

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY].

**THE CATALYTIC PREPARATION OF MERCAPTANS.<sup>1</sup>**

BY R. L. KRAMER AND E. EMMET REID.

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**Introduction.**

The problem of the preparation of alkyl mercaptans, especially *n*-butyl mercaptans, was assigned to this laboratory in connection with investigations carried out in the war work. A survey of the methods in the literature excited interest in a catalytic process which appeared to possess exceptional possibilities for development. Accordingly an investigation of it was made which resulted in the erection of a small plant for the production of butyl mercaptan which will be described in a separate article.<sup>2</sup> Later, after the war, the problem was more thoroughly investigated to clear up a number of difficulties which arose in the operation of the process and for its general scientific interest.

**Historical.**

Sabatier<sup>1</sup> discovered the catalytic method in his work with metallic oxides as dehydrating catalysts in organic reactions. The method as described consists in passing a mixture of alcohol vapor and hydrogen sulfide over thoria heated to 300–380°, the resulting product being a mixture of mercaptan, unchanged alcohol and some sulfide. A portion of the alcohol is converted into the olefine hydrocarbon, which in the case of secondary alcohols is quite large. The mercaptan was separated and purified by fractional distillation.<sup>3</sup> In a later communication,<sup>4</sup> Sabatier compared the activities of a number of metallic oxides by means of *iso*-amyl alcohol at 370–384°, and found thoria to be the best catalyst, crediting it with a 70% yield of *iso*-amyl mercaptan.

The description of the method does not include information as to the rate at which the mixture of alcohol and hydrogen sulfide was passed over the catalyst, the proportions of each in the mixture, or the amount of thoria used, though it may be inferred that the apparatus, quantities of materials and rates of passage were analogous to those used in his study of the dehydration of alcohols.<sup>5</sup>

**Apparatus.**

The catalyst was contained in a hard glass tube 20 × 640 mm., which was uniformly heated in a special horizontal electric-tube furnace auto-

<sup>1</sup> From doctor's dissertation of R. L. Kramer.

<sup>2</sup> In this investigation Dr. J. W. Kimball, Mr. George Holm, Mr. G. W. Livingston and Mr. R. W. Hale, Jr., also took part. Though their results are not included in the present article, credit is due them for assistance in laying the foundation for the present work.

<sup>3</sup> See section on distillation of mixtures of mercaptan and alcohol.

<sup>4</sup> Sabatier, *Compt. rend.*, 150, 1569 (1910).

<sup>5</sup> *Ibid.*, 146, 1377 (1908).

matically regulated to about  $1^{\circ}$ . The temperature was read on a thermometer placed between the catalyst tube and the wall of the furnace. Tests showed that this registered about  $20^{\circ}$  above the temperature inside the catalyst tube, hence the temperatures given in tables are  $20^{\circ}$  lower than those actually read.

The hydrogen sulfide was generated in a Kipp apparatus and was washed with water, dried over calcium chloride and measured by a calibrated flowmeter. It averaged 95% pure.

The alcohol was admitted from a dropping funnel with a calibrated tip to a tube reaching to the bottom of a distilling bulb through which the hydrogen sulfide was passed. This bulb was immersed in an oil-bath and served as a flash-boiler to vaporize the alcohol and as a mixing chamber for the vapor and the gas, the mixture being led directly into the furnace. The reaction products passed through a condenser cooled with ice-water into a receiver packed in ice. The uncondensed portion was led through caustic alkali solution and the remaining gas collected over water in a large calibrated aspirator bottle.

#### Method of Work.

While the furnace was heating, the rates of flow of hydrogen sulfide and alcohol vapor were adjusted, the products, being run out through a 3-way cock placed between the condenser and receiver. When the desired conditions were attained one gram molecule of the alcohol was placed in the dropping funnel, the stopcock turned so as to connect with the receiver and the time taken. As the last of the alcohol ran in, the receiver was disconnected and the time taken again.

#### The Product.

The condensate usually consisted of 2 layers; the lower, or water layer, was discarded and the other weighed and entered as "product." The upper layer in the receiver, except in the case of the methyl compound, which demanded special treatment, consisted of mercaptan, unchanged alcohol, aldehyde, ether, water and condensation products saturated with hydrogen sulfide and unsaturated hydrocarbon.

