

Synthesis and Physical Properties of Several Acetylenic Hydrocarbons

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As a part of researches conducted on hydrocarbons as jet-fuel components under the auspices of the National Advisory Committee for Aeronautics, a number of acetylenic hydrocarbons and their intermediates have been prepared. The details of these syntheses and the physical constants measured on the compounds are presented.

1. Introduction

The work described herein is the continuation of hydrocarbon research conducted at the Bureau since 1937 under the administrative sponsorship of the National Advisory Committee for Aeronautics. Previous papers [5, 12]³ have described the preparation and physical properties of a number of aliphatic hydrocarbons and their intermediates; these were used mainly in researches on the detonation proper-

ties of fuels for reciprocating engines. More recently, attention has been directed to fuels for reaction engines. The emphasis at the Bureau was thereby shifted to hydrocarbons useful in investigations of basic problems in jet-fuel combustion. The hydrocarbons selected for synthesis were alkynes, alkyadiynes, and an alkenyne, and were chosen in order to ascertain the effects of structure on flame speed and other properties. These compounds and the intermediates used in their syntheses are listed in table 1, in which are enumerated the physical constants of the material prepared, the purities of selected hydrocarbons, and the melting points of the mercury derivative of the 1-acetylenes [6].

TABLE 1. Physical properties of compounds prepared

Compound	Boiling point at 760 mm Hg	Freezing point in air	Density at 20° C	Refractive index at 20° C	Melting point of mercury derivative [6]	Purity ^a
	° C	° C	g/ml	<i>n</i> _D ²⁰	° C	Mole percent
Propyne.....	208 to 210	97.6 MS
1-Butyne.....	-125.87	161.5 to 162
2-Butyne.....	26.97	-32.33	0.6906	1.3918	99.88 FP
1-Pentyne.....	40.233	-106.5	.69400	1.38476	117 to 118	99.5 MS
2-Pentyne.....	56.12	-109.45	.71040	1.40336
3-Methyl-1-butyne.....	29.0	^b nf	.6727	1.3756	^c 76.5 to 77
1-Hexyne.....	71.38	-132.4	.7149	1.3986	95.7 to 96.7
2-Hexyne.....	84.52	-89.58	.73146	1.41382
3-Hexyne.....	81.43	-103.16	.7226	1.4112
3-Methyl-1-pentyne.....	57.7	nf	.7037	1.3916	74 to 75
4-Methyl-1-pentyne.....	61.3	-105.3	.7047	1.3932	100 to 100.5
4-Methyl-2-pentyne.....	73.13	-110.37	.7157	1.4057
3,3-Dimethyl-1-butyne.....	37.72	-78.21	.6678	1.3736	92.5 to 93.0
4-Methyl-2-hexyne.....	99.54	-107.63	.73855	1.4170	99.8 MS
5-Methyl-2-hexyne.....	102.46	^d -92.91	.73776	1.41762	99.89 LTC
2-Methyl-3-hexyne.....	95.2	-116.7	.7249	1.4120
1-Octyne.....	126.20	-79.6	.7468	1.4163	80.5 to 81.0
1-Pentyne-3-ene(<i>cis</i> and <i>trans</i>) ^e	43.8 to 44.0 ^f7304 to .7297	1.4293 to 1.4340
1-Pentyne-3-ene(<i>trans</i>) ^e	51.97270	1.4377	155.3 to 157
1,3-Butadiyne.....	10 to 11	99.8 MS
1,5-Hexadiyne.....	87.858	-4.266	.79943	1.43934	Polymer
1-Pentyne-4-ol.....	27.3	nf	.8957	1.4388
1,1-Dichloro-3-methylbutane.....	^f 129.6	nf	1.0473	1.4342
1,1-Dichloro-3-methylpentane.....	^g 157.2	nf	1.0373	1.4426
1,1-Dichloro-3,3-dimethylbutane.....	^h 146.0	-60.3	1.0272	1.4388
4-Methyl-2-chloro-1-pentene.....	102 to 103
1,2,5,6-Tetrabromohexane.....	49 to 50

^a FP, purity from freezing curve analysis [16]; LTC, purity by low-temperature calorimetry (by G. T. Furukawa, Thermodynamics Section [4]); MS, purity by mass spectrometry (by V. H. Dibeler and F. L. Mohler, Mass Spectrometry Section.)

^b nf is nonfreezing, glassy at low temperatures.

^c On freshly prepared material. After standing for 4 days, material became yellow and did not melt at 150° C.

^d Triple point, measured in calorimeter by G. T. Furukawa of Thermodynamics Section. Molar heat of fusion = 10,600 joules.

^e *cis* and *trans* designations from infrared spectrometry, performed and interpreted by F. A. Smith and J. E. Stewart.

^f 90° C at 240 mm.

^g 92° C at 100 mm.

^h 85° C at 104 mm.

2. Equipment

2.1. Reaction Vessels

Large-scale reactions were carried out in a commercial 50-gal stainless-steel reaction vessel designed to permit any jacket temperature from 5° to 150° C to be maintained. This kettle is described in a previous publication [5].

