[Contribution from the Chemistry Laboratory of Johns Hopkins University]

THE ACTION OF SODIUM ON ALKYL DISULFIDES

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Since alkyl sulfides are in some respects analogous to the halides it was thought of interest to try the action of sodium on them in anhydrous media to see whether any reactions take place analogous to the Wurtz-Fittig synthesis. Some reaction does take place between alkyl sulfides and sodium in anhydrous ether but it is extremely slow; after three months only a trifling amount of the reaction product was obtained. Hence, the more reactive disulfides were taken up.

Methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl and *iso*-amyl disulfides reacted more or less readily with sodium in dry ether to give sodium mercaptides: $R.S.S.R + 2Na \longrightarrow 2R.SNa$.

The ease of reaction appears to increase from methyl to butyl; the higher disulfides react readily and apparently quantitatively. This is a convenient way to prepare these sodium mercaptides which are otherwise difficult to obtain in solid form. Ether is retained strongly by the flaky mass and could not be eliminated entirely even by warming under reduced pressure.

The course of the reaction is followed by observing the formation of white or yellow coatings or scales on the sodium. Sodium wire was used at first but it proved difficult to free the product from residual metal. It was found best to use thick slices of sodium from which the product could be scraped. Methyl and ethyl disulfides reacted slowly and gave only scanty yields though the mixtures were confined in pressure bottles warmed and kept for two weeks. With benzyl disulfide, the reaction was extremely slow. Some reaction did take place in the course of several months, but nothing definite could be isolated. With *p*-nitrobenzyl disulfide there was deep seated decomposition as indicated by the development of the odor of ammonia.

The mercaptans produced by hydrolysis of the mercaptides were identified by preparing the α-anthraquinone-thio-ethers according to the method of Reid, Mackall and Miller,[1] and Hoffman and Reid.[2]

The melting points obtained were identical with those previously recorded with the exception of that of the *iso*butyl derivative. This, according to Reid, Mackall and Miller, melts at 144°. Repeated experiments by the present workers with compounds obtained from various sources (Industrial Alcohol Company, Eastman Kodak Company, and others) and made both by the disulfide and mercaptan methods, and also from the mercaptan itself, gave an anthraquinone derivative melting at 116°.

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[1] Reid, Mackall and Miller, This Journal, **43,** 2108 (1921).

[2] Hoffman and Reid, *ibid.,* **45,** 1835 (1923).

The colors of the anthraquinone derivatives were also found to be indeterminate and varied with the solvent used and the conditions of crystallization, though the orange predominated.

The effect of sodium in a medium of absolute alcohol was tried on several disulfides, according to the method used by Drogin and Rosanoff[3] for the estimation of halogens. The ethyl-, butyl- and *iso*-amyl disulfides gave mercaptans, while benzyl disulfide yielded dibenzyl and hydrogen sulfide.

As sodium reacts so readily, it was thought that magnesium, which attacks alkyl halides so vigorously, might react as well, but such was not found to be the case, although the mixtures were heated to boiling. Higher-boiling solvents such as benzene and xylene were also substituted for the ether but without result.

Some experiments were made with sodium and the disulfides without any solvent. The same sort of reaction appeared to take place, but not so readily.

Experimental Part

To 50 cc. of dry ether and 5 g. of freshly cut sodium in a flask provided with a reflux condenser protected by a calcium chloride tube, 9.5 g. of butyl disulfide was added in portions through the condenser. A vigorous reaction took place which was moderated by cooling. After the mixture had been heated on a water-bath for an hour the ether was poured off and the white-yellow material detached from the unreacted metal.

In several experiments an attempt was made to determine the yield by weighing the sodium mercaptide after warming it in a vacuum to remove the ether, but the weight was much greater than the calculated, which was found to be due to the ether which is strongly held by the flaky material. In other experiments the mercaptide was thrown onto ice in the presence of a weak acid and the mercaptan collected. In others, the flaky mercaptide was added directly to the sodium α-anthraquinone sulfonate.

To identify the mercaptan the product was added to 3.1 g. of sodium anthraquinone-α-sulfonate dissolved in 70 cc. of hot water containing 2 g. of sodium hydroxide. This mixture was boiled under a reflux condenser for about four hours, and the anthraquinone-thio-ether filtered off and recrystallized.

The reactions with the other disulfides were carried out in exactly the same way except with the methyl and ethyl disulfides—which reacted very slowly. These were warmed with the sodium and ether in pressure bottles for 10-20 hours. The excess of sodium was removed and the necessary alkaline solution of sodium anthraquinone sulfonate added to the residue in the pressure bottle which was then closed and again heated.

Summary

The action of sodium in anhydrous media on alkyl sulfides and disulfides has been studied. With the sulfides reaction is extremely slow and does not lead to definite products but most disulfides react readily to give sodium alkyl mercaptides. The same products are obtained in absolute alcohol. Magnesium does not react under these conditions.

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[3] Drogin and Rosanoff, THIS JOURNAL, **38**, 711 (1916).