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REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION

V. THE SYNTHESIS OF OXYGEN AND SULFUR ETHERS AND OF ALKYL DERIVATIVES OF AMMONO ACIDS

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Many organic compounds containing hydroxyl, sulfhydroxyl, amino or imino groups in their molecules have an acidic function in liquid ammonia, and form salts in that solvent with the alkali metals, or in some cases preferably with the alkali metal amides.[1] Such salts may react with certain organic halides, the hydrocarbon radical of the latter replacing the metal atom of the salt. The object of the present investigation was to study the general character of these reactions.

From a consideration of the stoichiometrical relations of the reacting materials it is apparent that the reactions between the salts and halides often proceed practically quantitatively, particularly in those cases where there is no action between the halide and liquid ammonia. However, it is sometimes difficult, especially in working with small amounts of materials, to isolate the entire product. This is particularly true with low-boiling liquids more or less soluble in water, since in these cases much of the products may be lost in distilling the ammonia according to the procedure employed. While the yields recorded in this article represent appreciable amounts of carefully purified products isolated from the reaction mixtures, they are not to be regarded as indicating the maximum yields which might be obtained if the yields were made the primary object of the investigation.

The reactions which occur at a temperature of approximately —33° are usually completed within five minutes or less time. Indeed, the rate of reaction is often determined by the solubility of intermediate products. They thus approach the ionic type of reactions, whereas similar syntheses in other media often require much higher temperatures and many hours time for only partial completion.

Numerous observations, more or less qualitative, have been made regarding the solubility and reactivity of substances in liquid ammonia, and these are presented since such observations are necessary for the further development of the study of organic reactions in liquid ammonia in general.

Oxygen ethers were synthesized by a method analogous to that of Williamson, ROMe + RX = ROR + MeX, the alcoholates being formed

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[1] Previous articles in this series are (a) Kraus and White, THIS JOURNAL, **45**, 768 (1923); (b) White, *ibid.*, **45**, 779 (1923); (c) White and Knight, *ibid.*, **45**, 1780 (1923); (d) Kraus and Kawamura, *ibid.*, **45**, 2756 (1923).

in liquid ammonia. The solubility of the alcoholates varies very largely and has a great influence on the yield of ether as obtained from a given amount of alcohol. The saturated aliphatic alcoholates are relatively insoluble and a quantitative reaction for their synthesis is often difficult to attain;[2] the alkali metal phenolates, however, are generally appreciably soluble in liquid ammonia and react more readily, especially with the alkyl halides.

Where the metal has a reducing action on the hydroxyl compound in the formation of the alcoholates, the ethers cannot be synthesized by the above methods. In forming the sodium naphtholates a reducing action was noted, tetrahydronaphthol derivatives being formed by the hydrogen set free by the action of the sodium on the naphthol hydroxyl group. On the addition of alkyl halide to the reduction mixture, where the naphthol and sodium were allowed to react in equivalent amounts, a mixture of ethers of naphthol and tetrahydronaphthol was obtained. The synthesis of a pure naphthol ether in liquid ammonia is very simple, however, since a pure alkali metal naphtholate may be readily formed by the action of the ammono base, potassium or sodium amide, on the naphthol: $C_{10}H_7OH + KNH_2 = C_{10}H_7OK + NH_3$. Alkyl ethers are readily produced from such naphtholates.

Alkyl-aryl thio-ethers were synthesized in liquid ammonia according to the general reaction expressed as follows: $RSMe + RX = RSR + MeX$. These thio-ethers are produced exceedingly readily, sodium thiophenolate being appreciably soluble in liquid ammonia, and thiophenol itself being more acidic than phenol.[3] The thiophenol ethers may also be synthesized from the alkyl halides and thiophenol directly without the necessity of intermediate sodium thiophenolate formation. It is very probable that true aliphatic thio-ethers could be easily made by the action of alkyl halides on sodium mercaptides in liquid ammonia or possibly on the mercaptans themselves.

