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
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RECEIVED MAY 7, 1945

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, $n^{20}\text{D}$ 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).

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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).

Noteworthy exceptions to this generalization appear in the results of earlier investigations by Howard who reported the formation of secondary alcohols containing the trichloromethyl group along with an alkyl group in those cases where the alkyl group is ethyl, *n*-propyl,[2] isopropyl or *n*-butyl.[3] The yields reported are not high and no mention is made of other reaction products. Gilman and Abbott[1] have studied the reaction of chloral with ethylmagnesium halides; they were unsuccessful in synthesizing the secondary alcohol, but obtained a considerable amount of trichloroethanol.

The research projects here reported were undertaken to investigate further the reaction of chloral with alkylmagnesium halides. The results are in accordance with the generalization of Gilman and Abbott.

Experimental

Chloral and *n*-Amylmagnesium Bromide.—The Grignard reagent was prepared in the usual manner by the slow addition of a 0.25-mole portion of *n*-amyl bromide dissolved in a like volume of anhydrous ether to 0.25 g. atom of magnesium turnings in 200 ml. of anhydrous ether. In those cases where the procedure of normal addition was followed 0.25 mole of freshly distilled chloral dissolved in a like volume of anhydrous ether was dropped slowly into the prepared Grignard reagent. The reaction flask was immersed in an ice–water-bath and the rate of addition was controlled so that no refluxing of the ether was evident. Following the addition of the chloral the mixture was warmed to room temperature and refluxed for one-half hour. In the inverse addition the Grignard reagent was removed and added slowly to 0.25 mole of chloral dissolved in 100 ml. of anhydrous ether. During addition of the reagent the reaction mixture was cooled as in the normal addition. In both types of addition a considerable amount of solid separated during the course of the reaction. The product was hydrolyzed by pouring into an ice–water mixture and then cleared by the addition of 10% aqueous acetic acid. The ether layer was removed and washed in turn with sodium bicarbonate solution, sodium bisulfite solution and water, then dried over anhydrous sodium sulfate.

The ether and the pentene-1 which was formed in the reaction were removed by distillation. The major portion of the ether and hydrocarbon was distilled off by using a hot water-bath; following this the residue was heated in an oil-bath to a bath temperature of 110°, and the distillate collected with the main portion. In order to facilitate the determination of the amount of pentene-1 present it was converted into 1,2-dibromopentane; this was accomplished by treating the ether solution with a slight excess of bromine in subdued light. Following this the ether was removed by distillation and the residual oil was washed in turn with sodium bicarbonate solution and water. After a period of drying over anhydrous calcium chloride the product was distilled under diminished pressure to obtain the 1,2-dibromopentane; boiling point 72–74° at 15 mm.

The oily residue from the removal of ether and pentene-1 was subjected to fractional distillation under diminished pressure. The fraction which distilled at 95–99° at 125 mm. was shown to be trichloroethanol through the preparation of the *m*-nitrobenzoate, melting point 75°, and the α-naphthyl urethan, melting point 119–120°. The results are summarized in Table I.

TABLE I

Experiment no.	1	2	1
Products isolated	Normal addition, g.		Inverse addition, g.
CCl_3CH_2OH	19	20	23
$C_5H_{10}Br_2$ (1, 2)	24	23	27
Tarry residue	5.5	5.0	5.0

Chloral and *n*-Hexylmagnesium Bromide.—The procedure employed was similar to that for chloral and *n*-amylmagnesium bromide. Twenty-five hundredths mole portions of *n*-hexyl bromide and chloral, and 0.25 g. atom of magnesium were used. In the separation of the ether and hexene-1 from the reaction mixture the distilling flask was heated in an oil-bath to a bath temperature of 130°. The 1,2-dibromohexane distilled at 87–89° at 15 mm. Results are given in Table II.

TABLE II

Experiment no.	1	2	1
Products isolated	Normal addition, g.		Inverse addition, g.
CCl_3CH_2OH	21	22.5	26
$C_6H_{12}Br_2$ (1,2)	28	27	33.5
Tarry residue	4.2	4.5	2.0

DEPARTMENT OF CHEMISTRY
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[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, AGRICULTURAL RESEARCH ADMINISTRATION, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE]

Optical Crystallographic Properties of DDT

BY ERNEST L. GOODEN

The prominence in insecticide research of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane, commonly called DDT, has prompted an investigation of the principal optical crystallographic properties of this compound. The results obtained to date are reported here.

The sample used was the para–para′ isomer (m. p. 108°)[1] purified by successive recrystallizations of technical DDT from ethanol.

Careful consideration was given to the changeability of the refractive index matching liquids. The liquids used for α and β were aqueous solutions of mercuric potassium iodide. Because these solutions are sensitive to changes in humidity, each use of a given liquid was accompanied by a measurement of its refractive index (nD) on the same day. Determination of γ, which is beyond the range of aqueous mercuric potassium iodide, was done with solutions of sulfur in methylene iodide, and the indices of these were checked within a day or two of their use. Since DDT is noticeably soluble in methylene iodide, allowance was made, in the following way, for the alteration of index of the matching liquid surrounding the crystals: A solution of sulfur in methylene iodide known to produce a nearly perfect match for DDT crystals in the γ-indicating position was transferred to a glass-stoppered hollow prism, and the refractive index measured on a spectrometer, with sodium light, both before and after the addition of DDT to practical saturation. The DDT was found to lower the index of

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(2) Howard, THIS JOURNAL, **48**, 774 (1926).

(3) Howard, *ibid.*, **49**, 1068 (1927).

(1) The pure material and melting point datum were supplied by Stanley A. Hall, of this Bureau.