Thermal and Photochemical Decomposition of Cyclopropylphenylmethane

Peter A. Leermakers and George F. Vesley

Hall Laboratory of Chemistry, Wesleyan University, Middletown, Connecticut

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Cyclopropylphenylmethane in the vapor phase has been pyrolyzed at 400° and photolyzed at 55 and 85°. The principal product of the thermal reaction was naphthalene. Lesser amounts of toluene, benzene, ethylbenzene, propane, ethylene, methane, and ethane were formed (in order of decreasing quantity). Photolysis in the absence of oxygen yielded as condensable products toluene, benzene, ethylbenzene, and styrene. The major gaseous product was cyclopropane, formed in addition to ethylene, propylene, propane, methane, ethane, 1-butene, and traces of either 2-butene or isobutylene and acetylene. The formation of considerable amounts of polymer was observed. The ratios of the above photoproducts changed slightly with temperature and substantially in the presence of oxygen. The mechanistic implications of these observations are discussed.

The problem of the conversion and transfer of electronic excitation energy in photochemical systems has been studied in several cases in recent years. A model molecular system for observation of the migration of energy, that may have been converted from electronic to vibrational, seems to be that containing some chromophore with a cyclopropane ring in its proximity. For instance, Pitts and Norman[1] have observed that irradiation of methyl cyclopropyl ketone leads to ring opening in the cyclopropyl function to yield methyl propenyl ketone. Further investigations in Pitts' and our laboratories[2] have shown that in ketones containing a cyclopropyl function there is considerable dependence on structure of photochemical reactivity in such molecules, and that "insulation" by even one methylene unit between the chromophore and the cyclopropane ring dramatically reduces efficiency of ring-opening isomerization with a subsequent increase in radical fragmentation processes.

The title compound, cyclopropylphenylmethane, appeared to be a compound quite suitable to the study of energy migration. The benzene chromophore is one methylene unit removed from the cyclopropane ring. Several pathways should be available for the photochemical dissipation of the electronic excitation energy; an investigation of the various fragmentation products and possible rearrangement products should indicate the feasability of these various pathways. As, perhaps, a side issue it was thought that a comparison of pyrolysis products to photochemical products might prove interesting.

Previous investigators have studied the photolysis of various substituted benzenes in the vapor phase including toluene, mesitylene, and ethylbenzene,[3] and the xylenes.[4] In each case the result was fragmentation of the substituent alkyl with formation of gases (mainly methane and hydrogen) and, in the case of the xylenes, also rearrangement, *e.g.*, *ortho* to *meta*.[4] In all cases there was extensive formation of polymer.

Results and Discussion

Photochemical Decomposition.—Irradiation of cyclopropylphenylmethane (2.5 mm.) at 55 and 85° in the absence of oxygen, and at 55° in the presence of 50 mm. of oxygen, with light of 2537 Å. gave the products listed in Table I. The yields of products are relative, based on methane equal to one for the gases and benzene equal to one for the condensables. All values are accurate to about ±10%. Absolute yields and quantum yields could not be determined owing to extensive formation of polymer which coated the walls of the reaction vessel requiring that photolyses be stopped after a few % conversion of starting material.

Table I

Photochemical Decomposition of Cyclopropylphenylmethane

Products	55°	85°	55° (50 mm. O_2)
	Gases		
Methane	1.0	1.0	1.0
Ethane	0.8	0.6	0.02
Ethylene	1.5	1.6	2.3
Propane	0.8	0.5	0.4
Propylene	1.3	0.9	0.5
Cyclopropane	4.3	2.0	0.3
1-Butene	0.4	*a*	*a*
2-Butene Isobutylene	0.2	*a*	*a*
Acetylene	Trace	Trace	
	Condensables		
Benzene	1.0	...	Trace
Toluene	1.2	...	0.0
Ethylbenzene	0.6	...	0.0
Styrene	0.2	...	0.0
Ethanol	...	...	Trace

[a] C_4 hydrocarbons were not analyzed for in these cases.

