Researches on Acetylenic Compounds. Part L. The Infrared Absorption of Some Conjugated Ethylenic and Acetylenic Systems.*

By J. L. H. Allan, G. D. Meakins, and M. C. Whiting.

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From the infrared spectra of various types of conjugated ethylenic and acetylenic compounds, correlations facilitating the recognition of these systems have been established. Study of the 1050—650 cm.$^{-1}$ region yielded more detailed information than that obtained from the higher frequency ranges. In many of the compounds investigated geometrical isomerism is possible: examination of both *cis-* and *trans*-isomers led to useful spectral distinctions between them.

Other correlations relate to acetylenic compounds in which the triple bond is conjugated with acid or ester groups, and to halides of the allylic and propargylic types.

Although much information about the infrared absorption of compounds containing isolated multiple bonds is available in the literature, conjugated systems have received less attention. Past studies have dealt mainly with higher frequency ranges (above 1500 cm.$^{-1}$), which contain the easily recognised stretching vibrations. While the results are useful in detecting conjugation they are not sufficiently sensitive to provide clear distinctions between closely related systems. Often the value of correlations established with systems capable of exhibiting geometrical isomerism has been reduced by examination of only some of the possible isomers.

The substances listed in Table 1 were therefore synthesised (preceding paper), rigorously purified, and examined under similar conditions: they represent a complete set of variations on two related structural themes. Correlations deduced from these results were supported by data from a wider range of compounds shown in Tables 2 and 3. In a separate study the spectra of allylic and progargylic halides (Table 4) were investigated.

Spectroscopic Work and Explanation of Tables 1—4.—Although the compounds in Table 1 were examined fairly recently, the remaining spectra were obtained during the last three years. This wide separation in time, and the fact that the main function of each determination was to facilitate contemporaneous research, account for the diversity of conditions used.

The spectra were recorded on a Perkin-Elmer model 21 double-beam spectrometer fitted with a sodium chloride prism. The condition specified at the heads of the columns of the Tables is that pertaining to the majority of cases for a particular band. Exceptions are indicated by the superscripts: * = Nujol, † = CCl_4, ‡ = CS_2, § = liquid, || = melt.

Where possible quantitative intensity values are given. These data are apparent extinction coefficients (ε) calculated in the usual way (Henbest, Meakins, and Wood, *J.*, 1954, 800). [With some of the bands, maximal absorption was not within the range (*ca.* 40—70%) generally considered most suitable for quantitative treatment. Thus in extreme cases the intensity values may be in error by factors as large as 1·5.] Elsewhere the usual terms (s = strong, m = medium, w = weak) are used. The two systems are connected by the approximate relations: w = ε, 35—70; m = ε, 70—150; s = $\varepsilon > 150$.

Frequencies are in cm.$^{-1}$, and the maximal errors, for sharp bands, are estimated as ±15, ±8, and ±5 cm.$^{-1}$ at 2300, 1700, and 900 cm.$^{-1}$, respectively. In the Tables the frequency of a band is followed by an intensity description.

Under the conditions used, the acids existed wholly *§|| or mainly †‡ in the dimeric form, and the bands quoted refer to this state. With solutions, weaker bands due to the monomers (*e.g.* C=O stretching ~1750 cm.$^{-1}$) were observed, but these have not been listed.

The meanings of other terms used are: sh = shoulder on a neighbouring (main) band,

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* Part XLIX, preceding paper.

— = no appreciable band ($\varepsilon > 40$) in the frequency range indicated, ni = frequency range not investigated, [ ] = " accidental band," *i.e.*, that a band does occur in the frequency range, but that it is not considered to be due to the vibration specified at the head of the column, ? = assignment indicated is doubtful, *c* and *t* = *cis* and *trans*, respectively.

The references in the Tables are :

a, unpublished work from these laboratories. b, Bates, Jones, and Whiting, *J.*, 1954, 1854. c, Nayler and Whiting, *J.*, in the press. d, Kuhn and Grundmann, *Ber.*, 1936, **69**, 1757. e, Nayler and Whiting, *J.*, 1954, 4006. f, Nayler, Jones, and Whiting, forthcoming publication. g, Allan and Whiting, *J.*, 1953, 3314. h, Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583. i, Preceding paper. j, Shaw and Whiting, *J.*, 1954, 3217. k, Marshall and Whiting, forthcoming publication. l, Heilbron, Sondheimer, and Jones, *J.*, 1947, 1586. m, Jones, Shaw, and Whiting, *J.*, 1954, 3212. n, Favorski and Sakara, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 43. o, Jones and Whiting, *J.*, 1949, 1423. p, Jones, Mansfield, and Whiting, *J.*, 1954, 3208. q, Jones, Thompson, and Whiting, forthcoming publication. r, Bu'Lock, Jones, Mansfield, Thompson, and Whiting, *Chem. and Ind.*, 1954, 990. s, Johnson, *J.*, 1946, 1009. t, Cook, Jones, and Whiting, *J.*, 1952, 2883.

