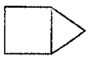
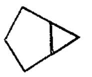
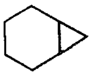
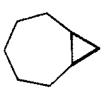
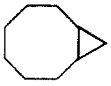
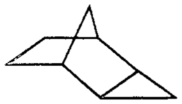
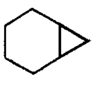
quist for these spectra. [i] Only near-infrared spectrum available. [j] We are indebted to Professor R. Criegee for a sample of bicyclo-[2.1.0]pentane. [k] Both bands absent. [l] N. M. Kishner and I. B. Losik, *Bull. Acad. Sci. USSR*, 49 (1941); *Chem. Abstr.*, **37**, 2728 (1943). [m] Unpublished results of E. P. Blanchard and H. E. Simmons. [n] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964). [o] G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960). [p] W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954). [q] We are indebted to Professor A. C. Cope for these spectra. [r] C≡C stretching frequency. [s] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961). [t] We are indebted to Dr. B. C. Anderson for this spectrum. [u] C=C stretching frequency. [v] H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964). [w] E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964). [x] H. D. Hartzler, *ibid.*, **83**, 4997 (1961). [y] Unpublished results of H. D. Hartzler.

Table II

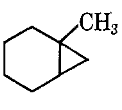
Compd.	ν, cm.$^{-1}$	
	1048	1025
	1074	1019
	1055	1025, 1017
	1049	1023
	1046	1022
	1033	1026

pane ring. In 20 compounds studied, the absorption occurred only over the range 6135–6060 cm.$^{-1}$. In this same series the overtone band ranged over 4515–4475 cm.$^{-1}$.

Chart II



6079



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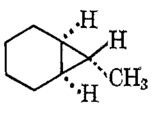
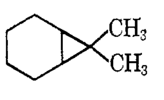


absent



absent

(3) Most reports place the allenic stretching frequencies in the range 1950–1970 cm.$^{-1}$.[5] A shift of 40 to 60 cm.$^{-1}$ to higher frequencies is found in the spectra of the alkenylidenecyclopropanes. The increased force constants of double bonds attached to a cyclopropane ring above those of acyclic double bonds is a result of the higher energy required for compression of the already strained cyclopropane bond angles. The magnitude of the shift is smaller than the shift of 100 cm.$^{-1}$ found in the double-bond stretching frequency of acyclic olefins *vs.* methylenecyclopropanes.[6,7] The smaller shift observed with the allenes is a result of the fact that the stretching vibration involves relatively small displacements of the terminal carbon atoms and is mainly due to the motion of the central carbon atom.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 61, 62.

(6) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

(7) H. D. Hartzler, *ibid.*, **86**, 526 (1964).

Photolysis and Pyrolysis of Phenylcyclopropane in the Vapor Phase

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Phenylcyclopropane has been decomposed in the vapor phase by 2537-Å. irradiation at 55 and 75° and by pyrolysis at 350°. In the photolysis the chief condensable products were (in order of decreasing yield) *n*-propylbenzene, α-methylstyrene, β-methylstyrene, styrene, ethylbenzene, toluene, and benzene. The gaseous products consisted of methane, ethane, ethylene, and acetylene. Considerable quantities of polymer deposited on the walls of the reaction vessel, requiring that photolyses be stopped after a few per cent conversion. In the presence of 50 mm. of oxygen during the photolysis, the yield of ethylene was unchanged, but all of the other products were totally inhibited with the exception of polymer. In the thermal decomposition, the principal condensable products were (in order of decreasing yields) *n*-propylbenzene, α-methylstyrene, toluene, ethylbenzene, styrene, and β-methylstyrene. The gaseous products were methane, ethylene, ethane, and acetylene. Traces of benzene, cyclopropane, and propylene were also found. Quantitative analysis of the products in the above reactions permits certain mechanistic conclusions.

The problem of energy migration in cyclopropyl-containing compounds has intrigued us for some time. The classic work of Pitts and Norman[1] on the photolysis of methyl cyclopropyl ketone showed that the Norrish type-I process could be suppressed in favor of energy migration to open the cyclopropane ring, yielding methyl propenyl ketone. Subsequent investigations in Pitts' and our laboratories[2] have shown that, in the photolysis of ketones containing a cyclopropane function "insulated" by even one methylene unit from the carbonyl, the efficiency of ring-opening isomerization is dramatically reduced with other, more conventional, processes taking over. We have recently investigated the photochemical behavior of cyclopropylphenylmethane,[3] where the benzene chromophore is removed by a methylene unit from cyclopropyl, and found complex radical decomposition rather than ring-opening isomerization, although we did observe a very interesting primary process, namely, the loss

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(1) J. N. Pitts and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(2) J. N. Pitts, L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. F. Vesley, *Photochem. Photobiol.*, **4**, 305 (1965).

