

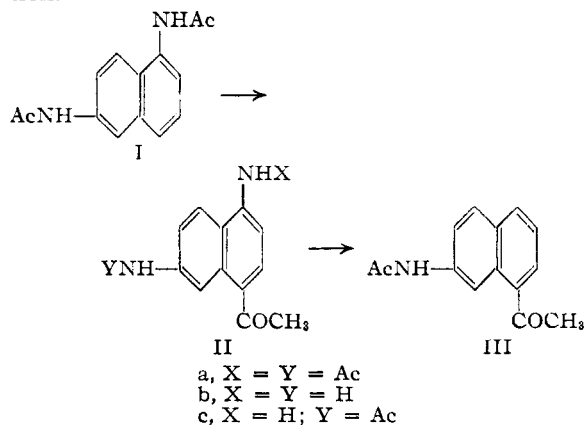
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Directive Influence of the Acetylamino Group in the Friedel-Crafts Acylation of the Diacetylaminonaphthalenes

BY NELSON J. LEONARD AND ARCHIBALD M. HYSON¹

Since complete identification of the products of Friedel-Crafts acetylation of acet-1- and acet-2-naphthalide^{2,3} indicated that the acetyl group does not enter a position ortho to the acetylamino group, it was of interest to determine if the same generalization holds true for the diacetylaminonaphthalenes. Accordingly the Friedel-Crafts acetylation of diacetylaminonaphthalenes has been studied under the same conditions, and it has been found that acetyl substitution does not occur at positions ortho or peri to either acetylamino group.

Eight of the ten possible naphthalenediamines were prepared and were subjected, as their acetyl derivatives, to Friedel-Crafts acylation with acetyl chloride in the presence of excess aluminum chloride either in carbon disulfide or in *sym*-tetrachloroethane. The choice of solvent was influenced by the solubility of the naphthalenediamine at the reaction temperature. The choice of reactant—free base or N,N'-diacetyl derivative—was guided by convenience since the previous study³ indicated that identical results were obtained whether the acetylaminonaphthalene was used as such initially or was generated under the reaction conditions. Of the eight naphthalenediamines prepared and subjected to Friedel-Crafts acetylation conditions, six failed to undergo ring-acetylation: 1,2-, 1,4-, 1,5-, 1,8-, 2,6- and 2,7-naphthalenediamine (although of course N-acetylation occurred when the free diamine was employed as reactant). Both 1,6- and 1,7-diacetylaminonaphthalene underwent ring-acetylation in the 4-position.



The structure of the Friedel-Crafts acetylation product of 1,6-diacetylaminonaphthalene (I) was

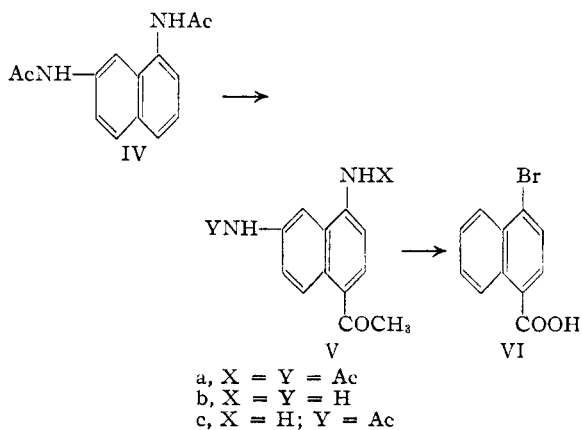
(1) Present address: Ammonia Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

(2) Leonard and Hyson, *J. Org. Chem.*, **13**, 164 (1948).

