254	260[b]	267	272[b]	274	nsec
n-Propylbenzene	0.090	0.230	0.280	0.290			145
sec-Butylbenzene	0.085	0.240	0.280	0.280			170
Phenylcyclopropane	0.100	0.205	0.400	0.470	0.480		130
trans-Methylphenylcyclopropane	0.100	0.200	0.380	0.470	0.470	0.47	140
Benzylcyclopropane	0.900	0.210	0.250	0.250			150

[a] Excluding any error in the absolute quantum yield of the benzene standard, the mean error in these values is ±5%. [b] All measurements were carried out on 1–5 mm of vapor, and 50 mm of *n*-butane was added to each molecule when irradiated near its 0–0 band to test for any low-pressure effects. [c] Calculated [S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962)] from the solution absorption spectra.

Experimental Section

Materials. *trans*- and *cis*-1-methyl-2-phenylcyclopropane (I and II) were prepared by the method of Simmons and Smith[9] using a mixture of *cis*- and *trans*-1-phenylprop-2-ene. The isomeric phenylcyclopropanes were separated and purified using a 20 ft × 0.25 in. 20% FFAF on Chromosorb P (45–60 mesh) vpc column. The *trans*-methylphenylcyclopropane was purified to better than 99.95% before use and the major impurity was the cis isomer. 1-Phenyl-2-methylprop-2-ene, *cis*- and *trans*-1-phenylbut-2-ene, phenylcyclopropane, and allylbenzene were obtained from Chemical Samples Co., Columbus, Ohio, and purified on the FFAF column before use. 4-Phenylbut-1-ene and *cis*- and *trans*-1-phenylbut-1-ene were obtained from K and K Laboratories, while the remaining two phenylbutenes were obtained from the chemistry department's stockpile and their structures checked by nmr analysis. Toluene, benzene, *n*-propylbenzene, *sec*-butylbenzene, *p*-xylene, *n*-butane and *cis*-but-2-ene were Phillips research grade and were used without further purification. *trans*-Penta-1,3-diene (piperylene) and benzylcyclopropane were obtained from Aldrich Chemical Co.

Fluorescence. A T-shaped cell 10 cm in length with the observation window centered 4 cm from the front window was housed in an oven which was held at 40°. A 1000-W Hanovia high-pressure xenon lamp was used as the light source. In all the fluorescence experiments the Bausch and Lomb high-intensity monochromator had 1-mm slits (a linear reciprocal dispersion of 1.6 nm). An RCA 935 phototube was used to measure absorption and 1P 28 photomultiplier tube for the emission. The cell was calibrated with respect to emission by using benzene and taking Q_f (10 mm at 253 nm) to be 0.18.[10] Using this calibration, the literature values for Q_f(toluene)[11] and Q_f(*p*-xylene)[12] from 240 nm to the respective 0–0 bands could be reproduced within the quoted error limits. There was no measurable difference in Q_f for toluene irradiated at its 0–0 band at 40 or at 21°.[11] Fluorescence spectra were measured in acetonitrile using an Aminco-Bowman spectrofluorimeter, and the absorption spectra were measured using a Cary 14 spectrometer.

Photolysis. The photolysis apparatus and procedure have been described previously.[13] All of the photolyses were run at 3–5 mm of I and at 45°. The ferrioxalate method of Hatchard and Parker[14] was used for actinometry. The expression used for obtaining the true number of quanta absorbed[15] can be derived from the paper of Hunt and Hill[16] with an added correction $(1 - f_{gas}/1 - f_{H_2O})$ for the different phases used in actinometry and in the photolysis of I.

$$I_a = I_i^t(1 - \Delta/\Delta_0^t)(1 - f_{gas}/1 - f_{H_2O}) \times \\ \{1 - \Delta/\Delta_0^t f_{gas}[1 + \Delta_0^t/\Delta_a(1 - f_{gas})^2]\}^{-1}$$

