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

The Structure of the Acids Obtained by the Oxidation of Triisobutylene. II.[1] The Alpha Acid of Conant and Wheland[2]

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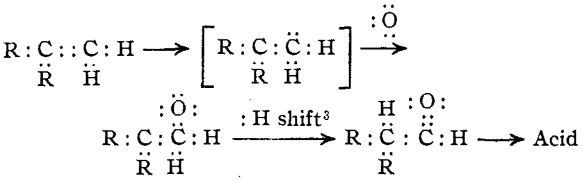
Since the formula suggested tentatively[2] for the alpha acid, $C_{12}H_{24}O_2$, m. p. 89°, has been shown to belong to the beta acid,[1] the structure of the alpha acid has been determined in this Laboratory. We find that the alpha acid is dineopentylacetic acid formed by the oxidation and rearrangement of 1,1-dineopentylethylene.



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

$$R:\underset{\ddot{R}}{C}:\overset{:\ddot{O}:}{\underset{\ddot{H}}{\ddot{C}}}:H \xrightarrow{:H\ \text{shift}^{3}} R:\overset{H}{\underset{\ddot{R}}{\ddot{C}}}:\overset{:O:}{\overset{::}{C}}:H \longrightarrow \text{Acid}$$

Butlerow discovered a similar process when he found isobutyric acid among the oxidation products of tertiary butyl alcohol by chromic acid mixture.[4] Undoubtedly this change involved the oxidation of isobutylene according to the indicated mechanism.

The structure of the alpha acid was determined by degradation to dineopentylcarbinol, which was identified by comparison with a known specimen of the synthetic material.

Experimental

Separation of the Acid Chlorides.—Crude Butlerow's acid,[5] prepared by N. H. Hale and K. C. Laughlin, was refluxed with thionyl chloride (130 g. for 145 g. of acid). The mixed acid chlorides were distilled through a 60 × 1.5 cm. helix[6] packed adiabatic column equivalent to twelve theoretical plates, at 4 mm. pressure to give twenty-one fractions and a residue of 14 g. Fractions 2–10, b. p. 78–79° (4 mm.), n^{20}_{D} 1.4399 were the alpha acid chloride, yield 34%. Hydrolysis gave alpha acid, m. p. 85–87°. Fractions 14–21, b. p. 81–81.5° (3.5 mm.), n^{20}_{D} 1.4640, were the beta acid chloride, yield 36%. Hydrolysis gave beta acid, m. p. 125°.

Reaction of the Alpha Acid Chloride with Sodium Azide and Hydrolysis of the Isocyanate.[1]—A solution of 43.7 g. of the alpha acid chloride in 125 cc. of dry toluene was treated with 19.5 g. of sodium azide (Eastman Kodak Co.) and heated to gentle refluxing in an oil-bath for forty hours. A total of 4.7 liters of gas was evolved. The solution was filtered from sodium chloride and added dropwise to 300 cc. of boiling hydrochloric acid. The steam distillation of the toluene was continued until a white solid began to collect in the condenser. The residue was treated with 15 cc. of concd. hydrochloric acid in 200 cc. of water, warmed and filtered. About 1.5 g. of greasy residue remained. This was probably the disubstituted urea. The filtrate was treated with an excess of sodium hydroxide and extracted with ether. The ether solution was dried and saturated with dry hydrogen chloride gas. The hydrochloride of dineopentylcarbinylamine precipitated, 24 g., 58% yield, m. p. 239–240°, acetyl derivative, m. p. 134.5°.

Anal. Calcd. for $C_{11}H_{26}NCl$: N, 6.7; Found: N, 6.8. Calcd. for $C_{13}H_{27}ON$: N, 6.6; Found: N, 6.8.

Conversion of the Amine to Dineopentylcarbinol by Nitrous Acid.—A solution of 20.7 g. of the amine hydrochloride in 125 cc. of water containing 0.3 cc. of concd. hydrochloric acid was treated with a solution of 8.5 g. of potassium nitrate in 15 cc. of water. A white solid separated but dissolved on warming. The solution was heated on the steam-bath until no more gas was evolved (18 hrs.). A brownish oil floated on the solution. The mixture was cooled and extracted with ether. After drying with potassium carbonate and removing the ether, the product was distilled at reduced pressure through a 25 × 0.7 cm. column,[6] with all precautions, to give thirteen fractions and a residue of 0.5 cc. Fractions 1–6, b. p. 44° (13 mm.), n^{20}_{D} 1.4160 were olefins. Fractions 7–13, b. p. 75–79° (11 mm.), m. p. 11–15°, were impure dineopentylcarbinol. A mixture with 10% of the synthetic substance (m. p. 39°) had m. p. 19–22°. The 3,5-dinitrobenzoate melted at 97°, known derivative, m. p. 98.5°, mixed m. p. 98°. Fraction 9 mixed with methylneopentyl-butylcarbinol (m. p. 10°)[1] melted below 0°.

Summary

1. The alpha acid of Conant and Wheland, obtained by the oxidation of triisobutylene, has been shown to be dineopentylacetic acid.

2. Further evidence has been obtained for the current theory of the mechanism of rearrangements.

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[1] Whitmore and Laughlin, THIS JOURNAL, **56**, 1128 (1934).

[2] Conant and Wheland, *ibid.*, **55**, 2499 (1933).

[3] *Cf.* Whitmore, *ibid.*, **54**, 3277 (1932). For the formation of an "open sextet" by addition to an olefin see Whitmore and Johnston, *ibid.*, **55**, 5020 (1933).

[4] Butlerow, *Z. Chem.*, (2) VII, 485 (1871); *J. Chem. Soc.*, **25**, 295 (1872).

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

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