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–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

---

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

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

1,2-Hexadiene[1]

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.

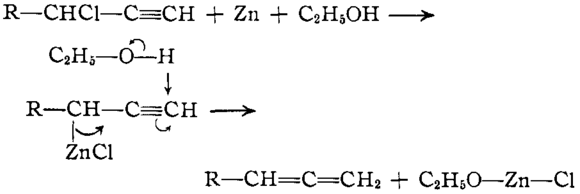
The best known synthesis of 1,2-dienes is that of Bouis[2] which involves the reaction of a Grignard reagent with acrolein, conversion of the unsaturated alcohol to the corresponding bromide, addition of bromine to the latter to form a 1,2,3-tribromoparaffin followed by elimination of hydrogen bromide 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 Ginzburg[3] who claims that 3-methyl-1,2-butadiene is produced by the zinc–copper-alcohol reduction of dimethylethynylcarbinyl 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.

$$n\text{-}C_3H_7\text{—}CHO + NaC{\equiv}CH \xrightarrow{(NH_3)}$$

$$n\text{-}C_3H_7\text{—}CHOH\text{—}C{\equiv}CH \xrightarrow{SOCl_2}$$

$$C_3H_7\text{—}CHCl\text{—}C{\equiv}CH \xrightarrow[C_2H_5OH]{Zn\text{-}Cu} C_3H_7\text{—}CH{=}C{=}CH_2$$

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.



$$R\text{—}CHCl\text{—}C{\equiv}CH + Zn + C_2H_5OH \longrightarrow$$

$$\begin{array}{l} C_2H_5\text{—}O\text{—}H \\ \qquad\quad\downarrow \\ R\text{—}\underset{ZnCl}{\underset{|}{CH}}\text{—}C{\equiv}CH \longrightarrow \end{array}$$

$$R\text{—}CH{=}C{=}CH_2 + C_2H_5O\text{—}Zn\text{—}Cl$$

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-dienes[4]; (g) the ultraviolet spectrum failed to show any strong absorption in the 200–400 mμ 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 conditions[6] and gave a good yield of 2,2-dimethoxyhexane. Reaction with dry hydrogen chloride and a small amount of bismuth chloride in benzene solution[7] 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).

erable isomerization to 1-hexyne which is not reduced by this treatment. Like 1-hexyne, 1,2-hexadiene may be distilled repeatedly at atmospheric pressure. It yellows slowly in contact with air but does not appear to polymerize appreciably. While silver and mercury derivatives were not formed in aqueous alkaline solution, neutral mercuric chloride in dilute alcohol gave a copious white precipitate.[2,8]

The physical properties of 1,2-hexadiene and some of its important isomers are summarized in Table I for comparison.

TABLE I

CONSTANTS FOR SOME C_6H_{10} HYDROCARBONS

Compound	B. p., °C.	Mm.	d^{20}	$n^{20}D$
1,2-Hexadiene	74.6–74.8	740	0.7149	1.4282
1,3-Hexadiene[a]	71–71.5		.707	1.4271
1-Hexyne[b]	71.4	760	.7156	1.3990
2-Hexyne[c]	83.8	742	.7317	1.4135

[a] Paul and Tchelitcheff, *Compt. rend.*, **223**, 1136 (1946).
[b] Henne and Greenlee, THIS JOURNAL, **67**, 485 (1945).
[c] Campbell and Eby, *ibid.*, **63**, 2684 (1941).

Experimental

n-**Propylethynylcarbinol.**—Pure *n*-butyraldehyde (2.5 moles) dissolved in an equal volume of anhydrous ether was added dropwise to 2.5 moles of sodium acetylide in 2.5 liters of liquid ammonia. The mixture was cooled to −45 to −50° and a slow stream of acetylene admitted with good stirring throughout the reaction. The carbinol was recovered (53% yield) in the usual manner[9]; b. p. 64° at 30 mm.; $n^{25}D$ 1.4344; d^{25} 0.8710. The literature values[10] are b. p. 140–141° at 760 mm.; $n^{20}D$ 1.43297; d^{20} 0.8704. The α-naphthyl urethan melted at 74–75°.

