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The alkylation of dimethylaniline with ethylene glycol sulfite

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THE ALKYLATION OF
DIMETHYLANILINE WITH ETHYLENE GLYCOL SULFITE

A thesis presented to the Department of
Chemistry at Union College in partial fulfilment
of the requirements for the degree of Bachelor
of Science with a major in Chemistry.

Name John R. Draves
Approved by H. F. Herbrandson
Date Jan. 21, 1948

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INTRODUCTION

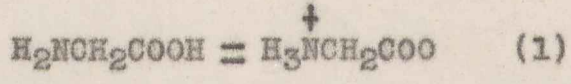
The alkylation of ter.-amines with alkylchlorosulfinates and alkylsulfites has been of interest in producing various betaine salts. Most of the work reported in the literature has been with ter.-aliphatic amines, amino acids, pyridine, straight-chain sulfites, and chlorosulfinates. No work has been reported on the alkylation of ter.-aromatic amines with cyclic sulfites and the betaine salts produced.

The purpose of this investigation was to isolate and characterize the betaine salt produced by the alkylation of a ter.-aromatic amine with a cyclic sulfite. The reaction chosen was that between dimethylaniline and ethylene glycol sulfite.

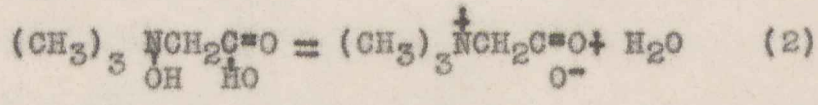
HISTORICAL

Certain types of organic compounds which contain acidic and basic functional groups are capable of existing in ionic form. These compounds are analogous to inorganic salts and are soluble in water but insoluble in non-polar organic solvents such as ether and benzene.

The most common examples of this type of compound occur in the amino acids. In alpha-amino acids the zwitter ion effect is observed.



Another possibility is exemplified by betaine which may be regarded as the internal salt of the quaternary ammonium hydroxide of dimethyl glycine.

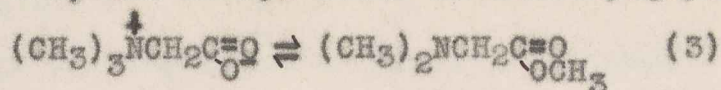


According to Karrer (1) when betaine is heated in a sealed

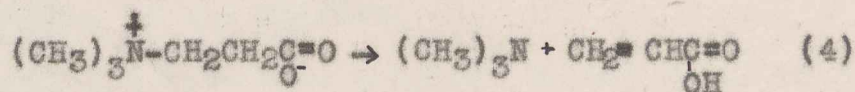
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tube at 170 to 200°, the methyl ester of dimethylglycine is formed.

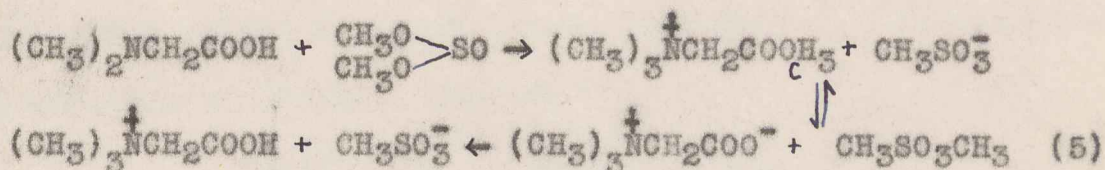


However, the betaine of beta-dimethyl alanine decomposes into trimethylamine and acrylic acid when heated.



A number of investigators have reported that betaine-type salts are formed by alkylation of ter.-amines with alkylchlorosulfonates and alkylsulfites.

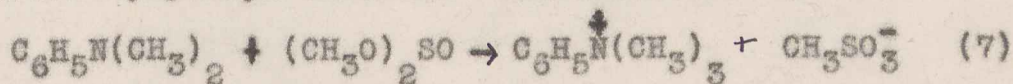
Using dimethylglycine and dimethylsulfite, Voss and Blanke (2) obtained a hygroscopic betaine salt plus the methyl ester of methane sulfonic acid.



With pyridine and dimethylsulfite at room temperature the product was N-methylpyridium methanesulfonate according to Voss and Blanke (3). The product was red, hygroscopic, and melted from 117° to 118°.



Dimethylaniline and dimethylsulfite at 140° gave a 99 per cent yield of trimethylphenyl ammonium methanesulfonate.



Gerrard (4) has reported that the alkylation of pyridine with alkylchlorosulfonates yields alkylpyridium salts.