$C\equiv C$ *Stretching.*—In unconjugated acetylenes this vibration gives weak bands in the 2300—2100 cm.$^{-1}$ region (Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441; Wotiz, Miller, and Palchak, *ibid.*, 1950, **72**, 5055). Conjugation with olefinic, or other acetylenic, bonds causes some intensification and (usually) a decrease in frequency, but these changes are much smaller than those observed in the $C=C$ stretching band of conjugated olefins (see, *inter al.*, Sheppard, *J. Chem. Phys.*, 1949, **17**, 74; Celmer and Solomons, *J. Amer. Chem. Soc.*, 1952, **74**, 3838; 1953, **75**, 1372, 3430, for $C\equiv C$ stretching : Blout, Fields, and Karplus, *ibid.*, 1948, **70**, 194, for $C=C$ stretching). Thus, it appears that a hydrocarbon must contain four triple bonds in conjugation to give an appreciable $C\equiv C$ stretching band {cf. $Me{\cdot}[C\equiv C]_3{\cdot}Me$, 2222 w, and $Me{\cdot}[C\equiv C]_4{\cdot}Me$, 2237 m (Cook, Jones, and Whiting, *J.*, 1952, 2883)}.

There does not appear to have been any systematic study of the effect of conjugation with carboxy- or methoxycarbonyl groups. The data in Tables 1 and 3 show that such conjugation causes the expected, marked intensification of the $C\equiv C$ stretching absorption. The results can be summarised : $C\equiv C$ stretching in ${\cdot}[C\equiv C]_n{\cdot}CO_2R$; R = H or Me, $n = 1$, medium band 2260—2235 cm.$^{-1}$, $n = 2$ or 3, strong band(s) 2270—2200 cm.$^{-1}$.

For $n = 1$ the frequency range is small; the exception (compound 70) would be expected to absorb at lower frequency. In the cases with $n = 2$ or 3 the band is split into two components (compounds 23, 24, and 81—87) presumably by mechanical coupling among the vibrations of the triple bonds. The higher-frequency band is generally the more intense in solution spectra, but we have often observed a reversal of this relation when using solid films or Nujol suspensions. It is remarkable that the frequency ranges are, in both cases, above rather than below the position (*ca.* 2200 cm.$^{-1}$) associated with the unconjugated disubstituted acetylenes.

Comparison of compounds 13—16 with 17—20 shows that the $C\equiv C$ band is weaker in the former group, apparently because the usual polarising influence of the CO_2R residue is here attenuated by the interposition of an ethylenic linkage. In compounds 72 and 73 the triple-bond vibration is centrosymmetric, and is therefore inactive in the infra-red.

$C=O$ *Stretching.*—The figures (Tables 1 and 3), which must be considered separately for acids and esters, illustrate the shift of the band to lower frequency when one $C=C$ or $C\equiv C$ is in conjugation with CO_2R. (The frequencies of corresponding saturated acids and esters are about 1710 and 1740 cm.$^{-1}$, respectively.) There is an indication that a slightly greater decrease in frequency of the $C=O$ stretching is produced by a conjugated triple bond than by a double bond. In other series it is known that as the conjugation is extended the addition of each *olefinic* bond makes progressively less difference to the $C=O$ frequency (Blout *et al.*, *loc. cit.*; R. N. Jones and Dobriner, *Vitamins and Hormones*, 1949, **7**, 293). With the conjugated acetylenic compounds the esters containing one or two triple bonds (nos. 21, 23, 66, 70, 74, 76, 78, and 81) have values close to 1717 cm.$^{-1}$, but when three such bonds are involved (84 and 87) a higher frequency, $\sim$1722 cm.$^{-1}$, is observed. Thus, extending the *acetylenic* conjugation causes first a drop, then a rise in frequency. An explanation of these differences is found by considering the p*K* values of the acids in the

