

the relative intensities reported here are based on visual estimates of blackening of the photographic plate at the band maxima. No account of deviations from linearity of the characteristic curve of the plate or of the effect of the appreciable width and overlapping of the absorption bands has been taken in making the estimates. Therefore the discrepancy in the relative intensities mentioned above cannot be considered to be a serious objection to the suggested interpretation of the spectra; at least not until accurate intensity measurements are made and until the changes of relative intensities with changes of temperature of the absorbing crystals are investigated.

Summary

1. The room temperature absorption spectra of crystals of pyridinium tetrabromocobaltate(II), quinolinium tetrabromocobaltate(II) and ethyl-

enediaminium hexachlorocobaltate(II) have been photographed.

2. The spectra of pyridinium tetrabromocobaltate(II) and quinolinium tetrabromocobaltate(II) were found to be essentially identical and to bear a very close resemblance to the previously observed spectra of similar double salts containing the tetrahedral tetrachlorocobaltate(II) ion. Therefore the bromides may be assumed to contain the tetrahedral tetrabromocobaltate(II) ion. The spectrum of ethylenediaminium hexachlorocobaltate(II) is distinctly different.

3. A vibration frequency of the tetrahedral complex ions has been identified from an analysis of the tetrahalide spectra. From the magnitude of this frequency, the force constants of the cobalt-bromine and cobalt-chlorine bonds have been determined.

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The Preparation of the Six *n*-Octynoic Acids^{1,2}

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In this paper are described the syntheses of the six *n*-octynoic acids and of many intermediates. This work was undertaken with a multiple purpose: (1) to add to our knowledge of the reactivity of the acetylenic function in acids having the triple bond at varying distances from the carboxyl group; (2) to study various methods of synthesis for such acids; (3) to obtain information about the odors of the methyl esters. Inasmuch as the synthetic problems consumed most of our efforts, the first objective must remain for future study. It was deemed of interest to investigate the odors of the methyl esters of these acids because of the commercial use of methyl heptyne-carboxylate in perfumery. The odors have been evaluated by men skilled in the art and are described as follows.⁴

$\text{HC}\equiv\text{C}(\text{CH}_2)_8\text{COOCH}_3$, very green but sharp, chemical, fatty, unpleasant; $\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_4\text{COOCH}_3$, reseda-like, fatty, weak, green seaweed; $\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}(\text{CH}_2)_3\text{COOCH}_3$, leafy, cucumber-like, something like talia, sweet, violet; $\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{C}(\text{CH}_2)_2\text{COOCH}_3$, cucumber-like but sharp, chemical, somewhat fruity; CH_3-

$(\text{CH}_2)_8\text{C}\equiv\text{CCH}_2\text{COOCH}_3$, something like fresh cut grass, but crude and fatty.

The synthetic methods used are described below and are summarized in a series of charts. Since many bifunctional acetylenic intermediates of either rare or previously non-existent types were prepared, we prefer to discuss the preparation of these compounds according to the functional group other than the triple bond. In this way the scope and limitations of the methods of synthesis will be emphasized.

Alkynes and Alkynols

The required 1-alkynes were prepared in high yields by known procedures.⁵ 2-Alkyn-1-ols were made in high yield by condensation of 1-alkynyl-magnesium bromides with gaseous formaldehyde⁶ while 3-alkyn-1-ols were prepared in poor yield by the reaction of acetylenic organometallic reagents with ethylene oxide.⁷

Acetylenic Halides

One useful method for preparation of halogenated acetylenes involved the reaction of alkynylsodium in liquid ammonia with polymethylene chlorobromides.⁸ This reaction failed with ethylene

(5) (a) Vaughn, *et al.*, *J. Org. Chem.*, **2**, 1 (1937); (b) Henne and Greenlee, *THIS JOURNAL*, **67**, 484 (1945).

(6) Lai, *Bull. soc. chim.*, **53**, 682 1533 (1933); Bartlett and Rosen, *THIS JOURNAL*, **64**, 545 (1942)

(7) Compare Faucounau, *Compt. rend.*, **199**, 605 (1934); Danehy, Vogt and Nieuwland, *THIS JOURNAL*, **57**, 2327 (1935); Greenlee, Ph.D. thesis, The Ohio State University, 1942, p. 60.

(8) In a paper which appeared while this manuscript was in preparation, Ahmad and Strong, *THIS JOURNAL*, **70**, 1699 (1948), mention a 36% yield of 1-chloro-5-decyne from 1-chloro-4-iodobutane and 1-hexynylsodium.

(1) The material herein presented was taken from the Ph.D. thesis of John H. Wotiz, The Ohio State University, June, 1948. Present address of John H. Wotiz, Chemistry Department, University of Pittsburgh.

(2) Presented before the Organic Division of the American Chemical Society at Chicago, Illinois, April, 1948.

(3) The authors wish to express their gratitude to The Ohio State University for a grant from funds donated by The Ohio State University Research Foundation and administered by the Graduate School.

(4) We are indebted to Dr. Ernst T. Theimer of the research department of van Ameringen-Haebler, Inc., Elizabeth, New Jersey, for securing the data on odor.

chlorobromide. The condensation of 1-pentynylmagnesium bromide with β -chloroethyl *p*-toluenesulfonate⁹ yielded 1-chloro-3-heptyne in 38% yield. This halide was also prepared in 72% yield from the corresponding alcohol, but, because of poor yields in preparation of the required alcohol, this route to 4-octynoic acid was not the best.