For experimental runs and for small-scale work, a 5-gal brass kettle was used. This was made of 12-in. brass tubing with a sheet-brass bottom brazed into place and a removable flanged top to facilitate emptying and cleaning. The top was equipped with openings for stirrer, addition vessel, reflux condenser, and observation hole, and was held in place by means of C-clamps and sealed by means of a neoprene gasket pressed between the flanges. This reactor was of sufficiently small size to allow immersion in a bath for heating or cooling, as necessary. Because of the relatively high heat conductivity of the metal, this apparatus permitted highly exothermic reactions, such as halide condensations (see sec. 3.4), to be run with appreciable savings of time and much greater safety than prevails with the use of glass equipment of equal capacity. Glass equipment was used only for very small-scale preliminary reactions.

For reactions using liquid ammonia as a solvent (see sec. 3.2 and 3.3), a 10-gal stainless-steel reaction vessel was installed. This was jacketed for temperature control and equipped with appropriate valves and flanged openings; on the bottom was a 2-in. drain valve, on the top were openings for a 2-in. peephole, gas inlet, and reflux condenser. The peephole was normally stoppered, but when necessary, it could be used for observation of the reaction or addition of reagents. Acetylene and other gases were introduced through a ¼-in. steel pipe brazed through a flange and extending almost to the bottom of the vessel. The condenser consisted of a 30-gal open-top insulated cylinder, through which passed two intertwined coils made of 20-ft lengths of ¾-in. steel pipe welded into a 1-in. tee at the bottom. The 1-in. tee connected to a sight-glass for observation of reflux and thence to the kettle. Stirring was effected by means of a built-in stirrer driven by an explosion-proof motor. The kettle was insulated on all sides with a 6-in. layer of ground cork. When in continuous operation, it was necessary to fill the condenser with dry ice only at 8-hr intervals.

2.2. Distillation Equipment

There were seven stills available for this work. These were used for purification of reagents, for the fractionation of final hydrocarbons and some of the intermediates, and have been described previously [5]. For convenience, the salient features of each are listed in table 2.

TABLE 2.

Still	Type	Size	Packing	Pot capacity
5----	Total reflux variable takeoff.	cm 150 by 2.2..	¾-in. stainless steel helices from 0.010-in. wire.	ml 200 to 5,000.
6-----	do.	150 by 2.2..	¾-in. glass helices.	200 to 5,000.
17-----	Podbielniak Hypercal.	127 by 0.8..	Heli-grid-----	250 to 5,000.
19-----	do.	250 by 2.5..	do.	250 to 5,000.
21-----	Total reflux variable takeoff.	120 by 3.5..	¾-in. glass helices.	22,000.
22-----	do.	183 by 2.5..	¾-in. stainless steel helices from 0.010-in. wire.	500 to 5,000.
28-----	do.	35 by 2.5..	¼-in. glass helices.	2,000.

3. Methods and Technique

3.1. Preparation of Grignard Reagents

The Grignard reagents necessary for some of the syntheses were prepared in the 50-gal stainless-steel kettle according to the methods used previously [5]. In all cases the Grignard reagent was then reacted in place.

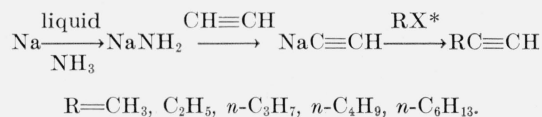
3.2. Preparation of Sodium Acetylide

For the preparation of many of the acetylene homologs, the starting material was monosodium or disodium acetylide. The flow sheets of the several synthetic schemes, using these compounds as starting materials, are given as methods A to C in table 3, in which are enumerated the several different synthetic routes used in this work and the compounds prepared thereby. The technique of preparing sodium acetylide was adapted from that used by K. W. Greenlee and his associates at Ohio State University, Columbus, Ohio. These sodium acetylides were conveniently prepared in the 10-gal stainless-steel reactor and alkylated in place to the desired alkyne. A typical preparation of 60 moles of monosodium acetylide is described below.

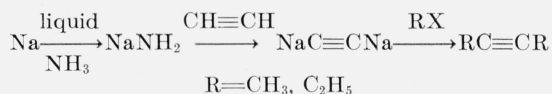
About 10 kg of commercial anhydrous ammonia was added in the liquid phase to the reactor through the gas-inlet tube, the cold refluxing ammonia being sufficient to cool the pot. Then 15 g of ferric chloride was added deftly in 3 portions through the peephole. The reaction was quite violent, and after the reflux had subsided, about 60 g of sodium cut in small pieces was added. After the sodium had dissolved, a stream of dry air was passed through the gas-inlet tube for about 1½ min, in order to form a catalyst, which would be effective in converting the sodium into the amide rapidly. Sodium cut into approximately ½-in. cubes was then added in portions with stirring until a total of 1,389 g (60 g-atoms) was added. The reaction was vigorous, and a continuous