Those organic compounds containing an amino or imino group of more or less acidic function in liquid ammonia react with the alkali metals or metal amides and form alkali metal salts: $>N\text{-}H + MeNH_2 = >N\text{-}Me + NH_3$. Franklin and Stafford[4] first observed this fact in connection with the reactions of potassium amide with certain acid amides, and later

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[2] This latter fact may be due to the physical condition of the mixture (Ref. 1a, p. 770), or perhaps to the formation of compounds of the general composition $(ROMe)_x\cdot(ROH)_y$ which are precipitated from solution whereby an excess of dissolved metal remains unattacked. The precipitates do not appear to be crystalline.

[3] The acids employed throughout this investigation were all weak acids and the relatively strong acids reacted more readily with alkyl halides than the weaker ones. It is possible that alkyl derivatives of even stronger acids could be synthesized in liquid ammonia.

[4] Franklin and Stafford, *Am. Chem. J.*, **28**, 95 (1902).

Franklin[5] prepared other metal derivatives of similar compounds. We have studied the reactions of such potassium salts with certain organic halides and have found that they react with alkyl halides but not with aryl halides. In this way N-ethyl derivatives of aceto-amide, aniline, acetanilide, diphenylamine, and of phthalimide (Gabriel synthesis in liquid ammonia) were formed.

Experimental Part

Apparatus and Procedure.—The apparatus and experimental procedure were in general similar to those that have been described by White.[6]

Action of Organic Halides on Liquid Ammonia.—Twenty-two g. of each halide mentioned below was introduced into about 25 cc. of liquid ammonia and any reaction was allowed to proceed for 30 minutes. Methyl iodide began to react almost immediately, a white crystalline precipitate soon forming and the reaction becoming very vigorous. The ammonia was evaporated and a large amount of residue, which proved to be tetramethylammonium iodide, was obtained.

Ethyl iodide treated with liquid ammonia as described above reacted with it but very little. A small amount of precipitate was obtained and little residue after evaporating the ammonia. Benzyl chloride was likewise found to react with liquid ammonia to a slight extent. Ethyl bromide, *n*-butyl bromide, ethylene bromide and phenyl iodide did not react.

The above-mentioned halides, with the exception of phenyl iodide, react with certain salts in liquid ammonia as shown below. Evidently, the yield of methyl or ethyl derivatives of such salts partly depends on the relative velocities of the reactions between methyl or ethyl *iodide* with the salt concerned and with the solvent ammonia. In alkylations of this kind this fact should be considered in attempts to obtain maximum yields of alkyl compounds. Of course, particularly in methylations, syntheses would not proceed quantitatively.

Oxygen Ethers

Ethyl Ether.—As has been noted,[7] ethyl alcohol and sodium do not react in the exact proportion of 1 molecule of alcohol to 1 atom of sodium in liquid ammonia, a white precipitate being formed and an excess of sodium being left in the solution.

In an experiment of this kind 1.6 g. of sodium was allowed to react with 6.4 g. of absolute alcohol whereby a white precipitate and a blue solution resulted. On the further addition of 5.6 g. of alcohol the precipitate dissolved and the solution became colorless. These quantities of reagents correspond approximately to the formation of a soluble compound of the formula $C_2H_5ONa.C_2H_5OH$. Similarly, 0.56 g. of potassium

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[5] Franklin, This Journal, **37**, 2279 (1915).

[6] Ref. 1b, p. 780.

[7] Ref. 1a, p. 770.

added to 0.66 g. of alcohol (1 molecular equivalent to 1 atomic equivalent) produced a white precipitate and a blue solution, showing incomplete action of the metal.

Ethyl ether was prepared from potassium ethylate made by the action of potassium amide on alcohol, since the reaction between potassium amide and alcohol proceeds quietly, and since it appears that the potassium alkylates are somewhat more soluble than the sodium alkylates.

Two and two-tenths g. of potassium was dissolved in liquid ammonia and converted into amide by the action of ferric oxide introduced into the reaction tube by the addition of a rusty iron nail; 2.6 g. of alcohol was added and a white precipitate of alcoholate resulted. The yellow color of the solution due to the presence of potassium amide disappeared, indicating that the amide had largely entered into reaction. On the addition of 8.8 g. of ethyl iodide a vigorous reaction ensued, the precipitate dissolved and a clear. colorless solution was obtained. The ammonia was distilled under water saturated with ether; yield of ethyl ether, 2.9 g. or 71%. This yield was considerably lowered due to the fact that the solubility of ether in water is markedly increased by the presence of ammonia.

