degradation alcohol and behaved similarly. The crude chloride obtained, 20 g., was distilled through column K to give three fractions and no residue. Fractions 1–2, 5 cc., 41.5° (10 mm.)–72.5 (8 mm.), n_D^{20} 1.4303–1.4307, were the olefin. Fraction 3, 8.5 g., 72.5–74° (8 mm.), 1.4525, was the chloride, d_4^{20} 0.894, MR_D 57.5, calcd. 57.8. The identity of this chloride with that obtained from the degradation alcohol confirms the identification of the beta acid as methyl-*tert*-butylneopentylacetic acid.

Action of Phosphorus Pentoxide on the Beta Acid.—The apparatus used was a 3-necked 1-liter flask fitted with a reflux condenser. One neck was used as the inlet for nitrogen which was dried with sulfuric acid and soda-lime. The other neck was used for the introduction of the reacting materials. The exit gas was led from the top of the reflux condenser to a 20-liter calibrated carboy filled with brine and equipped with a leveling bulb. The gas analysis was by means of an Orsat apparatus according to the methods given in "Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Gases." Pure beta acid, 15 g., m. p. $130-130.5^{\circ}$, was mixed with 40 g. of phosphorus pentoxide and the mixture was heated in an oil-bath at $140-150^{\circ}$ for one and one-half hours. The gas collected amounted to 3.5 liters. Its analysis showed the following percentages: CO₂ 0.1, olefins 14.9, O₂ 2.4, CO 44.2. This represents a yield of CO of 90% of the theoretical.

Summary

1. The beta acid of Conant and Wheland, obtained by the oxidation of triisobutylene, has been shown to be methyl-*tert*-butylneopentylacetic acid.

2. A mechanism has been formulated for the rearrangement involved.

3. The structure of the alpha acid is being studied.

STATE COLLEGE, PA. RECEIVED NOVEMBER 17, 1933

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

Condensation of Alkyl Acetylenes with Oxy Compounds

BY G. F. HENNION AND D. B. KILLIAN WITH THOMAS H. VAUGHN AND J. A. NIEUWLAND

Introduction

The condensation of acetylene with various oxy compounds by means of boron fluoride and mercuric oxide as a catalyst has recently been reported from these laboratories.^{1,2} This communication is a preliminary report on similar condensations of the alkyl acetylenes with alcohols and acids to form ketals and α -alkylvinyl esters. Ketals (ketone acetals) have been previously prepared by the condensation of ketones with alkyl orthoformates in the presence of appropriate alcohols.^{3,4,5} Their mode of formation from the alkyl acetylenes is believed to be as follows

$$CH_{3}OCH_{4}$$

$$2CH_{3}OH + C_{4}H_{9} - C \equiv CH \longrightarrow C_{4}H_{9} - C \equiv CH_{2} \longrightarrow C_{4}H_{9} - C(OCH_{3})_{2}CH_{3} \quad (I)$$

$$C_{5}H_{11}$$

$$CH_{2}OH + C_{5}H_{11} - C \equiv CH \longrightarrow CH_{2} - O - C \equiv CH_{2} \longrightarrow CH_{2}OH$$

$$CH_{2}OH \qquad CH_{2}OH$$

$$CH_{2}OH$$

$$CH_{2}OH$$

$$CH_{2}OH \qquad (II)$$

In the preparation of ketals of type (I) we have observed that washing the reaction product with carbonate solutions to neutralize the acid catalyst and to remove unreacted alcohol is to be avoided, otherwise the principal product is a ketone, formed by hydrolysis

 $C_4H_9C(OCH_3)_2CH_8 + H_2O \longrightarrow 2CH_3OH + C_4H_9COCH_3$ (III)

Neutralization of the reaction product with powdered anhydrous potassium carbonate followed by fractionation results in good yields of ketals of type (I). The purified ketals of both types (I) and (II), however, are quite stable to alkaline hydrolysis. Acid hydrolysis gives the theoretical yield of ketone.