I_a = light absorbed in quanta per second, I_i^t = light incident just inside the front window of the cell at a time *t*, if the cell were filled with an aqueous solution when an experiment was carried out $I_i^t = I_i^0\Delta_0^t/\Delta_0^0$, Δ_0^t/Δ^0 = the ratio of the phototube readings for the empty cell at the time of actinometry (Δ^0_0) and at the time of the experiment (Δ_0^t), Δ/Δ_0^t = the ratio of the phototube readings for the empty cell and the cell filled with reactant, Δ_0^t/Δ_a = the ratio of the phototube readings with an empty cell (Δ_0^t) and with the cell removed (Δ_a), f_{gas} = the Fresnel reflection coefficient for a quartz–gas interface, and f_{H_2O} = the Fresnel reflection coefficient for quartz–water interface.[17] The variation of phototube sensitivity was determined by the sodium salicylate film method and found to be close to the manufacturer's data. The gas chromatographic separation of the products of the reaction proved to be a considerable problem. The column used for quantitative measurements was a 50 ft × 0.02 in. *m*-bis(*m*-phenoxyphenoxy)benzene on Apiezon (MBMA) Golay column. This column is capable of separating all the phenylbutenes (geometric and structural isomers) and also separates the geometric isomers I and II. However, the *cis*-methylphenylcyclopropane and *trans*-1-phenyl-but-2-ene have identical retention times. Numerous columns were used in an attempt to achieve a separation of these two compounds. Included among these were 40 ft × 0.125 in. diisodecyl phthalate, 30 ft × 0.125 in. tricresyl phosphate, 25 ft × 0.125 in. Carbowax 20 M, and 30 ft × 0.125 in. FFAP columns. All the above columns failed and only when a 150 ft × 0.02 in. MBMA column was used was partial success achieved. This column is capable of a partial separation but in the case of ratios of II to the 1-phenyl-2-butene greater than 12 to 1 the latter would not be detected. The 150 ft MBMA column was used to detect the presence of 1-phenylbut-2-ene in the direct and sensitized photolysis.

Preparative photolysis was carried out using 100-ml quartz bulbs and irradiating in a Rayonet reactor (with the low-pressure mercury bulbs). After photolysis the *cis*-methylphenylcyclopropane was separated by chromatography and its structure confirmed by nmr analysis. The other two products, III and IV, could not be obtained in this way because of their low quantum yields of formation and the small difference in the retention times between them and I and II on the preparative column. The structures of III and IV are supported by the high-resolution chromatography results. Further support for the structure of III comes from the fact that when the crude gas-phase photolysis reaction mixture was dissolved in heptane and irradiated at 300 nm (only III should absorb at this wavelength), the concentration of III decreased and a new compound with a retention time identical with that of *cis*-1-phenylbut-1-ene was formed.

The sensitized photolysis of I by benzene (irradiated at 254 nm) was carried out as follows. The cell was filled with 4.5 ± 0.2 mm of I (measured by chromatography and absorbance) and the transmitted light measured (I_t^I). After introducing 38 mm of benzene and allowing the gases to mix for 3 hr, the transmitted light (I_t^M) was again measured. The fraction of light absorbed directly by I is given by

$$I_a(\mathrm{I}) = (I_0 - I_t^M)\frac{\log I_0/I_t^I}{\log I_0/I_t^M}$$

Under the conditions used, 74% of the total light absorbed was absorbed by the benzene and corrections were made for direct absorption by I. Corrections were also made to account for the formation of products by direct absorption.

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(17) For the refractive indices of water at a large number of wavelengths, see N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold, Princeton, N. J., 1940, p 285.

Results

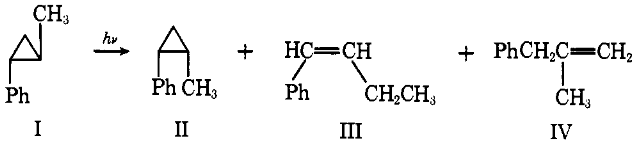
Fluorescence Yields. The vapor-phase fluorescence quantum yields of I were obtained for exciting radiation at the 0–0 band and at wavelengths down to 248 nm (Table I).[18] Since the values of Q_F were found to be very high compared to other alkylbenzenes, the fluorescence of phenylcyclopropane (VI) and benzylcyclopropane (VII) was studied. To allow direct comparison with the open-chain analogs, the fluorescence quantum yields of *n*-propylbenzene and *sec*-butylbenzene were also measured. The radiative lifetimes of these molecules were calculated in order to detect any trends which would account for the changes in the Q_F's. One value for Q_F of phenylcyclopropane in the vapor phase is available. The value obtained by Foote[8a] at 253.7 nm was 0.225 using benzene as a standard and taking $Q_F(253.7, \text{nm}) = 0.22$. Adjusting this latter value to 0.18, the value used in the present work, Q_F (phenylcyclopropane at 253.7), becomes 0.18. This is within the absolute error of the value in Table I.

