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THE USE OF SODAMIDE AS A CONDENSING AGENT

IN ORGANIC CHEMICAL SYNTHESIS

by

D. McDougall

Being a -

Thesis presented to the Department of
Chemistry, University of Manitoba, in partial
fulfilment of the requirements for the degree of
Master of Science.

University of Manitoba,

April, 1926.

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"The Use of Sodamide as a Condensing Agent
in Organic Chemical Synthesis."

"The Use of Sodamide as a Condensing Agent
in Organic Chemical Synthesis"

Introduction

Before synthetic research seriously occupied the attention of the earlier organic chemists, the old belief, that organic compounds could be formed only in organic beings, by the directing influence of a vital force, had necessarily to be overcome. Similarly the belief that in living nature the elements obeyed laws quite different from those in dead nature, acted as an effective barrier to any investigation of synthetic methods.

These conceptions prevailed for a considerable length of time. Even the preparation of urea from inorganic sources, by Wöhler in 1828, was at first regarded as of small importance, and for a number of years it was the only well known example of its kind. Finally, however, through the work of Kolbe in the synthesis of acetic acid; of Frankland in building up of hydrocarbons from substances of simpler composition; and the synthesis of fats by Berthelot, the growing conviction, that organic compounds were formed under the influence of the same forces as the inorganic, was gradually strengthened. When these barriers were finally removed, the value of synthetic research became more and more apparent.

Since that time the application of synthetic methods has met with marked success in every section of the wide field of organic chemistry. The application of these methods has led to the elucidation of the chemical constitution of many complex organic compounds. It is true that much can be deduced from the properties, modes of formation, and decomposition products of the compound. In fact from these observations, the structural formula may be deduced with reasonable certainty, but the proof of the correctness of

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these deductions lies in its synthesis, from its elements, or from substances of known composition. The further application of synthetic methods has led to the production of a vast number of new compounds, many of which are of immense value in the commercial world.

Of the many methods employed in synthetic research, perhaps none has proven of greater value, or wider application, than the condensation method. This method is inseparably connected with the earlier history of organic chemistry.

The fact that the chemical processes taking place in the plant and animal organisms, in the formation of complex organic compounds, is essentially one of condensation, has from earliest times served as a stimulus to the investigation of reactions of this type. (1)

Condensation is defined as "the union of two or more organic molecules, or parts of the same molecule (with or without elimination of component elements) in which the new combination is effected between carbon atoms." (2)

When condensation takes place between two or more different molecules it is referred to as external condensation. When union of the carbon atoms in the same molecule takes place leading to ring formation it is termed internal condensation.

Condensation is effected by the addition of some substance which acts as a condensing agent. A variety of substances are employed for this purpose, e.g. dilute sodium hydroxide solution in Claisen's reaction; ammonia, diethylamine, piperidine and aniline, in Knoevenagel's reaction; hydrogen chloride, potassium carbonate, dilute sodium hydroxide solution, and less frequently sulphuric acid, acetic acid, acetic anhydride, and zinc chloride,

(1) Practical plant biochemistry, Onslow, pp.3.

(2) Advanced Organic Chemistry, Cohen, Part I, page 195.

in the aldol condensation; sodium ethoxide in the acetoacetic ester condensation.

The following investigations have been undertaken with a view to extending the use of sodamide as a condensing agent in organic chemical synthesis. In addition to investigating its use, in cases where condensation readily takes place in the presence of other reagents, a number of new reactions have been tried, e.g. the action of chloroform, ethyl carbonate and ethyl oxalate on quinoline in the presence of sodamide, also the action of nitro compounds and bases in the presence of sodamide. The results of the latter reactions have proven of considerable interest, and appear to offer opportunities for further investigation.

I wish to express my appreciation to Dr. H. P. Arnes of the Department of Chemistry, University of Manitoba, at whose suggestion these investigations were undertaken, for his assistance and advice.

D. McDougall.

Winnipeg, Manitoba,

April 13th, 1926.

Review of Literature

The literature on this subject reveals a great diversity in the nature of the problems treated in the numerous papers. This review is intended to indicate only the outstanding contributors, with special reference to some of the more important papers.

