sis showed 67% yield of 1,2,4-trichlorobenzene and a small amount of 1,2,3- and/or 1,3,5-trichlorobenzene.

Anal. Calcd. for $C_6H_3Cl_3$: Cl, 58.30. Found: Cl, 58.49.

Reaction resulted in no change in the *p*-isomer content.

5. **Ferric Chloride and Toluene with Aluminum Chloride Catalyst** (By Dr. J. G. Burt).—Toluene (215 g., 2.34 moles) was allowed to react with ferric chloride (233 g., 1.44 moles) in the presence of aluminum chloride (12 g., 0.09 mole). Hydrogen chloride evolved at about 40–60° during three hours amounted to 117% of theory. The reaction product was isolated by steam distillation, drying and fractionation. The chlorotoluene fraction had b.p. 155–165°; 91 g., 64% yield based on the ferric chloride. Infrared analysis of all fractions showed a 69% yield of chlorotoluene ($p/o/m$ = 91/9/<1).

A mole ratio of toluene to ferric chloride of 3.5/1 under the same conditions gave a 62% yield of chlorotoluene (p/o = 89/11).

A black almost infusible, water and ether-insoluble solid was obtained in each case which contained carbon, chlorine, hydrogen and iron.

6. **Ferric Chloride and 1-Chloronaphthalene.**—To 40.4 g. (0.28 mole) of ferric chloride was added slowly 61.1 g. (0.376 mole) of 1-chloronaphthalene. The mixture evolved hydrogen chloride rapidly and was heated to 52° over three hours. Unreacted 1-chloronaphthalene was steam distilled out. The dark residue was extracted with chloroform, the solvent evaporated, and the residual oil recrystallized from acetic acid. Crystals, 4.3 g., m.p. 208–211°, were collected, dissolved in benzene and decolorized with carbon. The solid obtained, 0.7 g., m.p. 219–220°, was analyzed. Additional solid, 2.6 g., m.p. 213–216° and 216–217°, was obtained from the benzene solution.

Anal. Calcd. for $C_{20}H_{12}Cl_2$: C, 74.35; H, 3.74; Cl, 21.91. Found: C, 74.03; H, 3.52; Cl, 22.12.

7. **Ferric Chloride and Benzene.**—As reported by Thomas,[1] chlorination was sluggish. Ferric chloride (1 mole) and benzene (1.5 moles) produced only a 30% yield of hydrogen chloride after 17 hours at the reflux temperature, and 67 g. of benzene- and water-insoluble black solid (inorganic material present). Chlorobenzene was formed in no more than 6% yield (as distillation hold-up).

8. **Chlorination of Chlorobenzene with Chlorine Gas.**—Chlorobenzene (2 moles) was chlorinated with chlorine gas (0.59 mole) at 125–130° using ferric chloride (0.015 mole) as catalyst. Tan ferrous chloride was formed during the reaction. (Found: Fe, 46.6; Cl, 46.0.)

Analysis of the distilled products by infrared showed a 96% yield of dichlorobenzene ($p/o/m$ = 54/46/<1) based on weight increase during chlorination. The distillation residue contained 1,2,4- (3.5% yield) and 1,3,5-trichlorobenzene and unidentified material. The f.p. of the dichlorobenzene fraction corresponded to 56% *p*- and 44% *o*-dichlorobenzene, which confirmed the infrared analysis.

9. **Analytical Methods.**—The infrared spectra[15] of the following compounds were obtained in cyclohexane solution and the absorption coefficient calculated at the indicated wave lengths (microns): benzene (14.85), chlorobenzene (13.52, 14.23, 14.62), *o*-dichlorobenzene (13.38), *p*-dichlorobenzene (12.23), *m*-dichlorobenzene (12.75), 1,2,4-trichlorobenzene (12.35), toluene (13.75), *o*-chlorotoluene (13.40), *p*-chlorotoluene (12.45), *m*-chlorotoluene (13.0), 2,4-dichlorotoluene (12.0, 14.15), benzyl chloride (14.35), bromobenzene (13.62), *p*-chlorobromobenzene (12.30), *o*-dibromobenzene (13.42), fluorobenzene (13.3) and iodobenzene (13.7). The concentration of the various isomers in a mixture was obtained by calculation from the absorbance at the characteristic wave lengths.

A comparison of known mixtures showed the method to be accurate within 2%. The smallest detectable amount of *m*-chlorotoluene in a typical mixture was calculated to be 0.5% from the specific absorption coefficient and for *m*-dichlorobenzene the amount was 0.7%. A Perkin-Elmer infrared spectrophotometer model 12-C was used in this work.

