which melts at 68° and is sparingly soluble in ether, with one part of brominated mixed glyceride, containing one molecule of octobromo-arachidic acid. α-Octobromo-arachido-distearin should contain 41.3% of bromine. α-Palmito-distearin has been isolated from lard by Bömer.[11]

Fractionation of Methyl Esters.—Six hundred and twenty-five g. of the methyl esters from Lard 1 was distilled slowly from a 1-liter Claisen flask, four fractions being cut. The results of analysis of these fractions are given in Table II.

TABLE II

RESULTS OF FRACTIONATION OF METHYL ESTERS FROM LARD NO. 1

B. p., °C.	Wt., g.	Iodine number	Sapon. number	Polybromide number	Arachidonic acid, %
180–194	114	42.73	203.3	0.05	0.07
194–199	181	49.98	199.0	.07	.09
199–210	222	62.03	195.4	.13	.17
210–220	105	72.82	190.9	.51	.66

The identity of the methyl octobromo-arachidate isolated from the methyl esters from each specimen of lard is proved by the bromine analyses, which agree satisfactorily with the theoretical, 66.78%, and by the melting point, which in each case was 228–230°, the same as that found for this compound isolated from the glandular lipids.

Summary

Four specimens of typical commercial lard have been found to contain arachidonic acid in amounts varying from 0.31 to 0.40%. Two of the samples of lard yielded ether-insoluble bromine addition products which were shown to be a mixture, probably of α-palmito-distearin with a glyceride of octobromo-arachidic acid.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

ALLENE AND METHYLACETYLENE TETRABROMIDES[1]

BY CHARLES D. HURD,[2] R. N. MEINERT[3] AND L. U. SPENCE[3]

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Methylacetylene tetrabromide was studied by Oppenheim[4] in 1864, and by Gustavson and Demjanov[5] in 1888. The more recent and more

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[11] Bömer, *Z. Nahr. Genussm.*, **17**, 393 (1909); **25**, 354 (1913).

[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.

[4] Oppenheim, *Ann.*, **132**, 124 (1864).

[5] Gustavson and Demjanov, *J. prakt. Chem.*, [2] **38**, 201 (1888).

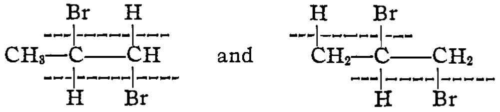
extensive data of both Risseghem[6] and of Demjanov and Dojarenka[7] seem to be more reliable, but in both cases the possibility of the presence of isomers seems not to have been eliminated. Risseghem prepared her material by the following steps: $CH_2{=}CBr{-}CH_3 \xrightarrow{Br_2} CH_2Br{-}CBr_2{-}CH_3 \xrightarrow{C_6H_5ONa} CHBr{=}CBr{-}CH_3 \xrightarrow{Br_2} CHBr_2CBr_2CH_3$. It will be noted that if sodium phenylate caused the detachment of hydrogen bromide in another direction, then $CH_2Br{-}CBr{=}CH_2$ would be formed, which, with bromine, would give allene tetrabromide, $CH_2Br{-}CBr_2{-}CH_2Br$. Demjanov and Dojarenka's tetrabromide is open to objection also. They decomposed trimethylcyclopropylammonium hydroxide at 300° to produce cyclopropene admixed with about 10% of allylene. Bromination yielded the tetrabromides $CHBr_2CH_2CHBr_2$ and $CH_3CBr_2CHBr_2$. Separation of these two compounds from each other, and possibly from traces of allene tetrabromide as well, by distillation methods makes it probable that the separation was not absolutely quantitative in spite of a rigorous procedure.

In the present work methylacetylene was prepared and passed into a solution of bromine in carbon tetrachloride. The methylacetylene tetrabromide thus produced was purified by fractional distillation. Three distinct methods were used in the synthesis of methylacetylene. In one method a satisfactory synthesis of propionaldehyde was effected, and this aldehyde was converted into propylidene chloride. The latter was then subjected to the action of potassium hydroxide in hot butyl alcohol

$$CH_3CH_2CHCl_2 + 2KOH \longrightarrow CH_3C{\equiv}CH + 2KCl + 2H_2O$$

Because of poor yields throughout, this method is not to be recommended. Reboul[8] carried out a similar reaction in a sealed tube at 150°, using ethyl alcohol.

