vigorous mechanical stirring to 30 g. of phenylmercuric acetate in 300 cc. of water. Stirring was continued for an hour, and then the grayish-black precipitate of mercury diphenyl and mercury was filtered off on a Büchner funnel, washed well with water, and sucked as dry as possible.

The residue was extracted twice with 75cc. portions of acetone. Finely divided mercury ran through the filter papers, and it was necessary to amalgamate the metal with powdered zinc before a clear filtrate could be obtained. Water was added to the filtrate until a slight permanent turbidity was obtained. Crystals of mercury diphenyl formed very slowly on cooling, so enough water was added to precipitate all of the mercury compound. Filtered off and dried, it weighed 13.2 g., a yield of 95.6%. The colorless microcrystalline product melted at 124.5° (uncorr.) with preliminary softening.

Summary

1. The analogy between mercuration and hydrolysis has received further confirmation.
2. An 80% yield of phenylmercuric acetate was obtained by the *direct mercuration of benzene in the presence of ethanol.*
3. Mercury diphenyl in 95.6% yield was obtained from phenylmercuric acetate by means of sodium stannite.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VERMONT]

TERTIARY-BUTYL ALCOHOL

BY R. R. READ AND FREDERIC PRISLEY

RECEIVED MARCH 18, 1924

The usual laboratory methods for the preparation of tertiary-butyl alcohol involve the use of methylmagnesium iodide. As the use of this reagent in even moderately large scale operations is attended by considerable difficulty it seemed desirable to make a study of other methods for the preparation of the alcohol.

Wischnegradsky[1] has pointed out that a commercial grade of amylene is very readily dissolved, in part, when shaken with 50% sulfuric acid in a salt-ice bath. Attention has been drawn recently to the ease with which trimethyl ethylene may be converted into *tertiary* amyl alcohol by the preliminary formation of amyl sulfuric acid and subsequent neutralization.[2]

The boiling point of *iso*butylene (—6°) is so low, however, that the absorption of the liquid hydrocarbon has been carried out only in closed tubes.[3] Moreover, the *iso*butylene obtained by the dehydration of

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[1] Wischnegradsky, *Ann.* **190**, 332 (1878). No temperatures were noted, but it would seem certain from the emphasis laid on the use of a strong walled bottle and the rate of reaction that the temperature of the reacting mixture was considerably above that of the surrounding bath; 300 g. of amylene dissolved in 30 minutes.

[2] Adams, THIS JOURNAL, **40**, 1950 (1918).

[3] (a) Butlerow (Butleroff), *Ann.*, **180**, 246 (1876); (b) **189**, 48 (1877); Compare (c) Le Bel and Greene, *Bull. soc. chim.*, [2] **29**, 306 (1878).

*iso*butyl alcohol in a furnace, as described below,[4] contains so high a percentage of non-condensable gas[5] that the liquid *iso*butylene is difficult to prepare by this method.

Butlerow and many others have shown that the liquid butylenes are readily absorbed in sulfuric acid of 50% concentration and over, *iso*butylene much more readily than the others.

The absorption of gaseous *iso*butylene by dil. and concd. sulfuric acid is very slow at low temperatures[6] and while quite rapid at higher temperatures, leads mainly to polymerization products.

While a diluent would decrease the rate of absorption, it would at the same time so lower the vapor pressure that the reaction could be carried on in an open flask. The solubility of the unsaturated hydrocarbons in many solvents led to the attempt to hydrate the dilute *iso*butylene instead of the pure hydrocarbon. Any material miscible with the hydrocarbon, inert to cold sulfuric acid, and of low molecular weight and freezing point would be suitable as solvent; a commercial grade of kerosene, repeatedly shaken out with concd. sulfuric acid was found well adapted for the purpose.

