

presence of a relative impurity and the first point taken was used as the "zero point."

Almost every one of the rate constants in Table I is the result of at least two runs of at least five points each. The concentration of at least one of the reagents was usually different, by a factor of about two, in the two runs.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

Cyclopropene. IV. The Infrared, Ultraviolet and N.m.r. Spectra of Cyclopropene and Some Related Compounds¹

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The infrared, ultraviolet and n.m.r. spectra of cyclopropene and a number of related compounds have been examined. The results are discussed in terms of the structures of the compounds.

Our interest in the effects of bond angle deformation on the properties of organic compounds has led us to investigate the infrared, ultraviolet and n.m.r. spectra of cyclopropene, and to compare these data with those for other cyclic compounds. The results obtained with each type of spectral transition will be discussed separately.

Infrared Spectra.—Before considering the infrared spectral data for the cycloalkenes and cycloalkanones given in Table II, it would seem appropriate to summarize the available data for the cycloalkanes. Table I gives the type A vibrational fre-

Vibration	Cyclopropane ²	Cyclobutane ³	Cyclopentane ⁴	Cyclohexane ⁵
A ₁ ' or A _{1g} C-H str.	3009	2870	2868	2853
A ₂ '' or A _{2u} C-H str.	3103	2896	2965	2960
A ₁ ' or A _{1g} ring breathing	1188	1003	886	802
K C-C stretching ^b	4.27	4.21	...	4.00
K C-H stretching ^c	5.1	4.5	4.6	4.6

^a Values are given in cm.⁻¹; A₁ frequencies are from liquid phase Raman spectra, and A₂ frequencies are from gas phase spectra. ^b Values were taken from ref. 3; it was assumed that the interaction constant for cyclopropane is zero as with cyclobutane. ^c The values for this force constant are not available from a normal coordinate analysis, and therefore they were roughly approximated from the average of the A₁ and A₂ frequencies.

quencies for carbon-hydrogen stretching and for ring breathing. The A₁' and A_{1g} vibrations are totally symmetric and are observed only in the Raman spectrum, whereas the A₂'' and A_{2u} frequencies are infrared active. The carbon-hydrogen vibrational modes which corresponds to these designa-

(1) This work was supported by the Office of Ordnance Research and in part by a Sloan Foundation grant. Part III: P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

(2) A. W. Baker and R. C. Lord, *ibid.*, **23**, 1636 (1955).

(3) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(4) F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

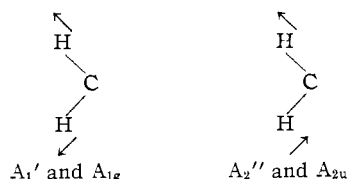
(5) C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947); R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943). The A_{1g} C-H frequency was taken as that of the most intense polarized Raman line in the 3000 cm.⁻¹ region, and the A_{2u} C-H frequency was taken as that of the strongest infrared active band in this region, in analogy with cyclopentane.

TABLE II
VIBRATIONAL FREQUENCIES FOR SOME CYCLIC COMPOUNDS^a

Ring size	Cycloalkene =CH		>C=C<	Cycloalkanone >C=O	Methylene-cycloalkene >C=CH ₂
	A	B			
3	3076	..	1641	1815 ^f	1730 ^g
4	3048	3126	1566 ^e	1788	1678
5	3061	..	1611	1746	1657 ^d
6	3024	3067	1649	1715	1651 ^d
7	3020	3059	1650	1703	...
8	3016	3053	1648	1702	...
Straight chain ^b	3023	..	1658	1720	1654