Béhal and Desgrez⁶ reported reaction between amylacetylene and acetic acid when these were heated at 280° for twenty-four hours in a sealed tube. Upon working up the product they identified only amyl methyl ketone, which they assumed was formed by the hydrolysis of α amylvinyl acetate (IV), which compound they did not isolate. While our method of reaction is not similar to that reported by Béhal and Desgrez, we have confirmed their observation with respect to the formation of ketone and have also (6) Béhal and Desgrez. Compt. rend., 114, 1074 (1892).

Nieuwland. Vogt and Foohey. THIS JOURNAL. 52, 1018 (1930).
 Hinton and Nieuwland. *ibid.*, 52, 2892 (1930).

⁽³⁾ Hess. German Patent 197.804 (1908): see Frdl. 9, 1004 (1908– 10).

⁽⁴⁾ Claisen, Ber., 31, 1012 (1898).

⁽⁵⁾ Evlampiev. J. Russ. Phys.-Chem. Soc., 54, 462 (1923).

May, 1934

isolated the corresponding unsaturated ester (IV). With amylacetylene and acetic acid the principal reaction proceeds as follows

$$C_{\delta}H_{11}$$

 $C_{5}H_{11}C \equiv CH + CH_{3}COOH \longrightarrow CH_{3}COC = CH_{2}$ (IV)

The exact origin of the ketone (amyl methyl ketone in this case) is uncertain. It may be formed by hydrolysis of the ester (IV) while washing the crude material with water and carbonate solution, or by the hydrolysis of the theoretical diacetate, $(CH_3COO)_2C(CH_3)(C_5H_{11})$, which was not isolated. The yield of ketone varied. As high as 18% of the acetylene was converted to ketone in one experiment, while the average conversion was about 7%. The purified α -amylvinyl acetate (IV) appears to be quite stable to dilute acids and alkalies.

Experimental

Catalyst.—The boron fluoride required as a catalyst was obtained from the ether-boron fluoride compound, $(C_2H_s)_2O$ ·BF₂, b. p. 125-126°. It was prepared as previously described.⁷

Acetylenes.—Butylacetylene, b. p. 70–71°, and amylacetylene, b. p. 99–100°, were prepared in 50–60% yields from the corresponding alky lbromides and sodium acetylide in liquid ammonia using a modification (to be described later) of the procedure described by Picon.⁸

Other Reagents.—C. P. methyl alcohol was purified by drying over anhydrous copper sulfate and distilling before use. Eastman ethylene glycol was distilled before use. Glacial acetic acid and acetic anhydride were used without further purification. The mercuric oxide was of the red variety.

Reaction of Butylacetylene with Methyl Alcohol .---Into a 500-ml. three-necked flask was weighed 4-5 g. of mercuric oxide. To this was added 2 ml. of (C₂H₅)₂O·BF₃ and 2 ml. of methyl alcohol. The pasty mass was warmed slightly to dissolve partially the mercuric oxide. The flask was equipped with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser. Twenty grams of methyl alcohol was added to the catalyst described above and an additional 20 g. (total 40 g., 1.25 moles) was mixed with 41 g. (0.5 mole) of butylacetylene. The catalyst with half the alcohol was heated on a water-bath at 30-40°, the stirrer started, and the remaining half of the alcohol and the butylacetylene added dropwise. This addition required half an hour. Stirring was continued for another one and one-half hours. The mercury catalyst blackened and settled as a sludge. After stirring, the flask was removed, 5 g. of powdered anhydrous potassium carbonate was added, and the solid sludge allowed to settle. The supernatant liquid was decanted and fractionated in vacuo through a 35-cm. Snyder 3-ball column. The yield of 2.2-dimethoxyhexane (I) was 51 g. (70% of the theoretical). The following characteristics were determined for this compound: b. p. 58-60° at 30 mm.; $n_{\rm D}^{19}$ 1.4076, $n_{\rm D}^{25}$ 1.4053; d_{28} 0.8536; MR[']_D found 41.96, MR[']_D calcd. (Smyth values⁹) 42.44; molecular weight found, cryoscopic in benzene, 144, calculated for C₈H₁₈O₂, 146.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.69; H, 12.41. Found: C, 65.56; H, 12.18.