Ethyl-*n*-butyl Ether.—Potassium amide, derived from 2.1 g. of potassium in liquid ammonia, was treated with 2.59 g. of absolute alcohol. The precipitated potassium ethylate dissolved after the addition of 7 g. of *n*-butyl bromide. On distillation under water 1.1 g. of ethyl-*n*-butyl ether, a 19% yield, was obtained. This yield was lowered because of the appreciable solubility of the ether in water.

A negligible amount of ethylbutyl ether was formed by treatment of potassium *n*-butylate with ethyl iodide, indicating that the butylate is more insoluble in liquid ammonia than the ethylate. Further, there was no appreciable reaction when potassium butylate was treated with *n*-butyl bromide, so that *n*-butyl ether cannot be synthesized by this method.

Ethylene Glycol Ethers.—Glycol, which is soluble in liquid ammonia, was found to react quantitatively with sodium with the evolution of hydrogen and the formation of the white, insoluble monosodium glycolate. This glycolate was stable toward an excess of sodium and hence must be very insoluble. It did not react with ethyl bromide but (as formed from 5.2 g. of sodium and 14.0 g. of glycol) reacted very slowly with ethyl iodide, and a small amount of glycol monoethyl ether was isolated.

Since the glycol monoethyl ether is soluble in liquid ammonia, it undoubtedly would form an alkali metal salt in liquid ammonia. Thus further alkylation should be possible. It is suggested that such progressive alkylations of polyhydroxy compounds may be more practicable in certain other cases where the alcoholates are more soluble.

Ethylbenzyl Ether.—To the colorless solution of 2.2 g. of potassium treated with 5.2 g. of absolute alcohol (1 atomic equivalent of metal to 2 molecular equivalents of alcohol) 7.1 g. of benzyl chloride was added, whereupon a white precipitate immediately formed. The ammonia was evaporated, water was added and the aqueous solution extracted with ether. The ether extract was dried with solid sodium hydroxide and distilled; yield of ethylbenzyl ether, 6.2 g., or 81%.

Two g. of potassium was treated with 5.5 g. of benzyl alcohol, the reaction being rapid and complete, potassium benzylate precipitating as a white solid; 10 g. of ethyl iodide was added, the benzylate dissolved and ethylbenzyl ether was isolated as described above; yield, 2.8 g., or 40%.

Benzyl Ether.—The reagents were 2.2 g. of potassium, 6.1 g. of benzyl alcohol and 7.2 g. of benzyl chloride; yield of benzyl ether, 6.1 g., or 55%.

Stability of Sodium Phenolate.—Four g. of phenol was dissolved in liquid ammonia and 1 g. of sodium was added (1 molecular equivalent of phenol to 1 atomic equivalent of sodium). Reaction was rapid, the sodium phenolate at first remaining in solution but precipitating as it increased in amount. All of the sodium was decolorized. On the addition of 0.45 g. more of sodium no action took place and the solution remained blue for 18 hours. Sodium phenolate is, therefore, not reduced by sodium.

Anisole.—The reaction between methyl iodide and sodium phenolate has been observed by Kraus and White.[8] A solution of 26.8 g. of phenol in liquid ammonia was treated with 6.6 g. of sodium. Gaseous methyl chloride was then passed into the mixture. It was difficult to observe any change in the character of the precipitate, since the insolubility of the sodium chloride formed obscured the disappearance of the sodium phenolate; 13.1 g. of anisole was isolated, a 42% yield. Considerable phenol was recovered, being partially set free from its sodium salt in the process by the action of ammonium chloride which was a by-product of the action of methyl chloride on ammonia.

