magnesium iodide prepared from 0.50 g. of magnesium and 1.5 ml. of methyl iodide in 25 ml. of ether was added dropwise over a period of 5 min. a solution of 4.30 g. of the lactone III in 25 ml. of ether. The mixture was heated under reflux for 15 min. and then hydrolyzed with dilute hydrochloric acid. The ether layer was washed with water and bisulfite solution and finally dried and evaporated to yield a colorless oil which resisted crystallization. It was dissolved in a mixture of 60 ml. of glacial acetic acid, 30 ml. of concentrated hydrochloric acid and 5 ml. of water and the solution heated under reflux for 2 hours. The reddish solution was diluted with 200 ml. of water and extracted with ether. The ether extract was washed with water and extracted twice with dilute aqueous sodium hydroxide. Acidification of the alkaline extract liberated 2.28 g. (49% recovery) of the crystalline β-(1-tetralone-2)-butyric acid (I) melting at 101–102° after recrystallization from heptane.[3] The ether layer was dried and evaporated to yield a yellow oil which when triturated under a little hexane deposited 640 mg. (15% yield) of white crystals, m.p. 119–125°. Two additional recrystallizations from methanol afforded large prisms of **1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI)** melting at 124–125° when alone or admixed with an authentic sample.[3]

The hexane filtrate from the preceding crystals was diluted to 200 ml. with more hexane and the solution passed through a column of 15 g. of activated alumina. The filtrate upon evaporation yielded 1.26 g. (30% yield) of a colorless oil solidifying when chilled and melting at 55–61°. Four recrystallizations from methanol produced colorless rods of **1,3-dimethyl-1,2,3,4-tetrahydrophenanthrene (X)**, m.p. 64–65°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.54. Found: C, 91.20; H, 8.26.

The picrate crystallized from methanol in the form of orange-colored needles, m.p. 133–135°.

Anal. Calcd. for $C_{22}H_{21}O_7N_3$: C, 60.13; H, 4.78. Found: C, 59.96; H, 5.06.

The ultraviolet absorption spectrum of the hydrocarbon was determined in methanol at a concentration of 1 mg. %. It showed absorption bands at 280 mμ (log *e* 3.75), 307 mμ (log *e* 2.98) and 322 mμ (log *e* 2.88) (see text). The spectrum coincides with that reported[5] for 1,2,3,4-tetrahydrophenanthrene.

Dehydrogenation of the hydrocarbon was carried out on 500 mg of product in the presence of 100 mg. of 10% palladium-on-charcoal. The mixture was heated to 300–320° for 45 min. then cooled and dissolved in 100 ml. of hexane. The solution was filtered through 10 g. of activated alumina and the filtrate evaporated to yield a colorless oil (420 mg. or 84% yield) which solidified on cooling. Recrystallization from methanol afforded colorless needles of **1,3-dimethylphenanthrene** melting at 74.5–75.5° when alone or admixed with a sample prepared from the ketone XI.[3] **The picrate** crystallized from methanol in the form of orange-colored needles, m.p. 155–156° (reported[6]: hydrocarbon, 75–76°; picrate, 154–155°).

Procedure b.—A solution of methylmagnesium iodide in ether was prepared in a dropping funnel from 0.72 of magnesium and 2 ml. of methyl iodide. This was added dropwise over a period of 45 min. to a stirred solution of 6.4 g. of the enol lactone III in 250 ml. of pure toluene cooled to −70° in a Dry Ice–acetone-bath. The reaction mixture was allowed to warm to room temperature and the reaction products isolated as described in the preceding experiment. The oily material was dissolved in a mixture of 80 ml. of glacial acetic acid, 40 ml. of concentrated hydrochloric acid and 8 ml. of water and the solution heated under reflux for 2 hours and worked up for β-(1-tetralone-2)-butyric acid, the ketone XI and the hydrocarbon X as described in the preceding experiment.

In this manner, there were obtained, respectively, 2.83 g. (41% recovery) of β-(1-tetralone-2)-butyric acid, m.p. 101–102°, 1.90 g. (30% yield) of 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI), m.p. 124–125°, and 0.82 g. (13% yield) of 1,3-dimethyl-1,2,3,4-tetrahydrophenanthrene (X). Identifications were made by means of mixed melting point determinations.

