

covered may, of course, approach unity even if the diatomic molecules are undissociated and retain their identity throughout the adsorption and subsequent surface diffusion processes. Thus, the results for the one- and the two-dimensional problems are similar.

Summary

Equilibria in reactions involving pairs of ad-

acent substituents on indefinitely long polymer chains are treated statistically. Although it should be difficult to carry a reaction of this type close to completion, there is no finite limit on the fraction of the functional groups remaining unreacted, which is in contrast to the limit $1/e^2$ beyond which a non-reversible reaction of such pairs cannot be carried.

ITHACA, NEW YORK

RECEIVED MAY 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, AND FROM MELLON INSTITUTE]

The Infrared Spectra of Propargylic Alcohols and Bromides

BY JOHN H. WOTIZ, FOIL A. MILLER AND ROBERT J. PALCHAK

In a recent publication¹ dealing with the infrared spectrum of isomeric normal acetylenic compounds, it was noted that compounds containing a functional group on the carbon atom once removed from the triple bond ($C_4H_9C\equiv C-CH_2X$; X equals OH, Cl, Br, CN) have a characteristic strong band near 1710 cm.^{-1} ($5.85\ \mu$). Strong absorption at this position is quite unexpected, and the present investigation was undertaken to see whether this band is attributed to a carbonyl-containing impurity, or whether it is characteristic of such substances. Propargylic

compounds of the type $R-C\equiv C-\overset{\overset{R_1}{|}}{\underset{\underset{R_2}{|}}{C}}-X$, where X is

OH or Br, R is hydrogen, alkyl, or phenyl, and R_1 and R_2 are hydrogen or alkyl groups, were synthesized and their infrared spectra determined. With the exception of the above-mentioned publication,⁴ there is no record of infrared spectra of propargylic compounds in the literature. Table I contains the structural formulas and characteristic absorption bands of all the compounds considered in this study. Figures 1 and 2 contain the spectra of some of the more representative propargylic alcohols and bromides, respectively.

Experimental

Propargylic alcohols were prepared by the action of acetylenic Grignard reagents on aldehydes or ketones. Dimethyl-1-heptynylcarbinol (XVII) is a new compound.

Propargylic bromides were prepared by the reaction of phosphorus tribromide with an ether solution of the propargylic alcohol in the presence of pyridine. Compounds 2-bromo-3-octyne (X), 2-bromo-3-nonyne (XII), 3-bromo-1-heptyne (XIV), 2-bromo-2-methyl-3-octyne (XVI), and 2-bromo-2-methyl-3-nonyne (XVIII) have not been previously reported. The boiling point and refractive index of the alcohols and the bromides used for the infrared investigation are listed in Table I, together with references to previous preparations.

Spectroscopic Measurements.²—The infrared spectra were obtained with a Baird double beam spectrometer using a sodium chloride prism. The samples were studied

as pure liquids in 0.05 mm. cells. In Fig. 1 portions of some of the spectra are also given for other thicknesses.

The Raman spectrum was obtained for compound VI. The apparatus consisted of a spectrograph modeled closely after one designed by Prof. R. C. Lord,³ and an illuminator unit similar to that of Crawford and Horwitz.⁴ Exposures of one-half and one hour were used.

Discussion of Results

A number of the bands can be attributed immediately to corresponding modes of vibration, and need not be discussed explicitly. The mono-substituted acetylenes exhibit the $C\equiv C$ stretching frequency near 2100 cm.^{-1} ($4.76\ \mu$), whereas the disubstituted acetylenes have it at 2210 to 2280 cm.^{-1} (4.52 to $4.38\ \mu$). Primary propargylic compounds $R-C\equiv C-CH_2-X$, where R is an alkyl group, show the band near 2260 cm.^{-1} (compounds III through VI). When R is a phenyl group (compounds VII and VIII), the band is lowered to 2210 cm.^{-1} . These results agree with our earlier findings¹ and with observations on the Raman spectra of various acetylenic compounds.⁵

We turn now to the unsuspected band at 1740 to 1600 cm.^{-1} which occurs in all but two of the compounds studied. The position depends upon whether the alcohol or bromide is primary, secondary, or tertiary, as shown in Table II. Within each of these classes there is a variation in intensity. However, as a group, the intensity diminishes in the order primary, secondary and tertiary. In general the band is more intense in the bromides than in the corresponding alcohols. The band is not observed for the two tertiary alcohols (compounds XV and XVII).

