o-Ethoxybenzaldehyde dimethylhydrazone. A solution of 15 g. (0.1 mole) of *o*-ethoxybenzaldehyde and 7.0 g. (0.116 mole) of dimethylhydrazine was refluxed 3 hr. Distillation of the reaction mixture, after evaporation of the excess hydrazine, gave 12.6 g., 66%, of the product, b.p. 136–138°/4 mm.

2,5-Diethoxyterephthalaldehyde bis(dimethylhydrazone). A solution of 6.6 g. (0.03 mole) of 2,5-diethoxyterephthalaldehyde and 5.0 g. (0.083 mole) of dimethylhydrazine in 25 ml. of alcohol was refluxed for 3 hr. The solid which precipitated on cooling was recrystallized from methanol-water to give 2.0 g., 22%, of the product, m.p. 147–148°.

p-Dimethylaminobenzaldehyde dimethylhydrazone. A solution of 15 g. (0.1 mole) of *p*-dimethylaminobenzaldehyde and 7.0 g. (0.116 mole) of dimethylhydrazine in 30 ml. of concentrated hydrochloric acid and 25 ml. of ethanol was refluxed for 3 hr. The solution was made basic with concentrated ammonium hydroxide, filtered hot, and cooled to precipitate the crude product. Recrystallization from ethanol-water gave 5.0 g., 26%, of the product, m.p. 74–75°.

Pyridine-2-carboxaldehyde dimethylhydrazone. A mixture of 5.35 g. (0.05 mole) of pyridine-2-carboxaldehyde and 4.0 g. (0.067 mole) of dimethylhydrazine was fractionated after standing 1 hr. to give 5.7 g., 77%, of the crude product, b.p. 128–132°/13 mm. Refractionation gave the pure product, b.p. 128–130°/13 mm., n_D^{28} 1.6038. The picrate prepared from this product melts at 185–186°.

Pyridine-4-carboxaldehyde dimethylhydrazone. This product was prepared by the procedure given for the isomeric 2-carboxaldehyde. The fraction b.p. 136–149°/21 mm. solidified in the receiver. Recrystallization from petroleum ether gave 73% of the product, m.p. 60–64°. Additional recrystallization from petroleum ether and from water gave the pure product, m.p. 65–66°.

Infrared spectra were determined using a Baird double beam recording spectrophotometer with sodium chloride optics. All measurements were calibrated against the 3.419μ band for polystyrene. The medium used is given in the tables of data. Solutions were run at approximately 5% concentrations. The abbreviations used signify w (weak), m (medium), s (strong), S or vs (very strong), sh (shoulder)

Acknowledgment. The authors wish to acknowledge support of this research through grant C-2457 from the National Cancer Institute of the United States Public Health Service and grant NSF-G1918 from the National Science Foundation.

LOUISVILLE, KY.

[CONTRIBUTION NO. 996 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Infrared Spectra of Allenic Compounds

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Received July 31, 1956

From the inspection of the infrared spectra of 58 allenic compounds, 48 of them from the literature, 2 resynthesized, and 8 synthesized for this study, it was concluded that the bands at 1950 and 850 cm.$^{-1}$ are characteristic of the allene bond system with certain variations due to substitution. The antisymmetrical stretching frequency at 1950 cm.$^{-1}$ appears as a doublet when the allene group is terminal and is substituted by an electron-attracting group (CO_2H, CO_2R, $CONH_2$, COCl, COR, CF_3, CN). Its intensity decreases with increasing substitution of electronically similar groups. The band at 850 cm.$^{-1}$ is characteristic of the terminal $=CH_2$ group and its absence is good evidence for the absence of terminal allenes. It has an overtone at 1700 cm.$^{-1}$ of low intensity. The synthesis of the new allenes is described.