TABLE 3. Flow sheet of alkyne syntheses

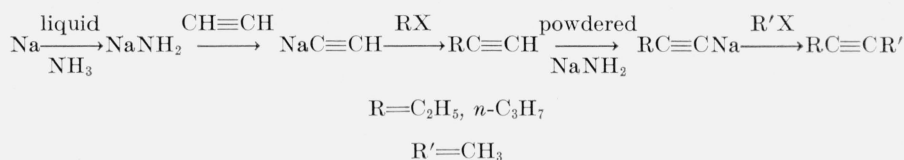
Method A. Alkylation of monosodium acetylide:



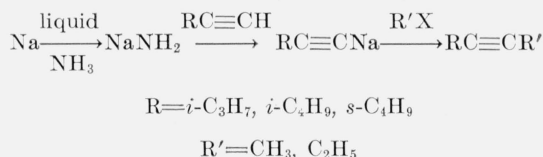
Method B. Symmetrical alkylation of disodium acetylide:



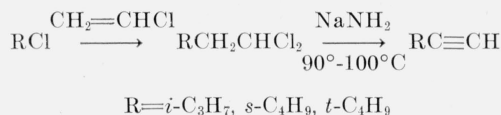
Method C. Unsymmetrical alkylation of acetylene (in situ):



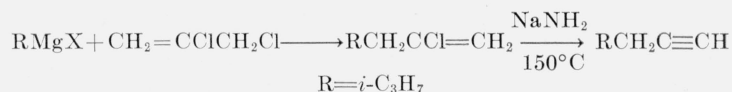
Method D. Alkylation of 1-alkynes:



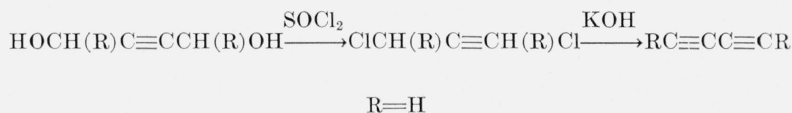
Method E. Vinylation and dehydrohalogenation reactions:



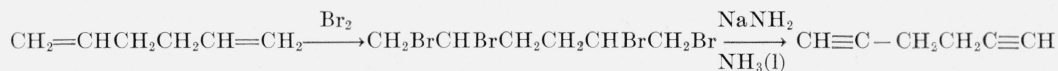
Method F. Alkylation and dehydrohalogenation reactions:



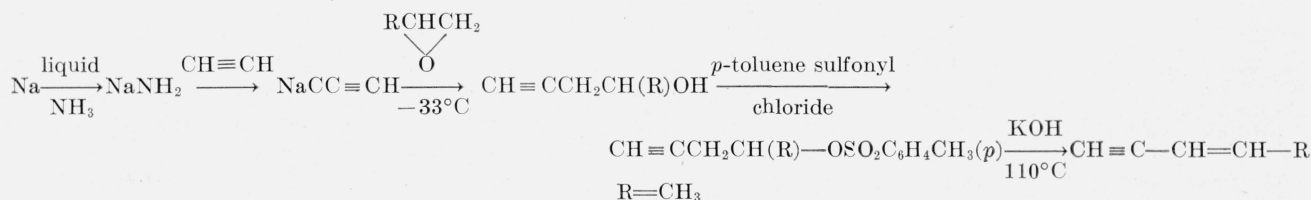
Method G. Dehydrohalogenation and isomerization reactions:



Method H. Halogenation and dehydrohalogenation:



Method I. Alkynylation and dehydration reactions:



*RX indicates alkyl halide or alkyl sulfate.

stream of hydrogen was evolved. The solution was then stirred for 2 hr before the addition of acetylene. In several cases the conversion of sodium to sodium amide was extremely slow, the sodium merely dissolving in the ammonia. This was evidenced by the persistent, intense blue color of the liquid. In such cases the solution was permitted to stand overnight, or until it attained a characteristic black hue and the blue coloration was completely gone.

Commercial acetylene gas was then passed into the sodium-amide solution through the gas-inlet tube after it had passed through a sulfuric acid scrubber to remove entrained acetone. Disodium acetylide was formed first and imparted a milky-white appearance to the liquid. For the preparation of disodium acetylide, the gas addition was stopped when the molal ratio of acetylene to sodium was one-half. Upon continued addition of acetylene, the disodium salt was converted to the monosodium acetylide, and as the theoretical quantity for monosodium-acetylide formation was approached, the color of the solution regained its black appearance. Thus, from 60 g-atoms of original sodium, 30 moles of disodium acetylide were formed with 780 g of acetylene, whereas the addition of 1,560 g of acetylene caused formation of 60 moles of monosodium acetylide.

3.3. Alkylation Reactions

The alkylation of the sodium acetylides and their homologs was carried out in the 10-gal stainless-steel reactor. Because of the variation in the technique, representative alkylations illustrating methods A to D in table 3 are described below. A résumé of the preparation of each acetylene made thereby is given in table 4.

(a) *Method A.* Propyne was prepared in 65-percent yield by treatment of monosodium acetylide with dimethyl sulfate in liquid ammonia. Sixty theoretical moles of monosodium acetylide was prepared from 1.70 kg of acetylene (65 moles), 1.61 kg of sodium (70 g-atoms), and 18 g of ferric chloride

in 11 kg of liquid ammonia, using a modification of the previously described method (see sec. 3.2). Because of the difficulty in separating acetylene from propyne, care had to be taken to avoid an excess of acetylene; consequently, only enough acetylene was added to make 60 moles of monosodium acetylide and 5 moles of disodium acetylide. In this case, the 2-butyne formed as a by-product from the disodium acetylide present offered no problem in the purification step.