TABLE 1. *Conjugated esters and acids.*

No.		C≡C stretching (CCl_4)		C=O stretching, esters (CS_2)	C=O stretching, acids (CCl_4)	C=C stretching (CCl_4)		Olefinic CH out-of-plane bending (CS_2)					C≡C·CO_2R (CS_2)
								trans			*cis*		
1	$Me\cdot CH\overset{t}{=}CH\cdot CO_2Me$	—	—	1726(850)	—	1659(180)	—	969(220)	—	—	—	—	—
2	$Me\cdot CH\overset{t}{=}CH\cdot CO_2H$	—	—	—	1694(750)	1651(250) ‡	—	970(350)	—	—	—	[695(55)]	—
3	$Me\cdot CH\overset{c}{=}CH\cdot CO_2Me$	—	—	1721(800)	—	1644(120)	—	—	—	—	812(160)	—	—
4	$Me\cdot CH\overset{c}{=}CH\cdot CO_2H$	—	—	—	1692(700) ‡	1639(250) ‡	—	—	—	—	818(130)	—	—
5	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2Me$	—	—	1716(850)	—	1642(200)	1614(100)	995(350)	943(60)	—	—	—	—
6	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	—	—	—	1702 s *	1639 s *	1613 s *	998 s *	945 w *	—	—	[697 m] *	—
7	$Me\cdot CH\overset{c}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2Me$	—	—	1715(800)	—	1634(200)	1598 m	990(150)	951(50)	936(30)	—	?687(100)	—
8	$Me\cdot CH\overset{c}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	—	—	—	1683(1100)	1627(230)	1601(140)	990(170)	949(100)	—	—	?683(110)	—
9	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2Me$	—	—	1715(700)	—	1639(200)	1597 m	996(200)	958(140)	938(100)	832(180)	—	—
10	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2H$	—	—	—	1687(450)	1636(200)	1600 m	996(200)	958(300)	—	837(170)	—	—
11	$Me\cdot CH\overset{c}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2Me$	—	—	1715(650)	—	1623(200)	1587 m	—	—	—	821(180)	?662(130)	—
12	$Me\cdot CH\overset{c}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2H$	—	—	—	1691s ‖	1620 s ‖	1598 m ‖	—	—	—	829(160)	?662(150)	—
13	$Me\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CO_2Me$	2270(70)	—	1719(850)	—	1615(200)	—	959(200)	—	—	—	—	—
14	$Me\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CO_2H$	2270(70)	—	—	1685 s	1619 s	—	959(400)	—	—	—	[660(80)]	—
15	$Me\cdot C{\equiv}C\cdot CH\overset{c}{\underset{c}{=}}CH\cdot CO_2Me$	2229(80)	—	1733(450) 1718(250)	—	1612(200)	—	—	—	—	812(200)	—	—
16	$Me\cdot C{\equiv}C\cdot CH{=}CH\cdot CO_2H$	2224(70)	—	—	1702(450)	1609(220)	—	—	—	—	819(160)	—	—
17	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CO_2Me$	2221(140)	—	1708(550)	—	1626(40)	—	948(250)	—	—	—	—	746(160)
18	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CO_2H$	2224 w *	2190 s *	—	1667 s *	1618 w *	—	951 m *	—	—	—	—	756 m *
19	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot CO_2Me$	2224(170)	—	1713(500)	—	1615(30)	—	—	—	—	721(120)	—	745(140)
20	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot CO_2H$	2219(220)	—	—	1692(450)	1615(45)	—	—	—	—	720(150)	[662(160)]	757(60)
21	$Me\cdot C{\equiv}C\cdot CO_2Me$	2242(150)	—	1718(600)	—	—	—	—	—	—	—	—	748(100)
22	$Me\cdot C{\equiv}C\cdot CO_2H$	2246(200)	2140(20)	—	1684(750) ‡	—	—	—	—	—	—	—	750(70)
23	$Me\cdot C{\equiv}C\cdot C{\equiv}C\cdot CO_2Me$	2260(400)	2190(80)	1716(850)	—	—	—	—	—	—	—	—	740(160)
24	$Me\cdot C{\equiv}C\cdot C{\equiv}C\cdot CO_2H$	2270(450)	2180(80)	—	1688(800) ‡	—	—	—	—	—	—	[700(95)]	742(80)