Since it was difficult to get a pure sample (required for infrared spectroscopy) of 1-chloro-5-heptyne from the reaction between propynylsodium and 1-chloro-4-bromobutane¹⁰ we attempted to prepare this intermediate by alkylating 1-chloro-5-hexyne with methyl bromide in liquid ammonia. In a similar manner, and for a similar reason, 1-chloro-4-heptyne was prepared by alkylating 1-chloro-4-pentyne with ethyl bromide. It is interesting to note that in each of these alkylations, small quantities of a terminal alkyne, possibly 1-chloro-6-heptyne, were found. This impurity was removed by a treatment with potassium iodomercurate reagent (see experimental). The presence of an acetylenic hydrogen in the distilled reaction products was first suspected when the infrared absorption spectra were examined.¹¹

Another method which proved useful for the preparation of acetylenic halides involved replacement of the hydroxyl group of acetylenic alcohols. The behavior of 2-heptyn-1-ol with thionyl chloride and phosphorus tribromide is especially noteworthy. The 1-chloro-2-heptyne thus prepared only reacted with alcoholic silver nitrate on standing and warming whereas the 1-bromo-2-heptyne reacted immediately. The chloro compound could not be brought to react with magnesium even by the "entrainment" method,¹² whereas the bromo compound reacted with such ease that coupling occurred predominantly. However, by using a special high dilution technique recently developed¹³ a 98% yield of organomagnesium derivative was obtained from the bromide. A mixture of acids, whose composition is now under investigation, was isolated on carbonation of this derivative.

Examples of an acetylenic-allenic isomerism, $R-C\equiv C-CH_2X \rightleftharpoons RCX=C=CH_2$, are described by Johnson.¹⁴ It may be that we were dealing with a similar isomerism. Further work on these halides is being done by one of us (J. H. W.).

Acetylenic Nitriles

Acetylenic halides having at least three methyl-

(9) Compare Johnson, Schwartz and Jacobs, *ibid.*, **60**, 1882 (1938).

(10) Greenlee, Ph.D. thesis, The Ohio State University, 1942, p. 49, points out that $CH_3C\equiv CR$ and RBr usually are difficult to separate by fractionation. Vaughn, *et al.*, ref. 5a, also showed that $RC\equiv CH$ and RCl boil at nearly the same point.

(11) The infrared absorption spectra of many of the intermediates described herein will shortly be published.

(12) Grignard, *Compt. rend.*, **198**, 625 (1934), showed that certain unreactive halides could be made to form Grignard reagents by admixture with ethyl bromide.

(13) M.S. Thesis of D. Rowlands, The Ohio State University, June, 1948, under supervision of Drs. K. Greenlee and C. E. Boord.

(14) Johnson, "Acetylenic Compounds." Edward Arnold and Company, London, 1946, Vol. I, p. 63.

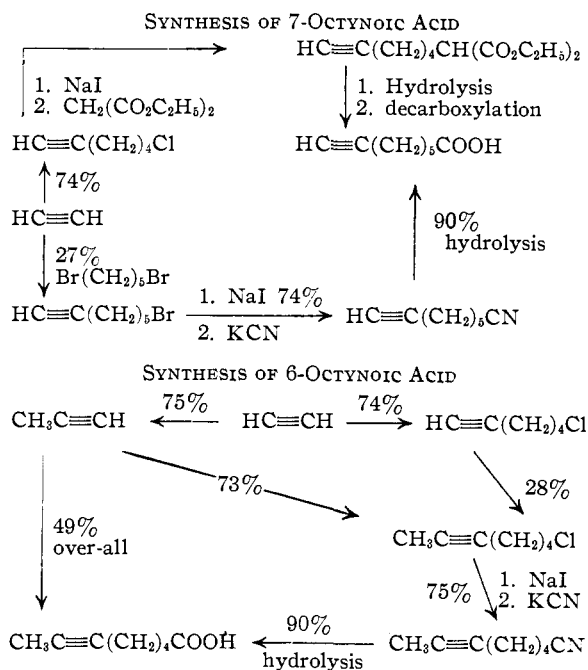
ene groups between the halogen and the triple bond were best converted into the cyanides *via* the iodides by standard procedures. However, neither 1-chloro-2-heptyne nor 1-bromo-2-heptyne yielded the corresponding iodide or cyanide in this way. Only by heating the bromide in anhydrous medium with cuprous cyanide at 150–160° could the nitrile be obtained. The yield by this method was excellent. It is interesting to note that attempts to prepare $NCCH_2C\equiv CCH_2CN$ from the chloride or bromide were unsuccessful.¹⁵

Similar difficulties were met in attempting to prepare nitriles from 1-halo-3-heptynes. However, since the corresponding acid could easily be prepared by the malonic ester synthesis from 1-bromo-2-hexyne no intensive study of this reaction was made.

