LVI.—*The Action of Ethyl Carbamate on Esters of Organic Acids and Mustard Oils.*

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IN continuation of the research on the esters of acetylenic acids, we have subjected the sodium derivative of ethyl carbamate to the action of ethyl phenylpropiolate with the view of ascertaining whether in this case, also, a union is effected as represented by the equation :

We find, however, that such an additive product is not formed, but

instead, alcohol is eliminated, and ethyl phenylpropiolylcarbamate, $C_6H_5 \cdot C \equiv C \cdot CO \cdot NH \cdot CO_2Et$, is produced.

Some time ago, Hantzsch (*Ber.*, 1894, **27**, 1250) showed that, in the presence of sodium ethoxide, ethyl carbamate does not condense with esters of fatty acids to yield acyl derivatives of ethyl carbamate, the only exception being ethyl oxalate, which yields diethyl oxalyl-dicarbamate, $(CO \cdot NH \cdot CO_2Et)_2$. The acyl derivatives of ethyl carbamate had to be prepared by the action of acid chlorides or acid anhydrides on ethyl carbamate. Those compounds may, however, be obtained also in a manner similar to the formation of ethyl phenylpropiolylcarbamate by the action of ethyl sodiocarbamate on the esters of fatty or fatty-aromatic acids. This reaction, moreover, allows of the preparation of ethyl formylcarbamate, which, on account of the non-existence of formyl chloride, cannot be produced by the old method. Owing to the fact that ethyl formylcarbamate is readily hydrolysed, a mixture of this substance and ethyl carbamate, which melts at a low temperature, is produced in the reaction. On being kept for several days in a desiccator, the oil deposits a small quantity only of the formyl compound, and, as a complete separation cannot be effected by fractional distillation in a vacuum, the yield of the pure ethyl formylcarbamate is rather small.

On applying this reaction to the esters of benzenecarboxylic acids, it has been found that ethyl benzoate forms only a small quantity of ethyl benzoylcarbamate, whereas ethyl *o*-phthalate does not yield a trace of the carbamate.

Of interest is the behaviour of ethyl sodiocarbamate towards ethyl benzylideneacetoacetate. This reaction furnishes diethyl acetyl-diphenylcyclohexanonedicarboxylate,

identical with the compound which one of us (Ruhemann, *Trans.*, 1909, **95**, 110) obtained by the action of sodium phenoxide or sodium ethoxide on ethyl benzylideneacetoacetate.

In connexion with this work, we have studied the behaviour of ethyl sodiocarbamate towards mustard oils. On using phenylthiocarbimides, the reaction takes place in two phases. At first, both substances unite to form carboxyethylphenylthiocarbimide,

which, indeed, could be isolated and identified with the product obtained by Doran (*Trans.*, 1896, **69**, 326) on treatment of carboxy-ethylthiocyanide with aniline. The yield of this substance from ethyl carbamate is very small, as the greater part of it subsequently condenses with another molecule of phenylthiocarbimide, thus :

and yields a compound the constitution of which is to be represented by the formula

This substance, which stands in a close relationship to carbonylthiocarbamilide, $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}\langle\text{N}(\text{C}_6\text{H}_5)\rangle\text{CO}$, the product of the action of carbonyl chloride on thiocarbamilide, is, therefore, to be regarded as *anhydrodiphenyldithiobiuretcарboxylic acid*. The compound is yellow, whereas its sodium and potassium derivatives are colourless. This fact leads to the view that the salts are derived from the tautomeric formula

The yellow substance is scarcely attacked on boiling with hydrochloric acid, but it is very sensitive towards potassium hydroxide. The colourless salt, which is first formed on the addition of the dilute alkali, decomposes when digested on the water-bath for a short time.

Analogous to the behaviour of phenylthiocarbimide is the action of ethyl sodiocarbamate on allylthiocarbimide, whereby *anhydrodiallyldithiobiuretcарboxylic acid*, $\text{C}_9\text{H}_{11}\text{ON}_3\text{S}_2$, is produced.

EXPERIMENTAL.

Ethyl Phenylpropiolylcarbamate, $\text{C}_6\text{H}_5\cdot\text{C}\equiv\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$.

This compound is formed by digesting a solution of ethyl carbamate (4.5 grams) in absolute ether with sodium wire (1.2 grams) on the water-bath until the metal has disappeared, then adding ethyl phenylpropiolate (8.7 grams) to the voluminous mass of ethyl sodiocarbamate, and keeping the mixture for a day or warming it on the water-bath for one to two hours. On pouring the whole into water, removing the ethereal layer (which contains only traces of ethyl carbamate and ethyl phenylpropiolate), and treating the aqueous solution with an excess of dilute sulphuric acid, an emulsion is produced. This, in a short time, deposits a solid, which is very soluble in alcohol, especially on boiling, and crystallises from dilute alcohol in colourless prisms melting at 100° :

0.2070 gave 0.5030 CO_2 and 0.9965 H_2O . $\text{C} = 66.27$; $\text{H} = 5.17$.