TABLE 2. *Miscellaneous ethylenic compounds.*

No.		Olefinic CH out-of-plane bending (CS_2) *trans*			*cis*	$C{\equiv}C\cdot CO_2R$ (CS_2)	Refs.
25	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CH_2\cdot OH$	985(270)	—	928(50)	—	—	
26	$HO\cdot CH_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CH_2\cdot OH$	993 s §	958 w §	—	—	—	b
27	$Me\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CH(OH)\cdot CHMe\cdot OH$	988 s §	—	—	—	—	c
28	$HO_2C\cdot CH_2\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CH_2\cdot CO_2H$	989 s *	937 m *	—	—	—	d
29	$[CH_2]_5{>}C(OH)\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot C(OH){<}[CH_2]_5$	990 s §	958 m §	—	—	—	b
30	$Me\cdot[CH{=}CH]_2\cdot CH(OH)\cdot C{\equiv}C\cdot CH(OH)\cdot[CH{=}CH]_3\cdot Me$ (all *trans*)	993 s *	—	923 m *	—	—	c
31	$\{Me\cdot[CH{=}CH]_5\cdot CH(OH)\cdot C{\equiv}\}_2$ (all *trans*)	1006 s *	964 m *	925 w *	—	—	c
32	$CH_2{=}CMe\cdot CH\overset{t}{=}CH\cdot CH{=}CMe\cdot CH{=}CH_2$	—	959 s §	—	—	—	e
33	$CH_2{=}CMe\cdot CH\overset{t}{=}CH\cdot CMe{=}CH_2$	—	959 s §	—	—	—	f
34	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}CH$	—	956(140)	—	—	—	g
35	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}CH$	—	[958(50)]	—	723(115)	—	g
36	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot CH\overset{t}{=}CHMe$	—	945(300)	—	—	—	a
37	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot C{\equiv}C\cdot CH\overset{c}{=}CHMe$	—	—	—	716(320)	—	a
38	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CH_2\cdot OH$	—	953(130)	—	—	—	a
39	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot CH_2\cdot OH$	—	—	—	718(150)	—	a
40	$HO\cdot CH_2\cdot CH_2\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CH_2\cdot CH_2\cdot OH$	—	957 s §	—	—	—	a
41	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CH_2Cl$	—	951(190)	—	—	—	a
42	$Me\cdot CH\overset{c}{=}CH\cdot C{\equiv}C\cdot CH_2Cl$	—	—	—	717(160)	—	a
43	$Me\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CH_2\cdot CO_2H$	—	950(170)	—	—	—	a
44	$HC{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH_2\cdot OH$	—	952(130)	—	—	—	h
45	$HC{\equiv}C\cdot CH\overset{t}{=}CH\cdot CHMe\cdot OH$	—	956(145)	—	—	—	a
46	$HC{\equiv}C\cdot CH\overset{c}{=}CH\cdot CHMe\cdot OH$	—	—	—	756(65)	—	a
47	$Me\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2\cdot OH$ (mainly *trans*)	—	953(130)	—	—	—	i
48	$HC{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH_2Cl$	—	950(150)	—	—	—	a
49	$Me\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2Cl$ (*cis-trans* mixture)	—	950(140)	—	764(25)	—	a
50	$Bu^n\cdot C{\equiv}C\cdot CH{=}CH\cdot CH_2Cl$ (mainly *trans*)	—	952(120)	—	—	—	a
51	$HC{\equiv}C\cdot CH\overset{t}{=}CH\cdot CHMeCl$	—	948(175)	—	—	—	a
52	$HC{\equiv}C\cdot CH\overset{c}{=}CH\cdot CHMeCl$	—	[948(20)]	—	759(125)	—	a
53	$HO\cdot CPh_2\cdot CH\overset{t}{=}CH\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CPh_2\cdot OH$	—	958 ms §	—	ni	ni	b
54	$(Me\cdot[CH{=}CH]_2\cdot C{\equiv})_2$ (all *trans*)	978 s †	—	930 m †	ni	ni	a
55	$Ph\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	1004 s *	—	—	—	—	
56	$MeO_2C\cdot[CH{=}CH]_4\cdot CO_2Me$ (all *trans*)	1022 s *	—	—	—	—	j
57	p-$MeO\cdot C_6H_4\cdot[CH{=}CH]_3\cdot CO_2Me$ (all *trans*)	1005 s *	—	—	—	—	k
58	p-$MeO\cdot C_6H_4\cdot[CH{=}CH]_5\cdot CO_2Me$ (all *trans*)	1010 s *	—	—	—	—	k
59	p-$MeO\cdot C_6H_4\cdot[CH{=}CH]_7\cdot CO_2Me$ (all *trans*)	1014 s *	—	—	—	—	k
60	$HC{\equiv}C\cdot CH\overset{t}{=}CH\cdot CO_2H$	—	958 s	—	[685 m]	—	e
61	$MeO_2C\cdot[C{\equiv}C]_2\cdot CH\overset{t}{=}CH\cdot CO_2Me$	—	956(290)	—	[710(55)]	742(50)	m
62	$MeO_2C\cdot[C{\equiv}C]_2\cdot CH\overset{t}{=}CH\cdot CO_2H$	—	958(120) †	—	ni	ni	m
63	$MeO_2C\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2Me$	991 s	940 w	—	—	742 m	m
64	$HO_2C\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH\overset{t}{=}CH\cdot CO_2H$	1000 s *	950 w *	—	—	747 m ‖	m
65	$MeO_2C\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH\overset{c}{=}CH\cdot CO_2Me$	990 s	955 w	—	822 m	745 m	m