Acetylenic Acids

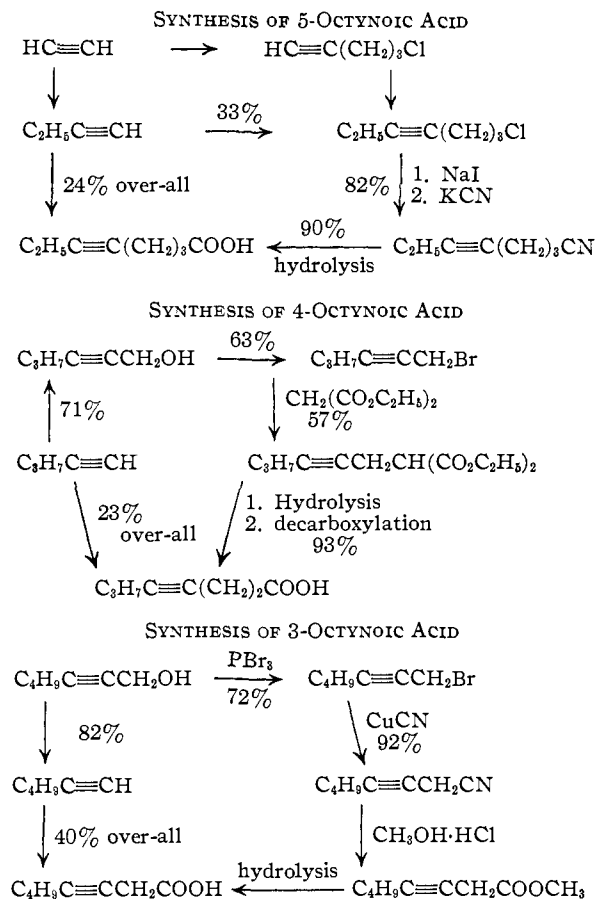
Except for 1-cyano-3-heptyne the hydrolysis of acetylenic nitriles proceeded very well by refluxing in aqueous alcoholic alkali until the evolution of ammonia ceased. 1-Cyano-3-heptyne was converted into the corresponding ester by heating with alcoholic hydrogen chloride followed by alkaline hydrolysis of the ester thus produced. Several other methods of hydrolysis were tried without success. 4- and 5-octynoic acids were prepared by decarboxylation of the corresponding malonic acids. 2-Octynoic acid was prepared by carbonation of 1-heptynyl sodium.¹⁶

The structures of the isomeric *n*-octynoic acids



(15) Johnson, *J. Chem. Soc.*, 1009 (1946). In ref. 14, p. 66, Johnson states that no information is available on β,γ -acetylenic nitriles, so that we have evidently prepared the first compound of this type.

(16) Moureu and Delange, *Bull. soc. chim.*, [3] **29**, 648 (1903), Zoss and Hennion, *THIS JOURNAL*, **63**, 1151 (1941).



were established by ozonization and by hydrogenation to *n*-octanoic acid. Comparison with the latter of the various samples was effected through the amide.

Experimental¹⁷

Tetramethylene Chlorobromide.—A fairly rapid stream of hydrogen chloride (cylinder) was passed into a heated mixture of 1 g. of aluminum chloride, 3 cc. of water, and 720 g. (10 moles) of tetrahydrofuran (du Pont). When the temperature levelled off at 105° the heater was removed and hydrogen chloride was introduced until the reaction mixture returned to room temperature. This crude mixture was added slowly to 2 kg. (7.4 moles) of phosphorus tribromide with stirring and ice cooling. After all had been added, the mixture was heated on a steam-bath for one hour and cooled. The upper layer was washed, dried, and rectified to yield 2.13 kg. (62%) of tetramethylene chlorobromide, b. p. 80–82° at 30 mm.

Pentamethylene Chlorobromide.—5-Chloroamyl acetate, b. p. 82–84° at 2 mm., was prepared in 93% yield from 430 g. (5 moles) of tetrahydropyran (du Pont), 429 g. (5.5 moles) of acetyl chloride, and 40 g. of freshly fused zinc chloride.¹⁸ A mixture of this ester (329 g., 2 moles), 320 g. of methanol, and 5 g. of *p*-toluenesulfonic acid was rectified until 180 g. of the methanol-methyl acetate azeotrope, b. p. 54°, had been collected. The remaining solvent was removed under reduced pressure at room temperature. The residue was reacted with phosphorus tri-

bromide (271 g.) as in the case of tetramethylene chlorohydrin (above) to yield 325 g. (88% over-all) of pentamethylene chlorobromide, b. p. 92–93° at 20 mm., *n*^{20D} 1.4815.

Anal. Calcd. for C₅H₁₀ClBr: C, 32.3; H, 5.4. Found: C, 32.8, 32.9; H, 5.4, 5.3.

2-Heptyn-1-ol.—A solution of 82 g. (1 mole) of 1-hexyne in 300 cc. of dry ether was added slowly to 1.1 moles of ethylmagnesium bromide in 300 cc. of ether. After refluxing for six hours the mixture was cooled (nitrogen atmosphere). Gaseous formaldehyde was introduced (at a rate to maintain gentle refluxing) by passing dry nitrogen through a flask containing paraformaldehyde (dried over phosphorus pentoxide for at least two weeks) and heated by a bath at 180°. The exothermic reaction ceased when about one equivalent of formaldehyde had been introduced. On working up in the usual manner 92 g. (82%) of 2-heptyn-1-ol, b. p. 113–16° at 56 mm., was obtained.⁹ Larger runs gave yields 5 to 10% smaller.

2-Hexyn-1-ol.—By a procedure similar to that described above, 2 moles of 1-pentyne yielded 140 g. (71%) of 2-hexyn-1-ol, b. p. 87–89° at 58 mm.

Anal. Calcd. for C₆H₁₀O: C, 73.4; H, 10.2. Found: C, 73.2, 73.3; H, 10.2, 10.3.

The 3,5-dinitrobenzoate, prepared in high yield, melted at 64–65°.

Anal. Calcd. for C₁₈H₁₂O₆N₂: C, 53.4; H, 4.1; N, 9.6. Found: C, 53.6, 53.3; H, 4.1, 4.4; N, 9.5, 9.2.

3-Hexyn-1-ol.—This compound,¹⁹ prepared in 48% yield from 1-butylnylsodium and ethylene oxide in liquid ammonia^{5b} boiled at 160–170°. On redistillation almost all of it boiled at 161°. The 3,5-dinitrobenzoate melted at 72–73°, in agreement with Takei.¹⁹

Anal. Calcd. for C₁₃H₁₂O₆N₂: C, 53.4; H, 4.1; N, 9.6. Found: C, 53.1, 53.1; H, 4.1, 4.2; N, 9.3, 9.3.

