

to produce a crystalline product. VII forms a dehydro compound, as noted by van Sillevoldt, but contrary to his results the compound having the higher m. p. of 262° with decomposition was obtained as the principal product. The same compound in approximately the same yield (35%) was obtained on treatment of VII with alcoholic sulfuric acid either with or without previous treatment with iodine and sodium acetate. On boiling the dehydro compound with alcoholic alkali, a bicarbonate-soluble material is formed, giving a blue-green color with ferric chloride. Treatment of VII with alcoholic alkali gives little reaction, most of the original compound being precipitated apparently unchanged from the reaction mixture on the addition of water. A small alkali-soluble fraction was obtained. In the presence of zinc a reaction occurs, yielding a bicarbonate-insoluble but alkali-soluble oil giving a reddish-brown color with ferric chloride.

The compound resembles the rotenoids in empirical formula, toxicity (Table III), optical activity and response to the Meyer and Rogers-Calamari color tests, but differs in response to the Goodhue and Durham tests and reaction with alkali. The formation of the dehydro compound by dehydration alone suggests that VII may be a hydroxy derivative of the tephrosin type. This interpretation is supported by the high oxygen content, the irregular responses to the color tests, and the normal reaction of the dehydro compound with alkali to be expected in the rotenoid series.

No compound corresponding to van Sillevoldt's red-yellow crystals of m. p. 207° was isolated.

Toxicity (Tables II and III).—A number of points of interest are apparent from the toxicity data. Two of the compounds, V and VII, show a toxicity to the silkworm equal or nearly equal to that of rotenone itself. Great specificity is shown by these two compounds, however, since they showed a negligible mortality on the bean beetle under comparable conditions. The reduction in the feeding of the bean beetle caused by these two materials indicates that they have some effect on this insect also, even

though less intense. The other compounds are either conclusively non-toxic or of such small effect that the presence of toxicity is highly questionable. The very high toxicity shown by the residues, particularly residue G, is very probably not accounted for by their content of rotenone or the other isolated compounds, because their toxic action on the silkworm is even more rapid than that of any of the pure compounds. Accordingly, unless the compounds show synergism, which was found by Martin²⁴ to be negligible in several mixtures of rotenoids, one or more highly toxic materials in addition to those isolated are probably present.

Summary

The ether extract of yam beans was divided into a non-toxic oil and a resin toxic to insects. The resin was fractionated by chromatographic methods, yielding one non-crystalline and six crystalline compounds, and three heterogeneous fractions.

One of the crystalline compounds was identified as rotenone, and a second, designated "erosone," was shown to be closely related to elliptone.

Four of the compounds showed evidence of a relation to the rotenoid structure, but differed in containing a single methoxyl group.

Three of the compounds and one of the heterogeneous fractions were toxic to the silkworm, but two of these compounds were of low toxicity to the Mexican bean beetle.

The toxic heterogeneous fraction probably contained at least one toxic compound not isolated.

(24) Martin, *Ann. Appl. Biol.*, **29**, 69 (1942).

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RECEIVED APRIL 30, 1945

NOTES

Minimum Explosive Concentration of Chlorine Monoxide Diluted with Oxygen

BY GEORGE H. CADY AND ROBERT E. BROWN¹

Although it has long been known that chlorine monoxide is an explosive compound, no determinations have been made of the explosive limits of mixtures of this substance with other gases. Since the compound is used in high dilution for the industrial production of hypochlorous acid and calcium hypochlorite,² it is desirable to know the minimum explosive concentration of the gas. This limit has been measured for mixtures of chlorine monoxide and oxygen at one atmosphere pressure and at 23°. Under these conditions an explosion can be obtained only when the mixture contains over 23.5% chlorine monoxide by vol-

ume. Since this amount is much greater than the concentration used commercially, there appears to be no chance that the gas will explode in the plant.

Experimental

Each mixture containing chlorine monoxide was obtained by passing a dry mixture of chlorine in oxygen over a large excess of yellow mercuric oxide which had been dried in an oven at about 110°. The reaction proceeded so far toward completion that no free chlorine was found in any of the mixtures when analyzed by the iodometric technique described by Spinks.³ The mixture passed through a sampling bulb, an explosion chamber, and finally through a second sampling bulb. Mixtures ranging in concentration from 22 to 40% by volume were tested, the compositions being known to within 0.3%. The explosion chamber was a Pyrex glass tube having a length of 90 cm. and an internal diameter of 34 mm. It was mounted in a vertical position and was equipped with two tungsten wire electrodes located 3 cm. from the bottom of the tube with a spark gap of 2 mm. A hot spark produced by an induction coil was used to initiate an explosion. Tests were made in faint day-light at a temperature within 1° of 23°.

(1) Present address: Lt.(j.g.) Robert E. Brown, U.S.N.R., c/o C.O.P., Navy 163, F.P.O., San Francisco, California.

(2) Geo. H. Cady, U. S. Patent 2,157,524, May 9, 1939; I. E. Muskat and Geo. H. Cady, U. S. Patent 2,240,344, April 29, 1941; U. S. Patent 2,240,342, April 29, 1941.

(3) J. W. T. Spinks, *This Journal*, **53**, 3015-3016 (1931)

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.

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RECEIVED MAY 7, 1945

Preparation of Ethylene Glycol Dimethyl Ether

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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 this¹ and the higher² 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}^{20} 0.8664, n_D^{20} 1.3813; yield, 78% based on the sodium.

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RECEIVED JUNE 25, 1945

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

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

(3) Calingsaert, *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.

Müller¹ 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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RECEIVED JULY 30, 1945

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 Abbott¹ 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).