^a Values in cm.⁻¹ for CCl₄ solutions (10%) using an instrument with a calcium fluoride prism, except for the data to which reference is given below. Estimated error in frequency is ±5 cm.⁻¹ at 3000 cm.⁻¹ and ±2 cm.⁻¹ at 1600 cm.⁻¹. The frequencies for a number of these compounds have been reported elsewhere. All the values given here, with the exceptions noted, were determined with the same instrument in order to make them more comparable. ^b The compounds are *cis*-2-butene, diethyl ketone and isobutene. ^c Raman frequency, ref. 10. ^d Raman frequencies: P. A. Akishin and V. M. Tatevskii, *Vestnik Moskov Univ.*, 6, No. 2 Ser. Fiz. Mat. i Estestven Nauk, No. 1, 103 (1951). ^e This datum was kindly supplied by Dr. B. E. Anderson, E. I. du Pont de Nemours and Co. ^f W. B. De More, H. D. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5878 (1959), gas phase spectrum. This datum does not refer to material which has been isolated and identified as cyclopropanone, but rather to the product of the reaction of methylene with ketene in a solid matrix. Its properties makes it appear likely that it is cyclopropanone.

tions are approximately as noted

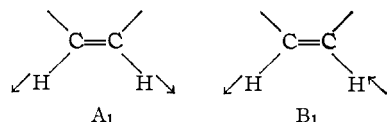


As has been noted previously,⁶ the frequencies of the symmetrical carbon-hydrogen vibration show a general increase as the bond angle deformation is increased. Unfortunately, the more fundamental quantity, the carbon-hydrogen stretching force constant, has not been determined for these compounds. It has been roughly approxima-

(6) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

ted by using the average of the A_1 and A_2 frequencies, giving the values shown in Table I. The values for cyclopropane are similar to those for *cis*-2-butene which has its A_1 frequency at 3034 cm.^{-1} ,⁷ and for which the force constant is approximately 5.0×10^5 dynes/cm. The similarity of values suggests⁸ that the carbon orbitals forming the C-H bonds of cyclopropane have increased s-character compared to the other cycloalkanes. This would be in good accord with the models of cyclopropane which have been suggested by Walsh⁸ and by Coulson and Moffitt.⁹

With the cycloalkenes, there are two carbon-hydrogen vibrational frequencies of type A_1 and B_1 , which correspond approximately to



With cyclobutene, the frequencies corresponding to these normal modes of vibration have been assigned by Lord and Rea.¹⁰ It was noted that these vibrations gave rise to bands at the high frequency side of the methylene carbon-hydrogen band; that the A_1 band was considerably more intense than the B_1 band; and that the A_1 band appeared at a lower frequency than the B_1 band.

Cyclohexene, cycloheptene and cyclooctene have a band of fairly high intensity at the high frequency side of the methylene absorption (Table II) which probably corresponds to the A type vibration. There is also a much weaker band at a somewhat higher frequency which is tentatively suggested to correspond to the B type vibration. With cyclopentene, a band corresponding to the B type vibration is not observed; it may be of too low intensity, or it may coincide with the position of the A type vibration. The same appears to also be the case with cyclopropene.

The A type vibrations of the cycloalkenes show a smaller frequency variation with change in ring size than do the corresponding vibrations of the cycloalkanes. The trend is, however, in the same direction. The B type vibrations appear to have a larger change with ring size, although it has not as yet been possible to determine the frequency of this vibration for cyclopropene and cyclopentene. The study of this problem by the synthesis of suitable deuterium-substituted derivatives is in progress. A complete vibrational analysis which would lead to the force constants for the carbon-hydrogen bonds would be of great value in helping to decide whether or not the carbon orbitals in the vinyl C-H bonds have greater s-character than those of a simple alkene.

The change in the carbon-carbon double bond frequencies is particularly interesting in that a marked drop in frequency is noted with cyclobutene, whereas the frequency for cyclopropene is

about normal in comparison with the other cycloalkenes. A simple-minded approach to predicting the change in frequency with ring size would involve the assumption that the carbon p-orbitals forming the double bond π -orbital, being orthogonal to the orbitals forming the σ -bonds, would be unaffected by bond angle deformation, and the strength of the π -bond would increase in going from cyclopentene to cyclopropene in view of the decrease in carbon-carbon double bond distance.^{1,11} As noted previously, the force constants for C-C stretching for the cycloalkanes increase only slightly with increasing ring size. Thus, the two effects should cancel each other and should result in essentially constant carbon-carbon double bond frequencies. Possibly, the across-ring repulsions which are assumed to be operative in cyclobutene in view of the long carbon-carbon bond distance,¹² are in part responsible for the value observed with cyclobutene, and when this interaction is no longer present, as in cyclopropene, the frequency returns to a normal value.

