

4. The inhibitive effect has been shown in all cases to be not instantaneous, but to develop somewhat slowly with the oxidation of the solution. Ernst¹ noticed the same phenomenon in studying the influence of foreign substances on the catalytic acceleration of the oxidation of hydrogen by colloidal platinum solution. Bigelow² noticed the same depression of the oxidation rate toward the end of the reaction, but ascribed it to other causes.

5. As a very common accompaniment of these phenomena, initial accelerations have been found. It is possible that the method of procedure is alone the cause of these not being observed in all cases.

6. The limit of the dilution at which substances still show inhibitive effects differs for different substances, being in some cases still noticeable at a dilution of $\frac{1}{2,600,000}$ molar. Investigations are now being carried on whose purpose is to subject these phenomena of development periods and of initial accelerations to a careful study in the hope of finding some simple explanation of them. Until this can be done and the phenomena in question either eliminated or controlled, it is hopeless to attempt any exact quantitative investigation of the subject as a whole.

STANFORD UNIV., CAL.,
January 9, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF METHYL AND ETHYL ALCOHOLS UPON THE BROMIDES OF CERTAIN PROPENYL COMPOUNDS.

BY F. J. POND, E. S. ERB, AND A. G. FORD.

Received December 21, 1901.

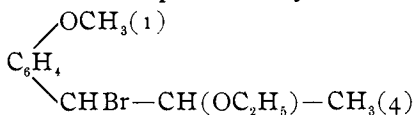
IT has been known for a number of years that certain bromine derivatives of anethol, isosafrol, isoapiol, and other analogous compounds, containing a propenyl group, C_3H_5 , joined to a benzene nucleus, dissolve in ethyl alcohol with apparent decomposition, or on boiling with alcohol, they are converted into compounds which contain a less percentage of bromine. Thus Hell and Günthert³ found that anethol dibromide, $C_{10}H_{12}O.Br_2$, is changed into a dark-colored oil on boiling with absolute alcohol; this oil was not prepared in a chemically pure condition, but on

¹ Ernst: *Ztschr. phys. Chem.*, **37**, 478.

² *Loc. cit.*

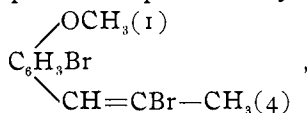
³ Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

analysis it gave figures indicating the composition $C_{12}H_{17}O_2Br$, and its constitution was represented by the formula



Nothing further appears to have been learned regarding this compound, nor has the action of methyl alcohol on anethol dibromide hitherto been studied.

Also, according to Hell and Günthert,¹ when monobromanethol dibromide, $C_{10}H_{11}OBr.Br_2$, is boiled for some time with absolute ethyl alcohol, ethyl bromide is formed and an oil results which soon solidifies; it separates from ether in crystals melting at 62° . This compound is represented by the formula



and its formation is said to be due to the elimination of 1 molecule of hydrogen bromide from monobromanethol dibromide by means of ethyl alcohol; that is, when anethol dibromide is heated with ethyl alcohol, hydrobromic acid is eliminated and the elements of ethyl alcohol are added, while with the tribromide, hydrogen bromide is given off and an unsaturated bromide, $C_{10}H_{10}OBr_2$, is obtained. The action of methyl alcohol upon the tribromide does not appear to have been investigated.

No definite chemical compounds have been obtained by the action of methyl or ethyl alcohol upon the bromides of other propenyl compounds, although several cases are noted in the literature in which the action of alcohol seems to give rise to non-characteristic oils. For example, Ciamician and Silber² found that monobromisafrol dibromide is changed by the action of boiling ethyl alcohol; they refer to this reaction in the following words: "Mit Wasser oder namentlich mit Alkohol gekocht scheint es Bromwasserstoff abzuspalten." Hell and Hoering³ state that a non-characteristic oil is formed when monobromisafrol dibromide is boiled with ethyl alcohol: "Mit Alkohol erhitzt gaben die Krystalle eine Schmiere, woraus keine Krystalle mehr zu erhalten waren."

¹ Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

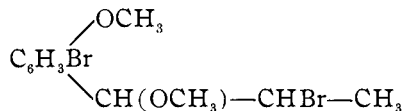
² Ciamician and Silber: *Ber. d. chem. Ges.*, **23**, 1164.

³ Hoering: *Inaug. Diss.* (Rostock), p. 59 (1897).

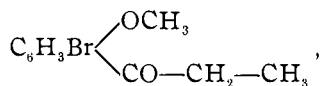
The fact that anisylidene acetophenone dibromide is converted by boiling ethyl alcohol into a definite and crystalline ethyl alcohol addition-product of monobromanisylidene acetophenone,¹ and by methyl alcohol into a corresponding, higher melting methyl alcohol addition-product, led to the belief that similar changes take place when the bromides of certain propenyl compounds are boiled with alcohols. This belief has been justified by the preparation of several characteristic alcohol addition-products.

In our experimental work we have succeeded in preparing the methyl and ethyl alcohol addition-products of monobromanethol by boiling anethol dibromide with the corresponding alcohols. Both compounds are liquids, and are converted into anisyl ethyl ketone,² $C_{10}H_{12}O_2$, on treatment with *one* molecular proportion of sodium methylate or alcoholic potash; this ketone was first prepared by Wallach and Pond by treating anethol dibromide with *two* molecules of sodium methylate.