(3) Leonard and Hyson, *This Journal*, **71**, 1392 (1949)

established as 4,7-diacetylaminonaphthalene (IIa) by the following series of conversions. The product (IIa) was hydrolyzed to 4,7-diamino-1-acetonaphthone (IIb), and selective acetylation of the 7-amino group was utilized in the next step. It was considered that if monoacetylation would occur, the 7-amino group would be acylated in preference to the 4-amino group, since the latter is less basic due to its location para to the carbonyl function. Monoacetylation did occur quantitatively when IIb was treated with acetic anhydride in hot, dry benzene, and the expected location of the acetyl group on the β -nitrogen was established by further degradation of IIc, which also established the structure of the initial Friedel-Crafts product. The 4-amino group of the 4-amino-7-acetylaminonaphthalene (IIc) was converted to the diazonium group, which was replaced smoothly by hydrogen through treatment with hypophosphorous acid to give 7-acetylaminonaphthalene-4-carboxylic acid (III). This product was identical with an authentic sample² of 7-acetylaminonaphthalene.

1,7-Diacetylaminonaphthalene (IV) likewise underwent Friedel-Crafts acetylation in the position para to the α -acetylamino group, and 4,6-diacetylaminonaphthalene (Va) was the



product. The proof of structure of compound Va was achieved as follows. It was hydrolyzed to the diamine Vb, and Vb was monoacetylated, as with the 4,7-isomer, to form 4-amino-6-acetylaminonaphthalene-1-acetonaphthone (Vc). The α -amino group was converted to the diazonium group, which was replaced by bromine to give 4-bromo-6-acetylaminonaphthalene-1-acetonaphthone. In succession, acid hydrolysis, diazotization, and hypophosphorous acid treatment converted this compound to 4-bromo-1-acetonaphthone, which was not isolated but was oxidized directly to 4-bromo-1-naphthoic

acid (VI). Compound VI was identical with an authentic sample of 4-bromo-1-naphthoic acid.

From these experiments on the Friedel-Crafts reaction with N-acetylated naphthalenediamines, it can be stated empirically that substitution does not occur at positions ortho or peri to the acetyl-amino group, evidently due to steric hindrance. When, as in certain of the diacetylaminonaphthalenes, the ortho and peri positions are the only activated ones, no ring-acetylation will occur. For example, no ring-acetylation takes place with the 1,4-, 1,5- and 2,7-diacetylaminonaphthalenes. Substitution in 1,6-diacetylaminonaphthalene occurs at the 4-position, which is the only activated position not adjacent to an amino group. Substitution in 1,7-diacetylaminonaphthalene likewise occurs at the most activated and unhindered position. That no substitution (at the 5-position) takes place in the ring of 1,7-diacetylaminonaphthalene which contains the β -acetyl-amino group is consistent with the lack of substitution at the analogous 4-position of the 2,6-compound.

Experimental⁴

Preparation of Naphthalenediamines

1,2-Naphthalenediamine.—1-Nitro-2-naphthylamine⁵ was reduced catalytically in ethanol solution over Raney nickel at 25° and 100–130 atm. The 1,2-naphthalenediamine was recrystallized from water as glistening plates, m. p. 96–98° (reported, 98°)⁶; 1,2-diacetylaminonaphthalene, m. p. 234–236° (reported, 234°).⁷

1,4-Naphthalenediamine.—4-Nitroacet-1-naphthalide,⁸ prepared by the nitration of acet-1-naphthalide,^{8,9} was reduced catalytically in ethanol over Raney nickel, and the product was acetylated to give 1,4-diacetylaminonaphthalene; colorless needles from aqueous acetic acid, m. p. 295.5–297.5° (reported, 303°).¹⁰

1,5-Naphthalenediamine.—1,5-Dinitronaphthalene⁷ was reduced catalytically to give the diamine, m. p. 187.5–189° (reported, 190°).¹¹

1,5-Diformylaminonaphthalene was obtained by the action of formic acid on 1,5-naphthalenediamine following the method of Hodgson and Whitehurst¹²; m. p. 283°, with decomposition.