To this acetylide solution was added 8.8 kg (70 moles) of dimethylsulfate over a period of 3 hr. The reaction was quite vigorous but easily controllable. The mixture was stirred overnight, after which it was treated with 11.5 liters of water. The condenser was then blocked off at the sight glass, and a delivery tube attached through the peephole flange. The evolved gas was passed through a train consisting of a water trap with a constant-level continuous-flow siphon, cold 10-percent sulfuric acid, a calcium-chloride drying tower, a dry-ice condenser, and was caught in a chilled steel cylinder containing a small amount of acetone. The product from two runs was fractionated in column 19 to recover 3.25 kg (81 moles) of purified 1-propyne (65-percent yield).

(b) *Method B.* 2-butyne was prepared by the reaction of dimethylsulfate with disodium acetylide in liquid ammonia. Forty moles of disodium acetylide were prepared from 1,840 g of sodium (80 g-atoms), 1.05 kg (40 moles) of acetylene, and 20 g of ferric chloride in 14.5 kg of liquid ammonia, by the technique previously described (see sec. 3.2). To this mixture was added 10.6 kg (84 moles) of dimethylsulfate over a period of 6 hr; the reaction was vigorous, but controllable. The solution was stirred for 16 hr, and the 2-butyne was recovered in the same manner used for propyne. In this case, however, most of the 2-butyne condensed in the chilled dilute sulfuric acid, and was distilled from this flask through a calcium-chloride tower into a steel bomb by heating the flask with an electric heating mantle. This run

TABLE 4. Alkynes by alkylation

Hydrocarbon	Prepara- tive method	Reactants				Alkylation agents				Product yield	
		Na	C ₂ H ₂	FeCl ₃	NH ₃ (l)	RX (first)		R'X (second)			
		<i>g-atoms</i>	<i>Moles</i>	<i>g</i>	<i>kg</i>	<i>Compound</i>	<i>Moles</i>	<i>Compound</i>	<i>Moles</i>	<i>Moles</i>	<i>Percent</i>
Propyne.....	A	70	65	18	11.0	CH ₃ Br.....	60	40.5	65
1-Butyne.....	A	70	65	18	11.0	(C ₂ H ₅) ₂ SO ₄	60	43.7	67
2-Butyne.....	B	80	40	20	14.5	CH ₃ Br.....	84	17.0	42
1-Pentyne.....	A	21	(^a)	5.5	3.5	n-C ₃ H ₇ Cl.....	21	7.4	35
2-Pentyne.....	C	45	45	12	9.1	C ₂ H ₅ Br.....	45	CH ₃ Br.....	^b 48	36.3	81
1-Hexyne.....	A	60	60	15	10.3	n-C ₄ H ₉ Br.....	60	28.8	48
2-Hexyne.....	C	45	45	12	9.1	n-C ₃ H ₇ Br.....	45	(CH ₃) ₂ SO ₄	^b 48.5	27	60
3-Hexyne.....	B	80	40	20	10.0	(C ₂ H ₅) ₂ SO ₄	80.5	25.6	^c 64
4-Methyl-2-pentyne.....	D	63	(^d)	15	10.0	(CH ₃) ₂ SO ₄	63	24	42
4-Methyl-2-hexyne.....	D	40	(^e)	9	7.5	CH ₃ Br.....	40	25	^f 69
5-Methyl-2-hexyne.....	D	35	(^g)	12	9.1	CH ₃ Br.....	40	28.4	81
2-Methyl-3-hexyne.....	D	48	(^h)	12	9.1	C ₂ H ₅ Br.....	50	38.6	80
1-Octyne.....	A	30	30	7	5.5	n-C ₆ H ₁₃ Br.....	30	11.2	38

^a Sufficient to attain black color. ^b Preceded by 46 moles of sodium amide. ^c One run, using ethyl bromide gave 93 percent yield. ^d 57 moles of 3-methyl-1-butyne used. ^e 36 moles of 3-methyl-1-pentyne used. ^f Purified through azeotrope with ethanol, bp 74° C [10]. ^g 35 moles of 4-methyl-1-pentyne used. ^h 45 moles of 3-methyl-1-butyne used.

produced a total of 0.91 kg (17 moles) of crude 2-butyne; yield, 42 percent. The crude was fractionated through column 19 to yield 2-butyne with the properties listed in table 1.

