XCVII.—*Allylamine Derivatives.*

By WILHELM GLUUD, Ph.D.

THE production of pyrrole from allyl derivatives has been described by Königs (*Ber.*, 1879, **12**, 2344), who passed ethylallylamine over lead oxide at 400—500°. Since then no progress has been effected in this method of preparing pyrrole, and the description of the following compounds may therefore be of interest. The reaction and its application to similar substances will be dealt with in another communication.

The simplest acyl derivative of allylamine is allylformamide, the empirical formula of which differs from that of pyrrole only by one molecule of water :

It seems, however, to have only a slight tendency to pass into pyrrole derivatives, although these can be obtained by heating allylformamide to 260° , but the yield was so small that the reaction did not repay further investigation. The high temperature caused the formation of many decomposition products, including carbon monoxide and ammonium carbonate. Dehydrating agents gave no better results.

Allylthiocarbimide on heating with sodium in a sealed tube gave compounds which showed the pyrrole reaction with pine-wood quite distinctly, and a similar result was obtained by passing the vapour of the compound over heated copper, but in both cases the yield was very small owing to the violent character of the reaction. It is a remarkable fact, however, that small quantities of pyrrole compounds are formed during the preparation of allylformamide from allylthiocarbimide and formic acid.

It occurred to me that better results might be obtained by using allyloxamic acid, an expectation which has been satisfactorily confirmed, as this substance was found to be an excellent material for the production of pyrrole derivatives. For this purpose it was necessary to find an easy way of preparing it. An attempt was made to obtain it by a method analogous to that used by Clayton (*Ber.*, 1895, **28**, 1666) in the preparation of allylformamide, namely, from oxalic acid and allylthiocarbimide, but the products of the reaction are complicated and difficult to separate, being for the most part allylamine oxalates, besides the allylamine salt of allyloxamic acid, and some compounds containing sulphur. The latter were not investigated, as they were of no use for the purpose of this research, but possibly they may be of interest as intermediate products, as they readily evolve carbonyl sulphide, and may therefore be assumed to contain this substance only loosely combined. A better method was to prepare the ethyl ester of allyloxamic acid from allylamine and ethyl oxalate, and then to hydrolyse the ester.

EXPERIMENTAL.

Allylformamide, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CHO}$.

This substance was previously prepared by Clayton (*Ber.*, 1895, **28**, 1666), but as no details of the yield are given, some improvements may be noted which ensure a rapid preparation of any quantity of the compound. If anhydrous formic acid is used, the reaction takes much less time, and can be carried out on a water-bath, and the oil need not be distilled under diminished pressure.

Allylthiocarbimide (102 grams) and anhydrous formic acid (53 grams) are heated under reflux on the water-bath, the condenser

being connected to a gas wash-bottle filled with water. The evolution of gas begins at once, but after about an hour the reaction suddenly becomes violent, and should be moderated by slightly lowering the temperature. When the liquid stops boiling the reaction is completed by heating for half an hour on the water-bath. The liquid is then distilled; much carbonyl sulphide is evolved below 190° , and the allylformamide passes over at $213\text{--}218^{\circ}$, the yield being about 70 per cent. of the theoretical. The residue in the flask gave the pyrrole reaction with pine-wood. In another experiment, from 150 grams of allylthiocarbimide 91 grams of allylformamide were obtained, which boiled at $215\text{--}216^{\circ}$. It is an oily liquid with an unpleasant odour, readily soluble in water, ether, or alcohol. When prepared in this way, it is pure enough for most purposes, but can be purified by extraction with light petroleum or by redistillation over charcoal; the compound then still contains traces of sulphur.