(3) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **30**, 539 (1965).

of ethylene, to produce, presumably, benzylcarbene. The recent work of Richardson, *et al.*,[4] which shows that phenylcyclopropane photoeliminates methylene (which was trapped by conventional techniques) when irradiated in solution, has prompted us to study the photolysis of this compound in the vapor phase. This system, of course, is a direct analog of Pitts' cyclopropyl methyl ketone, since the chromophore is directly adjacent to the cyclopropane ring. Thus, one might expect ring opening, possibly elimination of methylene as in the work of Richardson, *et al.*,[4] more complex processes as in the case of cyclopropylphenylmethane,[3] or an unholy combination of them all.

Pyrolysis of the compound was also studied to see if there might be any analogy to pyrolysis of cyclopropylphenylmethane, the latter surprisingly rearranging to naphthalene in high yield.[3]

Results and Discussion

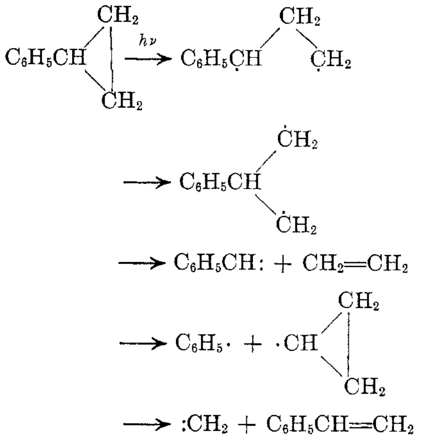
Photochemical Decomposition.—Irradiation of phenylcyclopropane (~6 mm.) at 55 and 75° in the absence of oxygen and at 55° in the presence of 50 mm. of oxygen, with light of 2537 Å. for a period of 2 hr., yielded the products listed in Table I. The figures reported are mole per cent, based on the amount of starting material *originally present*, and are not net yields. Extensive formation of polymer limited conversion to a very few per cent. (The values in Table I are accurate to ±10%.) At the higher temperature, the yields of gases were slightly higher, but the relative yields were virtually the same as at 55°. Condensables were not analyzed at the higher temperature.

TABLE I

Product	Mole % 75°	55°	55° (50 mm. of O_2)
Methane	2.51	1.67	0^a
Ethane	1.45	1.02	0
Ethylene	2.26	1.45	1.68
Acetylene	0.89	0.57	0
Benzene	...	Trace	0
Toluene	...	0.007	0
Ethylbenzene	...	0.023	0
Styrene	...	0.050	0
n-Propylbenzene	...	0.494	0
α-Methylstyrene	...	0.097	0
β-Methylstyrene	...	0.069	0

[a] All zero values are within the limits of detection, less than 0.001.

A striking feature of the data is that there was no trace of any C_3 gas in the products, corresponding to the virtual absence of benzene. This was certainly not the case in the photolysis of cyclopropylphenylmethane[3] (where, in fact, cyclopropane was the major gas); thus we see that other photolytic paths, all involving cleavage in some manner of the three-membered ring, are available. The presence of the methylstyrenes, and the *n*-propylbenzene would indicate that an appreciable amount of the phenylcyclopropane undergoes simple ring opening, followed either by isomerization (as in the case of the methylstyrenes) or abstraction of hydrogen (as in the *n*-propylbenzene). The sizeable presence of the gaseous products would indicate that some of the starting material also undergoes extensive fragmentation in primary or secondary processes. Equations 1–5, of varying importance,



(1)

(2)

$$\longrightarrow C_6H_5CH: + CH_2{=}CH_2 \qquad (3)$$

(4)

$$\longrightarrow :CH_2 + C_6H_5CH{=}CH_2 \qquad (5)$$

represent the five most likely primary processes in the photolysis. Process 1 apparently takes place to an appreciable extent in view of the yields of *n*-propylbenzene and β-methylstyrene. The preponderance of the *n*-propyl compound over β-methylstyrene and *the total lack of both in the presence of oxygen* strongly suggest the intermediacy of a diradical rather than a concerted ring opening–hydrogen migration that would give rise to β-methylstyrene (the analog of Pitts' methyl propenyl ketone[1]). The diradical intermediate, presumably partially stabilized by the benzene ring, must exist long enough in order to abstract hydrogen from some species in the system to give the saturated side-chain product, in preference to hydrogen migration to give the side-chain unsaturated product, in view of the relative product distribution.

