able pair of bands was found so that there is no value for ΔH by the dilute solution method forthcoming for this molecule.

1,1,2-Trichloroethane.—The sample of trichloroethane used in this work was found to be different from that used in the previous investigation[3] in one important respect, namely, that one of the bands (at 547 cm.$^{-1}$), whose temperature dependence relative to the band at 524 cm.$^{-1}$ had been measured, was absent in the infrared spectra of the liquid and solid material. The other pair of bands (at 1050 and 1010 cm.$^{-1}$) was present, however, in the spectrum of the liquid and it was confirmed that they belonged to different species, since of the pair only the band at 1050 cm.$^{-1}$ is present in the spectrum of the solid trichloroethane. The temperature dependence of this pair of bands was measured in the liquid and the plot of log (ratio of peak heights) *vs.* $1/T$ is shown in Fig. 1; the value found for ΔH was approximately 0.1 cal. The infrared spectra of 1,1,2-trichloroethane in the liquid, solid and vapor state are given in Table I.

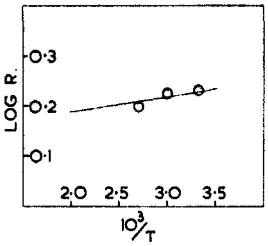

Fig. 1.

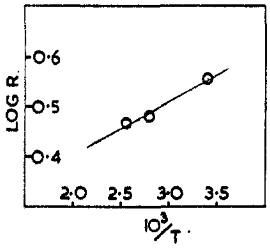

Fig. 2.

1,1,2,2-Tetrabromoethane.—No suitable pair of bands was found in the infrared spectrum of liquid tetrabromoethane. The spectrum of the liquid shows three bands at 636, 614 and 584 cm.$^{-1}$, respectively, whereas of these only the band at 614 cm.$^{-1}$ is present in the spectrum of the solid. The attempt to investigate the temperature dependence of the pair of bands at 614 and 584 cm.$^{-1}$ in the pure liquid and in solution proved unsatisfactory, owing to the large amount of overlap of the bands. The spectra of 1,1,2,2-tetrabromoethane in the liquid and solid states are given in Table II.

TABLE II

INFRARED SPECTRA OF 1,1,2,2-TETRABROMOETHANE (*cf.* TABLE I)

Liquid	Solid	Liquid	Solid
2986 (8)	2986 (9)	925 (0)	927 (0)
2430 (1)		895 (1)	903 (0)
2260 (2)	2264 (3)	828 (4)	831 (2)
1932 (1)	1938 (0)	788 (4)	794 (1)
1355 (1)	1358 (1)	761 (4)	766 (2)
1304 (1)	1310 (1)		748 (sh)
1275 (sh)		707 (9)	707 (8)
1240 (9)	1243 (9)	636 (6)	
1194 (6)	1198 (5)	614 (8)	614 (8)
1135 (10)	1135 (9)	584 (4)	
1073 (1)	1065 (0)		562 (1)
1006 (8)	1009 (6)	536 (4)	533 (8)
		449 (2)[a]	449 (3)

[a] 0.2 mm. cell.

1,1,2-Tribromoethane.—In the infrared spectrum of liquid tribromoethane there is a pair of bands at 1041 and 1000 cm.$^{-1}$, respectively, which belong to different isomeric forms, since again, of this pair, only the band at 1041 cm.$^{-1}$ is present in the spectrum of the solid tribromoethane. The temperature dependence of this pair of bands was measured in the liquid state, and the plot of log (ratio of peak heights) *vs.* $1/T$ is shown in Fig. 2; the value of ΔH for the liquid is approximately 0.5 cal. The infrared spectra of the 1,1,2-tribromoethane in the liquid and solid state are given in Table III.

Discussion

It is apparent that the latitude of error in the infrared methods for measuring the energy difference between the isomeric forms is wider than previously reported.[3] In making measurements on pure liquids the greatest difficulty is the correct positioning of the background, since the scattering in an empty cell is greater than in one containing liquid between the plates. Furthermore, the effect of temperature and solvent on the shapes of bands requires further investigation and work along these lines is in progress in this Laboratory. In the previous dilute solution technique,[3] the peak heights of bands have been taken as a measure of their concentrations and further investigation is in progress to determine whether this is adequate or not.