3-Heptyn-1-ol.—This compound (Table II) was prepared in 30% yield from 1-pentylnylsodium and ethylene oxide in liquid ammonia.^{5b} The yield was about the same when prepared from 1-pentylnylmagnesium bromide and ethylene oxide. In the latter case, enough 1-pentyne could be recovered to raise the yield to 45% (based on pentyne consumed). No attempt to recover pentyne was made in the liquid ammonia run.

3-Octyn-1-ol (Table II).—Using the liquid ammonia procedure^{5b} 164 g. of 1-hexyne yielded 53 g. (21%) of 3-octyn-1-ol, b. p. 105–106° at 25 mm. The yield was 37% if based on hexyne consumed (70 g. recovered).

4-Heptyn-1-ol, 5-Heptyn-1-ol and 6-Heptyn-1-ol (Table II).—The corresponding chloroalkynes were converted through the iodides to the acetates by heating with potassium acetate in absolute alcohol. After hydrolysis the alcohols were separated from unreacted halide by conversion to the benzoates, distillation, and saponification. No yields for these steps are available because of uncertain purity of starting halides.

1-Chloroacetylenic Compounds (Table II).—To a mixture of sodium acetylide (5 moles) in 3 l. of liquid ammonia^{5b} was added 858 g. (5 moles) of tetramethylene chlorobromide during four hours and the whole stirred under reflux for seven hours. After most of the ammonia had evaporated (eight hours) 2 l. of water was added slowly. The organic layer was taken into ether, washed with dilute acid and water, and dried. Rectification yielded 430 g. (74%) of 1-chloro-5-hexyne, b. p. 143–144°. In a similar way 1-chloro-6-heptyne (70% yield) and 1-chloro-5-heptyne (73% yield) were prepared from the reaction of sodium acetylide with pentamethylene chlorobromide and of propynyl sodium with tetramethylene chlorobromide. The yield of 1-chloro-4-heptyne by this method was about 30%. Improvement by adding 1-butylnylsodium to trimethylene chlorobromide was not achieved.

1-Chloro-4-heptyne.—To a solution of 205 g. of 1-chloro-4-pentyne in 2 l. of liquid ammonia was added 78

(17) Microanalyses by Mrs. Klotz and Mr. Polglase, OSU, Arlington Laboratories, and Clarke Microanalytical Laboratories, Urbana, Illinois.

(18) Synerholm, *THIS JOURNAL*, **69**, 2581 (1947).

(19) Takei, *Ber.*, **73**, 950 (1940).

TABLE I

R	PHYSICAL PROPERTIES AND ANALYSES OF NEW ACETYLENIC COMPOUNDS ^a																
	Alcohols, ROH			3,5-Dinitrobenzoates ^a			Acids RCOOH			Amides, RCONH ₂							
	B. p., °C. Mm. ^b	n _D ²⁰	Found, % ^p C (75.0) H (10.7)	M. p., ^e °C. (54.9)	Found, % ^p C (54.9) H (4.6) N (9.1)	B. p., ^f °C. (2 M. p. mm.)	n _D ²⁰	Neut. equiv. (140)	Found, % ^p C (68.6) H (8.6)	M. p., ^g °C. (69.1)	Found, % ^p C (9.3) H (10.1)	N					
HC≡C(CH ₂) ₅	98 20	1.4534	74.6	10.6	46	55.0	4.5	9.5	123 20	1.4502	140.5	68.1	8.6	86	69.9	9.5	10.5
CH ₃ C≡C(CH ₂) ₄	96 15	1.4590	74.2	10.7	53	54.8	4.4	9.2	116 37		139.5	67.9	8.6	113	68.7	9.3	10.2
C ₂ H ₅ C≡C(CH ₂) ₃	91 15	1.4593	75.7	10.4	52	54.8	4.6	9.2	111 8	1.4540	140	69.2	9.0	105	69.8	9.3	10.1
C ₃ H ₇ C≡C(CH ₂) ₂	111 70	1.4530	74.8	10.5	61	54.8	4.9	9.4	121 49		140.5	68.9	8.6	118	69.9	9.2	10.0
C ₄ H ₉ C≡CCH ₂	98 28 ^d	1.4523	74.8	10.8	62	55.4	4.5	9.7	110 18	1.4577	140.5	68.8	8.6	52	69.1	9.1	10.1
C ₅ H ₁₁ C≡C									114 5 ⁿ	1.4588				91 ⁿ			
C ₇ H ₁₅ ^c	93 30 ^e	1.4218			47 ^f				99 16 ^m	1.4150				105 ^m			
R	Chlorides, RCl			Bromides, RBr			Nitriles, RCN			Methyl esters, RCOOCH ₃							
	B. p., °C. Mm. ^b	n _D ²⁰	Found, % ^p C (84.3) H (8.4)	B. p., °C. Mm. ^l	n _D ²⁰	Found, % ^p C (83.0) H (6.3)	B. p., °C. Mm. ^b	n _D ²⁰	Found, % ^p C (79.3) H (9.1) N (11.5)	B. p., mm. ^b	n _D ²⁰	Found, % ^p C (70.1) H (9.1)					
	atm.																
HCC≡(CH ₂) ₅	166	1.4507	64.3	8.4	92 20	1.4750	48.5	6.6	80 3	1.4460	79.0	9.0	11.6	64	1.4380	70.1	9.4
CH ₃ C≡C(CH ₂) ₄	175	1.4599	64.4	8.4					79 2	1.4530	79.4	9.2	11.6	68	1.4433	70.1	9.2
C ₂ H ₅ C≡C(CH ₂) ₃	164	1.4540	64.8	8.5					111 29	1.4514	80.0	9.2	11.1	64	1.4421	70.2	9.1
C ₃ H ₇ C≡C(CH ₂) ₂	162	1.4520	64.7	8.9	100 65	1.4785	49.5	6.6	71 3	1.4492	79.4	8.9	12.0	63	1.4414	70.0	9.4
C ₄ H ₉ C≡CCH ₂	167	1.4570	64.8	8.4	84 20	1.4878	49.1	6.2	124 56	1.4475	79.7	9.2	11.3	64	1.4448	70.2	9.0
C ₅ H ₁₁ C≡C					69 25 ^h	1.4678			86 17 ⁱ	1.4551				70 ⁿ	1.4442		
C ₇ H ₁₅ ^c	159 ^g	1.4264			70 15 ^j	1.4476 ^k			66 4 ^k	1.4178				57 ^m	1.4150		

