tionated by means of a Glinsky column. Permanganate oxidation of the *o*-tolylcarbinol fraction, in accordance with the procedure employed with benzylmagnesium chloride and formaldehyde,[1a] gave *o*-toluic acid, the identification of which was completed by a mixed melting point determination.

The experiment was checked.

Summary

It has been shown that benzyl-lithium, like benzylmagnesium chloride, undergoes a nuclear allylic rearrangement with formaldehyde.

AMES, IOWA RECEIVED NOVEMBER 8, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

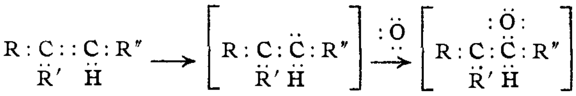
The Structure of the Acids Obtained by the Oxidation of Triisobutylene. I. The Beta Acid of Conant and Wheland[1]

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN

Since the formula suggested tentatively by Conant and Wheland[1] for the beta acid, $C_{12}H_{24}O_2$, m. p. 129°, obtained by the oxidation of triisobutylene would involve a rearrangement entirely at variance with known rearrangements as well as contrary to the modern conceptions of such processes, we decided to study the structure of this acid. We find that the beta acid is methyl-*tert*-butylneopentylacetic acid.

The separation of the acids was accomplished by the fractional distillation of their acid chlorides through an effective column under diminished pressure.[2] The beta chloride was degraded to the corresponding amine by the sodium azide procedure of Naegeli.[3] The amine with nitrous acid gave a tertiary alcohol which was converted to its chloride by hydrochloric acid and was proved to be identical with methyl-*tert*-butylneopentylcarbinol synthesized from methylmagnesium chloride and *tert*-butyl neopentyl ketone.

The formation of the beta acid from 2,2,4,6,6-pentamethylheptene-3[4] probably involves the addition of a neutral oxygen atom (with its six valence electrons) to the electron pair in the activated ethylene bond.



$$\mathrm{R:\underset{\ddot{R}'}{C}::\underset{\ddot{H}}{C}:R''} \longrightarrow \left[\mathrm{R:\underset{\ddot{R}'}{C}:\underset{\ddot{H}}{\ddot{C}}:R''}\right] \xrightarrow{:\underset{..}{\ddot{O}}} \left[\mathrm{R:\underset{\ddot{R}'}{C}:\overset{:\ddot{O}:}{\underset{\ddot{H}}{\ddot{C}}}:R''}\right]$$

R, R′, and R″ = neopentyl, methyl and *tert*-butyl, respectively.

The carbon with the open sextet then attracts the electron pair and R″, thus forming an aldehyde which, under the oxidizing conditions, is changed to a tri-substituted acetic acid. If the process followed other courses, ketonic products would be formed. Such products are actually formed with the alpha and beta acids in the oxidation of triisobutylene. They are being studied in this Laboratory.

The structure now proved for the beta acid was tentatively assigned by Conant and Wheland to the alpha acid, $C_{12}H_{24}O_2$, m. p. 89°. Preliminary studies show that the alpha acid corresponds to neither formula suggested by these authors for the two acids obtained from triisobutylene. By means of the mechanism used in the present paper to explain the formation of the beta acid, the formula of the alpha acid and its formation from 2-neopentyl-4,4-dimethylpentene-1[4] become obvious. These will be published later.

Experimental

Oxidation of Triisobutylene.—At first the acids were prepared by N. H. Hale by the oxidation of crude triisobutylene according to Butlerow.[5] The rest was prepared by the following method. A solution of 2 kg. (6.7 moles) of sodium dichromate in 2 liters of 50% acetic acid was placed in a 12-liter flask equipped with dropping funnel, reflux condenser and stirrer. To this was added 1680 g. (10 moles) of the lower-boiling fractions of triisobutylene, separated by M. R. Fenske and his coworkers in this Laboratory, b. p. 175.6° (738 mm., Cottrell), n^{20}_{D} 1.4300. The mixture was stirred vigorously and 1600 cc. of sulfuric acid was added dropwise over a period of four days, with the temperature not above 60°. The reaction mixture was steam distilled from the same flask, and the oil layer of the distillate was set aside for future investigation. The lower layer was siphoned from the hot residue and the remaining oil layer, after washing with 200 cc. of hot water, was distilled to 120° (22 mm.) through column K, 44 × 1.4 cm., 9.6 theoretical plates, glass helix packing.[6] The distillate was combined with

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(1) Conant and Wheland, THIS JOURNAL, **55**, 2499 (1933).

(2) *Cf.* Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

(3) Naegeli, *Helv. Chim. Acta*, **15**, 49 (1932).

