The Infrared Spectra of Some Cyclopropanes

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Received June 3, 1965

This paper presents a collection of infrared spectral data for some 100 organic compounds containing cyclopropane rings. These are drawn from several sources and include simple cyclopropane hydrocarbons, bicyclic hydrocarbons, functionally substituted cyclopropanes, methylenecyclopropanes, allenic cyclopropanes, and spiropentanes. The major absorptions in the regions of cyclopropyl carbon–hydrogen stretching (infrared and near-infrared) and the characteristic cyclopropyl ring deformation are given along with the allenic stretching frequencies.

Because of the interest in organic molecules containing cyclopropane rings, we have collected infrared spectral data of some 100 cyclopropanes which have been studied in this and other laboratories. Since the spectra were obtained from different sources and were measured in different media, only calibrated data obtained from similar spectrometers are included. Furthermore, only the solvent is indicated in Table I and the original literature should be consulted for instrument data. All spectra from this laboratory were obtained on a Perkin-Elmer Model 21 double-beam infrared spectrometer equipped with sodium chloride optics.

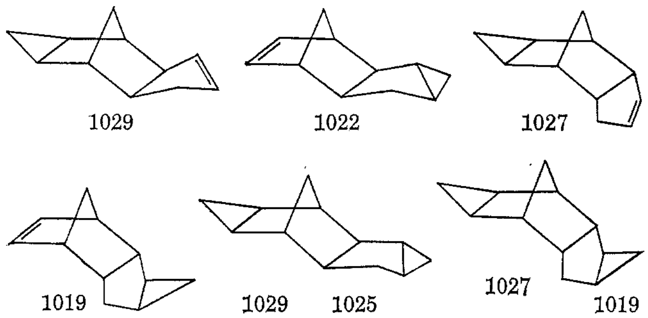
The spectral data are collected in Table I. Three regions seemed of most interest: carbon–hydrogen stretching near 3090 cm.$^{-1}$, the first overtone of this band ($\sim$6250 cm.$^{-1}$) and the combination band ($\sim$4545 cm.$^{-1}$) in the near-infrared, and the characteristic ring deformation near 1020 cm.$^{-1}$. Several allenic stretching frequencies were also included because of the paucity of such data.

The characteristic vibrational frequencies of compounds containing cyclopropane rings have been discussed in many articles, and other compilations of data have appeared.[1] Since the assignments of frequencies and their reliability have been discussed at length,[1] we note only a few points.

(1) The moderately strong band in the 1020-cm.$^{-1}$ region has been ascribed by Herzberg[2] to a symmetric vibration of the cyclopropyl ring. Several authors[1a,b,f,l,m] have found this assignment useful for the identification of cyclopropanes, while others[1c,d,h,n] have pointed out that the absorption is sometimes weak or obscured by other functionality, especially oxygen. Josien, Fuson, and Cary[1d] suggested that the absorption at 890 cm.$^{-1}$, which is often seen in cyclopropanes, is useful for identification, but this has been disputed.[1e,n]

In this study, we find that the absorption at 1020 cm.$^{-1}$ occurs in most samples and is often valuable in determining not only the presence of cyclopropane rings in certain circumstances, but also their environment. This absorption, however, is generally missing in hexasubstituted derivatives and is obscured by the presence of carbon–oxygen bonds. In the simple, bicyclic hydrocarbon series, this region appears to be reasonably characteristic and exhibits two well-defined peaks between 1010 and 1089 cm.$^{-1}$ (Table II). The highest frequency absorption decreases monotonically, while the stronger, low-frequency band varies only slightly. The high-frequency absorption in bicyclo[2.1.0]pentane (1048 cm.$^{-1}$) seems anomalously low, and this may be due to strain in the ring to which the cyclopropane is fused, since tricyclo-[3.2.1.0^{2,4}]octane also absorbs at a low frequency (1033 cm.$^{-1}$). The stronger, low-frequency absorption is fairly characteristic of the cyclopropane environment, as shown by the correlation in the series of methylene adducts of *exo*- and *endo*-dicyclopentadiene[3] (see Chart I, absorptions given in reciprocal centimeters).