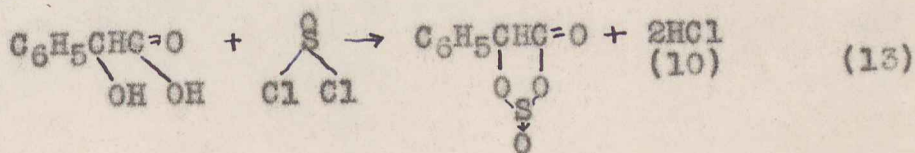
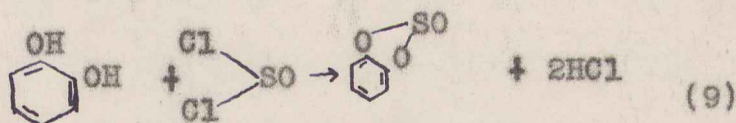
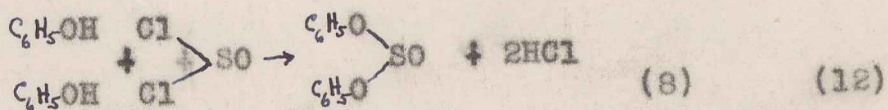
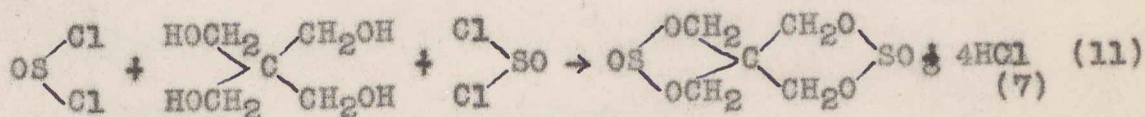
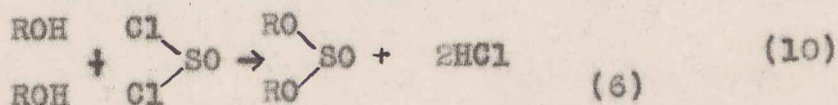
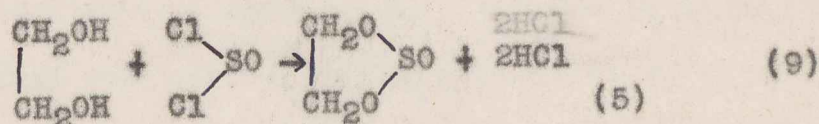


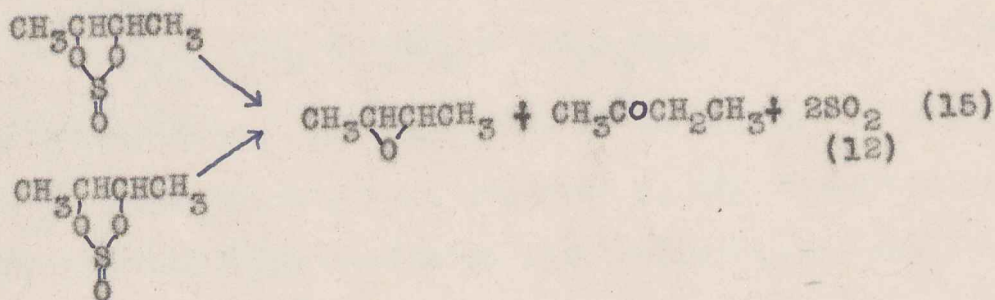
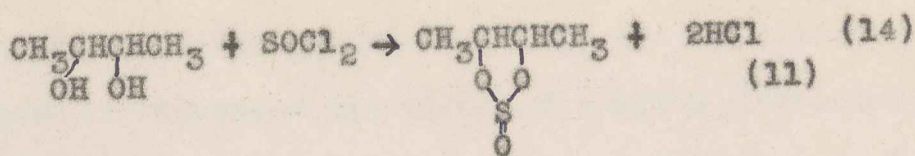
where R equals methyl, ethyl, propyl, butyl, iso-propyl, iso-

butyl, and iso-amyl.

Because it was necessary to prepare the sulfite of ethylene glycol used in the reaction under consideration in this paper, the literature was consulted in order to find a suitable method for the preparation of the sulfite.

Organic sulfites have been prepared by the reaction of thionylchloride on certain hydroxy compounds. According to the literature the reaction appears to be general for primary and secondary alcohols, phenol, and polyhydroxy compounds in which the hydroxyl groups are adjacently located so as not to be affected by steric hindrance. In any case the reaction proceeds generally by the formation of two molecules of hydrogen chloride from the hydrogen atoms of two hydroxyl groups and the two chlorine atoms from a molecule of thionyl chloride.