Product Formation. On the photolysis of *trans*-1-methyl-2-phenylcyclopropane (I) in the aromatic absorption region three major products could be detected. The most important product was *cis*-methylphenylcyclopropane (II), while *trans*-1-phenylbut-1-ene (III) and 1-phenyl-2-methylprop-2-ene (IV) were also formed. As discussed in the Experimental Section, *trans*-1-phenylbut-2-ene (V) may also be formed, but its quantum yield of formation must be $<\Phi_{II}/12$. Toluene and benzene were observed as minor products ($\Phi < 5 \times 10^{-3}$). However, on irradiation of an empty (pumped out) cell, which had been used for more than three photolyses without cleaning, the toluene and benzene were formed in significant amounts. These products may therefore be formed either partly or solely by polymer photodegradation. The formation of IV has no precedent in the solution photolysis of phenylcyclopropanes. However, the benzene-sensitized photolysis of 1,2-dimethylcyclopropane[8b] results in the formation of 3-methyl-1-butene. The latter must be formed by a process similar to, though not identical with, the process involved here (Scheme II). Table II shows the wavelength dependence of quantum yields of formation II, III, IV. Chromatographic analysis using authentic samples of all the remaining phenylbutenes, the phenylpropenes, 1-methylindane, and 1-methylindene showed that they were not products under the conditions used. The effect of wavelength on the quantum yields is small for Φ_{II} and Φ_{III} until 240 nm, at which point there is a rapid drop in efficiencies of these processes. Such behavior seems to be typical of processes which emanate from the singlet state of benzenoid compounds[12,13] and has been attributed to the increased efficiency of reactions to form unstable isomers

Table II. The Wavelength Dependence of Product Quantum Yields

λ, nm	Φ_{II}	Φ_{III}	Φ_{IV}
275	0.12 ± 0.01	0.011 ± 0.001	0.007 ± 0.0015
271	0.12 ± 0.01	0.011 ± 0.001	0.007 ± 0.0015
267	0.12 ± 0.01	0.012 ± 0.001	0.007 ± 0.0015
254	0.13 ± 0.01	0.015 ± 0.002	
248	0.10 ± 0.01	0.015 ± 0.002	
240	<0.005		

Scheme II



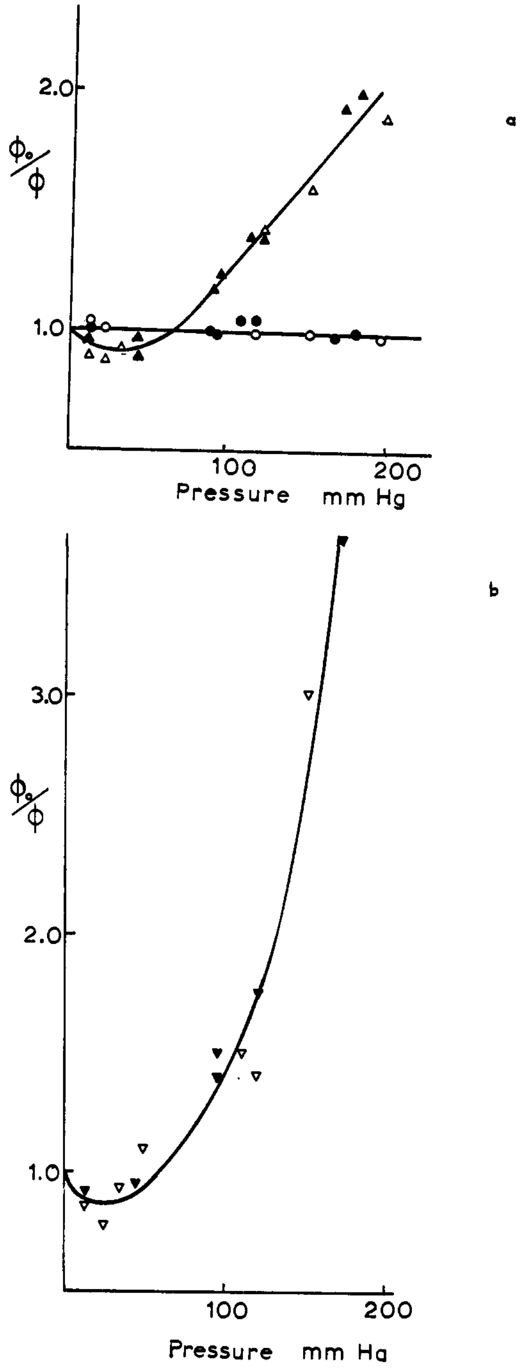


Figure 1. (a) The effect of added *n*-butane (filled symbols) and *cis*-but-2-ene (empty symbols) on the quantum yields of formation of II (●, ○) and III (▲, △). The wavelength was 267 nm, 2.0-mm slits were used, and the temperature was 45°. (b) The effect of added *n*-butane (▼) and *cis*-but-2-ene (▽) on the quantum yields of formation of IV. The wavelength was 267 nm, 2.0-mm slits were used, and the temperature was 45°.