1,6-Naphthalenediamine.—5-Nitroacet-2-naphthalide,¹³ prepared by the nitration of acet-2-naphthalide,^{14,15,9} was reduced catalytically to give 5-aminoacet-2-naphthalide; colorless needles from benzene-acetone, m. p. 139–140°.

Anal. Calcd. for C₁₂H₁₂N₂O: C, 71.97; H, 6.04; N, 14.00. Found: C, 72.23; H, 6.24; N, 13.63.

1,6-Diacetylaminonaphthalene crystallized as colorless needles from aqueous acetic acid; m. p. 267–268° (reported, 263.5°).¹³

1,7-Naphthalenediamine.—8-Nitroacet-2-naphthalide,¹⁵ prepared by the nitration of acet-2-naphthalide,^{14,15,9} was reduced catalytically to give 8-aminoacet-2-naphthalide; colorless needles from benzene-ligroin, m. p. 149–149.5°.

Anal. Calcd. for C₁₂H₁₂N₂O: C, 71.97; H, 6.04; N, 14.00. Found: C, 71.68; H, 6.01; N, 13.75.

1,7-Diacetylaminonaphthalene crystallized as colorless prisms from acetone-ligroin; m. p. 217–220° (reported, 213°).¹⁶

1,8-Naphthalenediamine.—1,8-Dinitronaphthalene, obtained from a technical mixture of the 1,5- and 1,8-isomers, was reduced catalytically to give the diamine; colorless needles from benzene-ligroin, m. p. 65–66.5° (reported, 66.5°).¹⁷

2,6-Naphthalenediamine.—Catalytic reduction of 6-nitro-2-naphthylamine¹⁸ gave 2,6-naphthalenediamine, m. p. 226° (reported, 217°).¹⁷

2,7-Naphthalenediamine.—The catalytic reduction of 2,7-dinitronaphthalene,¹⁹ followed by acetylation of the product, gave colorless needles of 2,7-diacetylaminonaphthalene from water (3 l. of water per gram of solid), m. p. 264–265° (reported, 261°).²⁰

Friedel-Crafts Acetylation

The Friedel-Crafts acetylation of the naphthalenediamines (or of their N,N'-diacyl derivatives) was carried out in carbon disulfide or *sym*-tetrachloroethane, using at least seven moles of aluminum chloride per mole of diamine and two to three moles of acetyl chloride per mole of diamine. Larger proportions of aluminum chloride or acetyl chloride did not influence the course of the reaction. The temperature was maintained at 25° for twelve hours and then at 45° (for carbon disulfide) or 100° (for tetrachloroethane) for two to ten hours. The results were not altered when the tetrachloroethane was substituted for carbon disulfide, when the N,N'-diacyl derivative was used in place of the diamine, or when the reaction temperatures and times were varied.

Only starting material and, in some cases, traces of the N,N'-diacyl compounds were isolated in the reactions of 1,5-naphthalenediamine, 1,5-diformylaminonaphthalene, 2,6-naphthalenediamine, and 2,7-diacetylaminonaphthalene under these conditions. Where the reaction product was other than the starting diamine, the methods of isolation and structure-proof are given below.

Characterization of the Product of Friedel-Crafts Acetylation of 1,2-Naphthalenediamine.—The crude solid, which was obtained after removal of carbon disulfide and decomposition of the complex with hydrochloric acid and ice, was suspended in water and was treated with alkali. The mixture was extracted thoroughly with ether and the ether was removed. The residue crystallized from aqueous ethanol as long, faintly yellow needles, m. p. 171.5–172.5° (plates from water).

Anal. Calcd. for C₁₂H₁₂N₂O: C, 71.97; H, 6.04; N, 14.00. Found: C, 72.22; H, 6.18; N, 14.01.