The intensity of the band is also of interest. It increases in going from cyclooctene to cyclohexene and is about the same for cyclohexene and cyclopentene. However, with cyclobutene, it is so weak that it can barely be detected. Cyclopropene, on the other hand, has a band which is as intense as that for cyclopentene. This again suggests that the abnormality in the series lies with cyclobutene and that the bond angle deformation itself has little effect on the carbon-carbon double bond vibration.

In connection with the carbon-carbon double bond frequency observed with cyclopropene, it is interesting to note that Faure and Smith observed a weak band in sterculic acid at 1865 cm.^{-1} which they assumed to be the cyclopropene ring carbon-carbon double bond frequency, and Doering and Mole observed a similar weak band at 1898 cm.^{-1} with 1,2-dimethylcyclopropene.¹³ There seems to be little doubt about the assignment for the 1641 cm.^{-1} band of cyclopropene since it is supported by Raman data (unpublished), and therefore it would appear either that alkyl groups have a remarkably large effect on the position of this vibration, or that the band in the cyclopropene derivatives has been assigned incorrectly.

As noted previously¹⁴ the carbonyl frequency for the cycloalkanones increases in a regular fashion as the ring size decreases. This may also be attributed to an increase in the s-character of the carbon orbitals forming the bond. The same effect is noted with the methylenecycloalkanes. Thus, with an exocyclic double bond, there is no abnormality observed with the four-membered ring.

Ultraviolet Spectra.—It is known that the cycloalkenes have an absorption band starting at about $200\text{ m}\mu$ which results from the excitation of a π -electron to an antibonding state.¹⁵ Although in

(7) H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.*, **6**, 247 (1938).

(8) A. D. Walsh, *Nature*, **159**, 164 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

(9) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

(10) R. C. Lord and D. G. Rea, *J. Am. Chem. Soc.*, **79**, 2401 (1957).

(11) E. Goldish, K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.*, **78**, 2714 (1956).

(12) J. D. Dunitz and V. Shomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(13) P. K. Faure and J. C. Smith, *J. Chem. Soc.*, 1818 (1956); W. v. E. Doering and T. Mole, *Tetrahedron*, **10**, 85 (1960).

(14) Cf. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 128.

(15) E. P. Carr and H. Stuecklen, *J. Chem. Phys.*, **6**, 55 (1938).

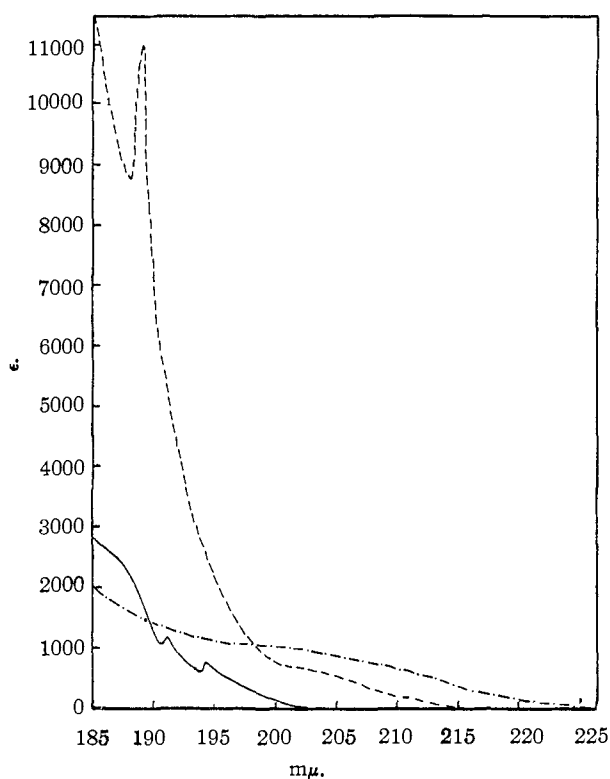


Fig. 1.—Ultraviolet spectra of cycloalkenes. The broken line is cyclopentene, the solid line is cyclobutene, and the dot-dash line is cyclopropene.

accordance with the Frank-Condon principle no nuclear motion may occur during such a transition, the rehybridization which may accompany the transition may result in a change in the strain energy in the excited state. The possibility of observing such an effect has been investigated by determining the ultraviolet spectra of cyclopropene and cyclobutene down to 185 $m\mu$ in the vapor phase. The data are shown in Fig. 1, and the spectrum of cyclopentene is included for comparison.