Because of the increasing interest in allenic compounds it became important to develop fast and safe methods for their identification. The present paper deals with the application of infrared spectroscopy to this problem. Certain empirical rules became apparent which were successfully tested and applied to all available allenic compounds. Some allenic compounds were especially synthesized for this study; other data were collected from the literature or obtained by personal communications with other investigators. In some cases infrared spectra of the allenic compounds prepared by other workers was determined in our laboratories.[2]

For the identification of allenes two bands are of special interest. In the 1950 cm.$^{-1}$ region, v_1 (due to the antisymmetrical C=C=C stretching vibration) sometimes appears as a doublet,[3] and v_2 (due to torsional motion of an allenic terminal methylene) in the 850 cm.$^{-1}$ region. The latter band has an overtone, $2v_2$ at 1700 cm.$^{-1}$ The presence of v_1 and v_2 and their relative intensities clearly differentiates between allenes containing various substituents. Tables I to V list the allenic compounds available for this study and the position and intensities of the v_1, v_2 and $2v_2$ bands.

Explanation of Tables I to V. Tables I to V contain pertinent infrared data collected during this study for allenic compounds. These data were obtained from many different sources, under diversified conditions and using many different instruments. Therefore, the actual frequencies of the absorption bands listed in these tables are quite uncertain.

Frequencies are in reciprocal centimeters (cm.$^{-1}$). The frequency of a band is followed by an intensity description. The usual terms (v = very, s = strong, m = medium, w = weak) are used.

The meanings of other terms are: — = no appreciable absorption band; na = information for this frequency range is not available; [] = "ac-

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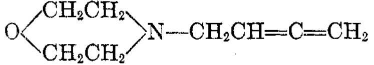
[1] Abstracted from the Ph.D. thesis of D.E.M., University of Pittsburgh, 1956. The authors wish to acknowledge the financial support of the Air Reduction Company.

[2] We wish to thank Dr. Foil A. Miller and his coworkers for all the determinations and for the fruitful discussions.

[3] J. H. Wotiz and W. D. Celmer, *J. Am. Chem. Soc.*, **74**, 1860 (1952).

TABLE I

MONOSUBSTITUTED ALLENES

No.	Compound	Reference	v_1	$2v_2$	v_2
1	$H_2C{=}C{=}CH_2$	4	1957 v s	1687 w	842 m
2	$CH_3CH{=}C{=}CH_2$	5	1961 v s	1701 m	858 v s
3	$C_4H_9CH{=}C{=}CH_2$	6	1945 v s	1685 m	848 v s
4	$C_6H_5CH{=}C{=}CH_2$	7	1925 s	—	860 m
5	$ClCH{=}C{=}CH_2$	8,9	1960 w	1750 w	—
6	$BrCH{=}C{=}CH_2$	8,9	1960 w	1750 w	875 v s
7	$ICH{=}C{=}CH_2$	8	1940 w	na	na
8	$HO_2CCH{=}C{=}CH_2$	10,11	1930, 1900 s	[1670] v s	850 s
9	$CF_3CH{=}C{=}CH_2$	12	2000, 1970 s	1695	na
10	$C_2H_5OCH{=}C{=}CH_2$	13	1970 (?)	na	na
11	$C_6H_5OCH{=}C{=}CH_2$	14	1950 m	—	835 m
12	$HO_2CCH_2CH{=}C{=}CH_2$	15,16	1967 v s	na	na
13	$HOCH_2CH{=}C{=}CH_2$	17	1980 s	1707 m	853 v s
14	$CH_3(CH_2)_5CHOHCH{=}C{=}CH_2$	18	1953	na	na
15	$(C_2H_5)_2NCH_2CH{=}C{=}CH_2$	19,20	1960 s	1965 m	850 s
16	 $O{<}\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}{>}N{-}CH_2CH{=}C{=}CH_2$	19,20	1957 s	1700 m	855 s
17	$CH_3NHCH_2CH{=}C{=}CH_2$	19,20	1957 s	1700 m	850 s
18	$(CH_3)_2NCH_2CH{=}C{=}CH_2$	19,20	1960 s	1705 m	844 s
19	$HOCH_2CH_2CH{=}C{=}CH_2$	21,22	1957 s	—	842 s
20	$CH_3CHOHCH_2CH{=}C{=}CH_2$	21	1970 (?)	na	na

cidental band," *i.e.*, that a band occurs 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; (?) = relative intensity not known.