The liquid was freed from hydrogen sulfide by boiling under a well-cooled reflux condenser for 20 minutes, or until a test portion showed no hydrogen sulfide with alcoholic lead-acetate solution. The mercaptan present was then determined iodometrically.<sup>1</sup> The gaseous products collected consisted of the unsaturated hydrocarbon resulting from dehydration of a part of the alcohol, hydrogen corresponding to the aldehyde produced and hydrogen originally present as impurity in the hydrogen sulfide, together with a small amount of air from the receiver. A measured sample was shaken with bromine water to determine the unsaturated

<sup>1</sup> Kimball, Kramer and Reid, *THIS JOURNAL* (to be published later).

hydrocarbon. The analysis of the residue from an average run showed it to be nearly pure hydrogen.

Methyl mercaptan boiling at 6° required special treatment. It was absorbed in the caustic soda wash-bottles, the resultant alkaline solution placed in a flask, the exit tube of which was connected with a coil condenser surrounded with freezing mixture, and the mercaptan was displaced by passing hydrogen sulfide into the solution. No hydrogen sulfide passed through till all of the mercaptan had been displaced. The mercaptan was collected in well-cooled tared tubes which were sealed and weighed.

### The Catalyst.

Thoria has been used as a catalyst throughout the work; much time has been spent studying different methods of its preparation so as to obtain maximum activity. Comparing this oxide with alumina and others the activity of which is greatly influenced by mode of preparation,<sup>1</sup> Sabatier says,<sup>2</sup> "On the contrary thoria does not present this inconvenience and its activity is not sensibly diminished when it is ignited at a red heat; it seems that so heavy a molecule can not undergo further important molecular condensations."

Our experiments show that the mode of preparation of thoria greatly influences its activity in this reaction, some preparations being absolutely inactive.

Commercial thoria and discs cut from Welsbach gas mantles were found to be inactive. When thorium nitrate is heated suddenly to a high temperature by being dropped into a red hot crucible a very light porous thoria is obtained, 7 g. of it occupying 200 cc. of space. On account of its enormous surface we expected this to be a wonderfully active form but found it inactive. A thoria gel prepared according to Müller<sup>3</sup> was found to be inactive alone but when the concentrated hydrosol was distributed on pumice, Catalyst E, before the final evaporation a fair catalyst was obtained. The precipitated and carefully washed hydroxide from 44 g. of pure thorium nitrate was suspended in 300 cc. of pure water, which was rapidly stirred at 90° while 4 g. of thorium nitrate in 20 cc. of water was added. The hydroxide dissolved to form an orange-yellow hydrosol. The volume was reduced to 20 cc. on the water-bath and the hydrosol evaporated in a vacuum desiccator to a hard glass-brittle light green solid. This was dehydrated at 400° in a current of air.

On account of the high cost of thoria, its density, and tendency to pack, a number of experiments were made with different proportions of thoria on pumice as a carrier.

<sup>1</sup> Sabatier, *Compt. rend.*, 147, 106 (1909).

<sup>2</sup> Sabatier, "La Catalyse," 2nd Ed., Paris, 1920, p. 26.

<sup>3</sup> Müller, *Ber.*, 39, 2857 (1906).

The best catalyst obtained was prepared as follows. Pumice sized between 6- and 12-mesh sieves was placed in a dish on a water-bath and a conc. water solution of analyzed thorium nitrate poured over it, the quantities being so taken that the ratio of pumice to thoria should be 3:1. Other ratios were tried but gave poorer results. The mass was continually turned during the evaporation of the water. The material may be further dried in an oven at 120°. This was done with Catalyst F while G and H were not so dried. Catalyst F was easily duplicated and proved to be reliable and efficient; it was used in all of our subsequent work. The thorium-nitrate-pumice was placed in a tube in a current of air and heated to 270°, the decomposition temperature of the nitrate, till decomposition was nearly complete, after which the temperature was gradually raised to 400°, and air passed until the issuing gas would no longer redden moist litmus. A snow-like coating of thoria covered the pumice.