The analysis indicated that an acetyl group had entered the molecule, and its attachment to one of the nitrogens rather than to the ring was established by the fact that the product gave a negative iodoform test. Diazotization of the product as a suspension in 10 *N* hydrochloric acid gave a colorless solid, m. p. 188.5–189.5°, soluble in aqueous alkali and insoluble in aqueous acid, identified as naphtho-1',2':4,5-triazole (reported, 188°).²¹

Characterization of the Product of Friedel-Crafts Acetylation of 1,2-Diacetylaminonaphthalene.—The solid, which was obtained after removal of carbon disulfide and decomposition of the complex with ice, was recrystallized from water to constant melting point, 249°.

Anal. Calcd. for C₁₆H₁₆N₂O₃: C, 67.58; H, 5.68; N, 9.86. Found: C, 67.62; H, 5.76; N, 10.21.

The analysis and negative iodoform test indicated that a third N-acetyl group had entered the molecule. Hydrolysis of a 10-g. sample was effected by heating under

(4) All melting points are corrected.

(5) "Organic Syntheses," **13**, 72 (1933).

(6) Lellmann and Remy, *Ber.*, **19**, 796 (1886).

(7) Lawson, *ibid.*, **18**, 796 (1885).

(8) Hodgson and Walker, *J. Chem. Soc.*, 1205 (1933).

(9) Hodgson and Ward, *ibid.*, 1060 (1947).

(10) Kleeman, *Ber.*, **19**, 334 (1886).

(11) Krollpfeiffer, *Ann.*, **430**, 199 (1923).

(12) Hodgson and Whitehurst, *J. Chem. Soc.*, 202 (1945).

(13) Sachs, *Ber.*, **39**, 3022 (1906).

(14) Friedländer and Szymanski, *ibid.*, **25**, 2076 (1892).

(15) Morgan and Gilmour, *J. Soc. Chem. Ind.*, **41**, 61T (1922).

(16) Friedländer, *Ber.*, **29**, 41 (1896).

(17) Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 79 (1928).

(18) Saunders and Hamilton, *THIS JOURNAL*, **54**, 636 (1932).

(19) Hodgson and Ward, *J. Chem. Soc.*, 590 (1945).

(20) Windaus, *Ber.*, **57**, 1731 (1924).

(21) Diels, *ibid.*, **54**, 226 (1921).

reflux with 200 ml. of 1 *N* hydrochloric acid for one hour. After decolorization of the solution, 100 ml. of 10 *N* hydrochloric acid was added, and a hydrochloride salt was precipitated. Recrystallization from ethanol-ether gave colorless crystals, m. p. > 320°, identified as 2-methyl-3-naphth[1,2]imidazole hydrochloride.²²

Anal. Calcd. for $C_{12}H_{11}ClN_2$: C, 65.89; H, 5.07; N, 12.81. Found: C, 65.85; H, 5.22; N, 12.81.

Characterization of the Product of Friedel-Crafts Acetylation of 1,5-Naphthalenediamine.—The solid obtained after solvent-removal and complex-decomposition was extracted with ether. The ether-soluble material proved to be 1,5-naphthalenediamine. The small amount of ether-insoluble material had no definite melting point but decomposed about 350°. The compound was unchanged by cold 2 *N* hydrochloric acid, with or without nitrous acid, but slowly gave a clear yellow solution with 10 *N* hydrochloric acid and nitrous acid. This solution added to an alkaline solution of 2-naphthol produced the same shade of red as did diazotized 1,5-naphthalenediamine. The compound was undoubtedly 1,5-diacetylaminonaphthalene, reported as decomposing above 360° by Kunckell and Schneider.²³

Friedel-Crafts Acetylation of 1,6-Diacetylaminonaphthalene

4,7-Diacetylaminonaphthalene.—The crude Friedel-Crafts product was dissolved in boiling glacial acetic acid, with decolorization, and 1 l. of water was added to the hot, clear solution. Pure 4,7-diacetylaminonaphthalene, m. p. 249.5–250.5, was obtained in 76% yield after one recrystallization from water.