The spectrum of cyclopentene has been investigated by Carr and Stucklen¹⁵ and by Pickett, Muntz and McPherson,¹⁶ who concluded that there were two transitions, one having a low intensity and centered at about 200 $m\mu$, and the other having much higher intensity and a shorter wave length. The beginning of the more intense band has a marked vibrational component with separations of 1520 and 2470 cm^{-1} . With cyclobutene, the transition, at least as far as 185 $m\mu$, is of much lower intensity. A vibrational component may be seen at the beginning of the band and corresponds to a separation of about 1000 cm^{-1} . Thus, one of the A_1 ring expansion modes at 1182 and 1137 cm^{-1} may be the vibration which is coupled with the electronic excitation. If the first vibrational component of the spectra of cyclobutene and cyclopentene corresponds to the O—O transition for the same type of band, then this band of cyclobutene has been shifted by 6 $m\mu$ to the

(16) L. W. Pickett, M. Muntz and E. M. McPherson, *J. Am. Chem. Soc.*, **73**, 4862 (1951).

red, corresponding to a change in excitation energy of 4.5 kcal./mole.

The absorption of cyclopropene above 200 $m\mu$ is higher than that for cyclopentene, but the intensity at 185 $m\mu$ is markedly less than that for either cyclopentene or cyclobutene. It would appear that the higher wave length band of cyclopentene has increased in intensity, and that the lower wave length band has decreased in intensity in going to cyclopropene.

The presently available data on the electronic spectra of alkenes is not adequate to permit a more detailed consideration of the spectra. However, there are features of the spectra of both cyclobutene and cyclopropene which deserve further investigation, and such work is now planned.

N.m.r. Spectra.—The n.m.r. spectra of a series of cycloalkanes, cycloalkenes and cycloalkanones are given in Table III. They were determined as 15% solutions in carbon tetrachloride using tetramethylsilane as a reference and a 60 mc. oscillator frequency. In a few cases, the spectra were determined at a lower concentration but no significant shifts were observed.

TABLE III
N.M.R. SPECTRA OF SOME CYCLIC COMPOUNDS^a

Ring size	Cycloalkenes		Cycloalkenes		$\Delta\tau^b$	J^c
	=CH	CH ₂ C=	$\Delta\tau^b$	CCH ₂ C		
3	9.78(s)	2.99(t)	9.08(t)	0.70 1.8
4	8.04(s)	4.03(s)	7.46(s)	.56 0.0
5	8.49(s)	4.40(t)	7.72(m)	.77	8.10(m)	0.39 0.5
6	8.56(s)	4.41(t)	8.04(m)	.53	8.35(m)	.20 1.5
7	8.46(s)	4.29(t)	7.89(b)	.57	8.38(b) 8.51(b)	.08 3.7 - .05
8	8.46(s)	4.44(t)	7.89(b)	.54	8.50(b)	- .04 5.3
Ring size	CH ₂ -C=O	$\Delta\tau^b$	Cycloalkanones		$\Delta\tau^b$	$J^{\alpha,\beta}$
			C-CH ₂ -C			
4	6.97(t)	1.07	8.04(p)	0.00		8.2
5	7.94(s)	0.55	7.98(s)	.51		
6	7.78(b)	.78	8.21(b)	.35		
7	7.62(b)	.84	8.34(b)	.12		
8	7.70(b)	.76	8.19(b)	.27		
			8.50(b)	-.04		

^a All values are given in p.p.m. referred to tetramethylsilane (internal standard) as 10.00 (G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)). Spectra were taken as 15% solutions in carbon tetrachloride at room temperature with the exception of cyclopropene which was determined at -9° . The spectrum of cyclobutene at -9° was identical with that obtained at 25° . The letters refer to the number of components of each line: s, single; t, triplet; p, pentuplet; m, incompletely resolved multiplet; b, broad unresolved multiplet. The probable error is ± 0.02 . ^b Shift with respect to corresponding cycloalkane. ^c Apparent coupling constant between the olefinic and allyl protons, ± 0.2 cycle per sec.