In some cases, isomer ratios were obtained from freezing and melting points of the main portion of the product consisting of a mixture of *o*- and *p*-dichlorobenzene, and were found to deviate from infrared data usually by no more than 2%. Use was made of a freezing point curve for mixtures of *o*- and *p*-dichlorobenzene similar to the one reported by Holleman and van der Linden.[4]

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[15] *Cf.* J. Le Comte, *Compt. rend.*, **204**, 1186 (1937); *C. A.*, **31**, 4205 (1937); **32**, 2833 (1938).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS LIMITED]

Acetylene Polymers: Preparation, Physical Properties, Infrared and Ultraviolet Spectra[1]

BY K. K. GEORGIEFF, W. T. CAVE AND K. G. BLAIKIE

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Monovinylacetylene (M.V.A.), divinylacetylene (D.V.A.), 1,3-butadienylacetylene (B.D.A.), 1,3,7-octatrien-5-yne (I) and a 7-yne acetylene tetramer thought to be 1,3,5-octatrien-7-yne (II) have been prepared by the Nieuwland reaction and separated by the high vacuum, fractional distillation–condensation technique. Some of their physical properties have been measured and vapor pressure curves, infrared spectra with band assignments and ultraviolet spectra with extinction coefficients are reported. Mass spectra were obtained but details are not given. The ultraviolet spectra of polymers of monovinylacetylene and divinylacetylene also were obtained. Evidence in support of the 1,3,5-octatrien-7-yne constitution for the 7-yne tetramer is given and a mechanism of formation is suggested.

Many of the lower polymers of acetylene occur as impurities in acetylene generated from calcium carbide[2] and as by-products in many reactions of acetylene, *e.g.*, the synthesis of acrylonitrile,[3–7] and monovinylacetylene for chloroprene.[8,9] Their identification and quantitative estimation is a matter of practical and theoretical importance, but known chemical methods are impractically difficult.

It has been found that the infrared and ultraviolet spectra provide convenient methods for both qualitative and quantitative determinations. This paper presents spectroscopic and other physical

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[1] The authors wish to thank Shawinigan Chemicals Ltd. for permission to publish this paper.

[2] A. Müller, *Angew. Chem.*, **62**, 166 (1950).

[3] R. L. Hasche and J. G. McNally, F.I.A.T. Final Report No. 836 (1946).

[4] D. Brundrit and W. Hunter, B.I.O.S. Final Report No. 1057 (1947).

[5] A. S. Carter, F.I.A.T. Final Report No. 1025 (1947).

[6] F. Nill and R. Largent, F.I.A.T. Final Report No. 1125 (1947).

[7] A. S. Fromholz, B.I.O.S. Miscellaneous Report No. 90.

[8] P. V. Zhavoronkov, A. P. Alekhina and R. S. Shter, *Sintet. Kauchuk*, No. 2, 12 (1934); *C. A.*, **29**, 3976 (1935).

[9] A. L. Klebanskiĭ, L. G. Tzyurikh and I. M. Dolgopol'skiĭ, *Bull. acad. sci. U.R.S.S.*, No. 2, 189 (1935); *C. A.*, **30**, 1259 (1936).

data which are in addition to or at variance with previously published work.[10-14]

A mixture of acetylene polymers was obtained by the Nieuwland reaction,[15,16] but in contrast to previous investigations, separation was carried out using the high vacuum, low temperature, fractional distillation–condensation technique described by Sanderson.[17] This permitted reasonably efficient fractionation with a minimum risk of polymerization, formation of dangerous peroxides or isomerization.

Experimental

Crude mixtures of acetylene polymers were prepared by a modification of the continuous method of Zhavoronkov,[8] Klebanskiĭ[9] and Schmitz,[18] and the batch method of Nieuwland.[15] In the continuous method, acetylene generated from calcium carbide and purified by scrubbing with 88% sulfuric acid and 1.5% sodium hydroxide solution was passed at a rate of 220–250 liters per hour into a mixture of 1272 g. of cuprous chloride (95% reagent grade), 685 g. of ammonium chloride, 39.3 g. of 37% hydrochloric acid and 1097 g. of water at 80°.

The crude product was distilled using the high vacuum apparatus of Sanderson[19] modified by the addition of several vertical tubes with stopcocks and semi-ball connections along the underside of the main line to permit the quick attachment of reaction, distilling and receiving flasks. These flasks consisted of closed straight tubes 8–25 mm. i.d. × 10–20 cm. long fitted with stopcocks and female semi-ball connections and were used for the preliminary separation into 8–10 fractions. Those having roughly the same vapor pressure were combined. Three main cuts were thus obtained and subsequently redistilled into series of fractions using the fractional distillation–condensation technique.[17] Losses due to polymerization were kept small by carrying out the purification reactions in evacuated tubes at relatively low temperatures and by storing the samples under vacuum at −10 to −78°. Apiezon "N" was used as stopcock lubricant. This grease has, however, fairly strong absorption bands at 231 and 260 mμ in the ultraviolet and at about 3008, 2936, 1460 and 1380 cm.$^{-1}$ in the infrared, and contamination of spectral samples with it must be avoided.