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(18) K. Salisbury, *J. Chem. Soc. D*, 934 (1971).

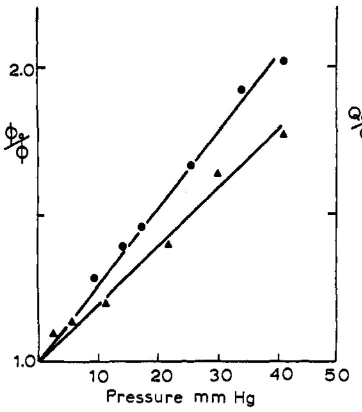

Figure 2. The effect of added piperylene on the quantum yields of formation of II (▲) and on the fluorescence quantum yields of I (●). The wavelength was 267 nm, 1-mm slits were used for the fluorescence work and 2.0-mm for product quantum yield measurement, and the temperatures at which the experiments were run were 40 and 45°, respectively.

of the benzenes with increase in vibrational energy in the first excited singlet states.

Figure 1 shows the effect of added *n*-butane and *cis*-but-2-ene on the quantum yields of formation. There is no effect on Φ_{II}. In the case of Φ_{III} and Φ_{IV}, however, there is quenching, although the processes involved seem to be complex. There is considerable scatter in this quenching, and although part of this may be attributed to the low quantum yields, especially at high pressures, with the resulting need for long irradiation times and analyses of small amounts of products, there may be other factors involved. Certainly, polymerization increases with increasing pressures of added gases. In several of the *cis*-but-2-ene quenching experiments, the butene was analyzed at the end of the experiments to determine the extent of geometric isomerization. It was hoped that in this way a triplet quantum yield might be obtained (the method of Cundall[19]). No detectable isomerization ($<0.20\%$) occurred in agreement with the lack of product quenching by the butene. The maximum pressure of butene for which an analysis was carried out was 50 mm and the maximum number of quanta absorbed 2×10^{19}. Figure 2 shows the quenching of geometric isomerization of I on addition of *trans*-piperylene (slope = 0.0192, average error = 0.040). Also shown is the fluorescence quenching on the addition of piperylene (slope = 0.0255, average error = 0.020). In the quenching of formation of III and IV the scatter was extremely large and, since any interpretation of the quenching, which would include a complex vibrational quenching plus electronic quenching, would be difficult, the results will not be presented.

A few solution experiments were carried out. On irradiation of a heptane solution of I, hydrocarbon II was the major product and although III was a detectable product, the ratio of Φ_{III} to Φ_{II} was lower by at least an order of magnitude than in the gas phase, below 100 mm. The formation of IV was not detectable.

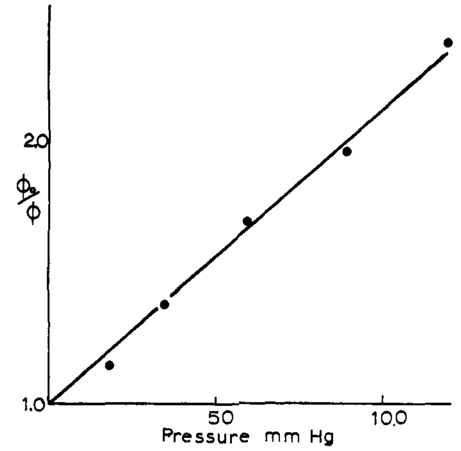

Figure 3. The effect of added *cis*-but-2-ene on the benzene-sensitized formation of II. The wavelength was 254 nm, 2-mm slits were used, and the temperature was 45°.

Sensitized Photolysis. Sensitization of I by benzene irradiated at 254 nm results in the formation of the same three products as observed on direct photolysis. The quantum yield of formation of II by sensitization was 0.085 ± 0.0080, while the yields of III and IV were 0.0060 ± 0.0010 and 0.0030 ± 0.0007. The ratio of quantum yields of formation of the three products is, within a large experimental error, the same as direct photolysis. To confirm that triplet energy transfer was involved in the sensitization, *cis*-but-2-ene was added to the benzene and methylphenylcyclopropane (Figure 3; slope = +0.0110, average error = 0.040). Since butene does not affect the efficiency of formation of II on direct excitation (Figure 1a) and 2-butene does not quench benzene singles, Figure 3 represents the competitive quenching of benzene triplets by the 2-butene and methylphenylcyclopropane. The variation of the ratio of Φ_{II} to Φ_{III} and Φ_{IV} with increasing butene pressure is to a good approximation the same as observed in the direct photolysis. Any small differences would be hidden by the uncertainties in measuring Φ_{III} and Φ_{IV} at high pressures.