It has been found that when monobromanethol dibromide is boiled with, or crystallized from, methyl alcohol, it is converted into the methyl alcohol addition-product,



This substance forms large, magnificent crystals, which melt at $72^\circ\text{—}74^\circ$. The corresponding ethyl alcohol addition-product is an oil. When these compounds are treated with *one* molecule of sodium alcoholate or alcoholic potash and the resulting product is hydrolyzed with hydrochloric acid, monobromanisyl ethyl ketone,



is obtained. This ketone forms long needles, melts at 100° , and was first prepared by Hell and Hollenberg³ by the action of *two* molecules of sodium alcoholate upon monobromanethol dibromide.

Two new compounds are obtained by the action of methyl and

¹ Pond and Shoffsall: This Journal, **22**, 668 and 670.

² Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2715; see also Hell and Hollenberg: *Ibid.*, **29**, 687.

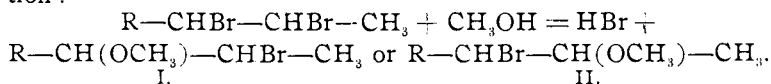
³ Hell and Hollenberg: *Ber. d. chem. Ges.*, **29**, 686; See Hell and Gärtner: *J. prakt. Chem.*, **51**, 428.

ethyl alcohol on monobromisafrol dibromide, $C_{10}H_9O_2Br.Br_2$; the methyl alcohol product separates in well-formed crystals, and melts at $75^\circ-76^\circ$, and the ethyl alcohol compound forms large crystals, melting at $59^\circ-60^\circ$. The corresponding monobromoketone, $C_{10}H_9O_3Br$, has not been obtained.

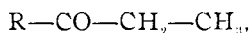
Ethylisoeugenol dibromide, $C_{12}H_{16}O_2.Br_2$, is also changed by boiling with methyl and ethyl alcohol; the former gives rise to a crystalline compound melting at 68° , while the latter yields an oil.

Monobromisoapiol dibromide, $C_{12}H_{13}O_4Br.Br_2$, is converted into a crystalline product on boiling with methyl alcohol; it melts at 92° . The ethyl alcohol addition-product is an oil.

The reaction by which these various alcohol addition-products are formed, is probably to be represented by the following equation:



For the present we prefer to represent the alcohol addition-products by the general formula I. This formula more readily explains the formation of ketones,

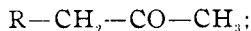


by the action of *one* molecular proportion of sodium alcoholate or alcoholic potash:

1. $R-CH(OCH_3)-CHBr-CH_3 + KOH = \\ R-C(OCH_3)=CH-CH_3 + KBr + H_2O.$
2. $R-C(OCH_3)=CH-CH_3 + H_2O = \\ R-C(OH)=CH-CH_3 + CH_3OH.$
3. $R-C(OH)=CH-CH_3 = R-CO-CH_2-CH_3.$

It has previously¹ been proved that these ketones contain the carbonyl group in the α -position to the benzene ring.

If formula II be accepted for these alcohol additive compounds, it would be expected that alcoholic potash would eliminate hydrogen bromide with the ultimate formation of isomeric ketones,



this, however, is not apparently the case.

Owing to the limited time for our work, the investigation of the compounds which are mentioned in the following pages, is

¹ Wallach and Pond: *Ber. d. chem. Ges.* **28**, 2718; see also Hell and Hollenberg: *Ibid.*, **29**, 688.

very far from complete, but we deem it desirable to publish the results obtained at this time with the view of reserving this line of research. During the current year we propose to continue these investigations and to extend them to some other propenyl compounds.

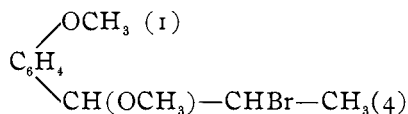
EXPERIMENTAL.

Anethol Dibromide, $C_6H_4(OCH_3).C_3H_5Br_2$, was prepared according to Ladenburg's method.¹

Forty grams of anethol were dissolved in 200 cc. of ether, and the solution was well cooled with a freezing-mixture; one molecular proportion (43.2 grams) of bromine was added very slowly and with constant shaking. The slight excess of bromine was then removed by shaking the ethereal solution with sulphurous acid, and the ether allowed to evaporate slowly; the resulting crystalline mass was recrystallized from petroleum ether, yielding white needles, which melted at 62° - 64° .

The Action of Methyl Alcohol upon Anethol Dibromide.

Methyl Alcohol Addition-Product of Monobromanethol,



A solution of 30 grams of anethol dibromide in 90 cc. of methyl alcohol was boiled for one hour in a reflux apparatus; the solution at first assumed a light pink color, but darkened as the boiling continued. On completion of the reaction the liquid reacted acid, due to the elimination of hydrobromic acid. The contents of the flask were then poured into a large quantity of cold water, and the resulting oil was separated, washed with water and extracted with ether; the ethereal solution was repeatedly shaken with water, dried over anhydrous sodium sulphate, and the ether evaporated. A mobile oil resulted, which had a light yellow color, and was decomposed on distillation. It dissolves readily in alcohol, ether, chloroform and acetic acid, but could not be obtained in a crystalline form. The bromine determination gave:

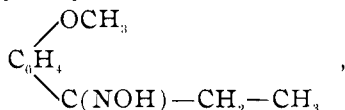
¹ Ladenburg: *Ann. Chem.* (Liebig), Suppl., 8, 94; *Ber. d. chem. Ges.*, 2, 372.