Monovinylacetylene (M.V.A.).—The lowest boiling series of fractions consisted chiefly of M.V.A. (1-buten-3-yne) with some acetylene, vinyl chloride and acetaldehyde. The acetylene and vinyl chloride were removed by fractional distillation–condensation using traps at −78, −95 and −196°. The acetaldehyde was removed by shaking with a 15% aqueous sodium bisulfite solution in a reaction flask at 0°. The M.V.A. was distilled into another flask, treated with a 20% aqueous potassium hydroxide solution at 0°, and then distilled away from the latter. To confirm its purity, some M.V.A. was converted to its copper salt and regenerated with hydrochloric acid. The vapor pressure and infrared spectrum of the final product were found to be identical to those of the starting material.

Divinylacetylene (D.V.A.).—The next highest boiling series of fractions consisted chiefly of D.V.A. (1,5-hexadien-3-yne) with some 1,3-butadienyl acetylene (B.D.A., 1,3-hexadien-5-yne), chloroprene and water. The chloroprene was separated by fractional distillation–condensation using traps at −40 to −20, −50 to −30 and −196°. The B.D.A. was precipitated with ammoniacal cuprous chloride solution. The D.V.A. was distilled away from the yellowish-orange copper salt of B.D.A. but could not be completely dried by distillation. This was done by slowly distilling it through 14-mesh calcium carbide; $d^{20}{}_{20}$ 0.772, $n^{20.2}{}_{\mathrm{D}}$ 1.5055.

1,3-Butadienylacetylene (B.D.A.).—The copper salt of B.D.A. was washed with ammoniacal methanol and dried, and part of it was regenerated by treatment with sodium cyanide solution according to the procedure of Carter.[20] The wet B.D.A. was then distilled in the high vacuum apparatus and dried with calcium carbide. This procedure produced reasonably pure B.D.A. but some high boiling material was also obtained. The remainder of the copper salt was regenerated with 7% hydrochloric acid in the presence of a little Aerosol OT wetting agent. Several treatments were made starting with 110% of the theoretical amount of acid at 25° for 15–20 minutes, followed by distillation of the regenerated B.D.A. after adjusting the temperature of the mixture to just above its freezing point. Subsequent treatments were carried out with increasing amounts of acid and increasing temperature up to a maximum of 45–50°. Chlorinated by-products were not formed as in the method of Klebanskiĭ[21]; $d^{28}{}_{20}$ 0.780 ± 0.005.

1,3,7-Octatrien-5-yne (I).—The highest boiling series of fractions consisted chiefly of I, 0.5–1% of a 7-yne acetylene tetramer, several per cent. of vinyl chloroprene and small percentages of unknown impurities. The vinyl chloroprene was removed by fractional distillation–condensation with traps at −11 to −9, −20 to −15 and −196°, and the tetramers were separated from the high boiling impurities at slightly higher bath temperatures. The 7-yne tetramer was precipitated with ammoniacal cuprous chloride as a yellowish-orange salt. After pumping off most of the ammonia, I was distilled together with considerable water into a very narrow distilling tube. By melting the mixture to permit I to float to the top, freezing it again and then warming only the organic layer through the glass by suitable means, it was possible to distill I with only a little water. Final drying was done with calcium carbide; $n^{20}{}_{\mathrm{D}}$ 1.5834. Mass and infrared spectra indicated the presence of traces of vinyl chloroprene and a compound of molecular weight 121 or 122, and titration with Karl Fischer reagent showed less than 1% water. Attempts to obtain carbon-hydrogen analyses by combustion resulted in explosions.

7-yne Acetylene Tetramer (II).—The copper salt of II was washed, dried and regenerated with 7–20% hydrochloric acid in the same manner as B.D.A. However, even at 40–45° in the presence of excess acid, the regeneration was not complete in 45 minutes. Some of the copper salt, which was salvaged when the trap accidentally broke, was heated on a spatula and found to sparkle. Only sufficient II was recovered to obtain the ultraviolet and mass spectra. II could not be completely dried by repeated passage through calcium carbide which suggests the existence of a hydrate.

Preparation of Polymers of M.V.A. and D.V.A.—Samples of M.V.A. and D.V.A. were sealed in glass tubes both under vacuum and in the presence of 200–300 mm. pressure of air, and heated in a water-bath. The temperature was increased every few hours until slow polymerization commenced. Polymerization was stopped when 20–50% of the monomer had been converted. In the presence of air, M.V.A. (chiefly vapor) polymerized at 40° in 24 hours and D.V.A. (chiefly liquid) at 50–60° in 40 hours. In the absence of air, M.V.A. (chiefly liquid) required a temperature of 75–85° for 7 days and D.V.A. (vapor) 90–95° for 3–7 days. To remove occluded monomer, the polymers were dissolved in methanol, evaporated to dryness and redissolved in methanol. The solubilities of both polymers were low in methanol and very much lower in isoöctane and chloroform.

Infrared, Ultraviolet and Mass Spectra.—The infrared spectra were obtained on a Perkin-Elmer spectrometer, model 12-C, using a rock-salt prism. The recommended calibration standards[22] were used with frequent checks so

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(10) N. Sheppard, *J. Chem. Phys.*, **17**, 74 (1949).

(11) R. F. Stamm, F. Halverson and J. J. Whalen, *ibid.*, **17**, 104 (1949).

(12) E. Bartholomé and J. Karweil, *Z. physik. Chem.*, **B35**, 442 (1937).

