tract. It was found necessary to wash the ether or ligroin solution with aqueous alcohol, although this caused some loss of linolenyl alcohol in the resulting emulsions. After copious washing, the dried alcohol was distilled at 133° (2 mm.). The distillate still contained 1.63% of free acid, which was removed with dilute alkali. The final yield of pure alcohol was 13 g.

Properties of Linolenyl Alcohol.—The linolenyl alcohol was a colorless, oily liquid. Its iodine value was 287.0 (calcd. 288.2); it had an $E^{1\%}_{1\,\text{cm.}}$ of less than 1 at 2700 Å. and about 6 at 2300 Å. Its $n^{23}\text{D}$ was 1.4792, compared to 1.4800 for linolenic acid. On bromination in ether, it produced an immediate precipitate of a granular bromide corresponding to approximately 25% of the theoretical yield. After one crystallization from benzene, the hexabromide sintered at 171° and melted sharply at 172°. An additional recrystallization did not alter the m. p. The alcohol thus closely resembles the corresponding acid.

Summary

Unconjugated alpha-linoleyl and alpha-linolenyl alcohols were prepared by the reduction of methyl linoleate and methyl linolenate with sodium in absolute ethanol.

The physical and chemical properties of the alcohols were shown to parallel closely the properties of the parent acids.

alpha-Linoleyl alcohol was characterized by its tetrabromide, m. p. 88°, while alpha-linolenyl alcohol formed a hexabromide, m. p. 172°.

alpha-Linoleyl alcohol was rearranged by potassium hydroxide in butanol to isomeric octadecadiene-10,12-ols, among them a solid 10,12-linoleyl alcohol, m. p. 43.5°. The properties of the isomerized alcohols were related to the characteristics of the products of reduction of methyl linoleate with sodium in butanol.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 8, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Tertiary Acetylenes[1]

BY KENNETH N. CAMPBELL AND LAWRENCE T. EBY

The catalytic reduction of acetylenes offers a good means of preparing olefins of known position of the double bond,[2] but so far this work has been confined to the straight chain compounds, as acetylenes containing branches near the triple bond have been difficult to prepare, and but few of them are known. In order to extend the reduction studies to this type of acetylene it therefore was necessary first to develop a method of preparing such compounds. The simplest method of making acetylenes, the reaction of an alkyl halide with a sodium acetylide, fails with secondary and tertiary halides.[3] *t*-Butylacetylene has been prepared[4] by treatment of 3,3-dimethyl-2,2-dichlorobutane with sodium hydroxide, and neopentylacetylene has been made by a similar produre.[5] This method is not, however, of general application, since in most cases the intermediate halide is difficult to prepare.

Attention was therefore turned to the Grignard reaction as a means of making the desired acetylenes. Just as neopentane can be made from methylmagnesium chloride and *t*-butyl chloride,[6] it was hoped that acetylenic hydrocarbons could be prepared from acetylenic Grignard reagents and tertiary alkyl halides. Although these Grignard reagents will couple with activated halides such as allyl bromide,[7] it was found in the present study that only poor yields of hydrocarbon were obtained when *t*-butyl or *t*-amyl bromides were used, and the method does not seem a promising one for the preparation of branched chain acetylenes.

The possibility of preparing such acetylenes from tertiary acetylenic chlorides and primary aliphatic Grignard reagents was then investigated. Tertiary acetylenic carbinols, which are easily prepared from sodium acetylide or a sodium alkylacetylide and a ketone in liquid ammonia,[8] can be readily converted to the corresponding chlorides by means of anhydrous hydrogen chloride at low temperatures. The chlorides are unstable, but can be distilled and kept without decomposition if reasonable care is used. They show the usual reactions of tertiary chlorides,

---

[1] Paper XL on the chemistry of substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **62**, 1368 (1940). This material was presented before the Organic Division at the Cincinnati meeting, April, 1940.

[2] Campbell and O'Connor, *ibid.*, **61**, 2897 (1939).

