

phosphorus and liquid white phosphorus are identical, we can change the single equation of these investigators for the vapor pressure of both liquid violet and liquid white phosphorus over the range 145° to 634° from

$$\log_{10} P(\text{mm. Hg}) = 19.2189 - 3585.96/T - 3.59 \log_{10} T$$

to

$$\log_{10} P(\text{mm. Hg}) = 11.5694 - 2898.1/T - 1.2566 \log_{10} T \quad (3)$$

which represents all the data on liquid violet and liquid white phosphorus (except those of Schroetter) from 44° to 634° with deviations seldom greater than 5%. However a plot of the deviations of these data from the equation showed, in each set of measurements, decided trends that would be difficult to eliminate by a single smooth curve. It does however appear that the vapor pressure of liquid violet and liquid white phosphorus can be represented approximately by a single smooth curve.

Summary.

1. The vapor pressure of liquid white phosphorus has been measured in the range 44° to 150° by the static isoteniscope method of Smith and Menzies.

2. The relation between temperature and vapor pressure in this range is given by equation

$$\log_{10} P(\text{mm. Hg}) = 7.9542 - 2757.5/T$$

with maximum error probably as small as 0.5% from 100° to 150° and probably increasing below this temperature to a value not greater than 5% at 44.0°.

3. The measurements reported in this paper are not inconsistent with the measurements of Centnerszwer on the solid and are from 30 to 60% higher than values obtained by extrapolating the equation of Smits and Bokhorst to temperatures between 150° and 44°.

EAST PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

ARISTOL.

BY G. H. WOOLLETT.

Received June 11, 1920.

Little is known concerning the chemistry of aristol,¹ although the substance has been on the market for about 30 years.

It is an amorphous powder made by the action, at ordinary temperature, of an excess of a solution of iodine and potassium iodide on a solution of thymol and approximately 4 equivalents of alkali. When fresh it has a dark red color but soon fades to a buff or brown, a change which is hastened by light.

The red variety is capable of producing, more or less slowly, about 2

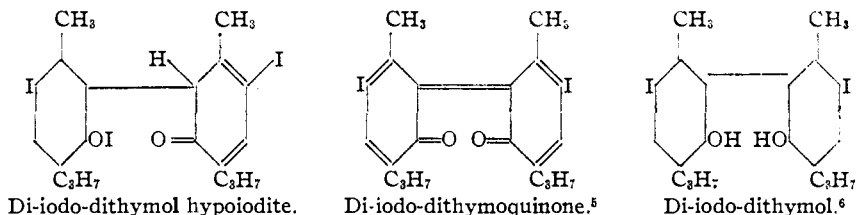
¹ Other names for this substance are annidalin, thymotol and diiododithymol.

to 3% of its weight of free iodine, and owes its pharmaceutical value to this property. The buff or brown variety evolves no iodine.¹

The constitution and molecular weight of the substance, as well as the cause of the color, and the mechanism of the reaction by which iodine is evolved, are not satisfactorily explained in the literature.

Three reports of the molecular weight were found: the first made ebullioscopically,² is given as 550 and has been assumed generally to be the normal weight. Later determinations³ made cryoscopically in thymol gave approximately this value, but those made cryoscopically in benzene by the same authors gave values 2.2 to 2.3 times the normal.

Analyses of aristol have shown that its composition varies considerably, but that it may be fairly well represented by the empirical formula $C_{10}H_{11}IO$. The molecular weight of 550 necessitates doubling this, and several structural formulas have been advanced, based on these data. The original one proposed by the discoverers⁴ and the 2 latest formulas are given below.



The hypoiodite formula has been shown by Bougault to be wrong, and as no author has succeeded in obtaining dithymol from aristol by reduction, although several have tried, the dithymol⁷ formulas may be questioned.

The idea that aristol contains adsorbed iodine, which is responsible for the evolution of iodine and also for the color of the material, has been advanced, since the hypoiodite formula was discarded.

During a study in this laboratory of Lautemann's Red,⁸ a supposed analogue of aristol, certain facts were discovered which did not agree with the data on aristol. The present research was undertaken both to substantiate the work on Lautemann's Red and to straighten out, if possible, the chemistry of aristol.

¹ J. Bougault, *J. pharm. chim.*, **17**, 221-7 (1918); *C. A.*, **12**, 1517 (1918).