The amide of sodium was discovered during the early part of the 19th century by Gay Lussac and Thénard, and shortly afterward by Humphrey Davy (1). The amide of potassium was discovered at the same time by these investigators.

Synthesis with derivatives of sodamide were carried out as early as 1893 by Carl Blacher (2).

The earliest account of the action of sodamide as a condensing agent appears to be communicated by Freund and Speyer in 1902. An abstract of this appears in the Journal of the Chemical Society of that year. (3) Since that time a considerable amount of work has been carried out on the use of 'sodamide in organic chemical synthesis'.

The principal contributors are:

Haller and Bauer

Haller and Ramert-Lucas

Haller and Louvrier

Haller and Benoit

Haller and Cornibert

(1) J. C. S. T. 1894, page 504.

(2) J. C. S. A1. 1895, page 289. Ber. 1895, 28; 432-37.

(3) J. C. S. A1. 1902, page 584. Ber. 1902, 35; 2321-22

Titherley, A.W.

Tschitschibabin and Zeida

Tschitschibabin and Oparina

Tschitschibabin and Zecopina

A. W. Titherley, of University College, Liverpool, has contributed a number of papers on this subject. These appear in the transactions of the Chemical Society. In his communication of 1894 he described:

- "1. Preparation, properties, and composition of sodamide, and
2. Experiments, disproving the alleged existence of nitride of sodium; and attempts to prepare disodamide."

The paper also refers to a number of experiments on potassamide and lithamide. (1)

In 1897 he described a number of substitution derivatives of sodamide. A series of derivatives were obtained by the substitution of one or both atoms of hydrogen in Na NH_2 by radicals. (2)

In a later communication he has described the action of sodamide and of acyl-substituted sodamides on organic esters. (3)

Later investigations of some interest have been carried out by Tschitschibabin and Zecopina and Tschitschibabin and Oparina on the action of sodamide on quinoline, and iso quinoline. (4) With quinoline the main products of the reaction are diquinoline $\text{C}_{18} \text{H}_{14} \text{N}_2$ and diquinolyl $\text{C}_{18} \text{H}_{12} \text{N}_2$. The former is readily oxidized to the latter. The preparation of 2-amino-quinoline by the action of sodamide on quinoline has been re-investigated in an endeavour to improve the yield of the amino compound. This has not been successful. Iso quinoline reacts in a similar way with sodamide, in the presence of neutral solvents, amino iso quinoline being produced. (5)

(1) J.C.S. T. 1894, 504.

(2) J.C.S. T. 1897, 460

(3) J.C.S. T. 1902, 1520

(4) J.C.S. 1923 A1 page 603, J.Russ. Phys.Chem. Soc. 1920, 50; 553-7

(5) J.C.S. 1923 A1 page 604 " " " " " 1920, 50; 543-8

In 1915 Tschitschibabin and Zeide published a paper on "New reactions of compounds containing the pyridine nucleus." (1) In this paper mention is made of the interaction of sodamide and pyridine at a temperature not exceeding 120°C. This yields 2-amino-pyridine. 2,6. di-amino-pyridine may also be obtained by the further action of sodamide on pyridine. Secondary products are also obtained, these appear to increase in amount as the temperature of the reaction is raised. No reference has been found in the literature to the action of sodamide in effecting condensation between nitro-compounds and bases, or as a condensing agent in the aldol type of condensation.

(1) J.G.S. 1915 A1 page 590. J.Russ. Phys.Chem.Soc. 1910., 46; 1216-36

Experimental

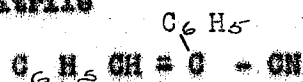
Part I

Experiments to determine the value of sodamide as a condensing agent in the aldol type of condensation:

- (1) Benzaldehyde and Benzyl cyanide
- (2) Benzaldehyde and Acetophenone
- (3) Benzaldehyde and Acetone

Condensation may be effected in all these cases using dilute sodium hydroxide solution, yielding in

- (1) α phenyl-cinnamic nitrile



- (2) Benzylidene acetophenone



- (3) Benzylidene acetone



Condensation of Benzaldehyde and Benzyl
by Means of Sodamide

Quantities used:

Benzaldehyde	25 grams
Benzyl cyanide	29 "
Sodamide	8 "

Method of preparation -

The two liquids were mixed in a beaker, dry ether added, and the sodamide powdered very fine, then added in small quantities at a time. A brisk reaction ensued, and a light coloured solid product separated out, practically the whole solidified. Water was added gradually to decompose excess of sodamide. The mixture was then filtered on the suction pump, and the solid product, dried and porous plate at room temperature.