[3] Picon, *Compt. rend.*, **168**, 825 (1919).

[4] Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[5] Ozanne and Marvel, THIS JOURNAL, **52**, 5267 (1930).

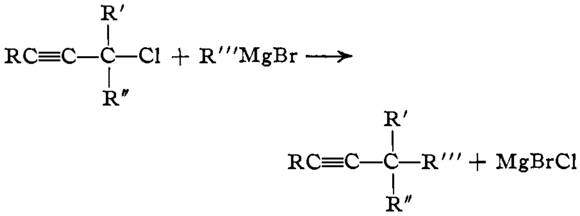
[6] Whitmore and Fleming, *ibid.*, **55**, 3803 (1933).

[7] Danehy, Killian and Nieuwland, *ibid.*, **58**, 611 (1936).

[8] Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).

somewhat enhanced by the presence of the unsaturated group. It has not been found possible so far to prepare Grignard reagents from these chlorides.

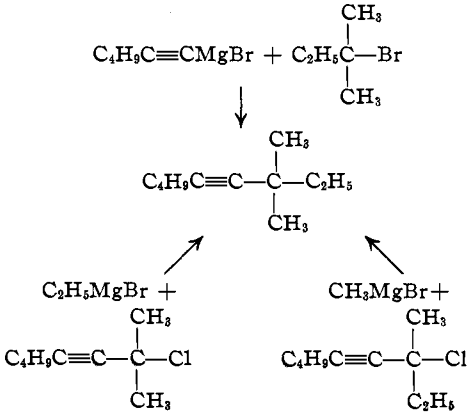
It was found, however, that the chlorides which do not contain an acetylenic hydrogen atom couple easily at about 80° with aliphatic magnesium bromides, to give branched chain acetylenic hydrocarbons in good yields.



$$RC{\equiv}C{-}\overset{R'}{\underset{R''}{C}}{-}Cl + R'''MgBr \longrightarrow RC{\equiv}C{-}\overset{R'}{\underset{R''}{C}}{-}R''' + MgBrCl$$

The reaction does not go well when R is hydrogen, possibly because an insoluble acetylenic magnesium bromide is formed, which does not easily react further.

Acetylenic hydrocarbons were obtained from 3-chloro-3-methyl-4-heptyne with methyl- and ethylmagnesium bromides, 2-chloro-2-methyl-3-octyne with methyl- and ethylmagnesium bromides, 3-chloro-3-methyl-4-nonyne with methylmagnesium bromide, and 3-chloro-3-methyl-4-decyne with methylmagnesium bromide. The identity of the products was established by means of physical constants, analyses and by reduction to the saturated hydrocarbons. In two cases the expected saturated hydrocarbon was synthesized in fair yields from a primary alkylmagnesium bromide and a tertiary alkyl bromide, and the synthetic material compared with that obtained by reduction. As a further proof that the acetylenic hydrocarbons had the structures assigned to them, 3,3-dimethyl-4-nonyne was made in three ways, as indicated below, and the products shown to be identical.



$$C_4H_9C{\equiv}CMgBr + C_2H_5\overset{CH_3}{\underset{CH_3}{C}}{-}Br \longrightarrow C_4H_9C{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C_2H_5$$

$$C_2H_5MgBr + C_4H_9C{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl \longrightarrow C_4H_9C{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C_2H_5 \longleftarrow CH_3MgBr + C_4H_9C{\equiv}C{-}\overset{CH_3}{\underset{C_2H_5}{C}}{-}Cl$$

Experimental

Preparation of Acetylenic Carbinols.—These were made by the general procedure of Campbell, Campbell and Eby.[8]

Preparation of Acetylenic Chlorides.—Hydrogen chloride gas, dried by means of sulfuric acid and calcium chloride, was passed into the pure carbinol, which was kept cold in an ice–salt bath. The passage of gas was continued for one hour after the liquid became saturated. The water layer formed by the reaction was then removed, and anhydrous potassium carbonate was added slowly, with shaking and cooling, to the crude halide until the pink color disappeared. The chlorides were stored in a refrigerator and fractionated from fresh potassium carbonate through a helix-packed column under reduced pressure. In the case of methylethylethynylcarbinol, it was necessary to allow the reaction mixture to stand overnight under pressure with hydrogen chloride, and the best yield of chloride was obtained by shaking the carbinol with concentrated hydrochloric acid.[8]