Discussion

The fluorescence quantum yields of the phenylcyclopropanes I and VI are considerably larger than those of any monoalkylbenzene. The interposition of a methylene between the benzene and cyclopropane rings, as in benzylcyclopropane, destroys this fluorescence enhancement. To determine the cause of the increased Q_F's, it is necessary to consider changes in the rates of all of the processes by which the first excited singlet state may decay. In Scheme III, k_1 is the radiative rate

Scheme III

$$h\nu + \mathrm{I} \longrightarrow {}^1\mathrm{I}$$

$$^1\mathrm{I} \longrightarrow \mathrm{I} + h\nu^1 \qquad (1)$$

$$\longrightarrow {}^3\mathrm{I} \qquad (2)$$

$$\longrightarrow \mathrm{I} \qquad (3)$$

$$\longrightarrow \text{products} + \mathrm{I} \qquad (4)$$

$$Q_F = k_1/k_1 + k_2 + k_3 + k_4$$

constant, k_2 is the intersystem crossing rate constant, k_3 is the rate constant for internal conversion, and k_4 is the

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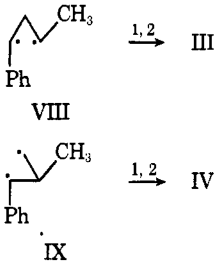
[19] R. B. Cundall and D. G. Milne, *J. Amer. Chem. Soc.*, **83**, 3902 (1961); R. B. Cundall, F. J. Fletcher, and D. G. Milne, *J. Chem. Phys.*, **39**, 3536 (1963); R. B. Cundall, F. J. Milne, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964); R. B. Cundall and A. S. Davies, *ibid.*, **62**, 1151 (1966).

sum of the unimolecular rate constants which result in chemistry (k_4 may include a chemical internal conversion process such as suggested by O'Connell and coworkers[20]). The radiative lifetimes ($1/k_1$) may be obtained from the absorption spectra and as is shown in Table I. There is only a small decrease in τ_{rad} on going from alkylbenzenes to the phenylcyclopropanes, not enough to account for the increase in Q_F's. The effect of the cyclopropyl substituent on k_3 is unknown, but since internal conversion is of little importance in alkylbenzenes, k_3 is probably not important here. Thus, there remains only one possibility; namely, that there is a decrease in intersystem crossing rate constant (k_2) compared to the monoalkylbenzenes. The reason for such a decrease in k_2 is being sought in modern theories of radiationless transitions. It has been suggested that a ring opening in an excited singlet state followed by a rapid ring closure to a ground-state molecule may provide an efficient route for internal conversion in arylcyclopropanes.[20] If such a process is in operation for singlet to ground state internal conversion in phenylcyclopropanes, then an even larger decrease in k_2 would be necessary to account for the increase in the Q_F's.

The difference in the variation of product quantum yields and fluorescence quantum yields with varying excitation wavelengths can be explained in one of two ways. (i) If the observed chemistry occurs directly from the singlet state, in the case of III and IV *via* the trimethylene species VIII and IX (Scheme IV), the rate constants for formation of these intermediates may increase with increasing vibrational energy in the singlet state. In competition with these processes, reactions to form unstable isomers (benzvalenes) are also probable processes with increasing vibrational energy.[21] If the radiative rate constant (k_1) is independent of the excited singlet vibrational level,[22] the results would be explained. (ii) Equally possible, the chemistry may emanate from the triplet manifold *via* the same trimethylene species, and the observed trend in Q_F and product yields may reflect an increase in intersystem crossing rate constant with increasing vibrational energy in the excited singlet state.[22] Competitive benzvalene formation and a constancy of k_2 would again give the observed results. Certainly the triplet state can give the three products as is conclusively shown by the benzene sensitization experiments.