^a Boiling points represent middle cuts taken for analyses; melting points are usually over a one degree range, the upper limit being that recorded. Duplicate analyses were obtained for almost every sample. To save space, only the best analysis is included in this table. ^b These boiling points were observed with different vacuum systems and flasks and hence are not directly comparable. ^c Known compounds; properties listed for comparison. ^d Reported by Toussaint and Wenzke, *THIS JOURNAL*, 57, 668 (1935), without analysis. ^e Ellis and Reid, *ibid.*, 54, 1678 (1932). ^f Adamson and Kenner, *J. Chem. Soc.*, 287 (1935). ^g Heilbron, "Dictionary of Organic Compounds," Vol. I, p. 473. ^h McCusker and Vogt, *THIS JOURNAL*, 59, 1307 (1937). ⁱ Our values. Heilbron (footnote *g*) p. 296, gives b. p. 70.6° at 19 mm. and *n*_D²⁰ 1.4480. ^j Moureu and Lazennec, *Bull. soc. chim.*, [3] 35, 524 (1906). ^k Footnote *g*, page 393. ^l Boiling points taken in same apparatus, hence comparable. ^m Footnote *g*, p. 393. ⁿ Moureu and Delange, *Bull. soc. chim.*, [3] 29, 655 (1903). ^o The 3,5-dinitrobenzoates were prepared in 90% yields by heating with pure 3,5-dinitrobenzoyl chloride until evolution of hydrogen chloride slackened. The products were isolated and recrystallized to constant melting point from petroleum ether (b. p. 30–60°) and benzene. Mixed melting points between the various derivatives all gave large depressions. ^p Values in parentheses are calculated. ^q Of the alcohols, ROH.

g. of sodium amide. After stirring for thirty minutes 218 g. of ethyl bromide was added during three hours. By rectification of this reaction product there was obtained 35 g. (17%) of crude 1-chloro-4-pentyne, b. p. 110–112°, and 45 g. (17%) of crude 1-chloro-4-heptyne, b. p. 163–165°. When the infrared absorption spectrum¹¹ of this fraction showed the presence of a terminal acetylenic function, 19 g. was treated with a mercuric iodide, reagent²⁰ until no further precipitate formed. The white solid was collected and recrystallized to a melting point of 66–67°. Analysis showed 48.6% carbon and 4.7% hydrogen, which did not indicate any compound to be expected. The excess mercury reagent was removed by precipitating with 1-hexane and on rectification 4 g. of a pure sample of 1-chloro-4-heptyne (Table II) was obtained.

1-Chloro-5-heptyne (Table II).—By a procedure similar to that used above, there was obtained 50 g. (38%) of crude 1-chloro-5-heptyne, b. p. 173–174°, by treating 116 g. of 1-chloro-5-hexyne with sodium amide and then methyl bromide. Purification of this entire fraction as above yielded 25 g. of pure 1-chloro-5-heptyne. The mercury derivative²⁰ obtained in this case (4 g.) melted at 76–77° and contained 48.9% of carbon and 4.8% of hydrogen.

1-Chloro-3-heptyne (Table II).—1-Chloro-3-heptyne, b. p. 71–75° at 30 mm., b. p. 90–93° at 70 mm., was prepared in 38% yield (calculated on 1-pentyne) essentially as described by Johnson for a similar reaction.⁹ This chloride was also prepared in 72% yield from a reaction between thionyl chloride, pyridine, and 3-heptyn-1-ol by the procedure described below, except that a glass stirrer was used.

1-Chloro-2-heptyne (Table II).—In the best of several experiments a solution of 112 g. (1 mole) of 2-heptyn-1-ol and 78 g. (1 mole) of dry pyridine in 100 cc. of dry ether was added to a solution of 131 g. (1.1 mole) of thionyl chloride (obtained from the Columbia Chemical Division

of the Pittsburgh Plate Glass Company) in 100 cc. of dry ether at such a rate as to maintain refluxing. After the addition was complete ether (about 150 cc.) was distilled until the inside temperature was 80°. Then 13 g. more of thionyl chloride was added and the stirring and heating continued for an hour. The chromel (nickel and chromium alloy) wire stirrer had completely dissolved and the mixture was green. We do not know whether this happening aided or harmed the reaction. The mixture was treated with 500 cc. of cold water and the ether layer was separated, washed with sodium carbonate solution and water, and was dried over calcium chloride. After a rapid vacuum distillation the product was redistilled to yield 100 g. (77%) of 1-chloro-2-heptyne, b. p. 73° at 24 mm. This product gave a precipitate with alcoholic silver nitrate only on warming or long standing.

