

Pressed juice from banana pulp also contains this activator.

The aqueous extract may be heated to boiling for a few minutes without loss of its activating property, but when evaporated to dryness on the steam-bath at P_H 6.4, it is rendered inert.

The glycolytic activator is more resistant to acid (P_H 1) than to alkali (P_H 9.4).

The activator passes through a collodion membrane on dialysis.

The effect of the activator, in the crude extract, on yeast apo-zymase is much less than that of yeast cozymase.

The effect of the activator on yeast apo-zymase is increased by small amounts of magnesium chloride, but hardly at all by acetic aldehyde.

The extract from the banana pulp also contained phosphatase and carboxylase.

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Studies on the Rearrangement of Tertiarybutylmethylcarbinol (Pinacolyl Alcohol). I

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In spite of the large amount of work on pinacolyl alcohol, its dehydration products and its halides, the subject is still confused. This is shown by the fact that the fourth edition of Beilstein's "Handbuch" gives the halides the tertiary structure, $(CH_3)_2CXCH(CH_3)_2$, corresponding to a complete rearrangement, while the supplement to the fourth edition gives the structure, $(CH_3)_3CCHXCH_3$.

In the present work the chloride has been prepared from pinacolyl alcohol and saturated aqueous hydrochloric acid at -10° . The product reacted with moist silver oxide to give the rearranged product dimethylisopropylcarbinol. A bromide was prepared from pinacolyl alcohol. This was studied by the freezing point method² and was found to consist of about 90% of the rearranged tertiary bromide, $(CH_3)_2CBrCH(CH_3)_2$. The composition of the impure bromide was not changed by heating for sixteen hours at 125° . Hydrolysis experiments^{2,3} also indicated that the mixture was about 90% tertiary.

The dehydration of *tert.*-butylmethylcarbinol was studied. Attempts to dehydrate the boiling alcohol by means of traces of benzene sulfonic acid and iodine failed. Dehydration of the alcohol with oxalic acid gave tetra-

(1) Submitted in partial fulfillment of the requirements for the Ph.D. degree at the Pennsylvania State College. Most of this work was done at Northwestern University in 1928-1929.

(2) Whitmore and Rothrock, *THIS JOURNAL*, **54**, 3431 (1932).

(3) Delacre, *Bull. soc. chim.*, [4] **1**, 575, 978 (1907).

methylethylene and *unsym.*-methylisopropylethylene in the ratio 5:2. The fraction boiling at 65–67° observed by other workers⁴ was shown to be a mixture of these olefins. By heating the —OMgBr derivative of the alcohol to 250–300°, a 3:2 mixture of the same olefins was obtained.⁵ Dehydration of the alcohol with iodine in a sealed tube at 140° gave a 6:1 mixture. When the acetate of pinacolyl alcohol was decomposed at about 300°, *tert.*-butylethylene was formed with only small amounts of rearranged products. This recalls the formation of the unrearranged olefin from the xanthate of pinacolyl alcohol.⁶

The alcohol itself has been found to be stable to long heating at 200°, in spite of suggestions in the literature that it undergoes rearrangement on repeated distillation.⁷

Experimental

The pinacolyl alcohol, b. p. 116.5–121° (740 mm.), was obtained by the action of acetaldehyde with *tert.*-butylmagnesium chloride. The yield was 28% based on the tertiary butyl chloride used. The alcohol was also made by reducing pinacolone,⁸ with moist ether and sodium. The yields of material of b. p. 117–121° and m. p. 1.0–2.5°, were about 70%.

Stability of Tertiarybutylmethylcarbinol and its Acetate to Heat.—The freezing point constant of the alcohol was found to be 5.6. Two duplicate sealed tubes containing samples of the alcohol, m. p. +1°, and filled with carbon dioxide, were heated at 200°. The first tube was cooled and opened after eighteen hours and the second after forty-eight hours. The freezing points of the two samples were –1.5 and –2.0°.² Mixed melting point determinations with unheated samples of the alcohol showed no depression. A sample of the alcohol of m. p. 1.6° was refluxed with protection from atmospheric moisture for forty-one hours. Its melting point was then found to be 1.4°. These experiments indicate that the thermal decomposition of the alcohol was very slight.

