

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°, was mixed with 40 g. of phosphorus pentoxide and the mixture was heated in an oil-bath at 140-150° 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.

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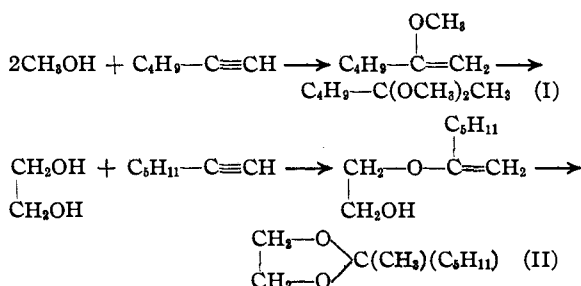
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Condensation of Alkyl Acetylenes with Oxy Compounds

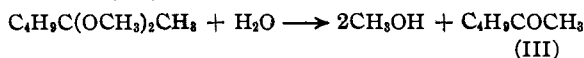
BY G. F. HENNION AND D. B. KILLIAN WITH THOMAS H. VAUGHN AND J. A. NIEUWLAND

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



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



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

(1) Nieuwland, Vogt and Foohey, *THIS JOURNAL*, **52**, 1018 (1930).

(2) Hinton and Nieuwland, *ibid.*, **52**, 2892 (1930).

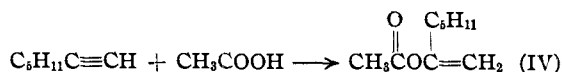
(3) Hess, German Patent 197,804 (1908); see *Frdl.*, **9**, 1004 (1908-10).

(4) Claisen, *Ber.*, **31**, 1012 (1898).

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

(6) Béhal and Desgrez, *Compt. rend.*, **114**, 1074 (1892).

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



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, $(\text{CH}_3\text{COO})_2\text{C}(\text{CH}_3)(\text{C}_5\text{H}_{11})$, 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 alkalis.

Experimental

Catalyst.—The boron fluoride required as a catalyst was obtained from the ether-boron fluoride compound, $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$, 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 alkyl bromides 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 $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ 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_D^{19} 1.4076, n_D^{25} 1.4053; d_{25} 0.8536; MR'_D found 41.96, MR'_D calcd. (Smyth values⁹) 42.44; molecular weight found, cryoscopic in benzene, 144, calculated for $\text{C}_8\text{H}_{18}\text{O}_2$, 146.

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{O}_2$: 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 Glycol.—A similar procedure was used in preparing the cyclic glycol ketal, 1-methyl-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°. 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° at 745 mm.; n_D^{27} 1.4227, n_D^{30} 1.4224; d_{30} 0.8984; MR'_D found 44.77, MR'_D calcd. 44.85.

Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{O}_2$: 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 α -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 $\text{C}_9\text{H}_{18}\text{O}_2$: 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) Heanion, Hinton and Nieuwland, *THIS JOURNAL*, **55**, 2858 (1933).

(8) Picon, *Compt. rend.*, **158**, 1346 (1914); **159**, 32 (1919).

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

