

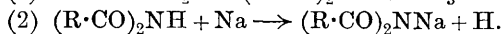
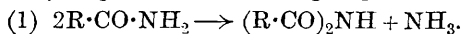
CLXVIII.—*Preparation of Secondary and Tertiary Acid Amides from their Metallic Derivatives.*

By JITENDRA NATH RAKSHIT.

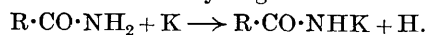
THE replacement of hydrogen in the amido-group of aliphatic amides by alkali metals had been attempted by different investigators through different methods. Curtius (*Ber.*, 1890, **23**, 3037) tried the direct action of metallic sodium on acetamide, and he obtained hydrogen and ammonia as evolved gases, and a yellow, oily liquid, which solidified on cooling. He suspected the substance to be sodium diacetamide, but the investigation was not completed. The formation of sodium diacetamide by the above reaction was indirectly supported by Blacher (*Ber.*, 1895, **28**, 432), who succeeded in isolating diacetamide by the action of an alcoholic solution of sodium ethoxide on the crude product obtained by Curtius's method.

An extensive investigation on the preparation of sodium derivatives of acid amides was undertaken by Titherley (*T.*, 1897, **71**, 466). The principle involved in his process is the interaction of the free acid amides with sodamide in indifferent solvents: $R \cdot CO \cdot NH_2 + NaNH_2 = R \cdot CO \cdot NHNa + NH_2$.

In the present investigation, acid amides were acted on by sodium or potassium in an indifferent solvent, such as benzene or light petroleum. As a rule, sodium causes the condensation of the primary acid amides to secondary ones, and next itself replaces one atom of hydrogen of the amido-group:



It is very curious that the behaviour of potassium under similar conditions is quite different from that of sodium. With formamide it yields potassium diformamide, but with acetamide and propionamide it produces only potassium monacid amides by the simple displacement of one atom of hydrogen:



Sodium Diformamide, $(H \cdot CO)_2NNa$.

Light petroleum was dried by boiling under a reflux condenser with anhydrous potassium carbonate for about three hours, and

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the fraction boiling between 65° and 75° was collected and kept in a bottle containing sticks of potassium hydroxide. Two hundred c.c. of light petroleum and 10 grams of formamide are placed in a 750 c.c. flask, then 5 grams of freshly-cut sodium are dropped into the flask, which is immediately attached to a spiral reflux condenser. As soon as sodium dips under the petroleum and reaches the layer of formamide, a brisk evolution of gas commences. The separate pieces of sodium, being covered by layers of amide and bubbles of gas, float again on the surface, during which time a very strong odour of ammonia is perceived at the open end of the condenser. In an hour the reaction practically ceases, when the mass solidifies. It is then heated to boiling over a liquid paraffin bath for four hours to convert any unchanged amide. When cooled, the crystalline, solidified mass is collected with the aid of the pump, and washed three times with light petroleum. It is then kept in a vacuum desiccator over sulphuric acid for twenty-four hours.

0.1243, by Kjeldahl's method, required 13.0 c.c. $N/10\text{-HCl}$.
 $N = 14.72$.

0.6480 gave 0.4840 Na_2SO_4 . $\text{Na} = 24.21$.

$\text{C}_2\text{H}_5\text{O}_2\text{NNa}$ requires $N = 14.73$; $\text{Na} = 24.21$ per cent.

The liberation of hydrogen was estimated quantitatively by the following process. In the above-mentioned flask the sodium is kept in suspension above the liquid by means of a spiral of platinum wire. A tube for the entrance of dry ammonia is introduced into the flask, the end of which just reaches the surface of the light petroleum. The upper end of the condenser is connected to a delivery tube for the collection of gas. The end of the delivery is dipped under a surface of mercury, and the gas is collected by the displacement of dilute sulphuric acid in an inverted cylinder on the trough containing mercury, the mercury preventing the direct contact of gas inside the delivery tube and the dilute acid. The apparatus is freed from air by passing a current of dry ammonia, and, after the air is expelled, the sodium is dropped by vigorous shaking and the reaction at once commences; finally, the flask is heated to boiling. When the reaction is practically finished, a current of ammonia is passed until no more gas is collected over the acid. One gram gave 141 c.c. of moist hydrogen at 33° and 760 mm. pressure, that calculated from the above general equation being 145 c.c. under similar conditions. Hence the reaction is fairly quantitative.