- I. 0.2029 gram gave 0.1456 gram silver bromide.
 II. 0.2027 gram gave 0.1447 gram silver bromide.

	Calculated for $C_{11}H_{15}O_2$ br.	I.	Found. II.
Bromine.....	30.88	30.54	30.37

When this oil is treated with one molecular proportion of sodium alcoholate and the resulting product is boiled with hydrochloric acid, anisyl ethyl ketone, $C_{10}H_{12}O_2$, is obtained.

Forty-four grams of the methyl alcohol addition-product of bromanethol were added to a solution of one molecule of sodium methylate (4 grams of sodium in 100 cc. of methyl alcohol), and boiled for four hours. At the end of this time, the liquid reacted slightly alkaline, and contained considerable sodium bromide. Sufficient water was added to dissolve the sodium bromide and to precipitate the resulting oil. The latter was separated and warmed for about fifteen minutes with dilute hydrochloric acid; it was then distilled with steam. An almost colorless oil was obtained, which, on treatment with hydroxylamine, was converted into a solid oxime. The oxime crystallized from alcohol-ether in large prisms, melting at 73° - 74° ; it is identical in all respects with anisyl ethyl ketoxime,



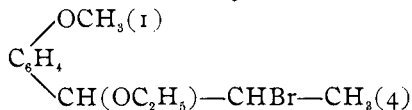
which Wallach and Pond¹ obtained from the oil resulting on the treatment of anethol dibromide with *two* molecules of sodium methylate. On treating this oxime with dilute sulphuric acid, anisyl ethyl ketone (iii. p. 26° - 27°) was formed.

The same oxime (iii. p. 74°) was also obtained by a similar treatment of the methyl alcohol addition-product of monobromanethol with one molecule of sodium ethylate and alcoholic potassium hydroxide.

The yield of anisyl ethyl ketone by this method of preparation is better than by the direct action of two molecules of sodium methylate on anethol dibromide.

The Action of Ethyl Alcohol upon Anethol Dibromide.

Ethyl Alcohol Addition-Product of Monobromanethol,



¹ Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2715.

It was mentioned in the introduction that Hell and Günthert¹ studied this reaction. They found that boiling ethyl alcohol converts anethol dibromide into a dark brown, resinous mass which possesses a strong anethol-like odor; it dissolves in ether, alcohol, benzene, chloroform, and acetic acid. Analysis of this oil gave 28.57 per cent. of bromine, and from this it was regarded that the oil was the ethyl alcohol addition-product of monobromanethol, $C_{12}H_{17}O_2Br$.

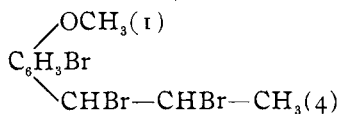
The results of our investigation fully confirm this view. Thirty grams of anethol dibromide were boiled with 90 cc. of ethyl alcohol for one hour, and the reaction-product was poured into cold water. The resulting dark-colored oil was washed repeatedly with water, extracted with ether, again washed, and dried over anhydrous sodium sulphate. On evaporation of the ether, a dark, rather mobile oil resulted; it could not be purified by distillation, but on analysis gave the following results:

- I. 0.2020 gram gave 0.1398 gram silver bromide.
 II. 0.2028 gram gave 0.1399 gram silver bromide.

	Calculated for $C_{12}H_{17}O_2Br$.	I.	Found.	II.
Bromine.....	29.30	29.45		29.35

This compound was also readily converted into anisyl ethyl ketone, $C_{10}H_{12}O_2$, by the action of sodium alcoholate or alcoholic potash; its oxime melted at 72° – 74° .

Monobromanethol Dibromide,



This compound was first prepared by Cahours² by the addition of bromine to anethol; he regarded it as tribromanethol, $C_{10}H_9Br_3O$. In 1895, Hell and Gärttner³ obtained it by adding slowly to a cold, ethereal solution of anethol, the calculated amount of bromine (two molecules). We have found the following method to be the most satisfactory for the preparation of large quantities of the substance.

To a solution of 100 grams of anethol in 75 cc. of ether, 216.2 grams (2 molecules) of bromine are added quite rapidly, the flask

¹ Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

² Cahours: *Ann. Chem.* (Liebig), **41**, 60.

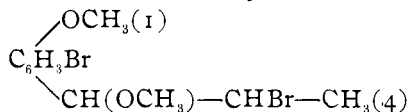
³ Hell and Gärttner: *J. prakt. Chem.*, **51**, 425; **52**, 193; see also Orudorff and Morton: *Am. Chem. J.*, **23**, 185.

in which the bromination is carried on being placed in ordinary cold water; an especially low temperature and a gradual addition of the bromine are not only unnecessary, but retard the process. When the addition of bromine is complete, the black, oily product is poured into an open dish and allowed to stand, or may be stirred for a few minutes; the product then solidifies with violent evolution of hydrogen bromide. It is now placed on a suction filter, washed very sparingly with ether, and then spread out on a large filter-paper. After twelve hours, it is again washed on a suction filter with a little ether until it assumes a permanent white color. This product melts at 108° – 112° , and is quite pure; it was used in the following described experiments.