Anal. Calcd. for $C_{16}H_{18}N_2O_2$: C, 67.58; H, 5.68; N, 9.86. Found: C, 67.80; H, 5.66; N, 9.90.

Hydrolysis of 10 g. of this compound by boiling with 120 ml. of 2 *N* hydrochloric acid during one-half hour, followed by decolorization, filtration, and neutralization of the cooled filtrate with ammonia, gave 6.8 g. (96%) of 4,7-diamino-1-acetonaphthone. Recrystallization from benzene-ligroin gave yellow rods, m. p. 151–152°.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.97; H, 6.04; N, 14.00. Found: C, 72.17; H, 6.21; N, 13.72.

Proof of Structure of 4,7-Diamino-1-acetonaphthone

Conversion to 4-Amino-7-acetylaminonaphthalene.—One gram of 4,7-diamino-1-acetonaphthone was dissolved in 250 ml. of hot benzene, and 0.5 ml. of acetic anhydride was added in one portion to the hot solution. The mixture was allowed to stand at 25° overnight, and the monoacetyl derivative which separated in quantitative yield was recrystallized first from water, then from benzene-acetone; m. p. 251–253°, depressed on admixture with the diacetyl derivative.

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.39; H, 5.83; N, 11.57. Found: C, 69.42; H, 5.93; N, 11.64.

Diazotization and Deamination of 4-Amino-7-acetylaminonaphthalene.—A 250-mg. sample of 4-amino-7-acetylaminonaphthalene was suspended in 10 ml. of ice-water, and 0.75 ml. of 10 *N* hydrochloric acid was added, followed immediately by excess solid sodium nitrite until a clear orange solution resulted. The excess nitrous acid was then destroyed by the addition of urea. The cold solution was treated with 5 ml. of 30% hypophosphorous acid and the reaction mixture was kept at 0° overnight. The solid which separated was collected and was washed with 2.5 *N* sodium hydroxide followed by water. The dried material (150 mg.) was recrystallized from benzene-ligroin with decolorization and finally from aqueous ethanol to give needles, m. p. 149–150°, which did not depress the melting point of an authentic sample of 7-acetylaminonaphthalene.²

(22) Fischer and Hepp, *Ber.*, **20**, 2471 (1887); Meldola and Eynon, *J. Chem. Soc.*, **77**, 1159 (1900); Fischer, Reindl and Fezer, *Ber.*, **34**, 930 (1901).

(23) Kunckell and Schneider, *Chem. Ztg.*, **36**, 1021 (1912).

Friedel-Crafts Acetylation of 1,7-Diacetylaminonaphthalene

4,6-Diacetylaminonaphthalene.—The crude Friedel-Crafts product was extracted with 3 l. of boiling water, with decolorization. The filtered aqueous extract, upon cooling, deposited light cream-colored, silky needles. Pure 4,6-diacetylaminonaphthalene, m. p. 263.5–264.5°, was obtained in 60% yield after one recrystallization from water.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 67.58; H, 5.68; N, 9.86. Found: C, 67.76; H, 5.81; N, 9.79.

Hydrolysis of 1 g. of this compound by boiling with 50 ml. of 2 *N* hydrochloric acid during one-half hour, followed by decolorization, filtration and neutralization of the cooled filtrate with ammonia, gave 0.55 g. (78%) of 4,6-diamino-1-acetonaphthone. The melting point, 140–141°, was not improved by recrystallization from benzene.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.97; H, 6.04; N, 14.00. Found: C, 71.80; H, 6.15; N, 13.86.

Proof of Structure of 4,6-Diamino-1-acetonaphthone

Conversion to 4-Amino-6-acetylaminonaphthalene.—4,6-Diamino-1-acetonaphthone was converted to 4-amino-6-acetylaminonaphthalene following the procedure employed with the 4,7-isomer; needles from water, m. p. 209–211°.

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.39; H, 5.83; N, 11.57. Found: C, 69.34; H, 6.07; N, 11.81.