TABLE 3. *Conjugated acetylenic esters and acids.*

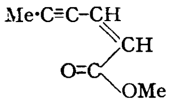
No.		$C\equiv C$ stretching (CCl_4)			$C=O$ stretching (CCl_4) esters	acids	$C\equiv C\cdot CO_2R$ (CS_2)	Refs.
66	$HC\equiv C\cdot CO_2Me$	ni	—	—	1719 s ‡	—	750(150)	
67	$Et\cdot C\equiv C\cdot CO_2H$	2258 m	—	—	—	1690 s	ni	
68	$Bu^t\cdot CH_2\cdot C\equiv C\cdot CO_2H$	2250 m ‡	—	—	—	1685 s ‡	751(60)	n
69	$Ph\cdot CH_2\cdot CH_2\cdot C\equiv C\cdot CO_2H$	2250 m	—	—	—	1693 s	ni	a
70	$[CH_2]_5{>}C(OH)\cdot C\equiv C\cdot CO_2Me$	2208 m ‡	—	—	1715 s	—	747(120)	o
71	$HO_2C\cdot CH_2\cdot CH_2\cdot C\equiv C\cdot CO_2H$	2250 m *	—	—	—	1695 s •	744 w *	p
72	$MeO_2C\cdot C\equiv C\cdot CO_2Me$	—	—	—	1722 s §	—	749 m §	
73	$HO_2C\cdot C\equiv C\cdot CO_2H$	—	—	—	—	1700 s *	745 m *	
74	$HC\equiv C\cdot CH_2\cdot CH_2\cdot C\equiv C\cdot CO_2Me$	2242(135)	—	—	1715 s	—	ni	j
75	$HC\equiv C\cdot CH_2\cdot CH_2\cdot C\equiv C\cdot CO_2H$	2248(190)	2215 Sh	—	—	1693 s	ni	j
76	$(MeO_2C\cdot C\equiv C\cdot CH_2\cdot)_2$	2252(185)	—	—	1717 s	—	ni	m
77	$(HO_2C\cdot C\equiv C\cdot CH_2\cdot)_2$	2245 s •	—	—	—	1680 s •	750 m *	m
78	$(MeO_2C\cdot C\equiv C\cdot CH_2\cdot CH_2)_2$	2242(220)	—	—	1717 s	—	ni	m
79	$(HO_2C\cdot C\equiv C\cdot CH_2\cdot CH_2)_2$	2236 s *	—	—	—	1680 s •	752 m *	m
80	$Ph\cdot C\equiv C\cdot CO_2Me$	ni	—	—	ni	—	747 Sh (on 755 Ph)	
81	$Et\cdot[C\equiv C]_2\cdot CO_2Me$	2243 s §	2187 Sh §	2160 m §	1717 s §	—	745 m §	q
82	$Et\cdot[C\equiv C]_2\cdot CO_2H$	2240 s *	2195 Sh *	2160 m •	—	1680 s *	743 m *	q
83	$Bu^n\cdot[C\equiv C]_2\cdot CO_2H$	2252 s	2170 m	—	—	1693 s	742(55)	q
84	$Me\cdot[C\equiv C]_3\cdot CO_2Me$	2210 s	2125 m	—	1721 s	—	740(135)	r
85	$Me\cdot[C\equiv C]_3\cdot CO_2H$	2210 s	2135 w	—	—	1694 s	ni	r
86	$Et\cdot[C\equiv C]_3\cdot CO_2H$	2200 s	2130 m	—	—	1684 s	ni	q
87	$HO\cdot CH_2\cdot[C\equiv C]_3\cdot CO_2Me$	2220 s	2133 w	—	1724 s	—	ni	r

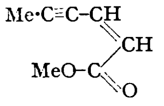
TABLE 4. *Allylic and propargylic halides.*

No.		$C=C\cdot C\cdot Hal$ and $C\equiv C\cdot C\cdot Hal$ (CS_2)					Refs.
48	$HC\equiv C\cdot CH=CH\cdot CH_2Cl$	1244(75)	—	—	691(75)	—	a
49	$Me\cdot C\equiv C\cdot CH=CH\cdot CH_2Cl$ (*cis-trans* mixture)	1246(80)	—	—	681(70)	—	a
50	$Bu^n\cdot C\equiv C\cdot CH=CH\cdot CH_2Cl$ (mainly *trans*)	1250(60)	1244(75)	—	680(60)	—	a
41	$Me\cdot CH\overset{t}{=}CH\cdot C\equiv C\cdot CH_2Cl$	1260(200)	—	—	693(200)	—	a
42	$Me\cdot CH\overset{c}{=}CH\cdot C\equiv C\cdot CH_2Cl$	1260(200)	—	—	693(200)	—	a
88	$Me\cdot C\equiv C\cdot CH_2Cl$	1260(140)	—	—	702(75)	688(90)	
89	$ClCH_2\cdot C\equiv C\cdot CH_2Cl$	1262 s §	—	—	699 s §	—	s
90	$Me\cdot CHCl\cdot[C\equiv C]_2\cdot CH_2Cl$	1269 s §	1243 s §	1220 s §	700 s	—	q
91	$Et\cdot CHCl\cdot[C\equiv C]_2\cdot CH_2Cl$	1267 s §	1256 s §	—	700 s §	—	q
92	$ClCH_2\cdot[C\equiv C]_2\cdot CH_2Cl$	1254 s §	—	—	699 s §	—	t
93	$ClCH_2\cdot[C\equiv C]_4\cdot CH_2Cl$	1261 s	—	—	721 m	703 m	t
94	$Me\cdot C\equiv C\cdot CH_2Br$	1221 s §	1211 s §	—	—	—	
95	$Bu^n\cdot C\equiv C\cdot CHMeBr$	1184(145)	—	—	—	—	a
96	$Me\cdot C\equiv C\cdot CH_2I$	1180 s §	1146 s §	—	—	—	
97	$Bu^n\cdot C\equiv C\cdot CH_2I$	1172 s §	1143 s §	—	—	—	