Purification -

It was soluble in chloroform at ordinary temperatures, and in methyl alcohol at a slightly higher temperature. The entire product was purified by repeated crystallization from methyl alcohol.

Yield - 7 grams.

Melting Point - 85° C.

Description - White glistening plates.

α phenyl cinnamic nitrile was then prepared by condensing benzaldehyde and benzyl cyanide, using dilute sodium hydroxide as a condensing agent. The products obtained by these two methods were similar. α phenyl cinnamic nitrile prepared by this method melted at 86° C.

This experiment was repeated, and the reaction carried out with the pure substances, the ether was omitted. This was carried out to determine if the ether had any effect on the yield. Under these conditions the yield was about 8 grams. There was not sufficient difference between the two yields to indicate any influence by the ether.

Condensation of Benzaldehyde and Acetophenone
by Means of Sodamide

Quantities used:

Benzaldehyde	25 grams
Acetophenone	30 "
Sodamide	10 "

Method of preparation -

The benzaldehyde and acetophenone were mixed in a beaker, and dissolved in dry ether. The sodamide which was finely powdered, was added in small quantities. A light yellow coloured product separated out, which was quite sticky and viscous. Any excess of sodamide was decomposed by the addition of water. The mixture was filtered, and the residue, dried at room temperature.

Purification -

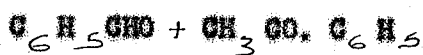
The product obtained was soluble in hot water, soluble with difficulty in alcohol, easily soluble in chloroform and ether. It was purified by crystallization from a mixture of equal parts of alcohol 90% and chloroform.

Description - White crystalline powder.

Yield - 4 grams.

Melting Point - Decomposes.

It was expected that this reaction would result in condensation between the benzaldehyde and acetophenone, with the production of Benzal acetophenone



This substance may be prepared from benzaldehyde and acetophenone, by using a dilute solution of sodium hydroxide as a condensing agent. It may also be prepared by treating a mixture of 12 parts of acetophenone and 10.5 parts of benzaldehyde with 3 parts of a 20% solution of sodium methylate. (1)

Benzal acetophenone obtained in this way occurs as large trimetric tables, easily soluble in chloroform, ether and benzene, soluble in alcohol and petroleum ether, melting point 58° C.

The product obtained by the use of sodamide as a condensing agent, differed entirely from that prepared by the above methods.

Result of analysis for percentage of Carbon and Hydrogen:

	<u>C.</u>	<u>H.</u>
1st trial	69.28%	5.99%
2nd "	67.70%	5.68%
3rd "	72.27%	6.01%
4th "	78.88%	9.07%
Theoretical for $C_6H_5CH=CH.CO.C_6H_5$	82.19%	6.94%

These results indicate that the product obtained was not a definite chemical substance.

A number of experiments were carried out, with a view to determining the conditions favourable to the formation of Benzal acetophenone.

1. The finely powdered sodamide was added to the benzaldehyde first, a white solid substance was produced. This was then placed in a 250 c.c. flask, and the flask attached to an upright condenser, and heated on the water bath. The acetophenone was then added, and the reaction allowed to proceed for two hours. No combination evidently occurred.

(1) Dictionary of Chemistry, Watts Vol.1, pp. 495

2. The benzaldehyde and acetophenone were mixed in a beaker, and the beaker surrounded by a freezing mixture. The finely powdered sodamide was then added in small quantities, and the temperature kept below 10° C. In this experiment dry ether was not used, the pure substances alone were employed. A solid product separated out. Further investigation in isolating a definite substance from the product proved unsuccessful.

