

Summary

1. Tetramethylene bromide was prepared by the action of a solution of hydrobromic acid and sulfuric acid on tetramethylene glycol. Monomethylmalonic diethyl ester was prepared from ethyl α -cyanopropionate, and the conditions for the maximum yield of the latter product from α -bromopropionate were elaborated.

2. Methylmalonic ester and tetramethylene bromide were condensed to give ethyl dimethylhexane-tetracarboxylate, which on hydrolysis and decomposition at 240° gave α, α' -dimethylsuberic acid.

3. α, α' -Dimethylsuberic acid exists in two isomeric forms, both of which were isolated pure. Bromination of either acid gave as the principal product one and the same α, α' -dibromo- α, α' -dimethylsuberic acid.

4. Attempts to form a cyclohexane ring by removal of bromine with copper bronze and molecular silver were unsuccessful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

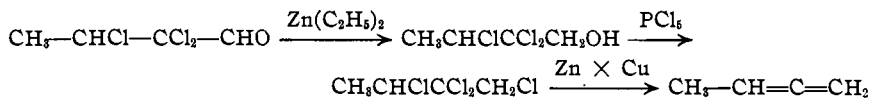
SYNTHESIS AND PYROLYSIS OF METHYLLALLENE AND ETHYLACETYLENE¹

BY CHARLES D. HURD² AND RICHARD N. MEINERT³

RECEIVED NOVEMBER 3, 1930

PUBLISHED JANUARY 12, 1931

The only previous mention of methylallene in the literature is its synthesis in 1888 by Norton and Noyes.⁴ They listed its boiling point at 19° and prepared its tetrabromide. The synthesis was effected through "butyric chloral" by the following steps



Since that time a few general methods of synthesis for allenes have been developed, none of which, however, has received application in the synthesis of methylallene. Bouis' general method⁵ seemed to possess definite advantages and was therefore selected.

Crotonaldehyde was the starting point in the synthesis. It was reduced

¹ This paper contains results obtained in an investigation on "The Pyrolysis of Pure Hydrocarbons" listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

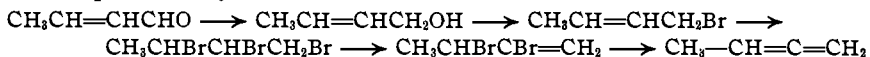
² Director of Project No. 18.

³ American Petroleum Institute Junior Research Fellow.

⁴ Norton and Noyes, *Am. Chem. J.*, 10, 430 (1888).

⁵ Bouis, *Compt. rend.*, 182, 788 (1926); 183, 133 (1926).

to crotyl alcohol, which, in turn, was changed into crotyl bromide. On bromination the latter yielded 1,2,3-tribromobutane. Treatment of this with potassium hydroxide gave rise to 2,3-dibromo-1-butene which, on treatment with zinc dust suspended in ethyl alcohol, yielded methylallene. The steps in this synthesis are



The boiling point of methylallene was found to be 10.3° instead of 19° as was reported by Norton and Noyes. This boiling point was obtained with a standardized thermometer, using a vacuum-jacketed spiral column having a cooling cup at the top of the column so that a drip-back could be maintained. From this, it seems that the older value is in error, possibly due to superheating of the vapor. Other physical constants of methylallene were also determined, as no values for the density or the refractive index have been previously recorded.

No mention of 2,3-dibromo-1-butene is made in the literature. For this reason it was studied in some detail. Methylallene tetrabromide was mentioned in Norton and Noyes' paper but none of its properties was listed. Therefore, it was synthesized, analyzed and its physical properties determined. It was prepared both by bromination of methylallene and by bromination of 2,3-dibromo-1-butene.

Comparison of the Pyrolysis of Allene and Methylallene.—It was found that methylallene resembles allene in its mode of pyrolysis. At temperatures from 500 to 550° , a complete decomposition was effected in thirty-six seconds and three-fourths of the methylallene was converted into liquids of a polymeric nature. Some tarry material and a little carbon were deposited on the walls of the reaction tube.

The liquids were separated as efficiently as possible into fractions containing but one polymer. The lowest boiling fraction was obtained in a state of fairly high purity. It boiled at 110 – 115° and a molecular weight determination showed that it was a dimer of methylallene. Attempts to prove its structure by permanganate oxidation or by ozonization were not fruitful.