² P. Dannenberg, *Monatsh.*, **24**, 67 (1903).

³ Moles and Marquina, *Anal. fis. quim.*, **17**, 59 (1919); *C. A.*, **13**, 3156 (1919).

⁴ Messinger and Vortmann, *Ber.*, **22**, 2312 (1889).

⁵ Bougault, *loc. cit.*

⁶ Moles and Marquina, *loc. cit.*

⁷ Cousin states that aristol consists of products more highly condensed than dithymol. *Compt. rend.*, **146**, 292 (1908).

⁸ Hunter and Woollett, *THIS JOURNAL*, **43**, 135 (1921).

The work on aritol showed first that it is not a single substance,¹ and that it can be separated by extraction with cold alcohol into a brown tarry fraction, soluble in alcohol, which constitutes on the average about 40% of the whole, and a colorless or faintly yellow fraction, insoluble in alcohol. No crystalline substance could be found in the soluble fraction other than a small amount of free iodine. This fraction produced more aritol on treatment with alkali, if the free iodine were not removed first.

It was further shown that by varying the proportions of iodine, thymol and alkali, but otherwise proceeding as in the manufacture of aritol, quite different results were obtained; thus, with 1 equivalent of each, iodothymol was formed, with 1 equivalent of thymol to 2 of the others, a gum was formed which was nearly all soluble in alcohol and which acted in every way like the soluble fraction of aritol. With 1 equivalent of thymol and 4 of iodine and alkali, aritol was formed. When iodothymol was treated with one equivalent of iodine and one of alkali the soluble gum resulted, 2 equivalents, however, gave aritol. It would appear from this observation that the soluble fraction of aritol is at least in part an intermediate product, although, as shown by analysis, it contains practically as much combined iodine as the insoluble part. Iodothymol would also appear to be an intermediate substance.

The insoluble part of aritol resembles leuco Lautemann's Red and, as would be expected, can be oxidized to a red substance like fresh aritol and Lautemann's Red in appearance, but not at all soluble in alcohol. The oxidation is somewhat more difficult than in the case of leuco Lautemann's Red. The re-oxidized insoluble fraction retains its color much longer than fresh aritol and also gives off less iodine. The idea that the color of aritol is due to adsorbed iodine was disposed of when besides this it was further shown that the insoluble fraction shows no tendency to adsorb iodine.

The presence of the soluble fraction or some similar substance was found to be necessary for the rapid loss of color and production of iodine and the change taking place during this action was found to be an oxidation of the soluble part by the insoluble part. Fig. 1 follows this reaction graphically. Curve I was obtained from a sample of comparatively fresh aritol, II from the re-oxidized insoluble fraction plus some iodothymol which was chosen as representative of the soluble fraction, III from the re-oxidized insoluble fraction alone, and IV from the insoluble fraction before re-oxidation. Curves V, VI, VII and VIII were obtained from similar samples kept in the dark except during titration, and show that there is a noticeable effect due to the action of light.

¹ This was also pointed out by T. R. Carswell, who, however, did not succeed in separating it into fractions which could be identified. *Chem. News*, 68, 87, 99, 131, 153, 166, 181, 195, 203, 214, 237 (1893).

The higher initial and final values in the case of fresh aristol are due to the presence of free iodine. Part of this had been present since the manufacture and part was due to the sample being partly "run down" when taken.

Iodothymol alone gave no iodine under similar circumstances, but Lautemann's Red, as was expected, when mixed with iodothymol acted in every respect like the re-oxidized insoluble fraction of aristol. In both cases as the production of iodine progressed the red color of the material became fainter.