With the cycloalkanes, there is a shift of the proton resonance to a lower field as the ring size is decreased. However, with cyclopropane, there is a marked shift to higher field. This has been observed previously with both cyclopropane, and its derivatives.¹⁷ The shift will be discussed in connection with the spectrum of cyclopropene.

The position of the vinyl proton resonance in the cycloalkenes is essentially constant with the 5–8 membered rings. Again, with cyclobutene, a shift to lower field is noted, corresponding to the increase in bond angle deformation, and with cyclopropene

(17) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, N. Y., 1959, pp. 236, 285, 289.

the effect is even larger. A similar change may be seen in the spectra of cyclohexene, norbornene and norbornadiene for which the vinyl resonance appears at 4.41, 4.06, and 3.35 respectively, although here, other factors may also be operative.

The value of the apparent coupling constant between the olefinic and allyl protons in cyclohexene, cycloheptene and cyclooctene increases from 1.5 to 3.7 to 5.3. The coupling in these compounds should be treated as an $X_2AA'X_2'$ case, and there will be two coupling constants, J_{AX} and $J_{AX'}$. Bothner-By¹⁸ has found that to a good approximation, the apparent coupling constants are equal to $J_{AX} + J_{AX'}$, and that $J_{AX'}$ is usually negative. Thus the true coupling constants are somewhat larger than the above numbers. Since $J_{AX'}$ would be expected to be considerably smaller than J_{AX} , the apparent coupling constants still indicate the trend in the true coupling constants.

In the half-chair form of cyclohexane (Fig. 2) the olefinic protons occupy a position nearly half-way between the allylic hydrogens. The dihedral angle between these protons is about 60° , for which a coupling constant of about 2 cycles would be expected.¹⁹ It may be noted that the boat form would require that the olefinic hydrogens eclipse one of the allylic hydrogens, and this would result in a higher coupling constant than was observed. Thus the n.m.r. data are in good accord with the prediction based on the minimization of hydrogen repulsion.

With cycloheptene, however, the more stable conformation no longer puts the olefinic hydrogen half-way between the allylic hydrogens, and with cyclooctene, the eclipsing of these hydrogens becomes even more severe. This is in good accord with the increase in the coupling constant. It may be noted that these rings should have a relatively low energy barrier for going from one stable form to the other (interchanging the hydrogens which eclipse the olefinic hydrogens) and thus one observes only an average value of the coupling constant rather than two values corresponding to the two dihedral angles in the more stable form.

The apparent coupling constant decreases on going from cyclohexene to cyclopentene and cyclobutene. This may be due either to a change in J_{AX} or $J_{AX'}$ or both, and it is not possible at this time to decide which is the major factor. The larger apparent coupling constant for cyclopropene may be a result of the fact that there is only one coupling constant (A_2X_2 case) or, the coupling constant may have decreased further and become negative.

It is interesting to note that the relative shifts for the allyl protons with respect to the corresponding cycloalkane are approximately constant. Again, with cyclopropene a marked shift to a higher field is noted. There are several possible reasons for the shift observed with cyclopropene derivatives. Bothner-By and Naar-Colin²⁰ have noted that the

(18) Private communication from A. A. Bothner-By. We wish to thank him for supplying us with this information prior to publication. Cf. R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960), and references cited therein.

(19) Cf. M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959), for a correlation between the dihedral angle and the coupling constant.