The following possible explanations for this band have occurred to us:

1. **It May Be an Overtone or Combination Tone.**—An overtone is out of the question because there is no strong fundamental at the proper position. Two arguments suggest that it cannot be a combination tone. First, for many

(3) Harrison, Lord and Loofbourow, "Practical Spectroscopy," Prentice Hall, Inc., New York, N. Y., 1948, p. 515 ff.

(4) Crawford and Horwitz, *J. Chem. Phys.*, **15**, 268 (1947).

(5) Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, pp. 200-206.

(1) Wotiz and Miller, *THIS JOURNAL*, **71**, 3441 (1949).

(2) The authors wish to thank Mr. R. B. Haunan for his able assistance in these determinations.

TABLE I

LIST OF COMPOUNDS, PHYSICAL CONSTANTS AND SELECTED INFRARED BANDS

Intensities: s, strong; m, medium; w, weak; v, very. All cell thickness 0.05 mm. Microanalyses by G. L. Stragand at the Microchemical Analytical Laboratory of the University of Pittsburgh.

I	Compound	Reference to previous synthesis	°C.	B. p., Mm.	n_D^{25}	Absorption bands (cm. ⁻¹)	
						C≡C	New bands
II	HC≡C—CH ₂ OH	e	e	e	e	2100 m	1710 w
III	HC≡C—CH ₂ Br	e	e	e	e	2105 m	1715 m
IV	C ₄ H ₉ C≡C—CH ₂ OH ^a	f	98	28	1.4523	2240 s	1700 w
V	C ₄ H ₉ C≡C—CH ₂ Br ^a	g	54	4	1.4844	2260 vs	1735 vs
VI	C ₃ H ₇ C≡C—CH ₂ Br ^b	g	38	4	1.4886	2260 vs	1740 s
VII	C ₆ H ₁₁ C≡C—CH ₂ Br	g	68	4	1.4818	2270 vs	1740 vs
VIII	C ₆ H ₅ C≡C—CH ₂ OH	h	107	2	1.5835	2201 m	1710 s
IX	C ₆ H ₅ C≡C—CH ₂ Br	i	93	1	1.6195	2210 s	1720 s
	C ₄ H ₉ C≡C—CHCH ₃	i	66	4	1.4452	2260 m	1695 s
X	$\begin{array}{c} \text{OH} \\ \\ \text{C}_4\text{H}_9\text{C}\equiv\text{C}-\text{CHCH}_3 \end{array}$	k	57	2	1.4805	2210 vs	1695 vw ^v
XI	$\begin{array}{c} \text{Br} \\ \\ \text{C}_5\text{H}_{11}\text{C}\equiv\text{C}-\text{CHCH}_3 \end{array}$	h	63	2	1.4409	2230 m	1650 w
XII	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_{11}\text{C}\equiv\text{C}-\text{CHCH}_3 \end{array}$	i	56	<1	1.4800	2230 s ^t	1670 m
XIII	$\begin{array}{c} \text{Br} \\ \\ \text{C}_4\text{H}_9\text{CH}-\text{C}\equiv\text{C}-\text{H} \end{array}$	m	69	18	1.4360	2080 w	1695 w
XIV	$\begin{array}{c} \text{OH} \\ \\ \text{C}_4\text{H}_9\text{CH}-\text{C}\equiv\text{C}-\text{H} \end{array}$	n	64	20	1.4695	2090 w ^u	1700 vw
XV	$\begin{array}{c} \text{Br} \\ \\ \text{C}_4\text{H}_9\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \end{array}$	o	97	33	1.4418	2230 w	x
XVI	$\begin{array}{c} \text{OH} \\ \\ \text{C}_4\text{H}_9\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \end{array}$	p	49	1	1.4755	2230 s	1630 s
XVII	$\begin{array}{c} \text{Br} \\ \\ \text{C}_6\text{H}_{11}\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \end{array}$	q	73	4	1.4420	2270 m	x
XVIII	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_{11}\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \\ \\ \text{Br} \end{array}$	r	78	<1	1.4920	x	1600 s