Orndorff and Morton¹ purified this compound by dissolving it in a small amount of chloroform and then precipitating with ethyl alcohol. Our experience has been that, although this method gives a pure, crystalline product, a large quantity of the substance suffers decomposition by such treatment, doubtless due to the action of the alcohol.

The Action of Methyl Alcohol upon Monobromanethol Dibromide.

Methyl Alcohol Addition-Product of Dibromanethol,



—Thirty grams of monobromanethol dibromide were dissolved in 100 cc. of methyl alcohol in a flask fitted with a reflux condenser and boiled for two hours on a steam-bath. The resulting, slightly yellow colored solution had an acid reaction, and gave off fumes of hydrobromic acid; it was poured into a beaker and allowed to stand. In a few hours crystals separated, which were removed and recrystallized from acetone; beautiful, large, colorless prisms resulted, which melted at 71° – 74° .

In another preparation, 135 grams of monobromanethol dibromide were boiled with 380 cc. of methyl alcohol for one hour, the slightly colored solution was filtered and allowed to crystallize. The resultant crystals were repeatedly crystallized from methyl alcohol and finally obtained in large, colorless prisms, melting at 73° – 74° .

It was further learned that the same compound may be readily

¹ Orndorff and Morton: *Am. Chem. J.*, **23**, 185.

obtained by dissolving monobromauethol dibromide in methyl alcohol in a beaker, heating the solution to the boiling point, and allowing to crystallize; on recrystallization from methyl alcohol, the compound is obtained pure and melts at 73° – 74° .

Analyses gave the following results:¹

- I. 0.2052 gram gave 0.2952 gram carbon dioxide and 0.0816 gram water.
- II. 0.3000 gram gave 0.4308 gram carbon dioxide and 0.1114 gram water.
- III. 0.2128 gram gave 0.2378 gram silver bromide.
- IV. 0.2128 gram gave 0.2380 gram silver bromide.

	Calculated for $C_{11}H_{14}O_2Br_2$	Found.			
		I.	II.	III.	IV.
Carbon.....	39.05	39.23	39.16
Hydrogen.....	4.14	4.42	4.12
Bromine.....	47.34	47.55	47.59

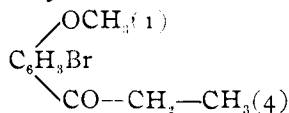
This compound is readily soluble in the usual organic solvents, and may be recrystallized, without change, from boiling ethyl alcohol. On distillation under a pressure of 14 to 15 mm., it boils without decomposition at 160° – 164° yielding a colorless and odorless oil, which solidifies after standing a few hours, and again melts at 72° – 74° ; if the pressure be slightly increased, the compound suffers some decomposition with evolution of hydrogen bromide, and the distillate does not become solid.

When the compound was heated carefully at the atmospheric pressure, it melted to a colorless liquid; at 130° , the liquid assumed a yellowish color, which rapidly became darker as the temperature increased. From 170° – 195° , a colorless liquid distilled over and was proved to be methyl alcohol. At 195° , the heat was removed, and on cooling, the contents of the flask appeared as a black thick oil, which did not solidify after standing for several months.

It reacts as a saturated compound, since it does not decolorize permanganate and its ethereal solution does not absorb bromine.

An attempt was made to remove the elements of hydrogen bromide by boiling a solution of 20 grams of the compound in 100 cc. of methyl alcohol with 4 grams of anhydrous sodium acetate for twelve hours, but after filtering the reaction-product, the unchanged substance was obtained and melted at 72° – 73° . Hydrobromic acid may be readily removed, however, by the action of sodium alcoholate or alcoholic potash.

¹ These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

Monobromanisyl Ethyl Ketone.

—Ten grams of the methyl alcohol addition-product of dibrom-anethol, $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Br}_2$, were added to a solution of one molecule of sodium methylate (0.8 gram of sodium in 25 cc. of methyl alcohol), and boiled for two hours. At the end of this time sodium bromide had separated and the liquid reacted slightly alkaline; water was added and the liquid was made slightly acid with hydrochloric acid, when a colorless oil, heavier than water, separated. The aqueous, alcoholic liquid was decanted, and the oil treated with concentrated hydrochloric acid; after stirring for a few seconds, the oil was completely converted into a white solid. The latter was washed free from acid and crystallized from alcohol; it separated in beautiful, long needles, which melted at $100^\circ-101^\circ$.

Analyses gave the following results:

- I. 0.3000 gram gave 0.5403 gram carbon dioxide and 0.1364 gram water.
- II. 0.2008 gram gave 0.1549 gram silver bromide.
- III. 0.2000 gram gave 0.1549 gram silver bromide.

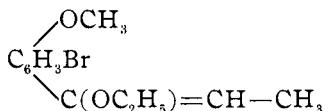
	Calculated for $\text{C}_{10}\text{H}_{11}\text{BrO}_2$	I.	Found. II.	III.
Carbon	49.38	49.11
Hydrogen	4.53	5.05
Bromine	32.92	32.82	32.95

The formation of this ketone is to be explained by the fact that sodium methylate removes one molecule of hydrogen bromide yielding an unsaturated ether; the latter is hydrolyzed by hydrochloric acid, and the resulting unsaturated alcohol suffers an intramolecular change into the more stable, saturated ketone.