TABLE III

INFRARED SPECTRA OF 1,1,2-TRIBROMOETHANE (*cf.* TABLE I)

Liquid	Solid	Liquid	Solid
	3548 (1)	1142 (10)	1145 (8)
3021 (10)		1119 (9)	1124 (6)
3002 (9)		1041 (4)	1042 (4)
2960 (6)	2979 (3)		1022 (sh)
2924 (sh)		1000 (1)	
2821 (1)			895 (sh)
2773 (1)		879 (10)	880 (10)
2534 (0)			847 (0)
2484 (0)		812 (1)	812 (0)
2456 (0)		769 (0)	767 (0)
2420 (0)		752 (0)	
2290 (2)		720 (0)	
2094 (0)	2130 (sh)		695 (sh)
2073 (0)	2062 (0)	686 (8)	682 (5)
1413 (9)	1415 (5)		642 (sh)
1315 (sh)	1306 (0)	609 (8)	605 (8)
1269 (9)	1272 (10)	562 (8)	560 (8)
1258 (8)		525 (2)	547 (1)
	1245 (1)	479 (0)	
1213 (10)	1214 (10)	426 (1)	
1181 (9)		334 (3) 0.2 mm. cell	

In obtaining the infrared spectra of compounds in the solid state extreme care has to be taken to ensure that one has the true crystalline solid, rather than a glassy solid, the formation of which has been previously reported.[5,6] In many cases, especially for volatile liquids, the most satisfactory solids are obtained by condensation of the vapor in a Hornig-type cell,[6] and allowing the glassy solid to heat up slowly until it crystallizes.

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(5) J. K. Brown and N. Sheppard, *Discus. Farad. Soc.*, **9**, 144 (1950); *J. Chem. Phys.*, **19**, 976 (1951); F. E. Malherbe and H. J. Bernstein, *ibid.*, **19**, 1607 (1951).

(6) E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

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The Infrared Spectra of Some Allenic Compounds

BY JOHN H. WOTIZ AND WALTER D. CELMER

The characteristic allenic bond (C=C=C) absorption band is usually listed near 1970 cm.$^{-1}$.[1] This bond is of considerable analytical value as it is

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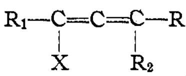
(1) R. B. Barnes, R. C. Gore and R. W. Stafford, *Anal. Chem.*, **20**, 402 (1948).

usually strong and occurs in a relatively unobscured infrared region. A number of new allenic compounds became available recently and the study of their spectra now reveals that the very strong allenic absorption band is near 1940 cm.$^{-1}$ and that it often splits into two strong bands near 1930 and 1950 cm.$^{-1}$, respectively. In Table I are listed the compounds studied and the position and intensities of the allenic absorption band(s). The upper curve in Fig. 1 is an example of a compound showing the doublet whereas the lower curve illustrates the single allenic absorption band.

With the exception of compounds I, VIII and XI the compounds studied are solids at room temperature. Their spectra were determined in carbon tetrachloride or nujol suspensions. It was observed that the doublet is especially noticeable when carbon tetrachloride was used as solvent, whereas it is not as apparent in nujol suspensions. We also found that compounds which often showed a broad band near 1940 cm.$^{-1}$ when studied with the Baird I. R. Spectrograph using a sodium chloride prism, showed a sharp doublet with a Perkin-Elmer instrument using a calcium fluoride prism. Thus we resolved the broad band near 1950 cm.$^{-1}$ of VIII in the recently published spectrum[2] into a doublet. We have also tried to determine the Raman spectrum of compound IV, but were unsuccessful due to absorption and (or) fluorescence in the region of 4358 Å.

TABLE I



$$R_1—\underset{X}{C}=C=\underset{R_2}{C}—R_3$$

Comp.	R_1	X	R_2	R_3	Synthesis reference	Allenic absorption band, cm.$^{-1}$ 1930	1940	1950
I	C_4H_9	H	H	H	*a*	−	++	−
II	H	CO_2H	H	H	*d*	+	−	+
III	C_3H_7	CO_2H	H	H	*b*	+	−	+
IV	C_4H_9	CO_2H	H	H	*b*	+	−	+
V	C_5H_{11}	CO_2H	H	H	*b*	+	−	+
VI	C_4H_9	CO_2H	H	CH_3	*c*	−	++	−
VII	C_4H_9	CO_2H	CH_3	CH_3	*c*	−	++	−
VIII	C_4H_9	CO_2CH_3	H	H	*b*	+	−	+
IX	C_3H_7	$CONH_2$	H	H	*b*	+	−	+
X	C_4H_9	$CONH_2$	H	H	*b*	+	−	+
XI	C_4H_9	CH_2OH	H	H	*e*	−	++	−

