

LXVI.—*Preparation and Reactions of Bromopicrin.*

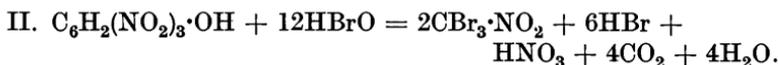
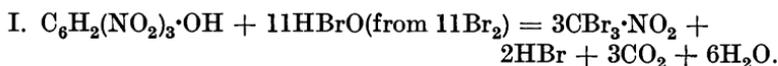
By LOUIS HUNTER.

BROMOPICRIN was first prepared by Stenhouse (*Annalen*, 1854, **91**, 307) by distillation of an aqueous mixture of picric acid, lime, and bromine. This method was repeated by Bolas and Groves (this *Journal*, 1870, **23**, 153), who claim that the conversion of picric acid into bromopicrin according to the scheme  $C_6H_2(NO_2)_3 \cdot OH \rightarrow 3CBr_3 \cdot NO_2$  is almost quantitative. According to Scholl and Brenneisen (*Ber.*, 1898, **31**, 654), however, the product contains a small admixture of dibromodinitromethane.

Orton and McKie (*T.*, 1921, **119**, 29) were successful in modifying the Stenhouse-Hofmann process for the preparation of chloropicrin to suit laboratory and industrial conditions. The process described in the present paper is an attempt to apply the results of these authors to the case of bromopicrin. Archetti (*Boll. Chim. farm.*, 1903, **42**, 673) states that exposure of aqueous picric acid and bromine to direct sunlight for several months produces a yellow oil. This experiment has been repeated and the oil found to be impure bromopicrin. By working in the presence of sodium carbonate the time of exposure can be reduced to a few days, and a

suitable choice of conditions ensures a good yield of practically pure bromopicrin. In the absence of light, the reaction proceeds in the same way, but requires a somewhat longer period for completion.

The reaction follows a course similar to that proposed by Orton and McKie (*loc. cit.*) in the case of chloropicrin, hypobromous acid or its sodium salt being the active agent.



Measurements of the amount of bromine required to decompose a known weight of picric acid, and estimations of bromide and bromate produced during the reaction, give results which are in close agreement with the above equations. Equation I indicates the reappearance as bromopicrin of the whole of the nitro-groups present in the picric acid; the yield in this case would amount to 390 per cent. calculated on the original picric acid. Equation II requires a yield of 260 per cent., the remainder of the nitrogen appearing as nitric acid. Estimations of the nitrate-content of the liquors by the Schulze-Tiemann method serve as a means of measuring the extent to which the reaction follows equation II. Under the best conditions—a faintly alkaline medium—the yield of bromopicrin can be raised to 353 per cent., the proportion of nitrate in the liquors being correspondingly small.

When prepared in an acid or in a strongly alkaline medium, bromopicrin is formed only in poor yield, much of the picric acid remaining unchanged even after long exposure (see Table I).

The chief impurity contained in the crude oil is carbon tetrabromide, arising either by the further bromination of bromopicrin, or directly by bromination of the non-nitrated carbon atoms in the picric acid molecule. In no case does the amount of carbon tetrabromide in the crude bromopicrin exceed 0.5 per cent. Since such small amounts do not materially alter the figures for total bromine, the carbon tetrabromide is detected only by such reactions as involve bromopicrin but leave the tetrabromide unaffected. The reaction with caustic alkali has been used to estimate carbon tetrabromide in the crude oil.

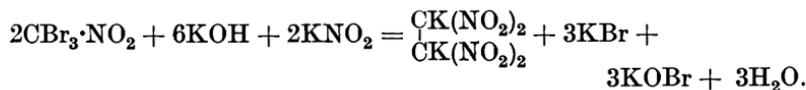
*Reaction with Concentrated Alkali.*—It was observed by Wolff and Rüdell (*Annalen*, 1897, 294, 201) that bromopicrin reacts vigorously with 50 per cent. caustic potash to form potassium bromide and a yellow explosive salt. Although this salt was not examined by them, they suggested that it was the potassium salt of bromonitromethane, from analogy with the case of dibromo-

dinitromethane (Losanitsch, *Ber.*, 1882, **15**, 471), which is attacked by caustic potash as follows :



Investigation of the reaction, however, has shown this suggestion to be incorrect. The yellow salt is bromine-free, and is the *s.*-dipotassium tetranitroethane which was obtained by Scholl and Brenneisen (*Ber.*, 1898, **31**, 642) by the action of alcoholic potassium cyanide on bromopicrin.