(c) *Method C.* 2-pentyne was prepared by the treatment of monosodium acetylide with ethyl bromide in liquid ammonia, followed by the reaction of methyl bromide with the sodium derivative (formed in situ) of the resulting 1-butyne. Monosodium acetylide (45 moles) was formed from 1,035 g (45 g-atoms) of sodium, 1.17 kg (45 moles) of acetylene and 12 g of ferric chloride in 9.1 kg of ammonia by the usual technique (see sec. 3.2). To this solution was added 4.91 kg of ethyl bromide (45 moles) over a period of 2½ hr, during which the reaction was quite vigorous. After the addition was completed, the reaction mixture was stirred for 1½ hr before adding 1.82 kg of commercial sodium amide over a period of 45 min. The solution was stirred for 1 hr, and then 4.58 kg of methyl bromide was added to the reaction in the liquid phase. The mixture became quite viscous and was allowed to stand overnight. The next morning it had solidified and the stirrer would not operate. To loosen it, 2.7 kg of liquid ammonia was added. This was followed by 3.8 liters of isooctane⁴ as solvent and 15 liters of water. There was no vigorous reflux during this decomposition. The organic layer was separated, washed twice with cold water, once with dilute hydrochloric acid, and dried over anhydrous sodium carbonate.

On distillation there was obtained 2.47 kg (36.3 moles) of pure 2-pentyne with the properties listed in table 1. This recovery corresponds to a yield of 81 percent.

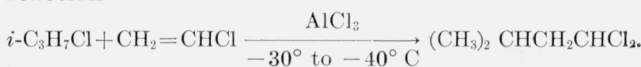
(d) *Method D.* 5-methyl-2-hexyne was formed by the methylation of 4-methyl-1-pentyne prepared by method E. To a solution of sodium amide prepared in the usual way from 805 g (35 g-atoms) of sodium, 12 g of ferric chloride, and 9.1 kg of ammonia, was added 2.87 kg (35 moles) of 4-methyl-1-pentyne. The addition took 1 hr and did not cause very vigorous refluxing. After 2 hr of stirring, 3.64 kg (38 moles) of methyl bromide was added rapidly through the gas-inlet tube. The reaction mixture was stirred overnight, after which it was treated with 19 liters of water. The organic layer was filtered and washed three times with water, and then dried over

anhydrous sodium carbonate. Distillation of the crude through column 6 yielded 2.73 kg of material, boiling at 102° to 103° C (yield, 81 percent). Redistillation in still 19 yielded a product with the properties listed in table 1.

3.4. Preparation of Halides—Methods E to H

Direct alkylation of sodium acetylide is not successful with branched-chain adducts. Therefore, it was necessary to prepare branched acetylenes by dehydrohalogenation of appropriate halogen compounds [17]. Several dihalides used in method E (see table 3) were prepared by adaptations of the vinylation method of Schmerling [15]; one chlorolefin was prepared by the Grignard reaction [9]. Dehydrohalogenation reactions were also used for the syntheses of two diacetylenes (methods G and H). The halides for these were made by chlorination of a polyalcohol and by addition of bromine to a diolefin. In table 5 are given data on typical syntheses of the intermediate halides used in preparing 3-methyl-1-butyne, 3-methyl-1-pentyne, 3,3-dimethyl-1-butyne, 4-methyl-1-pentyne, 1,3-butanediene, and 1,5-hexadiene, respectively, some of which were used in additional preparations utilizing alkylation techniques (see table 4).

(a) *Halides for method E.* Inasmuch as the quantities involved in these syntheses were many times greater than those used by Schmerling, it was necessary to develop techniques for the addition of reagents and control of the reaction in order to assure adequate yield. Typical of the several vinylation reactions is the preparation of 1,1-dichloro-3-methylbutane, which proceeds according to the reaction



To the 5-gal brass reactor equipped with stirrer, condenser cooled to -78° C, thermometer, and inlet tube were added 3.92 kg (50 moles) of isopropyl chloride and 340 g (2.5 moles) of aluminum chloride. Effervescence and darkening of the liquid began immediately upon this addition; the former ceased after a short time and did not resume during the subsequent addition of vinyl chloride. After the initial heat of reaction had been dissipated, the contents of the pot was cooled to -30° C, and 3,286 g (53 moles)

TABLE 5. Halide intermediates

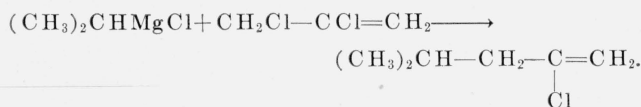
Compound prepared	Method (see table 3)	Reactants			Yields	
					Moles	Percent
(CH ₃) ₂ CHCH ₂ CHCl ₂	E	(CH ₃) ₂ CHCl(50 moles).....	CH ₂ =CHCl(53 moles).....	AlCl ₃ (340 g).....	36	72
CH ₃ CH ₂ CH(CH ₃)CH ₂ CHCl ₂	E	CH ₃ CH ₂ C(CH ₃)Cl(60 moles).....	CH ₂ =CHCl(60 moles).....	AlCl ₃ (351 g).....	40.7	68
(CH ₃) ₃ CCH ₂ CHCl ₂	E	(CH ₃) ₃ CCl(50 moles).....	CH ₂ =CHCl(53 moles).....	AlCl ₃ (454 g).....	35	70
(CH ₃) ₂ CHCH ₂ CCl=CH ₂	F	CH ₂ =CClCH ₂ Cl(153 moles).....	^a (CH ₃) ₂ CHMgCl.....		70	^b 59
ClCH ₂ C≡CCH ₂ Cl.....	G	HOCH ₂ C≡CCH ₂ OH(4.7 moles).....	SOCl ₂ (8.4 moles).....		3.3	70
CH ₂ BrCHBrCH ₂ CH ₂ CHBrCH ₂ Br.....	H	CH ₂ =CHCH ₂ CH ₂ CH=CH ₂ (24 moles).....	Br ₂ (48 moles).....		20.4	84

^a Prepared from 170 moles of isopropylchloride, 170 g-atoms of magnesium in 52 liters of ether.