C and D were preliminary catalysts prepared in this way except that the proportion of thoria and the decomposition temperatures varied.

Catalyst A was prepared by igniting precipitated thorium hydroxide which had been carefully washed to remove electrolytes. It was mixed with glass wool to keep it suspended.

The table below gives the results with various catalysts, 74 g. of *n*-butyl alcohol with an equivalent amount of hydrogen sulfide being passed over the catalyst at 380° in 6 hours except with Catalysts E and H, where it was 4 hours.

TABLE I.—COMPARISON OF CATALYSTS.

Expt.	Catalyst.	Thoria. G.	Pumice. G.	Temp. of prep. C.	Yield. %
1	A	20	none	Below red	35.8
2	B	19	37.5	Below red	43.5
3	C	6	44	400	34.4
4	C	6	44	450	26.6
5	C	6	44	550	21.1
6	D	12.5	37.5	400	44.4
7	D	12.5	37.5	500	42.7
8	E	25	X	...	38.8
9	F	12.5	37.5	270-400	50.2
10	F	12.5	37.5	270-400	52.1
11	F	12.5	37.5	270-400	52.7
12	G	8	42	270-400	44.0
13	G	8	42	270-400	45.7
14	H	12.5	37.5	270-400	49.9
15	H	12.5	37.5	270-400	50.1

From these figures it appears that a given weight of thoria is considerably more effective if distributed on a carrier. From Expts. 3, 4, 5, and 6-7, it appears that the activity of the thoria is considerably diminished by heating much above 400°. Catalyst H is the most efficient.

### Regeneration of Catalyst.

The catalyst becomes coated slowly at 380°, and more rapidly at higher temperatures, with carbonaceous material and its activity diminishes. A fouled catalyst may be cleaned by passing steam through it at 380° until all volatile material is removed and following this with nitrogen peroxide at the same temperature as long as there is any action. The oxides of nitrogen are then completely displaced with steam. The regenerated catalyst is snow-white and shows its original activity.

### Effect of Temperature.

One gram mol of *n*-butyl alcohol was passed with an equivalent amount of hydrogen sulfide over Catalyst F in 6 hours, the product weighed, and the mercaptan determined. For the higher temperatures the butylene was determined and the aldehyde estimated from the amount of hydrogen remaining, allowing for the hydrogen present in the hydrogen sulfide, the alcohol being taken by difference. Some butyl sulfide was doubtless formed but it was not taken into account as the amount is relatively small and no convenient method of estimating it is known. The results are given in Table II below and in Fig. 1 the yields are plotted against temperature. In order to show the effect of the catalyst on the alcohol alone the last three runs were made without the hydrogen sulfide, under the same conditions.

TABLE II.—EFFECT OF TEMPERATURE.

Expt.	Temp. ° C.	Product.		Alcohol converted.			Alcohol by dif. %.
		Weight. G.	Analysis. %.	BuSH. %.	C <sub>4</sub> H <sub>8</sub> . %.	PrCHO. %.	
1	260	75	9.3	7.7	...	....	....
2	280	78	14.3	12.4	...	....	....
3	300	82	21.7	19.7	...	....	....
4	320	84	29.3	27.4	...	....	....
5	340	80.5	38.2	34.2	0.3	5.1	60.4
6	360	82.5	47.3	43.4	1.2	10.0	45.4
7	360	78.5	48.5	42.3	1.7	11.3	44.7
8	380	77	59.6	50.2	...	....	....
9	380	76.5	61.3	52.1	1.8	15.1	31.0
10	380	73.5	64.6	52.7	2.1	17.4	27.8
Alcohol alone.							
11	340	....	....	....	0.5	7.7	91.8
12	360	....	....	....	2.1	17.7	80.2
13	380	....	....	....	2.7	32.7	64.6

From these results it appears that the yield of mercaptan increase regularly with the temperature but on account of the increasing prominence of side reaction it is not advisable to go above 380°. Fouling of the catalyst interferes above this temperature.

The rate of formation of butylene is surprisingly low, and is not serious even at 380°; that is, this catalyst appears to be more active in the de-

hydrogenation than in the dehydration of butyl alcohol. This is surprising in view of Sabatier's<sup>1</sup> statement that thoria is exclusively a dehydrating catalyst for alcohols.