The frequency assignments are: v_1 = band near 1950 cm.$^{-1}$ due to antisymmetrical C=C=C stretching vibration; v_2 = band near 850 cm.$^{-1}$ due to torsional motion of an allenic terminal methylene group; $2v_2$ = overtone of v_2.

Certain correlations between the structures of allenic compounds and their infrared spectra can now be made:

1. The only allenic compounds for which v_1 appears as a doublet (*e.g.* 1930 and 1950 cm.$^{-1}$) are those containing a terminal allenic grouping ($C{=}C{=}CH_2$) and which have one of the following groups directly attached to the allenic system: $—CO_2H$, $—CO_2R$, $—CONH_2$, —COCl, —CO—R, $—CF_3$, —CN. The same groups are predominately *meta*-directing when attached to a benzene nucleus. It is likely that the origin of the splitting of v_1 is in the electron-withdrawing property of these groups.

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(19) V. A. Engelhardt, *J. Am. Chem. Soc.*, **78**, 107 (1956).

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(23) Resynthesized especially for this study.

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(25) J. H. Wotiz, *J. Am. Chem. Soc.*, **72**, 1639 (1950).

(26) Synthesis described in this study. The spectra are recorded on a Baird Associates double-beam spectrophotometer, using a NaCl prism, by Dr. F. A. Miller and associates of the Mellon Institute. Copies of spectrograms are available from the authors upon request.

(27) J. H. Wotiz and E. S. Hudak, *J. Org. Chem.*, **19**, 1580 (1954).

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(37) W. Oroshnik, A. D. Mebane, and G. Karinas, *J. Am. Chem. Soc.*, **75**, 1050 (1953).

(38) J. H. Wotiz and R. J. Palchak, *J. Am. Chem. Soc.*, **73**, 1971 (1951).

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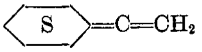
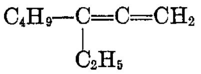
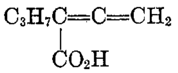
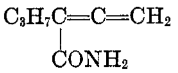
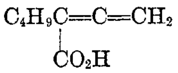
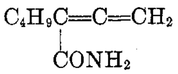
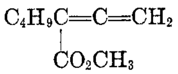
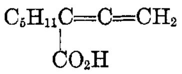
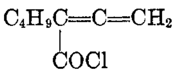
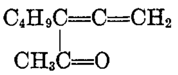
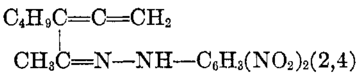
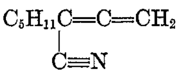
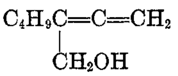
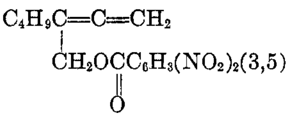
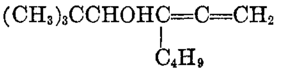
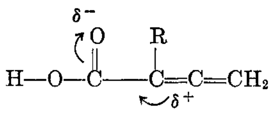
(40) Incorrectly identified in the original reference.

