

4. The two hydroquinones may be brominated to the same hexabromo derivative, 2,5-di-(3,5-dibromo-2,4,6-trimethylphenyl)-3,6-dibromohydroquinone, thus indicating that symmetry in the end rings eliminates the stereoisomerism.

5. The hexabromo compound just mentioned forms a characteristic diacetate and quinone. Moreover, it is oxidized by sodium hydroxide and hydrogen peroxide to dibromomesitylcarboxylic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

THE REACTION BETWEEN CERTAIN ORGANIC SULFUR COMPOUNDS AND SODIUM IN LIQUID AMMONIA¹

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In connection with certain investigations on the sulfur compounds in crude untreated petroleum, it was found necessary to determine the effect of sodium on some simple organic sulfur compounds. Sulfides, disulfides and mercaptans were chosen for this study, since they are representative of divalent sulfur compounds which are supposed to exist in crude petroleum.

Very little work has been done on the effect of sodium on these types of sulfur compounds. Moses and Reid² found that organic sulfides are unattacked by sodium in ether even after standing for three months. Disulfides are converted into the corresponding mercaptans.

Kraus and White,³ using a solution of sodium in liquid ammonia, converted diphenyl sulfide into benzene and sodium sulfide. No other reaction products were isolated. Apparently, the solution of sodium in liquid ammonia is more reactive than the ether-sodium system. We found this idea borne out in the present investigation.

With the three types of compounds studied, sulfides, disulfides and mercaptans, sodium might be expected to react in liquid ammonia, at least in two ways: first, it might carry the reduction to completion, yielding as

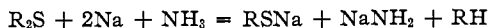
¹ The investigation was carried out in 1928-1929 under a grant from the American Petroleum Institute, and specified as Project 17.

² Moses and Reid, *THIS JOURNAL*, **48**, 776 (1926).

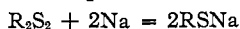
³ Kraus and White, *ibid.*, **45**, 775 (1923). We repeated Kraus' work on the reaction between diphenyl sulfide and sodium in liquid ammonia. Four experiments were made, two in which the procedure was identical with that described in the experimental part, and two in which the diphenyl sulfide was dropped into a solution of sodium in liquid ammonia as Kraus carried out the reaction. Our results were the same in all four experiments. A deep red solution was obtained when reaction was complete. The solid reaction product was a brown powder which ignited when exposed to moist air for a few minutes. Thiophenol and aniline were the only products identified. Benzene and sodium sulfide were watched for closely, since Kraus reported these, but we were unable to detect either compound.

final products sodium sulfide, hydrocarbons or amines or both; or second, the reduction might stop at an intermediate stage, forming sodium mercaptides, and hydrocarbons, or amines, or both.

So far as our present investigations show, only the second course is followed. Aliphatic sulfides are reduced to the corresponding mercaptides, and hydrocarbons, according to the equation



Disulfides are formed by oxidation of mercaptans. Treatment with a reducing agent should reform the mercaptans. This was found to be the case as indicated by the general equation



Mercaptans, being weak acids, react with liquid ammonia to form slightly soluble, white crystalline ammonium mercaptides. If to a liquid ammonia solution of a mercaptide, sodium is added, the ammonium mercaptides are decomposed with the formation of sodium mercaptides, and the evolution of one-half mole of hydrogen



Experimental

Materials.—The liquid ammonia was the regular commercial grade dried over sodium. The mercaptans, sulfides and disulfides were Eastman C. P. products.

Apparatus.—A new type of reaction chamber was designed for this investigation (see accompanying diagram). It was equipped with a mercury-sealed stirrer and connections for collecting gaseous reaction products.

Procedure.—Five grams of the compound under investigation was placed in the thoroughly dried reaction chamber, the stirrer placed in position and the two spiral exit tubes closed with two soda lime tubes. The reaction tube was then submerged slowly in the Dewar flask containing crude liquid ammonia. A stream of dried air was bubbled through the latter to cool it below the boiling point of liquid ammonia. One of the soda lime tubes was then removed and the exit tube of a small tank containing ammonia dried over sodium was connected by means of rubber tubing. A slow stream of gaseous ammonia was then run into the reaction chamber, where it condensed onto the sulfur compound and partially dissolved it. When 75 cc. of liquid ammonia had been condensed, the ammonia stream was stopped, but the connection allowed to stand. The remaining soda lime tube was then connected through a Bunsen valve to the gasometer.