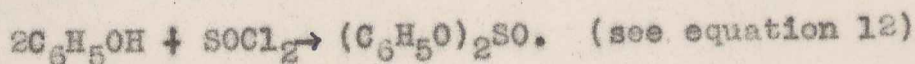




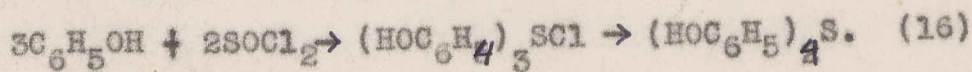
Denivelle (11) used the sulfite of 2,3-butanediol (equation 14) to obtain a ten per cent yield of butadiene. He has reported that in the presence of kaolin the sulfite decomposes at 575° to give a small amount of butadiene. At 275° without kaolin the sulfite decomposes to 2,3-epoxybutane and methyl ethyl ketone (equation 15).

From the literature it appears that the reaction of phenol with thionylchloride can give three products depending on the conditions of the reaction and the relative amounts of reactants used.

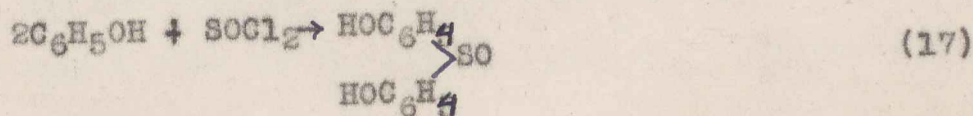
According to Richter (6)



Carre and Liebermann(13) have reported that

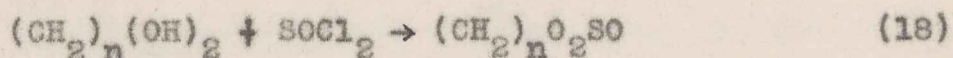


By carrying out the reaction in carbondisulfide at zero degrees and in the presence of anhydrous aluminum chloride, Smiles and Baine(14) obtained a sulfone.



Polyhydroxy compounds with the hydroxyls adjacently located

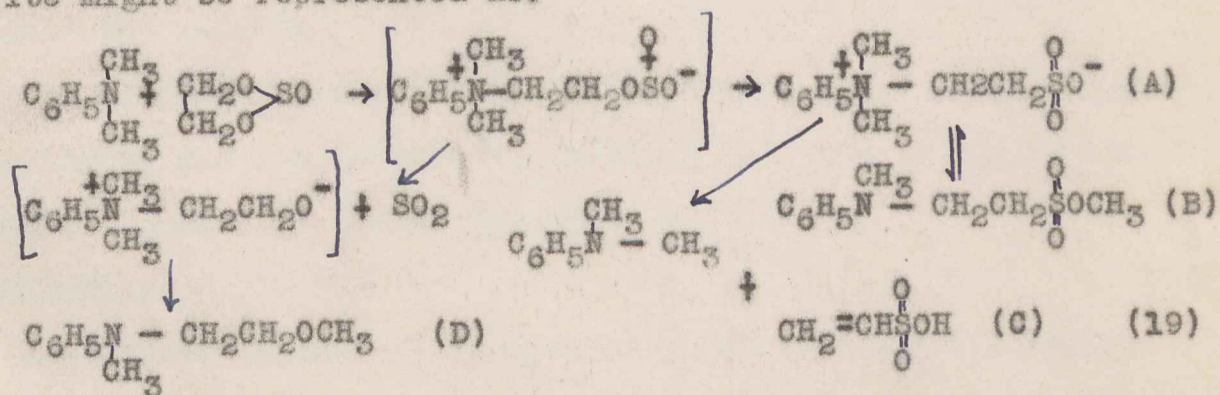
give quantitative yields of the sulfite. As the distance between the hydroxyls is increased the yield of sulfite decreases and the dichloride is formed. Weist(15) has reported that



up to n equals four. But Majima(5) in an attempt to prepare the sulfite of trimethyleneglycol obtained mostly trimethylenechloride. Green(9) reacted thionylchloride with hydroquinone and obtained only para- $\text{C}_6\text{H}_4(\text{OSOCl})_2$.