(4) McCubbin, THIS JOURNAL, **53**, 356 (1931), confirmed by C. D. Wilson of this Laboratory.

(5) Butlerow, *Ber.*, **12**, 1482 (1879).

(6) Wilson, Parker and Laughlin, THIS JOURNAL **55**, 2795 (1933).

the oil layer from the steam distillation for further study. The residue, 310 g., was a mixture of the alpha and beta acids of Conant and Wheland, together with some higher isobutylene polymers.

Separation of the Acids.—To 600 g. of the acid mixture obtained by this method was added an equal weight of thionyl chloride. The mixture was allowed to stand for twelve hours in a flask vented through a calcium chloride tube (hood), and was then distilled through column K under reduced pressure, using an oil-bath to avoid decomposition. After removal of the excess thionyl chloride 220 g. of distillate was obtained, b. p. 65–83 (2 mm.), n^{20}_{D} 1.4417–1.4433. This was mainly the crude alpha acid chloride and was set aside in a sealed bottle for future investigation. The residue was treated with 50 cc. of water. The beta acid thus formed, after filtering and drying in air, weighed 210 g. The filtrate, 115 g., was a dark brown, viscous liquid.

Preparation of the Pure Beta Acid Chloride.—Crude beta acid, 240 g., was treated with an equal weight of thionyl chloride in the usual way. The product was distilled through column K to give 11 fractions with b. p., amounts, and n^{20}_{D} as follows: Nos. 1–8, 86 cc., 98° (15 mm.)–98.5° (8 mm.), 1.4437–1.4613; No. 9, 120 g., 96° (6 mm.), 1.4641; No. 10, 3 cc., 96–7° (6 mm.), 1.4628; No. 11, 25 cc., residue. Fraction 9 had d^{20}_{4} 0.967 and MR_D 62.2 (calcd. for $C_{12}H_{23}OCl$ 62.8). A small portion was hydrolyzed with water to give the beta acid with m. p. 130–130.5°.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.9; H, 12.1. Found: C, 71.71; H, 12.09.

Degradation of the Beta Acid Chloride.—The sodium azide used in this reaction was activated by precipitation from water solution with acetone according to the method of Nelles.[7] A solution of 120 g. of the beta acid chloride in 350 cc. of dry toluene was placed in a 1-liter flask equipped with stirrer and reflux condenser and connected to a gas meter. The freshly precipitated sodium azide, 55 g., was added and the mixture was heated to gentle refluxing with stirring for five hours, when 14.4 liters of gas had been evolved (theoretical volume of nitrogen 13.4 liters). The mixture was filtered and the precipitate was washed with 50 cc. of dry toluene. The filtrate was divided into two equal parts. One part was placed in a dropping funnel connected to a 1-liter flask fitted with stirrer and condenser. To this flask was added 350 cc. of hydrochloric acid, which was then heated until some distilled over, then the solution was added dropwise with stirring, at such a rate that the solvent toluene was distilled from the reaction flask as rapidly as it was added. The residue in the reaction flask was partially neutralized with 20% sodium hydroxide and was filtered warm. The precipitate, less than 1 g., was probably the disubstituted urea. The filtrate was neutralized with sodium hydroxide and an excess of 0.25 mole was added. The oil layer was separated and the water layer was washed with two 100-cc. portions of ether. The combined oil and ether extracts were dried with 20 g. of potassium carbonate, and were then saturated with hydrogen chloride. The ether and hydrogen chloride were removed under reduced pressure to give 31.5 g. of the amine hydrochloride, m. p. 215–217°. Treatment of the second part of the solution in the same way yielded 33 g. of the amine hydrochloride (yield, 57% based on the acid chloride). The phenyl urea prepared from this material by means of phenyl isocyanate melted at 175–176°.

Conversion of the Degradation Amine to Methyl-*tert*-butylneopentylcarbinol.—A portion, 10.3 g., of the amine hydrochloride was dissolved in 25 cc. of water containing 0.1 cc. of hydrochloric acid. A cold solution of 4.25 g. of potassium nitrite in 10 cc. of water was added, whereupon a white solid was formed (probably the amine nitrite). The mixture was diluted with 100 cc. of water and was heated on the steam-bath for eight hours. Nitrogen was evolved and an oil layer formed. This was separated and the water layer was washed with two 50-cc. portions of ether which were combined with the oil layer and dried over 10 g. of potassium carbonate.