It is significant that hydrogen, while expected, was not found in any of the runs, nor was any C_{10} hydrocarbon other than starting material. Ring-opening isomerization should have yielded 1-phenyl-2-butene in a fashion analogous to the photoisomerization of methyl cyclopropyl ketone to methyl propenyl ketone.[1]

It is obvious from the data that extensive fragmentation and hydrogen migration has occurred. Of the observed products ethylene is the only one that could be formed in a primary photochemical process (which would also ultimately result in the formation of styrene *and polymeric material*). The other products must inevitably be formed by hydrogen abstraction. We feel that eq. 1–4 represent the primary reaction pathways, the observed products being derived from the fragments indicated. The fact that ethylene formation shows virtually no temperature sensitivity and is apparently not inhibited by oxygen (it is the only product to increase relative to methane) would make it reasonable that eq. 1 is a primary path and that, indeed,

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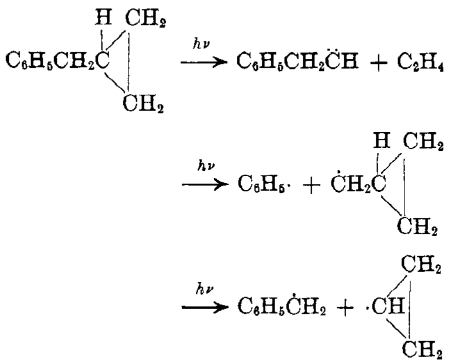
(1) J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

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

(3) R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).

(4) K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964).



$$C_6H_5CH_2C(H)\langle(CH_2)_2 \xrightarrow{h\nu} C_6H_5CH_2\ddot{C}H + C_2H_4 \quad (1)$$

$$\xrightarrow{h\nu} C_6H_5\cdot + \dot{C}H_2C(H)\langle(CH_2)_2 \quad (2)$$

$$\xrightarrow{h\nu} C_6H_5\dot{C}H_2 + \cdot CH\langle(CH_2)_2 \quad (3)$$

$$\xrightarrow{h\nu} C_6H_5CH_2\dot{C}HCH_2\dot{C}H_2 \quad (4)$$

most of the ethylene arises from eq. 1. The formation of benzene suggests eq. 2, and the high proportion of cyclopropane in the gaseous products probably justifies eq. 3. Equation 4 may not be important, but is included since the C–C bond ruptured is the weakest in the molecule. Probably process 3 is the most important, since cyclopropane is the major gas and toluene the major condensable. It is unlikely that most of the toluene could be formed from coupling of methyl and phenyl radicals, although this cannot be rigorously ruled out.

Absorption of a 2537-Å. photon injects 112.5 kcal./mole of energy in the π-electron system of the aromatic nucleus. This energy may be reradiated, lost by internal conversion, or utilized to achieve bond cleavage. Two factors will determine which C–C bond is cleaved. One is the proximity of the bond to the excitation center; the other is the strength of the bond. In cyclopropylphenylmethane the bonds become successively weaker as they become further from the aromatic nucleus[5]; thus the two effects are in opposition to each other. Although phenyl–methylene C–C bond rupture does occur to a substantial extent, in an even larger number of excited molecules apparently energy migrates past this bond to achieve the result of eq. 3.

In the limited range studied, the effect of temperature was not very pronounced except, perhaps, on the yield of cyclopropane which was reduced by half with a 30°-rise in temperature. This might be anticipated since the cyclopropyl radical should be less stable at higher temperatures; however, the yields of propylene and propane did not correspondingly increase. Thus, either the result is not of consequence, or else the cyclopropyl radical became incorporated into the polymer.

The effect of oxygen is more noteworthy. All of the gaseous products, with the exception of ethylene, were diminished with respect to methane; ethane was virtually eliminated, and the absolute yield of the combined gases was somewhat reduced by qualitative but not quantitative observation. Of the condensable products only a trace of benzene could be found along with ethanol as expected. We do not attribute this to quenching of excited states, since products were obviously formed (including more polymer than in runs without oxygen). Rather the oxygen almost surely combined with the copious radical intermediates forming peroxides and polymer.

Thermal Decomposition.—In an effort to determine whether there was a direct relationship between the photolysis and pyrolysis of cyclopropylphenylmethane, 50- and 10-μl. samples of the latter were degassed, sealed off in 5-ml. ampoules, and heated.

At temperatures of 350° and below, little reaction took place. However, samples heated to 400° for 20 hr. reacted virtually to completion to yield the products, with indicated molar stoichiometry, given in Table II. As can be seen, the actual mass balance is better than 90%. We are then quite sure that no important product has been overlooked. Formation of polymer was not apparent. Conspicuously absent from the products were cyclopropane and propylene, products of importance in the photolysis. In addition, as in the case of the photolysis, hydrogen was not detected.