Preparation of 4-Bromo-6-acetylaminonaphthalene.—One gram of 4-amino-6-acetylaminonaphthalene was suspended in 20 ml. of ice-water. To this suspension was added 1 ml. of 5 *N* hydrobromic acid, followed immediately by solid sodium nitrite in small portions until a clear red solution resulted. The excess nitrous acid was destroyed by addition of urea. The solution of the diazonium bromide was poured into a cooled solution of 4 g. of cuprous bromide in 45 ml. of 5 *N* hydrobromic acid. The reaction mixture was allowed to stand at 25° overnight, and the solid was removed by filtration and was washed several times with 3.5 *N* hydrobromic acid and finally with water. The 4-bromo-6-acetylaminonaphthalene (0.52 g.) crystallized as needles from ethanol; m. p. 194–195°.

Anal. Calcd. for $C_{14}H_{13}BrNO_2$: C, 54.91; H, 3.95; N, 4.58. Found: C, 55.14; H, 4.06; N, 4.55.

Conversion to 4-Bromo-1-naphthoic Acid.—4-Bromo-6-acetylaminonaphthalene (100 mg.) was converted to the amine hydrochloride. A suspension of the finely-divided salt in 18 ml. of 4 *N* hydrochloric acid was treated with solid sodium nitrite until a clear yellow solution was obtained. Excess nitrous acid was destroyed by the addition of urea, and to the solution was added 6 ml. of a 30% solution of hypophosphorous acid. The mixture was kept at 0° for twelve hours, then at 25° for twelve hours. The supernatant liquid was decanted, and the oily semi-solid residue was subjected to hypochlorite oxidation. The product was worked up in the usual manner. An acid was obtained which melted at 221–222° after recrystallization from aqueous ethanol. The melting point of 4-bromo-1-naphthoic acid as reported by Gomberg and Blicke²⁴ was 217–220°. An authentic sample of 4-bromo-1-naphthoic acid was prepared from 4-amino-1-acetonaphthalene by replacement of the amino group by bromine, followed by hypochlorite oxidation of the 4-bromo-1-acetonaphthalene. The melting point of the authentic sample was 221–222° and a mixed melting point of the two specimens showed no depression.

Characterization of the Product of Friedel-Crafts Acetylation of 1,8-Naphthalenediamine.—The crude Friedel-Crafts product was extracted with 300 ml. of hot 2 *N* hydrochloric acid. The extract was decolorized and the resulting clear yellow solution was kept at 0° overnight. The silky yellow needles which appeared were collected and dried; yield, 40%; m. p. > 360°, with decomposition.

(24) Gomberg and Blicke, *This Journal*, **45**, 1765 (1923).

Anal. Calcd. for $C_{12}H_{11}ClN_2$: C, 65.89; H, 5.07. Found: C, 66.11; H, 5.48.

The analysis and properties indicated that the compound was 2-methylperimidine hydrochloride.²⁵

Summary

1. In the series of naphthalenediamines subjected, as their acetyl derivatives, to the Friedel-

(25) Holljes and Wagner, *J. Org. Chem.*, **9**, 31 (1944).

Crafts acetylation reaction, ring-acetylation was found to take place at the 4-position in 1,6-diacetylaminonaphthalene, at the 4-position in 1,7-diacetylaminonaphthalene, and failed to take place with the 1,2-, 1,4-, 1,5-, 1,8-, 2,6- and 2,7- isomers.