0.2560 „ 14.6 c.c. N_2 at 18° and 752 mm. $\text{N} = 6.51$.

$\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$ requires $\text{C} = 66.35$; $\text{H} = 5.07$; $\text{N} = 6.45$ per cent.

Ethyl phenylpropiolylcarbamate, on being in contact with concentrated aqueous ammonia for a few hours, dissolves, and, in the course

of a day, the solution sets to a semi-solid mass of crystals. These readily dissolve in boiling water, and, on cooling, crystallise in colourless prisms. The compound is phenylpropiolamide,

which Stockhausen and Gattermann (*Ber.*, 1892, 25, 3537) obtained by the action of ammonium carbonate on phenylpropiolyl chloride. They gave the melting point as 99—100°, whereas we find it to be 108—109°:

0.2060 gave 0.5620 CO_2 and 0.0928 H_2O . $\text{C} = 74.40$; $\text{H} = 5.0$.

0.2158 „ 18 c.c. N_2 at 15° and 764 mm. $\text{N} = 9.82$.

$\text{C}_9\text{H}_7\text{ON}$ requires $\text{C} = 74.48$; $\text{H} = 4.83$; $\text{N} = 9.65$ per cent.

Ethyl Phenylacetylcarbamate, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$.

It has been mentioned in the introduction to this paper that ethyl benzoate, on treatment with ethyl sodiocarbamate, yields only a very small quantity of ethyl benzoylcarbamate, and that no trace of an acylcarbamate is formed from ethyl *o*-phthalate. This result is probably due to steric hindrance, for, as shown before, ethyl phenylpropiolate readily reacts with ethyl sodiocarbamate, and gives a good yield of the acylcarbamate. Ethyl phenylacetate (16.4 grams) also condenses with ethyl sodiocarbamate (produced from 9 grams of ethyl carbamate and 2.3 grams of sodium in absolute ether). The mixture, after being kept for two days, is poured into water, the ethereal layer separated from the aqueous solution, and the latter treated with dilute hydrochloric acid, when a solid is precipitated. This is readily soluble in alcohol, and crystallises from dilute alcohol in colourless, silky needles melting at 114—115°:

0.2075 gave 0.4845 CO_2 and 0.1175 H_2O . $\text{C} = 63.68$; $\text{H} = 6.29$.

0.2255 „ 13.2 c.c. N_2 at 14° and 767 mm. $\text{N} = 6.94$.

$\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C} = 63.76$; $\text{H} = 6.28$; $\text{N} = 6.76$ per cent.

This compound, also, is hydrolysed by ammonia, and yields phenylacetamide in addition to phenylacetic acid. The former separates on leaving the carbamate in contact with concentrated aqueous ammonia for several days, and crystallises from boiling water in colourless plates. It was identified by the melting point (154—155°) and a nitrogen estimation:

0.1474 gave 13.6 c.c. N_2 at 24° and 772 mm. $\text{N} = 10.5$.

$\text{C}_8\text{H}_9\text{ON}$ requires $\text{N} = 10.37$ per cent.

Action of Ethyl Sodiocarbamate on Ethyl Benzylideneacetoacetate.

On adding to ethyl sodiocarbamate (from 2.3 grams of sodium and 9 grams of ethylcarbamate), suspended in absolute ether, ethyl

benzylideneacetoacetate (21·8 grams), heat is developed, the ethyl sodiocarbamate disappears, and a yellow solid separates. After being kept overnight, the whole is poured into water. The aqueous solution contains only a small quantity of a viscous product; the ethereal layer, on evaporation of the ether, yields an oil which, when stirred with a little alcohol, partly solidifies. The product is filtered with the aid of the pump, and washed with alcohol until the filtrate ceases to be yellow. The solid is free from nitrogen, and, after crystallisation from alcohol, has the same melting point and chemical behaviour as diethyl 6-acetyl-1 : 5-diphenylcyclohexan-3-one-2 : 6-dicarboxylate,

which has recently been described by one of us (*loc. cit.*). The formula, moreover, was verified by analysis :

0·2122 gave 0·5565 CO_2 and 0·1240 H_2O . $\text{C} = 71\cdot52$; $\text{H} = 6\cdot49$.