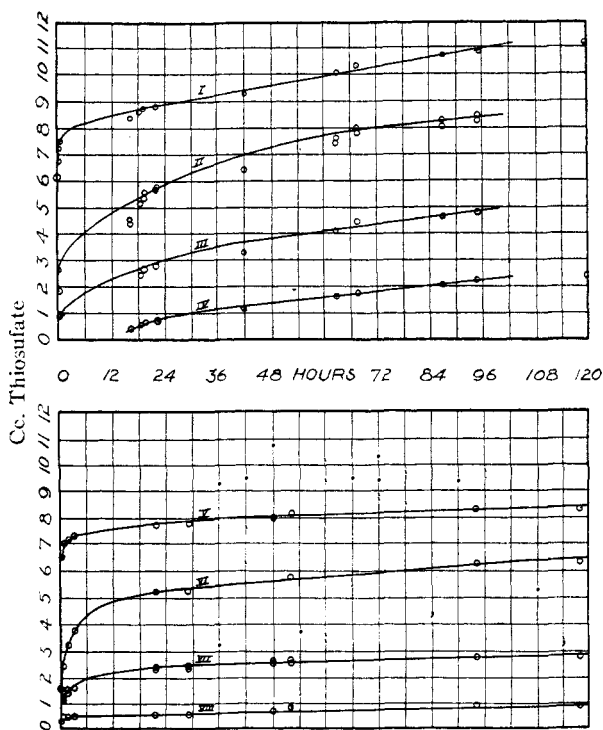


Fig. 1.

The molecular weight of the insoluble fraction taken cryoscopically in benzene was found to vary in different samples from 1940 to 2266. After oxidation it became 3670 to 4430. Taken cryoscopically in thymol, the values for one unoxidized sample were 1290 and 1360. These values are much the highest yet reported and are so, no doubt, because the former determinations were made on aristol containing much more of the soluble fraction. The high molecular weight substantiates our view that the red part of aristol is analogous to Lautemann's Red.

The lower value obtained with thymol as solvent may be due to dis-

sociation as suggested by Moles and Marquina, but it is not improbable that the lowering is due to reaction between solvent and solute. Such a reaction would be favored by the higher temperature necessary in working with thymol as solvent.

The iodine content of the insoluble fraction both before and after oxidation was never equal to the amount required by the formula $(C_{10}H_{11}IO)_n$, which is not surprising when one considers the ease with which iodine is lost by the substance and the manipulation necessary to separate the fractions and to oxidize the insoluble one.

Experimental.

Preparation of Aristol.—The method used in making aristol was essentially that of Messinger and Vortmann.¹ An average sample was prepared as follows: Fifteen g. (0.1 mol.) thymol and 16 g. (0.4 mol) sodium hydroxide were dissolved in 500 cc. of water. To this solution, at ordinary temperature and with efficient stirring, a solution of 70 g. of iodine and 50 g. of potassium iodide in 250 cc. of water was added until an excess of iodine was present which could be detected by the color of the solution after the precipitate had settled slightly. This usually consumed the entire amount.

The deep red precipitate of aristol was washed for several hours by decantation. filtered on a plaited filter, washed 3 or 4 times and transferred to a Büchner filter. The cake so formed was broken up in 500 cc. water and re-filtered. This was repeated several times. It was found impracticable to wash the product until it was entirely free from iodine, but the treatment outlined furnished filtrates which gave only slight opalescence with silver nitrate.

The aristol was dried in air in the dark and, when dry, consisted of soft lumps of dusty powder of a color which may best be described as "old rose." Twenty-eight g. was obtained in this case.

Samples as carefully washed as this one retained most of their color for at least 2 years if kept dry and in the dark.

Analysis for Iodine (Carius).—Sample 1: subs., 0.2054, 0.2069: AgI, 0.1789, 0.1809. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found: 47.13, 47.25. Sample 6 (Bayer's aristol, bought for comparison): subs., 0.2702: AgI, 0.2188. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found: 43.76.

Separation of the Fractions.—Various samples were extracted with cold alcohol, the insoluble part weighed and the weight of the soluble part calculated. In all cases, the alcoholic solution was brown and contained free iodine as shown by tests with starch.

The insoluble part was a nearly white powder in all cases except Sample 9 which was still slightly pink. None of the samples of insoluble aristol gave tests for iodine when fresh, nor did they show any free iodine if they were kept dry and in the dark for more than 2 years.

Analyses.—Sample 1, 2.00: loss 0.75 = 37.5%; insoluble, 1.25. Sample 5, 2.00: loss 0.84 = 41%; insoluble, 1.16. Sample 6, (Bayer's; this sample yellow), 5.00, 4.00: loss 2.00 = 40%, 1.62 = 40.5%; insoluble, 3.00, 2.38. average loss, 39.7%.

Carius, insoluble part. Sample 1: subs. 0.1714, 0.1848: AgI, 0.1454, 0.1583. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found: 45.83, 46.28. Sample 5: subs., 0.1990, 0.1847: AgI, 0.1679, 0.1549. Found: 45.58, 45.31. Sample 6 (3.00 g. sample): subs., 0.2055, 0.2368: AgI, 0.1598, 0.1839. Found: 42.01, 41.96.