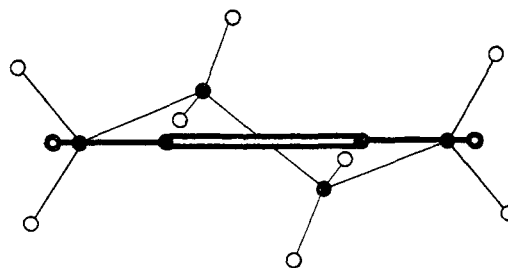


Fig. 2.—The conformation of cyclohexane. The vinyl hydrogens are indicated as semi-filled circles.

chemical shifts between cyclopentane, cyclohexane and an open-chain methylene may be attributed to the magnetic anisotropy of the carbon-carbon bond. The magnitude of this contribution to the shielding is given approximately by

$$\sigma_{i,xy} = (1 - 3 \cos^2 B)(\chi_{xy})/3r^3$$

where $\sigma_{i,xy}$ is the part of the shielding of the i th proton due to the anisotropy, χ_{xy} , in the X-Y bond, and B is the angle between the axis of the X-Y bond and the line joining the center of the bond to the i th proton.

In cyclopropane, the angle B is 90° and r is approximately 2.36×10^{-8} cm. Using 5×10^{-30} for χ_{C-C} ,¹⁹ the shielding due to this factor is calculated to be 0.25 p.p.m. The value for cyclopentane is -0.08 , giving a net shift of 0.33. This effect is in the right direction, but it is too small by a factor of 4.

It has been observed that cyclopropane has an unusually large molar diamagnetic susceptibility,²¹ and it was suggested that the observed value could be accounted for if one were to assume that three electrons precessed in a ring of radius 1.46 Å. It is clear from the theoretical studies of cyclopropane^{8,9} that the ring electrons possess greater mobility than those of ordinary saturated compounds, but the value 1.46 Å. seems rather large. However, if this is correct, it may account for the upfield shift of the proton resonance. In a magnetic field, a ring current would be induced which would lead to an induced magnetic field opposing the applied field at distances smaller than the radius of the ring, and reinforcing the applied field at larger distances. The methylene hydrogens would be within this radius and would be more shielded. This is in contrast to the protons in benzene which are outside the radius of the ring current, and consequently experience an induced magnetic field in the same direction as the applied field.²² The vinyl protons, being farther from the center of the ring, would not experience as large a shift, and if at the proper distance might be shifted downfield (*i.e.*, if the distance were greater than the radius for the ring current).

Cycloalkanones.—With cyclobutanone, a large shift with respect to cyclobutane is noted for the α -hydrogens, whereas no shift is observed for the β -hydrogens. This suggests that the force respon-

(20) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

(21) J. R. Lacher, J. W. Pollack and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

(22) J. A. Pople, *ibid.*, **24**, 111 (1956).

sible for the chemical shift has a strong directional character. The coupling constant of the α - and β -hydrogens (8.2 sec.⁻¹) is the value expected for the case in which the hydrogens on adjacent carbons are close to being completely eclipsed. Only a single value of the coupling constant is obtained from a first-order consideration of the spectrum. Bothner-By¹⁸ has found that the coupling constants for the *cis*- and *trans*- α - and β -protons will appear to approach that for a single coupling constant if

$$\frac{J_{\alpha\alpha'} + J_{\beta\beta'}}{J_{\alpha\beta} - J_{\alpha\beta'}} \gg 1$$

and this will probably be the case here.

In complete contrast to cyclobutanone, the chemical shifts of the α - and β -hydrogens of cyclopentanone are almost the same (differing by only 2.4 cycles at 60 mc.), and the coupling constant must be very small. The spectrum consists of only two peaks of approximately equal intensity. For the A₂B₂ case, if the coupling constant were equal to or larger than the chemical shift, the spectrum would be much more complex than that observed. Thus the coupling constant must be much smaller than 2.4 sec.⁻¹. This seems unreasonable in view of the results which have been obtained with other compounds. Also, it is strange that the α - and β -hydrogens are almost equally shielded.

The spectra of the other cycloalkanones are about what one might expect. The chemical shift for the α -hydrogens with respect to the corresponding saturated hydrocarbon is about the same for the 6-, 7- and 8-membered ring ketones, and in each case the resonance band is rather broad. The far ring protons give bands with half-widths of 9 and 6 cycles for the 6- and 7-membered rings, respectively. However, the band for cyclooctanone is very broad, and there is a suggestion of it being in two parts with chemical shifts of 8.19 and 8.50, respectively. The former band has a half-width of about 25 sec.⁻¹, and the half-width of the latter is about 10 sec.⁻¹. It can be seen that there is far less regularity in the spectra of the ketones than there was with the alkenes.

