Barometric pressures ranged from 757 to 765 mm., the tests which established the explosive limit being made at 759 and 760.5 mm.

Mixtures containing over 30% by volume of chlorine monoxide exploded with some violence, emitting an orange-colored flash of light extending the length of the tube. The higher the concentration of the oxide, the more vigorous was the explosion. Mixtures containing 25 to 30% chlorine monoxide exploded weakly and, as the reaction occurred, a yellow band of light was observed moving up through the tube. A hot spark was required to start the explosion of such a mixture. When the concentration was below 25% the flame was not seen, but an explosion was detected by a rattling of the glass cover of the explosion tube. Mixtures containing 22.1, 23.0, and 23.2% by volume of chlorine monoxide failed to explode while two mixtures containing 23.8% did explode.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON
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Preparation of Ethylene Glycol Dimethyl Ether

BY JOHN V. CAPINJOLA

In connection with studies in this Laboratory for which several dialkyl ethers of ethylene glycol were required, it was found that the dimethyl ether of ethylene glycol can be prepared simply and in good yield by a modification of the procedures already reported for this[1] and the higher[2] dialkyl ethers.

Methyl chloride is simply passed into a solution of sodium in excess ethylene glycol monomethyl ether (Methyl Cellosolve) until the mixture has gained the required weight, after which the mixture is decanted from the precipitated sodium chloride and the product is recovered by distillation.

Experimental

The following is a description of a typical preparation. To 1830 g. (24 moles) of methyl cellosolve contained in a 3-liter, three-neck flask, equipped with a reflux condenser and mechanical stirrer,[3] was added portionwise while stirring 138 g. (6.0 moles) of sodium in small pieces. As the sodium dissolved, the mixture thickened and became dark brown in color. When all the sodium had dissolved, the flask was fitted with a thermometer and an inlet tube extending beneath the surface of the solution. Methyl chloride was passed into the mixture at such a rate that very little escaped reaction. Reaction started immediately and proceeded smoothly and rapidly. Some heat was evolved, and this was removed by means of a water-bath applied when the temperature of the mixture reached 60°. When the reaction was complete, as determined by the gain in weight (the time for complete methylation was usually about three hours), the mixture was cooled and the liquid portion was decanted from the sodium chloride. The liquid portion was distilled from an ordinary distilling flask, collecting the material distilling below 123°. Fractional distillation of this material gave 422 g. of ethylene glycol dimethyl ether boiling at 83.5–84.0°, d^{20}_{4} 0.8664, n^{20}_{D} 1.3813; yield, 78% based on the sodium.

RESEARCH LABORATORIES
OF THE ETHYL CORPORATION
DETROIT, MICHIGAN
RECEIVED JUNE 25, 1945

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(1) Lippert, *Ann.*, **276**, 171 (1893); Clarke, *J. Chem. Soc.*, **101**, 1802 (1912).

(2) Van Duzee and Adkins, THIS JOURNAL, **57**, 147 (1935); Liston and Dehn, *ibid.*, **60**, 1264 (1938).

(3) Calingaert, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 51 (1940).

The Decomposition of Picrates of Organic Bases with Lithium Hydroxide

BY ALFRED BURGER

When an organic base is to be recovered from its picrate the salt is usually suspended or dissolved in the solution of sodium, potassium or ammonium hydroxide, or the corresponding carbonates, and the base extracted into a suitable solvent. Owing to the low solubility of sodium, potassium and ammonium picrates, these salts invariably crystallize out during the extraction, and necessitate considerable dilution of the aqueous layer, or removal by filtration. If the organic base is appreciably soluble in water, the efficiency of the extraction into the solvent is greatly decreased by dilution.

Müller[1] suggested to adsorb the picric acid on wool in 0.1 N hydrochloric acid solution, and to recover the hydrochloride of the base from the filtrate by evaporation. This method is recommended especially for bases sensitive to alkali and oxidation. However, for larger amounts of picrates, it is time-consuming, and the traditional methods of extracting the base will be preferred in many cases.

The present author has found that lithium hydroxide may be employed advantageously for the decomposition of picrates. The picrate is suspended in a saturated aqueous solution (about 13%) of the hydroxide, and the base extracted in a separatory funnel or continuous extractor without fear of separation of lithium picrate. The last traces of picric acid may be removed easily by washing the ether extract once or twice with a saturated lithium hydroxide solution.

(1) Müller, *Z. physiol. Chem.*, **209**, 207 (1932).

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VA.
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The Reaction of Chloral with *n*-Amylmagnesium Bromide and *n*-Hexylmagnesium Bromide

BY VAUGHN W. FLOUTZ

A number of investigators have studied the reaction of chloral with organomagnesium halides, and have reported various reaction products which depend, in general, upon the type of organomagnesium halide used. With some exceptions, the literature which covers studies of this nature bears out the conclusion of Gilman and Abbott[1] to the effect that reduction of chloral to trichloroethanol predominates in the use of Grignard reagents, RMgX, which can be oxidized with the loss of two hydrogen atoms and the formation of a carbon to carbon double bond. In other cases, where R cannot be so oxidized, the main reaction is normal addition leading to the formation of the secondary alcohol. The methyl, benzyl and aryl groups are of this nature.

(1) Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1943).