The Soluble Fraction.—Four g. of Sample 6 was extracted with about 40 cc. of methyl alcohol. Fifteen cc. of the extract was evaporated quickly *in vacuo* at ordi-

¹ *Loc. cit.*

nary temperature. The brown tar which resulted was analyzed for iodine. (Carius.)

Subs., 0.1808, 0.1940: AgI, 0.1557, 0.1687. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found 46.52, 46.95.

One g. of Sample 6 was moistened with alcohol and added to about 100 cc. of water and 1 cc. of starch paste. This was titrated for iodine with sodium thiosulfate solution (1 cc. = 0.0101 g. of I_2) and used 0.6 cc., equivalent to 0.6% of I_2 free in the original sample.

Correcting the above analyses for the 1.9% of I_2 which should be free in the 1.215 g. of extract, the per cent. of I_2 becomes 44.4 and 45.1.

Aristol from the Soluble Fraction.—Five cc. portions of alcoholic extract from 2 g. of Sample 5 were used.

Each of the first two was treated with 1 cc. of 5% sodium carbonate solution and then about 100 cc. of water, filtered and washed. The precipitates were red and resembled the original aristol in all observed properties. 0.108 g. and 0.107 g. were obtained.

Analysis (Carius).—Subs., 0.1004 g.: AgI, 0.0800. Found: I, 43.05.

Two other portions titrated for iodine required 1.85 and 1.90 cc. of thiosulfate solution, equivalent to about 0.018 g. of I_2 . These samples when treated with sodium carbonate solution gave a gummy precipitate which could not be filtered but with no trace of red color.

Samples of extract when treated with water alone also gave the gummy precipitate.

Portions of alcoholic extract from 2 g. of Sample 1 were treated in the same way. Sample 1 was at this time 18 months old and still red.

Each of two 5-cc. portions took 0.8 cc. of thiosulfate solution equivalent to 0.008 g. iodine.

Two 5-cc. portions treated with sodium carbonate solution gave 0.119 and 0.120 g. of aristol.

Analysis (Carius).—Subs., 0.1851: AgI, 0.1504. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found: 43.90.

Preparation of Aristol Having a High Percentage Soluble in Alcohol.—Five g. of iodothymol was dissolved in 100 cc. of water together with a little more than an equimolecular proportion of sodium hydroxide, and dil. acetic acid was added until a slight precipitate was formed. Then the solution was filtered into 1 liter of carbon dioxide-free water contained in a 2-liter bottle. This solution was shaken vigorously and a solution of 4.6 g. of iodine in 100 cc. of potassium iodide solution was added to it rapidly.

A sticky brown precipitate was formed, which adhered to the walls of the bottle after the liquid contents were poured away. This was washed with a thiosulfate solution and with water, after which nearly all of it could be dissolved, if 40 cc. of alcohol was added and the bottle was shaken.

The alcoholic solution in 10-cc. portions was treated with a 5% sodium carbonate solution, iodine and water; the aristol which formed was filtered, washed and weighed as follows.

Sample.	Na_2CO_3 . Cc.	I_2 added. G.	Aristol formed. G.
I.....	1.75	0.015	0.290
II.....	2.50	0.031	0.288
III.....	3.30	0.048	0.294
IV.....	5.00	0.025	0.290

Analysis (Carius).—Subs., (I), 0.1415; (II) 0.2088; (III) 0.1288: AgI; (I) 0.1229; (II) 0.1806; (III) 0.1102. Found: (I) 46.91; (II) 46.82; (III) 46.22.

Another sample made in the same way upon treatment with iodine and sodium carbonate gave an aristol of the following analysis.

Subs., 0.2154: AgI, 0.1847. Calc. for $(C_{10}H_{11}IO)_n$: I, 46.33. Found: 46.32.

A third sample of the highly soluble aristol was made in the following way.

Fifteen g. (0.1 mol) of thymol and 8 g. (0.2 mol) of sodium hydroxide in 1 liter of water were placed in a wide-mouthed vessel, and treated with an iodine-potassium iodide solution containing 50.8 g. of iodine (0.2 mol).

The sticky residue was washed as usual and scraped out, weighed, and dissolved in chloroform. Alcohol was added and the material insoluble in alcohol was weighed.