Propylene bromide, in the second method, was converted into methylacetylene[9] by the action of potassium hydroxide in butyl alcohol. This methylacetylene was shown to be admixed with 4 to 7% of allene. Inspection of the formula of propylene bromide shows why this is possible



$$CH_3{-}\overset{Br}{\underset{H}{C}}{-}\overset{H}{\underset{Br}{C}}H \quad \text{and} \quad \overset{H}{CH_2}{-}\overset{Br}{\underset{H}{C}}{-}\underset{Br}{CH_2}$$

By liquefaction of the methylacetylene, and by two fractionations with a very efficient column the allene content was lowered from 5.5 to 1.2%.

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[6] Risseghem, *Bull. soc. chim. Belg.*, **28,** 376 (1919); *Chem. Zentr.*, **I,** 892 (1923).

[7] Demjanov and Dojarenka, *Ber.*, **56,** 2200 (1923).

[8] Reboul, *Compt. rend.*, **82,** 377 (1876).

[9] Tapley and Giesy, *J. Am. Pharm. Assocn.*, **15,** 115 (1926).

The difficulty of complete purification by this means is obvious, since allene boils at −32° and methylacetylene at −27.5°.

It would seem that a mixture of methylacetylene and allene could be separated readily through metallic derivatives of the former, and further study may show this to be the case. Our preliminary experiences, however, with the cuprous salt and with the chloromagnesium derivative were so unsatisfactory that further efforts in this direction were abandoned. The cuprous salt was precipitated by passing the gas (83% methylacetylene, 10% allene, 7% air) into an ammoniacal solution of cuprous chloride. Decomposition of this cuprous methylacetylide with hydrochloric acid was unsatisfactory since it gave only a small yield of methylacetylene. In another attempt to purify a similar mixture of methylacetylene and allene, it was allowed to react with ethylmagnesium chloride in dry ether. This gave a precipitate of methylethynylmagnesium chloride, $CH_3C{\equiv}C{-}Mg{-}Cl$. Hydrolysis of this substance yielded a gas which was about 85% methylacetylene and the remainder hydrogen, ethane, etc. Since the recovery was only about 30% of the theoretical, no efforts were made to perfect the method.

In the third method, pure methylacetylene (entirely free from allene) was prepared by the action of sodium acetylide and methyl iodide in liquid ammonia. This is the method of Lebeau and Picon.[10] It has been used by Maass and Wright[11] for the synthesis of pure methylacetylene. As in the second method, this methylacetylene was purified by liquefaction and distillation. Admixed acetylene was thereby removed.

Boiling point, index of refraction and density determinations on these samples of methylacetylene tetrabromide were made and studied. Similar determinations were made on pure allene tetrabromide, $CH_2Br{-}CBr_2{-}CH_2Br$. This was prepared by the addition of bromine to allene, and by the addition of bromine to dibromo-2,3-propene-1, $CH_2{=}CBr{-}CH_2Br$. Work on allene tetrabromide has been reported by Gustavson and Demjanov[5] and by Lespieau.[12]

Experimental Part

Preparation of Propionaldehyde.—Propionaldehyde was prepared by the gradual addition of dichromate oxidizing mixture to hot *n*-propyl alcohol. Thus, for 100 g. of the alcohol, the oxidizing agent was composed of 164 g. of potassium dichromate, 120 cc. of concd. sulfuric acid and one liter of water. The alcohol was kept boiling during the addition, which took about thirty minutes. Efficient mechanical stirring was essential to facilitate the rapid escape of the aldehyde. A reflux condenser kept at 60° allowed this escape, but at the same time prevented the unoxidized propyl alcohol from distilling away. Propionaldehyde was then condensed and purified in the usual way. The yield of aldehyde, b. p. 48–55°, was 44–47 g., or 45–49% of the theoretical.

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[10] Lebeau and Picon, *Compt. rend.*, **156,** 1077 (1913).

[11] Maass and Wright, This Journal, **43,** 1098 (1921).

[12] Lespieau, *Ann. chim. phys.*, [7] **11,** 252 (1897).

Propylidene chloride was prepared in about 30% yields from propionaldehyde and phosphorus pentachloride by the method of Reboul.[13] It boiled at 86–88°.

Preparation of Methylacetylene. First Method.—Since preliminary dehalogenation experiments using a suspension of sodamide in paraffin oil gave very unsatisfactory yields of methylacetylene, this reagent was discarded in favor of potassium hydroxide in butyl alcohol.