two series. In the olefinic compounds the pK value is not appreciably affected by conjugation, and this factor is not involved in determining the C=O values. However, the strength of the acetylenic acids increases with the number of conjugated triple bonds (Jones, Mansfield, and Whiting, forthcoming publication). This would indicate increased bond order of the C=O in the acids, and presumably a similar effect operates in the derived esters. Some analogy is found in the relations between pK and the OH and CO stretching frequencies of acids (Goulden, *Spectrochim. Acta*, 1954, **6**, 129; Flett, *Trans. Faraday Soc.*, 1948, **44**, 767).

The intensity of the C=O band in the esters (Table 1) varies slightly with the nature of the unsaturated bond, diminishing in the order *trans* > *cis* > acetylenic. Compound 15 is most unusual in that the spectrum of its solution shows two C=O bands. The occurrence of two stretching bands from one C=O group implies the existence of two different " states " for the C=O group. Such states generally arise through differences in the type or degree of hydrogen bonding operating in them (R. N. Jones, Humphries, Herling, and Dobriner. *J. Amer. Chem. Soc.*, 1952, **74**, 2820), and doubling in the spectra of solid materials is quite common (see, *e.g.*, Zürcher, Heusser, Jeger, and Geistlich, *Helv. Chim. Acta*, 1954, **37**, 1562). A second cause is exemplified with 2-bromo*cyclo*hexanone (Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2301), where the two states are those having different conformations of the bromine atom. The extent of dipolar interaction differs in the two, with consequential separation of the $\mathrm{C{=}O}$ frequencies. An explanation along these lines can be employed with compound 15, the two forms being the rotational isomers (I) and (II). In the absence of dipolar interaction the frequency separation of the $\mathrm{C{=}O}$ bands of (I) and (II) would be small (cf. Short, *J.*, 1952, 206). However, the $\mathrm{C{-}C{\equiv}C}$ and $\mathrm{C{=}O}$ dipoles will be almost parallel, and nearly perpendicular, to each other in (I) and (II) respectively. Thus the large frequency separation, 15 cm.$^{-1}$, might reasonably be expected.*


(I)


(II)

$\mathrm{C{=}C}$ *Stretching.*—The spectra of compounds 1—20 show the expected numbers of $\mathrm{C{=}C}$ bands, two in nos. 5—12, one in the rest. The operation of a geometric effect is apparent (see, *inter al.*, Sinclair, McKay, Myers, and R. N. Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2578). The conversion of either the $\alpha\beta$- or the $\gamma\delta$-ethylenic bond from *trans* into *cis* causes a shift of the band to lower frequency. Thus, the stereochemistry influences the *intensity* of the $\mathrm{C{=}O}$ stretching band, and the *frequency* of the $\mathrm{C{=}C}$ stretching band : no such regularities are found in the complementary properties.

Compounds 17—20 absorb strongly in this region, whereas 13—16 have only weak bands : this is the converse of their behaviour in the $\mathrm{C{\equiv}C}$ range. The relative intensities of the $\mathrm{C{=}C}$ and $\mathrm{C{\equiv}C}$ bands clearly indicate which linkage is adjacent to the $\mathrm{CO_2R}$ group.