Analysis.—Subs., 16.193 g. Insoluble in alcohol, 0.840 g. = 5%.

On treatment with a sodium carbonate solution and iodine, the alcoholic solution of this preparation gave red aristol as did the preceding 2 samples.

The Insoluble Fraction.—All samples of this fraction were nearly white or faint pink in color and were dusty powders when dry. The fraction is insoluble in water acids, alkali, and alcohol, easily soluble in benzene, chloroform, carbon disulfide, etc., less soluble in ether, and in petroleum ether. Alcohol throws it out of solution in the above solvents as an amorphous precipitate nearly white which when dry resembles the original material. Evaporation of solutions of the substance leave it as a brittle varnish; no trace of crystalline structure was ever noticed.

No free iodine could be detected in dry samples of the substance even after storage for 2 years in the dark. A test for iodine with material dissolved in chloroform and shaken with diluted starch paste never revealed iodine in less than 10 minutes.

Attempts to Adsorb Iodine.—About 0.5 g. of the white insoluble fraction of aristol (Sample 6) was dissolved in 5 cc. of chloroform and 10 cc. of ethyl bromide, and crystals of iodine were added until about 0.1 g. was present. At this stage the solution was deep violet in color. After a few minutes, when nearly all the ethyl bromide had evaporated, alcohol was added to precipitate the aristol. This precipitate was filtered, washed with a few cc. of alcohol and then dried. It was as white as the original substance.

Re-oxidation.—Two g. of the same sample was dissolved in 10 cc. of ethyl bromide and 5 cc. of chloroform containing a few drops of glacial acetic acid. To this solution 3 g. of lead dioxide was added and the whole was shaken for about a minute, then filtered. The filtrate was deeply colored. Alcohol formed a red precipitate which resembled the original aristol in color, and when dry weighed 0.9 g. This red product remained in a window for several days without fading, while crude red aristol would not do this.

The ethyl bromide was used in the above experiments to give bulk to the solutions to assist filtration and because it could be removed easily without heat before precipitation.

The re-oxidation was repeated with a 5-g. sample of insoluble aristol from Sample 8. In this case 10 g. of lead dioxide, 30 cc. of ethyl bromide, 10 cc. of chloroform and 1 cc. of glacial acetic acid were used. The red product (Sample 8a) resembled the one obtained from Sample 6 and weighed 4 g. Free iodine was shown in the filtrate by the starch test.

Analysis, Sample 8a (Carius).—Subs., 0.2230: AgI, 0.1747. Found: I, 42.32.

Sample 9 was treated in the same way and gave results apparently identical. The red re-oxidation product from the insoluble fraction was analyzed.

Analysis (Carius).—Subs., 0.1325: AgI, 0.1052. Found: I, 42.89.

Molecular weights were determined cryoscopically as follows.

In Benzene K = 5000.				
	Wt. subs. G.	Wt. solvent. G.	Δ °C.	Mol. wt. found.
Insol. frac., Sample 6.....	0.9380	30	0.069	2270
Re-oxidized product from this sample..	0.8916	24.6	0.041	2430
Insol. frac., Sample 8, I.....	0.9134	27.1	0.087	1940
II.....	1.4238	27.1	0.135	1950
Re-oxidized Sample 8a.....	0.3610	24.6	0.020	2670
In Thymol, ^a K = 8000.				
Insoluble fraction, I.....	0.661	25	0.166	1290
II.....	1.506	25	0.355	1360

^a Kahlbaum's thymol used. M. p. 48.96°.

Determination of Evolved Iodine.—Four-tenths g. of each of the following samples was dissolved in 5 cc. of chloroform placed in a small glass-stoppered bottle, to which 10 cc. of water and about 0.5 cc. of starch paste were added: Sample 8 (1); insoluble fraction from Sample 8 (IV); re-oxidized insoluble fraction from Sample 8 (III); re-oxidized insoluble fraction from Sample 8 and 0.05 g. of iodothymol (II); polydibromophenylene oxide (blank). These samples were left near a large window but not in direct sunlight and the iodine was titrated with thiosulfate solution (1 cc. equivalent to 0.00106 g. of iodine) from time to time, as shown by Fig. 1. As the amounts of iodine are small (2.5% maximum) the values are stated in terms of thiosulfate solution. No iodine appeared in the blank.