The presence of α-methylstyrene suggests the occurence of eq. 2. However, the complete absence of cumene among the reaction products would tend to indicate that in this system, with a diradical nonstabilized by any means, hydrogen atom transfer (to give the methylstyrene) is much more rapid than hydrogen abstraction from an external source. The process yielding α-methylstyrene cannot be concerted, however, since oxygen completely scavenges any intermediate so that none of the hydrocarbon is formed in photolysis with oxygen (Table I). The ratio of the combined yield of *n*-propylbenzene and β-methylstyrene (products of an initial cleavage like that in eq. 1) to the yield of α-methylstyrene (as from the cleavage of the carbon–carbon bond as in eq. 2) is about 9:1. Since the energy from the irradiation is being initially absorbed in the benzene ring, this preferential breaking of the nearer carbon–carbon bond in the cyclopropyl ring is to be expected.

Process 3 is of the greatest interest and perhaps the most important. Ethylene is the second most abundant gaseous product, and *it is the only product formed, with approximately the same efficiency in the presence of oxygen.* Oxygen is acting as a chemical and *not* a physical quencher[5]; thus the formation of ethylene, even in 50 mm. of oxygen, demands that it is not formed *via* radical intermediates but rather in a primary process. This is quite analogous to our previous observation in the cyclopropylphenylmethane system.[3]

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[4] D. B. Richardson, L. R. Durrett, J. M. Martin, W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Am. Chem. Soc.*, **87**, 2763 (1965).

[5] G. F. Vesley and P. A. Leermakers, *J. Phys. Chem.*, **68**, 2364 (1964).

The remaining fragment from this process could abstract hydrogen to form eventually the toluene which was observed (in the nonoxygen runs), or this fragment might become incorporated into the polymer. The absence of the various other products (both condensables and gases) in the presence of oxygen would tend to indicate that they are being formed through processes which go through radical intermediates, and hence, in the presence of oxygen, are incorporated into either various polymers or peroxides.

Equation 4 certainly is of little significance in the photochemical decomposition. The trace of benzene among the condensable products, but lack of any C_3 gases, would indicate that benzene must be formed *via* a secondary pathway in the reaction.

Process 5 must be considered as a possibility in the light of the formation of ethylbenzene and styrene, both of which suggest some initial step which yields an eight-carbon fragment. It is possible, though, that these products are being derived through secondary processes following from eq. 1 and 2. More importantly, it certainly cannot be excluded as a primary process in light of the results of Richardson, *et al.*,[4] where, as mentioned previously, methylene is photoeliminated from phenylcyclopropane in solution. We have no evidence that this is a really *important* process in the gas phase, but it seems to be much more important in *solution*[4] where thermal deactivation allows more selective (and possibly totally different) photochemical pathways.

Thermal Decomposition.—Temperatures up to 300° leave phenylcyclopropane unchanged. Thus, pyrolytic studies were carried out at 350° for a period of 20 hr. Under these conditions, the phenylcyclopropane decomposed to the extent of about 10%, the rest was recovered unchanged. The results of this decomposition are given in Table II, in which the yields are expressed in mole per cent, based on the amount of phenylcyclopropane consumed. The values are accurate to ±10%.

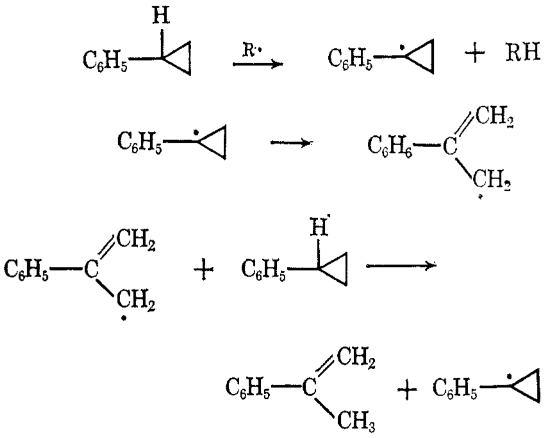
TABLE II

Product	Yield, %
Methane	10.8
Ethane	4.2
Ethylene	7.9
Acetylene	1.4
Cyclopropane	Trace
Propylene	Trace
Benzene	<0.5
Toluene	4.9
Ethylbenzene	3.0
Styrene	2.9
n-Propylbenzene	39.7
α-Methylstyrene	38.2
β-Methylstyrene	3.3

The products formed in this pyrolysis are essentially the same as those of the photolysis (with the exception of the C_3 gases), even though the relative yields of the various products have changed. In the pyrolysis no polymeric material was observed, and the mass balance (carbon 95%, hydrogen 109%) accounted for essentially all of the starting material consumed.