The compound has a rather pleasant odor. Its structure was definitely proved by hydrolysis (with dilute acid) to butyl methyl ketone (III), b. p. 126-128°, n_D^{20} 1.4010, which gave a semicarbazone of m. p. 118-119°.

Amylacetylene with Ethylene Giycol.—A similar procedure was used in preparing the cyclic glycol ketal, 1methyl-1-amyl-dioxole-2,5 (II), with the following changes. All of the glycol was added to the catalyst and the amylacetylene was added to the mixture dropwise at $60-70^{\circ}$. The crude product was taken up in ether, washed with sodium carbonate solution, dried over calcium chloride and fractionated. The yield was 75% of the theoretical. The compound has the following characteristics: b. p. $180-181^{\circ}$ at 745 mm.; n_{27}^{27} 1.4227, n_{20}^{30} 1.4224; d_{30} 0.8984; MR_D found 44.77, MR_D calcd. 44.85.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.29; H, 11.48. Found: C, 67.88; H, 11.50.

Amylacetylene with Acetic Acid .-- The procedure described under methyl alcohol was used in this reaction except for the following changes: 144 g. (1.5 moles) of amylacetylene was used and a mixture of 105 g. (1.75 moles) of acetic acid and 10 g. of acetic anhydride was used in place of methyl alcohol. The reaction flask was cooled in an ice-bath. After the stirring was completed, the flask was removed, 150 ml. of ether was added and the extract washed twice with 300-ml. portions of water and then with 100-ml. portions of 10% sodium carbonate until neutral to litmus. It was then dried over calcium chloride and fractionated through a 125-cm. glass-jacketed Vigreux column at 40 mm. pressure. Repeated fractionation yielded 5.5 g. (3% yield) of amyl methyl ketone. b. p. 146-150°; n_{D}^{25} 1.4036; which gave a semicarbazone, m. p. 122-123°; and 80 g. (34% yield) of a-amylvinyl acetate (IV).

The low yield of ester is partially accounted for by distillation losses and polymerization during the reaction. α -Amylvinyl acetate has the following physical properties: b. p. 92–94° at 40 mm.; n_D^{25} 1.4217, n_D^{20} 1.4237; d_{25} 0.8800; MR_D found 45.06, MR_D calcd. 44.95.

Anal. Calcd. for C₉H₁₀O₂: C, 69.23; H, 10.33. Found: C, 69.17; H, 10.24.

Its structure was determined definitely by saponification.

Saponification of α -Amylvinyl Acetate.—Twenty grams of ester was added dropwise to 50 ml. of a 20% solution of alcoholic potash and boiled for thirty minutes. The solution was diluted with water, the top layer removed, dried over calcium chloride and distilled. The aqueous layer was evaporated to dryness and the solid acidified with sulfuric acid. The products from the saponification reaction were identified as (1) unreacted ester, (2) amyl methyl ketone (V), b. p. 148–150°; n_D^{24} 1.4080; semicarbazone

⁽⁷⁾ Hennion. Hinton and Nieuwland. THIS JOURNAL. 55, 2858 (1933).

⁽⁸⁾ Picon, Compt. rend., 158, 1346 (1914); 169, 32 (1919).

⁽⁹⁾ Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 152.

m. p. 122–123° and (3) acetic acid. The reaction may be formulated as follows

Reactions of α -Amylvinyl Acetate.—This compound (IV) dissolved in carbon tetrachloride adds bromine very readily to form an unstable bromide with distinct lachrymatory properties. It dissolves completely in cold concentrated sulfuric acid and is not reprecipitated by careful dilution with cold water. Ammonolysis of the ester (IV) yields acetamide and amyl methyl ketone (V).

This work is being continued in order to complete several

homologous series of these ketals and esters, and to investigate their reactions and properties.