The same ketone (m. p., 100°) is also formed by the action of one molecule of potassium hydroxide, dissolved in alcohol, on the methyl alcohol addition-product, and subsequent treatment with hydrochloric acid.

This ketone was prepared by Hell and Hollenberg¹ by the action of two molecules of sodium ethylate upon one molecular proportion of monobromanethol dibromide; they also isolated the unsaturated ether,

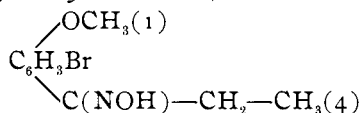
¹ Hell and Hollenberg: *Ber. d. chem. Ges.*, **29**, 635; see also Hell and Gärtner: *J. prakt. Chem.*, **51**, 424.



which is an oil boiling at $180^\circ-182^\circ$ (16 mm.), but they did not obtain the first reaction-product, *viz.*, the alcohol addition-product.

To further characterize this ketone, we have converted it into the oxime.

Monobromanisyl Ethyl Ketoxime,



—Ten grams of the ketone were dissolved in alcohol and treated in the usual manner with hydroxylamine; on precipitating the reaction-product with water, an oil resulted which soon solidified. It was crystallized from alcohol and separated in splendid crystals, melting at 108° .

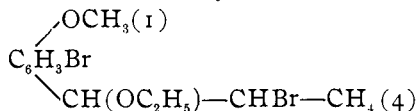
On analysis, it gave the following results for bromine :

- I. 0.2004 gram gave 0.1464 gram silver bromide.
 II. 0.2003 gram gave 0.1457 gram silver bromide.

	Calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{BrN}$.	I.	Found.	II.
Bromine	31.01	31.08		30.95

The Action of Ethyl Alcohol upon Monobromanethol Dibromide.

Ethyl Alcohol Addition-Product of Dibromanethol,



A solution of 20 grams of monobromanethol dibromide in 50 cc. of absolute ethyl alcohol was boiled for three minutes on a water-bath; on evaporation of the alcohol, an oil resulted, which was washed with water, extracted with ether, and dried over anhydrous sodium sulphate. After evaporation of the ether over fused calcium chloride in vacuum, a mobile, amber-colored oil was obtained, which gave the following figures on analysis :

- I. 0.2021 gram gave 0.2161 gram silver bromide.
 II. 0.2012 gram gave 0.2153 gram silver bromide.

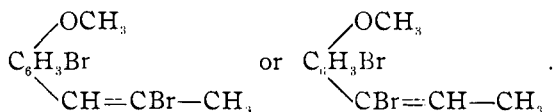
	Calculated for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Br}_2$.	I.	Found.	II.
Bromine.....	45.45	45.50		45.53

This compound could not be obtained in a solid condition. The same oil was found in a number of other experiments in which different proportions of alcohol were used, and the boiling was carried on for various lengths of time, from four minutes to three hours.

On heating this oil in a flask to 196° under atmospheric pressure, ethyl alcohol is given off and is recognized by the iodoform reaction. The oil does not reduce permanganate in the cold, and its ethereal solution absorbs no bromine.

When this oil is treated with one molecular proportion of sodium alcoholate or alcoholic potash, and then with concentrated hydrochloric acid, it is readily and quantitatively converted into monobromanisl ethyl ketone, melting at 99°–100°.

According to Hell and Günthert,¹ when monobromanethol dibromide is boiled with absolute ethyl alcohol for twenty-four hours and the alcohol is then distilled off, ethyl bromide is formed and an oil results which gradually solidifies after pouring into cold water; it crystallizes from ether in long, prismatic crystals which melt at 62°. On analysis this compound gave results indicating the formula $C_{10}H_{16}Br_2O$, and Hell regards it as an unsaturated bromide,



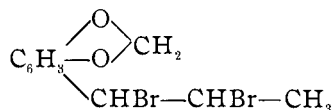
On repeating this experiment, following as closely as possible the directions indicated by Hell, we were unable to obtain the substance in a solid form until the oil had remained for several hours at a temperature below 0°. By this method, a small proportion of the oil gradually became solid and, after recrystallization from ether, melted at 64°–66°; most of the reaction-product remained as an oil which consisted largely of the ethyl alcohol addition-product above mentioned.

It appears, therefore, that the reaction may take place in two ways, depending on the time that the bromide is heated with the alcohol, and on the subsequent treatment, as the removal of alcohol by gradual evaporation at the ordinary temperature or by distillation; by the former treatment, a product consisting almost entirely of the liquid addition-product results, while the latter

¹ Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

method yields some of the solid, unsaturated bromide, together with considerable liquid addition-product.

Isosafrol Dibromide,



—The isosafrol necessary for our work was prepared from safrol according to the method of Eykman.¹ It was readily converted into the dibromide² by the gradual addition of one molecule of bromine to its cold, ethereal solution. The dibromide remained as a colorless oil after evaporation of the ether.

The Action of Methyl and Ethyl Alcohols upon Isosafrol Dibromide.