^b Based on dichloride consumed.

of vinyl chloride was bubbled rapidly into the stirred solution. This reaction is extremely exothermic, and rapid removal of heat is essential to prevent its becoming violent. In this case the addition required about 2 hr with the temperature at -30° to -40° C. The solution was stirred for 90 min after the addition was completed; the entire brownish reaction mixture was then poured onto cracked ice. After the colors of the aluminum-chloride complexes disappeared, a yellow liquid, heavier than water, remained. About 2,000 ml of ligroin was added as solvent; the resulting organic solution was washed once with dilute sodium carbonate and twice with water, dried over anhydrous sodium carbonate, and fractionated through column 6. After the ligroin forerun, there was collected a main product of 1,600 ml, boiling 127° to 130.5° C. The yield was 72 percent.

(b) *Halide for method F.* The chloroolefin used in method F was prepared by the reaction of isopropylmagnesium chloride on 2,3-dichloro-1-propene, according to the equation



Isopropylmagnesium chloride was prepared in the usual manner from 13.4 kg (170 moles) of isopropyl chloride, 4.09 kg of magnesium turnings (170 g-atoms), and 52 liters of anhydrous ether in the 50-gal stainless-steel kettle. To this stirred solution 16.95 kg (153 moles) of 2,3-dichloro-1-propene dissolved in 16 liters of ether was added over a period of 3 days. At the end of this time, the reaction mixture was treated in the usual manner with 5.45 kg of concentrated hydrochloric acid in 75 liters of water. The ether layer was washed four times with water and dried over anhydrous sodium carbonate. On distillation through column 6, the organic layer yielded 3.82 kg (34 moles) of unreacted 2,3-dichloro-1-propene (bp 88° to 96° C) and 8.27 kg (70 moles) of 4-methyl-2-chloro-1-pentene (bp 100° to 104° C). The yield, based on material consumed, was 59 percent.

(c) *Halide for method G.* The 1,4-dichloro-2-butyne used in this work was prepared by reaction of commercial 1,4-dihydroxy-2-butyne with thionyl

chloride [1]. To a 5-liter flask fitted with stirrer, dropping funnel, and reflux condenser, and containing 400 g of pulverized 1,4-butyne-2-ol was added 1,000 g of pure thionyl chloride; during this addition, the temperature of the mixture decreased to about -15° C. The mixture was warmed to 10° C with stirring for 12 hr and was then heated to 60° C, as long as sulfur dioxide evolved. The direct vacuum distillation of this mixture yielded 399 g of 1,4-dichloro-2-butyne, bp 50° to 70° C at 6.5 mm Hg (yield, 70 percent).

(d) *Halide for method H.* The tetrabromide for this synthesis was made by addition of bromine to 1,5-hexadiene in several runs. In one of these, 800 ml of chloroform and 490 g (6 moles) of 1,5-hexadiene were added to a 5-liter 3-necked ice-cooled flask equipped with stirrer, addition vessel, and condenser. Approximately 0.98 kg (6 moles) of bromine was added slowly over a period of 2 hr, followed by 100 ml of additional chloroform and then by another charge of 0.98 kg (6 moles) of bromine. After the addition was complete, the mixture was filtered. The first crop of crystals weighed 517 g; when the filtrate was cooled to -20° C, an additional 502 g of crystals were obtained in the second crop, and 228 g in the third. From four such runs, a total of 8,104 g of 1,2,5,6-tetrabromohexane was prepared, representing an over-all yield of 85 percent.

3.5. Dehydrohalogenation Reactions

Some of the dehydrohalogenations of dichlorides and of the chloroolefin to the corresponding acetylenes were carried out in the 50-gal stainless-steel vessel. Table 6 lists some of the compounds prepared in this manner. The most convenient method of dehydrohalogenation utilized sodium amide suspended in refined light mineral oil at about 100° to 150° C [2]. The technique employed in dehydrochlorinations in methods E and F is illustrated by the conversion of 1,1-dichloro-3-methylbutane to 3-methyl-1-butyne.