Over 80% of the starting material is formally accounted for by ring opening, followed by either isomerization or hydrogen abstraction to yield the product (following probably the same processes as in the photolysis eq. 1 and 2). However, for the pyrolysis, the ratio of the combined yields of β-methylstyrene and *n*-propylbenzene to the yield of α-methylstyrene is about 1.1:1 (compared with about 9:1 in the photolysis). Apparently, the thermal energy is equilibrated throughout the molecule, and there thus is no specificity in the site of the initial cleavage of the cyclopropyl ring (whereas, in the photolysis, with the benzene ring serving as the chromophore, the rupture was preferably occurring in the carbon–carbon bond nearer the benzene ring).

Formation of the relatively large amounts of α-methylstyrene may also be accounted for by a chain process[6] such as eq. 6.



(6)

The ratio of *n*-propylbenzene to β-methylstyrene remained roughly the same as in the photolysis, with a heavy preponderance of the *n*-propylbenzene. This favoring of the hydrogen abstraction over internal isomerization may again be due to the stabilization provided to the radical by the presence of the benzene ring, but it is still rather puzzling. The complete absence of any cumene in either the pyrolysis of the photolysis would indicate that the corresponding diradical, if formed, is not stable enough to exist for a sufficient length of time for hydrogen abstraction to occur.

The presence of trace amounts of cyclopropane and propylene in the pyrolysis, along with limited quantities of benzene, would tend to indicate that to some extent the pyrolysis was going by the route indicated in eq. 4. It would be highly unlikely that the cyclopropane would be formed by any route other than this initial cleavage from the benzene ring.

Once again, as in the photolysis, the elimination of ethylene from the starting material appears to be an important part of the reaction process. Similarly, the more complex forms of fragmentation, possibly the same as those in eq. 4 and 5, are necessary to explain the remaining products.

We have previously reported[3] that the principal reaction product in the thermal decomposition of cyclopropylphenylmethane is naphthalene. It was postulated that the mechanism involved opening of the three-membered ring and attack on the benzene ring by the diradical so formed, followed by rapid aromatization (loss of hydrogen). An alternative mechanism

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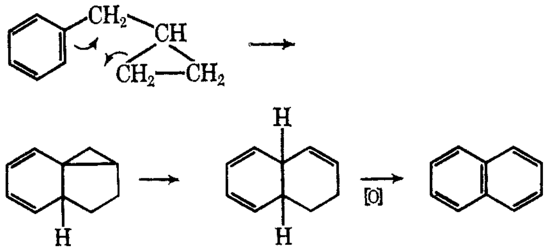
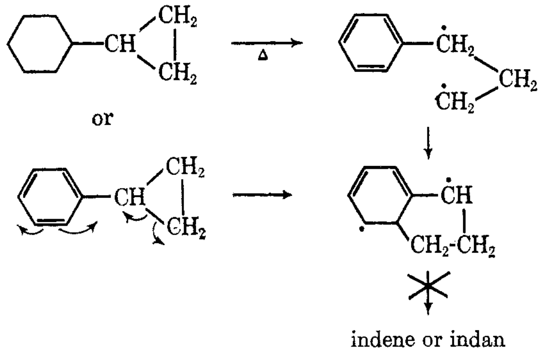
[6] We wish to thank a referee for pointing this pathway out to us.



(7)

is given in eq. 7, which better accounts for the apparent smoothness of the reaction.

By analogy to either of the above mechanisms, some indene or indan should have been formed in the pyrolysis of phenylcyclopropane (eq. 8). However, not even a trace of indan or indene could be detected; thus, in cyclopropylphenylmethane the driving force in the formation of naphthalene is apparently the attainment of additional aromatic resonance energy, this driving force being absent in the present system.