CHART I



(2) The finding of Washburn and Mahoney[1j] that the carbon–hydrogen stretching frequency in cyclopropanes in the near-infrared ($\sim$6250 cm.$^{-1}$) is highly characteristic has been confirmed and extended by Gassman[4] and by Weitkamp and Korte.[1o]

We find that 1,2,3-tri- and 1,1,2,3-tetrasubstituted cyclopropanes show no absorption in this region of the near-infrared. An example is provided by the series of norcaranes (Chart II, absorptions given in reciprocal centimeters). In cyclopropanes where electronegative groups are not bonded directly to the ring, this absorption is of little value as a structural parameter other than ascertaining the presence of the cyclopro-

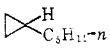
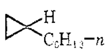
(1) (a) J. D. Bartelson, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946); (b) J. M. Derfer, E. E. Pickett, and C. E. Boord, *ibid.*, **71**, 2482 (1949); (c) S. E. Wiberly and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952); (d) M. Josien, N. Fuson, and A. S. Cary, *J. Am. Chem. Soc.*, **73**, 4445 (1951); (e) E. K. Plyler and N. Acquista, *J. Res. Natl. Bur. Std.*, **43**, 37 (1949); (f) V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954); (g) Hs. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956); (h) C. F. H. Allen, T. J. Davis, W. J. Humphlett, and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957); (i) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, **79**, 3467 (1957); (j) W. H. Washburn and M. J. Mahoney, *ibid.*, **80**, 504 (1958); (k) G. W. Cannon, A. A. Santilli, and P. Shenian, *ibid.*, **81**, 1660 (1959); (l) C. F. Wilcox, Jr., and R. R. Craig, *ibid.*, **83**, 3866 (1961); (m) H. Weitkamp, U. Hasserodt, and F. Korte, *Ber.*, **95**, 2280 (1962); (n) A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 2012 (1959); (o) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964)

(2) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 352.

(3) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964).

(4) P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

TABLE I. CYCLOPROPANE INFRARED SPECTRA

Compounds	ν (C–H), cm.$^{-1}$ [a]	A (C–H)[b]	ν (ring), cm.$^{-1}$ [a]	A (ring)[b]	Near-infrared,[c] cm.$^{-1}$	ν (allenic C=C), cm.$^{-1}$	A (allenic)[b]	Conditions[d]	Ref.
	3086	s	1040	m				A	*e*
	3003	s	1013	s					
	3067	m	1042	m				A	*e*
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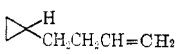	3106	s	1045	m				A	*e*
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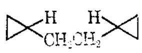	3070	s	1040	s				A	*e*
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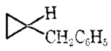
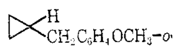
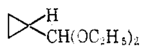
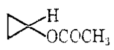
	3077	s	1045	m				A	*e*
	3021	s	1031	s					
			1016	s					
	3077	s	1050	m	6098			A	*e*
	3003	s	1032	m	4484[f]				
			1015	m					
	3096	m	1045	w				A	*e*
	3003	m	1019	w					
	3096	m	1046 (sh)	w				A	*e*
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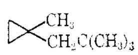
	3080	m	1015	m				C	*e*
	3077	m	1043	w				A	*e*
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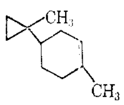
			1009	s					
	3067	s	1050	w				A	*e*
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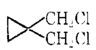	3080	w	1023	m				A	*h*
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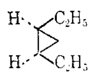
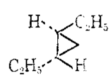
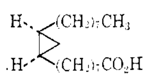
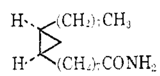
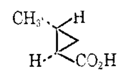
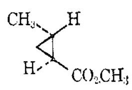
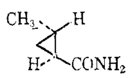
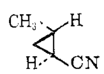
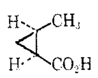
	3072	s	1048	w	6098			A	*e*
			1019	s	4505				
			1005	m	4454				
	3086	s	1022	s	6098			A	*e*
					4515				
					4464				
			1020	m				E	*e*
					6098				*e*
					4505				
					4464				
			1012	m				D	*h*
			1041	s					
	3086 (sh)	w	1042	w				A	*e*
	2994	s							
			1012	w				H	*h*
			1041	w					
			1028	m				A	*h*
			1054	m					
			998	w				D	*h*
			1043	m					
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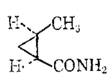			1003	w				H	*h*
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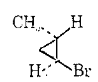
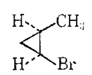
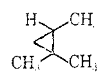
			1029	m				B	*h*
			1060	w					
			1032	w				B	*h*
	3077	m	1025	w				C	*e*

