

116.5°. The ortho acid, 1.5 g., was somewhat impure and melted at 47.1–49.3° (recorded value 51°). A small amount of material<sup>3</sup> which was probably a disubstitution product was also present.

A preparation, carried out in the apparatus which was used before the high speed stirrer was developed, consisted of the addition of 250 ml. of isopropylbenzene to the product of the reaction of 42 g. (0.4 mole) of amyl chloride and 37 g. of sodium in 200 ml. of petroleum ether. The mixture was refluxed at 52° for two and one-half hours. Cumic acid, 3.8 g., was isolated and characterized by the melting point, 154°, of the amide. The recorded value is 155°.<sup>4</sup>

(3) Persoz, *Ann.*, **44**, 312 (1842).

(4) Gattermann and Schmidt, *ibid.*, **244**, 52 (1888).

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RESEARCH LABORATORY OF ORGANIC CHEMISTRY  
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### An Improved Method for the Preparation of 1-Isobutyryl-2-phenylhydrazine

BY MARTIN JACOBSON AND FRED ACREE, JR.

The preparation of 1-isobutyryl-2-phenylhydrazine has been reported by several investigators in either very low or unspecified yields. Bölsing and Tafel,<sup>1</sup> Brunner,<sup>2</sup> Leighton<sup>3</sup> (25% yield) and van Alphen<sup>4</sup> (38% yield) prepared the hydrazine from phenylhydrazine and isobutyric acid. Ponzio<sup>5</sup> prepared the substance from isobutyryldinitroethane and phenylhydrazine, while Widman<sup>6</sup> and van Alphen<sup>4</sup> treated phenylhydrazine with isobutyryl chloride and isobutyryl bromide, respectively.

In this Laboratory 67% of the theoretical quantity of the hydrazine has been obtained by the following procedure: A mixture of 378 g. (3.5 moles) of phenylhydrazine (technical), 700 g. (7 moles, 100% excess) of isobutyric acid (technical), and 250 ml. of toluene was refluxed under a condenser equipped with a water trap. After forty-eight hours 77 ml. of water had been collected (theory for 3.5 moles, 63 ml.) and the reaction mixture was then cooled in an ice-box overnight. The substance which separated was filtered and washed with ether, and the crude air-dried product (425 g., 68% yield), consisting of colorless, shining plates, melted at 139–141°. After it was recrystallized from ethanol the substance weighed 418 g. (67% yield) and had a constant melting point of 143° (cor.). Reworking of the toluene and ethanol mother liquors caused an additional 12 g. of crude material to separate, from which 2 g. (0.3%) of the pure hydrazine was obtained on recrystallization.

(1) Bölsing and Tafel, *Ber.*, **25**, 1552 (1892).

(2) Brunner, *Monatsh.*, **18**, 97 (1897).

(3) Leighton, *Am. Chem. J.*, **20**, 678 (1898).

(4) van Alphen, *Rec. trav. chim.*, **43**, 823 (1924).

(5) Ponzio, *Gazz. chim. ital.*, **35**, 395 (1905).

(6) Widman, *Ber.*, **27**, 1967 (1894).

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### Improved Preparation of Isopropylidene Glycerol

BY MELVIN S. NEWMAN AND MARY RENOLL

We have recently modified Fischer's<sup>1</sup> procedure for making isopropylidene glycerol so that this compound may be prepared quite easily in almost quantitative yield. The physical properties of our once-distilled product compare favorably with those for Fischer's thrice-distilled material.

#### Experimental

A mixture of 100 g. (1.09 moles) of anhydrous distilled glycerol, 300 cc. of acetone, 300 cc. of petroleum ether (b. p. 35–55°, Skellysolve F) and 3.0 g. of *p*-toluenesulfonic acid monohydrate was placed in a one-liter three-necked flask fitted with a stirrer and a helices-packed (18 inches) total-reflux column topped by a total-reflux phase-separating head. The mixture was stirred and refluxed (temperature at head 25–28°) for forty-three hours. The mixture was homogeneous after eighteen hours. After twenty-four hours the reaction was almost complete as judged by the amount of lower aqueous phase being formed in the head. The cooled reaction mixture was neutralized with 1.3 g. of powdered fused sodium acetate. After filtration and evaporation of solvent, the isopropylidene glycerol was obtained in 96.6% yield (139 g.) as a colorless liquid, b. p. 80.5–80.8° (11 mm.),  $n_D^{20}$  1.4326,  $d_4^{25}$  1.0626,  $M_{RD}$  32.30, calcd. 32.43 (using values in Gilman<sup>2</sup> except for ether oxygen which was calculated as 1.60 by means of the Lorentz-Lorenz formula using  $n_D^{20}$  1.42227 and  $d_4^{20}$  1.03361 for dioxane<sup>3</sup>). In a similar experiment using 100 g. of about 95% glycerol the yield of isopropylidene glycerol was 125 g.

(1) E. Fischer and Pfähler, *Ber.*, **53**, 1606 (1920).

(2) Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1751.

(3) Allsopp and Willis, *Proc. Roy. Soc. (London)*, **A153**, 392 (1936).

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### Reaction of Theophylline with Gibbs' Reagent

BY HARRY W. RAYBIN

Recently, the use of Gibbs' reagent (2,6-dichloroquinone-chloro-imide) has been proposed for the detection and determination of uric acid.<sup>1</sup>

The interaction of various compounds including the purines, with Gibbs' reagent have been studied by Scudi,<sup>2</sup> Leahy,<sup>3</sup> and Fearon,<sup>1</sup> and among the purines only uric acid has been noted as reacting. The statement of Fearon<sup>1</sup> that "Less oxidized purines, such as hypoxanthine and xanthine, give no colours with this reagent" needs qualification in view of the readily obtained blue color given by theophylline (1,3-dimethylxanthine) with this reagent. The addition of a few drops of 0.4% alcoholic Gibbs' reagent to a borax or sesquicarbonate solution of theophylline produces a blue color, with the noteworthy property of giving an insoluble red-violet precipitate by the addition of solid sesquicarbonate to saturation. The violet-red precipitate is obtained with 0.2 mg. of theophylline per cc. (aminophylline is not suited

(1) W. R. Fearon, *Biochem. J.*, **38**, 399 (1944).

(2) J. V. Scudi, *J. Biol. Chem.*, **139**, 715 (1941).

(3) H. W. Leahy, et al., *J. Milk Technology*, **3**, 183 (1940).