^a Infrared spectrum previously described; Wotiz and Miller, *THIS JOURNAL*, 71, 3441 (1949). ^b Spectrum similar to compounds IV and VI. ^c Spectrum similar to compound XV. ^d Spectrum similar to compound XVI. ^e Purchased from Farchan Research Laboratories, Cleveland, Ohio. ^f Newman and Wotiz, *THIS JOURNAL*, 71, 1292 (1949). ^g Wotiz, *ibid.*, 72, 1639 (1950). ^h Gredy, *Ann. chim.*, 4, 5 (1935). ⁱ Murray and Cleveland, *THIS JOURNAL*, 60, 2664 (1938). ^j Campbell, Campbell and Eby, *ibid.*, 60, 2882 (1938). ^k New compound. *Anal.* Calcd. for C₆H₁₃Br: C, 50.8; H, 6.9; Br, 42.3. Found: C, 51.0; H, 6.7; Br, 42.2. ^l New compound. *Anal.* Calcd. for C₉H₁₃Br: C, 53.2; H, 7.4; Br, 39.4. Found: C, 53.2; H, 7.3; Br, 39.3. ^m Trouchet, *Compt. rend.*, 196, 706 (1933). ⁿ New compound. *Anal.* Calcd. for C₇H₁₁Br: C, 48.0; H, 6.3; Br, 45.6. Found: C, 48.2; H, 6.2; Br, 45.4. ^o Danehy, Killian and Nieuwland, *THIS JOURNAL*, 58, 611 (1936). ^p New compound. *Anal.* Calcd. for C₉H₁₃Br: C, 53.2; H, 7.4; Br, 39.4. Found: C, 53.2; H, 7.3; Br, 39.4. ^q New compound. *Anal.* Calcd. for C₁₀H₁₅O: C, 77.9; H, 11.6. Found: C, 77.8; H, 11.4. ^r New compound. *Anal.* Calcd. for C₁₀H₁₇Br: C, 55.3; H, 7.8; Br, 36.9. Found: C, 55.5; H, 7.8; Br, 36.9. ^s Also a very weak band at 1700 cm.⁻¹. ^t Also a medium strong band at 1940 cm.⁻¹. ^u A thicker sample clearly shows this band.

TABLE II

LOCATION AND INTENSITY OF THE NEW BAND

Class	Cpd. nos.	cm. ⁻¹	Position		Intensity
			μ	μ	
Primary	R—C≡C—CH ₂ X	I-VI	1740-1700	5.75-5.88	vs to w
Secondary	R—C≡C—CHX—CH ₃	IX-XII	1700-1650	5.88-6.07	s to vw
Secondary	R—CHX—C≡C—H	XIII, XIV	1700-1650	5.88-6.07	s to vw
Tertiary	R—C≡C—CXCH ₃ —CH ₃	XV-XVIII	1630-1600	6.13-6.25	s to missing

of the compounds one cannot make up a suitable combination tone from among the observed frequencies. It must be granted that this is a weak argument because an unobserved frequency

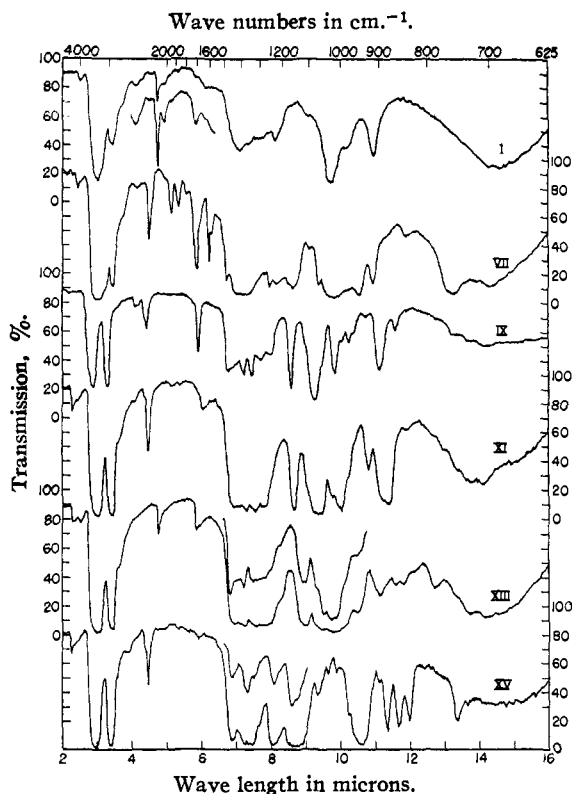


Fig. 1.—Propargylic alcohols: all cell thicknesses 0.05 mm. except VI (0.1 mm.) and IX (<0.05 mm.).

below 650 cm.^{-1} might be involved. Much more convincing is the fact that this band, in at least some of the compounds, is among the most intense bands in the spectrum and therefore cannot possibly be a combination tone (*cf.* IV, VI, VIII). Consequently we reject this explanation.