Preparation of 3,3-Dimethyl-4-nonyne from Butylacetylenemagnesium Bromide.—Ethylmagnesium bromide was prepared in the usual way from 80.2 g. of magnesium turnings and 359.7 g. of ethyl bromide. A solution of 246 g. of butylacetylene in an equal volume of dry ether was added slowly, and then the mixture was refluxed gently to complete the expulsion of ethane. Ether was added as necessary to keep the mixture fluid. Three hundred and fifty-three grams of *t*-amyl bromide was added dropwise, with refluxing, to the acetylenic Grignard reagent, over a period of five hours, and the reaction mixture was refluxed for seven hours after addition was complete. The mixture was poured onto ice and dilute hydrochloric acid, the ether layer separated, washed with water and dried over magnesium sulfate. Distillation of the material left after removal of the ether yielded only 13 g. of 3,3-dimethyl-4-nonyne, a 3% yield. No better results were obtained when *t*-amyl chloride was used, or when the reaction was carried out in toluene solution.

Preparation of Acetylenic Hydrocarbons from the Chlorides.—The procedure was the same in all cases, and so only a typical example is given. Ethylmagnesium bromide was prepared from 14 g. of magnesium turnings, 70 g. of ethyl bromide and 125 cc. of dry ether. When the reaction was complete, ether was removed from the reagent by distillation until the temperature of the Grignard mixture was about 80°. One-half mole (79.3 g.) of undiluted 2-methyl-2-chloro-3-octyne was added slowly, with stirring, while the inside temperature was maintained at 60–80°. After all the halide was added, the mixture was stirred and kept at a temperature above 50° for five hours. Ether was added, if necessary, to keep the reaction mass mobile. Hydrolysis was accomplished by pouring the mixture onto crushed ice and hydrochloric acid. The organic layer was separated, dried over potassium carbonate and the ether removed at atmospheric pressure. The residue was fractionated through a helix-packed column under reduced pressure.

Reduction of Acetylenes.—The acetylene (0.2 mole) was dissolved in 50 cc. of reagent-grade methyl alcohol and 3 g. of Raney nickel catalyst[9] was added. The mixture was

---

(9) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

TABLE I

YIELDS AND PHYSICAL CONSTANTS OF CHLORIDES

Compound	Yield, %	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	*MR*D Obsd.	*MR*D Calcd.	Cl analyses, % Found	Cl analyses, % Calcd.
3-Cl-3-Me-4-pentyne	60	55	130	1.4330	0.9163	33.04	32.77	30.42	30.41
3-Cl-3-Me-4-heptyne	66	64	25	1.4514	.9100	42.76	42.28	24.56	24.52
2-Cl-2-Me-3-octyne	85	68	15	1.4480	.8929	47.52	46.90	22.29	22.35
3-Cl-3-Me-4-nonyne	72	82	17	1.4543	.8968	52.18	51.52	20.48	20.53
3-Cl-3-Me-4-decyne	86	90	10	1.4549	.8849	57.20	56.13	18.41	18.99

TABLE II

YIELDS AND PHYSICAL CONSTANTS OF ACETYLENES

Compound	Yield, %	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	*MR*D Obsd.	*MR*D Calcd.
3,3-Di-Me-4-heptyne	66	69	100	1.4360	0.7610	42.67	42.08
3-Me-3-Et-4-heptyne	61	88	100	1.4386	.7714	47.10	46.68
2,2-Di-Me-3-octyne	74	79	70	1.4270	.7491	47.38	46.68
3,3-Di-Me-4-nonyne[a]	73	82	40	1.4313	.7658	51.45	51.28
3,3-Di-Me-4-nonyne[b]	60	82	40	1.4312	.7650	51.60	51.28
3,3-Di-Me-4-nonyne[c]	3	80	40	1.4300	.7669	51.2	51.28
3,3-Di-Me-4-decyne	72	86	20	1.4399	.7731	56.68	55.90