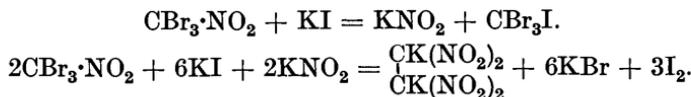
The yellow precipitate obtained by the action of concentrated potash on bromopicrin contains large quantities of potassium bromide and bromate, and the actual yield of the organic salt is small. Its formation is the result of a series of simultaneous reactions, the effect of which may be expressed thus :



The nitrite is supplied by side-decompositions of the bromopicrin; for example,  $\text{CBr}_3\cdot\text{NO}_2 + 6\text{KOH} = 3\text{KBr} + \text{KNO}_2 + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$ . Potassium hypobromite is present in considerable quantity in the filtrate.

Attempts to obtain the corresponding sodium salt in a pure state by a similar method were unsuccessful owing to its much greater solubility. That the reaction with concentrated sodium hydroxide is exactly parallel, however, is shown by the formation of a yellow, explosive precipitate containing bromide and having properties similar to those of the potassium salt.

*Reaction with Potassium and Sodium Iodides.*—In the same paper, Wolff and Rüdél state that bromopicrin liberates iodine from aqueous or alcoholic solutions of potassium iodide with formation of a yellow, crystalline, explosive salt. Repetition of this work reveals the fact that the explosive salt in this case also is *s.*-dipotassium tetranitroethane. The reaction may be compared with that between bromopicrin and aqueous alcoholic potassium cyanide (Scholl and Brenneisen, *loc. cit.*), yielding the same potassium salt together with potassium bromide and cyanogen bromide. A series of equations similar to those put forward by these authors may be suggested and summarised thus :

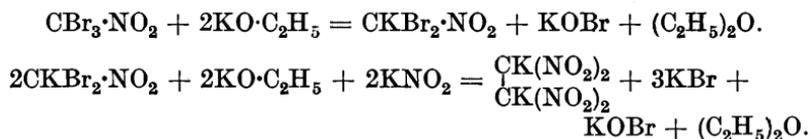


After standing for some hours, the alcoholic filtrate from the

potassium salts deposits crystals of potassium nitrate, without doubt produced by oxidation of the potassium nitrite.

With alcoholic sodium iodide, bromopicrin liberates iodine and produces a yellow solid containing the corresponding sodium salt. The extreme solubility of the latter makes its isolation in the pure state impossible.

*Reaction with Sodium and Potassium Ethoxides.*—It has been shown by Röse (*Annalen*, 1880, 205, 249) that chloropicrin reacts with alcoholic sodium ethoxide with formation of ethyl orthocarbonate. The yield, however, is not good, and under the best conditions amounts only to 30 per cent. of the theoretical. It was thought, therefore, that the use of bromopicrin in a similar reaction might lead to a more satisfactory yield of orthocarbonate. This proves not to be the case, however, only traces of orthocarbonate being formed and a yellow mixture containing bromide, bromate, and an organic salt precipitated. As in the previous experiments, the sodium salt proves too soluble for isolation; but by use of potassium ethoxide an organic potassium salt can be obtained, which by its properties and analysis is shown to be *s.*-dipotassium tetranitroethane. An intermediate mixture of organic salts, the analysis of which suggests the presence of potassium dibromonitromethane, has been isolated; and consequently the course of the reaction is represented thus:



As before, the nitrite is generated by side-decompositions of the bromopicrin. The ether is obtained as a first fraction in the recovery of alcohol from the filtrate.