2. The Band May Be Due to an Impurity, Especially a Carbonyl-containing Impurity.

The following points argue against this suggestion. (a) The band is found in all but two of the compounds studied. It occurs in well-defined and different spectral regions for the primary, secondary and tertiary compounds. It is unlikely that an impurity would be so consistent in its behavior. (b) The analysis for carbon, hydrogen and bromine for all of the synthesized bromides gave values very close to theoretical, thus leaving no place for oxygen in the compound. (c) It was already noted¹ that bromide IV shows no evidence for the presence of aldehyde or ketone impurities in its ultraviolet spectrum. (d) The Raman spectrum of VI was measured. The 1740 cm.^{-1} infrared band is more intense in this compound than in any other studied. If this band actually is due to a carbonyl group, it would also be apparent in the Raman spectrum, since carbonyl bands are fairly intense in the Raman effect. Actually no Raman displacement is observed between 1430 and 2230 cm.^{-1} . This again suggests that it is not due to the $\text{C}=\text{O}$

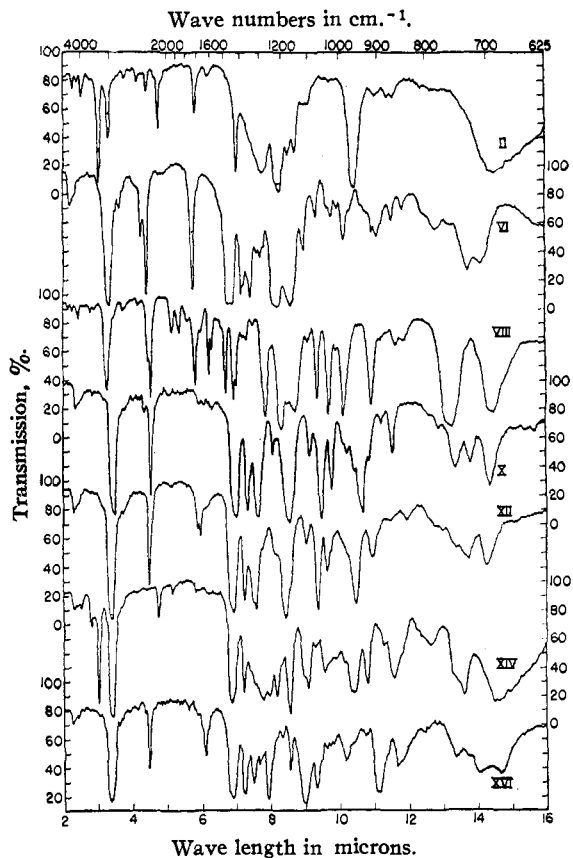


Fig. 2.—Propargylic bromides: all cell thicknesses 0.05 mm.

group. The Raman spectra of VII and VIII have been reported⁶ and again the band is absent. None of these reasons by itself proves that the band may not arise from some impurities, but together they are quite convincing.

(3) **The Band May Be to an Isomer.**—There is evidence⁷ that propargylic bromides yield mixtures of acetylenic and allenic products. This can be explained by assuming that the starting halide consisted of a mixture of $\text{R}-\text{C}\equiv\text{C}-\text{CH}_2\text{Br}$ and $\text{R}-\text{C}=\text{C}=\text{CH}_2$. The allenic group $\text{C}=\text{C}=\text{C}$ nor-

mally has a band at 1900 to 2000 cm.^{-1} . It is possible that the substitution of a bromine atom directly on the allenic group may lower the allenic band to 1750 – 1700 cm.^{-1} . This point cannot be checked until the spectra of some authentic bromoallenes is determined. In the case of the propargylic alcohols, one would also have to assume a mixture of isomers, as for example $\text{R}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ and $\text{R}-\text{C}=\text{C}=\text{CH}_2$. The later

substance is the enol form of the unsaturated

(6) Murray and Cleveland, *THIS JOURNAL*, **60**, 2664 (1938).

(7) Wotiz, *ibid.*, **72**, 1639 (1950); Hennion and Sheehan, *ibid.*, **71**, 1964 (1949).

ketone $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$. This structure could account for the band in propargylic alcohols, but offers no solution in the case of the bromides. This makes the explanation of the band in bromides essentially different from that in the alcohols, since it would be attributed to the allenic group in the bromides and to the ketone group in the "alcohols." This is unlikely in view of their similar behavior, and casts doubt on the postulate. (It is assumed that the enol form is far less prevalent than the keto form.)