Olefinic C–H *Out-of-plane Bending.*—While the 1 : 2-disubstituted *trans*-olefinic system

TABLE 5. *Out-of-plane bending frequencies of conjugated* trans- *and* cis-*bonds.*

	trans	Refs.	*cis*		Refs.
(CH=CH	965 s	u	$\mathrm{CH\overset{c}{=}CH}$	~700 m, variable	u, v
$\mathrm{CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CH}$	990 s	w, x, ii	—	—	
*$\mathrm{CH\overset{t}{=}CH{\cdot}CH\overset{c}{=}CH}$	985 s, 950 m	w, y	—	—	
$\mathrm{CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CH}$	997 s	x, z, cc, ii	—	—	
$\mathrm{CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CH{\cdot}CH\overset{c}{=}CH}$	990 s, 965 m	x, z, cc	—	—	
$\mathrm{[CH\overset{t}{=}CH]}_n(n>3)$	increases with *n* ; upper limit ~1000 s	x, aa, ii	—	—	
$\mathrm{CH\overset{t}{=}CH{\cdot}CO{\cdot}X}$ (X = OH, OR, NHR)	980 s	bb, dd, ee, ff, ii	$\mathrm{CH\overset{c}{=}CH{\cdot}CO{\cdot}X}$ (X = (OH, OR, NHR)	820 s	bb, dd, ii
$\mathrm{CH\overset{t}{=}CH{\cdot}C{\equiv}C}$	950 s	w, gg, hh, ii	$\mathrm{CH\overset{c}{=}CH{\cdot}C{\equiv}C}$	720 s	ii

* Ref. w gives a third band (1020) for this system. It is probable, however, that this band is associated with the ester group present in the compounds studied (cf. Sinclair, McKay, and R. N. Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570).

u, Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1. v, Henbest *et al.*, *loc. cit.* w, Celmer *et al.*, *locc. cit.* x, Ahlers, Brett, and McTaggart, *J. Appl. Chem.*, 1953, **3**, 433. y, Jackson, Paschke, Tolberg, Boyd, and Wheeler, *J. Amer. Oil Chem. Soc.*, 1952, **29**, 229. z, Bickford, Du Pré, Mack, and O'Connor, *ibid.*, 1953, **30**, 376. aa, Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1949, **71**, 1396. bb, Crombie, *J.*, 1952, 2997, 4338. cc, Crombie and Taylor, *J.*, 1954, 2816. dd, Sinclair *et al.*, *loc. cit.*, p. 2578. ee, Kitson, *Analyt. Chem.*, 1953, **25**, 1470. ff, Freeman, *J. Amer. Chem. Soc.*, 1953, **75**, 1859. gg, Ahlers and Ligthelm, *J.*, 1952, 5039. hh, Gunstone and McGee, *Chem. and Ind.*, 1954, 1112. ii, this paper.

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* Since this paper was prepared, it has been possible, through the courtesy of Professor N. A. Sörensen, to examine the infrared spectra of the naturally-occurring methyl deca-*cis*-2-ene-4 : 6-diynoate and methyl deca-*cis*-2 : 8-diene-4 : 6-diynoate. Both show double carbonyl bands at 1730 and 1717 cm.$^{-1}$ which are evidently characteristic of the grouping *cis*-$\mathrm{R{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2Me}$. Both also absorbed strongly at 813 cm.$^{-1}$ (*cis*-$\mathrm{CH{=}CH{\cdot}CO_2Me}$), and the latter only showed a strong band at 713 cm.$^{-1}$ (*cis*-$\mathrm{Me{\cdot}CH{=}CH{\cdot}C{\equiv}C}$).

can be readily detected by the out-of-plane bending vibration, use of the corresponding band for the *cis*-bond has been regarded as less satisfactory (Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 42). The frequency of the *cis*-band is certainly more variable than that of the *trans* (Henbest *et al.*, *loc. cit.*), but this variability should actually enhance its value once the necessary correlations have been established.

The information available about the bands of conjugated ethylenic bonds is summarised in Table 5. Average frequencies, rather than frequency ranges, are given in view of the small numbers of examples of each type. [A few representatives of other systems, *e.g.*, the *cis-cis-trans*-conjugated trienes (Ahlers and Dennison, *Chem. and Ind.*, 1954, **603**; Ahlers, Dennison and O'Neill, *Nature*, 1954, **173**, 1045) have been studied, but no generalisations are possible in these cases.]

Strong bands at 820 cm.$^{-1}$ (Table 1) are characteristic of the *cis*-CH=CH·CO·X system, and are of obvious diagnostic value. The tentative correlations by Sinclair *et al.* (*loc. cit.*) and by Crombie (*locc. cit.*) are thus confirmed. (The presence of this band was used in assigning the bond configurations in compound 65.) The shift (*ca.* 100 cm.$^{-1}$) in passing from simple *cis*-olefins to conjugated *cis*-olefinic acids and their derivatives is much bigger than that (*ca.* 15 cm.$^{-1}$) found with *trans*-systems. A comparable shift (*ca.* 60 cm.$^{-1}$) was, however, observed by Freeman (*loc. cit.*) in the α-methylidene acids.