THEORY OF THE ALKYLATION OF DIMETHYLANILINE WITH ETHYLENE GLYCOL SULFITE

From preliminary considerations based on equations (1) through (8) the reaction between dimethylaniline and the glycol sulfite might be represented as:



Product (A) is of the betaine type and analogous to that of equations (3) and (4). Product (D) was suggested as a further possibility when sulfur dioxide was detected during the reaction. Equation (19) is hypothetical and was formulated, on the basis of reactions given in the literature, merely as an aid in interpreting the reaction here in question. At the most it probably represents only a part of the actual reaction. Preparation of the sulfite of Ethylene Glycol:

The glycol sulfite was prepared at room temperature according

to equation (9) by the dropwise addition of three moles of thionylchloride to three moles of ethyleneglycol contained in a three-neck flask equipped with a dropping funnel and reflux condenser. The time of addition was approximately one hour during which period the flask was occasionally shaken. To prevent hydrolysis of the thionylchloride by atmospheric moisture the condenser and funnel were fitted with drying tubes.

Although the reaction was carried out at room temperature, the initial stage of the reaction produced much heat thereby necessitating the condenser to prevent the escape of thionylchloride before it had reacted. During the remainder of the reaction the temperature dropped gradually to below that of the room. After the addition of the thionylchloride, the mixture was heated to complete the reaction.

The sulfite was distilled from the reaction at reduced pressure. The material was a colorless oil boiling from 166° to 168° at atmospheric pressure. Majima (5) gives 169° to 172°.

EXPERIMENTAL

Equivalent amounts of anhydrous dimethylaniline and glycol-sulfite were mixed in the cold giving a reddish color. The mixture was refluxed for three hours or as long as sulfur dioxide could be detected at the top of the condenser with litmus paper. The temperature of reflux ranged from 163° to 205° approximately. The reaction mixture was extracted with water and ether.

The water layer was evaporated leaving a reddish brown, highly viscous, material soluble in ethanol and insoluble in ethyl acetate, and benzene. When treated with a sodium hydroxide solution, an aqueous solution of the material gave a precipitate

soluble with effervescence in hydrochloric acid. The gas evolved may have been sulfur dioxide.

On dissolving a portion of the material in ethanol a small amount of solid precipitated which did not melt below 250°. When heated in a porcelain spatula over an open flame the solid decomposed giving off an amine-like odor. An attempt was made to obtain more of the solid by using an excess of ethylacetate as a precipitating agent. However, when ethylacetate was added to an alcoholic solution of the viscous material, only a milky color resulted.

Because the samples taken probably contained enough water to effect the solution of any salt that might have been present, an attempt was made to dehydrate the viscous material. Absolute ethanol and ethylacetate might then be used for precipitation.

Accordingly benzene was added to the material followed by evaporation. Failure resulted because it was mechanically impossible to break up the material. Direct distillation at a high vacuum might have succeeded in reducing the material to an anhydrous state but a vacuum pump was not available. Further attempts to characterize the material had to be discontinued at this point. The only additional information obtained about the material was that when left exposed to the air, particularly while in solution, it turned a deep blue.

The ether layer, dried over anhydrous magnesium sulfate, was evaporated leaving a brownish liquid with an amine odor. A methiodide derivative was made to determine whether or not the liquid was dimethylaniline. A decomposition point of 173° instead of 223° was obtained. To purify the liquid fractionation was conducted at atmospheric pressure. The liquid began to distill at

197°. Fractionation was impossible because the boiling point rose steadily without leveling off. Only a low-boiling fraction from 197° to 250° and a high-boiling fraction from 250° to 330° were cut.

Attention was immediately directed to the high-boiling liquid which was steam distilled to remove any decomposition products. A small amount of oil was recovered which tested for sulfur.

To avoid high temperatures the fractionation procedure was modified and repeated on another sample of the liquid recovered from the ether layer. The liquid was first steam distilled in acid solution to remove any non-amine products. A few milliliters of oil came over. Next the solution was made alkaline and the liberated oil steam distilled. About half of this material came over as a light yellow oil which when distilled at a atmospheric pressure yielded a small amount of oil boiling from 192° to 195° and characterized as dimethylanilin. The remainder of the oil boiled up to 210° and higher.

The oil which did not steam distil was extracted with benzene followed by evaporation and the oil recovered distilled at reduced pressure of the water pump. Distillation began at 124° and again the temperature rose steadily without leveling off. A low-boiling fraction was taken from 124° to 160° and a high-boiling fraction from 160° to 250° which was a yellow, syrupy oil that gave a slight test for sulfur. Higher boiling material remained in the claisen flask when distillation was stopped at 250°.

Because an efficient column was available to fractionate the oil, no further work could be done on separating the components

of the ether-soluable products.

