XC.—*Formation of Pyrazolone Derivatives from
Chlorofumaric acid.*

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CLAUS and Voeller (*Ber.*, 1881, **14**, 151), and W. H. Perkin, senior (*Trans.*, 1888, **53**, 702), by the action of ammonia on ethylic chlorofumarate, obtained, in addition to ethylic chlorofumaramate, the diamide of amidofumaric acid. The readiness with which the chlorine atom of the ethereal salt is replaced by the amido-group, rendered it probable that hydrazine would also effect a similar substitution, and at the same time bring about a condensation to a pyrazolone compound. Such a change does, in fact, take place, and gives rise to the formation of ethylic 5-pyrazolone-3-carboxylate, as represented by the equation

This substance is identical with the compound which v. Rothenburg (*J. pr. Chem.*, 1895, **51**, 53) obtained from the ethereal salts of oxalacetic and acetylenedicarboxylic acids. We have, therefore, to assume that the condensation of ethylic chlorofumarate and hydrazine hydrate to the pyrazolone derivative is accompanied by a molecular transformation similar to that which brings about the formation of ethylic 5-pyrazolone-4-carboxylate from ethylic dicarboxyglutamate and the hydrazine (*Ber.*, 1894, **27**, 1658; 1895, **28**, 987).

The action of hydrazine hydrate on ethylic chlorofumarate proceeds with great development of heat. The product, on cooling, sets to a mass of crystals if the reagents are employed in the proportion of 1 mol. of the ethereal salt to 2 mols. of hydrazine hydrate; but, in using an excess of the base, no solid separates until the liquid is neutralised with hydrochloric acid. The crystals are collected, and dissolved in boiling water, from which, on cooling, colourless needles separate, softening at 180° and melting at $184-185^{\circ}$. They are readily soluble in alcohol and ether, and their aqueous solution is coloured red by ferric chloride.

The following analytical data correspond with the formula $C_6H_8N_2O_3$.

0.2500 gave 0.4220 CO_2 and 0.1116 H_2O . $C = 46.03$; $H = 4.96$.

0.2794 „ 40 c.c. moist nitrogen at 22° and 762 mm. $N = 17.87$.

$C_6H_8N_2O_3$ requires $C = 46.15$; $H = 5.12$; $N = 17.94$ per cent.

For identification, the compound obtained by v. Rothenburg was prepared from ethylic oxalacetate. This product gives the same reactions, and melts at the same temperature as does the substance produced from ethylic chlorofumarate, whilst v. Rothenburg gives the melting point 179° , and states that the ethereal salt is almost insoluble in water.

Besides ethylic 5-pyrazolone-3-carboxylate, there is formed a compound which is very readily soluble in water, and is contained in the mother liquor from the pyrazolone derivative. This reduces Fehling's solution, and crystallises from concentrated aqueous solution in plates decomposing at about 236° . It was not further examined, but there can be no doubt that it is identical with the substance formed along with ethylic pyrazolonecarboxylate from the ethereal salt of oxalacetic acid, which v. Rothenburg characterised as pyrazolone-3-carbonylhydrazine.

Ethylic pyrazolone-3-carboxylate dissolves readily in potash and in ammonia; its solution in water, after being neutralised with ammonia, yields, with silver nitrate, a white precipitate; this is washed with water and dried at 100° . Analysis of the silver compound proves it to have the formula $C_6H_6Ag_2N_2O_3$.

0.3810 left on ignition 0.2218 Ag. $Ag = 58.21$.

$C_6H_6Ag_2N_2O_3$ requires $Ag = 58.38$ per cent.

The *hydrolysis* of the ethereal salt is brought about by boiling its solution in potash, and is complete after two hours' heating. On addition of an excess of hydrochloric acid to the alkaline liquid, the pyrazolonecarboxylic acid is thrown down; this dissolves in boiling water, and, on cooling, separates in microscopic plates. On account

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of the difficulty with which the acid dissolves in water, there is no danger of its becoming contaminated with inorganic matter, as v. Rothenburg (*loc. cit.*) states to be the case if potash is used as the hydrolytic agent. The acid, prepared according to the above directions, burns away without leaving a trace of ash, and, on analysis, gives numbers closely agreeing with the formula $C_4H_4N_2O_3$.

0.2238 gave 0.3062 CO_2 and 0.0658 H_2O . $C = 37.31$; $H = 3.26$.

0.2386 „ 46 c.c. moist nitrogen at 25° and 765 mm. $N = 21.64$.

$C_4H_4N_2O_3$ requires $C = 37.50$; $H = 3.36$; $N = 21.87$ per cent.

The acid does not melt, but begins to decompose at about 260° ; its aqueous solution becomes violet on addition of ferric chloride.

Action of Phenylhydrazine on Ethylic Chlorofumarate.

Whilst the interaction of hydrazine hydrate and ethylic chlorofumarate is accompanied with development of heat, no perceptible change takes place on mixing the ethereal salt with phenylhydrazine, and, even on allowing the mixture to stand at the ordinary temperature for several days only a small quantity of phenylhydrazine hydrochloride separates. Reaction, however, takes place more readily on heating the mixture on the water bath for a few hours. The product is then allowed to cool, and, after addition of ether, the hydrochloride of phenylhydrazine is filtered off. On removal of the ether, an oil remains which does not solidify, but, when heated in an oil bath at 170° , yields, in addition to a resin, a sparingly soluble, crystalline substance. Their separation may be effected by digesting with alcohol, which dissolves the resin, leaving the white solid behind. This is soluble with difficulty in boiling glacial acetic acid, and, on cooling, separates in colourless needles which melt and decompose at 272° .

Analysis of this substance gave numbers corresponding with the formula $C_{24}H_{22}N_4O_6$.

0.2068 gave 0.4706 CO_2 and 0.0936 H_2O . $C = 62.06$; $H = 5.02$.

0.2226 „ 0.5078 „ 0.1024 „ $C = 62.19$; $H = 5.11$.

0.1266 „ 14 c.c. moist nitrogen at 24° and 758 mm. $N = 12.36$.

$C_{24}H_{22}N_4O_6$ requires $C = 62.33$; $H = 4.76$; $N = 12.12$ per cent.

The compound dissolves in potash and in ammonia, forming yellow solutions; the ammoniacal solution, on addition of silver nitrate, yields a precipitate which darkens on warming. The product gives the pyrazole-blue reaction with ferric chloride, bromine water, or potassium nitrite. The reagents are to be added carefully to the substance suspended in acetic acid, as an excess of the reagent destroys the colour. These properties characterise the compound as

a pyrazolone derivative, and it is to be looked upon as the ethereal salt of bis-phenylpyrazolonecarboxylic acid,

The formation of this ethereal salt may be interpreted by assuming that at first partial transformation of ethylic chlorofumarate into ethylic phenylhydrazofumarate takes place, which then, under the oxidising influence of phenylhydrazine, suffers a condensation to the bis-pyrazolone compound. Ethylic phenylpyrazolone-3-carboxylate, which W. Wislicenus (*Annalen*, 1888, **246**, 320) obtained from ethylic oxalacetate, might have been expected to be formed, but could not be isolated.

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