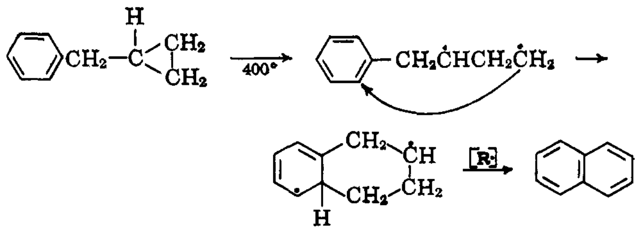
TABLE II

PYROLYSIS OF CYCLOPROPYLPHENYLMETHANE

Product	Moles of product/mole of starting material consumed
Naphthalene	0.65
Toluene	0.15
Benzene	0.06
Ethylbenzene	0.09
Propane	0.07
Ethylene	0.04
Ethane	0.03
Methane	0.03

Two facts emerge. First, there seems to be little correlation between the photolytic and pyrolytic behavior of the compound of interest. Second, and of more interest, is the highly efficient and novel rearrangement of the starting material to naphthalene, the mechanism of which is not entirely clear. The rearrangement requires the loss of four hydrogen atoms from the system. Other decomposition does occur to yield the saturated gases methane, ethane, and propane, as well as the saturated side-chain benzenes, toluene and ethylbenzene, so that one can account for the fate of some of the hydrogen but by no means all of it. Since molecular hydrogen is not observed, and the mass balance is good, the question of complete stoichiometry remains.

For the formation of naphthalene, the following rearrangement mechanism seems plausible (where the R· is a radical derived from a fragmentation side reaction). Since no trace of tetralin was observed, the aromatization step probably occurs exceedingly rapidly after ring closure. It is quite clear that to round out this work the system cyclopropylbenzene should be studied with respect to its photolytic and pyrolytic behavior. To our knowledge this is currently being initiated in another laboratory.[7]



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[5] Cleavage as indicated in eq. 2 should require 85–90 kcal., whereas that indicated in eq. 3, if the corresponding bond in ethylbenzene may serve as a model, may be as low as 65 kcal.[3] Cyclopropane C–C bond energies have been reported to be below 65 kcal.[6]

[6] F. Seubold, *J. Chem. Phys.*, **21**, 1616 (1953).

[7] J. N. Pitts, Jr., private communication.

Experimental

Photolysis.—In a 1.5-l. quartz reaction vessel, 20-μl. samples of cyclopropylphenylmethane (Aldrich Chemical Co.) were frozen out at Dry Ice temperatures and the system was evacuated. The system was then closed, either by a vacuum stopcock or by sealing off a glass tube, and irradiated for 1 hr. Photolyses were carried out in a Rayonet reactor (Southern New England Ultraviolet Co.) which has previously been described.[8] Radiation wave length was primarily 2537 Å.; reaction temperatures were maintained at 55 and 85°.

The condensable products were frozen out at liquid nitrogen temperature and sealed in tubes, several of which were then opened and combined, using ether as solvent, for analysis. Benzene, toluene, ethylbenzene, and styrene were identified by vapor chromatography retention times (on a 12-ft. di-*n*-decyl phthalate column, 140°), and, except for styrene, also by mass spectral analysis which was completely unambiguous.[9] For gas analysis the reaction vessel was connected to a conventional vacuum system. Condensables were trapped at Dry Ice–acetone temperature; gases were then collected and compressed, by use of a mercury diffusion pump and Toepler pump, into a sample cell connected to a flame ionization gas chromatograph. Gases were identified by comparison of retention times and coinjections with standards on a 3-ft. silica gel column and a 12-ft. β,β'-oxydipropionitrile column, both at room temperature. All C_1–C_3 and several C_4 hydrocarbons were tested and no two of these gases had identical retention times under our conditions.

In some runs 50 mm. of oxygen was bled in prior to irradiation. Identification of gaseous and condensable products was handled the same as in the runs without oxygen except that condensables were analyzed on a tricresyl phosphate column at 50°.

A sample of cyclopropylphenylmethane was degassed and treated identically except that irradiation was omitted. Analysis of any possible gaseous products showed that no reaction ensued under the reaction conditions (85°, 1 hr.).

