

TABLE II  
ANALYSES

Chloride	Derivative	Nitrogen, %	
		Found	Calcd.
s-Butyl	<i>p</i> -Toluide	7.48	7.61
	$\alpha$ -Naphthalide	6.42	6.17
<i>t</i> -Butyl	<i>p</i> -Toluide	7.39	7.52
	$\alpha$ -Naphthalide	6.21	6.17
Isoamyl	<i>p</i> -Toluide	7.27	7.42
	$\alpha$ -Naphthalide	5.90	5.97
<i>t</i> -Amyl	<i>p</i> -Toluide	7.06	7.14
	$\alpha$ -Naphthalide	6.19	6.23
2-Chloropentane	<i>p</i> -Toluide	7.00	6.83
	$\alpha$ -Naphthalide	5.95	5.97
3-Chloropentane	<i>p</i> -Toluide	6.98	6.83
	$\alpha$ -Naphthalide	6.01	5.81
2-Chlorohexane	Anilide	6.99	7.23

chloride method. These results indicated that the supposedly pure 3-chloropentanes contained some 2-chloropentane. No product was obtained from the derivatives of 2-chloropentane which corresponded to 3-chloropentane.

Schwartz and Johnson<sup>4</sup> stated that the purification of the anilide made from 3-bromopentane

was difficult and involved great loss of material. Sherrill, Otto and Pickett<sup>11</sup> found that 3-bromopentane could be prepared pure only by great care in the hydrobromination of 3-pentanol, otherwise a mixture of 3- and 2-bromopentanes was obtained. Ayres<sup>12</sup> reported that 2-chloropentane could be converted into 3-chloropentane by the action of heat and pressure and that this conversion was accelerated by catalysts.

### Summary

A method has been developed for the preparation of crystalline derivatives from eighteen alkyl chlorides, including a number of isomers. *p*-Tolyl isocyanate has been used as a characterizing agent for organomagnesium halides and has enabled us to distinguish between chlorides of closely similar boiling point.

(11) M. L. Sherrill, B. Otto and L. Pickett, *THIS JOURNAL*, **51**, 3023 (1929).

(12) E. E. Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929).

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## A Rapid Catalytic Preparation of Sodamide in Liquid Ammonia and Some of its Uses in the Preparation of Acetylenic Materials

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A solution of sodamide in liquid ammonia is known to be a valuable reagent in a number of organic reactions, but the difficulty of obtaining such a solution has limited its use. Sodamide is prepared commercially by the action of gaseous ammonia on molten sodium, but the necessity of storing and grinding it out of contact with both air and moisture, and the hazards of prolonged storage, make it undesirable for general laboratory use.

Sodamide is also formed slowly<sup>1</sup> in solutions of sodium in liquid ammonia, and a few attempts have been made to catalyze this reaction.<sup>2</sup>

We have found that in the presence of sodium oxides, sodamide can be prepared quickly at  $-33^\circ$  by adding ammonia-soluble iron, nickel or cobalt salts to the solution of sodium in liquid ammonia in the ratio of 0.001 mole or less of the salt to one gram atom of sodium. It was found that a number of factors influenced the rate of

reaction. The reaction is more rapid in dilute sodium solutions and the rate is a direct function of the iron, nickel or cobalt salt concentration.

In most of our work we have used the salt  $\text{Fe}(\text{NO}_2)_3 \cdot 6\text{H}_2\text{O}$  as a catalyst, 0.3 g. of the material being used for each mole of sodium. Sodium hydroxide is a pronounced, though weak, negative catalyst, while sodium oxides are active catalysts, being about equally effective in large or small amounts, which must be present along with the iron salt to effect the conversion. The oxide may be formed by the action of atmospheric oxygen on the sodium solution or sodium peroxide may be added. The first form is more active, no doubt due to its finely divided state, and is usually more convenient to employ.

The exact method of adding the catalyst is also important. The most rapid conversion is produced by adding the finely powdered ferric nitrate to the total amount of ammonia, adding 1-3% of the sodium and bubbling dry air through the solution until the excess sodium is oxidized.

(1) Joannis, *Compt. rend.*, **112**, 392 (1891).

(2) Ewan, British Patent, 222,718 (1923); McGee, *THIS JOURNAL*, **43**, 586 (1921); Burgess and Smoker, *Chem. Rev.*, **8**, 265 (1931).

The remainder of the sodium is then added. If the conversion is to be conducted in contact with air, as is usual, it suffices to add the powdered catalyst to the ammonia, add one gram of sodium and then after several minutes add the remainder.

While iron, cobalt and nickel salts are all catalysts, it was found by comparison of the rates of conversion effected by the nitrates that iron was about 40% more efficient than nickel and approximately 20% more efficient than cobalt.