n-**Propylethynylcarbinyl Chloride.**—Sixty-five grams of *n*-propylethynylcarbinol and 1 g. of dry pyridine were placed in a three-necked, 500-ml., round-bottom flask, equipped with a mercury-sealed sweep-stirrer, dropping funnel, and air condenser. Eighty grams of freshly distilled thionyl chloride was added dropwise with moderate stirring and at the conclusion of the addition, the mixture was heated to 70° for thirty minutes. The mixture was cooled, poured on 200 g. of ice and 50 ml. of ether added. The ether layer was washed twice with water, twice with a sodium bicarbonate solution, and again with water. It was dried with calcium chloride and after removal of the ether, the residue was distilled through a helix-packed column at 100 mm. yielding 55.5 g. of material (72% yield) boiling at 60–66°. Redistillation gave the following constants: b. p. 63–64° at 100 mm.; $n^{25}D$ 1.4375; d^{25} 0.9240.

1,2-Hexadiene.—The zinc-copper couple was prepared in the following manner. Sixty-two grams of zinc dust was washed four times with 50-ml. portions of 3% hydrochloric acid solution, twice with 50-ml. portions of distilled water, twice with 100-ml. portions of 2% copper sulfate solution, twice with distilled water, once with 100 ml. of 95% alcohol, and once with 100 ml. of absolute alcohol. The couple was then washed with 150 ml. of absolute alcohol into a three-necked, 500-ml., round-bottom flask equipped with a mercury-sealed stirrer, reflux condenser and dropping funnel. Fifty-six grams of *n*-propylethynylcarbinyl chloride was added dropwise with stirring. It was necessary to cool the flask occasionally during the addition since the reaction was exothermic. The mixture was finally heated to reflux for four hours with good stirring. The cooling water was removed from the condenser and the allene–alcohol azeotrope boiling from 63–66° was distilled through the condenser, the latter serving as a fractionating column. The distillate was washed three times with water and the hydrocarbon layer dried with calcium chloride. Distillation through a helix-packed column gave 28 g. of material (71% yield) boiling at 73.8–74.6° at 744 mm. Redistillation through a Todd column gave a product with the following constants: b. p. 74.6–74.8° at 740 mm.; $n^{25}D$ 1.4252, $n^{20}D$ 1.4282; d^{25} 0.7102, d^{20} 0.7149; *MR* calcd. 28.98, obsd. 29.58. Bouis[2] reported: b. p. 78–79° at 760 mm.; $n^{17}D$ 1.4298; d^{17} 0.7198.

Catalytic Hydrogenation.—A mixture of 0.05 g. of Adams platinum catalyst, 0.8646 g. (0.0105 mole) of 1,2-hexadiene and 100 ml. of 95% ethyl alcohol was shaken with hydrogen in a Parr machine at an initial pressure of 40 p. s. i. Reaction was complete in thirty minutes with absorption of 0.02 mole of hydrogen.

A mixture of 16.5 g. (0.2 mole) of 1,2-hexadiene, 1 g. of Raney nickel, and 50 ml. of 95% ethyl alcohol was shaken with hydrogen at an initial pressure of 56.3 p. s. i. until 0.2 mole had been absorbed. The reaction mixture was filtered from the catalyst, washed twice with water, and dried over anhydrous potassium carbonate. Fractional distillation gave a product boiling at 63–68°, mostly 67–68°, indicating that it was a mixture of the 1- and 2-hexenes. The 67–68° fraction had $n^{20}D$ 1.3925, in good agreement with 2-hexene.

Oxidation.—Two grams of 1,2-hexadiene, 175 ml. of water and 1 g. of sodium hydroxide were agitated with a mechanical stirrer and 7 g. of potassium permanganate was added in small portions over a period of twelve hours. Excess permanganate was removed with a little oxalic acid, the manganese dioxide removed by filtration, and the filtrate concentrated to 25 ml. The solution was acidified with 50% sulfuric acid and distilled. The distillate was exactly neutralized, 20 ml. of alcohol and 1 g. of *p*-bromophenacyl bromide added, and the solution refluxed for one hour. On cooling, *p*-bromophenacyl butyrate crystallized. Two recrystallizations from aqueous alcohol yielded a product (0.9 g.) whose m. p. and mixed m. p. was 62–62.5°.