Stirring was then started, and clean sodium in the form of wire one-eighth inch in diameter and as long was dropped in, two pieces at a time. When the blue color had disappeared, another portion was added, and this was continued until the blue color remained permanent for two hours. At the end of this time the residual gaseous products were flushed into the gasometer with a fairly rapid stream of gaseous ammonia, the stirrer then quickly removed and the reaction chamber stoppered. Both exit tubes

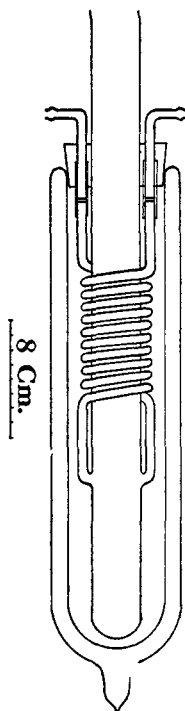


Fig. 1.

were connected to soda lime tubes and the reaction chamber set back into the Dewar flask from which the liquid ammonia had been removed. This precaution was necessary to prevent ebullition of the ammonia, which would force solid reaction products into the exit tubes. After about twelve hours, all of the ammonia had evaporated and a white crystalline product remained. This was scraped out, rapidly pulverized and preserved in a vacuum desiccator.

Sulfur was determined by oxidation with sodium peroxide in a Parr bomb and precipitated as barium sulfate.

Sodamide was determined by decomposing the sample with 10% sodium hydroxide solution, distilling the ammonia into standard acid as in the Kjeldahl method for nitrogen.

The gaseous products were analyzed by the conventional methods.

Aliphatic Sulfides

The reaction between *n*-propyl sulfide and *n*-heptyl sulfide and sodium in liquid ammonia was studied qualitatively with the following results: *n*-propyl sulfide yields *n*-propyl sodium mercaptide, sodamide and propane.

Normal heptyl sulfide crystallized when dropped into liquid ammonia and the solid appeared very insoluble. The reaction with sodium was very slow, but after fifty-five hours sufficient reaction had taken place to permit the identification of *n*-heptyl sodium mercaptide and sodamide. The amount of hydrocarbons produced was too small for identification and was mixed with unreacted organic sulfide.

Neither of these reactions produced a trace of sodium sulfide; the reaction always stopped with the formation of mercaptide.

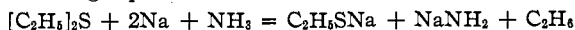
Sodium sulfide was tested for in both alkaline and acid solutions. In the former case, a dilute sodium plumbite solution was mixed with a dilute solution of the solid reaction product. Not the slightest trace of black lead sulfide was produced.

To test for sodium sulfide in acid solution, a dilute solution of the solid reaction product, acidified with dilute hydrochloric acid, was treated with a few drops of lead acetate solution. No darkening of the solution or precipitation of black lead sulfide was noticeable.

Of a semi-quantitative nature was the study of the reaction between ethyl sulfide and sodium in liquid ammonia. The results of two representative runs are given in Table I. These values were calculated on the assumption of the ratio



The yields of sodamide and ethane conform closely to the above ratio and suggest the following equation for the reaction



The ratio $\text{C}_2\text{H}_5\text{SNa}:\text{NaNH}_2 \rightleftharpoons 1$ probably arises from a concomitant reaction



Butane was not identified, however.