At the end of the reaction most of the catalytic material is in the form of a finely divided black precipitate which is easily removed by filtration. The sodamide solution purified by filtration contains only traces of sodium compounds and catalytic metals. Generally, however, filtration is unnecessary since the catalytic residues cause no trouble in most cases where the sodamide is used.

We were unable to prepare calcium amide by this procedure.

Hunt and Boncyk<sup>3</sup> have reported recently that sodamide is only soluble to the extent of 0.04 g. per liter of ammonia. Our experience has been that roughly a mole of sodamide will dissolve in a liter of ammonia. Hunt<sup>4</sup> has informed us that the sodamide on which solubility data were reported was of the commercial variety. This divergence in data, together with the large difference in reactivity, seems to indicate some deep-seated difference in the two varieties of sodamide.

Sodamide prepared by this method has been found useful in a number of reactions. In the ammonia in which it is prepared it is an excellent reagent for forming the sodium salts of a number of compounds such as acetylenes, amines, alcohols, etc., which subsequently may be used in ammonia solution. In the case of acetylenes it is particularly advantageous to use sodamide rather than sodium in order to avoid losses by hydrogenation.<sup>5</sup> Should the ammonia be undesirable the salt may be freed of it by evacuation at 100°. Where it is desired to conduct a reaction with sodamide in mineral oil, etc., at high temperatures the amide may be conveniently prepared by this method and the ammonia solution added to the oil at room temperature. On heating the ammonia is driven off and the amide is left suspended in the oil in a very finely divided and reactive state.

(3) Hunt and Boncyk, *THIS JOURNAL*, **55**, 3530 (1933).

(4) Hunt, private communication.

(5) Picon, *Compt. rend.*, **173**, 155 (1921); Bourguel, *Ann. chim.*, [10], **3**, 203 (1925).

Desaturation by dehydrohalogenation with sodamide at elevated temperatures is a standard method for the preparation of a number of acetylenes. Since it has been shown that under these same conditions of temperature sodamide also rearranges certain acetylenes,<sup>6</sup> the applicability of the method is limited. It is of interest to know whether or not sodamide in liquid ammonia is an effective dehydrohalogenation agent and also whether or not it is a rearrangement catalyst at low temperatures. We have accordingly subjected several halogeno compounds which ordinarily desaturate to acetylenes, to the action of sodamide in ammonia and have found that either dehalogenation or dehydrohalogenation, depending on the compound taken, results. The experimental data are tabulated below.

TABLE I  
ACTION OF SODAMIDE ON ORGANO-HALIDES

Compound	Product <sup>a</sup>	Yield, % <sup>e</sup>	
		Over-all	Accounted for
Butyliodoacetylene	Butylacetylene	31	34
1,2-Dibromoheptene	Amylacetylene <sup>b</sup>	55	
Stilbene dibromide	Stilbene <sup>c</sup>	86	
$\beta$ -Bromostyrene	Phenylacetylene	75	83
$\alpha$ -Chlorostyrene <sup>d</sup>	Phenylacetylene	57	
Styrene dibromide	Phenylacetylene	64	
2-Bromooctene-1	Hexylacetylene	73	90
<i>p</i> -Methyl $\alpha$ -chloro-styrene	Tolylacetylene	49	64
1,2-Dibromodecane	Octylacetylene	54	78

<sup>a</sup> All acetylenes were identified by conversion to the mercury derivative. Purity was established by the physical constants. <sup>b</sup> Hydrolyzed with ammonium nitrate. Much tar formed. <sup>c</sup> Identified as dibromide. <sup>d</sup> Experiment performed by Dr. D. J. Pflaum. <sup>e</sup> All yields are expressed in terms of purified materials.

Since none of the acetylenes obtained were capable of rearrangement by sodamide, ethylamylacetylene was treated with sodamide in ammonia at  $-34^\circ$  for sixteen hours. No rearrangement was observed. This indicates that sodamide in ammonia may be of great value in the preparation of disubstituted acetylenes which are easily rearranged.

### Experimental Part

**Preparation of Sodamide.**<sup>7</sup>—To a mechanically stirred mixture of 0.3 g. of finely powdered ferric nitrate in 500

(6) Bourguel, *Ann. chim.*, [10] **3**, 205 (1925); Guest, *THIS JOURNAL*, **50**, 1744 (1928).