Methanol Addition.—In a three-necked, 500-ml., round-bottom flask equipped with a mercury-sealed stirrer, dropping funnel, and condenser, there was placed 3 g. of red mercuric oxide, 2 ml. of boron trifluoride–diethyl ether and 3 ml. of methyl alcohol. Sixteen grams of methyl alcohol was added to the mixture and stirring begun. Twenty and one-half grams (0.25 mole) of 1,2-hexadiene in 16 g. of methyl alcohol was added dropwise to this mixture with good stirring. After one and one-half hours 5 g. of potassium carbonate was added and stirring continued for another hour. The solids were allowed to settle overnight and the clear yellow liquid decanted and distilled. Nineteen and one-half grams of product was collected and had the following constants: b. p. 64–65° at 30 mm.; $n^{25}D$ 1.4053; d^{25} 0.8527. Literature values[6] for 2,2-dimethoxyhexane are: b. p. 58–60° at 30 mm.; $n^{25}D$ 1.4053; d^{25} 0.8536.

Hydrolysis of the above product yielded a ketone whose semicarbazone melted at 124°. Mixed m. p. with the semicarbazone from authentic methyl *n*-butyl ketone was 124–125°.

Hydration.—Two grams of 1,2-hexadiene was added to 0.8 g. of concentrated sulfuric acid, 0.3 g. of mercuric sulfate, 2.0 g. of water and 5 g. of methyl alcohol. The exothermic reaction was complete within fifteen minutes. One gram of sodium acetate was added and the mixture distilled to near dryness. The distillate was treated with semicarbazide hydrochloride in the usual manner and methyl *n*-butyl ketone semicarbazone, m. p. 123°, recovered in 70% yield. The experiment was repeated and the methyl *n*-butyl ketone treated with 2,4-dinitrophenylhydrazine. The derivative melted correctly at 106°.

Hydrogen Chloride Addition.—Twenty grams of 1,2-hexadiene, 80 ml. of dry benzene and 1 g. of bismuth trichloride was placed in a three-necked, 500-ml., round-bottom flask provided with a mercury-sealed stirrer, re-

---

(8) Bouis, *Compt. rend.*, **182**, 790 (1926).

(9) Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938).

(10) Zalkind and Gverdsiteli, *J. Gen. Chem.* (*U. S. S R.*), **9**, 971 (1939); *C. A.*, **33**, 8569 (1939).

flux condenser, and gas inlet tube. Dry hydrogen chloride gas was passed into the rapidly stirred mixture for two and one-half hours with an increase in weight of 3.5 g. The temperature was kept between 65 and 70° during the addition. The mixture was washed with hydrochloric acid, water, sodium carbonate solution, again with water, and dried over calcium chloride. Distillation gave two fractions. The high boiling fraction had the following constants: b. p. 68–71° at 49 mm.; $n^{25}\text{D}$ 1.4369; d^{25} 1.0137. Literature values[7] for 2,2-dichlorohexane are: b. p. 68° at 49 mm.; $n^{25}\text{D}$ 1.4353; d^{25} 1.0150. The lower boiling fraction had the following constants: b. p. 117–118°; $n^{25}\text{D}$ 1.4300; d^{25} 0.8937; % chlorine, obsd. 26.15; calcd. 29.89. Permanganate oxidation of this material, as described above, produced *n*-butyric acid whose *p*-bromophenacyl ester was identical with that obtained from an authentic sample.

Isomerization of 1,2-Hexadiene.—Ten grams of 1,2-hexadiene was added to 5 g. of sodium under 100 ml. of moist ether and heated to gentle reflux. Eight grams of water was added, a few drops at a time, over a period of two days. Distillation of the ether layer gave about 2 g. of 1-hexyne, whose mercury derivative[11] melted correctly at 96–97°. Three grams of unreacted 1,2-hexadiene was also recovered.

Acknowledgment.—The authors express their sincere appreciation to Drs. A. S. Carter and A. A. Ebert, Jr., of the Jackson Laboratory, E. I. du Pont De Nemours and Company, for determination and interpretation of the infrared spectra of 1,2-hexadiene and its antecedents, 3-hydroxy- and 3-chloro-1-hexyne.

Summary

1. 1,2-Hexadiene has been prepared by a three-step synthesis starting with *n*-butyraldehyde and sodium acetylide.