Phenetole.—The preparation of this ether was carried out on a larger scale. Fifty-one g. of melted phenol was pipetted into 300 cc. of liquid ammonia contained in a large Dewar tube; 14 g. of sodium cut into small pieces was slowly added, the reaction being rapid with continuous evolution of hydrogen. A slight excess of sodium at the end of the reaction was evidenced by the blue color of the solution, the water in the crude ammonia employed thus being eliminated; 63 g. of ethyl bromide was then slowly added to the clear solution, the excess of sodium first reacting with the halide with the evolution of ethane and ethyl amine. The phenetole formed was soluble in the liquid ammonia, the decrease in quantity of which was made up by refilling the tube with ammonia. The ammonia was allowed to evaporate overnight, water was added to the residue, an ether extraction was made, and 39.4 g. of phenetole was obtained; yield, 59.5%.

Twenty g. of phenol and 45 g. of ethyl iodide in liquid ammonia were allowed to stand for 44 hours. The clear solution was distilled from an oil-bath and 3 g. of phenetole obtained. There was very little ethyl iodide in the final reaction mixture, indicating that it had partially volatilized with the ammonia and partly been converted into a substituted ammonium salt, this being left as a white residue after distillation of the phenetole. Evidently, phenol is not sufficiently acidic to react very rapidly with ethyl iodide.

***n*-Butylphenyl Ether.**—The reagents were 10 g. of phenol, 2.4 g. of sodium and 14.6 g. of *n*-butyl bromide; yield of *n*-butylphenyl ether, 4.5 g., or 28%.

Ethylene-diphenyl Ether.—Sodium phenolate was found to react neither with ethylene bromide nor with ethylene chloride.

Reduction of α-Naphthol.—To 2.88 g. of α-naphthol suspended in liquid ammonia was added 0.46 g. of sodium (1 molecular equivalent of naphthol to 1 atomic equivalent of sodium). The naphthol dissolved, and a clear, light yellow solution with no precipitate was obtained. No gas was given off during the reduction. From the evidence presented below the reaction may be expressed as follows: $4C_{10}H_7OH + 4Na = 3C_{10}H_7ONa + C_{10}H_{11}ONa$, the naphthol being partially reduced to tetrahydronaphthol; 0.46 g. of sodium was then added and this entered into complete reaction after three hours, the solution becoming light yellow and a white crystalline precipitate being formed. Water was added, the ammonia was evaporated, and a clear, aqueous solution resulted. This was acidified with hydrochloric acid and a white precipitate was obtained which melted to an oil when warmed. This mixture was extracted with petroleum ether and from the petroleum ether solution crystals of *ar*-tetrahydro-α-naphthol were isolated.

The white precipitate formed with an excess of sodium in the above reduction was sodium amide as is apparent from the following experiment. One g. of sodium was dissolved in liquid ammonia and 1.57 g. of α-naphthol was added. A white crystalline precipitate settled out and the solution was still blue after three hours; 0.2 g. of naphthol was added and this caused the blue color to disappear, so that the ratio was 1 molecule of

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[8] Ref. 1a, p. 770.

naphthol to 3.5 atoms of sodium, approximately agreeing with the following equation, $C_{10}H_7OH + 4Na + 3NH_3 = C_{10}H_{11}ONa + 3NaNH_2$, the complete reduction probably requiring a considerably longer time. Three cc. of phenyl iodide was now added to the mixture; the white precipitate dissolved and the solution assumed a deep red color. This color is produced in the action of sodium amide on aniline. The ammonia was evaporated and a little aniline was isolated from the residue after treatment with water. The aniline resulted from the action of sodium amide on phenyl iodide: $C_6H_5I + NaNH_2 = C_6H_5NH_2 + NaI$.

Reduction of β-Naphthol.—In experiments similar to those with α-naphthol, it was found that β-naphthol is reduced by an excess of sodium in liquid ammonia. *ac*-Tetrahydro-β-naphthol and *ar*-tetrahydro-β-naphthol were isolated as reduction products. Ethers prepared from the naphtholates in liquid ammonia in the usual way would hence be contaminated with the ethers of the tetrahydronaphthols, which latter would be difficult to separate on account of their relatively small quantities. The ethers are best made by the action of alkyl halides on naphtholates prepared by the action of metal amides on the naphthols.