In the hope of attributing the low yield of ethyl orthocarbonate—at least partly—to the formation of similar organic salts in the reaction between sodium ethoxide and chloropicrin, the salt mixture obtained from this reaction was examined. Very small amounts of organic salts were obtained, hence this contributes in only a small degree to the poorness of yield of orthocarbonate.

In the various reactions of bromopicrin described above, the equations are not to be regarded as an exact representation of the changes going on, since side-reactions are known to occur. The low yield of the organic potassium salt together with the high proportion of bromide found in the crude mixtures points to other and more complete decompositions of the bromopicrin molecule.

## E X P E R I M E N T A L.

*Bromopicrin*.—Picric acid (10 grams) and sodium carbonate (60 grams) were dissolved in a litre of water, and bromine (26 c.c.) was added. The mixture was exposed to sunlight for a period of five to seven days, when the colour had faded to a light yellow and the layer of bromine had been replaced by a yellowish-brown oil. Longer exposures are not to be recommended, since diminution of yield occurs. The oil was removed in a current of steam, washed several times with aqueous caustic soda followed by water, and finally dried over anhydrous sodium sulphate. The product was practically pure bromopicrin. Yield 35 grams (Found: Br = 80.73. Calc., Br = 80.54 per cent.). It gave the following constants: m. p. 9.7—10.3°,  $d_4^{18.3}$  2.799,  $[R_L]_D^{25}$  35.51 ( $\text{CBr}_3 \cdot \text{NO}_2$  requires 36.08).

Table I indicates the yield of bromopicrin and the time required for the completion of the reaction under various conditions, the end of the reaction being judged roughly by the fading of the bromine colour. The table refers to 10 grams of picric acid, 26 c.c. of bromine, and 1000 c.c. of water. The equivalent proportions of sodium carbonate are calculated on the weight of picric acid used.

TABLE I.

	Yield of bromopicrin per cent.	Time of reaction.
No sodium carbonate .....	285	6 weeks
5 equivs. $\text{Na}_2\text{CO}_3$ (11.6 grams) .....	330	3 "
10 " $\text{Na}_2\text{CO}_3$ (23.2 " ) .....	342	10—14 days
15 " $\text{Na}_2\text{CO}_3$ (34.7 " ) .....	342	10 "
20 " $\text{Na}_2\text{CO}_3$ (46.3 " ) .....	350	7 "
25 " $\text{Na}_2\text{CO}_3$ (57.9 " ) .....	353	5 "
30 " $\text{Na}_2\text{CO}_3$ (69.6 " ) .....	353	5 "
100 grams NaOH .....	190	2 weeks
100 " $\text{H}_2\text{SO}_4$ .....	146	Unfinished after 8 weeks

s.-*Dipotassium Tetranitroethane*,  $\begin{matrix} \text{C}(\text{NO}_2)_2 \cdot \text{NO} \cdot \text{OK} \\ | \\ \text{C}(\text{NO}_2)_2 \cdot \text{NO} \cdot \text{OK} \end{matrix}$ .—(a) *By the action of caustic potash*. Bromopicrin was slowly added in small amounts to a cooled solution of potassium hydroxide ( $\text{KOH} : \text{H}_2\text{O} = 1 : 1$ ). A pale yellow solid immediately separated and the oil became semi-solid. After a short time, a violent reaction commenced with considerable heating and further separation of the yellow salt. The precipitate contained potassium bromide and bromate together with the organic salt. Owing to the comparative insolubility of potassium bromate, numerous crystallisations from water were necessary to obtain the pure organic salt, thus entailing great loss. By addition of carbamide to the reaction mixture no bromate is formed, and there is no need for repeated crystallisation.

To 5 grams of carbamide, dissolved in 50 c.c. of 50 per cent. caustic potash, 25 grams of bromopicrin were slowly added with cooling. The precipitate was washed with alcohol, and thereafter two crystallisations from hot water yielded a pure product. Yield of crude mixture (uncrystallised), 18 grams. Yield of pure dipotassium tetranitroethane, 0.5 gram.

s.-Dipotassium tetranitroethane prepared in this way is a bright yellow, crystalline powder, most easily crystallised from aqueous alcohol. It explodes on heating at 269—273°, or by contact with strong acids (Found: K = 27.3; N = 19.33. Calc., K = 27.3; N = 19.58 per cent.).