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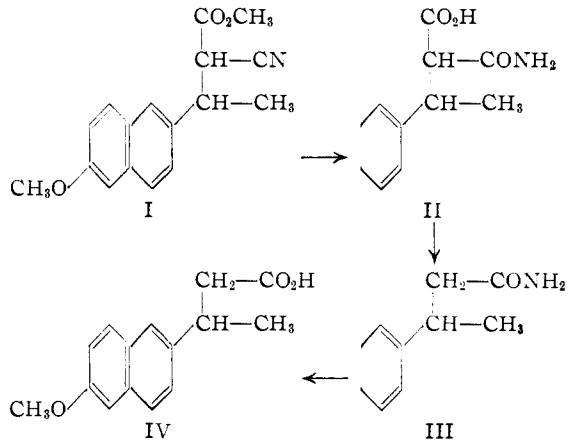
A New Route to the Allenolic Acid Type of Compound[1]

BY B. BELLEAU[2]

With the discovery by Courrier, Horeau and Jacques[3] of the high estrogenic activity exhibited by α,α-dimethyl-β-ethylallenolic acid (α,α-dimethyl - β - ethyl - 6 - hydroxy - 2 - naphthalenepropionic acid), interest in analogs of the latter was stimulated with the purpose of extending correlative studies between molecular structure and estrogenic activity. A sequence described by Horeau and Jacques[4] for the synthesis of this interesting estrogen, involves Blaise condensation of 2-cyano-6-methoxynaphthalene with methyl α-bromoisobutyrate followed by addition of ethyl Grignard reagent to the resulting β-ketoester; the carbinol so obtained is then dehydrated and hydrogenation of the double bond constitutes the final step.

This paper deals with a new and simplified approach to Horeau's type of acid. We exemplified our method by preparing β-methylallenolic acid methyl ether (IV). By analogy with the observation of Kohler and Reimer,[5] that ethyl α-cyanocinnamate reacts with phenylmagnesium bromide to yield exclusively ethyl α-cyano-β,β-diphenylpropionate through a 1,4-addition mechanism, we attempted the reaction of methyl α-cyanocrotonate with 6-methoxy-2-naphthylmagnesium bromide. This led to an oily reaction product (I) which upon heating with alkali produced a crystalline acid formulated as II. When



heated above the melting point, the latter lost carbon dioxide to give the amide III which was then saponified to β-methylallenolic acid methyl ether (IV). The resistance of the amide group of II toward strong alkali is only apparent and finds an explanation in the very low solubility of the sodium salt of II in alcohol. Since a 1,2-addition of the Grignard reagent to methyl α-

(1) Abstracted from the Ph.D. thesis of B. Belleau, presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, McGill University, 1950.

(2) The Sloan-Kettering Institute for Cancer Research, New York, N. Y.

(3) R. Courrier, A. Horeau and J. Jacques, *Compt. rend. soc. biol.*, **141**, 747 (1947).

(4) A. Horeau and J. Jacques, *Bull. soc. chim. France*, 58 (1947); J. Jacques and A. Horeau, *ibid.*, 707 (1948).

(5) E. P. Kohler and M. Reimer, *Am. Chem. J.*, **33**, 333 (1905).

cyanocrotonate cannot account for the production of intermediates II and III and the end product IV, it is obvious that 1,4-addition leading to I took place as expected. This addition product I should be especially useful as a starting material in the preparation of α-substituted allenolic acids (under investigation).

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Experimental[6]

Preparation of Starting Materials.—The 2-bromo-6-methoxynaphthalene was prepared by bromination of β-naphthol followed by reduction with tin and hydrochloric acid according to Koelsch.[7] Methylation and conversion to the Grignard reagent were carried out as described in the literature.[8] The methyl α-cyanocrotonate was prepared from acetaldehyde and cyanoacetic acid according to Young and co-workers.[9]

α-Carboxy-β-(6-methoxy-2-naphthyl)-butyramide (II).—A solution of 6-methoxy-2-naphthylmagnesium bromide was prepared from 1.07 g. of magnesium, 6.40 g. of 6-methoxy-2-bromonaphthalene and 1.0 g. of ethyl bromide in 50 ml. of a 3:5 mixture of ether–benzene. The dark brown solution was cooled to 5° and treated dropwise while stirring with a solution of 5.60 g. of methyl α-cyanocrotonate in 25 ml. of ether over a period of 20 min. The mixture was hydrolyzed with dilute sulfuric acid and more ether added. After two water-washes, the ether–benzene phase was dried and evaporated to yield an oil which was distilled *in vacuo*. A volatile fraction, b.p. 80–90° (0.1 mm.), was discarded and a sirupy fraction, b.p. 200–210° (0.1 mm.), consisting of methyl α-cyano-β-(6-methoxy-2-naphthyl)-butyrate (I) weighed 4.30 g. (56% yield).

This oil was dissolved in 25 ml. of methanol and 5 ml. of a 70% aqueous sodium hydroxide solution added. The mixture was heated under reflux for 4 hours after which time a considerable precipitate was collected by filtration. It was dissolved in 200 ml. of water and the solution after one ether-wash was acidified to liberate 1.80 g. (40% yield based on I) of needles m.p. 135–140° dec. Four recrystallizations from methanol afforded colorless prisms of α-carboxy-β-(6-methoxy-2-naphthyl)-butyramide (II) m.p. 138–139° dec.