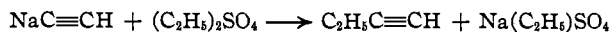
Inasmuch as allene was found⁶ to pyrolyze 66 and 81% in fifty-five and eighty-six seconds, it is evident that it is more resistant to heat than methylallene which was almost completely altered in thirty-six seconds. Although the gaseous products from both allene and methylallene were the lesser products of the reaction, it is interesting to note that methylallene, even with its considerably shorter contact time, gave more than twice the volume of gaseous products. As compared with 77–132 cc. of gas from each liter of allene pyrolyzed, methylallene gave rise to 235–308 cc. Evidently the methyl group is the responsible factor, for much of the

⁶ Meinert and Hurd, *THIS JOURNAL*, **52**, 4540 (1930).

increased volume was due to methane. Paraffin hydrocarbons made up about half of the total volume of the gases, and the n in C_nH_{2n+2} was considerably nearer unity in the gases from methylallene.

There is another interesting difference between allene and its homolog. Whereas the former is isomeric with only one member of the acetylene series, methylallene is isomeric with two, namely with ethylacetylene and dimethylacetylene. In addition, butadiene-1,3 is also isomeric. Of these three, ethylacetylene would be analyzed with acetylene as "acetylenes" with the alkaline potassium iodomercurate reagent. Dimethylacetylene and butadiene would be taken up in the 82.5% sulfuric acid pipet, if not in the 62.5% pipet. Such a mixture of propylene, allene, butadiene and dimethylacetylene would defy identification with the present methods of analysis, but since the total quantity of these gases was small it is evident that such transformations, even if present, must be very minor effects.

Ethylacetylene.—Ethylacetylene has been prepared by several workers, but there is no record of its pyrolysis. Both Reboul's and Lespieau's methods⁷ of preparation are open to the criticism that the ethylacetylene might be contaminated with methylallene. In the former method hydrogen bromide is detached from 2-bromo-1-butene by alcoholic potassium hydroxide. In the latter method, two moles of hydrogen bromide are detached from 1,2-dibromobutane. Picon's method,⁸ wherein ethyl iodide is made to react with sodium acetylide in liquid ammonia, is not open to this objection. Therefore this method, or rather a modification of it, was used in the present study. It was found that diethyl sulfate could be substituted for the much more expensive ethyl iodide. Both methods were tried and it was found that the reaction proceeded more smoothly when the sulfate was used than when the iodide was employed. The equation is



A similar synthesis of methylacetylene, using sodium acetylide and dimethyl sulfate, has been described recently.⁶ There is every reason to believe that this reaction with alkyl sulfates is general. No doubt alkyl *p*-toluenesulfonates could also be used with success.

The boiling point of the ethylacetylene, made by the diethyl sulfate procedure, was 8.5°. This is in agreement with Picon, who also reported 8.5°, but contradicts the work of Reboul, who reported 14–14.5°, and also contradicts the work of Lespieau, who reported 18°.

The relationship between allene and methylacetylene has been shown previously⁶ to be a predictable one on the basis of the three-carbon system inasmuch as methylacetylene pyrolyzed into allene. In the present study we were interested to see if ethylacetylene and methylallene bore a

⁷ Reboul, *Compt. rend.*, 113, 591 (1891); Lespieau, *Ann. chim.*, [8] 27, 146 (1912).

⁸ Picon, *Compt. rend.*, 158, 1184 (1914).

similar relationship, in which case an equation to represent it would be: $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} \longrightarrow \text{CH}_3\text{CH}=\text{C}=\text{CH}_2$. The reverse change, that of methylallene into ethylacetylene, has been brought about⁹ by heating with sodium.