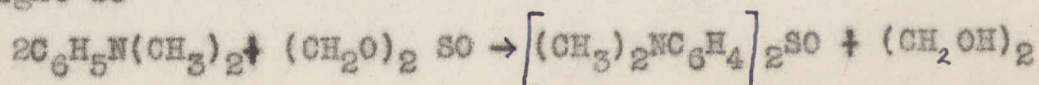
To compare with the previous derivative taken of the oil a methiodide was made of the high-boiling cut just mentioned (160° to 250°). It decomposed from 203° to 207°. As with the former derivative the latter decomposed slowly over a 10° to 15° range. The final stage of decomposition was more rapid and the greater part of the material decomposed over a comparatively narrower range.

Like the aqueous material the ether-soluable material, particularly the high boiling, oxidized to a deep blue color when exposed to the air.

RESULTS

Because no products were characterized, a definite conclusion can not be made as to their identity. However, it can be said with certainty that equation (19) is far from giving a complete picture of the reaction. The presence of water soluable material does, in this case, imply a salt. The high decomposition point of the solid recovered is a further indication of a salt which might be compound (A) of equation (19). The milky color obtained by adding ethylacetate to an alcoholic solution of the viscous material indicates a liquid, possibly compound (C)

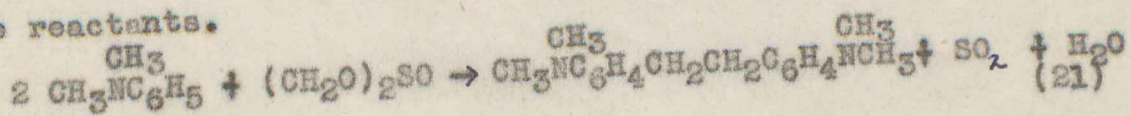
However, the reaction is complicated by the presence of some substance which readily oxidizes to a blue dye. The theoretical reaction does not account for such a compound. Smiles and Baine (14) have reported that $(\text{HOC}_6\text{H}_4)_2\text{SO}$ turns a prussian blue when treated with sulfuric acid. An analogous compound in the present case might be



Although Richter (6) has reported that the sulfites of dihydroxy aromatics are highly viscous and often waxy (a description which fits the state of the aqueous product), it is unlikely that the sulfone of equation (20), despite its similarity to $(\text{HO-C}_6\text{H}_4)_2\text{SO}$ and to a dihydroxy aromatic sulfite, would be water-soluble. It would probably be ether-soluble, however.

Work with the ether-soluble material showed that all the sulfite and most of the dimethylaniline were used up in the reaction. The fact that the ether residue gave no material boiling lower than 193° indicates that the sulfite, b.p. 167° , must have been consumed in the reaction. The ether residue is obviously a mixture of several compounds with increasingly higher boiling points starting with 193° of dimethylaniline. The sulfur-containing component appears to be low-boiling compared to the rest of the material and can be steam distilled. The high-boiling material which did not steam distil contains little or no sulfur-containing components. Compound (B) of equation (19) probably boils above 200° and might be the sulfur containing-component as might the sulfone of equation (20). Although compound (D) contains no sulfur it probably boils above 193° and would also be present in the low-boiling material.

The high boiling material must be a mixture of high molecular weight amines not accounted for in the theoretical reaction and which can be oxidized to a blue dye. To account for these observations it must be that along with the addition reaction (19) there is also a substitution reaction involving several molecules of the reactants.



The above reaction exemplifies this substitution. In turn the product might react with two more molecules of the sulfite by addition to the nitrogens as in equation (19). Containing four benzene rings, the final compound would have a sufficiently high molecular weight to account for the high boiling point observed and might conceivably be oxidized to a dye.

CONCLUSION

The alkylation of dimethylaniline with ethylene glycolsulfite was expected, on the basis of similar reactions reported in the literature, to give a salt of the betaine type. During the investigation of the products of the reaction in an effort to isolate and characterize the expected salt it was found, that the reaction is complicated by the formation of some high-boiling compound (or compounds) which is easily oxidized to a blue dye.

Although the reaction gave a considerable amount of water soluble material which appeared to be salt-like in nature, mechanical difficulties with this highly viscous and hygroscopic material prevented the characterization of any salt which might have been present.

The ether-soluble material revealed a mixture of high molecular weight amines with increasingly higher boiling points. Sulfur was detected in the lower boiling fraction of this mixture but only slightly in the higher boiling fraction, leading to the conclusion that the ether-soluble dye is probably a very complex amine containing no sulfur.

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