If allylformamide, however, is distilled over phosphoric oxide or zinc chloride, a small quantity of oil passes over about $120\text{--}140^{\circ}$. This oil is lighter than water, and does not mix with it; it gives the pyrrole reaction distinctly. On heating allylformamide in a sealed tube for several hours, decomposition begins about 260° . There is a high pressure in the tubes, due to carbon monoxide, and a small quantity of a pyrrole derivative of high boiling point is formed, along with resinous products and ammonium carbonate. Similar results were obtained when allylacetamide was used.

Diallyloxamide, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$.

This compound was prepared by Wallach and Stricker (*Ber.*, 1880, **13**, 513), but no accurate description of the preparation, properties, or details of analysis are given in their paper. Allylamine (3.8 grams) dissolved in 25 c.c. of ether is mixed with freshly distilled ethyl oxalate (3.5 grams) dissolved in 25 c.c. of ether, and the mixture cooled to 0° . After several hours the crystals formed (3.5 grams) are collected and recrystallised from acetone. Analysis of the compound, dried in a desiccator, showed that it was quite pure, the yield being about 87 per cent. of the theoretical:

0.1631 gave 0.3412 CO_2 and 0.1020 H_2O . $\text{C}=57.05$; $\text{H}=7.00$.

0.1700 „ 23.8 c.c. N_2 at 16° and 768 mm. $\text{N}=16.54$.

$\text{C}_8\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C}=57.10$; $\text{H}=7.19$; $\text{N}=16.67$ per cent.

The compound crystallises in long, narrow plates, fairly soluble in hot alcohol, chloroform, benzene, and excess of hot water or ether. It is readily soluble in warm dilute acetic acid, and addition of calcium chloride and sodium acetate to the solution

produces no precipitation of oxalate even on boiling for a short time.

The aqueous solution rapidly decolorises bromine water. When boiled with alkalis, allylamine is evolved.

Allyloxamic Acid, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$.

In order to obtain this compound, it is first necessary to prepare the *ethyl ester*, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$. This is done by mixing 100 grams of ethyl oxalate in 100 c.c. of ether with 37 grams of allylamine in 60 c.c. of ether and cooling to 0° . After an hour, the ether is evaporated off, and the residue which contains crystals is shaken with light petroleum. The solid remains suspended in the ether, and the ethyl allyloxamate which forms the lower layer is easily separated. On distillation, a small fraction passes over below 100° , then the temperature rises rapidly, and at 252° the ester (66 grams) distils over, the yield being 65 per cent. of the theoretical. It still, however, contains a small quantity of diallyloxamide, which partly separates on cooling. If the whole is hydrolysed this impurity can be completely removed.

The ester is a pale yellow liquid with an unpleasant, garlic odour. It is heavier than water, and readily soluble in the usual organic solvents or in excess of hot water, from which it separates on cooling. The aqueous solution decolorises bromine-water immediately.

In the following experiments it was unnecessary to use the pure product. The ester (2.3 grams) is shaken with 15 c.c. of *N*-sodium hydroxide until, after half an hour, the garlic odour has disappeared. Then 15 c.c. of *N*-hydrochloric acid are added, when crystals of diallyloxamide separate out. These are collected, and the filtrate is evaporated to dryness. The residue is extracted with ether and the solution evaporated, leaving a syrupy mass, which, on mixing with light petroleum, soon becomes crystalline (1.3 grams). The crystals can be purified by recrystallisation from a very small quantity of benzene and then from chloroform, from which allyloxamic acid (0.85 gram) separates in silky, square plates, which melt at $97\text{--}98^\circ$, forming a colourless liquid. They are very soluble in water, alcohol, or acetone, readily so in ether, hot chloroform or benzene, and sparingly soluble in hot light petroleum. From the last three solvents the substance crystallises on cooling the solution. The aqueous solution decolorises bromine-water at once. The substance, after being left in a desiccator, was analysed:

0.2093 gave 0.3563 CO_2 and 0.1032 H_2O . $\text{C}=46.43$; $\text{H}=5.52$.

0.2024 „ 18.8 c.c. N_2 at 18° and 760 mm. $\text{N}=10.86$.