When ethylacetylene was pyrolyzed, it was found that liquids were not so abundantly formed as was the case with methylacetylene. At 580 and 600° only one-third of the gas pyrolyzed appeared as liquids. Comparatively large amounts of gaseous products were formed. Thus, at 600° there were formed from each liter of ethylacetylene pyrolyzed the following amounts of gases: 94 cc. of acetylenes, of which less than a fifth was methylacetylene; 70 cc. of propylene, with possibly a small admixture of allene; 108 cc. of ethylene; 170 cc. of hydrogen, and 435 cc. of paraffins, practically all of which was methane. This total volume of 883 cc. of gas is a little more than double the volume obtained when a temperature of 550° was employed. However, the 403 cc. in the latter case is considerably in excess of the 308 cc. which was produced from ethylallene under almost duplicate conditions. Ethylacetylene was quite stable at 500° using a contact time of thirty-five seconds. Only 23% of it underwent pyrolysis. However, the pyrolysis was practically 100% at 580°.

The liquids obtained were separated into fractions with difficulty, owing to the small amount available. They were shown to be not aromatic in type. Their resemblance to the liquids obtained from the allenes and from methylacetylene was striking, but no definite polymers were identified. Although the refractive index data were of the same order of magnitude as the data from the corresponding fractions obtained from methylallene, the agreement was not close enough to warrant a claim that the two liquids were identical. Certainly, however, they were similar.

Experimental Part

Crotonaldehyde was reduced to crotyl alcohol with ethoxymagnesium chloride using the method of Meerwein.¹⁰ This was converted in 68% yield into crotyl bromide¹¹ by interaction with 48% hydrobromic acid.

1,2,3-Tribromobutane.—Bromine (80 cc., dried with concd. sulfuric acid) was slowly dropped into a cold and rapidly-stirred solution of 203 g. of crotyl bromide in 300 cc. of carbon tetrachloride. The details for this preparation of tribromobutane were analogous to those for the preparation of 1,2,3-tribromopropane (by adding bromine to allyl bromide) which are given in "Organic Syntheses."¹² The tribromobutane thus produced was twice distilled at 14 mm. The yield was 95% of the theoretical. At 14 mm. it boiled at 100–101° and at 20° its index of refraction was 1.5680. Charon¹³

⁹ Jocicz, *J. Russ. Phys.-Chem. Soc.*, 29, 90 (1897).

¹⁰ Meerwein, *Ann.*, 444, 221 (1925).

¹¹ Charon, *Ann. chim.*, [7] 17, 233 (1899).

¹² Johnson and McEwen, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 99.

¹³ Charon, Ref. 11, p. 239.

reported the b. p. to be 113–114° at 21 mm. Delaby¹⁴ reported the b. p. at 19 mm. to be 110–113° and the index of refraction, n_D^{15} 1.569.

2,3-Dibromo-1-butene.—In a one-liter balloon flask were placed 419 g. of 1,2,3-tribromobutane, 20 cc. of water and 100 g. of sodium hydroxide. The flask was connected to an efficient condenser by a wide bent tube and a receiving flask was fitted to the condenser by means of an adapter. The receiver was immersed in a bath of ice water. The contents of the flask were heated directly with a small, slightly luminous flame which was directed by the hand against the flask with a rotary motion. The flask was shaken from time to time, and gradually the alkaline layer became emulsified as the reaction progressed. The reaction proceeded very rapidly at first and developed considerable heat, enough in fact to cause spontaneous distillation of some of the product. After the first rapid reaction had subsided, the flask was again heated until all the liquid had distilled over, after which the solid material in the flask was strongly heated until no more distillate was obtained. The bromide in the receiving flask was washed with water, and the bromide layer separated from the water layer. The 2,3-dibromo-1-butene, which contained some unchanged tribromobutane, was then distilled under reduced pressure. The fraction boiling in the range of 85–90° at 40 mm. was collected. The residue, consisting of unchanged tribromobutane, was saved to be worked up with sodium hydroxide after a sufficient amount had accumulated from several runs. The fraction consisting of the dibromobutene with a small amount of the tribromobutane was redistilled; b. p. 75° at 20 mm. The small amount of residue was combined with the previous residues. The yield was 86%. Analyses of the dibromobutene and of the methylallene tetrabromide which follows were performed by Mr. Forrest Pilgrim.

Anal. Subs., 0.2212: AgBr, 0.3875. Calcd. for $C_4H_6Br_2$: Br, 74.72. Found: Br, 74.55.