3. The benzaldehyde and acetophenone were mixed in a flask, and the mixture dissolved in dry ether. The flask was then attached to an upright condenser, and the mixture heated on the water bath. The sodamide was added in small pieces to the mixture through the top of the condenser. A brisk reaction resulted. No apparent change took place for about fifteen minutes, a light yellow flaky solid separated out, practically the whole of the mixture solidified. The mixture was kept on the water bath for about an hour. The ether was then evaporated off, the product separated on the filter pump, and the residue dried at room temperature.

The product was purified by crystallization from alcohol 90%. The yield was very small, about .5 grams, yellow coloured plates.

A small quantity of benzal acetophenone, which had been prepared by using dilute sodium hydroxide as a condensing agent was then purified by crystallization from alcohol 90%. Both products were similar. Both had the same melting point 54° C, a mixture of the two substances gave the same melting point.

It would appear from these experiments that while condensation is effected in this case by sodamide, the yield is too small to warrant its use. The method of preparation is much more troublesome than by the use of dilute sodium hydroxide.

Condensation of Benzaldehyde and Acetone
by Means of Sodamide

Quantities used:

Benzaldehyde	25 grams
Acetone	14 "
Sodamide	10 "

Method of preparation -

The benzaldehyde and acetone were mixed in a beaker and the mixture dissolved in dry ether. The sodamide was finely powdered and added in small quantities. A very brisk reaction ensued. A dark reddish coloured substance separated out. The ether was then evaporated off; and the product decomposed with water. The portion of the product exposed to the air was reddish in colour, the part not exposed was yellow in colour.

Purification -

The product was soluble in chloroform. When concentrated on the water bath and allowed to cool, a yellowish viscous product was obtained. Attempts to isolate any definite substance were unsuccessful.

This experiment was repeated, the same method was used, but the temperature was kept below 10°C , no positive results were obtained.

The experiment was repeated again, this time the benzaldehyde and acetone were mixed in a flask, dry ether added, and the flask then attached to an upright condenser, and heated on the water bath. The sodamide was added in small quantities. A brisk reaction ensued, followed by the separation of a yellow product. The reaction was allowed to proceed at the temperature of the water bath for about one hour. The ether was then evaporated off, the product separated on the filter pump and dried. Purification from chloroform yielded similar results to the other two cases.

In 1902 Freund and Speyer (1) communicated the result of their investigations on the action of sodamide on acetone. They report isophrone as the principal product, formed together with mesityl oxide, xylitone and a viscid substance.

In these experiments with benzaldehyde and acetone apparently condensation is not effected. It may be that the only action is the action of the sodamide on the acetone.

(1) J.C.S. 1902, A1 page 584, Rev. 1902, 35; 2321-22

Experimental

Part II.

Attempts to effect condensation between:

- (1) Quinoline and oxalic ester
- (2) Quinoline and chloroform
- (3) Quinoline and ethyl carbonate
- (4) Benzaldehyde and ethyl carbonate
- (5) Benzaldehyde and p-nitro-toluene
- (6) p-nitro-toluene and Benzyl cyanide

Condensation of Quinoline and Oxalic Ester
by Means of Sodamide

Quantities used:

Oxalic ester	18	grams
Quinoline	10	"
Sodamide	5	"

Method of preparation -

The quinoline and oxalic ester were mixed in a beaker, and the mixture dissolved in dry ether. The reaction appeared to be much more easily controlled in the presence of the ether. The sodamide was reduced to a very fine powder, and a small quantity of it added at a time. A brown coloured solid product separated out. The mixture was then decomposed with water. A gelatinous product was obtained. This was filtered on the suction pump and dried on a porous plate.

Purification -

The product was soluble in boiling water, and was precipitated on the addition of methyl alcohol. The entire yield was purified by crystallization from dilute methyl alcohol.

Description - White amorphous powder.

Yield - 4.2 grams.

Tests - Nitrogen test negative.

Melting point - Decomposes on heating to a high temperature.

Condensation of Quinoline and Chloroform
by Means of Sodamide

Quantities used:

Quinoline	32 grams
Chloroform	30 "
Sodamide	10 "

Method of preparation -

The quinoline and chloroform were mixed in a beaker, and the mixture dissolved in dry ether. The sodamide was reduced to a fine powder, and a small quantity added at a time. A dark brownish coloured product separated out. The mixture was decomposed with water, the product filtered on the suction pump, and the residue dried on a porous plate.