(a) *Large-scale dehydrohalogenations in methods E and F.* The top of the condenser of the kettle was connected to another condenser kept at -20° C and thence to a 5-liter trap at -20° C. To the 50-gal stainless-steel kettle was added 26.5 liters of

TABLE 6. Hydrocarbons by dehydrohalogenation

Hydrocarbon	Synthetic method (see table 3)	Halide		Sodium amide	Dispersion medium		Yield	
		Formula	Quantity		Volume	Temperature		
3-Methyl-1-butyne.....	E	$(\text{CH}_3)_2\text{CHCH}_2\text{CHCl}_2$	Moles 80	Moles 281	Liters a26.5	$^{\circ}\text{C}$ 94	Moles 49	Percent 62
3-Methyl-1-pentyne.....	E	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHCl}_2$	107	375	a38	100	62.5	59
3,3-Dimethyl-1-butyne.....	E	$(\text{CH}_3)_3\text{CCH}_2\text{CHCl}_2$	60	210	a19	90 to 95	28.5	45
4-Methyl-1-pentyne.....	F	$(\text{CH}_3)_2\text{CHCH}_2\text{CCl}=\text{CH}_2$	67.3	168	a38	140	53.7	80
1,3-Butadiyne.....	G	$\text{CH}_2\text{ClC}\equiv\text{CCH}_2\text{Cl}$	b1.5	c7.0	d0.80	e75	0.9	60
1,5-Hexadiyne.....	H	$\text{CH}_2\text{BrCHBrCH}_2\text{CH}_2\text{CHBrCH}_2\text{Br}$	f6.6	58	g17.5	-33	4.16	63

aMineral oil. bDissolved in 1,200 g of 95% ethanol. cKOH. dWater. eInverse addition. KOH-in-water solution added to heated ethanol solution. fDissolved in 7 liters of diethylether. gLiquid ammonia.

light oil and 4.5 kg of sodium amide. The suspension was heated to 140° C, and an initial 200 ml of 1,1-dichloro-3-methylbutane was started to initiate the reaction; dehydrochlorination began immediately, as evidenced by the evolution of ammonia. The temperature of the suspension was reduced to 94° C, and 3,630 g of the dihalide was added over a period of 3 hr. Ammonia was evolved during the entire course of the addition.

The next day, the contents of the kettle were cooled and an additional 6.36 kg of sodium amide was added to the pot (total 281 moles). Again the reaction mixture was heated to 94° C, and the remainder of the dihalide, total 11.4 kg (80 moles), was added over a 7-hr period. There was a continuous evolution of ammonia during the addition, and the reaction mixture assumed the consistency of a thick grease. The mixture was then heated for 48 hr, and it was noted that refluxing had ceased.

After cooling the reaction mixture, 7.5 liters of water was added cautiously with stirring. Only slight amounts of ammonia were evolved at this stage. Then there was added 3,500 ml sulfuric acid (63 moles) in 95 liters of water. The reaction mixture was then distilled from the kettle until the distillate reached a temperature of 95° C. The distillate was caught in isooctane, dried, and redistilled to recover 3.36 kg (49 moles) of 3-methyl-1-butyne, bp 27° to 32° C, yield, 62 percent.

For the preparation of butadiyne and 1,5-hexadiyne, this method of dehydrohalogenation was not used; the data on these dehydrohalogenations are given in table 6, and the description of the syntheses of these compounds are given below. Because of the ease of polymerization and peroxidation of these compounds, the syntheses and purifications were conducted in an inert atmosphere, and the final products sealed under their own vapor pressure.

(b) *Dehydrochlorination in method G.* The starting material for the synthesis of 1,3-butadiyne was 1,4-dihydroxy-2-butyne [14] purchased from a commercial source. This alcohol was converted to 1,4-dichloro-2-butyne [5], as described in section 3.4(c). The dichloride was converted to butadiyne by reaction with potassium hydroxide [7]. To a solution of 195 g of 1,4-dichloro-2-butyne in 1,200 g of 95-percent ethanol at 75° C was added with stirring a solution of 400 g of potassium hydroxide and 800 g of water. The evolved 1,3-butadiyne was scrubbed with dilute potassium hydroxide and dried with calcium chloride. The yield in this step was 60 percent. The product from several such runs was fractionated in still 28. Mass-spectrometer analysis of the center cut indicated this distillate to be 99.8 percent pure.

(c) *Dehydrobromination in method H.* 1,5-Hexadiyne was obtained from the dehydrobromination of 1,2,5,6-tetrabromohexane with sodium amide in liquid ammonia.

As a starting material for this synthesis, large quantities of 1,5-hexadiene were prepared in the stainless-steel reactor in two identical runs. One of these is described below.

To 2.83 kg (118 moles) of magnesium in the kettle

was added 3 liters of a solution prepared by mixing 15.2 kg (200 moles) of allyl chloride and 60 liters of ether. After reaction had started, 20 liters of ether and the remainder of the allyl chloride-ether mixture were added while the kettle jacket was kept cold. The reaction was not a very violent one, but as the addition proceeded, the mixture thickened considerably and became milky-white. Stirring was continued for 3 days; the mixture was then treated with 49 liters of water and about 3.6 kg of hydrochloric acid. The ether layer was washed three times with water and dried over anhydrous sodium carbonate. The products of two such runs were combined and distilled in column 6 to give 11.31 kg (138 moles) diallyl boiling 56° to 63° C. This recovery corresponds to a 69-percent yield.

The 1,5-hexadiene was converted to the tetrabromide by treatment with bromine, as described in section 3.4(d); the 1,2,5,6-tetrabromohexane was then converted to 1,5-hexadiyne by an adaptation of the method of Raphael and Sandheimer [13]. One of the four dehydrobrominations is described.