$\text{C}_{26}\text{H}_{28}\text{O}_6$ requires $\text{C} = 71\cdot56$; $\text{H} = 6\cdot42$ per cent.

The alcoholic washings from the compound contain a yellow, viscous product, from which no crystalline substance could be extracted.

Diethyl Oxalylidodicarbamate, $(\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$.

This compound, which Hantzsch (*loc. cit.*) obtained by the action of an alcoholic solution of sodium ethoxide on a mixture of ethyl carbamate and ethyl oxalate, is formed, also, by dissolving sodium (2·3 grams) in a solution of ethyl carbamate (9 grams) in absolute ether, then adding ethyl oxalate (7·5 grams), and digesting the mixture on the water-bath for two to three hours. The product is poured into water, and the aqueous layer treated with dilute hydrochloric acid, when a solid is precipitated. This is almost insoluble in cold water, but readily dissolves in boiling water, and, on cooling, separates in colourless, stout prisms, which melt at the same temperature (170°) as observed by Hantzsch :

0·2054 gave 0·3115 CO_2 and 0·0980 H_2O . $\text{C} = 41\cdot36$; $\text{H} = 5\cdot30$.

0·2265 „ 23·2 c.c. N_2 at 15° and 777 mm. $\text{N} = 12\cdot27$.

$\text{C}_8\text{H}_{12}\text{O}_6\text{N}_2$ requires $\text{C} = 41\cdot38$; $\text{H} = 5\cdot17$; $\text{N} = 12\cdot07$ per cent.

This substance, on hydrolysis with concentrated aqueous ammonia, yields oxamide.

Ethyl Chloroacetylcarbamate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$.

Frerichs (*Arch. Pharm.*, 1899, 237, 288) prepared this compound from chloroacetyl chloride and ethyl carbamate. We obtained it by digesting the mixture of ethyl sodiocarbamate (from 2·3 grams of sodium and 9 grams of ethyl carbamate), suspended in absolute ether,

and ethyl chloroacetate (12·3 grams) on the water-bath for two hours. The whole is then poured into water, and the aqueous solution, after treatment with dilute sulphuric acid, frequently extracted with ether. On evaporation of the ether, a solid is left, which is sparingly soluble in ether but dissolves readily in boiling water, and, on cooling, crystallises in colourless prisms melting at 129—130°:

0·2154 gave 15·8 c.c. N_2 at 18° and 764 mm. $N = 8·49$.

$C_5H_8O_3NCl$ requires $N = 8·46$ per cent.

Ethyl Formylcarbamate, $CHO \cdot NH \cdot CO_2Et$.

On adding freshly distilled ethyl formate (8 grams) to ethyl sodiocarbamate (prepared by dissolving 2·3 grams of sodium in a solution of 9 grams of ethyl carbamate in absolute ether) and frequently shaking the mixture, the powdery ethyl sodiocarbamate is transformed into a white solid, which adheres to the sides of the vessel. The mixture, after being kept overnight, is poured into water, when the whole dissolves. The ethereal layer, which contains only a small quantity of ethyl carbamate, is removed from the aqueous solution, the latter treated with dilute sulphuric acid, and extracted ten times with ether. On evaporation of the ether, an oil is left from which, in the course of three to four days, a crystalline solid separates. This is collected with the aid of the pump, and the adhering oil pressed off between filter paper. The substance is very soluble in ether, but almost insoluble in light petroleum, and crystallises from a mixture of both solvents in colourless prisms, which are rather volatile in a vacuum, even at the ordinary temperature, and melt at 51—52°:

0·1994 gave 0·3007 CO_2 and 0·1097 H_2O . $C = 41·12$; $H = 6·11$.

0·1800 „ 18·4 c.c. N_2 at 17° and 774 mm. $N = 12·06$.

$C_4H_7O_3N$ requires $C = 41·02$; $H = 5·96$; $N = 11·97$ per cent.

Although almost the total quantity of ethyl sodiocarbamate reacts with ethyl formate, as indicated by the fact that the ethereal solution after treatment of the product with water contains only a little ethyl carbamate, yet the yield of ethyl formylcarbamate is rather small. This circumstance is partly due to the volatility of the compound, especially, however, to the ease with which it is hydrolysed by mineral acids, even in the cold. The oil which is left on evaporation of the ether from the ethereal extract of the acidified aqueous solution of the product of the reaction, is a mixture of ethyl carbamate and its formyl derivative. This melts at a low temperature; it distils at 73—82°/13 mm., and cannot be completely separated by fractional distillation. A nitrogen estimation of the fraction which boils at 73—77°/13 mm. and melts at 35—39° gave the following result:

0.1639 gave 21.4 c.c. N_2 at 19° and 776 mm. $N = 15.29$.