(13) M. de Maldé, C. Mussa, I. V. Nebbia and L. Nebbia, *Chim. anal.*, **34**, 172 (1952).

(14) I. M. Heilbron, E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 134 (1944).

(15) J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, THIS JOURNAL, **53**, 4197 (1931).

(16) J. A. Nieuwland, U. S. Patent 1,811,959 (1931).

(17) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 86.

(18) H. Schmitz and H. J. Schumacher, *Z. Elektrochem.*, **45**, 503 (1939).

(19) R. T. Sanderson, ref. 17, p. 105.

(20) A. S. Carter, U. S. Patents 2,173,272 (1939) and 2,228,752 (1941).

(21) A. L. Klebanskiĭ, U. A. Dranitzina and I. M. Dobromil'skaya, *Compt. rend. acad. sci. U.R.S.S.*, **2**, 229, 232 (1935); *C. A.*, **29**, 6205 (1935).

(22) Perkin-Elmer Manual for 12-C Spectrometer.

that accuracy limits are believed to be ±10 cm.$^{-1}$ at high frequencies and ±1 cm.$^{-1}$ at lower frequencies. In one instance the 10-cm. gas cell was modified to raise the temperature of the sample by winding the barrel of the cell with resistance wire and sealing the salt windows with polyvinyl acetate.

The ultraviolet spectra were obtained on a Beckman DU instrument using standard 1-cm. quartz cells. The spectrum of benzene was used for frequent calibration and accuracy is believed to be within the limits of ±0.5 mμ.

The mass spectra were obtained by Dr. F. P. Lossing (National Research Council, Ottawa) using an ionization potential of 50 electron volts.

Results

Nieuwland's batch procedure for the preparation of acetylene polymers[15] was found to give a much higher proportion of chlorinated by-products than did the continuous method. Vinyl chloride, chloroprene and higher boiling compounds, some with a specific gravity greater than one, were obtained. Butadienylacetylene and the 7-yne tetramer were not present in sufficient quantity to permit positive identification, but this is not surprising since the long time of reaction would be expected to allow the addition of hydrochloric acid to these compounds, if any were formed. In the continuous procedure, vinyl chloride was not present in appreciable quantities but chloroprene, vinyl chloroprene and higher boiling compounds, as well as B.D.A. and the 7-yne tetramer, were obtained.

The constitutions of all the above acetylene polymers except the 7-yne tetramer appear to have been satisfactorily established by previous investigators. Klebanskii[9] who has reported values for the specific gravity, refractive index and boiling point of 1,3,5-octatrien-7-yne (*i.e.*, d^{20}_{20} 0.857, n^{20}_D 1.489, b.p. 44° at 20 mm. abs.) does not appear to have given any information on its preparation or proof of its constitution. Our mass spectrum[23] establishes its molecular weight as 104 with 8 carbon atoms and therefore its empirical formula must be C_8H_8. Since it was regenerated from its copper salt, at least one end of its chain must be terminated by the $HC{\equiv}C{-}$ group. Nieuwland[15] and Dolgopol'skii[24] have previously shown that only 1,3,7-octatrien-5-yne is formed when M.V.A. is passed into the Nieuwland catalyst in the absence of acetylene. It would thus appear that an eight-carbon chain, terminated with $HC{\equiv}C{-}$ can be formed only by the addition of acetylene to B.D.A. since the latter is the only monosubstituted acetylene with six carbon atoms present. The equation for its formation would appear to be exactly analogous to that previously postulated for B.D.A.[15]

$$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH$$

$$\Big\downarrow \text{CuCl catalyst}$$

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}C{=} + HC{\equiv}CH \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}C{\equiv}CH$$

II

Its mass spectrum, which has substantially the same peaks as that of 1,3,7-octatrien-5-yne but of different proportions, is qualitatively consistent with the structure of 1,3,5-octatrien-7-yne as well as several isomers in which the relative positions of the double bonds are different. Only a partial ultraviolet spectrum was obtained due to contamination of the sample with grease but the wave lengths of the main bands are in good agreement with those predicted for 1,3,5-octatrien-7-yne. This is more fully discussed later.

Vapor Pressure Data.—The vapor pressures were determined in the high vacuum apparatus by the static method and are given in Table I. The vapor pressure of 1,3,7-octatrien-5-yne is 3.0 mm. at 20.0°.

TABLE I

Temp., °C.	Vapor pressures, mm. M.V.A.	D.V.A.	B.D.A.
−100	0.6		
−90	1.5		
−80	4.6		
−70	10.9		
−60	22.5		
−50	43.5	0.35 ± 0.05	0.35 ± 0.05
−40	84.0	1.2	1.2
−30	144	3.1	2.9
−20	245	6.4	6.0
−10		11.6	12.0
0.0		20.1	22.1
10		33.5	39.2
20		57.0	

Infrared Spectra.—The assignments of Sheppard[10] and Stamm, *et al.*,[11] for M.V.A. form a reasonable basis for attempting a description of the origins of the bands shown in Fig. 1. Comment follows where features of the spectra require additional discussion.