Conjugation of the *trans*-CH=CH bond with a CO·X group increases the bending frequency. Compounds 1 and 2, the simplest members of the series, show a smaller shift than is usual. Conjugation with other *trans*-bonds or with vinyl groups (Rasmussen and Brattain, *J. Chem. Phys.*, 1947, **15**, 131; refs. w, x, and aa of Table 5) also increases the frequency of this band. Conjugation with tri- or tetra-substituted olefinic bonds (Inhoffen, Brückner, Gründel, and Quinkert, *Ber.*, 1954, **87**, 1407) or with CH_2=CMe· and ·CH=CMe groupings (compounds 32 and 33) produces a small displacement to *lower* frequency.

Acetylenic conjugation moves the *trans*-band to lower frequency (compounds 34, 36, 38, 40, 41, 43, and 54). The compounds containing the *cis*-Me·CH=CH·C≡C· unit absorb fairly consistently at 720 cm.$^{-1}$ (compounds 35, 37, 39, and 42). The stability of the *trans*-band towards α-substitution (·C≡C·CH=CH·CX, X = Cl or OH; compounds 44, 45, and 47—51) contrasts with the behaviour of the *cis*-band (nos. 46, 49, and 52) in which a displacement to higher frequency is produced (cf. Hatch and Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72**, 727; Mislow and Hellman, *ibid.*, 1951, **73**, 244).

In the remaining compounds of Table 2, and in compounds 5—20 of Table 1, the conjugated system contains at least three multiple bonds. Two effects will influence the bending frequencies, and the results are interpreted in terms of the tendencies already discussed. In some cases the effects will act in the same direction: thus in compound 5 (Table 1) the system *trans-trans*-C=C·C=C·CO_2Me is regarded as *trans-trans*-C=C·C=C plus *trans*-C=C·CO_2Me, and the observed value (995) accords well with shifts to higher frequency of both the diene and ester components. With other systems (*e.g.*, compound **60**; *trans*-C≡C·C=C·CO_2Me divided into *trans*-C≡C·C=C and *trans*-C=C·CO_2Me) the factors are opposed, and the net effect is small. In related pairs of acids and esters (*e.g.*, 1 and 2, 13 and 14) the former usually have the stronger *trans*-band. This is caused by the contribution at the ethylenic frequency of the acidic hydroxyl out-of-plane bending vibration (a broad band centred around 930 cm.$^{-1}$).

It was not possible to identify the bending bands of the γδ-*cis*-bonds in compounds 7, 8, 11, and 12. Tentative assignments are given in Table 1, but their value is somewhat decreased by the occurrence of similar bands in the spectra of some of the acids lacking a *cis*-bond.

Band Characteristic of C≡C·CO_2R (R = H, Me).—These compounds are listed in Tables 3, 1 (nos. 17—24), and 2 (nos. 62—65). The thirteen esters examined have a medium band in the 750—740 cm.$^{-1}$ range, while the acids show a weaker band between 757 and 742 cm.$^{-1}$. These useful bands appear to be characteristic of conjugated acetylenic acids and esters—they do not occur in the spectra of the corresponding olefinic compounds. The vibrational assignments are not known. With saturated acids a band in the range 700—575 cm.$^{-1}$ has been correlated with a skeletal deformation involving the O–C=O angle of the acid dimer (Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247). Such an assignment could be applied to the acetylenic acids, but in the (monomeric) esters the frequency of the corresponding vibration would be appreciably different.

Allylic and Propargylic Halides.—Previous work on propargylic halides (Wotiz *et al.*, *locc. cit.*; Jacobs and Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314; Hatch and Kidwell, *ibid.*, 1954, **76**, 289) has been confined to the C≡C stretching vibration, and to the presence or absence of bands in the 1700 cm.$^{-1}$ region.

The results in Table 4 show that both the systems $C{\equiv}C{\cdot}CH_2Cl$ and $CH{=}CH{\cdot}CH_2Cl$ give two bands, near 1255 and 700 cm.$^{-1}$, which are strong in the propargylic chlorides and of medium intensity in the allylic chlorides. In some cases (88, 90, 91, and 93) splitting of either the higher- or the lower-frequency band occurs. With the propargylic bromides and iodides the higher band moves to lower frequency, and the lower one disappears, presumably by displacement to below 650 cm.$^{-1}$, the end of the sodium chloride range. These findings parallel those of Kitson (*loc. cit.*) who observed the higher-frequency band in both series, and reported frequencies for the allylic chlorides, bromides, and iodides of 1248, 1204, and 1150 cm.$^{-1}$, respectively.

The band near 700 cm.$^{-1}$ in the chlorides is probably due to C–Cl stretching: the absence of corresponding bands above 650 cm.$^{-1}$ in the bromides and iodides supports this suggestion. For the higher-frequency band there is no obvious assignment. None of the compounds in Table 4 showed selective absorption around 1700 cm.$^{-1}$ (cf. Wotiz *et al.*, *locc. cit.*).

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