1-Bromo-2-heptyne (Table II).—To a solution of 310 g. (2.75 mole) of 2-heptyn-1-ol and 5 g. of pyridine in 800 cc. of dry ether was added 271 g. (1 mole) of phosphorus tribromide at a rate to maintain refluxing. After heating and stirring for an additional two hours the mixture was cooled and the upper layer poured on ice. The organic matter was taken into ether, washed with sodium carbonate and saturated sodium chloride, and was dried over calcium chloride. The crude mixture remaining after removal of the ether was rapidly vacuum distilled to remove high boiling material and then rectified to yield 340 g. (72%) of 1-bromo-2-heptyne, b. p. 104–105° at 56 mm., and 55 g. (7%) of a hydrogen bromide addition compound presumably 1,3-dibromo-2-heptene, b. p. 112° at 25 mm., 70° at 2 mm., *n*_D²⁰ 1.5172.

Anal. Calcd. for C₇H₁₂Br₂: C, 32.8; H, 4.7. Found: C, 33.3, 33.7; H, 4.8, 4.5.

Repetition of the above reaction under slightly modified conditions gave yields in the range of 60 to 70%. None of the desired product was obtained when one equivalent of pyridine was used.

In a manner similar to the above, 2-hexyn-1-ol was con-

(20) Johnson and McEwen, *THIS JOURNAL*, 48, 469 (1926).

verted into 1-bromo-2-hexyne, b. p. 97–98° at 80 mm., n_D^{25} 1.4884, in 63% yield.

Anal. Calcd. for C_6H_9Br : C, 44.7; H, 5.6; Br, 49.7. Found: C, 44.4; H, 5.8; Br, 50.2.

The hydrogen bromide addition product (12% yield) formed here, probably 1,3-dibromo-2-hexene, had a boiling point of 100° at 25 mm., or 62° at 2 mm. and n_D^{25} 1.5235.

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.9; H, 4.1. Found: C, 30.4, 30.1; H, 4.3, 4.4.

Both 1-bromo-2-heptyne and 1-bromo-2-hexyne gave immediate precipitates when added to alcoholic silver nitrate.

The yield in the conversion of 3-heptyn-1-ol to 1-bromo-3-heptyne (Table II) by this method was considerably less (crude, 41%).

1-Bromo-6-heptyne.—A suspension of 3.2 mole of sodium acetylide in 1.5 l. of liquid ammonia was added during one hour to a stirred mixture of 1050 g. (4.6 mole) of pentamethylene dibromide, 500 cc. of dry ether, and 1 l. of ammonia. The addition was accomplished through a tube dipping into the bottom of the sodium acetylide flask and leading into the other. The rate of addition was controlled by partial release of the ammonia pressure in the acetylide flask as needed. The last amounts of acetylide were transferred by using three 50-cc. portions of ammonia for washing. After stirring for two more hours, the product was isolated as usual as a colorless oil, b. p. 80–100° at 20 mm. in 27% yield. On redistillation, pure 1-bromo-6-heptyne of b. p. of 92° at 20 mm., n_D^{25} 1.4750, was obtained with little loss.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.0; H, 6.3. Found: C, 48.8, 48.5; H, 6.5, 6.6.

1,2,3-Tribromo-2-heptene.—Because of difficulties met with in the attempted conversion of 1-bromo-2-heptyne to the corresponding cyanide, we thought it might prove useful to add bromine to the triple bond and remove it later. However, we never attempted to do the latter. By adding 80 g. of bromine in 80 cc. of carbon tetrachloride to 56 g. of 2-heptyn-1-ol in 75 cc. of carbon tetrachloride at 0° and waiting until decolorization after adding each drop, there was obtained 110 g. (81%) of 2,3-dibromo-2-hepten-1-ol, b. p. 113–115° at 4 mm.

Anal. Calcd. for $C_7H_{12}OBr_2$: C, 30.9; H, 4.4. Found: C, 30.8, 30.6; H, 4.5, 4.8.

The 3,5-dinitrobenzoate melted at 84–85°.

Anal. Calcd. for $C_{14}H_{14}O_8Br_2N_2$: C, 36.1; H, 3.0; N, 6.0. Found: C, 36.3; H, 3.0; N, 6.1.

By the procedure described above, this alcohol was converted into 1,2,3-tribromo-2-heptene, b. p. 112–114° at 4 mm., 96° at 2 mm., n_D^{25} 1.5540, in 87% yield.

Anal. Calcd. for $C_7H_{11}Br_3$: C, 25.1; H, 3.2. Found: C, 25.3, 25.4; H, 3.7, 3.6.

3,4-Dibromo-3-octen-1-ol.—In a similar way, 3-octyn-1-ol was converted into its dibromide, b. p. 111–113° at 2 mm. *Anal.* Calcd. for $C_8H_{14}OBr_2$: C, 33.5; H, 4.9. Found: C, 33.5, 33.8; H, 5.2, 5.3. The 3,5-dinitrobenzoate melted at 85–86°. *Anal.* Calcd. for $C_{15}H_{16}O_8Br_2N_2$: C, 37.5; H, 3.3; N, 5.8. Found: C, 37.4, 37.2; H, 3.5, 3.7; N, 6.3, 6.2. No further useful experiments with these bromine addition products were performed.

1-Iodo-5-hexyne.—Crude 1-chloro-5-hexyne prepared as described above was converted into 1-iodo-5-hexyne, b. p. 94–95° at 35 mm., n_D^{25} 1.5286, in 82% yield by refluxing with an excess of sodium iodide in acetone for twenty hours.

Anal. Calcd. for C_6H_9I : C, 34.4; H, 4.3. Found: C, 35.3; H, 4.4.