$\text{C}_5\text{H}_7\text{O}_3\text{N}$ requires $\text{C}=46.49$; $\text{H}=5.47$; $\text{N}=10.85$ per cent.

The *calcium* salt is prepared by mixing the crude ethyl ester (50 grams) with 160 c.c. of 2*N*-sodium hydroxide and cooling to 0°. When all the oil has disappeared, the liquid is filtered, and a solution of anhydrous calcium chloride (20 grams in 50 c.c. of water) is added to the filtrate. On cooling to 0° the calcium salt separates in crystals, which are collected and dried on a water-bath (40.5 grams), the yield being about 80 per cent. of the theoretical. They can be redissolved in about twenty times their volume of boiling water, and the solution cleared with charcoal. From this solution the salt separates in characteristic, narrow, compact prisms, which acquire a syrupy consistency about 160°. Analysis shows that the air-dried crystals contain two molecules of water:

0.2002 * at 100° over phosphoric acid under 10—12 mm. pressure gave 0.0215 H₂O. H₂O = 10.74.

C₁₀H₁₂O₆N₂Ca.2H₂O requires H₂O = 10.84 per cent.

0.1787 † gave 0.0340 CaO. Ca = 13.60.

C₁₀H₁₂O₆N₂Ca requires Ca = 13.53 per cent.

The salt, when heated alone, or with lime, or equivalent substances, easily yields a yellow oil, which does not mix with water, resinifies with acids, and gives the pyrrole reaction.

The *potassium* salt is prepared by boiling the aqueous solution of the calcium salt for some minutes with the required quantity of anhydrous potassium hydroxide. The solution is filtered and evaporated on a water-bath, leaving a waxy mass. This is mixed with alcohol, and becomes instantly solid. One gram of this solid is dissolved in a mixture of 20 c.c. of alcohol and 0.5 c.c. of water, from which solution 0.7 gram of the salt crystallises in thin plates. The air-dried salt contains no water of crystallisation, as it loses practically no weight when dried at 100° over phosphoric acid at 10—12 mm. pressure. When heated to 230° it forms a syrupy liquid, which decomposes at a higher temperature, giving oily distillates, which contain pyrrole derivatives.

Action of Oxalic Acid on Allylthiocarbimide.

Crystallised oxalic acid (30 grams) and allylthiocarbimide (30 grams) were heated under reflux for five hours at 125°. The action was not then complete, as the evolution of gas still continued. The product, which solidified on cooling, was washed with light petroleum to remove any unchanged allylthiocarbimide, and 23 grams were crystallised from alcohol, from which transparent prisms separated, melting at 135—136°, readily soluble in hot

* Air dried.

† Anhydrous.

water or alcohol, but practically insoluble in most organic solvents. It was dried in a vacuum desiccator, and then analysed:

0.1943 gave 0.2905 CO_2 and 0.1105 H_2O . $\text{C}=40.78$; $\text{H}=6.36$.

$\text{C}_8\text{H}_9\text{O}_4\text{N}$ requires $\text{C}=40.80$; $\text{H}=6.17$ per cent.

The product is therefore *allylamine hydrogen oxalate*. When heated above its melting point much gas is evolved, and a colourless residue left, which does not give the pyrrole reaction. It can also be prepared by mixing 1.2 grams of allylamine with a solution of 2 grams of oxalic acid in alcohol or acetone in the cold.