One mole (56 g.) of potassium hydroxide was dissolved in 150 cc. of *n*-butyl alcohol in a 500-cc. flask fitted with a 5-bulb reflux condenser. The upper end of the condenser was fitted with a stopper which held a dropping funnel and a gas delivery tube. This tube was connected to two bromine wash bottles which contained a total of 30 cc. of bromine covered by water. Propylidene chloride (20 g.) was added dropwise through the funnel during twenty minutes. Heating was continued for an hour. Then the gas was swept out by a current of air for fifteen minutes.

The bromine layer was washed with saturated sodium sulfite solution, then with water. Five cc. of carbon tetrachloride was used to extract the emulsified portion. After drying and removal of the solvent, 1.8 g. was collected at 6 mm. below 93°, chiefly at 55–60°. This was undoubtedly CH_3—CHBr—CHClBr. The allylene tetrabromide fraction, 93–99°, weighed 4.1 g., leaving 1.4 g. of residue. The allylene tetrabromide was fractionated and the constants taken on the portion boiling at 95–98° and 5.5–6 mm.

Preparation of Methylacetylene. Second Method.—Propylene[14] was converted into propylene bromide, which (202 g.), in turn, was dropped slowly into a flask containing a boiling solution of potassium hydroxide (180 g.) in *n*-butyl alcohol (400 cc.) as recommended by Tapley and Giesy. The methylacetylene and allene mixture thus produced escaped through an attached reflux condenser and was dried by passage through a calcium chloride tower. It was then liquefied by passing it into a small steel gas-bottle which was cooled to −55°; yield, 75%. For analysis, 100-cc. gaseous portions were treated with alkaline potassium iodomercurate solution for the acetylene content, and then with 82.5% sulfuric acid for the allene content.[15] In this way it was established that the gas contained about 5.5% (by volume) of allene and 94.5% of methylacetylene.

The liquefied hydrocarbon mixture was fractionally distilled from a spiral, vacuum-jacketed column such as has been described by Davis.[16] The distillate was collected in two portions of about equal volume, the first analyzing 9.2% of allene and the second 2.6%. Refractionation of the second fraction similarly yielded a higher-boiling portion which was found to contain 1.2% of allene. This material was converted into the tetrabromide, since it was not considered practical to fractionate it further.

For the bromination, the methylacetylene was allowed to escape slowly from its steel container and to pass into a solution of bromine in carbon tetrachloride. At the conclusion of the reaction, the excess of bromine was destroyed with an alkaline wash, and the tetrabromide dried and distilled *in vacuo*. The portion boiling from 95–110° (10 mm.) was collected. It weighed 23 g. This fraction, on redistillation, gave 13 g. of material boiling from 106–110° (10 mm.), which was used for the determination of its physical constants.

Preparation of Methylacetylene. Third Method.—Pure methylacetylene, free from allene, was made essentially by the method of Lebeau and Picon[10] from 36 g. of sodium metal (dissolved in liquid ammonia), an equivalent quantity of acetylene and

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[13] Reboul, *Ann. chim. phys.*, [5] **14,** 458 (1878).

[14] The propylene was generously furnished by E. R. Squibb and Sons. This courtesy is gratefully acknowledged.

[15] Hurd and Spence, THIS JOURNAL, **51,** 3356 (1929).

[16] Davis, *Ind. Eng. Chem., Anal. Edition,* **1,** 61 (1929); the column was constructed by Mr. George Reppert.

210 g. of methyl iodide. During the addition of methyl iodide, the temperature was maintained at −60 to −50°. When completed, the reaction flask was lifted from the cooling bath and the effluent gas was washed with water, with 10% sulfuric acid, then dried with calcium chloride, liquefied at −75° and finally fractionally distilled with the efficient column mentioned above to separate it from admixed acetylene. The last two-thirds of the distillate was used in preparing the tetrabromide, a step which was carried out in precisely the manner outlined in the second method. Fifty-eight g. of the tetrabromide, b. p. (10 mm.) 95–110°, was collected. On fractionation, 39 g. at 105–107° and 9 mm. was isolated.

Physical Constants of Methylacetylene Tetrabromide.—Our data will be compared and supplemented with the data of other workers. As stated above, our most reliable data were obtained on the material from the third method. That from the second contained small amounts of allene tetrabromide, whereas the quantity of material from the first was too small for rigorous purification.