Summary

1. Alkyl acetylenes react with methyl alcohol and glycol in the presence of boron fluoride and mercuric oxide to form good yields of ketals.

2. Alkyl acetylenes react with acetic acid in a similar manner to form α -alkylvinyl esters, some ketone being formed as a by-product.

3. Hydrolysis of these ketals and esters yields ketones in high yields.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Synthesis of Some Halogenated Thiophenols

By R. C. Dosser and G. Holmes Richter

Hammet and his co-workers¹ have observed that thiocresol not only accelerates the rate of healing of wounds of long standing, but also exerts a bacteriostatic action not shown by other compounds commonly used as tissue proliferants. It is well known that the introduction of chlorine into phenols increases their antiseptic properties, hence the chlorinated thiophenols should possess a specific interest. The synthesis of a number of compounds of this type not previously described in the literature is here reported. Their biological properties will be described elsewhere.

The method of synthesis employed in each case was to sulfonate the suitable aromatic amine by the baking process; after which the aminosulfonic acid was put through a Sandmeyer reaction in which the amino group was replaced by chlorine. The chlorosulfonic acids were usually isolated as the sodium salts, which were treated with phosphorus pentachloride. The resulting chlorosulfonyl chlorides were then reduced with hydrochloric acid and zinc in benzene suspension. A portion of the chlorosulfonyl chloride was usually converted into the corresponding sulfonamide. The mercury salts were prepared by treating an alcoholic solution with mercuric chloride. The disulfides were prepared by exposing an ammoniacal solution of the thiol to air for several hours.

Experimental

1. 6-Chloro-1-methyl-3-thiolbenzene.—o-Toluidine was used as the starting material. The chlorosulfonyl chloride melted at 64°. The final product was isolated by distillation; b. p. 122–123° at 26 mm.; d_4^{20} 1.2217; n_D^{20} 1.5967.

Anal. Calcd. for C_7H_7SC1 : S, 20.22. Found: S. 20.17.

2. Mercury Salt of 6-Chloro-1-methyl-3-thiolbenzene.—The product recrystallized from alcohol and dried over phosphorus pentoxide melted at 193-194°.

Anal. Calcd. for $C_{14}H_{12}Cl_2S_2Hg$: C, 32.57; H, 2.34. Found: C, 32.50; H, 2.57.

3. Disulfide of 6-Chloro-1-methyl-3-thiolbenzene.— The product was purified by recrystallization from alcohol, m. p. 65°.

Anal. Calcd. for $C_{14}H_{12}Cl_2S_2$: C, 53.31; H, 3.83. Found: C, 52.70; H, 3.62.

4. 2-Chloro-1,3-dimethyl-5-thiolbenzene.—The starting material was 1,3-dimethyl-2-aminobenzene. The chlorosulfonyl chloride recrystallized from ligroin melted at 121°. The sulfonamide, recrystallized from alcohol. melted at 205°. The final product purified by distillation boiled at 141-142° at 29 mm.; d_4^{20} 1.1906; n_D^{20} 1.5911.

Anal. Calcd. for C_8H_9ClS : S, 18.58. Found: S. 18.62.

5. The Mercury Salt of 2-Chloro-1,3-dimethyl-5-thiolbenzene.—The product recrystallized from alcohol melted at $240-245^{\circ}$ (dec.).

Anal. Calcd. for $C_8H_8Cl_2SHg$: C, 23.55; H, 1.98. Found: C, 23.32; H. 2.30.

6. Disulfide of 2-Chloro-1,3-dimethyl-5-thiolbenzene.—The product separates out from alcohol as needles with a slight yellowish cast, m. p. 124-125°.

Anal. Calcd. for $C_{16}H_{16}Cl_2S_2$: C. 55.95: H, 4.69. Found: C, 56.08; H. 4.63.

^{(1) &}quot;Synthetic Organic Chemicals," Eastman Kodak Publication, Vol. III, No. 5, 1930; J. Exptl. Med., 50, 445 (1929); Proc. Soc. Exptl. Biol. Med., 27, 20 (1929).