At 380° 52% of the alcohol is converted into mercaptan and 33% of the remaining 48% into aldehyde, while in the run with alcohol alone 32.7% of aldehyde formation was observed. At lower temperatures somewhat the same relations hold, indicating that the aldehyde formation depends on the remaining alcohol rather than on that originally present.

Less butylene is formed when hydrogen sulfide is present, though the difference is not great.

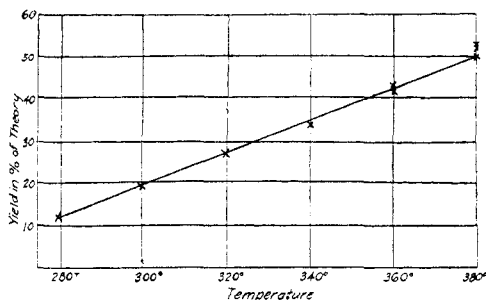


Fig. 1.

#### Rate of Flow.

The influence of rate of passage of the vapor mixture over the catalyst was investigated by making a series of runs at 380° using 74 g. of butyl alcohol for each run, and hydrogen sulfide in equivalent amounts.

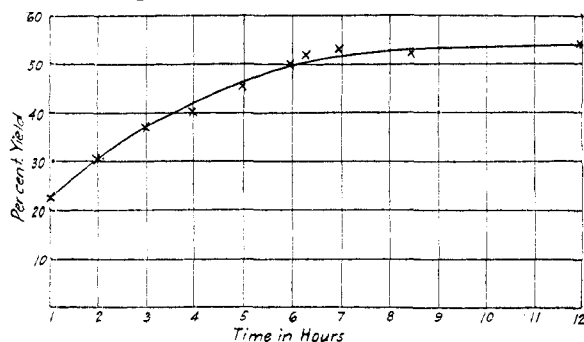


Fig. 2.

The results are given in Table III and plotted in Fig. 2. The yield of mercaptan increases with the time until the rate of 6 hours for 1 gram mole is reached. For the amount of catalyst used, this is the

TABLE III.—INFLUENCE OF RATE OF FLOW OF VAPOR MIXTURE.

Expt.	Time, Hours.	Product.		Alcohol converted.			Remaining by dif. %.
		Wgt. G.	BuSH. %.	BuSH. %.	C <sub>2</sub> H <sub>5</sub> . %.	PrCHO. %.	
1	1	72.5	29.9	22.4	0.3	3.4	73.9
2	2	79.0	35.1	30.8	0.5	7.4	61.3
3	3	78.0	43.1	37.3	0.5	10.5	51.7
4	3	78.5	43.0	37.5	0.8	8.7	53.0
5	4	77.5	46.9	40.4	1.0	11.0	47.6
6	5	76.0	54.0	45.6	1.4	13.1	39.9
7	6	77.0	59.6	50.2	...	...	...
8	6.3	76.5	61.3	52.1	1.8	15.1	31.0
9	7.1	73.5	64.6	52.7	2.1	17.4	27.8
10	8.5	76.0	61.3	51.8	1.4	17.6	29.2
11	12	68.0	71.4	53.8	2.0	23.2	21.0

<sup>1</sup> Sabatier, "La Catalyse," 2nd Ed., Paris, 1920, p. 251.

best rate. Doubling the time results in a very slight increase in the amount of mercaptan with a considerable increase in the by-products.

### Ratio of Reactants.

A brief study was made of the ratio of the reactants. The hydrogen sulfide which passes out of the reaction tube mixed with hydrogen and hydrocarbon is a loss and the greater its volume the more of the mercaptan it carries along with it. On the other hand, the amount of alcohol lost in side reactions is greater when it is in excess. A series of determinations was made at 380° passing 74 g. of *n*-butyl alcohol over the catalyst mixed with varying amounts of hydrogen sulfide. The results are given

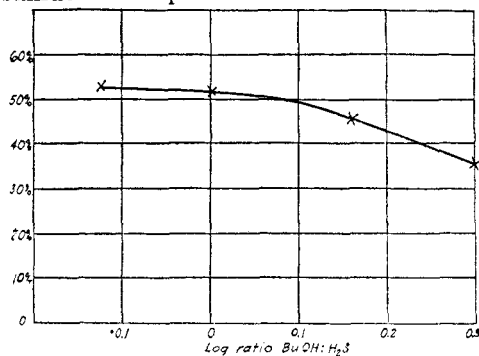


Fig. 3.

in Table IV and plotted in Fig. 3. The 1:1 ratio gives the best results.