PHYSICAL CONSTANTS OF METHYLACETYLENE TETRABROMIDE

The melting point, as noted by Risseghem, is −12.5°

Investigator		Boiling point		Density		Index of refraction	
		°C.	Mm.	d	Temp., °C.	n_D	Temp., °C.
Oppenheim		225–230	760	2.94	0/0	....	...
Oppenheim		110–130	10	....	....	....	...
Risseghem		111	11	2.6661	17.4/4	1.6148	17.4
Demjanov and Dojarenka		122–123	19	2.6835[a]	0/0	1.6142	10
Demjanov and Dojarenka		.....	...	2.6652[a]	10/0	1.6169	20.5
Petersen[17]		119–121	17	....	....	....	...
Present investigation	First method	95–98	5.5/6	2.698	20/4	1.6217	11
		.....	...	....	....	1.6165	21
	Second method	106–110	10	2.693	20/4	1.6204	10.0
		.....	...	2.680	25/4	1.6159	18.7
		.....	...	....	....	1.6153	20.0
		.....	...	....	....	1.6131	24.4
		.....	...	....	....	1.6119	27.0
	Third method	105–107	9	2.699	15/4	1.6207	12.3
		.....	...	2.687	20/4	1.6186	16.6
		.....	...	2.676	25/4	1.6166	20.0
		.....	...	....	....	1.6140	25.4

[a] Also from different material, these values are given: 2.7225, 0°/4°; 2.7011, 10°/4°; 2.6800, 21°/4°.

Discussion of Data

The boiling point data have been plotted as a Dühring line[18] in Fig. 1. Thus the boiling point of methylacetylene tetrabromide and the boiling point of water at the same pressure are plotted on the same coördinate. Extrapolation of the curve to 100° for water (atm. press.) gives a value of 229° for the boiling point of methylacetylene tetrabromide. This is well in keeping with Oppenheim's observation. His value at 10 mm.,

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[17] Petersen, *Z. Elektrochem.*, **18**, 712 (1912).

[18] Leslie and Carr, *Ind. Eng. Chem.*, **17**, 810 (1925).

however, is distinctly off the curve. The remaining values fit the straight line curve fairly well

The density values, referred to water at 4°, are plotted on Fig. 2, and the index of refraction data on Fig. 3. In Fig. 2 the results of Demjanov and Dojarenka are included. Our most reliable density values, those from the third method, were taken for this. This reliability was caused not only by the greater purity of the material but also by the fact that a 12-cc. specific gravity bottle was used as opposed to a 2.3-cc. Ostwald pycnometer which was employed for the other two methods. The other density values recorded in the literature vary considerably from these, all except Oppenheim's being smaller.

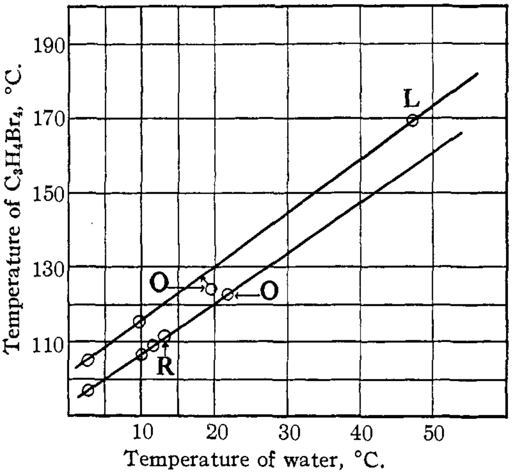

Fig. 1.—Dühring lines: O,O, data of Demjanov and Dojarenka; L, Lespieau's observation; R, Risseghem's datum; unmarked points from this investigation. Upper, allene tetrabromide–water; lower, methylacetylene tetrabromide–water.

The index of refraction values of Methods 1 and 3 are plotted in Fig. 3. The values for the material of Method 2 (from propylene bromide), if plotted, would show a parallel curve, the values throughout being somewhat smaller. Demjanov and Dojarenka's value at 21° (1.617) is of the correct order of magnitude but the value at 10° (1.6142) is evidently in error. This becomes obvious on plotting these two points. Risseghem's observation is somewhat low.