(7) It is not advisable to allow sodamide prepared by this method to stand in a dry condition for any considerable length of time, since, due to its finely divided condition and the presence of oxides, it rapidly forms unstable, explosive compounds. It should always be covered with ammonia, mineral oil, etc., and is best used when freshly prepared.

ml. of liquid ammonia contained in a 2-liter round-bottomed flask 1 g. of sodium was added. Air was bubbled through the solution until the blue color was discharged and 25 g. of sodium was added in small chunks. A reaction set in at once and in ten to twenty minutes the blue color was replaced by a gray, indicating the end of the conversion. In larger runs, employing similar catalyst and sodium concentrations, the time of conversion was about ten minutes per mole. If the solution was to be freed of catalyst it was diluted to about 1.2 liters and filtered through ordinary filter paper in a closed funnel.

**Preparation and Properties of 1,2-Dibromoheptene.**—This compound was prepared in 90% yield by the bromination of amylacetylene dissolved in carbon tetrachloride and cooled to  $-34^{\circ}$  by a bath of liquid ammonia. The pure substance has the following properties: b. p. 93–96 at 11 mm.;  $n_D^{27}$  1.5064;  $d_{30}$  1.462.

*Anal.*<sup>8</sup> Calcd. for  $C_7H_{12}Br_2$ : Br, 62.45. Found: Br, 62.39

**Reactions with Sodamide.**—The procedure employed is illustrated by the case of  $\beta$ -bromostyrene. To a mechanically stirred solution of 2 moles of sodamide in 1.5 liters of ammonia contained in a 4-liter beaker there was added dropwise over a period of twenty minutes 135 g. of  $\beta$ -bromostyrene. A vigorous reaction soon set in which appeared to be complete when the addition was finished. Stirring was continued for ten minutes and the mixture was hydrolyzed by the addition of 600 ml. of water. The solution was extracted twice with ether and the combined extracts were washed with dilute hydrochloric acid, dried over a mixture of potassium hydroxide and calcium chloride and fractionated. A yield of 56 g. of phenylacetylene, b. p. 140–143°,  $n_D^{26}$  1.5461, and a recovery of 14 g. of  $\beta$ -bromostyrene, b. p. 120–122 at 35 mm.,  $n_D^{25}$  1.6023, was obtained. This corresponds to an over-all yield of 75% or an accounted yield of 83% of the theoretical. This yield compares most favorably with the 67% yields obtained by Hessler's<sup>9</sup> synthesis and the reaction requires less time and attention.

**Preparation of Ethylamylacetylene.**—Amyl sodium acetylide was prepared by adding 50 g. of amylacetylene to a well-stirred solution of 40 g. of sodamide in 1 liter of ammonia contained in a covered 4-liter beaker. Stirring was continued for one hour, ammonia being added to main-

tain the volume, and 75 g. of liquid ethyl chloride was dropped in. After stirring for three hours water was added and the oil which separated was washed well with water and dried over calcium chloride. On fractionation 15 g. of ethylamylacetylene of b. p. 151–154° was obtained.

Alkyl sodium acetylides prepared from more concentrated mixtures of sodamide have been used for a number of other purposes in this Laboratory, *e. g.*, iodination with elementary iodine.<sup>10</sup> In several cases the ammonia has been distilled off and the solid sodium derivative easily suspended in ether or benzene and treated with various reagents, such as carbon dioxide and benzene chlorosulfonic acid, which cannot be used in ammonia.

**Attempted Rearrangement of Ethylamylacetylene.**—To a mixture of 13 g. of sodamide and 100 cc. of ammonia contained in a 250-cc. test-tube was added 10.6 g. of ethylamylacetylene. The tube was closed by a rubber stopper bearing a long length of capillary tubing and kept in a bath of liquid ammonia for sixteen hours. The solution was hydrolyzed with 200 ml. of water to remove the ammonia. The oil gave no precipitate with alkaline mercuric cyanide solution, indicating that it contained no  $\alpha$ -acetylenic material.

### Summary

1. It has been found that in the presence of sodium oxides and iron, cobalt, or nickel salts solutions of sodium in liquid ammonia are rapidly converted to sodamide.
2. Sodamide prepared by this method is more reactive and more soluble in ammonia than the sodamide of commerce.
3. Nine compounds which give acetylenes when treated with the usual dehalogenation or dehydrohalogenation agents have been subjected to the action of this sodamide in ammonia. All of them give acetylenes in good yields excepting stilbene dibromide, which gives stilbene.
4. Sodamide in ammonia at  $-34^{\circ}$  does not rearrange ethylamylacetylene.
5. 1,2-Dibromoheptene has been described.

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(8) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(9) Hessler, *THIS JOURNAL*, **44**, 425 (1922); "Organic Syntheses," 1932, John Wiley and Sons, Inc., New York, Collective Vol. I, p. 428.

(10) Vaughn and Nieuwland, *THIS JOURNAL*, **55**, 2152 (1933); Dr. D. J. Pfaum, unpublished.