With the use of an all-glass dehydrating tube the production of non-condensable gas was eliminated so that solutions of the unsaturated hydrocarbon in kerosene of any desired concentration were readily obtained, as was the hydrocarbon itself. All attempts to use phosphoric acid on coke as catalyst, as recommended by King[7] for the dehydration of *n*-butyl alcohol, were most unsatisfactory, as at even low temperatures (210–230°) half of the total hydrocarbon was lost through polymerization.

As has been frequently pointed out[8] a rearrangement in the carbon linking occurs during the dehydration of *n*- and *iso*butyl alcohols. In this work, 30–35% of 2,3-butylene was obtained from *iso*butyl alcohol, but as this hydrocarbon is far less reactive toward sulfuric acid, it remained after the removal of the *iso*butylene, liquid *iso*butylene being rapidly absorbed by 50% sulfuric acid at temperatures below its boiling point.

Experimental Part

1. The vapors of *iso*butyl alcohol (b. p., 106–108°) were passed over lump pumice coated with a paste of aluminum oxide, contained in an iron tube maintained at 500–520°. Water and undecomposed alcohol were removed from the resulting gases by

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[4] The furnace consisted of an electrically heated iron tube filled with aluminum oxide on pumice. The oxide was prepared by the dehydration in the furnace of carefully washed precipitated aluminum hydroxide.

[5] Analysis showed 85–90% of unsaturated hydrocarbon; *iso*butyraldehyde was recovered from the aqueous condensate in appreciable amounts.

[6] Michael and Brunel, *Am. Chem. J.*, **41**, 135 (1909).

[7] King, *J. Chem. Soc.*, **115**, 1404 (1919).

[8] Ref. 3c. *Am. Chem. J.*, **2**, 23 (1880). Nef, *Ann.*, **318**, 22 (1901). Senderens, *Compt. rend.*, **144**, 1110 (1907). Ipatiew, *Ber.*, **36**, 2012 (1903).

means of a water-cooled condenser, a separatory funnel set to collect the condensed liquid, and a calcium chloride tower. The gas was cooled by passage through a copper tube 7 meters long which was immersed in a salt-ice mixture, and then bubbled through three absorption bottles partially filled with kerosene and cooled in the same mixture. When the volume of the solvent had increased by half, it was replaced by a fresh portion.

An equal volume of cooled 50% sulfuric acid was added to the butylene solution and the mixture stirred vigorously during several hours, the temperature being allowed to rise from 0° to that of the room. Cooling was necessary at first to prevent the heat of reaction from bringing the temperature up to the boiling point. After separating the two layers, the kerosene was used again as solvent, thus conserving the *iso*butylene still contained in it. The acid was neutralized by slowly adding it to a well cooled, vigorously stirred, concentrated solution of sodium hydroxide. Steam distillation of the alkaline solution gave the constant-boiling mixture of *tertiary*-butyl alcohol and water, from which the former was salted out with potassium carbonate; partial crystallization of the material and renewed drying of the liquid fraction gave a product boiling at 81–83°, and solidifying above 16°. The yield varied according to the speed with which the *iso*butylene was passed through the solvent, and usually amounted to 40%, calculated on the amount of alcohol actually used.

2. The iron reaction chamber was replaced by one of glass, 3.5 cm. × 90 cm., constricted at the bottom to a 2-cm. tube, and at the top to a 2.5-cm. tube bearing a side neck, the thermometer well being sunk into the chamber, down to the catalyst, several centimeters below the top of the heating coil; 1000 g. of alcohol was boiled through the furnace during two hours; temperature, 450–475°.

The hydrocarbon which then liquefied in the copper condenser was passed directly into the kerosene. Upon subsequent treatment as previously noted, 500 g. of alcohol melting above 15° was obtained.