These reactions were carried on in a manner similar to that mentioned under anethol dibromide by boiling about 50 grams of the dibromide with 150 cc. of the alcohol for one hour. In this case, oils were formed which could not be obtained in a pure condition. Bromine analyses were made of the crude oils, which were purified as carefully as possible. The results are as follows :

1. Oil resulting by boiling isosafrol dibromide with methyl alcohol.

- I. 0.2024 gram gave 0.1452 gram silver bromide.
 II. 0.2029 gram gave 0.1465 gram silver bromide.

		Calculated for	
		$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \text{---} \text{O} \text{---} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \\ \text{CH(OCH}_3\text{)}\text{---CHBr---CH}_3 \end{array} $	
		I.	II.
Bromine.....	29.30	30.52	31.09

2. Oil resulting by boiling isosafrol dibromide with ethyl alcohol.

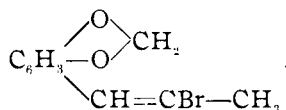
- I. 0.2017 gram gave 0.1388 gram silver bromide.
 II. 0.2005 gram gave 0.1376 gram silver bromide.

		Calculated for.	
		$ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \text{---} \text{O} \text{---} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \\ \text{CH(OC}_2\text{H}_5\text{)}\text{---CHBr---CH}_3 \end{array} $	
		I.	II.
Bromine.....	27.87	29.28	29.20

¹ Eykman : *Ber. d. chem. Ges.*, **23**, 855; Ciamician and Silber : *Ibid.*, **23**, 1159; Angeli : *Gazz. chim. ital.*, (2) **23**, 101.

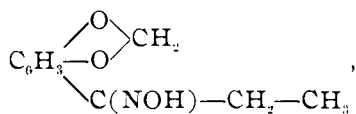
² Wallach and Pond : *Ber. d. chem. Ges.*, **28**, 2719.

These analyses are, of course, of no value in determining the exact constitution of the two compounds under consideration, but they indicate that the oils are the methyl and ethyl alcohol addition-products of monobromisafrol; for if the action of the alcohols caused the elimination of hydrogen bromide without the addition of the elements of the alcohols, it should give rise, in both cases, to the same compound, monobromisafrol,



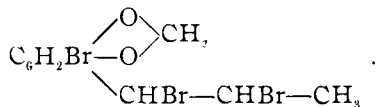
This compound would demand 33.19 per cent. of bromine, which is considerably in excess of that found. In the near future, we hope to obtain these two compounds in a pure condition.

Another circumstance which inclines us to the view that the two oils are alcohol addition-products of monobromisafrol is the behavior of the methyl alcohol product towards sodium alcoholate. When it is boiled with one molecule of sodium alcoholate or alcoholic potash, and the resulting product is treated as usual with hydrochloric acid, a liquid is obtained, which yields an oxime on treatment with hydroxylamine; this oxime crystallizes from alcohol in short prisms, melts at $101^\circ-102^\circ$, and is identical with the oxime¹



which is produced from the compound resulting by the treatment of isosafrol dibromide with two molecules of sodium methylate.

Monobromisafrol Dibromide,



—This compound was first prepared by Ciamician and Silber² by adding an excess of bromine to a solution of isosafrol in carbon bisulphide, and then heating for a considerable time in a reflux apparatus. It was subsequently obtained by Hell and Hoering³

¹ Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2719.

² Ciamician and Silber: *Ibid.*, **23**, 1163.

³ Hoering: *Inaug. Diss. (Rostock)*, p. 55. (1897).

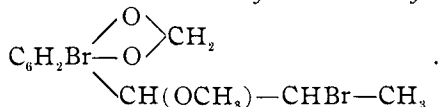
by slowly adding two molecules of bromine to an ethereal solution of isosafrol; the product was recrystallized from petroleum ether, and melted at 109.5° .

We find the following method well adapted for the preparation of this compound.

Thirty grams of isosafrol are dissolved in 90 cc. of ether, and 59.3 grams (2 molecules) of bromine are added as rapidly as the reaction will permit, without cooling. The dark-colored reaction-product is allowed to stand in an open vessel until the ether evaporates, when the substance remains as a crystalline mass. It is filtered by suction, washed with a little ether and then with a small quantity of cold alcohol, and crystallized from ethyl acetate; the crystals melt at 110° – 111° . It also crystallizes in large, colorless prisms from a solution in acetone to which an equal volume of ether is added.

The Action of Methyl Alcohol upon Monobromisosafrol Dibromide.

Methyl Alcohol Addition-Product of Dibromisosafrol,



—Thirty grams of monobromisosafrol dibromide were dissolved in 80 cc. of methyl alcohol and boiled with reflux condenser on the steam-bath for about two hours. The solution became slightly colored and gave an acid reaction; hydrobromic acid was given off. The reaction-product was poured into a beaker and the alcohol allowed to evaporate; the residue consisted of a light-colored, heavy oil, which solidified to a white mass after standing during several days. It was subsequently learned that the same solid compound is more readily formed by boiling the methyl alcoholic solution of the tribromide for about three minutes, and then adding a small quantity of water to the solution; the compound is then precipitated *at once* in fine crystals.

It is recrystallized from methyl alcohol; it separates from a concentrated solution in very fine needles, but from dilute solutions in large, prismatic crystals; both forms of crystals melt at 75° – 76.5° . It may be recrystallized without change from ethyl alcohol.