4. **The Band May Be a Characteristic Fundamental Frequency of These Molecules or, More Precisely, of the Conventional Molecular Structures Written in Table I.**—This seems highly unlikely. The nearest fundamental on the high wave number side, the $\text{C}\equiv\text{C}$ band, is in its normal position. Similarly the nearest fundamental on the other side, the methylene deformational frequencies near 1450 cm.^{-1} (6.9μ), are in their normal position (see, for example $\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{Br}$, compound II). Consequently we reject this explanation.

None of these four explanations is convincing,

and we must conclude that we do not know why these compounds exhibit this band. It may be worth noting that there are other properties of these compounds which are also unusual and which have not been clearly understood. For example the carbon-halogen bond length has been shown to be surprisingly long in propargyl chloride, bromide and iodide by electron diffraction measurements.⁸ The ease with which propargylic alcohols can be rearranged into unsaturated aldehydes and ketones⁹ and the fact that propargylic bromides yield acetylenic and allenic products⁹ should also be kept in mind when the structure of propargylic compounds is considered.

Summary

Infrared spectra of eighteen propargylic halides and alcohols have been measured. Many of these spectra exhibit a band in the range of 1740 to 1600 cm.^{-1} which may be very intense. The reason for a band at this position is still not known.

(8) Pauling, Gordy and Saylor, *THIS JOURNAL*, **64**, 1753 (1942).

(9) For a recent review of the Meyer-Schuster rearrangement, see Hannon, Davis and Maloney, *ibid.*, **71**, 2813 (1949); MacGregor, *ibid.*, **70**, 3953 (1948); Chanley, *ibid.*, **70**, 244 (1948).

PITTSBURGH 13, PA.

RECEIVED APRIL 24, 1950

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA AND THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND]

A Spectroscopic Study of *cis*- and *trans*-Dibenzoylethylenes and Related Compounds

BY LESTER P. KUHN,¹ ROBERT E. LUTZ² AND CARL R. BAUER^{2,3}

It is the purpose of this paper to show how the spectra of various dibenzoylethylenes and related compounds are affected by geometrical isomerism and by the introduction of substituents, and to determine what spectral characteristics there are which can enable one to distinguish a more stable isomer from its less stable counterpart in various pairs of geometric isomers. The absorption spectra were obtained in the ultraviolet and the infrared.

The important resonance forms of the dibenzoylethylenes are shown as formulas A, B, C and D. For all of these resonance forms to contribute to the actual state of the molecule it is necessary that the molecule be planar. The relative stability of each member of a pair of isomers will depend largely upon the resonance energy of each isomer, the larger the resonance energy the more stable the molecule. The resonance energy of a molecule will be large when the energy of the various important resonance forms lie close together. Form A is of lower energy than the other forms and both electrostatic and steric factors can raise the energy of the other forms thus decreasing the resonance energy of the molecule.

(1) Aberdeen Proving Ground.

(2) University of Virginia.

(3) du Pont Company Research Fellow, 1949-1950.

In dibenzoylene ($\text{R} = \text{R}' = \text{H}$) the *trans* isomer would be expected to be more stable than the *cis*. Each oxygen atom is at the negative end of a dipole and tends to repel the other thus raising the energy of the B, C and D forms of the *cis* isomer where they are required to lie close together. Furthermore as shown in Fig. 1,⁴ the oxygen atoms of the *cis* isomer overlap thus interfering with the planarity of the molecule. Actually the *trans* isomer has been found to be more stable than the *cis*, since the *cis* is converted to *trans* catalytically by acid, base or iodine.⁵

In the case of methyl dibenzoylene ($\text{R} = \text{H}$, $\text{R}' = \text{methyl}$) the choice of the more stable isomer is not so obvious. The electrostatic factor favors the *trans* isomer because in the *cis* isomer, as in the case of the parent compound cited above, the oxygen atoms must lie close to each other. Inspection of Fig. 1 shows that the amount of overlap in each isomer is about the same; the methyl group overlaps the oxygen of the *trans* isomer to about the same extent as the oxygens of the *cis* isomer overlap each other, and the overlap of the methyl groups with the hydrogen

(4) For data on which drawing is based, cf. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(5) Lutz, *THIS JOURNAL*, **62**, 3423 (1930); (b) Conant and Lutz, *ibid.*, **45**, 1303 (1923); (c) Paal and Schülze, *Ber.*, **35**, 168 (1902).