The physical constants were found to be as follows: density, d_4^{20} 1.8881, index of refraction, n_D^{20} 1.5556; n_D^{20} 1.5464; $n_D^{26.5}$ 1.5430. The change of the index of refraction with change of temperature, $dn_D/dT = -0.00053$; at 20 mm., the boiling point was 75°.

Preparation of Methylallene Tetrabromide.—Fifty grams of 2,3-dibromo-1-butene was added to an equal volume of dry carbon tetrachloride, and the calculated amount of bromide was added slowly. The reaction was slow in starting. As a matter of fact it was necessary to warm the flask gently to start the reaction but after once started it became so exothermic that it was necessary to cool the reacting mixture. When all of the bromine had been added, the solvent was removed and the methylallene tetrabromide was distilled at reduced pressure. The distillate was redistilled, only the middle portion being retained for the determination of the constants.

Anal. Subs., 0.2218: AgBr, 0.4463. Calcd. for $C_4H_6Br_4$: Br, 85.53. Found: Br, 85.63.

The physical constants were found to be as follows: melting point, -2° ; b. p. at 7 mm., 97.5° ; specific gravity, d_4^{20} 2.510 (the average of 2.5097 and 2.5103); index of refraction at 3.6° , 1.6152 and at 20.0° , 1.6070. From these data, $dn_D/dT = -0.00050$.

The only previous mention of this compound is in the paper of Norton and Noyes in 1888. Therein it was stated to be prepared from methylallene and bromine, and it was stated not to solidify at -17° . In determining the melting point it was found in the present work that the bromide had to be cooled to -40° until solidification occurred, but with a little of the solid material in contact with the liquid bromide, it could be solidified at -2° , and melted within half a degree of this point.

Preparation of Methylallene.—A one-liter, three-necked flask was fitted with a

¹⁴ Delaby, *Compt. rend.*, 176, 589 (1923). These values are used in "International Critical Tables," Vol. I, p. 186.

reflux condenser inclined at an angle of 45° , a dropping funnel, and a tube reaching nearly to the bottom of the flask, so that an inert gas could be used to flush out the apparatus. A delivery tube leading from the top of the condenser was fitted to a 100-cc. distilling flask which served as a trap and was kept at a temperature of 30° by a water-bath. A spiral condenser and receiver was fitted to the side arm of the trap flask. This condenser-receiver was kept at a temperature of -12° by ice and salt. The receiver was so arranged that the condensed liquid could be blown into a bottle for storage without removing any connections. The main reaction flask was heated with a water-bath.

Ethyl alcohol (300 cc.) and zinc dust (160 g.) were placed in the reaction flask. The 2,3-dibromo-1-butene (131 g.) was added slowly through the dropping funnel, during which time the alcohol in the flask was kept boiling vigorously. The methylallene all passed over into the condenser and was liquefied. There was a small amount of alcohol which collected in the trap. The reflux condenser was kept at $35-40^\circ$ in order to retain the alcohol but at the same time to permit the methylallene to escape. After all of the bromide had been added, the alcohol in the flask was boiled for several minutes and carbon dioxide was bubbled through to sweep out all of the methylallene. The crude material thus obtained was fractionated, using the spiral column previously described. The yield was 72%, calculated on the basis of the pure, distilled methylallene.

The physical properties of the liquid methylallene were as follows: b. p. 10.3° ; d_4^0 0.676; $n_D^{1.3}$ 1.4205.

Pyrolysis

Apparatus.—The apparatus used in the pyrolysis of both methylallene and ethylacetylene was the same as has been described by the authors in a previous paper,¹⁵ except for the manner in which the hydrocarbon was introduced into the system. The liquefied hydrocarbon was placed in a 25-cc. water-jacketed buret. The buret was attached by means of a rubber stopper to a 100-cc. distilling flask immersed in a bath at 35° . This served as a vaporizing chamber, and the gas was then led from the side arm of the distilling flask through the flowmeter and manometer connections into the reaction chamber as previously described. A spiral condenser which was immersed in a bath at -15° served to condense any unchanged methylallene which came off with the exit gases.