In another experiment the evolved gas was led into dilute hydrochloric acid and converted into the platinichloride (Found, $\text{Pt} = 44.23$; $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ requires $\text{Pt} = 44.22$ per cent.).

Sodium diformamide is a white, transparent, crystalline compound of pearly lustre. It is extremely deliquescent, readily soluble in water or alcohol, but less soluble in ether or light petroleum.

Potassium Diformamide, $(\text{H}\cdot\text{CO})_2\text{NK}$.

The above experiment was repeated, using, however, 8 grams of potassium instead of the sodium. The reaction with potassium is very vigorous, and a very brisk effervescence takes place. Hydrogen and ammonia gases are evolved. In some cases sparks of light are visible in the earlier stages of the reaction. After the reaction is practically finished, it is boiled for about three hours, when the whole solidifies on cooling. It is collected, washed three times with hot light petroleum, and kept in a vacuum desiccator over sulphuric acid for twenty-four hours:

0.4532 gave 0.3532 K_2SO_4 . $\text{K} = 34.96$.

0.3620, by Kjeldahl's method, required 32.6 $N/10\text{-HCl}$. $\text{N} = 12.62$.

$\text{C}_2\text{H}_2\text{O}_2\text{NK}$ requires $\text{K} = 35.13$; $\text{N} = 12.61$ per cent.

Potassium diformamide is a faintly yellow, crystalline compound; it is extremely deliquescent and readily soluble in water or alcohol, less so in ether or light petroleum.

Sodium Diacetamide, $(\text{CH}_3\cdot\text{CO})_2\text{NNa}$.

Ten grams of acetamide (purified by recrystallisation from benzene), 200 c.c. of anhydrous thiophen-free benzene, and 5 grams of sodium are mixed in a 750 c.c. flask, fitted with a reflux condenser. The reaction does not commence at once. On heating, the acetamide partly dissolves in the benzene, and the rest melts, and the reaction starts at once with the evolution of ammonia and hydrogen. After twenty to thirty minutes, white, flaky crystals begin to separate, and on continuing boiling for three hours the quantity of crystals increases. When cooled, the unconverted acetamide forms a solid crust at the bottom of the flask, and the crystals remain suspended in the benzene, which are then collected and washed three times with hot benzene, and kept in a vacuum desiccator over sulphuric acid (Found, $\text{Na} = 18.45$; $\text{N} = 11.37$. $\text{C}_4\text{H}_6\text{O}_2\text{NNa}$ requires $\text{Na} = 18.69$; $\text{N} = 11.38$ per cent.).

Sodium diacetamide forms yellowish-white, shining, flaky crystals. It is deliquescent, readily soluble in water, or alcohol, less so in ether, and practically insoluble in benzene or light petroleum.

Potassium Acetamide, $\text{CH}_3\cdot\text{CO}\cdot\text{NHK}$.

In the preparation of this substance, 10 grams of acetamide, 200 c.c. of benzene, and 4 grams of potassium are boiled as

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described above. The reaction commences only on boiling, a faint odour of ammonia is perceived at the beginning, and throughout the reaction hydrogen is evolved. After boiling for an hour, shining, white crystals separate out, and boiling is continued for about four hours. When cold, the crystals are collected, washed with hot benzene, and kept in a vacuum desiccator:

0.3620 gave 0.3254 K_2SO_4 . $K=40.27$.

0.1101 „ 14.3 c.c. N_2 (moist) at 30° and 760 mm. $N=14.48$.

C_2H_4ONK requires $K=40.21$; $N=14.43$ per cent.

Potassium acetamide forms white, flaky, glistening crystals, rapidly deliquescent in air. It is readily soluble in water or alcohol, and sparingly so in ether, benzene, or light petroleum.

Sodium Dipropionamide, $(C_2H_5 \cdot CO)_2NNa$.