Ethyl-β-naphthol Ether.—The reagents were 2.8 g. of potassium converted into amide, 10.3 g. of β-naphthol and 14 g. of ethyl iodide. At first the solution contained no precipitate, but in 10 minutes a white crystalline precipitate of the ether formed; yield of ethyl-β-naphthol ether, 7.5 g., or 61%.

A trace of the same ether was obtained by treating free β-naphthol with ethyl iodide in liquid ammonia.

Resorcinol-monoethyl Ether.—Resorcinol dissolves very readily in liquid ammonia. To 8 g. of resorcinol in liquid ammonia 1.67 g. of sodium was added (1 molecular equivalent of resorcinol to 1 atomic equivalent of sodium). The monosodium salt was found to be very soluble; 11.4 g. of ethyl iodide was then added. The reaction was rapid and was complete in one minute, a clear greenish-yellow solution being obtained. The subsequent operations of isolating the pure product, involving distillation with steam from an acid solution and extraction with ether of the distillate made alkaline with sodium hydroxide, account for the low yield—9%—of monoethyl ether which was obtained. Also, considerable diethyl ether was formed.

Resorcinol-diethyl Ether.—The reagents were 3 g. of resorcinol, 0.63 g. of sodium (1 molecular equivalent of resorcinol to 2 atomic equivalents of sodium) and 5.7 g. of ethyl bromide. The disodium salt of resorcinol was found to be rather insoluble in liquid ammonia, and it reacted only slowly with the ethyl bromide. Hence, 8 g. of ethyl iodide was added to the mixture. The reaction was then more rapid and a clear greenish-yellow solution with a little precipitate of sodium bromide was obtained; yield of resorcinol-diethyl ether, 1.4 g. or 32%.

Thiophenol Ethers

Thiophenolates.—As was pointed out in the first article of this series,[7] thiophenol reacts with liquid ammonia to form a compound, undoubtedly ammonium thiophenolate, which is somewhat soluble in liquid ammonia. The same compound is formed when ammonia gas is passed into thiophenol; a white, crystalline, odorless solid is formed which slowly hydrolyzes in the air with the evolution of ammonia and the formation of thiophenol. The ammonium thiophenolate is insoluble in petroleum ether and may be washed free from any excess of thiophenol with that liquid.

On adding sodium to the liquid ammonia solution of the ammonium thiophenolate, sodium thiophenolate is formed and this salt is very soluble in liquid ammonia.

Ethylphenyl Thio-ether.—The reagents were 16.1 g. of thiophenol, 3.4 g. of sodium and 20 g. of ethyl bromide. The thio-ether separated from ammonia solution as a waxy solid; yield, 16.6 g., or 82%.

It is unnecessary to prepare the sodium phenolate in the synthesis of the thio-ether as the ammonium thiophenolate readily reacts with alkyl halides. Thus when 5.3 g. of thiophenol was added to 6 g. of ethyl bromide in liquid ammonia, reaction soon occurred and the thio-ether precipitated; yield, 5 g., or 76%.

***n*-Propylphenyl Thio-ether.**—The reagents were 10.7 g. of thiophenol and 20.0 g. of *n*-propyl iodide; yield, 12.7 g., or 86%.

Dithioglycol-diphenyl Ether.—The reagents were 10 g. of thiophenol, 2.1 g. of sodium and 10 g. of ethylene bromide; yield, 10.5 g., or 98%.

N-Alkyl Derivatives of Ammono Acids

Ethyl Acetamide.—Seven-tenths g. of potassium was converted into amide in liquid ammonia and to this solution was added 1.05 g. of acetamide. Potassium acetamide precipitated and to the mixture was then added 1.90 g. of ethyl bromide. The reaction was rather slow, the precipitate requiring more than five hours to dissolve (probably ethyl iodide would be more reactive). The ammonia was evaporated and a residue of crystals (potassium bromide) and a colorless liquid remained. The mixture was transferred to a small distilling flask and distilled; yield, 0.5 g., or 34%.