TABLE IV.—EFFECT OF CHANGE OF RATIO OF REACTANTS.

Expt.	H <sub>2</sub> S : BuOH.	Product.		Alcohol converted.			Remaining by dif. %.
		Weight. G.	Analysis. %.	BuSH. %.	C <sub>4</sub> H <sub>8</sub> . %.	PrCHO. %.	
1	2 : 1	74	43.4	35.6	0.7	15.8	47.8
2	1.5 : 1	76	54.0	45.6	1.2	11.3	41.9
3	1 : 1	76.5	61.3	52.1	1.8	15.1	31.0
4	0.75 : 1	73.5	63.3	52.7	1.0	12.1	33.3

### Comparison of Alcohols.

A brief study was made of other alcohols under the conditions that had been found best for butyl alcohol, namely, passing one mole of the alcohol vapor mixed with an equivalent amount of hydrogen sulfide in 6 hours over Catalyst F at 380°, except for methyl and ethyl alcohols which were run at several temperatures. The alcohols were anhydrous except as noted for one run with ethyl alcohol. The results are given in Table V.

At 380° methyl and ethyl alcohols give about the same results, the yield increasing with propyl and still more with *n*-butyl alcohol. The *iso*-alcohols give somewhat lower yields but better with the larger molecular weight. These two alcohols give notably less aldehyde than the others.

Methyl alcohol gives a somewhat better yield at 370° than at 380°.

### Purification of Product.

The purification of the crude product from the furnace varies considerably with the alcohol used. A method of recovering and purifying methyl mercaptan has already been outlined. In the case of ethyl and

propyl mercaptans advantage is taken of the fact that the alcohols are extremely soluble in water and can be washed out of the crude material. After washing with water the residue consisting of mercaptan, sulfide and other products is treated with alkali to dissolve the mercaptan and separated. The addition of mineral acid to the alkaline solution frees the mercaptan which is washed, dried and fractioned.

TABLE V.—COMPARISON OF ALCOHOLS.

Expt.	Alcohol.	Temp. ° C.	Product.		Alcohol converted.			Remaining by dif. %.
			Weight. G.	Analysis. %.	RSH. %.	C <sub>n</sub> H <sub>2n</sub> . %.	RCHO. %.	
1	Methyl	370	20	100	41.6	....	14.3	44.1
2	Methyl	380	17.3	100	36.0	....	15.9	49.1
3	Ethyl	350	35	49.4	27.8	....	....	....
4	Ethyl	360	32	66.3	35.4	....	....	....
5	Ethyl	360	31	68.0	35.0	....	....	....
6	Ethyl	370	28	77.4	34.9	....	....	....
7	Ethyl 95%	365	29	67.1	32.4	7.16	11.0	49.4
8	Propyl	380	60	56.7	44.7	0.6	14.1	40.2
9	Propyl	380	61	56.1	45.1	0.7	13.2	41.0
10	<i>n</i> -Butyl	380	76.5	61.3	52.1	1.8	15.1	31.0
11	<i>iso</i> -Butyl	380	72	44.6	35.7	3.0	7.2	54.1
12	<i>iso</i> -Amyl	380	92	47.3	41.8	2.8	9.5	45.9
13	<i>iso</i> -Amyl	380	94	47.4	41.8	2.8	6.7	47.7

The higher alcohols are difficultly soluble in water, but an alkali separation cannot be used because the alcohol dissolves in an alkaline solution containing mercaptan. For example, 100 g. of water dissolves but 8.3 g. of *n*-butyl alcohol; but a mixture of the alcohol and mercaptan where the latter is present to the extent of 50% or better is completely soluble in a 20% solution of sodium hydroxide.