Eight grams of propionamide, 150 c.c. of light petroleum, and 3 grams of sodium are boiled together. The reaction then commences, hydrogen and ammonia being evolved. After about an hour, white crystals separate out, the boiling being continued for four hours. When cold, the crystals are collected, washed, and kept in a vacuum desiccator in the usual manner:

0.4530 gave 0.2110 Na_2SO_4 . $Na=15.08$.

0.2446, by Kjeldahl's method, required 16.2 c.c. $N/10-HCl$. $N=9.25$.

$C_6H_{10}O_2NNa$ requires $Na=15.23$; $N=9.27$ per cent.

Sodium dipropionamide forms white, crystalline plates of pearly lustre. It is deliquescent and readily soluble in water or alcohol, but sparingly so in ether, light petroleum, or benzene.

Potassium Propionamide, $C_2H_5 \cdot CO \cdot NHK$.

Eight grams of propionamide, 150 c.c. of dry light petroleum, and 5 grams of potassium are boiled as before. The reaction commences on boiling, and after twenty minutes white crystals are formed. The mixture is boiled for three hours, when fine, white crystals separate. On cooling, these are collected, washed, and kept in a vacuum desiccator:

0.3698 gave 0.2907 K_2SO_4 . $K=35.26$.

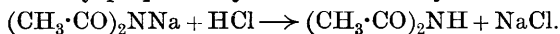
0.2680, by Kjeldahl's method, required 24.0 c.c. $N/10-HCl$. $N=12.55$.

C_3H_6ONK requires $K=35.13$; $N=12.61$ per cent.

Potassium propionamide is a white, scaly, crystalline compound, extremely deliquescent, readily soluble in water, or alcohol, but sparingly so in ether, benzene, or light petroleum.

Preparation of Secondary and Tertiary Acid Amides.

Consequent upon the convenient and ready method of preparing sodium derivatives of secondary acid amides, the preparation of diacetamide was undertaken from its derivative. Titherley (T., 1901, **79**, 411) obtained diacetamide by the interaction of acetyl chloride and sodium monoacetamide, and in this connexion he discovered a method of preparing diacetamide by the action of acetyl chloride on acetamide. From sodium diacetamide, however, it can be readily prepared by the action of hydrochloric acid :



Similarly, by the action of acetyl chloride, triacetamide can be obtained :

*Diacetamide, $(\text{CH}_3\cdot\text{CO})_2\text{NH}$.*

Fifteen grams of sodium diacetamide are placed in a 500 c.c. flask, and 62 c.c. of 2*N*-hydrochloric acid in alcoholic solution are added, 5 c.c. at a time; after the addition of each instalment the flask is immediately corked and shaken vigorously by rotatory motion. When all the acid has been added, the flask is connected with a reflux condenser, and heated to boiling for twenty minutes on the water-bath. On cooling, 30 c.c. of dry ether are added, the whole is shaken vigorously and filtered, and the filtrate evaporated on the water-bath. The residue is next extracted, first with 100 c.c., and then with 50 c.c. of warm light petroleum. The petroleum extracts are mixed, filtered, and evaporated on the water-bath. A transparent, shining, crystalline mass is obtained on cooling. The yield is 9.2 grams (Found, *N*=13.59. Calc., *N*=13.86 per cent.).

The diacetamide obtained in this way distilled at 216—218°, and melted at 79°.

Triacetamide, $(\text{CH}_3\cdot\text{CO})_3\text{N}$.

In the preparation of this compound, 10 grams of sodium diacetamide are suspended in 50 c.c. of benzene, and 5.8 c.c. of acetyl chloride are added drop by drop, the mixture being continually shaken; it is finally heated to boiling on the water-bath. The sodium chloride which separates is removed by filtration, and the filtrate evaporated on the water-bath. The residue solidifies on cooling; when crystallised from benzene, it gives transparent, glistening crystals, which melt at 77° (Found, *N*=9.72. Calc., *N*=9.79 per cent.)

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I take this opportunity of expressing my best thanks to Prof. P. C. Rây for the interest he has taken in this investigation.

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