TABLE I
RESULTS OF REPRESENTATIVE RUNS

Run	Residue, g.	Wt. calcd., g.	Sulfur, %	Calcd. S, %	Extent of reaction
I	5.93	5.71	23.3	25.9	93.4
II	5.75	5.71	23.9	25.9	93.4
	Run	Sodamide, %	Calcd., %	Extent of reaction	
	I	23.4	31.7	76.7	
	II	21.4	31.4	67.9	
Run	Gas [N. T. P.], liters	Ethane, %	Found	Calcd.	Extent
I	1.04	79.1	0.83	1.04	79.1
II	0.99	72.3	0.71	1.04	69.6

Aliphatic Disulfides

The reaction between sodium and aliphatic disulfides in liquid ammonia was studied with ethyl, *n*-propyl and iso-amyl disulfides. The procedure was identical with that for the sulfides.

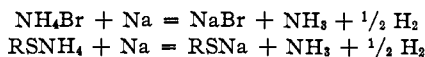
Qualitative examination of the reaction product showed that the alkyl sodium mercaptide was the only sulfur compound present, so the amount of mercaptide present was determined from the sulfur content of the solid product. The results for the three disulfides are tabulated in Table II.

TABLE II

ETHYL DISULFIDE					
Run	Residue, g.	Calcd. wt., g.	S, %	Calcd., %	Yield, %
I	6.90	6.83	36.8	38.0	97.8
II	6.91	6.83	36.0	38.0	95.4
<i>n</i> -PROPYL DISULFIDE					
I	6.47	6.20	31.9	32.6	102
II	6.38	6.20	32.0	32.6	102
ISO-AMYL DISULFIDE					
I	5.85	5.55	24.0	25.4	99.5
II	5.93	5.55	23.8	25.4	99.9

Aliphatic Mercaptans

When mercaptans⁴ are treated with liquid ammonia, slightly soluble white crystalline ammonium mercaptides are precipitated. When sodium is added to such a solution, a rapid reaction ensues with the formation of sodium mercaptides and the evolution of hydrogen, a reaction analogous to the reaction between ammonium bromide and sodium in liquid ammonia solutions.



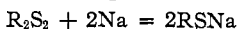
⁴ For the analogous reaction with thiophenols, see Ref. 3.

Summary

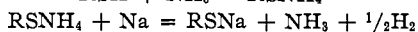
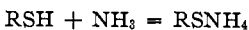
1. Aliphatic sulfides react with sodium in liquid ammonia chiefly according to the equation



2. Under the same conditions, aliphatic disulfides are reduced quantitatively to the corresponding mercaptides



3. Aliphatic mercaptans react as follows



4. No sodium sulfide is produced in any of these reactions; the reaction stops with the formation of mercaptide.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF "TRI-ISOBUTYLENE" BY OZONE

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The preparation of the so-called tri-isobutylene was first described in detail by Butlerow,¹ who dissolved isobutylene in a cold mixture of five parts of sulfuric acid to one part of water. The resulting oil boiled at 177.5–179° (749 mm.) and had a specific gravity of 0.774 at 0°. Dichromate oxidation yielded carbon dioxide, trimethylacetic acid, acetic acid, an acid C₁₁H₂₂O₂, acetone, and a neutral oil. The acid C₁₁H₂₂O₂ distilled at 266° and melted at 66–70°. The neutral oil had a boiling range of 100–220°, reacted with phosphorus trichloride and sodium, but did not reduce Tollens' reagent. In order to explain the formation of the solid acid Butlerow assumed the structure of the hydrocarbon to be [(CH₃)₃C]₂=C(CH₃)₂. He stated that the oxidation might first involve a pinacolone rearrangement with the formation of [(CH₃)₃C]₂C(CH₃)COCH₃. Further oxidation of this compound would result in the production of [(CH₃)₃C]₂C(CH₃)COOH, which would account for a solid acid having the formula C₁₁H₂₂O₂.

In a recent communication² the author described the preparation of di-isobutylene, the method of treating it with ozone, and the products resulting from the hydrolysis of the ozonide. In the work with tri-isobutylene a very similar procedure was followed.

Preparation of Tri-isobutylene.—Seven hundred fifty ml. of sulfuric acid and 250 ml. of water were mixed and cooled to about 5°. Then one liter of tertiary butyl

¹ Butlerow, *Ber.*, 12, 1482 (1879).

² McCubbin and Adkins, *THIS JOURNAL*, 52, 2547 (1930).