2. The reactions of 1,2-hexadiene are very similar to those undergone by the higher acetylenes and give products corresponding to those secured from either 1- or 2-hexyne.

NOTRE DAME, INDIANA RECEIVED JANUARY 22, 1949

---

[11] Vaughn, THIS JOURNAL, **55**, 3453 (1933).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

o-t-Butylphenol

BY HAROLD HART

In several recent papers[1,2,3] the effect of bulky groups in the ortho positions upon the spectra and reactivity of phenols has been investigated. It is to be noted, however, that in nearly all of the compounds studied, there was a substituent present in the para as well as the ortho position. Since both electrical and steric factors probably play a role in the effect of ortho substituents, it was desirable to have available for study compounds which contain groups in the ortho position only. It was the purpose of this investigation to devise a method of synthesizing such compounds. *o-t*-Butylphenol was selected as a typical example.

o-t-Butylphenol has been reported previously by several workers.[4,5,6] Direct alkylation of phenol, however, is not satisfactory for the laboratory synthesis of *o-t*-butylphenol.[5,7]

p-Bromophenol was alkylated with isobutylene using a procedure similar to that of Stillson, Sawyer and Hunt.[3] The 4-bromo-2-*t*-butylphenol obtained was reduced to *o-t*-butylphenol with Raney nickel–aluminum alloy and aqueous alkali.[8] This reduction, carried out in alkaline solution yields essentially no rearranged product. The over-all yield of *o-t*-butylphenol was 68%. Some of its physical and chemical properties are described in the Experimental Part.

The ultraviolet absorption spectrum of *o-t*-butylphenol in cyclohexane was determined and is shown in Fig. 1, with the spectra of phenol and *p-t*-butylphenol for comparison. It is seen that the spectrum of *o-t*-butylphenol is very similar to that of phenol, with peaks of almost identical extinction coefficients at 271 and 278 mμ and an incipient peak at 265 mμ corresponding to the peak at that wave length in the phenol spectrum. The peaks are somewhat broader, as one might expect, for the substituted phenol. *p-t*-Butylphenol has a spectrum which is almost identical with that of the ortho isomer, with the exception that the entire spectrum is shifted about 6 mμ toward the red (peaks at 277 and 283 mμ and an incipient peak at 271 mμ). The spectrum of *p*-cresol as determined by Wolf and Herold[9] shows a similar shift toward the red, whereas *o*-cresol has its maxima at almost

---

[1] N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

[2] N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[3] G. H. Stillson, D. W. Sawyer and C. K. Hunt, *ibid.*, **67**, 303 (1945).

[4] G. Vavon and N. Zaharia, *Compt. rend.*, **187**, 347 (1928).

[5] R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. Patent 1,972,599 (1934).

[6] W. A. Pardee and W. Weinrich, *Ind. Eng. Chem.*, **36**, 595 (1944).

[7] A. E. Chichibabin, *Bull. soc. chim.*, [5] **2**, 497–520 (1935); *Compt. rend.*, **198**, 1239 (1934). Chichibabin reported the synthesis of certain *o*-alkylphenols in good yields from tertiary alcohols, phenols and a phosphoric acid catalyst. The alkylation of phenol itself is not described by Chichibabin, but there is some reason to doubt the validity of the assignment of structure made by him to the mono-*t*-butyl-*o*-cresol. Dr. Donald R. Stevens of the Mellon Institute has kindly made available to us the boiling points which were obtained by Dr. Victor J. Anhorn of the Gulf Research and Development Company, Pittsburgh, Pa., for 6-*t*-butyl-*o*-cresol and 4-*t*-butyl-*o*-cresol. They are 110° and 124° (14 mm.), respectively. The mono-*t*-butyl-*o*-cresol described by Chichibabin is reported to boil at 122.5° (14 mm.) and is probably the 4-*t*-butyl- and not the 6-*t*-butyl-*o*-cresol as claimed.

[8] D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942); E. Schwenk, D. Papa, B. Whitman and H. Ginsberg, *ibid.*, **9**, 1 (1944).

[9] K. L. Wolf and W. Herold, *Z. physik. Chem.*, [B] **13**, 201 (1931).