Allene Tetrabromide

Preparation from Allene. **First Method.**—A sample of dibromo-2,3-propene-1, prepared according to the method of "Organic Syntheses,"[19] and of b. p. 73–76° at 75 mm., was dehalogenated into allene. To do this, 180 g. of it was added drop by drop to a boiling mixture of 300 cc. of alcohol and 150 g. of zinc dust. The effluent gas was washed, dried and then converted into allene tetrabromide by passing it into an ice-cold solution of bromine in carbon tetrachloride. This was worked up in the usual way by washing, drying and distilling, the fraction boiling at 95–110° (10 mm.) being collected. This fraction was redistilled for the portion which came over at 103–106° and 7 mm.; weight, 70 g. This sample was used for the physical constants.

Preparation from Dibromo-2,3-propene-1. Second Method.—The dibromopropene, dissolved in twice its volume of carbon tetrachloride, was placed in a flask fitted

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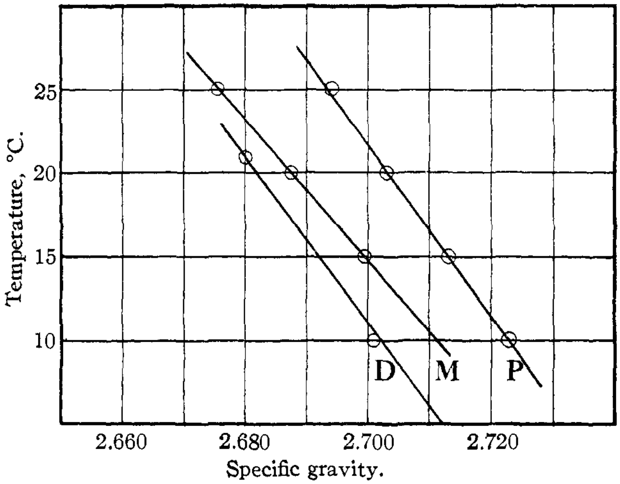
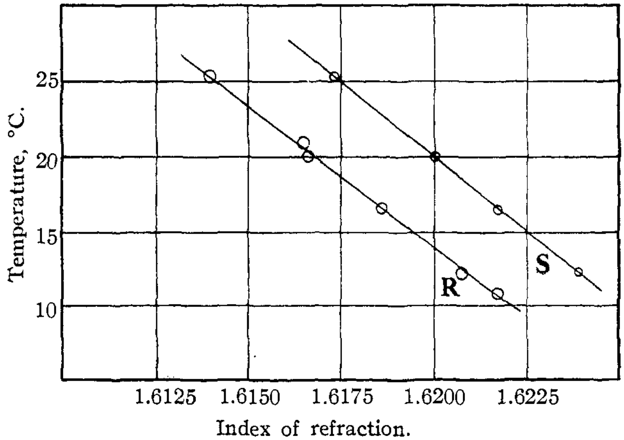
[19] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. V, p. 49.

with a dropping funnel and a mechanical stirrer. It was cooled by an ice-bath. Bromine was added slowly from the dropping funnel until an equivalent amount had been added. After drying and distillation, the fraction 93-104° (3 mm.) was collected; weight 120 g. Redistillation of this, discarding the first and last portions, gave 84 g. which boiled at 115.5° and 9 mm. This material was solidified by cooling it in an ice-bath. It was allowed to melt slowly, the first portions to melt being discarded. This process was thrice repeated and a sample of allene tetrabromide weighing 60 g. was obtained. This sample was used for determination of the constants.



Methylacetylene tetrabromide: D, results of Demjanov and Dojarenka; M, this investigation. Allene tetrabromide: P, this investigation.

Fig. 2.



R, Allene tetrabromide; S, methylacetylene tetrabromide.

Fig. 3.

In this investigation the melting points were determined by the cooling curve method, using a calibrated and standardized thermometer. It is pertinent to note that the greater purity of the material in the second method was occasioned by the fact that it was prepared in greater quantity and was crystallized several times. The value of 5.5–6° with one crystallization of a portion from a 60-g. sample was found to change to +1.9° when the size of the original preparation was but 17 g. Several fractionations are evidently essential for preparing allene tetrabromide of high purity.