The exit gaseous mixture was analyzed by the method of Hurd and Spence.¹⁶ Of supplementary interest, it was found that methylallene resembles propylene very decidedly in its rate of absorption in sulfuric acid solutions. Neither of these gases is appreciably soluble in the 62.5% sulfuric acid solution or in the alkaline potassium iodomercurate reagent. In 82.5% sulfuric acid, methylallene and propylene are absorbed at about the same rate. This rate is about 1.2 times faster than the rate for allene. It is interesting to note that in dilute acetic acid allene is absorbed about three times more rapidly than propylene. With a 2:1 solution of glacial acetic acid and water (in an Orsat pipet), 8.2 cc. of methylallene dissolved in two minutes, whereas only 2.7 cc. of propylene was absorbed. The same ratio held in more dilute solutions. For purposes of analysis of allene-propylene mixtures by this method, a ratio considerably greater than 3:1 would be required.

Pyrolysis of Methylallene.—The data obtained in four experiments are given in Table I.

In the first run, the off-gas consisted almost entirely of the carbon dioxide

¹⁵ Meinert and Hurd, *THIS JOURNAL*, **52**, 4540 (1930).

¹⁶ Hurd and Spence, *ibid.*, **51**, 3356-7 (1929).

TABLE I
 RESULTS OF THE PYROLYSIS OF METHYLALLENE

Run number	1	2	3	4
Temperature, °C.	405	500	500	550
Methylallene used, g.	13.1	20.1	20.1	11.2
Methylallene used, cc. as gas	5420	8340	8340	4640
Volume of off-gas, cc.	600	2160	3040	1838
Pressure in tube, mm.	725	720	737	727
Rate of flow of in-gas, cc./min.	132	135	137	129
Contact time, sec.	46.3	36.6	36.1	37.0
Analysis of off-gas, % by vol.				
Carbon dioxide	85	5.2	8.2	17.9
Acetylenes	..	3.3	2.7	0.7
Gas soluble in 62.5% H ₂ SO ₄	..	1.1	1.7	2.5
Gas soluble in 82.5% H ₂ SO ₄	..	19.1	19.0	19.0
Ethylene	..	8.1	8.1	5.7
Hydrogen	..	12.0	13.1	7.5
Paraffins	..	47.1	39.6	43.8
<i>n</i> in C _n H _{2n+2}	..	1.23	1.19	1.33
Percentage of pyrolysis	28	95-100	95-100	95-100
Weight of liquids, g.	3	14.6	14.8	8.0
% of liquids by wt. of methylallene pyrolyzed	22	72.7	73.6	73.2
Total volume of gaseous products formed, cc.				
Acetylenes	..	72	82	13
Soluble in 62.5% H ₂ SO ₄	..	24	52	46
Propylene, allene, etc.	..	410	577	349
Ethylene	..	175	246	105
Hydrogen	..	260	398	138
Paraffins	..	1018	1204	806
Cc. of gases formed per liter of entering methylallene				
Acetylenes	..	8.6	9.9	3.0
Soluble in 62.5% H ₂ SO ₄	..	3.0	6.2	10.0
Propylene, allene, etc.	..	49.2	69.2	75.8
Ethylene	..	21.0	29.5	22.6
Hydrogen	..	31.2	47.8	29.9
Paraffins	..	122.0	145.0	173.4

used to fill the system at the start of the experiment. No analysis of the remainder of this gas was made.

Reference to Table I shows that the reaction leading to the formation of liquids of high boiling point was the major effect in this pyrolysis. This was also the case with allene. The gaseous products were relatively unimportant, with the exception of the paraffin hydrocarbons which were present to the extent of 12-17% of the volume of methylallene pyrolyzed. Some carbon was deposited in the reaction tube.

The liquids which were obtained when methylallene was pyrolyzed were fractionally distilled using a 100-cc. Claisen flask which was equipped with a Vigreux column. The higher-boiling fraction was distilled under reduced pressure. The following fractions were obtained:

Fraction	B. p., °C.	n_D	Weight, g.
A	30-42	1.3
B	42-75	0.7
C	75-135	1.4815	6.6
D	135-200	1.4978	9.1
E	100-200 (33 mm.)	1.547	8.6
Residue			10.7

The residue was a very viscous, rubbery material that partially solidified on cooling.