Monovinylacetylene.—The doublet peak near 1850 cm.$^{-1}$ is identified with an overtone[25] of the prominent peak at 924 cm.$^{-1}$.[26,27] Although a band near 1285 cm.$^{-1}$ is expected for the $=C\langle^{H}$ bending mode, the band at 1240 cm.$^{-1}$ is substantially more intense than the corresponding one for acrylonitrile and appears much more like a distorted "C" type rather than a "B" type band. A strong overtone of the $\equiv C{-}H$ deformation is possible also in this region,[28] and this 1240 cm.$^{-1}$ band has been designated previously as an overtone.[12] Since the band envelope is obviously complex, it may be that both the $\equiv C{-}H$ (2 × ~630 cm.$^{-1}$) and the $=C{-}H$ deformations are represented, although this would introduce, for the latter mode, a discrepancy respecting its Raman displacement which has been given as 1288 cm.$^{-1}$.[10–12]

The weak bands at 873 and 673 cm.$^{-1}$ were not reported previously in the infrared spectrum.[12]

Divinylacetylene.—In spite of the most painstaking purification and several separate preparations, the relative intensities of the bands at 1613 and 1590 cm.$^{-1}$, presumably representing the $-C{=}C-$ stretching mode, remained unchanged. Al-

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(23) Private communications from F. P. Lossing, National Research Council, Ottawa, and J. L. Kerwin, Laval University, Quebec, P. Q.

(24) I. M. Dolgopol'skii, I. M. Dobromil'skaya and S. Yu Bokl, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1111 (1947); *C. A.*, **42**, 4517 (1948).

(25) N. Sheppard and D. M. Simpson, *Quart. Revs.* (*London*), **6**, 1 (1952).

(26) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

(27) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

(28) B. L. Crawford, Jr., *ibid.*, **8**, 526 (1940).

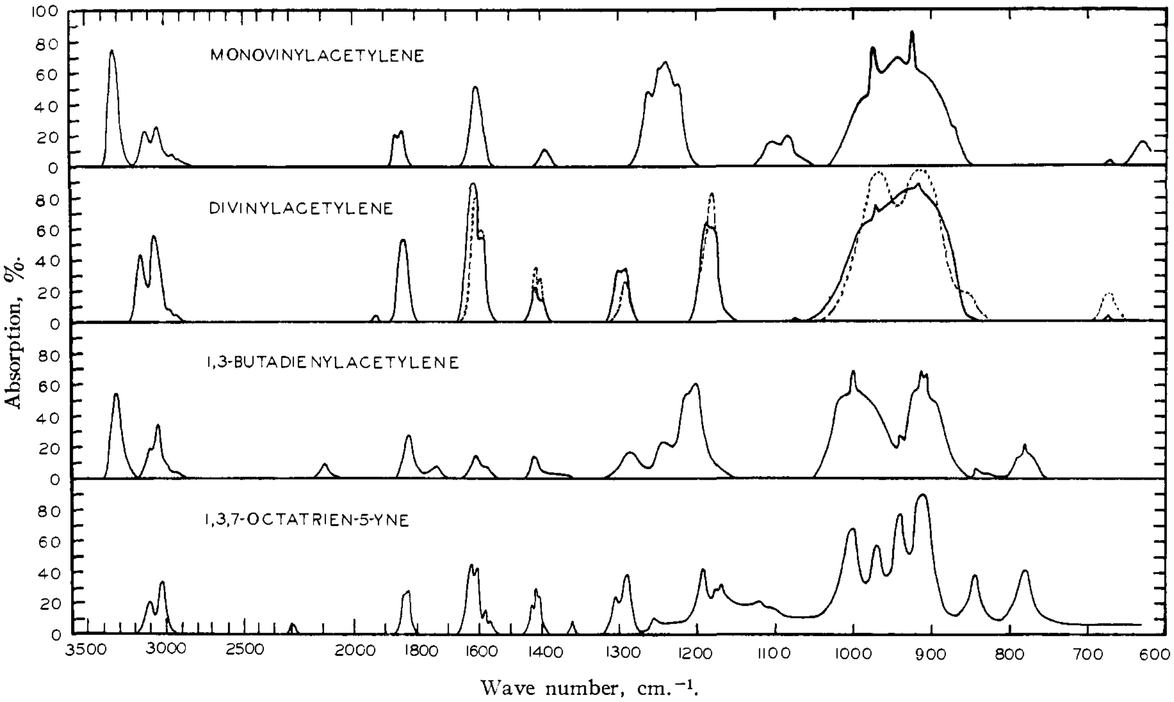

Fig. 1.—Infrared absorption spectra. Monovinylacetylene vapor, 47 mm. pressure, 10-cm. cell. Peaks: 3325, 3123, 3050, 2950, 2905, 1850, 1607, 1400, 1240, 1092, 972, 924, 873, 673 and 630 cm.$^{-1}$.