The above procedure was repeated with the remainder of the amine hydrochloride, and the combined products were distilled through column K, with a reflux ratio of 5 : 1 to give ten fractions with b. p. (at 15 mm.), amount, n^{20}_{D}, and m. p. as follows: Nos. 1–2, to 53°, 24 cc., 1.431; Nos. 3–4, 53–75°, 3 cc., 1.435 to 1.438; No. 5, 75–76.5°, 2 cc., 1.440; No. 6, 76.5°, 2 cc., 1.4407, 4.5°; No. 7, 76.8°, 2 cc., 1.4408, 5.5°; No. 8, 76.8°, 3 cc., 1.4410, 6.0°; No. 9, 76.8–78.0°, 5 cc., 1.4416, 5.0°; No. 10, residue, 3 cc. The first fractions were mainly olefins. Fractions 6–9 were combined and purified by partial melting and filtering. The product melted at 8–10°.

Analysis of the carbinol. Calcd. for $C_{11}H_{24}O$: C, 76.64; H, 14.05. Found: C, 76.54; H, 14.06.

Synthesis of Methyl-*tert*-butylneopentylcarbinol.—*tert*-Butyl neopentyl ketone (48 g.), prepared in 53% yield by J. W. Heyd from *tert*-butylmagnesium chloride and *tert*-butylacetyl chloride, was treated with methylmagnesium iodide with all the usual precautions for the preparation of complex tertiary alcohols. The product was carefully fractionated through Column K. The main fractions gave a 51% yield (27 g.) of methyl-*tert*-butylneopentylcarbinol, b. p. 61° (6 mm.), n^{20}_{D} 1.4406, m. p. 10–11°, d^{20}_{4} 0.840, MR_D 54.1, calcd. 54.5. A mixture with the carbinol obtained from the amine from the degradation of the beta acid melted at 9–11°, proving the identity of the two materials.

Conversion of the Degradation Carbinol to its Chloride.—The less pure carbinol obtained in the crystallization process, 14 cc., was treated at room temperature with 28 cc. of hydrochloric acid. The mixture solidified almost at once, forming what was probably the oxonium addition compound, which slowly decomposed to form the chloride and the olefin. After two hours the mixture consisted of two liquid layers. The oil layer was separated and was let stand overnight with an equal volume of hydrochloric acid. The oil layer, 10 cc., was separated, dried over 1 g. of potassium carbonate, and was distilled through a 63 × 0.9 cm. column equivalent to 15 theoretical plates,[2] to give three fractions and no residue. Fractions 1, 3 cc., 40–42° (10 mm.), n^{20}_{D} 1.4308 and 2, 1 cc., 42° (10 mm.)–72.5° (8 mm.), 1.4382 were mostly olefin. Fraction 3, 3 cc., 72.5–74° (8 mm.), 1.4522, was the chloride.

Conversion of the Synthetic Carbinol to its Chloride.—The carbinol, 25 g., was treated in the same manner as the

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[7] Nelles, *Ber.*, **65**, 1345 (1932).

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: CO_2 0.1, olefins 14.9, O_2 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

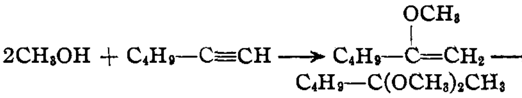
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Condensation of Alkyl Acetylenes with Oxy Compounds

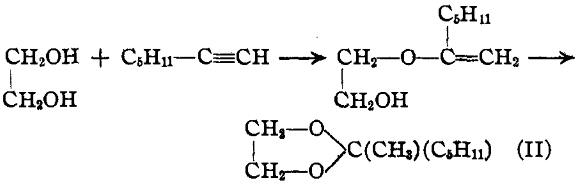
BY G. F. HENNION AND D. B. KILLIAN WITH THOMAS H. VAUGHN AND J. A. NIEUWLAND

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



$$2CH_3OH + C_4H_9{-}C{\equiv}CH \longrightarrow C_4H_9{-}\overset{\overset{\large OCH_3}{|}}{C}{=}CH_2 \longrightarrow C_4H_9{-}C(OCH_3)_2CH_3 \quad \text{(I)}$$



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + C_5H_{11}{-}C{\equiv}CH \longrightarrow \begin{matrix} CH_2{-}O{-}\overset{\overset{\large C_5H_{11}}{|}}{C}{=}CH_2 \\ | \\ CH_2OH \end{matrix} \longrightarrow \begin{matrix} CH_2{-}O \\ | \\ CH_2{-}O \end{matrix}\!\!\!>\!C(CH_3)(C_5H_{11}) \quad \text{(II)}$$

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

$$C_4H_9C(OCH_3)_2CH_3 + H_2O \longrightarrow 2CH_3OH + C_4H_9COCH_3 \quad \text{(III)}$$

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 Desgrez[6] 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

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(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).