Scheme IV



That *cis*-but-2-ene (up to 400 mm) is unable to quench any of the electronic states involved in product formation is evident from Figure 1. Here Φ_{II} is completely unaffected, while the quenching of formation of III and IV is only vibrational quenching the same as observed for *n*-butane. Now 2-butene is known to be a quencher of aromatic triplet states, and this quenching can be monitored by geometric isomerization of the olefin. The triplet energy of phenylcyclopropane as found by oxygen perturbed singlet–triplet absorption[23] is *ca.* 81 kcal mol^{-1}. Since *p*-xylene has a triplet energy[24,25] of *ca.* 81 kcal mol^{-1} and is an efficient sensitizer of butene isomerization, the absence of geometric isomerization on addition of 50 mm of *cis*-but-2-ene confirms the absence of electronic quenching. However, if the lifetime of the triplet is very short, this lack of quenching can be explained. It seems that this could be the case, for in the benzene sensitized photolysis of I a linear Stern–Volmer plot (Figure 3) is obtained on addition of *cis*-but-2-ene. Such linearity can only be explained by competitive quenching of the benzene triplet ($^3B_{1u}$) by the butene and by I. Any quenching of triplet I by butene would show as a deviation from linearity. Again the results can be explained in one of two ways; either by very fast reaction from the triplet manifold so that the triplet is too short-lived to be detected, or reaction from the singlet state with an intersystem crossing rate constant too low to populate the triplet state to a measurable extent.

We shall look more closely at the quantitative implications of the two possibilities. If all the reactions occur from the singlet state, then the lack of detectable sensitized isomerization of *cis*-but-2-ene under the conditions used sets a maximum value of $\Phi_T = 0.05$.[26] Since the singlet-state natural lifetime $\tau = Q_F\tau_{\text{rad}}$, $\tau = 66$ nsec (on irradiation near the 0–0 band), and since $\Phi_T = k_2\tau$, $k_3 < 7.6 \times 10^5$ sec^{-1}. This value is more than an order of magnitude lower than the intersystem crossing rate constants for alkylbenzenes; *e.g.*, for toluene[11] $k_{\text{ISC}} = 1.98 \times 10^7$ sec^{-1} and for *p*-xylene[12] $k_{\text{ISC}} = 1.08 \times 10^7$ sec^{-1}. On the other hand, the intersystem crossing rate constants in some constrained phenylalkenes do seem to be very low.[29] In the case of a triplet mechanism, it can be seen that the intersystem crossing rate constant would still be low compared to monoalkylbenzenes, having a maximum value (when $\Phi_T = 1 - Q_F$) of 7.9×10^6 sec^{-1}. In addition, if Φ_T is assumed to be 0.52 and making the same assumptions as before about collision diameter and energy transfer efficiency, from the absence of energy transfer to butene we can set an upper limit of 10^{-8} sec on the lifetime of the triplet.

The quantum yields of formation of the three products are measurably lower on sensitization with ben-

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(26) In this calculation, we have assumed a minimum lifetime of 0.1 μsec for the triplet of I, a collision diameter of 10^{-7} cm, and that only 1 collision in 20 will be effective in transferring electronic energy (see later and ref 27 and 28).

(27) A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968).

(28) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **73**, 1815 (1969); **71**, 3104 (1967).

(29) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *J. Amer. Chem. Soc.*, **90**, 4759 (1968).

zene than in direct irradiation, and since Φ_T for benzene vapor is 0.65 ± 0.05,[30] necessarily higher than Φ_T for I, this suggests that at least some reaction may be occurring from the singlet state. The indications are that the reactions may occur from either or both electronic states on direct irradiation. The very low value of the intersystem crossing rate constant necessary for a singlet mechanism has, as yet, found no theoretical justification and therefore tends to rule against this as an exclusive pathway. In many ways the uncertainties present in the mechanistic interpretation of this system are similar to those experienced in the direct irradiation of stilbenes,[31] and it is clear that some of the simple tests for the electronic states involved which have been used in phenylcyclopropane photochemistry[4] must be viewed with skepticism. Although no direct comparisons can be made between the work of Foote on the gas-phase photochemistry of phenylcyclopropane and the present study (since a simple alkyl substituent on occasions can have profound effects on the photochemistry of a system), there seem to be some obvious differences in the photochemistry of the systems. The quantum yields of the three major products, alkylbenzene, *cis*-1-phenylprop-1-ene and *trans*-1-phenylprop-1-ene, are very much higher than the quantum yields of olefins in this study ($\Phi_{253.7}$ allylbenzene at $46° = 0.27$ and $\Phi_{253.7}$ *cis*-1-phenylprop-1-ene at $46° = 0.19$). The effect of pressure was reported to give a linear positive Stern–Volmer plot up to *ca.* 2.0 mm in contrast to the present work. Foote came to the conclusion that the three major olefinic products were formed by reaction from the triplet state. However, all his evidence can be accommodated within the framework of either of the mechanisms presented here.