TABLE I (*Continued*)

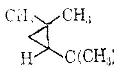
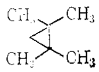
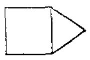
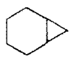
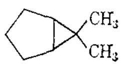
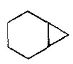
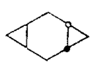
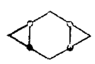
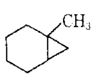
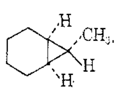
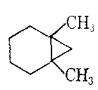
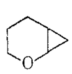
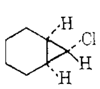
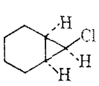
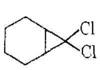
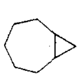
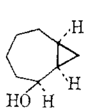
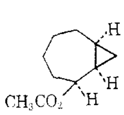
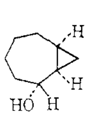
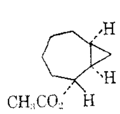
Compounds	ν (C–H), cm.$^{-1}$ [a]	A (C–H)[b]	ν (ring), cm.$^{-1}$ [a]	A (ring)[b]	Near-infrared,[c] cm.$^{-1}$	ν (allenic C=C), cm.$^{-1}$	A (allenic)[b]	Conditions[d]	Ref.
	3067 3021 (sh)	m m	1043 1014 (sh) 1011	w m m				A	*e*
	3067 2985	m s	1018	m				A	*e*
	3058	s	1025 1048	m s	6061 4484			A	*j*
	3067 3040 3003	s s s	1074 1019	m s	6098 4505			A	*e*
	3100 (sh) 3003	w s	1045	w	*k*			A	*l*
	3086 3021	s s	1055 1025 1017	w s s	6079 4494			A	*e*
	3058 3012	s s	1038 1019 1010	m s s				A	*e*
	3077 3021	m s	1064 1027 1024 (sh)	w m m				A	*e*
	3044	m	1020 1042	m m				A	*e*
	3058 3003	m s	1005 (sh) 1015 1047	m s w	6079 4494			A	*m*
	3106 2950	w s	1034 1011	m m	*k*			A	*n*
	3040 2976	m s	1015	s	6061 4474			A	*m*
	3086 3003	m s	1041 1009	m s	6116 4505			A	*e*
	3030	s	1015	w	*k*			A	*o*
	3030	s	1015	w	*k*			A	*o*
	3003	m	1033 1025	s s				A	*p*
	3058 2994	w m	1046 1020	m s	6116 4505 4464			A	*q*
	3070 2990 2915	w m s	1065 1027	w s				D	*q*
	3100 3025 2940	w m s	1048 1028 1018	m m m				D	*q*
	3070 2990	w m	1052 1025 1017	m m m				D	*q*
	3045 2970	m s	1044 1027 1020	s s s				D	*q*

TABLE I (*Continued*)