3. The copper condenser was wound around an all-copper kettle 25 cm. high and 16 cm. in diameter, fitted at the top with a press-ring cover having three holes for condenser, thermometer and stirrer, the kettle being immersed in a salt-ice bath (at —18° to —20°) so that the cooling mixture covered it entirely. 2600 g. of 50% sulfuric acid was placed in the kettle; 1000 g. of *iso*butyl alcohol was passed through the furnace during two hours, the small amount of undecomposed alcohol, together with the water, being sent through a second time, Only water then remained. Meanwhile the stirrer[9] was in vigorous action, this being continued during the next six hours while the temperature rose to —10°. The acid layer was then siphoned out. A mixture of 1300 g. of sodium hydroxide and 650 cc. of water was placed in a 5-liter flask fitted with a stirrer, reflux condenser and dropping funnel, the flask being placed in an ice-bath. The acid was run in as rapidly as was possible without causing more than slight refluxing (about one hour) the alcohol then being recovered as previously noted; yield, 550 to 580 g. of alcohol above 15°.

The remaining hydrocarbon, weighing 225–250 g., was recovered and found to consist almost entirely of 2,3-butylene, identified as its derivative 2,3-dibromobutane, b. p., 158–162°.

Summary

The details of a very satisfactory method for the preparation of *tertiary*-butyl alcohol have been described, which consist in the dehydration of

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[9] The stirrer was of the emulsifying type recently described in a communication from the Eastman Laboratories, "The Preparation of Synthetic Organic Chemicals at Rochester," p. 26.

*iso*butyl alcohol and the subsequent rehydration of the *iso*butylene thus formed. The method can be adapted to any laboratory scale.

BURLINGTON, VERMONT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TRIPHENYLFLUOROMETHANE

BY F. F. BLICKE

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Triphenylhalomethanes have been in continual demand for the preparation of substances containing a triphenylmethyl group; consequently, triphenylchloro-, bromo- and iodomethane are well-known compounds. In connection with certain work, however, it was found that the above-mentioned halides were not entirely suitable for our purpose.

The halogen in triphenylchloromethane is less reactive than the halogen in triphenylbromomethane and, normally, it might be expected that the fluorine compound would be even less reactive than the chloride. Still, considering the extreme chemical reactivity of fluorine itself and the abnormal behavior of so many inorganic fluorides it seemed not improbable that triphenylfluoromethane might prove to be an unusually reactive substance. Moreover, A. F. Holleman has shown that fluorine in certain substituted benzene compounds shows a remarkable reactivity.[1]

We were able to prepare triphenylfluoromethane by the action of acetyl fluoride on a benzene solution of triphenylcarbinol.[2] $(C_6H_5)_3C\text{-}OH + CH_3CO\text{-}F = (C_6H_5)_3C\text{-}F + CH_3CO\text{-}OH$.

Judging from the reactions studied, it can be said that the fluoride is unquestionably a less reactive substance than the corresponding chloride. The fluoride, unlike the chloride, is unacted upon by molecular silver, mercury or zinc. Even at 80° silver does not remove the fluorine.

The chloro compound reacts almost immediately and quantitatively with absolute ethyl alcohol with the formation of triphenylmethyl ethyl ether.[3] The fluoride can be recrystallized unchanged from alcohol.

Suspended in water for 12 hours, the fluoride shows no signs of hydrolysis and can be recovered unchanged. When boiled with aqueous sodium hydroxide, aqueous silver nitrate or with acetic acid the fluoride is converted into the carbinol.

The fluoro compound, dissolved in absolute ether, is reduced quanti-

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[1] Holleman, *Rec. trav. chim.*, **23**, 256 (1904); **24**, 28 (1905).

[2] Gomberg and Davis [THIS JOURNAL, **25**, 1271 (1903)] were the first to show that acetyl chloride reacts with triphenylcarbinol with the formation of triphenylchloromethane, and not triphenylmethyl acetate as might be expected. Later L. Henry [*Bull. acad. roy. Belg.*, **1905**, 537; **1906**, 261) showed that tertiary alcohols in general react with acetyl chloride with the formation of the corresponding carbinol chloride.

[3] Gomberg and Kamm, THIS JOURNAL, **39**, 2011 (1917).