+ Strong. ++ Very strong. − Missing. [a] H. Wotiz, THIS JOURNAL, **73**, 693 (1951). [b] Reference 2. [c] J. H. Wotiz and R. J. Palchak, THIS JOURNAL, **73**, 1971 (1951). [d] J. H. Wotiz, J. S. Matthews and J. A. Lieb, *ibid.*, **73**, 5503 (1915). [e] J. H. Wotiz and P. Mosso, unpublished results.

On the basis of the above listed findings we now have available a convenient method for the identification of compounds containing a carboxy, an amide or an ester grouping directly attached to an allenic bond. Such compounds containing a terminal allenic linkage show a doublet whereas the allenic bond inside the chain shows a single absorption band. The reason for such spectroscopic behavior is not apparent to us. We anticipate that other negative groups (electron attracting) will influence the allenic absorption band in the same manner as the groups listed above.

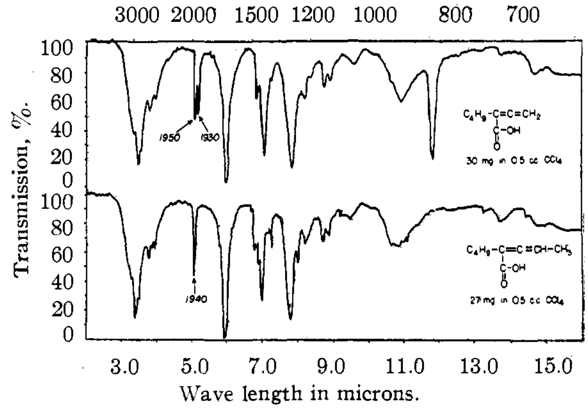


Fig. 1.

We wish to thank Dr. F. A. Miller and Mr. Robert Bauman of the Mellon Institute and Mr. G. B. Hess of Chas. Pfizer and Co. for the determination of the spectra used in this study.

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RECEIVED NOVEMBER 5, 1951

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[2] J. H. Wotiz, THIS JOURNAL, **72**, 1639 (1950)

The Reduction of Cyclohexanone Cyanohydrin by Lithium Aluminum Hydride

BY HAROLD R. NACE AND BILL B. SMITH[1]

RECEIVED NOVEMBER 12, 1951

The preparation of 1-aminomethyl-cyclohexanol by catalytic hydrogenation (Adams platinum) of cyclohexanone cyanohydrin has been reported by Tchoubar[2a,b] and Goldberg and Kirchensteiner.[2c] The hydrogenation was difficult to perform, and, consequently, unsatisfactory for the preparation of the aminoalcohol. Dauben, *et al.*,[3] developed a more convenient synthesis by reducing the corresponding nitroalcohol, 1-nitromethylcyclohexanol, to the aminoalcohol.

Difficulties with the hydrogenation of the cyanohydrin were also experienced in this Laboratory, and a second alternative synthesis, reduction of the cyanohydrin with lithium aluminum hydride, was developed.

Nystrom and Brown[4] reported the reduction of mandelonitrile (benzaldehyde cyanohydrin) in 48% yield using slightly more than one mole of hydride for two moles of cyanohydrin, and suggested that the use of a greater excess of hydride might improve the yield. Heusser, *et al.*,[5] reported the re-

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(1) Research Corporation Fellow, 1951–1952. This paper is based on a portion of the thesis to be submitted by Bill B. Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) (a) B. Tchoubar, *Compt. rend.*, **205**, 54 (1937). (b) B. Tchoubar, *Bull. soc. chim. France*, **216**, 160, 164, 169 (1949). (c) M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943).

(3) H. J. Dauben, H. J. Ringold, R. H. Wade and A. G. Anderson, THIS JOURNAL, **73**, 2359 (1951).

(4) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

(5) H. Heusser, P. th. Herzig, A. Fürst and Pl. A. Plattner, *Helv. Chim. Acta*, **33**, 1093 (1950).