Ethyl carbamate requires $N = 15.73$ per cent.

Ethyl formylcarbamate requires $N = 11.97$ per cent.

This indicates that the fraction is a mixture of about 88 per cent. ethyl carbamate and 12 per cent. ethyl formylcarbamate. The higher boiling fraction of the oil contains a larger percentage of the formyl derivative; on cooling, it solidifies, and the solid, after removal of the easily fusible portion by pressing between filter paper and crystallisation from a mixture of ether and light petroleum, yields a further quantity of the formyl compound.

Action of Ethyl Sodiocarbamate on Mustard Oils.

Anhydrodiphenyldithiobiuretcарboxylic Acid,

Phenylthiocarbimide (13.5 grams) reacts with ethyl sodiocarbamate (obtained by dissolving 2.3 grams of sodium in a solution of 9 grams of ethyl carbamate in absolute ether) on keeping the mixture at the ordinary temperature for two days. The product of the reaction is poured into water, and the aqueous solution separated from the ethereal layer. The latter contains ethyl carbamate besides traces of phenylthiocarbimide. The aqueous solution, when treated with dilute sulphuric acid, yields a yellow solid, which is a mixture of carboxyethylphenylthiocarbimide, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$, and anhydrodiphenyldithiobiuretcарboxylic acid, $\text{C}_{15}\text{H}_{11}\text{ON}_3\text{S}_2$; their separation is effected by shaking the ethereal solution of the mixture with sodium carbonate, which extracts the thiobiuret derivative. On evaporating the ethereal layer, a solid (3 grams) is left, which crystallises from dilute alcohol in colourless plates melting at 130° :

0.1432 gave 15.8 c.c. N_2 at 20° and 760 mm. $N = 12.62$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $N = 12.50$ per cent.

This substance is identical with the compound which Doran (*loc. cit.*) obtained by the action of aniline on carboxyethylthiocarbimide, $\text{CNS} \cdot \text{CO}_2\text{Et}$.

On adding dilute hydrochloric acid to the sodium carbonate solution of the mixture, a yellow solid (8 grams) is precipitated, which is readily soluble in ether or chloroform, sparingly so in cold, but readily so in boiling, alcohol, and, on cooling, crystallises in yellow prisms. These soften at 232° and melt and evolve gas at $234-235^\circ$:

0.1802 gave 0.3794 CO_2 and 0.0590 H_2O . $C = 57.42$; $H = 3.63$.

0.2115 „ 24.4 c.c. N_2 at 18° and 775 mm. $N = 13.58$.

0.2053 „ 0.3060 BaSO_4 . $S = 20.46$.

$\text{C}_{15}\text{H}_{11}\text{ON}_3\text{S}_2$ requires $C = 57.51$; $H = 3.51$; $N = 13.42$; $S = 20.44$ per cent.

The compound is scarcely attacked by dilute hydrochloric acid. It dissolves in dilute sodium carbonate to yield a colourless solution, from which the yellow substance is precipitated on the addition of mineral acids. This behaviour is due to the formation of a colourless salt, which is produced, also, on adding dilute sodium hydroxide to the yellow solid. Complete decomposition, however, takes place if the substance is digested with the dilute alkali for half an hour on the water-bath. Phenylthiocarbimide, aniline, thiocarbamilide, carbon dioxide, and hydrogen sulphide were identified as the products which are formed. The compound $C_{15}H_{11}ON_3S_2$ is readily soluble in dilute ammonia, yielding a colourless solution which gives silver sulphide on the addition of silver nitrate.

Anhydrodiallyldithiobiuretcарboxylic acid,

This compound is prepared in the same way as the former by keeping the mixture of allylthiocarbimide and ethyl sodiocarbamate suspended in absolute ether for two days. On proceeding as in the previous case, a small quantity of a colourless substance was obtained, which is insoluble in sodium carbonate. This has not been further examined, but there can be no doubt that it is carboxyethylallylthiocarbimide, $C_3H_5 \cdot NH \cdot CS \cdot NH \cdot CO_2Et$. The solution of the product of the reaction in sodium carbonate, on the addition of dilute hydrochloric acid, yields a yellow precipitate, which is readily soluble in ether or alcohol, and crystallises from dilute alcohol in pale yellow prisms; these soften at 129° and melt at $132-133^\circ$:

0.1933 gave 29.6 c.c. N_2 at 22° and 770 mm. $N = 17.57$.

$C_9H_{11}ON_3S_2$ requires $N = 17.43$ per cent.

This substance resembles in its behaviour the corresponding compound from phenylthiocarbimide; like the former, it dissolves in sodium carbonate to yield a colourless solution.

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