In another experiment a mixture of allylthiocarbimide (52 c.c.) and crystallised oxalic acid (77 grams) was heated on a water-bath for about twenty-five hours until no further evolution of gas was observed, and the odour of allylthiocarbimide had disappeared. The product was a clear liquid, which on cooling solidified to a waxy substance, consisting of an oil (24 grams) and a waxy solid (75 grams). The oil was evaporated on a water-bath, and the partly crystalline residue shaken with acetone, when allylamine oxalate (7.5 grams) separated out. The wax-like solid was also shaken with acetone, in which the greater part dissolved, leaving 29 grams of fine crystals melting at $130\text{--}134^\circ$. (Allylamine hydrogen oxalate melts at $135\text{--}136^\circ$.) The acetone solution was evaporated in a vacuum, yielding 21 grams of an unpleasant-smelling oil, which solidified on cooling, and appeared to be a mixture of various sulphur compounds, as on heating it gave off much carbonyl sulphide. The production of allylamine oxalate shows that if the reaction is allowed to be completed there is still not sufficient oxalic acid in spite of the excess used.

A mixture of anhydrous oxalic acid (55 grams) and allylthiocarbimide (50 grams) when heated for eighteen hours on a water-bath yielded 55 grams of crystals, more than 60 per cent. of which consisted of allylamine hydrogen oxalate, so that in this experiment also oxamic allyl acid could only have been formed in small quantity.

One experiment may be described, showing the course of this reaction in aqueous solution. Crystallised oxalic acid (70 grams), 50 grams of allylthiocarbimide, and 100 c.c. of water were boiled under reflux for thirty-six hours, the reaction being then complete. The liquid was evaporated on a water-bath until the aqueous layer acquired a syrupy consistency, when it was mixed with twice its volume of alcohol, and the crystals of allylamine oxalate (24 grams) formed were collected. The mother liquor was evaporated to dryness and the residue dissolved in alcohol, when a further separation of the oxalate (6 grams) took place. The filtrate was mixed with ether, and kept in ice for some hours. The crystals then

formed (8.5 grams) were removed from the solution, which on evaporation left an oil, which was not further investigated. The crystalline product was recrystallised from a very small quantity of hot chloroform and again from 50 c.c. of acetone; 3 grams of this product were again recrystallised from 75 c.c. of acetone, from which thin, transparent plates (2 grams) separated, melting at 111—112°. These were dried at 100° and analysed:

0.1622 gave 0.3044 CO₂ and 0.1091 H₂O. C=51.18; H=7.53.

0.1588 „ 19.8 c.c. N₂ at 17° and 772 mm. N=14.73.

C₈H₁₄O₃N₂ requires C=51.58; H=7.58; N=15.05 per cent.

This compound is *allylamine allyloxamate*,

It can also be prepared from the corresponding calcium salt. One gram of allylamine was added to 3 grams of the calcium salt dissolved in 75 c.c. of hot water, and the calcium precipitated with carbon dioxide. The hot solution was filtered, evaporated in a vacuum, and the residue dissolved in hot acetone. On cooling, 2.4 grams of crystals separated, which were identical with the above allylamine salt. It is extremely soluble in water or hot alcohol, very sparingly so in ether or benzene. The aqueous solution is neutral, decolorises bromine water instantly, and on addition of calcium chloride yields the corresponding very characteristic calcium salt.

Allylamine oxalate, as obtained in the above experiment, can be purified by crystallisation from 95 per cent. alcohol. Three grams of the purified product were dissolved in 100 c.c. of hot 97.5 per cent. alcohol, from which solution, on gradually cooling, small, compact prisms separated out on the sides of the flask. The liquid was then decanted and slowly cooled. This product was dried in a vacuum desiccator and analysed:

0.1522 gave 0.2638 CO₂ and 0.1027 H₂O. C=47.27; H=7.55.

0.1300 „ 15.2 c.c. N₂ at 18° and 770 mm. N=13.73.

C₈H₁₆O₄N₂ requires C=47.03; H=7.90; N=13.73 per cent.

It melts and decomposes at 181°, and is very soluble in water, but practically insoluble in organic solvents. It can also be prepared by mixing 2.5 grams of oxalic acid and 2.5 grams of allylamine in acetone solution at 0°. The crystals formed are collected and recrystallised from 97 per cent. alcohol.

DAVY FARADAY LABORATORY.