[a] Prepared from methylmagnesium bromide and 3-chloro-3-methyl-4-nonyne. [b] From 2-chloro-2-methyl-3-octyne and ethylmagnesium bromide. [c] From butylacetylenemagnesium bromide and *t*-amyl bromide. Since only small amounts were obtained in this reaction, the product could not be obtained in a very pure state..

TABLE III

ANALYSES OF ACETYLENES

Compound	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
3,3-Di-Me-4-heptyne	86.75	87.02	13.28	12.98
3-Me-3-Et-4-heptyne	86.34	86.52	13.60	13.48
2,2-Di-Me-3-octyne	86.45	86.52	13.56	13.48
3,3-Di-Me-4-nonyne[a]	87.00	86.76	13.07	13.24
3,3-Di-Me-4-nonyne[b]	86.55	86.76	13.35	13.24
3,3-Di-Me-4-nonyne[c]	86.81	86.76	13.53	13.24
3,3-Di-Me-4-decyne	86.43	86.66	13.40	13.34

(a), (b) and (c) have the same significance as in Table II.

TABLE IV

PHYSICAL CONSTANTS OF SATURATED HYDROCARBONS

Compound	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	*MR*D Obsd.	*MR*D Calcd.
3,3-Di-Me-heptane[a]	135	735	1.4078	0.7270	43.41	43.76
3,3-Di-Me-heptane[b]	136	745	1.4084	.7278	43.43	43.76
3-Me-3-Et-heptane[a]	155	734	1.4179	.7460	48.06	48.38
2,2-Di-Me-octane[a]	62	30	1.4082	.7245	48.47	48.38
3,3-Di-Me-nonane[a]	84	30	1.4212	.7469	52.98	53.00
3,3-Di-Me-nonane[b]	83	29	1.4200	.7478	52.80	53.00
3,3-Di-Me-decane[a]	89	20	1.4225	.7542	57.45	57.62

[a] Prepared by reduction of the acetylene. [b] Synthesized from *t*-amyl bromide and a primary alkylmagnesium bromide.

shaken with hydrogen in an Adams machine until no more hydrogen was absorbed. The catalyst was removed by filtration and the filtrate poured into 300 cc. of cold water. The organic layer was dried over anhydrous potassium carbonate and fractionated through a helix-packed column under reduced pressure. In some cases reduction did not go to completion, as shown by a high index of refraction of the product. In these cases the material was reduced again, using the Adams platinum oxide–platinum black catalyst, in absolute ethyl alcohol.

Preparation of Saturated Hydrocarbons by the Grignard Reaction.—*n*-Hexylmagnesium bromide was prepared from 24.3 g. of magnesium and 162 g. of *n*-hexyl bromide. Ether was removed by distillation until the temperature of the reaction mixture reached 70°. One hundred and fifty grams of *t*-amyl bromide was added over a period of two hours, with vigorous stirring, while the temperature was kept above 50°. The mixture was refluxed for an additional eight hours and was then hydrolyzed with ice and hydrochloric acid. The hydrocarbon was purified by distillation through a helix-packed column. A 23% yield of 3,3-dimethylnonane was obtained. Using the same procedure, 3,3-dimethylheptane was prepared from butylmagnesium bromide and *t*-amyl bromide in 28% yield.

Summary

1. Branched chain acetylenes have been prepared in good yields by coupling tertiary acetylenic chlorides with aliphatic Grignard reagents.

2. The coupling of acetylenic Grignard reagents with tertiary aliphatic halides is not at present a practical method for preparing branched chain acetylenes.

3. Several new acetylenes have been prepared and reduced to the saturated hydrocarbons.

NOTRE DAME, INDIANA

RECEIVED MAY 3, 1940