Experimental

Materials.—Except for cyclopropene, cyclobutane and cyclobutene, which were prepared by standard procedures, all of the compounds used were commercial samples. All compounds were analyzed by vapor phase chromatography, and if an impurity was found, the compound was purified by preparative scale vapor phase chromatography.

Instruments.—The infrared spectra were determined using a Perkin-Elmer model 21 spectrometer equipped with a calcium fluoride prism. It was calibrated using polystyrene and water vapor. The ultraviolet spectra were obtained using a Cary model 14 spectrometer. The n.m.r. spectra were obtained using a Varian spectrometer with a radio frequency of 60 mc.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Spin-Spin Coupling Constants between Non-bonded C¹³ and Protons in Some C¹³-Labeled Compounds

BY GERASIMOS J. KARABATSOS

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Spin-spin coupling constants between C¹³ and protons separated by one, two or three bonds have been measured in twelve compounds possessing either the isopropyl or the *t*-butyl group and labeled with C¹³ at specific carbon atoms. In diisopropyl ketone-carbonyl-C¹³, isobutyric acid-carbonyl-C¹³ and methyl isobutyrate-carbonyl-C¹³ the C¹³-proton coupling constants do not decrease monotonically with the number of bonds separating the two nuclei; $J_{C^{13}-C-H}$ corresponds to 80% $J_{C^{13}-C-C-H}$ in the ketone and 97% in the acid and ester; $J_{C^{13}-C-C-H}$ is found to vary over a range of 53% (5.8 c.p.s. in methyl isobutyrate-carbonyl-C¹³ to 3.8 c.p.s. in isobutyl alcohol-1-C¹³). In compounds possessing the isopropyl group $J_{C^{13}-C-C-H}$ has values in the range of 70–80% of the corresponding $J_{H-C-C-H}$; the two constants undergo changes which are, qualitatively, directly proportional to each other. The smallest spin-spin coupling constant between C¹³ and proton was found to be (3.5 c.p.s.) in the system C¹³-O-C-H of the methyl esters.

Spin-spin coupling constants between C¹³ and proton directly bonded to each other have been measured in compounds of C¹³ natural abundance, either from C¹³ or proton resonance n.m.r. studies, and some interesting correlations have been made.¹ No evaluation of such constants has been made when C¹³ and hydrogen are separated by more than one bond.² The possibility of using proton n.m.r. for ascertaining the position of C¹³ in specific atoms of products during mechanistic studies³ led to the examination of the proton n.m.r.

spectra of various C¹³-labeled compounds, available from such studies. This paper records various C¹³-proton spin-spin coupling constants together with some qualitative correlations.

Results and Discussion

All C¹³-labeled compounds whose proton n.m.r. spectra are reported in this paper contain either the isopropyl or the *t*-butyl group.⁴ The excess C¹³ content in the compounds varied from about 65% (diisopropyl ketone) to about 15% (dimethylacetic acid and its derivatives). Table I summarizes the measured spin-spin coupling constants between C¹³ and hydrogen, each value being the average of twelve measurements.

(3) For an example see G. J. Karabatsos and J. D. Graham, *J. Am. Chem. Soc.*, **82**, 5250 (1960).

(4) The author is indebted to Professor P. D. Bartlett for his encouragement in pursuing this work. Some of the compounds, namely diisopropyl ketone and its derivatives, dimethylacetic acid and trimethylacetic acid, were synthesized in his laboratories.

(1) (a) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957); (b) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, **118** (1958); (c) N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)*, **A252**, 506 (1959); (d) N. Sheppard and J. J. Turner, *Mol. Phys.*, **3**, 168 (1960); (e) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959); (f) N. Muller and D. E. Prichard, *ibid.*, **31**, 768, 1471 (1959); (g) G. V. D. Tiers, *ibid.*, **64**, 373 (1960); (h) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959).

(2) J. N. Shoolery has measured such constants in methylacetylene (private communication).