Pyrolysis.—Samples of cyclopropylphenylmethane were frozen in 5-ml ampoules, evacuated, and sealed off to a fine tip to serve as a break-seal. Samples of 10 μl. were used for quantitative runs and 50 μl. for product analysis. The tubes were heated in a furnace at 400° for 20 hr. The tubes were then placed in a larger vessel which was then evacuated. The vessel was agitated to effect breakage of the ampoule, and attached to the vacuum system for analysis of the gas, such analyses being similar to those described for the photochemical reactions. For quantitative yields all of the gas was compressed into the sample cell and the total gas formed in the reaction determined.

The liquid condensables were analyzed by gas chromatography under the same conditions employed in analysis of corresponding photochemical products. Naphthalene was also analyzed by gas chromatography (6-ft. Ucon polar, 150°). A portion was collected and identified by comparison of its infrared spectrum with an authentic sample, and by its melting point of 80°.

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

(9) We are indebted to Dr. G. P. Happ of the Eastman Kodak Co., for mass spectral analyses and interpretations.

Friedel-Crafts Isomerization. XI.[1] Aluminum Chloride Catalyzed Isomerization of the Haloethylbenzenes

GEORGE A. OLAH, JOAN C. LAPIERRE, AND CHARLES G. CARLSON

Eastern Research Laboratory, Dow Chemical Company, Framingham, Massachusetts

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The isomerization of the isomeric *o*-, *m*-, and *p*-fluoroethylbenzenes, -chloroethylbenzenes, and -bromoethylbenzenes has been investigated with water-promoted aluminum chloride. Fluoroethylbenzenes as well as the chloroethylbenzenes isomerize by an intramolecular 1,2-methyl shift mechanism. *m*-Bromoethylbenzene also isomerizes by an apparent 1,2-shift while the isomerization of *o*- and *p*-bromoethylbenzene involves an initial fast intermolecular bromine migration followed by a considerably slower rearrangement to the equilibrium mixture. The equilibrium isomer distributions consist, in the case of fluoroethylbenzenes, of 36% *ortho*, 52% *meta*, and 12% *para* isomer, in the case of chloroethylbenzenes, of 28% *ortho*, 52% *meta*, and 20% *para* isomer, and, in the case of bromoethylbenzenes, of 24% *ortho*, 56% *meta*, and 20% *para* isomer.

Many investigations of isomerization and disproportionation reactions of alkylbenzenes and halobenzenes under the influence of Lewis acids have been carried out. Less seems to be known of the behavior of substituted benzenes carrying both an alkyl and a halo substituent.

Olah and Meyer[2] as well as Crump and Gornowicz[3] and Kooyman and co-workers[4] previously reported on the aluminum halide catalyzed isomerization of halotoluenes. Our investigation was then extended to the isomerization of haloethylbenzenes. The isomerization of fluoroethylbenzenes and chloroethylbenzenes was not studied previously. Kooyman and co-workers[4] reported the equilibrium composition of the bromoethylbenzenes as consisting of 24–25% *ortho*, 53–54% *meta*, and 22% *para* isomer, without, however, providing any further data to the course of the isomerization.

In the present study, fluoroethylbenzenes, chloroethylbenzenes, and bromoethylbenzenes were isomerized with water-promoted aluminum chloride using gas–liquid chromotography to establish isomer distributions. The change of isomer distribution with time allows some insight into the three-compound equilibrium and provides qualitative information regarding the mechanism with which the individual isomers are formed.

Results

The isomerization of haloethylbenzenes through the catalytic effect of water-promoted aluminum chloride was investigated. Experimental conditions were similar to those used in the isomerization of halotoluenes.[2] All isomerizations were carried out at 25°. Results are given as normalized percentages of *ortho*, *meta*, and *para* isomer as a function of time.

Fluoroethylbenzenes.—Tables I–III show the data of isomerization of the three isomeric fluoroethylbenzenes. The equilibrium mixture contained 36%

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(1) Part X: *J. Org. Chem.*, **29**, 2687 (1964).

(2) G. A. Olah and M. W. Meyer, *ibid.*, **27**, 3464 (1962).

(3) J. W. Crump and G. A. Gornowicz, *ibid.*, **28**, 949 (1963).

(4) E. C. Kooyman, *Pure Appl. Chem.*, **7**, 193 (1963); G. J. P. Augustijn, E. C. Kooyman, and R. Louw, *Rec. trav. chim.*, **82**, 965 (1963).