Fraction A was shown to contain considerable unchanged methylallene by preparing the bromide. A mixture of the di- and tetrabromides was obtained as is always the case, and this was fractionally distilled in so far as the small volume would permit. The first portion boiled at 120-130° at 40 mm. and had a refractive index of 1.5408 at 26.5°. If pure, 2,3-dibromo-1-butene has a refractive index of 1.5430 at 26.5°. The second portion boiled at 150-160° at 40 mm. and had a refractive index of 1.5905 at 27.5°; $n_D^{27.5}$ for pure methylallene tetrabromide is 1.6033. The first portion was evidently the dibromide and the second was largely the tetrabromide of methylallene, with a small amount of the dibromide as an impurity. No solid tetrabromide was produced, which fact speaks for the absence of butadiene tetrabromide in this material.

Portion C of the liquids was purified by distillation. It was perfectly clear and had an odor resembling that of kerosene. The boiling point was 110-115° and the refractive index 1.4758 at 27°. The molecular weight of this sample was determined by the Victor Meyer method.

Mol. wt. Subs., 0.1582, 0.0809: cc. of gas formed, 41.7 at 26°, 752.7 mm.; 18.4 at 29°, 748.3 mm. (measured over water). *Mol. wt. found:* 97.7, 116. *Mean,* 105.9. *Calculated mol. wt. of C₈H₁₂:* 108.

This, together with the boiling point and the refractive index, shows that fraction C is a dimer of methylallene or perhaps a mixture of several dimers, inasmuch as several are possible.

Preparation of Ethylacetylene.—Thirty-six grams of sodium was dissolved in about 500 cc. of liquid ammonia. Then acetylene was passed into the solution till the blue color, characteristic of sodium in liquid ammonia, had disappeared. Following this, 230 g. of diethyl sulfate was added slowly, keeping the flask at -60°. Essentially the apparatus and procedure was identical to the one which has been recently described for the synthesis of methylacetylene¹⁷ from dimethyl sulfate and sodium acetylide. The preparation of ethylacetylene by this method proceeded even more smoothly than the preparation of methylacetylene.

The ethylacetylene was liquefied and fractionally distilled, using a low-pitched, vacuum-jacketed spiral¹⁸ column. It boiled at 8.5°, which is in agreement with the value found by Picon. The yield of the pure, redistilled ethylacetylene was 97.5 g. which represents a yield of 60%, based on the equation $\text{Et}_2\text{SO}_4 + \text{HC}\equiv\text{CNa} \longrightarrow \text{EtC}\equiv\text{CH} + \text{NaEtSO}_4$.

¹⁷ Meinert and Hurd, *THIS JOURNAL*, **52**, 4544 (1930).

¹⁸ Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

Pyrolysis of Ethylacetylene.—The ethylacetylene was pyrolyzed, using the same apparatus that was used for the methylallene experiments. In this case the spiral condenser-receiver was kept at a temperature of -20° so that all of the ethylacetylene which was not changed in the hot zone would be condensed and prevented from passing into the gas collection bottle along with the off-gas from the reaction. The data are given in Table II.

TABLE II
RESULTS OF THE PYROLYSIS OF ETHYLACETYLENE

Run	1	2	3	4
Temperature, $^{\circ}\text{C}$.	500	550	580	600
Contact time, seconds	34.8	34.5	35.0	30.0
Ethylacetylene used, g.	15.5	16.1	18.4	16.4
Ethylacetylene used, cc. of gas	6440	6680	7640	6800
Ethylacetylene recovered, g.	12.0	8.6	0.0	0.0
Ethylacetylene pyrolyzed, g.	3.5	7.5	18.4	16.4
Ethylacetylene pyrolyzed, cc. of gas	1450	3105	7640	6800
Off-gas not condensed at -20° , cc.	750	1750	6600	6800
Entering flow, cc./min.	163	150	146	180
Pressure in tube, mm.	725	732	737	740
Analysis of off-gas, % by volume				
Carbon dioxide	83.0	22.4	7.3	5.0
Acetylenes	..	15.6	12.8	9.4
Gas soluble in 82.5% H_2SO_4	..	7.8	8.7	7.6
Ethylene	..	6.6	9.7	10.8
Hydrogen	..	4.6	13.6	17.0
Paraffins	..	37.4	40.1	43.4
n in $\text{C}_n\text{H}_{2n+2}$..	1.49	1.23	1.18
Percentage decomposition	22.6	47	95-100	95-100
Wt. of liquids formed, g.	1.5	4.0	6.7	6.0
% of liquids formed by wt. of ethylacetylene pyrolyzed	43	53	36.5	36.6
Total volume of gaseous products, cc.				
Acetylenes	..	273	837	640
Gas soluble in 82.5% H_2SO_4	..	137	584	517
Ethylene	..	105	640	735
Hydrogen	..	81	897	1157
Paraffins	..	655	2640	2950
Cc. of gaseous products formed per liter of ethylacetylene pyrolyzed				
Acetylenes	..	88.4	110	94.2
Gas soluble in 82.5% H_2SO_4	..	43.9	76.5	76.2
Ethylene	..	33.8	83.8	108
Hydrogen	..	26.0	118	170
Paraffins	..	211.0	346	435