Purification -

The product was soluble in dilute alcohol (50%). The entire yield was dissolved in 50% alcohol, decolorized by digesting with animal charcoal, filtered, and the filtrate concentrated on the water bath.

Description -

By this method a very small yield of a cream coloured amorphous solid was obtained.

Yield - 0.5 grams

Nitrogen test negative

Halogen test positive.

Melting point - Decomposes on heating.

Condensation of Quinoline and Ethyl Carbonate

By Means of Sodamide

Quantities used:

Quinoline 32 grams

Ethyl carbonate 29 "

Sodamide 10 "

It was anticipated that in the event of condensation being effected between quinoline and oxalic ester, by means of sodamide, that it might also be effected between quinoline and ethyl carbonate. The latter reaction would very probably result in the production of a simpler product, one which would prove easier to identify and analyse.

Method of preparation -

The quinoline and ethyl carbonate were mixed in a beaker, and dry ether added. The sodamide, which had been reduced to a fine powder, was added in small quantities. This reaction takes place very slowly. The whole solidified yielding a brown mass. The mixture was then decomposed with water, filtered, and the residue dried at room temperature on a porous plate.

Purification -

The product was soluble in hot water, and precipitated by addition of ethyl alcohol. It was decolourized by digesting with animal charcoal. The entire yield was purified by precipitation from an aqueous solution by means of ethyl alcohol.

Description -

White fine crystalline powder.

Yield - 1.8 grams.

Tests - Nitrogen tests negative.

Melting point - Decomposes on heating.

Condensation of Benzaldehyde and Ethyl Carbonate

by Means of Sodamide

Quantities used:

Benzaldehyde	25 grams
Ethyl carbonate	29 "
Sodamide	10 "

Method of preparation -

The benzaldehyde and ethyl carbonate were mixed in a beaker, and dissolved in dry ether. This reaction, when carried out without the addition of the ether, gave rise to a very brisk reaction. It was much more easily controlled in the presence of the ether. An orange coloured product separated out. The mixture was then decomposed with water, filtered, and the residue dried on a porous plate at room temperature.

Purification -

The product was easily soluble in water, soluble with difficulty in alcohol 90%. Washing with alcohol appeared to remove the colour. A white powder remained. The entire yield was purified by precipitation from an aqueous solution, by 90% alcohol.

Description -

White, fine crystalline powder.

Yield - 0.3 grams.

Tests -

- (a) Aqueous solution alkaline.
- (b) When boiled with alkali or concentrated hydrochloric acid no odor of benzaldehyde was observed.

Melting point - Decomposes.

No further investigation of this product was carried out.

Condensation of Benzaldehyde and p-Nitro-Toluene
by Means of Sodamide

Quantities used:

p-Nitro-toluene	17 grams
Benzaldehyde	13 "
Sodamide	5 "

Method of preparation -

The p-nitro-toluene was dissolved in the benzaldehyde by the aid of gentle heat. Dry ether was added. The sodamide, finely powdered, was added in small quantities. A light coloured solid product separated out. The mixture was then decomposed with water, the product separated on the filter pump and dried at room temperature.

Purification -

The product was soluble in methyl alcohol, and precipitated out in crystalline form, on the addition of water. The entire yield was dissolved in dilute methyl alcohol, on standing long yellow needles separated out.

Melting point - 54° C.

This product was identified as p-nitro toluene. No condensation took place.

The experiment was repeated. The substances were heated in a flask attached to an upright condenser. The sodamide was added in small pieces. The results of this experiment were also negative.

Condensation of p-Nitro-toluene and Benzyl Cyanide
by Means of Sodamide

Quantities used:

p-Nitro-toluene	30 grams
Benzyl Cyanide	29 "
Sodamide	10 "

The p-nitro-toluene was dissolved in the benzyl cyanide by the aid of gentle heat. Dry ether was added, and the sodamide finely powdered added in small quantities. The solution became very dark in colour, and thickened slightly, no solid product was obtained. No definite results were obtained from this experiment.