PHYSICAL CONSTANTS OF ALLENE TETRABROMIDE

Investigator		Boiling point		M. p.,	Density		Index of refraction	
		°C.	Mm.	°C.	d	Temp., °C.	n_D	Temp., °C.
Reboul[20]		250–252	Atm.	...	2.64	...	.....	...
Gustavson and Demjanov		215–230 (dec.)	Atm.	−18–0	2.729	0/0	.....	...
Gustavson and Demjanov		.....	...	...	2.653	18/0	.....	...
Lespieau		230–250 (sl. dec.)	Atm.	10–11	2.739	0/4	.....	...
Lespieau		169–170	80	...	...	...	.....	...
Demjanov and Dojarenka		123–125	17	...	...	...	.....	...
This investigation	First method	104–106	5.5–6	One	2.714[a]	10/4	1.6213	12.6
		.....	...	cryst.	2.704	15/4	1.6194	16.5
		.....	...	5.5–6	2.694	20/4	1.6153	25.0
		.....	...	...	2.684	25/4	.....	...
	Second method	115.5	9	Reptd.	2.723	10/4	1.6238	12.4
		.....	...	cryst.	2.713	15/4	1.6217	16.4
		.....	...	10.7	2.703	20/4	1.6200	20.0
		.....	...	...	2.694	25/4	1.6173	25.2

[a] Taken in a 12-cc. specific gravity bottle.

Discussion of Data

As with methylacetylene tetrabromide, the Dühring line for allene tetrabromide is plotted in Fig. 1. The observation of Demjanov and Dojarenka fails to conform to the curve. If extrapolated, the boiling point at 760 mm. would be 245°, which is considerably higher than Gustavson and Demjanov's observation, but agrees with Lespieau's and with Reboul's.

The purity of our material used for the physical constants by the second method was evidenced by the sharpness and the constancy of the melting point. The results are considered accurate to 1 part in 3000 for the density, and to one part in the fourth decimal place for the refractive index. Lespieau's value for the density at 0° is only slightly lower than the extrapolated value from our curve. Because of the lesser purity of the material prepared by the first method, it has not been included on the chart. The slope of its curve would be identical but the values are lower throughout. So also, in Fig. 3, only the data of the second method have

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[20] Reboul, *Ann. chim. phys.*, [3] **60**, 51 (1860).

been included for the index of refraction curve. The values of the material of lesser purity would give a curve of similar slope and would come between the two curves of allene and methylacetylene tetrabromides. Curiously, however, it is nearer the latter than the former. This shows clearly that index of refraction data, and density data as well, are apt to be quite misleading in these two cases as a means of identification unless *pure* substances are at hand. In other words, a mixture of allene and methylacetylene could not be analyzed even with fair accuracy by conversion to the tetrabromide mixture, if boiling point, density or n_D values are the basis of evaluation. Fortunately, however, their analysis[15] may be effected readily in another manner.

Summary

Methylacetylene has been prepared in a high state of purity from methyl iodide and sodium acetylide in liquid ammonia. Preparing it by dehalogenation of propylidene chloride is not to be recommended because of poor yields, whereas similar preparation from propylene bromide invariably gives rise to allene as well. Such a mixture cannot be readily separated by fractional distillation, although the percentage of allene was lowered from 5.5 to 1.2 by this means. Methylacetylene tetrabromide was prepared from all three sources, and the physical constants studied.

Allene tetrabromide was made by the addition of bromine either to allene or to dibromo-2,3-propene-1. For purposes of high purity, it must be purified by several crystallizations as well as by fractional vacuum distillation. Such material melts at 10.7°. Boiling point, specific gravity and index of refraction data were obtained.

EVANSTON, ILLINOIS

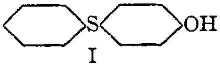
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF SOME IODATED DIPHENYL-SULFIDE PHENOLS[1]

BY SHAILER L. BASS AND TREAT B. JOHNSON

RECEIVED OCTOBER 16, 1929 PUBLISHED MARCH 6, 1930

In quest of phenolic compounds possessing properties requisite for their practical use in internal antisepsis, Hilbert and Johnson[2] have recently extended the research program of this Laboratory on germicides into the field of the diaryl-sulfide phenols. *p*-Hydroxydiphenyl-sulfide, I, with its high germicidal value and low toxicity (phenol coefficient 115) has proved the most promising of these derivatives thus far examined.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[1] Constructed from a dissertation presented by Shailer L. Bass in June, 1929, to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hilbert and Johnson, THIS JOURNAL, **51**, 1526 (1929).