1-Cyano-6-heptyne (Table II).—A mixture of 120 g. of 1-bromo-6-heptyne, 65 g. of potassium cyanide, 120 cc. of water, and 300 cc. of acetone was stirred and refluxed for forty-eight hours after which 250 cc. of mixed solvent was distilled. After suitable treatment the residue yielded 60 g. (74%) of 1-cyano-6-heptyne as a colorless liquid, b. p. 90–92° at 6 mm.

Similarly, 1-cyano-5-heptyne (Table II) b. p. 88–95° at 5 mm. was prepared from 1-iodo-5-heptyne (prepared from 1-chloro-5-heptyne as above described), the over-all yield from chloro compound being 75%. Likewise, 1-chloro-4-heptyne was converted (Table II) directly into 1-cyano-4-heptyne, b. p. 110–112° at 29 mm., in 82% yield.

1-Cyano-2-heptyne (Table II).—In the best of many experiments, a mixture of 70 g. of 1-bromo-2-heptyne, 45 g. of carefully dried cuprous cyanide, and 40 cc. of xylene was stirred and heated by a salt-bath at 160° until the inside temperature reached 157°. The temperature of the bath was lowered to 145° and the reaction proceeded exothermically for about thirty minutes during which time the inside temperature was not allowed to exceed 165°. After cooling the mixture was extracted thoroughly with benzene, all solids being removed by filtration. On distillation there was obtained 44 g. (92%) of nitrile, b. p. 123–126° at 56 mm. In other trials, the yields varied from 0 to 90%. Careful regulation of the temperature of the reaction mixture seems to be most important. Attempts to combine either the chloride or bromide with aqueous solutions of potassium cyanide were always fruitless.

1-Cyano-3-heptyne (Table II).—This nitrile was prepared from the corresponding acid via the amide and dehydration of the latter with phosphorus pentoxide. The yield on the last step was 50%.

5-, 6- and 7-Octynoic Acid (Table II).—The corresponding nitriles were hydrolyzed to the acids in about 90% yields by refluxing with an excess of 10% potassium hydroxide solution until the evolution of ammonia ceased.

3-Octynoic acid (Table II).—A stream of hydrogen chloride (tank) was passed into solution of 140 g. of 1-cyano-2-heptyne in 250 cc. of methanol and 25 cc. of water until it refluxed and later fell to 30°. The precipitated ammonium chloride was collected and the filtrate was concentrated. The crude ester was further hydrolyzed with alcoholic alkali to yield 120 g. (74%) of acid, b. p. 120–130° at 6 mm.

One attempt at hydrolysis involving shaking 6 g. of the cyanide with 20 cc. of concentrated hydrochloric acid for four days at room temperature yielded 3 g. (34%) of a product, b. p. 148 at 4 mm., m. p. 54–55° after crystallization from petroleum ether (b. p. 30–60°), which was presumably the amide of 4-chloro-3-octenoic acid.

Anal. Calcd. for $C_8H_{14}ONCl$: C, 54.9; H, 7.9; N, 8.0. Found: C, 54.9; H, 7.8; N, 8.1.

When the hydrolysis with concentrated hydrochloric acid was carried out at 80° for twelve hours, 8 g. (46%) of a chloro acid, presumably 4-chloro-3-octenoic acid, b. p. 125–126° at 3 mm., was obtained. The neutral equivalent was 177, 178; calculated for $C_8H_{13}O_2Cl$, 176.5.

When a mixture of 6 g. of 1-cyano-2-heptyne, 5 g. of concentrated sulfuric acid and 2 cc. of water was heated and stirred at 60° for two days little reaction had occurred. An additional 10 cc. of 6 N sulfuric acid was added and the heating and stirring continued for one day. The organic matter was then isolated and heated with aqueous potassium hydroxide until a homogeneous solution was obtained. The acid fraction after vacuum distillation and crystallization from petroleum ether (b. p. 30–60°) amounted to 4 g., m. p. 53–54°, neutral equivalent, 157. Calcd. for $C_8H_{14}O_3$, 156. This acid was thus 4-ketoöctanoic acid.²¹

Because of the difficulty in hydrolyzing 1-cyano-2-heptyne, it was brominated, as described for 1,2,3-tribromo-2-heptene, to yield 50% of the expected 1-cyano-2,3-dibromo-2-heptene, b. p. 118 at 4 mm.

Anal. Calcd. for $C_7H_{11}NBr_2$: N, 4.9. Found: N, 4.4.

Hydrolysis of this compound was likewise incomplete as heating 14 g. with 20 cc. of concentrated sulfuric acid to 80° for fifteen minutes, followed by standing at room temperature for three hours yielded only 7 g. (47%) of the amide of 3,4-dibromo-3-octenoic acid, m. p. 130–131°.

Anal. Calcd. for $C_8H_{13}ONBr_2$: C, 32.1; H, 4.3; N, 4.7. Found: C, 32.2; H, 4.5; N, 5.0.

(21) Blaise and Koehler, *Compt. rend.*, **148**, 489 (1909).

4-Octynoic acid (Table II).—In a typical malonic ester synthesis 280 g. (1.74 mole) of 1-bromo-2-hexyne was added to a solution of 1.5 l. of absolute alcohol, the sodium ethoxide prepared from 41.5 g. (1.8 mole) of sodium, and 320 g. (2 mole) of ethyl malonate. After refluxing for eight hours the product was treated as usual to yield 240 g. (57%) of ethyl 2-hexynylmalonate, b. p. 134–134° at 5 mm., and 75 g. (13%) of ethyl di-(2-hexynyl)-malonate, b. p. 168–170° at 5 mm., n_D^{25} 1.4600.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 65.0; H, 8.3. Found: C, 65.3, 65.2; H, 8.2, 8.2. Calcd. for $C_{18}H_{22}O_4$: C, 71.2; H, 8.7. Found: C, 71.2, 71.3; H, 8.8, 8.7.