It was analyzed with the following results:¹

¹ These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

- I. 0.2118 gram gave 0.2905 gram carbon dioxide and 0.0693 gram water.
 II. 0.1916 gram gave 0.2634 gram carbon dioxide and 0.0615 gram water.
 III. 0.2204 gram gave 0.2380 gram silver bromide.
 IV. 0.2204 gram gave 0.2382 gram silver bromide.

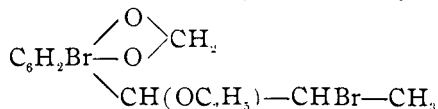
	Calculated for $C_{11}H_{12}O_3Br_2$.	I.	II. Found.	III.	IV.
Carbon	37.50	37.40	37.49
Hydrogen.....	3.41	3.63	3.56
Bromine	45.45	45.94	45.98

Although the corresponding methyl alcohol addition-product of dibromanethol is very readily converted into a ketone by treatment with one molecule of sodium alcoholate or alcoholic potash, no such change appears to take place with this isosafrol derivative. When 10 grams of the compound were heated with an excess of sodium methylate on the steam-bath for twenty-four hours, no reaction took place. The mixture was then heated in an oil-bath at a temperature of 150° until most of the excess of alcohol was removed; no sodium bromide was eliminated and, on the addition of water, an oil separated which soon solidified; this crystallized from alcohol and melted at 76° , indicating the unchanged compound.

Alcoholic potash, and even the action of an excess of metallic sodium on the alcoholic solution of the compound do not remove hydrogen bromide from this substance.

The Action of Ethyl Alcohol upon Monobromisosafrol Dibromide.

Ethyl Alcohol Addition-Product of Dibromisosafrol,



—It has already been mentioned that Hell and Hoering¹ have reported on this action; they state that when monobromisosafrol dibromide is boiled with alcohol, it yields a non-characteristic oil ("Schmiere") from which no crystalline compound is to be obtained. The results of our experiments do not quite confirm these observations.

When 30 grams of the tribromide were boiled with 80 cc. of absolute ethyl alcohol for about two hours, and the alcohol was then allowed to evaporate, a light-colored, heavy oil separated, which became solid after standing two weeks. It crystallized

¹ Hoering: Inaug. Diss. (Rostock), p. 59. (1897).

from an alcoholic solution in beautiful, large, rhombohedral crystals, and melted at 58°–60°. The same compound is more readily formed by dissolving the tribromide in ethyl alcohol, heating to the boiling-point for a few minutes, and then adding a small quantity of water; it then separates *at once* in small crystals, which, on recrystallization from alcohol, yield the large crystals above mentioned.

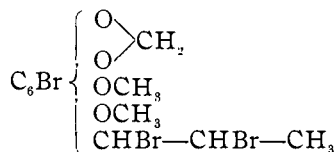
Analysis gave the following :¹

- I. 0.1835 gram gave 0.2650 gram carbon dioxide and 0.0665 gram water.
- II. 0.1892 gram gave 0.2686 gram carbon dioxide and 0.0658 gram water.
- III. 0.2070 gram gave 0.2130 gram silver bromide.
- IV. 0.2070 gram gave 0.2132 gram silver bromide.

	Calculated for C ₁₂ H ₁₄ O ₃ Br ₂ .	I.	Found.	III.	IV.
Carbon	39.34	39.38	38.71
Hydrogen.....	3.82	4.02	3.86
Bromine	43.71	43.78	43.82

When 10 grams of this compound are boiled with an excess of sodium alcoholate, no action appears to take place, the unchanged substance (m. p. 58°–60°) crystallizing from the reaction mixture.

*Monobromisoapiol Dibromide,*²



—The isoapiol,³ C₁₂H₁₄O₄, necessary for our experiments was prepared by boiling apiol with alcoholic potash; it was recrystallized from acetone and melted at 55°–56°.

Monobromisoapiol dibromide was first prepared by Ginsberg⁴ by the gradual addition of two parts of bromine dissolved in carbon bisulphide to a solution of one part of isoapiol in the same solvent; it was crystallized from glacial acetic acid and melted at 120°.

We find that it is more readily prepared by dissolving 52 grams of isoapiol in 52 cc. of ether, and adding 27.5 cc. (2 molecules) of bromine to the solution; the addition of the bromine may take place quite rapidly while the solution is cooled by ordinary cold

¹ These analyses were made by Mr. C. R. Siegfried.

² Ginsberg : *Ber. d. chem. Ges.*, **21**, 2515.

³ Ciamician and Silber : *Ber. d. chem. Ges.*, **21**, 1621; Ginsberg : *Ibid.*, **21**, 1192; See also Gerichten : *Ibid.*, **9**, 1479.

⁴ *Loc. cit.*

water. The reaction mixture is then placed in a beaker and the ether and hydrogen bromide removed by the aid of a vacuum desiccator. The resulting crystalline mass, which is only slightly colored, is recrystallized from acetone from which it separates in colorless prisms, melting at 120° .

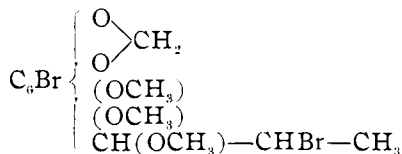
Analyses gave :

- I. 0.3000 gram gave 0.3445 gram carbon dioxide and 0.0772 gram water.
- II. 0.2000 gram gave 0.2448 gram silver bromide.
- III. 0.2010 gram gave 0.2451 gram silver bromide.