The off-gas from Runs 3 and 4 was combined and had a total volume of 11,200 cc. It was passed slowly through a spiral condenser and receiver maintained at a temperature of -78° by a bath of acetone and solid carbon

dioxide. About 2 cc. of liquid condensed. This was allowed to vaporize into two fractions by placing the receiver first in an ice-bath and collecting all the gas that came off at this temperature, and then allowing the receiver to warm up to room temperature and collecting this gas. The first fraction consisted of 500 cc. of gas, and the second fraction was also 500 cc. of gas. These two fractions (A and B) gave the following results upon analysis

Fraction	A	B
Acetylenes, %	16.2	41.6
Gas soluble in 82.5% H ₂ SO ₄ , %	32.4	47.2
Ethylene, %	12.2	0.0
Carbon dioxide, %	6.5	2.1

From this it can be calculated that the following volumes of substances were present in the two fractions

	A	B
Acetylenes, cc.	81	208
Gas soluble in 82.5% H ₂ SO ₄ , cc.	162	236
Ethylene, cc.	61	...

Since the total volume of gas treated in the experiment was 11,200 cc. by adding together the amounts from fractions A and B, it is possible to account for 289 cc. or 2.6% of acetylenes, 398 cc. or 3.5% of hydrocarbons absorbed in 82.5% sulfuric acid and 61 cc. or 0.56% of ethylene. Reference to Table II makes it evident that only about one-fourth of the total acetylenes present in the gas had condensed at -78° . Since methylacetylene boils at -23.8° and ethylacetylene at $+8.5^{\circ}$, the uncondensed acetylenes must represent ordinary acetylene (C₂H₂). The fact that a small amount of ethylene, which boils at -103° , was condensed makes it appear probable that some acetylene, which boils at -81° , would also condense. Hence the acetylenes found in fraction A are probably C₂H₂ for the most part.

About one-third of all the hydrocarbons from the pyrolysis which were absorbed in 82.4% sulfuric acid were condensed at -78° . This would certainly include any allene or methylallene which might be present, and would include much propylene as well, which boils at -50° .

In order to ascertain whether there was any methylallene present, all of the acetylenes were removed from a portion of sample B, and the gas which remained was placed in a cylinder inverted in a bath at -5° which completely surrounded it. There was no liquefaction as witnessed by the fact that there was no contraction in volume. Hence the gas of fraction B which was absorbed in 82.5% sulfuric acid could not have been methylallene, nor could any appreciable amounts of dimethylacetylene or butadiene-1,3 have been present. It may have been either allene or propylene. However, taking into account the velocity of the pyrolysis of allene at

temperatures above 550°, it is doubtful if any allene would be found in the off-gas from these experiments.

Referring again to Table II, these conclusions indicate that at least 80% of the gases listed as acetylenes consist of acetylene, C₂H₂, the remainder being methylacetylene. The gases absorbed in 82.5% sulfuric acid are considered to be almost entirely propylene, with possibly small amounts of allene, but with no methylallene.

Liquids.—The liquids obtained in the pyrolysis of ethylacetylene were all combined and fractionally distilled. The refractive indices of the various fractions were determined, with these results.