Divinylacetylene vapor (solid line), 50 mm. pressure, 10-cm. cell. Peaks: 3120, 3040, 2940, 2880, 1925, 1850, 1613, 1590, 1419, 1400, 1294, 1183, 1082, 973, 917, 856 and 673 cm.$^{-1}$. Divinylacetylene liquid (dashed line), 10% solution in CCl_4 or CS_2, 0.1 mm. cell.

Butadienylacetylene vapor, 40 mm. pressure, 10-cm. cell. Peaks: 3346, 3122, 3065, 2090, 1822, 1736, 1610, 1575, 1434, 1286, 1246, 1210, 1000, 942, 913, 908, 845 and 781 cm.$^{-1}$.

1,3,7-Octatrien-5-yne liquid, 10% solution in CCl_4 or CS_2, 0.1-mm. cell. Peaks: 3103, 3025, 2190, 1833, 1624, 1608, 1580, 1563, 1419, 1360, 1304, 1290, 1255, 1217, 1194, 1177, 1169, 1119, 1103, 1001, 969, 941, 911, 845 and 781 cm.$^{-1}$.

though less certain due to water vapor background, the same appeared true for the peaks representing the $-CH_2$ bending modes at 1419 and 1400 cm.$^{-1}$. Similar pairs of peaks appear in the liquid spectrum at 1608 and 1590 cm.$^{-1}$, and 1414 and 1403 cm.$^{-1}$ (*cf.* Fig. 1). A molecule with a center of symmetry would not be expected to show two bands for these modes. On the other hand, if the molecule were considered to exist in the *cis*-form its symmetry would be reduced and two bands could conceivably appear to represent each mode. Richards and Nielsen[29] discuss such a possibility for 1,3-butadiene, and Rasmussen and Brattain[30] deal specifically with the problem in describing the spectra for *cis*- and *trans*-pentadiene.

To discover whether further information on this point could be obtained, the spectrum of the gas at 65° was secured. Only slight modifications were observed. The band at 1613 cm.$^{-1}$ was reduced in width at the peak and a shoulder at about 1625 cm.$^{-1}$ was apparent. Very weak additional peaks were observed at 1000, 939 and 915 cm.$^{-1}$. No other significant changes in intensity were observed. To provide the necessary data a greater temperature difference clearly is necessary. However, incipient polymerization argued against the use of higher temperatures and the equipment for low temperature studies was not available.

Unfortunately, the Raman data which would help establish whether D.V.A. exists in both *cis*- and *trans*-forms are not yet available.

The band at 1183 cm.$^{-1}$ of much enhanced intensity (*cf.* M.V.A.[31,32]) seems most probably due to the planar $=CH_2$ rocking mode. Sheppard[10] has pointed out that a noticeable shifting of this band is not surprising due to the probability of interaction with the $>C-C<$ stretching mode.

Although there is a general agreement with the data of Maldé, *et al.*,[13] their liquid spectrum indicates a considerable number of extra bands. Even when allowance is made for differences in concentrations, the relative band intensities indicate the presence of an impurity in their sample. Their bands near 3300, 1300, 1230 and 800 cm.$^{-1}$ particularly, as well as the complexity of the 900–1000 cm.$^{-1}$ region, suggest the presence of B.D.A.

Butadienylacetylene.—At 2090 cm.$^{-1}$ there is a band representing the $-C\equiv C-$ stretching mode which was not apparent in the two preceding spectra, but which might be expected from the observations of Wotiz and Miller[33] that intensity increases when the $-C\equiv C-$ bond is terminal in a chain.

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(29) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Amer.*, **40**, 438 (1950).

(30) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

(31) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 597 (1944).

(32) F. Halverson, R. F. Stamm and J. J. Whalen, *J. Chem. Phys.*, **16**, 808 (1948).

(33) J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

The band at 1286 cm.$^{-1}$ can be associated with the $=\!C\!\begin{smallmatrix}\diagup H\\ \diagdown\end{smallmatrix}$ planar rocking mode, but the band at 1246 cm.$^{-1}$ has two possible origins. Since the molecule has no center of symmetry another band representing the $=\underset{\diagdown}{C}{-}H$ deformation is possible. Also, as with the M.V.A., the $\equiv C{-}H$ deformation might appear as an overtone in this region.

The bands at 1000, 942, 913 and 908 cm.$^{-1}$ are shifted obviously from their normal positions but deviations might reasonably be expected due to the conjugation of a $\begin{smallmatrix}\diagdown\\ H\diagup\end{smallmatrix}\!C{=}C\!\begin{smallmatrix}\diagup H\\ \diagdown\end{smallmatrix}$ group with a vinyl group at one end and with a triple bond at the other. The clear "C" type band at 781 cm.$^{-1}$, if a fundamental, must represent a non-planar mode. It seems too high a frequency for a skeletal deformation but it might be the $=CH_2$ torsional mode.