Experimental

Part III

Attempts to effect condensation between Nitro compounds and bases:

- (1) Nitro-benzene and Aniline
- (2) p-nitro-toluene and Aniline
- (3) p-nitro-toluidine and Aniline.

Condensation of Nitro-benzene and Aniline
by Means of Sodamide

Quantities used:

Nitro-benzene	62 grams
Aniline	47 "
Sodamide	20 "

Method of preparation -

The nitro-benzene and aniline were mixed in a 5 liter flask, and dry ether added. The mixture was heated gently on a water bath, and the sodamide finely powdered was added in small quantities. A fairly brisk reaction set in, and the liquid turned quite dark in colour. The Mixture did not solidify as in the other experiments. It became quite thick, practically semi-solid. When water was added to decompose excess of sodamide, the entire product was decomposed, a heavy dark oil settled to the bottom of the flask. The mixture was distilled in steam to remove unchanged aniline and nitro-benzene. When no more came over, a heavy dark oil remained in the bottom of the flask. This was separated from the aqueous layer by decantation. When allowed to cool at zero temperature practically the entire product solidified. The product was filtered, and dried on a porous plate at room temperature. It was dark brown in colour, and soluble in ether alcohol and ligroin.

Purification -

The product was dissolved in a mixture of alcohol and ether, digested with animal charcoal, and filtered. The filtrate was yellow, and on cooling deposited long yellow needle like crystals.

Yield - .8 grams.

Melting point - 173° C.

It was expected that in the event of condensation taking place, either azo-benzene or azoxy-benzene would be formed. The melting point corresponded to neither of these. It corresponds, however, to phenazene, a substance having the formula $C_6H_5N=N-C_6H_5$

A number of confirmatory tests were tried all of which indicated the substance to be phenazene.

(1) It dissolved in concentrated sulphuric acid with the production of a brilliant red colour.

(2) With stannous-chloride it gave a green colour.

(3) When precipitated from a solution in nitric acid, by silver nitrate solution a light yellow precipitate was obtained.

(4) The melting point of the two substances was identical.

Results of analysis to determine percentage of Nitrogen:

Trials	Theoretical percentage	Percentage obtained
1.	15.55%	16.97%
2.	-	16.45%
3.	-	16.41%

Results of analysis to determine the percentage of Carbon and Hydrogen:

Carbon		Hydrogen	
Theoretical percentage	Percentage obtained	Theoretical percentage	Percentage obtained
1. 80.00%	80.08%	4.44%	5.82%
2. -	80.24%	-	5.20%

Condensation of p-Nitro-Toluene and Aniline

and

Condensation of p-Nitro-Toluidine and Aniline

By Means of Sodamide

These reactions were carried out in a similar manner to that described under nitro-benzene and aniline. The result was similar in each case. The mixture darkened on the addition of sodamide, a semi solid was produced, which was decomposed on the addition of water, yielding a heavy oil which settled to the bottom of the flask, when subjected to distillation in steam, to remove unused substances, a heavy dark coloured oil remained in the bottom of the flask. Lack of time has prevented any further investigation of these products.

CONCLUSIONS

In summing up the results of these investigations, the following conclusions may be stated.

1. Sodamide is effective as a condensing agent in some cases in the aldol type of condensation. The yields obtained, in the cases tried, do not offer any advantages over other condensing agents.

2. Sodamide was found to be ineffective as a condensing agent in the following cases:-

- (a) Quinoline and oxalic ester.
- (b) Quinoline and chloroform.
- (c) Quinoline and ethyl carbonate
- (d) Benzaldehyde and acetone
- (e) Benzaldehyde and p-nitro-toluene
- (f) p-Nitro-toluene and benzyl cyanide.

3. A product was obtained by the interaction of benzaldehyde and ethyl carbonate in the presence of sodamide. Further investigation as to the nature of this product is necessary before it can be stated that condensation was effected.

4. Condensation is effected between nitro-compounds and bases, in the presence of sodamide. The nature of these reactions, and proper conditions under which they take place, warrants further investigation.

5. These investigations indicate that in the majority of cases, the reactions are very complex, and also that the conditions under which the reactions take place evidently affect very materially the nature of the product formed.

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