The acetate of *tert.*-butylmethylcarbinol, b. p. 141.2–141.4° (740 mm.), was prepared by means of acetyl chloride. Five grams of the acetate was heated in a sealed tube at 160–170° for one hundred and forty-four hours. The product was heated for eighteen hours with alcoholic potassium hydroxide and worked up. About 3 g. of material boiling at 119–120° was recovered. Treatment with phenyl isocyanate gave the phenylurethan of *tert.*-butylmethylcarbinol, m. p. 77.5–78.5°.

When 24 g. of the acetate was distilled over porous tile in a Pyrex tube heated in an electric furnace at about 300°, the product amounted to 8 g. of material of which 5 g. on refractionation boiled at 40–43.5° (740 mm.), a yield of *tert.*-butylethylene of about 35%. The olefin was oxidized with permanganate to trimethylacetic acid, which was identified by its odor and by conversion to the silver salt containing 51.7% silver (calcd. 52.1%).

Halides Obtained from Tertiarybutylmethylcarbinol

1. **The Chloride.**—Concentrated c. p. hydrochloric acid was cooled to –10° and saturated with hydrogen chloride gas. To 100 g. of this acid in a tube was added 20 g. of the carbinol, the tube was sealed and allowed to stand with occasional shaking

(4) Zelinsky and Zelikow, *Ber.*, **34**, 3248 (1901); Nybergh, "Hyllningskrift tillagnad Ossian Aschan," 1920, pp. 98–102; *Chemical Abstracts*, **16**, 2110 (1922).

(5) Whitmore and Houk, *THIS JOURNAL*, **54**, 3714 (1932).

(6) Fomin and Sochanski, *Ber.*, **46**, 244 (1913).

(7) Van Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921).

(8) "Organic Syntheses," 1925, Vol. V, pp. 87, 91.

(care!) at room temperature. The solution was at first red and homogeneous. After a few hours a violet upper layer separated. This gradually increased for five days. It was then removed and washed with concd. hydrochloric acid and twice with water. The violet color disappeared during the latter treatment. The weight of the crude chloride was 24 g.

A suspension of washed silver oxide (from 35 g. of silver nitrate) in 400 cc. of water was treated with 20 g. of the chloride and allowed to stand with shaking at room temperature for four days. The mixture was extracted with ether and the extract was fractionated. A small amount of olefin boiling at 70–80° was obtained. The main fraction boiled at 116–117.5° (738 mm.). This was treated with phenyl isocyanate. No product soluble in hot ligroin (phenylurethan of pinacolyl alcohol) was obtained. Crystallization of the product from alcohol gave diphenylurea, m. p. 235°, thus indicating that the alcohol formed by the silver oxide treatment was a tertiary alcohol. No *tert.*-butylmethylcarbinol was regenerated. This indicates that the chloride obtained from pinacolyl alcohol and cold hydrochloric acid is the rearranged tertiary chloride. A blank experiment with 3-chloropentane and silver oxide under like conditions gave no reaction.

2. The Bromide.—(a) Fifty grams of the carbinol was cooled with ice and treated with dry hydrogen bromide until saturated. The mixture turned red. After standing for two days at 0°, the saturation with hydrogen bromide was repeated. This was repeated twice more. Meantime an aqueous layer had separated. This was removed, the treatment with hydrogen bromide was repeated and the mixture was heated for three hours on the steam-bath under a reflux condenser. The bromide was then separated and distilled under reduced pressure. The product of b. p. 88–90° (200 mm.) and m. p. 6.6° weighed 68 g.

(b) For purposes of comparison dimethylisopropylcarbinyl bromide, b. p. 86–89° (180 mm.), m. p. 13.5°,¹⁰ was prepared by the action of hydrobromic acid on dimethylisopropylcarbinol, b. p. 116–120° (740 mm.), obtained in 40% yield by the action of acetone with isopropylmagnesium bromide. The melting point of 13.5° was obtained only after repeated fractional crystallizations.

(c) Freezing point determinations were taken on mixtures of the bromide prepared from *tert.*-butylmethylcarbinol (m. p. 6.6°) and that from dimethylisopropylcarbinol (m. p. 9.8°) made in the ratios 5:2 and 1:1. These were 7.4 and 8.5°, respectively, indicating that the two materials contained mainly the same bromide.

