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Summary

1. Iso, secondary and tertiary-butyl phenyl ethers have been prepared and catalytically rearranged to phenolic compounds.

2. The rearrangement of tertiary-butyl phenyl ether by the action of heat has been described.

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Studies on the Rearrangement of Tertiary-butylmethylcarbinol (Pinacolyl Alcohol). II.[1] Dehydration

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A primary alcohol containing the grouping R_3CCH_2OH can be dehydrated only with rearrangement.[3] On the other hand, a related tertiary alcohol, $R_3CC(OH)R_2$, is dehydrated mainly without rearrangement.[4] Conceivably a secondary alcohol, $R_3CCHOHR$, could be dehydrated either with or without rearrangement.[5] Until the present study, only rearranged products had been reported from the dehydration of such secondary alcohols.[1,6] The simplest of these alcohols, tertiaryl-butylmethylcarbinol, has been dehydrated by many workers.[7] The products obtained have been rearranged olefins, tetramethylethylene (b. p. 72°), and *unsym*-methylisopropylethylene (b. p. 54°). Previous work in this Laboratory has shown that the intermediate fraction, b. p. 65–67°, observed by some workers, is a mixture of the same two olefins.[1] The only preparations of the normal dehydration product, *tert*-butylethylene, have been made indirectly by the thermal decomposition of the xanthate of pinacolyl alcohol[8] and of the acetate.[1]

In the present work the pinacolyl alcohol was purified by repeated distillation and fractional crystallization and a large quantity was dehydrated at high pressure and temperature over a catalyst of phosphoric acid on silica gel. The usual rearranged olefins, tetramethylethylene and *unsym*-methylisopropylethylene, were obtained but, in addition, a small

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(1) Whitmore and Rothrock, THIS JOURNAL, **55**, 1106 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); Whitmore and Church, *ibid.*, **55**, 1119 (1933).

(4) Whitmore and Laughlin, *ibid.*, **54**, 4011 (1932).

(5) Whitmore, *ibid.*, **54**, 3274 (1932).

(6) Whitmore and Houk, *ibid.*, **54**, 3714 (1932); Whitmore and Krueger, *ibid.*, **55**, 1528 (1933).

(7) See citations to literature in Ref. 1.

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

amount (3%) of the unrearranged olefin, *tert*-butylethylene, was isolated and identified.

Experimental

Preparation and Purification of Tert-butylmethylcarbinol.—The alcohol, b. p. 118.7–119.7 (741 mm.), 120.4° (760 mm.), n^{20}_{D} 1.4148, was prepared by the action of acetaldehyde on *tert*-butylmagnesium chloride.[1] The yield for a 20-mole run, based on the chloride used, was 52.1%. The alcohol was distilled in an efficient laboratory column, 125 × 2.3 cm.,[9] after which it was further purified by fractional crystallization. In this way the freezing point was raised from 1.5 to 5.3°.

Dehydration of Tert-butylmethylcarbinol.—Ordinary laboratory methods for dehydrating the alcohol, using sulfuric acid, orthophosphoric acid, phosphoric anhydride, and oxalic acid, proved unsatisfactory for dehydrating large quantities. Finally, the alcohol was dehydrated in a high pressure flow system containing an electrically heated high pressure reactor made of Shelby seamless tubing, 91 cm. by 1.6 cm. (inside), partly filled with a catalyst of phosphoric acid on silica gel. A pump, adapted for handling small quantities of liquid, was used to pump the alcohol through the system. In a typical run 500 g. of the alcohol was dehydrated at 300° and 2500 lb. pressure. The loss was only 2%. The yield of olefins was 337 g. or 80%. These were repeatedly fractionated in a partial condensation column, 90 × 1.2 cm., using a reflux ratio of 200:1.[9] This gave three fractions of boiling range (740 mm.), wt., yield and n^{20}_{D} as follows: 38–43°, 10.5 g., 3%, 1.3775; 54–58°, 107 g., 31%, 1.3904; 69–72°, 208 g., 61%, 1.4121. The last two fractions were *unsym*-methylisopropylethylene and tetramethylethylene, respectively. The low-boiling fraction was identified as *tert*-butylethylene by ozonolysis.[10] In the aqueous layer of the decomposition products of the ozonide, qualitative tests for formaldehyde were obtained with fuchsin reagent and with aqueous resorcinol. The oily product oxidized in air to trimethylacetic acid, which was identified by conversion to the amide, m. p. 145–148°. Mixed with pure trimethylacetamide (m. p. 153–154°), it melted at 149–151°.

Summary

The catalytic dehydration of *tert*-butylmethylcarbinol at high temperature and pressure gave the rearranged olefins, tetramethylethylene and *unsym*-methylisopropylethylene, in the ratio 2:1 and, in addition, a small amount of the normal dehydration product, tertiary-butylethylene.

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[9] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[10] Whitmore and Church, *ibid*., **54**, 3712 (1932).