1,3,7-Octatrien-5-yne.—As would be expected, a low symmetry permits the appearance of many bands. Although individually less easily recognized, the bands can be grouped to conform with the previous suggestions. Bands at 1304, 1290, 1255 and 1217 cm.$^{-1}$ would appear to correspond to those at 1286 and 1246 cm.$^{-1}$ for B.D.A. Three bands, 1194, 1177 and 1169 cm.$^{-1}$, fall in the region in which the planar $-CH_2$ rocking mode is found. Peaks at 1624, 1608, 1580 and 1563 cm.$^{-1}$ fall in the range accorded to the $-C{=}C-$ stretching mode. Strong bands 1001, 969, 941 and 911 cm.$^{-1}$ represent the familiar $=\underset{\diagdown}{C}{-}H$ non-planar bending mode.

Of special interest is the absence of a band near 3300 cm.$^{-1}$ and of several more in the range 1700–1675 cm.$^{-1}$. These bands disappeared when the crude tetrameric mixture was treated with ammoniacal cuprous chloride solution to remove compounds containing acetylenic hydrogen. The bands disappearing, however, are not sufficient to make identification of the 7-yne tetramer possible.

Ultraviolet Spectra.—The ultraviolet data are given in Table II.[34]

Monovinylacetylene.—Partial spectra have been discussed by Lind and Livingston[35] and Dunicz.[36] Jones and McCombie[37] give the following values for dimethylvinylacetylene: λ_{max} 219.5 mμ, ϵ 9000; λ_{max} 226.0, ϵ 7000. These show a close similarity to our values for M.V.A. (*cf.* Table II). It is noted that the two peaks tend to merge at the higher concentrations and the extinction coefficients decrease rapidly as the concentration increases. In order to minimize the loss of M.V.A. due to its high volatility, a small weighed amount was dissolved in a large quantity of cold isoöctane and the lid of the quartz cell was sealed with wax.

The data concerning the polymers of M.V.A. and D.V.A. must be considered less reliable than for the monomers. Their low solubilities in the common solvents made difficult their purification and the accurate determination of concentrations. The spectrum of the polymer was obtained by heating monomeric M.V.A. for 7 days at 75–85°, mainly in the liquid phase, in the absence of air.

TABLE II

ULTRAVIOLET ABSORPTION DATA

Compound	Moles/l. × 10^5	λ_{max} mμ	ϵ_{max}
$CH_2{=}CH{-}C{\equiv}CH$	4.8	219	7,650
		227.5	7,750
	9.6	221	5,700 ± 100
		227.5	6,250 ± 50
	19	221sh	3,700
		227.5	4,250
M.V.A. polymer[a]	57	233	1,200
		~260sh	
$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$	5.1	232sh	7,100
		241	11,300 ± 500
		253	16,700 ± 300
		266	15,000 ± 400
	10.2	232sh	6,800
		241	10,600 ± 300
		253	14,500 ± 100
		266	12,300 ± 300
D.V.A. polymer[a]		234	
		~260sh	
$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH$	2.6	~240sh	
		252	26,300 ± 500
		~265sh	
	5.2	252	23,700 ± 1000
$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}C$ $\vert$ $CH_2{=}CH$	2.15	217	9,400
		227sh	7,500
		259sh	~13,500
		272	20,500 ± 400
		283	26,400 ± 500
		299	24,400 ± 600
	4.3	217	8,550 ± 100
		227sh	7,000 ± 100
		259sh	~13,000
		272	19,700 ± 200
		283	21,100 ± 100
		299	21,200 ± 200
$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}C{\equiv}CH$		271	
		282	
		298.5	

[a] Solvent is methanol, for all others isoöctane.

Divinylacetylene.—Two partial spectra have been published. Price and Walsh[38] recorded bands at 232, 241 and 253 mμ and Maldé, *et al.*,[13] reported bands at 253.6 and 265.3 mμ. The complete system of bands now has been observed and extinction coefficients calculated. Again, a deviation from the Beer–Lambert–Bouger absorption law is noted.

The band progression interval of about 2000 cm.$^{-1}$ indicates the vibration of the carbon–carbon triple bond.

Spectra were obtained for two concentrations of the polymer which had been prepared by heating the monomeric D.V.A. at 90–95° for 3 days in the vapor phase in the absence of air. The solubility of the polymer was too low even in methanol to permit a reasonably accurate determination of the concentration and consequently the extinction coefficient.

Butadienylacetylene.—In contrast to D.V.A., B.D.A. appears to possess a broad absorption band without clear substructure. There are suggestions of shoulders near 240 and 265 mμ, but unlike M.V.A. these features do not sharpen as the con-

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(34) The ultraviolet spectra discussed in this article have been deposited as Document number 4291 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

(35) S. C. Lind and R. Livingston, THIS JOURNAL, **55**, 1036 (1933).

(36) B. L. Dunicz, *ibid.*, **63**, 2461 (1941).

(37) E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 261 (1943).

(38) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A185**, 182 (1946).

centration is reduced. Again the extinction coefficients decrease with increase in concentration.

1,3,7-Octatrien-5-yne.—The spectrum of this compound is reminiscent of that of D.V.A. but the peaks have been shifted to longer wave lengths. The extinction coefficients decrease with increase in concentration but the deviations from ideal constancy are considerably less than for M.V.A. or D.V.A.