Anal. Calcd. for $C_{16}H_{17}O_4N$: C, 66.89; H, 5.92; N, 4.87; neut. equiv., 287. Found: C, 66.52; H, 6.20; N, 4.85; neut. equiv., 287.

β-(6-Methoxy-2-naphthyl)-butyramide (III).—Of the above α-carboxy-β-methyl-6-methoxy-2-naphthalenepropionamide, 500 mg. was heated to 150° in an oil-bath until gas evolution had ceased. Upon cooling, the melt solidified and was recrystallized from methanol to yield 414 mg. (98% yield) of colorless prisms, m.p. 173–173.5°.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.07; H, 6.99; N, 5.76. Found: C, 73.95; H, 6.74; N, 5.75.

β-(6-Methoxy-2-naphthyl)-butyric Acid (IV).—Twenty-five milligrams of the preceding β-methyl-6-methoxy-2-naphthalenepropionamide was dissolved in 10 ml. of 5% methanolic potassium hydroxide and the solution heated under reflux for 3 hours after which time it was poured into 50 ml. of water. After one ether-wash, the solution was acidified and extracted with ether. The ether was dried and evaporated to yield 23 mg. (92% yield) of material, m.p. 131–133°. Two recrystallizations from aqueous methanol afforded colorless needles, m.p. 133–133.5°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.77; H, 6.55; neut. equiv., 244. Found: C, 73.30; H, 6.76; neut. equiv., 244.

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(6) Melting points and boiling points are uncorrected and Mr. Y. Perron of University of Montreal kindly performed the microanalyses.

(7) C. F. Koelsch, *Org. Syntheses*, **20**, 29 (1940).

(8) K. Fries and K. Schimmelschmidt, *Ber.*, **58**, 2840 (1925).

(9) W. G. Young, L. J. Andrews, S. L. Lindenbaum and S. J. Cristol, THIS JOURNAL, **66**, 811 (1944).

Action of Lithium Aluminum Hydride on Acetylenic Acids

BY GLEN E. BENEDICT AND ROBERT R. RUSSELL

A study of the reduction of acetylenic acids with lithium aluminum hydride has been made during an investigation of a radio-carbon synthesis procedure. In an effort to reduce the number of steps in this procedure an attempt was made to reduce triple bond acids to double bond alcohols. The method used was essentially that of Nystrom and Brown[1] with the exception that the acids were left in contact with the ether solution of lithium aluminum hydride twice as long.

The acids used in this study were acetylenedicarboxylic and propiolic. Reductions were also carried out on fumaric and acrylic acids to check product behavior and the previously reported conclusions that aliphatic double bond acids were reduced to the corresponding double bond alcohols. All acids used were soluble except fumaric which was extracted into the reaction flask from a Soxhlet thimble.

The results of this investigation indicate the triple bond acids used were reduced and hydrogenated by the action of a 25% excess of lithium aluminum hydride at room temperature to the double bond alcohols.

All product alcohols decolorized bromine rapidly. The phenyl isocyanate derivatives of the reduction products from propiolic and acrylic acids showed no melting point depression when mixed with an authentic sample prepared from allyl alcohol.

A sample of the reduction product of acetylenedicarboxylic acid was titrated with a bromine in chloroform solution and the results indicated the formation of 2-butene-1,4-diol of 98% purity. The ethyl chlorocarbonate derivatives of the diols were prepared, melting points were taken for each separately and mixed. These corresponded closely and the mixed solid showed no tendency to melt lower than either alone.

Experimental

Reduction of Acetylenedicarboxylic Acid.—In a typical reaction 750 ml. of anhydrous ether was placed in a 2-liter, three-necked flask filled with a mechanical stirrer, dropping funnel and drying tube equipped condenser. An atmosphere of dry nitrogen was provided and 0.5 mole (19.5 g.) of lithium aluminum hydride was dissolved in the ether solution by stirring for three hours. When solution was complete 250 ml. of ether containing 0.2 mole (22.8 g.) of acetylenedicarboxylic acid was added dropwise and the resultant mixture stirred at room temperature for 16 hours. The excess hydride was then cautiously decomposed with water and the lithium aluminum organo intermediate was decomposed with 20% sulfuric acid. The two layers were separated and the aqueous layer was continuously extracted with ether. Ferrous ion was added to the water solution to decompose ether peroxide, so easily formed during continuous extraction operations. After drying with anhydrous sodium sulfate and treatment with potassium carbonate to remove any unreacted acid, the ether was removed by distillation. The residual 2-butene-1,4-diol, 15.7 g. (84%) was a liquid boiling at 128–130°. The purified product formed an oily granular mass when cooled in the ice-bath melting at room temperature.[2]

The **ethyl chlorocarbonate** derivative of the 2-butene-1,4-diol was prepared from 0.2 g. of alcohol 0.4 g. of pyridine in

(1) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

(2) W. E. Bissinger, *ibid.*, **69**, 2957 (1947), has reported the melting point of 2-butene-1,4-diol as 25°.