The Nature of the Intermediates. From the behavior of the three products toward vibrational quenching it seems clear that isomerization involves a different intermediate from olefin formation. Considerable theoretical interest in trimethylene has been recently generated.[32] However, firm conclusions concerning the structure of the ground-state trimethylene or its excited states have yet to be reached. It is suggested here that cis–trans isomerization may involve a "π-cyclopropane" in which the true diradical character may not have developed. That the intermediate VIII in the formation of *trans*-1-phenylbut-1-ene (III) does not feed into the isomerization pathway is indicated by the fact that although formation of III is quenched by increasing pressure, there is no enhancement of geometric isomerization (Figure 1).[33] The effect of vibrational quenchers on the formation of III and IV can be explained by a vibrational quenching of the hot radicals VIII and IX, which at low pressures may undergo destructive fission, thus enhancing the product formation, while at higher pressures so much vibrational energy is removed that the activation energy for product formation (*i.e.*, for hydrogen shifts) is unavailable.[34] This may be an oversimplified picture, and since the scatter in the Stern–Volmer plots for quenching of III and IV is large, no attempt will be made to pursue this quantitatively.

Quenching of the Excited Singlet State by *trans*-Piperylene. For the fluorescence quenching of I by piperylene

$$ {}^1\mathrm{I} + [\mathrm{pip}] \longrightarrow \mathrm{I} + [\mathrm{pip}]^* \qquad (5)$$

and

$$Q_{F_0}/Q_F = 1 + \tau k_5[\mathrm{pip}]$$

Now, since $\tau = 66$ nsec and the slope of the Stern–Volmer plot (Figure 2) is 5.16×10^2 l. mol^{-1}, $k_5 = 7.8 \times 10^9$ mol l.$^{-1}$ sec^{-1}. This figure is close to the piperylene quenching rate constants for other benzenoid singlets; *e.g.*, the mean value for the quenching of the xylenes is 1.40×10^{10} l. mol^{-1} sec^{-1}.[12]

Since up to 400 mm of butene had no effect on the quantum yield of II, no contribution due to triplet quenching would be expected in the quenching of geometric isomerization on the addition of piperylene. This is clearly the case, as is seen in Figure 2. In fact, the slope of the product quenching plot is lower (by 20%) than the fluorescence quenching plot. This difference is only just outside the estimated error but may reflect some naivity in the mechanism.[35]

Methylphenylcyclopropane Quenching of Benzene Triplets. A question which has aroused some interest in the literature recently is concerned with the importance of self-quenching of aromatic triplets.[36]

$$ {}^3\mathrm{Ar} + \mathrm{Ar} \longrightarrow \mathrm{Ar} + \mathrm{Ar}$$

Now the competitive quenching of benzene triplets by I and *cis*-butene can provide some information on the efficiency of the benzene to methylphenylcyclopropane triplet energy transfer process. Using Scheme V

Scheme V

$$\mathrm{Be} \xrightarrow{\Phi_T} {}^3\mathrm{Be} \qquad (6)$$

$$ {}^3\mathrm{Be} + \mathrm{Bu} \longrightarrow {}^3\mathrm{Bu} + \mathrm{Be} \qquad (7)$$

$$ {}^3\mathrm{Be} + \mathrm{I} \longrightarrow {}^3\mathrm{I} + \mathrm{Be} \qquad (8)$$

$$ {}^3\mathrm{Be} \longrightarrow \mathrm{Be} \qquad (9)$$

$$ {}^3\mathrm{Be} + \mathrm{Be} \longrightarrow \mathrm{Be} + \mathrm{Be} \qquad (10)$$

$$ {}^3\mathrm{I} \longrightarrow \mathrm{II} \qquad (11)$$

$$ \longrightarrow \text{other products} \qquad (12)$$

it can be shown that

$$\Phi_0/\Phi = 1 + [\mathrm{Bu}]\left[\frac{k_1}{k_8[\mathrm{I}] + k_9 + [\mathrm{Be}]k_{10}}\right] \qquad (13)$$

where Φ_0 is the quantum yield of II on triplet energy transfer from benzene in the absence of butene and Φ the quantum yield with added butene. From the slope in Figure 3

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[30] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970, p 293.

[31] J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, 88, 2336 (1966); J. Saltiel, *ibid.*, 90, 6394 (1968); W. M. Gelbart and S. A. Rice, *J. Chem. Phys.*, 50, 4775 (1969).

[32] R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968); K. G. Bergman, and W. L. Carter, *ibid.*, **91**, 7411 (1969).

[33] It should be pointed out that even if formation of III and IV were completely diverted to the formation of II, only a 5% increase in Φ_{II} would be expected. While it is felt that this increase would be detected, some doubt must remain.

[34] If the singlet excited state is involved in the reaction, III and IV may be formed by a concerted process, but in this case the increase in Φ_{III} and Φ_{IV} on the addition of low pressures of gas, followed by a decrease as the pressure is increased further, would be difficult to explain.