The alcohols can not be separated from the higher mercaptans by distillation because they form constant-boiling mixtures boiling only at slightly lower temperatures than do the mercaptans. When a simple distilling apparatus is used this is not evident except by analysis of the fraction corresponding to the pure mercaptan. Having observed this fact first in connection with *n*-butyl mercaptan an investigation was also made of propyl and *iso*-amyl mercaptans to determine accurately these mixtures and their compositions. As Sabatier had separated his product by fractional distillation it was expected that this information would throw some light on the wide variations in yield which he reported from those obtained in this work.

The method employed consisted in distilling the constant boiling mixture from a sample of equal parts of alcohol and mercaptan.<sup>1</sup> The frac-

<sup>1</sup> Note: It is very difficult to approach the constant-boiling mixture from the other side because of the slight difference in boiling points of the mixture and the mercaptan.



tion collected was analyzed and redistilled to check the first determination. When the customary fractionating columns were used the variation in the analyses of these fractions was large, becoming constant only after a considerable number of distillations. Therefore to make the separation as complete as possible a Dufton<sup>1</sup> column was used because of its high efficiency. As mercaptans attack metal it was necessary to construct the column entirely of glass. An example will illustrate the method. A mixture of equal parts of *n*-butyl alcohol and mercaptan was distilled and the first fraction from 97.6° to 98.0° collected which distilled constantly at 97.8°. This fraction analyzed 84.49% mercaptan. On redistillation it gave at the same temperature a distillate which was collected in three parts. The first, middle and last portion analyzed respectively 85.13%, 85.11%, 85.25% mercaptan. The results obtained for the mixtures of *n*-propyl, *n*-butyl and *iso*-amyl mercaptan and alcohol on distillation are recorded below, together with the boiling points of the components.

	B. p. of constituents. °C.	Composition. %
<i>n</i> -Propyl alcohol.....	97.4	8.65
<i>n</i> -Propyl mercaptan.....	67-68	91.35
Constant boiling mixture.....	66.4 at 765.6 mm.	
<i>n</i> -Butyl alcohol.....	117.02	14.84
<i>n</i> -Butyl mercaptan.....	97-98 at 753 mm.	85.16
Constant boiling mixture.....	97.8 at 770.3 mm.	
<i>iso</i> -Amyl alcohol.....	131	22.89
<i>iso</i> -Amyl mercaptan.....	116	77.11
Constant boiling mixture.....	115.6 at 766.9 mm.	

The compositions of the constant-boiling mixtures represent the limits of separation for mixtures of mercaptan and alcohol.

A better separation of these mixtures can be made by distilling with steam, but only in the case of propyl mercaptan is the separation sufficiently complete to be of any practical value. To determine the effect of distilling with steam, water was added to the mixture of alcohol and mercaptan. This insures good contact between the steam and mixture layer reducing the amount of water distilling to a minimum. The distillation was carried out as described above. The table gives the boiling point of the ternary vapor mixture and the analysis of the mercaptan-alcohol layer in the distillate.

#### TERNARY MIXTURES.

Mercaptan, alcohol and water.

	B. p. °C.	Pressure. Mm.	Mercaptan in upper layer. %
<i>n</i> -Propyl.....	60.8	771.6	96.00
<i>n</i> -Butyl.....	78.6	761.0	93.16
<i>iso</i> -Amyl.....	86.6	765.4	88.85

<sup>1</sup> *J. Soc. Chem. Ind.*, 38, 45T (1919).

According to Claison and others mercaptans can be prepared practically pure from a heavy metal salt. The lead salt is the one usually employed. It is precipitated in an alcoholic water solution, filtered and washed several times with alcohol. After drying to remove the alcohol the mercaptan is recovered by distilling the salt with dilute mineral acid. This method yields mercaptans which analyze better than 98.5%.