TABLE II

Disubstituted Allenes

No.	Compound	Reference	ν_1	$2\nu_2$	ν_2
21	$(CH_3)_2C=C=CH_2$	22,23	1930 s	1685 w	845 v s
22	$CH_3(C_2H_5)C=C=CH_2$	22	1960 s	1700 w	847 s
23		22	1955 s	1680 w	843 s
24	 $C_4H_9—\underset{C_2H_5}{\underset{\mid}{C}}=C=CH_2$	24	1925 m	1675 v w	845 s
25	 $C_3H_7\underset{CO_2H}{\underset{\mid}{C}}=C=CH_2$	3	1950, 1930 s	[1650] s	840 s
26	 $C_3H_7\underset{CONH_2}{\underset{\mid}{C}}=C=CH_2$	3	1950, 1930 s	na	na
27	 $C_4H_9\underset{CO_2H}{\underset{\mid}{C}}=C=CH_2$	25	1950, 1930 s	[1700] v s	850 s
28	 $C_4H_9\underset{CONH_2}{\underset{\mid}{C}}=C=CH_2$	3	1950, 1930 s	na	na
29	 $C_4H_9\underset{CO_2CH_3}{\underset{\mid}{C}}=C=CH_2$	25	1950, 1930 s	[1700] v s	850 s
30	 $C_5H_{11}\underset{CO_2H}{\underset{\mid}{C}}=C=CH_2$	3	1950, 1930 s	na	na
31	 $C_4H_9\underset{COCl}{\underset{\mid}{C}}=C=CH_2$	26	1930, 1900 s	[1720] v s	847 v s
32	 $C_4H_9\underset{CH_3C=O}{\underset{\mid}{C}}=C=CH_2$	26	1930, 1910 s	[1685] v s	855 s
33	 $C_4H_9\underset{CH_3C=N—NH—C_6H_3(NO_2)_2(2,4)}{\underset{\mid}{C}}=C=CH_2$	26	1910 m	[1700] s	856 m
34	 $C_5H_{11}\underset{C\equiv N}{\underset{\mid}{C}}=C=CH_2$	27	1925, 1910 w	[1700] w	?870 m
35	 $C_4H_9\underset{CH_2OH}{\underset{\mid}{C}}=C=CH_2$	26	1930 s	1700 w	848 s
36	 $C_4H_9\underset{CH_2O\underset{O}{\underset{\Vert}{C}}C_6H_3(NO_2)_2(3,5)}{\underset{\mid}{C}}=C=CH_2$	26	1925 s	[1700] v s	855 s
37	 $(CH_3)_3CCHOH\underset{C_4H_9}{\underset{\mid}{C}}=C=CH_2$	26	1940 w	[1725] w	845 m



$$H—O—\overset{\overset{\delta^-}{O}}{\overset{\Vert}{C}}—\overset{R}{\overset{\mid}{C}}=C=CH_2 \quad \delta^+$$

2. The increase in substitution about the allene by alkyl or aryl groups decreases the intensity of ν_1. In the case of tetraphenylallene (compound 54) this band is "absent." The presence of the allene grouping was recently demonstrated[41] by nuclear magnetic resonance studies.

3. The intensity of ν_1 is not greatly affected by an increase in substitution about the allene, if the substituents are different in their electronic behavior (*e.g.* compound 55).

4. The absence of ν_2 (850 cm.$^{-1}$) band is evidence for the absence of a terminal allene.

5. The $2\nu_2$ (1700 cm.$^{-1}$) absorption band is of little use for the characterization of allenes because it is a weak band which appears in a region frequently occupied by bands due to other bonds.

The position and intensities of ν_1 and ν_2 can be explained by making formal analogies between the allenic bond and a double bond.[1]

EXPERIMENTAL

A number of the compounds listed in Tables I to V are

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[41] J. H. Wotiz, D. O'Reilly and D. E. Mancuso, unpublished.

TABLE III

DISUBSTITUTED ALLENES (NON-TERMINAL)

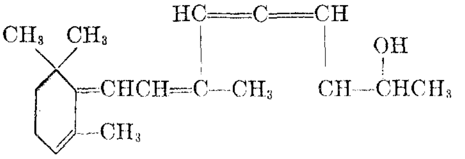
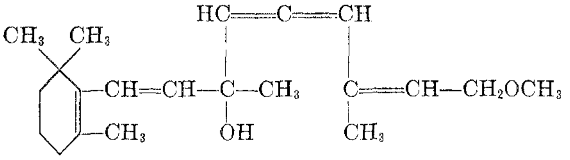
No.	Compound	Reference	v_1
38	2-Naphthyl—$CH{=}C{=}CH{-}C_6H_4Br$-*p*	28	1915 (?)
39	*p*-C_6H_5-$C_6H_4{-}CH{=}C{=}CH{-}C_6H_5$	29	1930 s
40	1,3-Heptamethyleneallene	30	1940 s
41	$CH_3CH{=}C{=}CHCO_2H$	31	1970 (?)
42	$HO_2CCH{=}C{=}CHCO_2H$	32,33	1970 s
43	$CH_3O_2CCH{=}C{=}CHCO_2CH_3$	32,33	1971 s
44	$(CH_3)_3CCOCH{=}C{=}CH{-}C_4H_9$	26	1925 w
45	$CH_3(CH_2)_5COCH{=}C{=}CH(CH_2)_7CO_2H$	18,34	1947 s
46	$H(C{\equiv}C)_2{-}CH{=}C{=}CH(CH{=}CH)_2CH_2CO_2H$	35	1930 w
47	$H(C{\equiv}C)_2{-}CH{=}C{=}CH(CH{=}CH)_2CH_2CO_2CH_3$	35	1930 w
48		36	1925 w
49		37	1940 m