[35] For example, collisions between piperylene and I may affect the intersystem crossing rate constant(s).

[36] C. S. Burton and H. E. Hunziker, *Chem. Phys. Lett.*, **6**, 352 (1970).

$$k_1/(k_8[\mathrm{I}] + k_1 + [\mathrm{Be}]k_{10}) = 225\ \mathrm{l.\ mol^{-1}}$$

If we neglect[24-26] the $k_9 + [\mathrm{Be}]k_{10}$ term in eq 13, and since $[\mathrm{I}] = 2.20 \pm 0.1 \times 10^{-4}$ mol $\mathrm{l.^{-1}}$, a minimum value for k_8/k_7 is 20. This very interesting piece of information shows that the quenching rate constant k_8 is one of the largest measured for quenching of benzenoid triplets by organic molecules. Lee and Haninger[28] and Morikawa and Cvetanović[27] have obtained values of 14 and 16, respectively, for k_q/k_7, where k_q is the quenching rate constant for quenching by 1,3-butadiene. The value of 20 for k_8/k_7 obtained here implies that triplet energy transfer between benzene derivatives is very efficient.

Acknowledgment. The author wishes to thank the Camille and Henry Dreyfus Foundation and the Robert A. Welch Foundation for financial support. The helpful guidance of Professor W. A. Noyes, Jr., and Professor G. J. Fonken is gratefully acknowledged.

A Molecular Orbital Study of the Low-Energy Electronic States of Ketene

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Abstract: *Ab initio* SCF and SCF–CI calculations with a minimal STO-3G basis set have been performed on the low-lying electronic states of ketene. Vertical excitation energies to the $^3A_2$, $^1A_2$, and $^3A_1$ states are calculated. These states are then geometry optimized, and 0–0 transition energies are obtained. The calculated excitation energies are compared with experimental data, and the transitions which give rise to the long wavelength bands in the uv spectrum are identified. The A_2 states are found to arise from $\pi \rightarrow \pi'^*$ transitions. The lowest triplet state of ketene results from optimization of the $^3A_1$ state, which arises from a $\pi \rightarrow \pi^*$ transition. Potential curves for the dissociation of ketene into CH_2 and CO are also presented and used as a basis for discussion of the photochemistry of this molecule.

The electronic absorption spectrum of ketene has been the subject of investigation by many spectroscopists. Among the first to measure the spectrum of this molecule were Lardy in 1924[1] and Norrish, Crone, and Saltmarsh in 1933.[2] More recently, Dixon and Kirby,[3] Rabalais, McDonald, Scherr, and McGlynn,[4] and Laufer and Keller[5] have recorded and analyzed the spectrum of ketene. Despite these detailed studies the nature of the low-energy excited states of this molecule have not been well characterized. Moreover, there is disagreement among recent studies in so fundamental a question as whether or not the ketene spectrum results only from spin-allowed transitions. Hence, a theoretical study of the geometries and energies of low-lying electronic states of ketene would be of value in answering questions posed by spectroscopic studies of this molecule.

Ketene is also of interest to photochemists, since irradiation of ketene has often been used as a source of both singlet and triplet methylene radicals. Spin conservation rules require that triplet ketene be the precursor of triplet methylene and that singlet ketene be the source of singlet methylene. Undoubtedly, an understanding of the mechanism of photolysis in ketene will be aided by a description of the electronic structures of states involved in photochemical processes.

Recently, *ab initio* self-consistent field (SCF) configuration interaction (CI) calculations have been reported for a rather large group of small molecules.[6,7] These studies have shown that minimal basis calculations can approximate the excitation energies of low-lying molecular electronic states quite well. In those cases where the excited state geometries have been determined experimentally, there was satisfactory agreement between calculated and experimental values for bond angles and bond lengths. It would therefore seem appropriate to carry out *ab initio* calculations on ketene in order to describe the geometries and electronic structures of the low-energy states of this molecule. This paper reports the results of such calculations. An analysis of these results should provide some insight into the spectroscopic and photochemical behavior of ketene.

Method of Calculation

For a molecule with $2n$ electrons the closed-shell ground state wave function can be written in the form of a single determinant

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!} \equiv |1\bar{1}\,2\bar{2}\ldots n\bar{n}|$$

in which n orbitals are each occupied by two electrons. A molecular orbital ψ_i may be expressed as a linear combination of atomic basis functions ϕ_μ (the LCAO

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(3) R. N. Dixon and G. H. Kirby, *Trans. Faraday Soc.*, **62**, 1406 (1966).

(4) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 73 (1971).

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