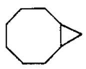
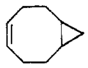
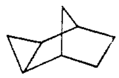
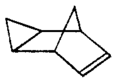
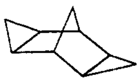
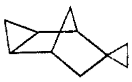
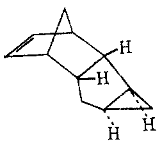
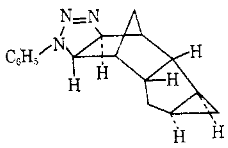
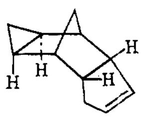
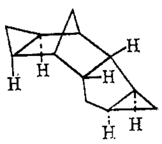
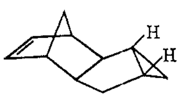
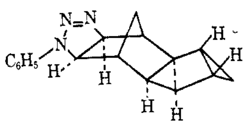
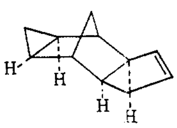
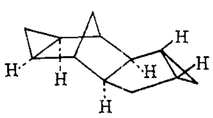
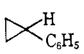
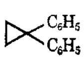
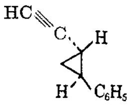
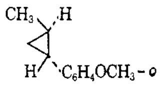
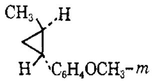
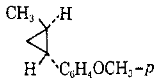
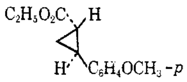
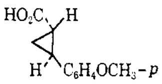
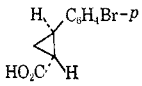
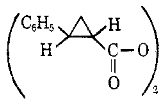
Compounds	ν (C–H), cm.$^{-1}$ [a]	A (C–H) [b]	ν (ring), cm.$^{-1}$ [a]	A (ring) [b]	Near-infrared,[c] cm.$^{-1}$	ν (allenic C=C), cm.$^{-1}$	A (allenic) [b]	Conditions [d]	Ref.
	3035 2965	w m	1004 1027	s s	6098 4505 4465			A	*q*
	3058 2994	m s	1028 1017	s s				A	*m*
	3058 3003	s s	1033 1026 (sh)	s m	6098 4505			A	*e*
	3115 (sh) 3067 (sh)	w s	1046 (sh) 1031 1012	m s s	6098 4494			A	*e*
	3075	s	1010 1042	m m				A	*n*
	3077 3021 (sh) 2994	m s s	1046 1035 1029 1008 1000	s s s s s				A	*n*
	3077 3040	s s	1038 1019	w s				A	*n*
	3049 3012	m m	1034 1020	s m				F	*n*
	3067 3040	s s	1042 (sh) 1027	w s				A	*n*
	3058 3021	w s	1053 1027 1019	m s s				A	*n*
	3067 3030	s s	1033 1022	m s				A	*n*
	3058 3021	w w	1038 1026 (sh) 1019	w w m				F	*n*
	3049 3021	s s	1041 1029	s s				A	*n*
	3049 3012	s s	1038 1025 1029 (sh)	s s s				A	*n*
	3058 3012	s s	1045 1025 1020 (sh)	m s m				A	*e*
	3086 (sh) 3058 3021	s s s	1052 1030 (sh) 1024	w m s				A	*e*

TABLE I (*Continued*)

Compounds	ν (C–H), cm.⁻¹[a]	A (C–H)[b]	ν (ring), cm.⁻¹[a]	A (ring)[b]	Near-infrared,[c] cm.⁻¹	ν (allenic C═C), cm.⁻¹	A (allenic)[b]	Conditions[d]	Ref.
	3279 3077 3058 3030 2976	s m m s m	1000 1020 (sh) 1033	w w s		2123[r]	s	A	*s*
	3067 3003	w w	1052 1030	m m	6098 4515			A	*e*
	3067 3012	m s	1064 (sh) 1048	w s	6098 4505			A	*e*
	3058 2994	m s	1064 1037	m s	6098 4515 4484			A	*e*
			1044 1022 1012	s w w	6135 4425[f]			B	*m*
			1040 1033 (sh) 1010	s m w	6154 4386[f]			B	*e*
			1016 1057	m s				H	*h*
			1020 1052	m m				H	*h*
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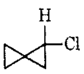
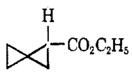
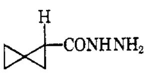
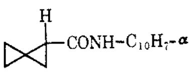
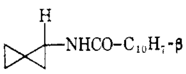
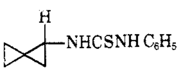
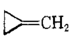
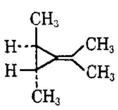
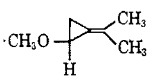
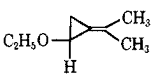
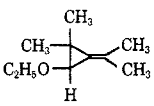
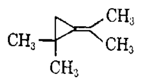
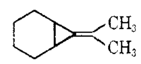
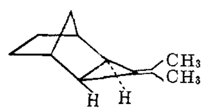
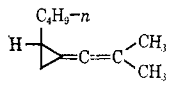
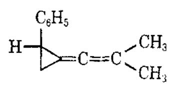
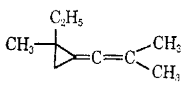
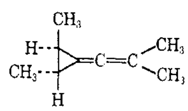
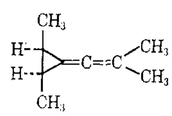
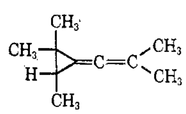
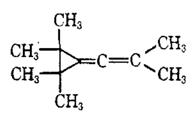
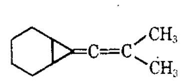
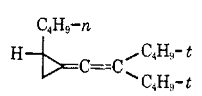
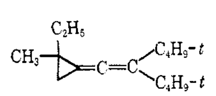
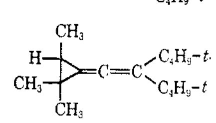
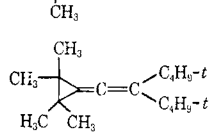
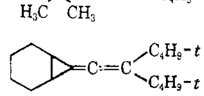
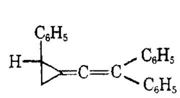
	3075	w	1010 1040	s w				B	*h*
			1010 1020 1050	w w m				A	*h*
			1000 1055	m w				H	*h*
			1008	w				H	*h*
			1005 1050	m w				D	*h*
			1000	w				H	*h*
	3077 2994	m m	1055 1034	m m				G	*t*
	3070 (sh)		990 1054	m m		1795[u]	m	A	*v*
	3070	m	1003 1025	s s		1780[u]	s	A	*v*
	3070	m	1000 1044	s s		1780[u]	s	A	*v*
	3070 (sh)		1025 1044	m m				A	*v*