TABLE IV

TRISUBSTITUTED ALLENES

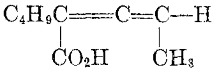
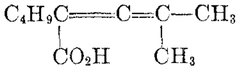
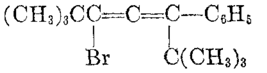
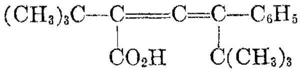
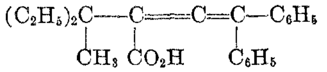
No.	Compound	Reference	v_1
50	 $C_4H_9\underset{CO_2H}{C}{=}C{=}\underset{CH_3}{C}{-}H$	38,3	1960 s
51	$(CH_3)_2C{=}C{=}CHCH_3$	26	1940 w
52	$(C_6H_5)_2C{=}C{=}CHC_6H_5$	29	(2000–1900) v w
53	$(CH_3)_2C{=}C{=}CHCH(CH_3)_2$	17	1940 w

TABLE V

TETRASUBSTITUTED ALLENES

No.	Compound	Reference	v_1
54	$(C_6H_5)C{=}C{=}C(C_6H_5)_2$	23	[1920] w
55	 $C_4H_9\underset{CO_2H}{C}{=}C{=}\underset{CH_3}{C}{-}CH_3$	38,3	1930 m
56	 $(CH_3)_3C\underset{Br}{C}{=}C{=}\underset{C(CH_3)_3}{C}{-}C_6H_5$	39,11	1925 m
57	 $(CH_3)_3C{-}\underset{CO_2H}{C}{=}C{=}\underset{C(CH_3)_3}{C}{-}C_6H_5$	39,11	1920 m
58	 $(C_2H_5)_2\underset{CH_3}{C}{-}\underset{CO_2H}{C}{=}C{=}\underset{C_6H_5}{C}{-}C_6H_5$	39,40	1900 s

new and their method of synthesis is described here along with some reactions which were found unsatisfactory.

Butylbutadienoyl Chloride (Comp. 31). Sodium butylbutadienoate was prepared in 99% yield by adding a solution of sodium hydroxide to butylbutadienoic acid[25] until the solution was slightly basic to Alkacid paper. The water was then removed by lyophilization (freeze drying). The sodium salt (53 g., 0.31 mole) was added in portions to a solution of 47 g. (0.37 mole) of oxalyl chloride in 100 ml. of dry, thiophene-free benzene.[42] After the gas evolution ceased, the sodium chloride was removed by filtration and the filtrate distilled yielding 35 g. (71% yield) of the acid chloride, b.p. 73–74° at 8 mm., n_D^{25} 1.4812.

Anal. Calcd for $C_8H_{11}OCl$: C, 60.6; H, 7.0. Found:[43] C, 60.0; H, 6.7.

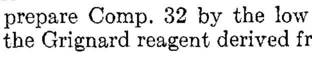
Attempted preparation of the acid chloride from the acid using thionylchloride gave products of high chlorine content which were difficult to avoid or to remove by distillation.

3-Butyl-3,4-pentadiene-2-one, (Comp. 33) was prepared by the method of Cason,[44] using 0.077 mole of methylmagnesium bromide, 7 g. (0.04 mole) of anhydrous cadmium chloride and 12 g. (0.076 mole) of butylbutadienoyl chloride in 50 ml. of benzene. The reaction product was hydrolyzed with ammonium chloride solution and the ether-benzene layer washed with sodium carbonate solution. Distillation yielded 4 g. of fraction, b.p. 47–51° at 2 mm., n_D^{25} 1.4740, which gave a positive halogen test with alcoholic silver nitrate. The unreacted acid chloride was removed by adding it to 10 ml. of liquid ammonia. After the vigorous reaction ceased the ammonia was evaporated, the residue suspended in ether and the ammonium chloride removed by filtration. The filtrate yielded 1 g. of the ketone, b.p. 60° at 3 mm.