(b) *By the action of potassium iodide.* Twenty-five grams of potassium iodide were dissolved in 500 c.c. of 90 per cent. alcohol. On addition of bromopicrin, a yellow, crystalline precipitate was immediately formed and iodine liberated. Considerable rise of temperature was observed. Addition of bromopicrin was continued in small amounts until a test portion of the liquor no longer gave a precipitate with bromopicrin. The amount of bromopicrin required was 33 grams. The precipitate, consisting of potassium bromide and the organic potassium salt, was collected, washed with alcohol, and dried. Yield 12 grams. Two crystallisations from water yielded pure dipotassium tetranitroethane (2.3 grams), explosion point 272° (Found: K = 27.13; N = 19.03 per cent.).

(c) *By the action of potassium ethoxide.* To 12 grams of potassium, dissolved in 150 c.c. of absolute alcohol, 25 grams of bromopicrin, dissolved in 30 c.c. of alcohol, were slowly added with frequent cooling, a cream-coloured precipitate immediately forming. When the addition of bromopicrin was complete, the mixture was warmed cautiously on the water-bath until a vigorous ebullition set in. At this stage the precipitate changed colour to orange and a considerable quantity of nitrogen was evolved. When the reaction had moderated, the mixture was boiled on the water-bath for half an hour, cooled, and filtered. Yield 33 grams. Two crystallisations from hot water gave 0.8 gram of the pure salt, explosion point 269—273° (Found: K = 27.39 per cent.).

A reaction similar to that with potassium ethoxide is obtained by use of alcoholic potash, but the yield of pure salt is not good. Carbamide or phenylhydrazine may be used to facilitate reaction, although the yield of the salt is not appreciably increased.

s.-Dipotassium tetranitroethane, prepared by any of the above methods, exhibits general properties which agree with those of the salt described by Scholl and Brenneisen (*loc. cit.*). It was further identified with this compound by its decomposition with acids, yielding dinitromethane; the preparation of the corresponding

silver salt (Found: Ag = 51.2. Calc., Ag = 50.9 per cent.); and its bromination in aqueous solution, yielding tribromotrinitroethane (Found: Br = 58.9. Calc., Br = 59.7 per cent.).

Table II compares the yield of dipotassium tetranitroethane when prepared by the various methods. Potassium cyanide is the reagent used by Scholl and Brenneisen, the yield of the organic salt having been worked out from the method of preparation given by these authors. The table shows that the most convenient and economical method for the preparation of *s.*-dipotassium tetranitroethane is by use of potassium iodide.

TABLE II.

Reagent.	Bromopicrin.	Crude product.	Pure salt.
KOH (50 grams) .....	25 grams	18 grams	0.5 gram
KI (18.8 grams).....	25 "	8.2 "	1.5 grams
KOEt (K 12 grams) .....	25 "	33 "	0.8 gram
KCN (23.5 grams) .....	25 "	9.5 "	1.7 grams

*Estimation of Carbon Tetrabromide in the Crude Bromopicrin.*—A known weight of the crude oil is decomposed with 50 per cent. caustic potash or soda. The precipitated solid is filtered through a porous crucible and washed with alcohol. On diluting the washings with water, the whole of the carbon tetrabromide contained in the original oil is precipitated. It is collected, dried, and weighed. After one crystallisation from alcohol, a specimen melted at 92—93° (Found: Br = 96.3. Calc., Br = 96.4 per cent.). Using this method of estimation, it is found that the crude oil contains least carbon tetrabromide when prepared in an alkaline medium; and that protracted exposure to light, especially with excess of bromine, tends to increase the proportion of carbon tetrabromide.

The author wishes to express his thanks to Professor K. J. P. Orton, F.R.S., for his help and criticism.

UNIVERSITY COLLEGE OF NORTH WALES,  
BANGOR.

[Received, January 30th, 1923.]