A mixture of 4.55 g. of dimethylisopropylcarbinyl bromide, m. p. 9.8°, with 0.389 g. of *tert.*-amyl bromide, b. p. 106.5–107° (735 mm.), froze at 2.3°, thus indicating a molecular lowering of 13. If the true melting point of this bromide is 15°, the bromide made from *tert.*-butylmethylcarbinol and freezing at 6.6° contains about 0.84 mole of impurity in 1000 g. of pure bromide and thus contains about 90% of the tertiary bromide, $(\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2$.

(d) A sample of the bromide of m. p. 6.6° prepared from *tert.*-butylmethylcarbinol was heated in a sealed tube at 125° for sixteen hours. The melting point was then 5.6°. If any unstable bromide had changed to the tertiary bromide, the melting point would have been raised.

(e) Weighed samples of dimethylisopropylcarbinyl bromide were shaken with distilled water and the water layers were titrated for bromide. In sixty-five minutes, 97% of the bromine in the bromide appeared as hydrogen bromide. Longer shaking gave no increase in this value.

In a similar way samples of the bromide of m. p. 6.6° were hydrolyzed by cold water to give 91–92.5% of the total bromine as hydrogen bromide, indicating a corresponding content of the tertiary bromide $(\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2$. The nature of the stable diffi-

(9) Couturier, *Ann. chim. phys.*, [6] **26**, 433 (1892); Delacre, *Bull. soc. chim.*, [3] **35**, 348 (1906).

(10) Zelinsky and Zelikow, *Ber.*, **34**, 2856 (1901).

cultly hydrolyzable bromide forming less than 10% of the product has not yet been determined.

Dehydration of Tertiarybutylmethylcarbinol

(a) Refluxing 30 g. of the carbinol (b. p. 118–120) with 0.1 g. of benzene sulfonic acid for 120 hours gave less than 0.5 g. of material boiling below 85°. A total of 27 g. of the carbinol was recovered unchanged.

(b) Dehydration of the carbinol with anhydrous oxalic acid gave a distillate boiling at 55–65°. When dried and carefully fractionated,¹¹ the chief fractions boiled at 740 mm. at 55–59° and 69.5–72° with only very small intermediate fractions. These were found in the ratio 2:5 and were the *unsym.*-methylisopropylethylene and tetramethylethylene reported by other workers. When careful fractionation was employed there was no indication of the 65–67° material reported by Zelinsky and Zelikow and by Nybergh.⁴

(c) The —OMgBr compound of the carbinol was made by treating a dry ether solution of 30 g. of the latter with the calculated amount of titrated ethylmagnesium bromide solution. The ether was evaporated and the residue was heated in an oil-bath. When the bath reached 170°, a distillate came over at 33.5–34.5°. Tests with bromine solution failed to indicate any unsaturated material (boiling point of *tert.*-butylethylene, 41°). The bath was then raised to 250° and then to 340°. A total of 20 g. of material boiling at 55–65° was obtained. Three careful fractionations of this material gave 4.5 g., b. p. 54–59°, and 6.5 g., b. p. 67–72°. No indication of *tert.*-butylethylene was detected.

(d) All attempts to dehydrate the carbinol by refluxing with iodine failed. Finally 19 g. of tertiarybutylmethylcarbinol and 1 g. of iodine were heated in a sealed tube at 140°. After eight hours two layers had formed. These did not change after heating for eight hours longer. The lower (water) layer amounted to 4 g. The upper layer was dried with sodium and fractionated carefully at 732 mm. The chief fractions were 1.4 g., b. p. 61.5–67°, and 8 g., b. p. 69–72.5°. Thus about 86% of the product was tetramethylethylene.

Summary

1. The stabilities of *tert.*-butylmethylcarbinol and its acetate have been studied. At high temperature, the acetate gives *tert.*-butylethylene without rearrangement.

2. The chloride and bromide obtained from the carbinol consist almost entirely of rearranged products.

3. A variety of means of dehydration of the carbinol give only tetramethylethylene and *unsym.*-methylisopropylethylene without any third product.

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(11) Whitmore and Lux, *THIS JOURNAL*, **54**, 3451 (1932).