Unlike the spectrum for D.V.A., however, it is not obvious what vibrational intervals make up the progression of bands. The difference between the two main peaks is about 1900 cm.$^{-1}$ suggesting that part of the spectrum, at least, finds its origin in a perturbed triple bond.

7-yne Tetramer.—It was evident from the original spectrum that inadvertent contamination of the tetramer with Apiezon "N" grease had occurred. By subtracting from this spectrum the absorption due to approximately the same concentration of grease as in the sample, a "difference curve" was obtained which gave an indication of the positions of the tetramer bands.[34]

The approximate wave lengths of the major bands of 1,3,5-octatrien-7-yne may be deduced from a consideration of the spectra published for the analogous alcohols by Heilbron, Jones and McCombie[14,37] as well as from data given previously in this paper.

TABLE III

Compound	Main band λ_{max}, mμ	Subsidiary bands λ_{max}, mμ	
$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH$ (B.D.A.)	252	240sh	265sh
$CH_3CH(OH)CH{=}CHCH{=}CHC{\equiv}CH$[14,37] (III)	260	247sh	273sh
$CH_3CH(OH)CH{=}CHCH{=}CHCH{=}CHC{\equiv}CH$[14,37] (IV)	292	279	305

In comparing B.D.A. with the corresponding alcohol III, an 8-mμ shift in the position of the main band is noted. If the same shift is assumed between 1,3,5-octatrien-7-yne and IV, the peaks for the former would be expected at 271, 284 and 297 mμ.

Another approach can be made through a consideration of the effect of the addition of conjugated ethylenic chromophores.

TABLE IV

Compound	Main band λ_{max}, mμ	Shift, mμ
$CH_2{=}CH{-}C{\equiv}CH$ (M.V.A.)	224 (mean)	28
$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH$ (B.D.A.)	252	
$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$ (D.V.A.)	253	30
$CH_2{=}CH{-}CH{=}CH{-}C{\equiv}C{-}CH{=}CH_2$ (I)	283	
$CH_3CH(OH)CH{=}CHCH{=}CHC{\equiv}CH$ (III)	260	32
$CH_3CH(OH)CH{=}CHCH{=}CHCH{=}CHC{\equiv}CH$ (IV)	292	

From the above data it would seem reasonable to expect that the main bands of 1,3,5-octatrien-7-yne would appear at wave lengths about 30 mμ longer than those for B.D.A. This would give values of 270, 282 and 295 mμ. The actual spectrum observed is in good agreement with these predictions. Without knowledge of the extinction coefficients, the identification of the 7-yne tetramer cannot be considered certain from the ultraviolet data alone. However, since no other constitution appears consistent with all of the chemical and spectral evidence, it seems very probable that the compound which has been prepared is 1,3,5-octatrien-7-yne.

Mass Spectra.—The mass spectra of all the acetylene polymers prepared were obtained and appeared to be at least qualitatively consistent with their accepted constitutions. They are not included here. It was noted that very large peaks of mass 78 were obtained with the tetramers. In 1,3,7-octatrien-5-yne this would appear to require the loss of a $CH_2{=}C{=}$ fragment after the migration of a hydrogen from a $CH_2{=}CH{-}$ group to an adjacent carbon. Analogous large peaks of mass 52 were obtained with both trimers.

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[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

Synthesis of Polyenes. V. α-Vitamin A Methyl Ether

BY WILLIAM OROSHNIK

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The synthesis and properties of α-vitamin A methyl ether are described.

Several studies attempting to correlate chemical structure with vitamin A activity have been reported during the past several years. Most of these have dealt with the effects of varying the number and position of methyl groups in the ring and side chain of vitamin A (I) and of vitamin A acid (II), as well as in some of their acetylenic analogs.[1] Except for 7-norvitamin A methyl ether, which was found to be 3.3% as active as vitamin A, these variants showed either negligible or no activity. Replacement of the β-ionone ring with a phenyl group in vitamin A,[2] or with a cyclopentenyl or cycloheptenyl group in 1,2-dehydrovitamin A acid,[3] results in complete loss of activity. The only analogs

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[1] N. A. Milas, *et al.*, THIS JOURNAL, **70**, 1591 (1948); I. Heilbron, E. R. H. Jones and R. W. Richardson, *J. Chem. Soc.*, 287 (1949); I. Heilbron, E. R. H. Jones, D. G. Lewis, R. W. Richardson and B. C. L. Weedon, *ibid.*, 742 (1949); I. Heilbron, E. R. H. Jones, D. G. Lewis and B. C. L. Weedon, *ibid.*, 2023 (1949); G. W. H. Cheeseman, I. Heilbron, E. R. H. Jones and B. C. L. Weedon, *ibid.*, 3120 (1949); J. B. Toogood and B. C. L. Weedon, *ibid.*, 3123 (1949).

[2] B. C. L. Weedon and R. J. Woods, *ibid.*, 2687 (1951).

[3] T. Bruun, I. Heilbron, B. C. L. Weedon and R. J. Woods, *ibid.*, 633 (1950).