Fraction	Weight, g.	B. p., °C.	n_D^{25}
A	0.5	30–65
B	1.0	65–100	1.4720
C	2.0	100–135	1.4925
D	5.0	135–200	1.5242
Residue	8.5		

Fractions B and C were combined and redistilled, and a fraction boiling from 110 to 120° was taken. Its refractive index was 1.4905. The boiling points were not sharp for the different fractions, and the temperature ascended gradually throughout the distillation with no indication of a pure compound distilling over. The very small volume of these fractions made it impossible to purify them further by distillation methods.

The odors and colors of the fractions were very similar to those obtained in the pyrolysis of allene, and especially of methylacetylene. A comparison of the index of refraction data of the corresponding fractions of the liquids obtained from ethylacetylene and methylacetylene shows a marked similarity. They are no doubt compounds of the same type, and there are some indications that some of the same liquids are present from both substances.

Summary

2,3-Dibromo-1-butene and 1,2,2,3-tetrabromobutane have been prepared and their physical properties determined. Methylallene has been prepared in a state of purity and its density and refractive index determined. A new synthesis for ethylacetylene has been developed.

It has been shown that methylallene polymerizes when pyrolyzed, and the presence of a dimer among the polymerization products has been demonstrated. In addition to the polymers, methane, ethane, ethylene, hydrogen, propylene and allene are formed in small amounts.

In the pyrolysis of ethylacetylene it has been shown that from one-third to one-half of the material was converted into liquids which resembled the liquids formed from methylallene, allene and methylacetylene. In addition to the liquids, there were produced paraffin hydrocarbons, hydrogen,

ethylene and propylene in the ratio approximately of 9:3:2:2, as well as small amounts of acetylene, methylacetylene and allene.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE KANSAS AGRICULTURAL EXPERIMENT STATION]

INDICATIONS OF GLUCOSE IN MILK¹

By CARRELL H. WHITNAH

RECEIVED NOVEMBER 3, 1930

PUBLISHED JANUARY 12, 1931

The work here reported was started by a request from the Dairy Department to determine if a large increase in the blood sugar of cows would cause the appearance of glucose in the milk. The samples of milk were furnished by the Dairy Department in connection with various projects in which the Department of Chemistry is cooperating.

The milk of lot number one was a composite from all herds supplying milk to the Dairy Department. That of lot number seven was taken separately from three of these herds. The other lots were individual milkings from each of three cows over the intervals indicated.

The official polarimetric method² for estimating milk sugar was modified to facilitate the estimation of small amounts of glucose in milk. Fifty cc. of milk was clarified, without further dilution, with 2.5 cc. of official mercuric nitrate solution. The mixture was filtered after standing for five minutes and the rotation of the filtrate measured at 20° in a 20-cm. water-jacketed tube.

Fermentation with yeast, as applied by Raymond and Blanco³ to other material, was tried as a method of removing any glucose in the milk. To determine whether this method was practicable, 0.5% of glucose was added to a sample of milk, the rotation of which was previously shown not to be changed by treatment with yeast. The extra rotation due to the added glucose was completely removed from 50-cc. samples of this sweetened milk by contact with 3 g. of yeast at 30° in between fifteen and thirty minutes, or with 1 g. of yeast in less than two hours. Samples treated with 3 g. of yeast showed no further change on standing for two hours with the yeast. It was therefore concluded that all the glucose and none of the lactose was removed, and that one hour would be a suitable time for the fermentation.

The yeast was prepared from Fleischmann's baker's yeast by washing and centrifuging five times.⁴ The last wash water was found to be clear and free from reducing sugars.

Analyses of 275 samples of milk showed decrease of rotation, after treating 50-cc. portions with 3 g. of yeast for one hour, varying from zero, in 20 cases, to a decrease corresponding to 0.35% of glucose in the milk. In eleven other samples the rotation was observed to increase from 0.01 to 0.07% of the original rotation on treatment with yeast. It is, at present, uncertain whether these apparent increases should be accepted

¹ Contribution No. 156 from the Department of Chemistry.

² Method of Analysis of the Association of Official Agricultural Chemists, 1925.

³ A. L. Raymond and J. G. Blanco, *J. Biol. Chem.*, 79, 649 (1928).

⁴ M. Somoji, *ibid.*, 75, 33 (1927).