Anal. Calcd. for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 78.8; H, 10.4.

Its 2,4-*dinitrophenylhydrazone* (Comp. 33) was recrystallized from ethanol and melted at 137–138°.

Attempts to prepare Comp. 32 by the low temperature acetylation[45] of the Grignard reagent derived from 1-bromo-2-heptyne[25]



$$\left[\begin{array}{c} C_4H_9C{\equiv}C{-}C^{-}H_2 \\ \updownarrow \\ C_4H_9\overset{-}{C}{=}C{=}CH_2 \end{array}\right]Mg^{+}Br$$

were unsuccessful as a complex mixture of products which contained mostly the acetylenic ketone $C_4H_9C{\equiv}CCH_2{-}CO{-}CH_3$ was formed. The reaction of the above mentioned Grignard reagent with propionitrile, followed by hydrolysis, also yielded a mixture from which it was impossible to isolate the desired allenic ketone.

2-Butyl-2,3-butadienol-1 (Comp. 35). The Grignard re-

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(42) R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, 42, 599 (1920).

(43) Microanalytical Laboratory, University of Pittsburgh.

(44) J. Cason, *J. Am. Chem. Soc.*, 68, 2078 (1946).

(45) M. S. Newman and A. S. Smith, *J. Org. Chem.*, 13, 592 (1948).

agent from 58 g. (0.33 mole) of 1-bromo-2-heptyne was prepared as previously described.[25] Gaseous formaldehyde was prepared by the thermal decomposition of 60 g. of paraformaldehyde. The reaction product of the formaldehyde with the Grignard reagent was hydrolyzed with ammonium chloride solution, the ether layer washed with sodium bisulfite and dried. Distillation yielded 69 g. of liquid boiling from 75–88° at 3 to 1 mm. pressure, n_D^{25} 1.4645–1.4630. Redistillation yielded 32 g. (76% yield) of the allenic alcohol, b.p. 57° at 0.6 mm. n_D^{25} 1.4686.

Anal. Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1; H, 11.8.

Its *3,5-dinitrobenzoate* (Comp. 36) was crystallized from petroleum ether (b.p. 30–60°) to a constant melting point of 36–37°.

Anal. Calcd. for $C_{15}H_{16}N_2O_6$: C, 56.2; H, 5.0. Found: C, 56.2; H, 5.4.

When a sample of it was mixed 3,5-dinitrobenzoate derived from 3-octynol-1[46] a ten degree melting point depression was noted.

2,2-Dimethyl-4-butyl-4,5-hexadiene-3-ol (Comp. 37) was prepared by the Reformatsky reaction using 18 g. (0.28 gram-atom) of freshly sanded zinc strips, 44 g. (0.25 mole) of 1-bromo-2-heptyne and 24 g. (0.3 mole) trimethylacetaldehyde, and a mixture of ether, benzene, tetrahydrofurane, and dioxane as solvents. The reaction started during the removal of ether by distillation. The reaction product was hydrolyzed by pouring it on a mixture of ice and acetic acid. The products were dissolved in ether and the ether solution washed with sodium carbonate. Distillation yielded 24.7 g. (66% yield) of product boiling from 76–84° at 2 mm., n_D^{25} 1.4551–1.4547, and 12 g. of higher boiling liquids.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.2. Found C, 79.1; H, 12.5.

Infrared analysis showed the fraction, b.p. 82° at 2 mm., n_D^{25} 1.4550 to be the allenic alcohol contaminated with some of its acetylenic isomer, $C_4H_9C \equiv CCH_2CHOH—C(CH_3)_3$ (very weak $C \equiv C$ band at 2200 cm.$^{-1}$).