Ethyl and Diethyl Anilines.—The formation of these compounds from the alkali metal anilides has been previously described.[9] We have further studied the action of potassium amide on aniline in liquid ammonia and have found that an excess of potassium amide has very little effect on monopotassium anilide, so that the dipotassium salt cannot be formed in appreciable quantity by this reaction within a few hours at least. By the action of ethyl bromide on the above mixture of monopotassium anilide treated with an excess of potassium amide, monoethyl aniline and only traces of diethyl aniline were obtained.

Ethyl-diphenyl Amine.—The reagents were 0.35 g. of potassium converted into amide, 1.5 g. of diphenylamine and 0.68 g. of ethyl bromide. Potassium diphenylamide was found to be soluble and to react immediately with ethyl bromide, a white precipitate of potassium bromide separating from the solution; yield, practically quantitative.

Ethyl Acetanilide.—The reagents were 1 g. of potassium converted into amide, 3.46 g. of acetanilide and 2.7 g. of ethyl bromide. Potassium acetanilide was soluble in ammonia and reacted readily with the ethyl bromide; yield, 1.6 g., or 40%.

Ethyl Phthalimide.—To a solution of 1.35 g. of phthalimide in liquid ammonia 0.36 g. of sodium amide, broken into small pieces, was added. Ethyl bromide was then introduced into the reaction mixture in small amounts at intervals of time in order to convert the insoluble sodium phthalimide which incrusted the surface of the sodium amide into soluble ethyl phthalimide. The ammonia was evaporated, water added, and long needles of ethyl phthalimide were isolated in small quantity.

Summary

Various oxygen and sulfur ethers and N-alkyl derivatives of ammono acids (alkyl esters of ammono acids) were synthesized in liquid ammonia by the action of potassium or sodium salts of the alcohols, phenols, naphthols, thiophenol and ammono acids on the alkyl and benzyl halides. Aryl halides such as phenyl iodide were found to react with no salt employed.

The reaction depends on the solubility of the alkali metal salts in liquid ammonia, on the degree of acidity of the compounds from which the salts are prepared, and on the relative rates of any reactions between the

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[9] Ref. 1c, pp. 1786–1787.

halides and liquid ammonia on the one hand and between the halides and the metal salts on the other.

Polyhydroxy compounds may be alkylated.

The naphthols are reduced by sodium in liquid ammonia to tetrahydronaphthols.

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THE CONSTITUTION OF KEROGEN[1]

BY J. W. McKINNEY[2]

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Introduction

Kerogen is the name given to the organic matter which occurs in pyrobituminous shale.[3] It is a mixture of complex compounds which is very difficult to work with, because it is largely insoluble in organic solvents, it cannot be separated from the inorganic mineral constituents which always accompany it, and its composition varies over a wide range, so that not much is known about the real nature of this material, although a certain amount of empirical data has been obtained.[4]

The pioneer in this field is Robertson,[5] who worked with some Scotch shales. By the action of nitric acid he obtained complex acidic bodies containing nitrogen, similar to those previously obtained by Anderson[6] from bituminous coal in the same manner. He found the carbon-hydrogen ratio of his shales, and attempted to establish a relation between it and the yield of oil. He found that pyridine was the best solvent, giving as much as 5% of extract, but could not get much information as to the nature of this material.

Other workers have extracted shales with a great variety of solvents invariably removing a small quantity of material, but have never attempted a detailed examination of the extracts. Many other methods of attack have also been tried, but the information gained is empirical and haphazard. The work described in this paper was an attempt to get a systematic knowledge of the action of solvents on pyrobituminous shale, and to work up the extracted material in detail.

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[1] Abstract of a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, McGill University, 1923.

[2] Fellow of the Advisory Research Council of Canada, 1922.

[3] Commonly called "oil-shale," which is a misnomer and should be reserved for shales from which all or most of the organic matter can be extracted by carbon disulfide.

[4] Gavin, "Oil-Shale," Bur. Mines, *Bull.*, **210** (1922).

[5] Robertson, *Proc. Roy. Soc. Edinburgh*, **34**, II, 190 (1913).

[6] Anderson, *J. Soc. Chem. Ind.*, **17**, 1018 (1898).