A second series of trials was carried out in the dark. The samples were exposed to light only during titration, otherwise the treatment was the same. The amounts used were the same as in the first series and the results are shown in Curves V, VI, VII, and VIII. The maximum amount of iodine liberated under these conditions was 1.5%.

Effect of Potassium Iodide.—As periodical titration with thiosulfate introduces potassium iodide as a new factor, the effect of this was tried out.

Three samples were made up: (1) 0.4 g. of re-oxidized insoluble aristol; (2) 0.4 g. of re-oxidized insoluble aristol + 0.05 g. of potassium iodide; (3) 0.4 g. of re-oxidized insoluble aristol + 0.05 g. of iodothymol. Each sample was dissolved in 5 cc. of chloroform in a glass-stoppered bottle to which 10 cc. of water and 0.5 cc. of starch paste were added. They were shaken for a few seconds and kept in a very dim light for 17 hours. They were then titrated as in the 2 preceding experiments, and required 1.1, 1.25 and 3.95 cc. of thiosulfate solution, respectively.

Free iodine appeared almost immediately in (2), in (3) after about 2 minutes, and in (1) after about 10 minutes. At the end of the 17-hour period the aristol in (3) was noticeably bleached, while that in the other 2 samples was apparently unchanged.

Lautemann's Red.—This was prepared by the directions given by Kammerer and Benzinger¹ and after it was thoroughly dry it was washed with alcohol and dried again. The sample prepared in this way was a bright red powder. Four samples were prepared, each containing chloroform, water and starch paste previously used, and the following quantities of materials: (1) and (2) 0.4 g. of Lautemann's Red; (3) and (4) 0.4 g. Lautemann's Red and 0.05 g. of iodothymol. These were kept in dim light for 20 hours, after which they were titrated as in the preceding experiment, and were found to require 1.20, 0.85, 5.80 and 5.65 cc. of thiosulfate solution, respectively.

Free iodine appeared in (3) and (4) in 25 minutes, in (1) and (2) in 3 hours. The Lautemann's Red was considerably bleached in (3) and (4) after the 20-hour period.

¹ *Loc. cit.*

Iodothymol.—This was first prepared by the method of Willgerodt¹ but later by a simpler method of our own, as follows.

Teng. (0.066 mol.) of thymol and a small excess of sodium hydroxide were dissolved in 100 cc. of water, dil. acetic acid was added till a slight permanent precipitate was formed, then the solution was filtered into 1000 cc. of water in a 2-liter bottle. A solution of 18.5 g. of iodine and 14 g. of potassium iodide was added rapidly while the mixture was shaken. At this point a brown oil separated. About 150 cc. of petroleum ether and a sufficient quantity of sodium thiosulfate solution to decolorize the mixture were added, and the whole was shaken well. The upper layer which contained the iodothymol was then separated, filtered and placed in a vacuum desiccator attached to a filter pump and left until a good crop of crystals formed. The yield of these first crystals was 6.5 g. and the melting point, without further treatment, 69°, the same as that given by Willgerodt.

This is the only iodothymol described in the literature and is stated by Willgerodt to be the *para* compound.

Summary.

Fresh aristol has been shown to be a mixture of a red substance, insoluble in alcohol, easily reducible, of high molecular weight ($C_{10}H_{11}IO$)_n, analogous to Lautemann's Red, and a tarry material, soluble in alcohol, which may be considered at least in part as an intermediate substance.

The red color is inherent in the insoluble fraction and is not due to adsorbed iodine.

The liberation of iodine is caused by the oxidizing action of the red substance.

During this action the red part is reduced to a leuco compound, which can be reoxidized.

The ordinary aristol of commerce consists of the leuco compound together with the soluble part, and more or less of the red substance, according to the length of time it has been kept. On this account it is not capable of giving much iodine.

MINNEAPOLIS, MINNESOTA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS.

BY ROGER F. BRUNEL, J. L. CRENSHAW AND ELISE TOBIN.

Received July 28, 1920.

We have found it necessary to prepare in this laboratory a series of aliphatic alcohols, in which there should be, if possible, no impurity exceeding 0.1 to 0.2%, and have undertaken to purify these alcohols by a somewhat more careful fractional distillation than is usually carried out.

A little examination of the literature will show that there is no criterion for the purity of any except a few of these simple substances. Except in the cases of methyl and ethyl alcohols agreement in boiling points to

¹ *J. prakt. Chem.*, [2] 39, 290 (1889).