To 12 kg of liquid ammonia in the 10-gal stainless-steel kettle was added 2.27 kg (58 moles) of powdered sodium amide. To this stirred solution was added 2.63 kg (6.6 moles) of 1,2,5,6-tetrabromohexane dissolved in 7 liters of ether, and the solution stirred for 2 days. During this period the dry-ice condenser was allowed to warm up, permitting some of the ammonia to boil off. At the end of this time the reaction mixture was treated with 20 moles of ammonium chloride and 15 liters of water. The organic layer was siphoned, washed three times with water, and dried over anhydrous sodium carbonate. After the bulk of the ether had been stripped, the organic layer was distilled in column 19, and 313 g of a fraction boiling 86° to 88° C was obtained, along with a forerun boiling 50° to 86° C. The total yield was 63 percent. Continued distillation past 90° C resulted in an explosion. The combined yield (bp 80° to 88° C) from four such runs was redistilled in column 19, under a nitrogen atmosphere, to give the material with the properties listed in table 1 for this diacetylene.

3.6. Miscellaneous Reactions—Method I

The reactions illustrated by method I in table 3 were used for the preparation of 1-pentyne-3-ene. Because of its reactivity, the compound was sealed in the absence of air.

(a) *1-Pentyne-3-ene.* This compound was prepared by treating the *p*-toluenesulfonate of 1-pentyne-4-ol with potassium hydroxide [3]. The 1-pentyne-4-ol was prepared by reacting propylene oxide with monosodium acetylide [8].

Sodium acetylide was prepared in the usual manner from 1,172 g of sodium, 15 g of ferric chloride, and 1.36 kg of acetylene in 10 ky of liquid ammonia. To this was added 2,500 g (43 moles) of propylene oxide, and the mixture was stirred all night. The ammonia was allowed to evaporate, and 6 liters of water were added slowly. The reaction mixture was transferred to a glass vessel, made slightly acid

with acetic acid, and steam distilled. The distillate was saturated with potassium carbonate and the organic layer separated, dried, and distilled. The portion boiling at 127.3° to 127.5° C was collected as 1-pentyne-4-ol. The yield was 1,377 g (38 percent).

A solution of 1,656 g of *p*-toluenesulfonyl chloride in 1,120 ml of warm pyridine was cooled rapidly to obtain small crystals. To this slurry was added slowly 675 g (8.05 moles) of 1-pentyne-4-ol. The solution was well stirred and the temperature kept below 30° C with external cooling. After the vigor of the reaction had subsided, it was allowed to stand at room temperature for 20 hr, after which 1 liter of water was added with cooling. The reaction mixture was extracted with 2 liters of ether and the extract washed 4 times with 1.5 liters of 30-percent sulfuric acid, 3 times with 1 liter of saturated sodium-bicarbonate solution, and, finally, 2 times with water and dried. The ether was removed by vacuum until a final pressure of 4 mm Hg was reached. The yield was 1,876 g (98 percent).

To a stirred solution of 600 g of potassium hydroxide in 2 liters of water was added slowly 1,876 g (7.85 moles) of the *p*-toluene-sulfonate of 1-pentyne-4-ol. The reaction temperature was kept at 110° C, and a small amount of wetting agent was added to facilitate the reaction. The evolved vapors were collected in a trap at -25° C; the frozen distillate was melted periodically and the layers separated. The organic material amounted to 486 g (7.36 moles), representing a yield of 94 percent. This material was dried with calcium chloride and distilled in column 19. The distillation gave first a mixture of *cis* and *trans* forms (bp 43.8° to 43.9° C, $n_D^{20}=1.4289$ to 1.4316) and then the pure *trans* form (bp 51.9° C, $n_D^{20}=1.4375$). Identification⁵ of the distillate fractions was made by infrared analysis, which demonstrated the presence of these two species and the absence of other isomers.

3.7. Measurements of Physical Properties

Because of the extremely reactive nature of several of the prepared compounds, final distillations of these were conducted from hydroquinone under a nitrogen atmosphere and bottled under their own vapor pressures [11]. This method of packaging reduced the amount of peroxides present and yielded samples suitable for physical-constants measurements. In general, the properties of the hydrocarbons measured included melting point or triple point, boiling point, refractive index, and density. The methods and techniques used in these determinations have been given previously [12].

Where feasible, the purities of samples were measured by mass spectrometry, calorimetrically [4], or by freezing-curve analysis [16]. For a more

complete characterization of some of the 1-acetylenes, mercury derivatives of these hydrocarbons were prepared according to the directions of Johnson and McEwen [6]. The data obtained on some of the compounds are listed in table 1, which is a summary of data obtained on the several compounds prepared.

4. Conclusions

Seventeen acetylenes, 1 olefin-acetylene, and 2 diacetylenes have been prepared in high states of purity. Physical constants are reported for these compounds; where feasible, the purity of the compound was determined.

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⁵ Determined and interpreted by F. A. Smith and J. E. Stewart of the Bureau's Gas Chemistry Section.