2,2-Dimethyldeca-4,5-dien-3-one. (Comp. 44). The mixture of Comp. 37 and its acetylenic isomer (7 g., 0.038 mole) was dissolved in 20 ml. of acetone, cooled to −4°, and oxidized by the addition of 3.3 g. (0.033 mole) of chromium trioxide in a solution of 2.8 ml. of sulfuric acid and 20 ml. of water.[47] The temperature was kept under 5° by external cooling. The reaction product was continuously extracted with ether for 12 hr. The ether extract was washed with a small portion of water and dried. Evaporation of the ether left 7.6 g. of a residue which upon distillation yielded 3.1 g. of product, b.p. 88–91° at 0.7 mm., n_D^{25} 1.4504–1.4495.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 77.9; H, 12.5.

Spectroscopic analysis showed that the allenic alcohol was destroyed by the oxidation and that the distillate was a mixture of the starting acetylenic alcohol and its oxidation product, $C_4H_9C \equiv C—CH_2—CO—C(CH_3)_3$. To 1 g. of this mixture in 10 ml. of ethanol was added 20 ml. of 5% aqueous sodium carbonate.[48] The mixture was agitated at 50° under nitrogen for 24 hr., and then extracted with ether. Distillation yielded Comp. 44, b.p. 65° at 0.8 mm., n_D^{25} 1.4523.

2-Methyl-2-chloro-3-pentyne. Into a solution of 151 g. (1.5 moles) of 2-methyl-3-pentynol[49] (prepared in 39% yield by the condensation of propynylmagnesium bromide and acetone, b.p. 55° at 25 mm., n_D^{18} 1.4438) in 400 ml. of dry petroleum ether (b.p. 30–60°) containing 2 g. of hydroquinone and 60 g. of powdered calcium chloride, was passed anhydrous hydrogen chloride.[50]

The temperature was kept at 0°. The solution was treated with solid anhydrous potassium carbonate, filtered and distilled, yielding 120 g. (67% yield), b.p. 55° at 70 mm., n_D^{25} 1.4475. Its infrared spectrum contained the $C \equiv C$ stretching frequency at 2210 cm.$^{-1}$ and was void of absorption bands in the double bond absorption region. Attempted preparation of the chloride as described by Zakharova[49] or by using thionyl chloride gave impure products.

2-Methyl-2,3-pentadiene (Comp. 51) was prepared by the dehalogenation[6,22] of 38 g. (0.33 mole) of 2-methyl-2-chloro-3-pentyne using 14 g. (0.37 mole) of lithium aluminum hydride in 1000 ml. of dry dioxane. Upon distillation, 4.7 g. (18% yield), b.p. 70–72°, n_D^{25} 1.4285, of the allene was isolated. Its infrared and Raman effect analyses revealed the presence of less than 20% of its acetylenic isomer, $(CH_3)_2CH—C \equiv C—CH_3$.[51]

Tetraphenylallene (Comp. 54) was prepared by the dehydrohalogenation of 213 g. (0.5 mole) of 2-bromo-1,1,3,3-tetraphenylpropene[52] (prepared by Wen-Yang Wen) using 100 g. of potassium hydroxide in 500 ml. of refluxing alcohol. From 190 g. of the crude product, 90 g. (53% yield) of the pure allene, m.p. 164–165°, was obtained by crystallization from acetone. Its infrared spectrum contains a band at 1920 cm.$^{-1}$, which is due, however, to the phenyl ring. Its Raman effect[2] analysis revealed a weak line at 1938 cm.$^{-1}$ due to the allene. Because of the large amount of light scattering which caused a heavy background on the Raman plate, it was impossible to establish the exact intensity of the bands.

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[CONTRIBUTION FROM DEPAUW UNIVERSITY AND THE INDIANA STATE BOARD OF HEALTH]

A Study of the Infrared Spectra of Some Alkyl-Substituted Carbostyrils

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Received August 8, 1956

The infrared spectra of several substituted carbostyrils are presented and discussed.

Characteristic absorption bands originating in the out-of-plane deformation vibrations of the hydrogen atoms on an aromatic ring have been found to appear in the infrared spectrum between 1225 and 650 cm.$^{-1}$ Well established correlations between the positions of these bands and various