2. The results indicate that the acetyl group does not enter a position ortho or peri to either acetylamino group.

URBANA, ILLINOIS

RECEIVED DECEMBER 10, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

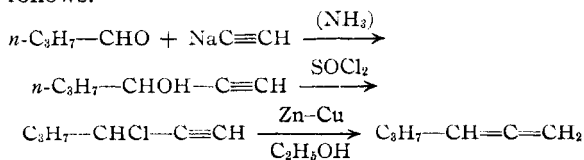
1,2-Hexadiene¹

BY G. F. HENNION AND J. J. SHEEHAN

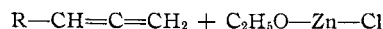
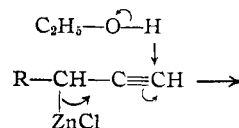
Introduction

Comparison of the chemical and physical properties of allenes and acetylenes has long been desirable. While a great deal is now known about higher acetylenes, much of the literature on the isomeric allenes is old and unreliable. The present study was undertaken to prepare authentic 1,2-hexadiene (*n*-propylallene) for comparison with the well-known 1-hexyne.

The best known synthesis of 1,2-dienes is that of Bouis² which involves the reaction of a Grignard reagent with acrolein, conversion of the unsaturated alcohol to the corresponding bromide, addition of bromine to the latter to form a 1,2,3-tribromoparaffin followed by elimination of hydrogen bromide and debromination with zinc dust. There are a number of disadvantages and uncertainties in this multi-stage synthesis. A more elegant approach is suggested by the recent work of Ginzburg³ who claims that 3-methyl-1,2-butadiene is produced by the zinc-copper-alcohol reduction of dimethylethynylcarbonyl chloride, $(CH_3)_2C(Cl)-C\equiv CH$. We have adapted this method to the preparation of 1,2-hexadiene. The over-all synthesis involves only three steps illustrated as follows.



The three reactions were studied in considerable detail and conditions found for a 50-70% yield at each stage. Since the infrared spectra clearly confirmed the acetylenic nature of the alcohol and the chloride, the reduction must involve an interesting rearrangement for which a possible mechanism may be pictured in the following manner.



The crude 1,2-hexadiene was contaminated with a small amount of 1-hexyne, most of which could be removed by careful fractional distillation. The allenic structure was proved by the following facts: (a) the physical constants differed from those for 1- and 2-hexyne; (b) hydrogenation with Adams platinum catalyst added exactly four atoms of hydrogen; (c) oxidation with alkaline permanganate yielded *n*-butyric acid; (d) hydration in the presence of mercuric sulfate and dilute sulfuric acid gave methyl *n*-butyl ketone; (e) the Diels-Alder reaction with maleic anhydride and attempted acetylide formation with ammoniacal silver nitrate solution were unsuccessful; (f) the infrared spectrum showed strong absorption at 4.8 and 6 microns, characteristic of 1,2-dienes⁴; (g) the ultraviolet spectrum failed to show any strong absorption in the 200-400 $m\mu$ region.

The similarity of the chemical and physical properties of 1,2-hexadiene and 1-hexyne was striking. In addition to rapid hydration in the presence of mercury catalysts,⁵ reaction with methanol proceeded well under similar conditions⁶ and gave a good yield of 2,2-dimethoxyhexane. Reaction with dry hydrogen chloride and a small amount of bismuth chloride in benzene solution⁷ gave 2-chloro-2-hexene and 2,2-dichlorohexane. Semihydrogenation over Raney nickel produced a mixture of 1- and 2-hexenes in which the latter appeared to predominate. Attempted reduction with sodium and moist ether resulted in consid-

(1) Paper LII on substituted acetylenes; previous paper, *THIS JOURNAL*, **70**, 427 (1948).

(2) Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927); *Ann. chim.*, [10] **9**, 402 (1928).

(3) Ginzburg, *J. Gen. Chem. (U. S. S. R.)*, **10**, 513 (1940); *C. A.*, **34**, 7843 (1940).

(4) The infrared examination disclosed the likely presence of a small amount of acetylenic impurity and the complete absence of conjugate dienes.

(5) Thomas, Campbell and Hennion, *THIS JOURNAL*, **60**, 718 (1938).

(6) Killian, Hennion and Nieuwland, *ibid.*, **56**, 1384 (1934).

(7) Hennion and Welsh, *ibid.*, **62**, 1367 (1940).