	Calculated for $C_{12}H_{18}O_4Br_2$		Found.	
		I.	II.	III.
Carbon	31.23	31.31
Hydrogen	2.82	2.86
Bromine	52.06	52.08	51.85

The Action of Methyl Alcohol upon Monobromisoapiol Dibromide.

Methyl Alcohol Addition-Product of Dibromisoapiol,



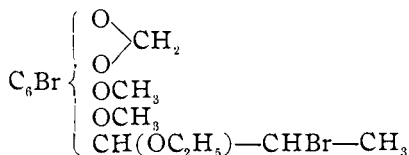
—This compound is formed by boiling monobromisoapiol dibromide with methyl alcohol for about fifteen minutes and then adding a small quantity of water to the hot solution. It usually separates at once in crystals, but under certain conditions it first forms an oil, which rapidly solidifies. It is recrystallized from methyl alcohol and obtained in large prisms, melting at 92° .

It was analyzed with the following results :

- I. 0.3001 gram gave 0.4148 gram carbon dioxide and 0.1069 gram water.
- II. 0.3006 gram gave 0.4143 gram carbon dioxide and 0.1092 gram water.
- III. 0.2006 gram gave 0.1828 gram silver bromide.
- IV. 0.2013 gram gave 0.1838 gram silver bromide.

	Calculated for $C_{13}H_{16}O_5Br_2$		Found.		
		I.	II.	III.	IV.
Carbon	37.86	37.69	37.58
Hydrogen	3.88	3.95	4.03
Bromine	38.83	38.78	38.85

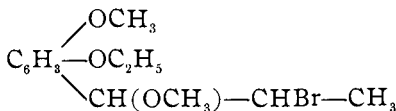
Sodium alcoholate is apparently without action upon this compound.

*The Action of Ethyl Alcohol upon Monobromisoapiol Dibromide.**Ethyl Alcohol Addition-Product of Dibromisoapiol,*

—Monobromisoapiol dibromide was boiled with three times its quantity of ethyl alcohol for about forty-five minutes. The solution had a dark color and an acid reaction; on the addition of water, an oil separated, which was carefully washed with water, extracted with ether and dried. On evaporation of the ether a rather dark-colored, viscous oil resulted, which gave the following results on analysis for bromine :

- I. 0.2077 gram gave 0.1805 gram silver bromide.
 II. 0.2137 gram gave 0.1840 gram silver bromide.

	Calculated for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{Br}_2$.	I. Found.	II.
Bromine	37.56	36.98	36.63

*The Action of Methyl Alcohol upon Ethylisoeugenol Dibromide.**Methyl Alcohol Addition-Product of Ethylmonobromisoeugenol,*

—Forty grams of ethylisoeugenol dibromide,¹ $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Br}_2$, were boiled with 100 cc. of methyl alcohol for about two hours, and the reaction-product allowed to stand in an open dish until the excess of alcohol evaporated. The residue consisted of an oil which gradually solidified; this was filtered by suction, washed sparingly with cold alcohol, and repeatedly crystallized from ethyl alcohol. It was rather difficult to remove some oily impurities from the compound, but after boiling with animal charcoal, it crystallized from alcohol in large colorless prisms, melting at 68°. It is quite soluble in methyl and ethyl alcohols, ether and acetone.

¹ Wallach and Pond : *Ber. d. chem. Ges.*, **28**, 2720.

Analysis gave the following :

- I. 0.2009 gram gave 0.1243 gram silver bromide.
 II. 0.2008 gram gave 0.1237 gram silver bromide.

	Calculated for $C_{17}H_{19}O_3Br$.	I.	Found.	II.
Bromine.....	26.40	26.32		26.21

It should also be mentioned that in one preparation of this compound by boiling ethylisoeugenol dibromide with methyl alcohol, another compound was formed, together with the methyl alcohol addition-product; it was separated by fractional crystallization from ethyl alcohol in which it is more sparingly soluble than the addition-product. It crystallizes in fine needles and melts at 128° ; it contains no bromine, but has not been further investigated.

[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION. COMMUNICATED BY W. A. WITHERS.]

THE DETERMINATION OF SULPHUR IN PLANTS.

BY G. S. FRAPS.

Received December 5, 1907.

IN a previous issue of this Journal¹ the author called attention to the loss of sulphur in preparing ash of plants. The conclusion reached was that "the sulphur obtained when the ash was burned by itself is from 4 to 100 per cent. less than when burned with calcium acetate. Whether the calcium acetate retains all the sulphur or not, is a point which requires further study." The facts which will be presented here show that the calcium acetate does not retain all the sulphur.

The object of the work was to compare the calcium acetate method with some method by the use of which we could be reasonably certain that all the sulphur contained in the plant in inorganic or organic combination would be retained and determined. A great difficulty is that a very small amount of sulphur is contained in a large quantity of plant material. The Liebig method (fusion with potassium hydroxide and a small amount of potassium nitrate in a silver dish) and the Carius method (heating in a sealed tube with fuming nitric acid) were considered, but offered difficulties on account of the large quantity of organic material to be handled. The following method was finally adopted for trial:

Fifteen grams material were placed in a flat porcelain dish of about 250 cc. capacity, 35 cc. of nitric acid (conc.) added, and the

¹ 23, 199 (1907).