In another experiment partial saponification occurred during isolation of the products from the reaction mixture and there was isolated a small amount of ethyl di-(2-hexynyl)-acetate, b. p. 135–137° at 3 mm.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7. Found: C, 77.0, 77.0; H, 9.7, 9.8.

On alkaline hydrolysis 2-hexynylmalonic acid, m. p. 109–110° with dec., and di-(2-hexynyl)-malonic acid, m. p. 138–139° with dec., were obtained. The neutralization equivalents were 92, 91 (theory, 92) and 131, 131 (theory, 132), respectively.

Anal. Calcd. for $C_8H_{12}O_4$: C, 58.9; H, 6.5. Found: C, 59.0, 59.0; H, 6.6, 6.7. Calcd. for $C_{18}H_{20}O_4$: C, 68.2; H, 7.6. Found: C, 68.4, 68.5; H, 7.6, 7.6.

Heating at 150 to 170° until the evolution of carbon dioxide ceased afforded 4-octynoic acid in 93% over-all yield from ester. The di-2-hexynylacetic acid was not isolated as such but was converted into the amide, m. p. 63–64°.

Anal. Calcd. for $C_{14}H_{21}ON$: C, 76.8; H, 9.6; N, 6.4. Found: C, 76.9, 77.0; H, 10.1, 10.1; N, 6.5, 6.5.

2-Octynoic Acid.—In a manner similar to the above, ethyl 2-heptynylmalonate, b. p. 146 at 5 mm., was prepared in 66% yield.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.1; H, 8.7. Found: C, 64.9; H, 8.5.²²

(22) The remaining malonic ester was saponified before the poor analytical result was obtained, hence we were unable to secure a good analysis.

On hydrolysis 2-heptynylmalonic acid, m. p. 93–94°, neutral equivalent 99 (theory, 99), was obtained.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 60.6; H, 7.1. Found: C, 59.9, 59.5; H, 7.1, 7.3.

Preparation of Methyl Esters.—The acetylenic acids were obtained in over 90% yields after refluxing for twelve hours in an excess of methanol containing small amounts of *p*-toluenesulfonic acid.

Ozonization of Octynoic Acids.—The octynoic acids were oxidized in acetic acid in an ozonizer of the Henne-Perilstein type²³ using a flow rate of 23 l. of oxygen, containing 1 g. of ozone, per hour. Only the dibasic fractions were isolated. The acids were checked by melting point and neutralization equivalent. The yields from solutions of about 4 g. of acids in 50 cc. of acetic acid (ozonized for four hours at room temperature) were as follows: 7-octynoic acid, 46% pimelic acid; 6-octynoic acid, 52% adipic acid; 5-octynoic acid, 71% glutaric acid; 4-octynoic acid, 67% succinic acid; and 3-octynoic acid, 80% malonic acid. No attempt to isolate maximum amounts of these dibasic acids was made.

Hydrogenation of Octynoic Acids.—The octynoic acids, 0.8 to 1.4 g., were dissolved in 20 cc. of pure ethyl alcohol and reduced over 0.20 g. of Adams platinum catalyst in a quantitative manner using an apparatus similar to that described by Joshel.²⁴ In each case almost exactly the theoretical amount of hydrogen was absorbed in times which varied from 150 to 300 minutes. 5-Octynoic acid was hydrogenated on a larger scale in a shaking device (Parr Instrument Company). In each case the saturated acid, obtained in almost theoretical yield, proved to be *n*-octanoic acid. Comparison was always effected by means of the amide, m. p. and mixed m. p., 103–104°.

Summary

The synthesis of 7-, 6-, 5-, 4- and 3-octynoic acids and the preparation and chemical behavior of many of the new acetylenic intermediates are described.

(23) Henne and Perilstein, *THIS JOURNAL*, **65**, 2183 (1943).

(24) Joshel, *Ind. Eng. Chem., Anal. Ed.*, **15**, 590 (1943).

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Native Lignin. II. Native Aspen Lignin^{1,2}

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The isolation of native lignin fractions from black spruce and western hemlock has been described by Brauns.³ These two preparations represent softwood (gymnosperm) lignin and are similar in nature. It is well known that hardwood (angiosperm) lignin differs from softwood lignin in that the former contains a greater amount of methoxyl and is built up of both syringyl and guaiacyl nuclei, whereas only the latter are found in softwood lignins. In recent years, the hardwoods have become increasingly important as a source of wood pulp. Consequently, it was of

interest to isolate and investigate the native lignin fraction from a typical hardwood.

Native aspen lignin was isolated by means of neutral ethanol under conditions designed to prevent any change in the lignin during its isolation and purification. The crude lignin contained 17.6% methoxyl, which agrees with the value of 17.5% reported by Lovell and Hibbert⁴ for a lignin preparation extracted from aspen with neutral alcohol. These investigators separated their product into three fractions by a fractional distribution between water, methanol, chloroform and carbon tetrachloride. They obtained one fraction having a methoxyl content of 18.4%, but apparently did not investigate their lignin further.

(1) For paper I of this series see F. E. Brauns, *THIS JOURNAL*, **61**, 2120–2127 (1939).

(2) Presented before the Division of Cellulose Chemistry at the 114th meeting of The American Chemical Society, Portland, Oregon, September 13–16, 1948.

(3) F. E. Brauns, *J. Org. Chem.*, **10**, 211–215 (1945).

(4) E. L. Lovell and H. Hibbert, *THIS JOURNAL*, **63**, 2070–2073 (1941).