(8)

Summary.—The results in both photolysis and pyrolysis of phenylcyclopropane indicate the lack of any clear-cut, low-energy pathway for destruction. Although parallels in the two methods of decomposition are not rigorously to be drawn, it appears that opening of the three-membered ring followed by either isomerization or hydrogen abstraction is of major importance in both (not a surprising result). Also, there is certainly a certain amount of more complex radical (and possibly carbene[4]) decomposition taking place in both photolysis and pyrolysis. The most interesting finding, in our judgment, is the occurrance of the photoelimination of ethylene (eq. 3) which, in view of our experiments, must be a primary process.

Experimental Section

Phenylcyclopropene.—The phenylcyclopropane used was prepared from styrene by means of dibromocarbene addition.[7] Styrene (8.3 moles, 167 g.) was added to a stirred solution of 8 g. of potassium (0.2 g.-atom) in 250 ml. of *t*-butyl alcohol. The reaction mixture was cooled to −10° with an ice–salt bath, and bromoform (50.6 g., 0.20 mole) was added dropwise over a period of 3 hr. The reaction mixture was then allowed to stir at room temperature for an additional 15 hr. About 200 ml. of water and 200 ml. of pentane were added, and the aqueous layer was extracted with pentane, which was added to the pentane layer. This was dried over magnesium sulfate and distilled. The phenyldibromocyclopropane distilled over at 102–106° at 1 mm. The yield was 27 g. (50%). The phenyl-2,2-dibromocyclopropane (14 g.) was added to 100 ml. of ether, and the solution was stirred. Sodium (24 g.) was added over a period of 3 hr., and simultaneously 150 ml. of 10% water–90% methanol was added. This was allowed to stir overnight. The mixture was then extracted with pentane, dried carefully over magnesium sulfate, and distilled. The desired phenylcyclopropane (b.p. 29–31° at 1 mm.) was thus obtained: yield, 4.2 g. In order to remove the remaining traces of olefin, the compound was then dissolved in pentane, cooled to Dry Ice temperatures, and bromine was added. This was then rinsed with 0.2 *N* sodium hydroxide until the color disappeared, dried over anhydrous sodium carbonate, and distilled. N.m.r., v.p.c., and ultraviolet analysis failed to indicate the presence of any impurities.

Photolysis.—Fifty-microliter samples of the phenylcyclopropane were frozen out in the bottom of a 1.5-l. quartz reaction vessel. The system was evacuated and then irradiated for a period of 2 hr. The irradiation was carried out at 2537 Å., and the temperature within the reactor during the photolyses was 55°, and for one run 75°.

The gases were analyzed by means of a flame-ionization detector vapor phase chromatograph. The gaseous products were sampled through a vacuum system which was connected directly into the chromatograph. The sampling technique was such that 2.5% of the total gas was "injected." Analyses were carried out utilizing a 3-ft. silica gel column at 30°. The gases were identified by retention time and by coinjections. Samples of all C_1–C_3 hydrocarbons, with the exception of allene and cyclopropene, were tested, and no two were found to have identical retention times. For the gases found among the products, standard volumes of the known gas were injected, and the amount of gas in the product was determined by the ratio of the peak areas.

The condensable products were analyzed by freezing out in tubes at 77°K. These were then diluted with a standard volume of ether. The solution of products, having a known dilution factor, was analyzed by v.p.c., comparing peak areas with those of authentic samples diluted to known volume. A 12-ft. di-*n*-decyl phthalate column at 100° was used for the analyses. Where retention times were not adequate to remove all ambiguity regarding identity, infrared and n.m.r. spectra were taken for confirmation.

Pyrolysis.—Fifty-microliter samples of the phenylcyclopropane were frozen in 5-ml. ampoules, which were evacuated and sealed. These ampoules were heated to 350° for a period of 20 hr. The ampoules were then opened into a evacuated system, and the gaseous products were analyzed by v.p.c., using the essentially same method as for the photolyses analyses. In the analyses of the gaseous products in the thermal decomposition, a 9.8% sample of the total gas was analyzed. In the analysis for the condensable products, the ampoules were opened, a standard volume of ether was added, and the contents were analyzed by v.p.c., again using the same quantitative method that was used for the photolysis analysis.

Acknowledgments.—The authors are indebted to Dr. A. J. Fry for helpful discussion, and to Dr. N. J. Turro for mass spectra and n.m.r. spectra. Financial assistance was provided by the Petroleum Research Fund of the American Chemical Society and by the National Science Foundation.

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[7] W. v. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).