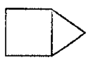
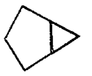
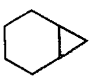
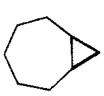
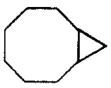
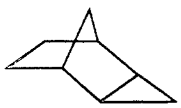
TABLE I (*Continued*)

Compounds	ν (C–H), cm.$^{-1}$ [a]	*A* (C–H)[b]	ν (ring), cm.$^{-1}$ [a]	*A* (ring)[b]	Near, infrared,[c] cm.$^{-1}$	ν (allenic C═C), cm.$^{-1}$	*A* (allenic)[b]	Conditions[d]	Ref.
	3070	m	985 1006 1028	s m w		1785[u]	m	A	*v*
	3070 (sh)		983 1027	m w		1783[u]	m	A	*v*
	3070 (sh)		1012	m		1783[u]	w	A	*v*
	3058 3020	w s	1017	m		2022	s	A	*s*
	3067 3030 2985	m s s	1003 1031	m s		2025	s	A	*s*
	3040 2985	m s	1005 (sh) 1013	s s		2020	s	A	*s*
	3100 2985	w s	1015 1029	w s		2020	s	A	*w*
	3100 3000	w s	1026	s		2020	s	A	*x*
	3100 2985	w s	1020	s		2020	s	A	*s*
						2020	w	A	*s*
	3090 (sh) 3030	w m	1026	w		2000 2024	m s	A	*s*
	3080 (sh) 3030 (sh)	m s	1017	m		2005	s	A	*y*
	3030 3003	m s	1005 1015	m m		2000	s	A	*y*
	3100 3030 3000	w w s	1025	w		1990	s	A	*y*
	3030	s	1032	m		2000	s	A	*y*
	3080 (sh)	w	1025	w		1980 2010	s s	A	*y*
	3080 3030 2985	w w w	998 1003 1022 1028	m w w w		2000	s	F	*s*

[a] Where no value is given this region of the spectrum is either blank or too complicated to analyze. [b] Relative absorbance (optical density); w = weak, m = medium, s = strong. [c] All near-infrared spectra taken in 10% carbon tetrachloride solution. [d] A = neat liquid, B = 10% carbon tetrachloride solution, C = gas phase, D = 10% carbon disulfide solution, E = melt, F = potassium bromide wafer, G = solid at −196°, H = 5% chloroform solution. [e] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959). [f] Strongest band in complicated region. [g] Optically active product from *d*-(+)-limonene. [h] We are indebted to Professor D. Apple-

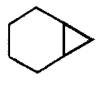
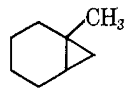
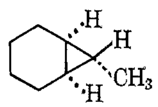
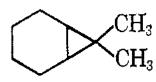
quist for these spectra. [i] Only near-infrared spectrum available. [j] We are indebted to Professor R. Criegee for a sample of bicyclo-[2.1.0]pentane. [k] Both bands absent. [l] N. M. Kishner and I. B. Losik, *Bull. Acad. Sci. USSR*, 49 (1941); *Chem. Abstr.*, **37**, 2728 (1943). [m] Unpublished results 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	6079	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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Received August 16, 1965

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

(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).