The lead salt of *n*-butyl mercaptan precipitated as described above is a yellow crystalline solid which melts at about 80° to an orange-red viscous liquid. This liquid is but very slowly hydrolyzed when boiled with water. This fact led to the following method for the preparation of pure butyl mercaptan. A crude sample was precipitated in alcoholic solution with lead acetate and filtered. The salt was transferred to a flask, warmed to 100° in an oil-bath and steam passed through the liquid to remove the volatile materials. Due to hydrolysis the condensate will always contain some mercaptan but when this becomes very small the steam is shut off. Dil. mineral acid was added in small portions at a time and the mercaptan driven over with steam. It was separated from the water, dried over anhydrous sodium carbonate and distilled. It came over in a fraction between 98° and 98.2° at 766.3 mm., the temperature remaining practically constant during the distillation at the higher temperature. An analysis of this sample gave the results 99.28 and 99.39%.

#### Comparison with Sabatier's Results.

It is difficult to compare the results obtained in this work with those of Sabatier because he gives a yield for but one alcohol. In comparing the activity of various oxides as catalysts for the reaction he stated that *iso*-amyl alcohol gave with thoria at 370° to 384° a yield of 70%. The temperatures agree very well, but the wide variations in yield are more difficult to explain. This, however, is probably due to the method which he used to separate and estimate his product, namely, fractional distillation. Assuming that he used a very good column for his separations and that he obtained the constant boiling mixture of 77.11% mercaptan, the actual yield would then have been but 54%. If he used only one of the customary columns the fraction which he collected boiling at 116° would unquestionably have had a much lower mercaptan content than the constant-boiling mixture, as has been found from experience. With these points in mind, our yield of 47% does not compare so unfavorably with his results. A specimen of *iso*-amyl mercaptan purchased before the war from Kahlbaum was found to contain 71% mercaptan.

#### Summary.

The catalytic preparation of mercaptan has been studied. By passing alcohol vapor and equivalent hydrogen sulfide at the rate of one mole per hour through a tube containing pumice coated with 12.5 g. of thoria at

380°, the following percentage yields of mercaptans were obtained: methyl 41%, ethyl 35%, propyl 45%, butyl 52%, *iso*-butyl 45%, *iso*-amyl 47%.

Propyl, butyl and *iso*-amyl mercaptans have been found to give constant-boiling mixtures with the corresponding alcohols and ternary mixtures with the alcohols and water.

BALTIMORE, MD.

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[CONTRIBUTION FROM THE LABORATORY OF THE WERNER DRUG AND CHEMICAL CO.]

## AN ALKYLENE AND SOME ALKYL HALIDES OF 2(4-HYDROXY-3-METHOXY-STYRYL)QUINOLINE.

BY LOUIS F. WERNER.

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In a recent paper,<sup>1</sup> the author showed that the methiodides of some of the 2(hydroxy-styryl)quinolines could be used as indicators. It was thought of interest to determine whether any variation in color exists in compounds of this type prepared from other alkyl halides. 2(4-hydroxy-3-methoxy-styryl)quinoline was the base selected for this work, as of the bases available this is the most readily prepared and purified.

The following halides were combined with 2(4-hydroxy-3-methoxy-styryl)quinoline: ethyl iodide, propyl iodide, *isopropyl* iodide, butyl iodide, *isobutyl* iodide, *iso*-amyl iodide and allyl bromide.

With the exception of the compounds resulting from *isopropyl* and *iso*-butyl iodides, all of these compounds were found to be indicators, and gave a fuchsin-red solution in aqueous alkaline solution, and a faintly yellow solution in neutral or acid acetate. The *isopropyl* and *isobutyl* derivatives, on the contrary, showed but little difference in color, the aqueous solution in each case being light yellow in acid or neutral solution, and only light brown in the presence of sodium hydroxide. This exceptional behavior is evidently associated with the branch chain structure of these alkyl derivatives, although the *iso*-amyl group showed the usual behavior. Possibly these groups were more mobile, and migrated to a position in the nucleus.

It was expected that the introduction of various alkyl groups might cause a modification of the colors of these dyes, but no variation could be detected in the shade of color of any of these derivatives, nor did the introduction of the allyl group cause any modification of the shade. A determination of the hydrogen-ion concentration at which the change from red to yellow takes place, would possibly show a difference for these various compounds.

### Experimental.

**General Method of Preparation.**—These compounds were prepared by heating 2(4-hydroxy-3-methoxy-styryl)quinoline with an excess of the

<sup>1</sup> Werner, THIS JOURNAL, 42, 2309 (1920).