LXXIX.—*Additive Compounds of Organic Bases and
Ethereal Salts of Unsaturated Acids.*

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WHILST engaged in the further study of the compounds obtained by the interaction of the sodium derivative of ethylic oxalacetate and ethylic chlorofumarate (Ruhemann and Hemmy, *Trans.*, 1897, **71**, 334) with the view of determining their constitution, we made certain observations which form the subject of this communication ; especially in relation to the substance forming blue salts with alkalis. This had been provisionally regarded as triethylic anhydro-oxalaconitate,

$$\text{COOC}_2\text{H}_5 \cdot \underset{\text{CO} \cdot \text{C}(\text{OH}) : \text{C} \cdot \text{COOC}_2\text{H}_5}{\text{C} \equiv \text{C}} \cdot \text{COOC}_2\text{H}_5$$

and its formation was attributed to the condensation of 2 mols. of ethylic oxalacetate, the ethylic

chlorofumarate being supposed to take no part in the reaction. This assumption was found to be correct, because it was ascertained that the same product was formed on digesting ethylic oxalacetate with sodium ethoxide, the yield, however, is very small as in the former case. In attempting to prepare this compound by the condensation of ethylic oxalacetate with ethylic aconitate, we observed that piperidine unites with ethylic aconitate, forming an oil of basic character. Similar additive products are also obtained by using other ethereal salts of unsaturated acids; we have, up to the present, also prepared corresponding compounds from ethylic fumarate and ethylic citraconate. We find, moreover, that piperidine not only combines with the ethereal salts of acids containing an ethylene linking, but also with those which have a triple bond. As examples of the latter, we have chosen ethylic phenylpropiolate, and have made the interesting observation that, in this case, the union with piperidine is accompanied by a strong evolution of heat. These additive compounds can be distilled under diminished pressure without undergoing decomposition, they are not affected by dilute potash, and with hydrogen chloride form salts which are extremely soluble in water.

These substances differ in their properties from the compound which is formed by mixing an ice cold ethereal solution of ethylic dicarboxyglutaconate with aniline (Guthzeit, *Ber.*, 1897, 30, 1757). Guthzeit regards this compound as ethylic anilidodicarboxyglutarate, whilst it might have been expected that a substance with such acid properties as ethylic dicarboxyglutaconate would yield with aniline a salt similar to those which it forms with alkalis, with guanidine, and with diethylamine (see Ruhemann and Hemmy, *Ber.*, 1897, 30, 2022).

Ethylic Piperidylsuccinate.

Ethylic fumarate and piperidine interact with development of heat. A mixture of the ethereal salt and the base in equivalent quantities is digested on the water bath for 8—10 hours, and the oily product subjected to fractional distillation under reduced pressure; the largest fraction, that which boils at 162—164°, on redistillation, distils at 159° under a pressure of 10 mm. The analysis of this oil corresponds with the formula $C_5H_{10}N \cdot \underset{\text{CH}_2 \cdot \text{COOC}_2\text{H}_5}{\underset{|}{\text{CH}}} \cdot \text{COOC}_2\text{H}_5$.

0.2406 gave 0.5354 CO_2 and 0.1963 H_2O . $\text{C} = 60.68$; $\text{H} = 9.06$.

0.2260 „ 11 c.c. nitrogen at 20° and 765 mm. $\text{N} = 5.59$.

$C_{13}H_{23}NO_4$ requires $\text{C} = 60.70$; $\text{H} = 8.94$; $\text{N} = 5.49$ per cent.

Ethylic piperidylsuccinate, freshly distilled, is a colourless oil having a density $d_{18^\circ/18^\circ} = 1.0469$, and a slight odour of piperidine,

which becomes yellow after standing for a day. It is readily soluble in alcohol and ether, but insoluble in water. On passing hydrogen chloride into the solution of the ethereal salt in ether dried over sodium, a white precipitate of the hydrochloride is thrown down in colourless prisms; this is very soluble in water and in alcohol, but insoluble in ether, it begins to soften at 135° , and melts at 140° to a clear liquid, which, on cooling, solidifies again after a time. The percentage of chlorine, as determined by precipitating the aqueous solution of the substance with silver nitrate, corresponds with the formula $C_{13}H_{23}NO_4.HCl$.

0.3563 gave 0.1743 AgCl. $Cl = 12.10$.

$C_{13}H_{23}NO_4.HCl$ requires $Cl = 12.095$ per cent.

Potash added to the aqueous solution of the hydrochloride precipitates the basic ethereal salt.

Ethylc Piperidylpyrotartrate.

This is formed in the same manner as the above, by digesting a mixture of piperidine with ethylic citraconate on the water bath, and fractionating the product. One redistillation of the fraction of higher boiling point suffices to obtain a pure compound boiling at $163-164^{\circ}$ under a pressure of 10 mm., and of the composition

0.2341 gave 0.5305 CO_2 and 0.1945 H_2O . $C = 61.80$; $H = 9.23$

0.2917 „ 13.5 c.c. of moist nitrogen at 21° and 756 mm. $N = 5.24$.

$C_{14}H_{25}NO_4$ requires $C = 61.99$; $H = 9.22$; $N = 5.17$ per cent.

Ethylc piperidylpyrotartrate is also colourless when freshly distilled, but becomes yellow after some time; its density is $d_{18^{\circ}/18^{\circ}} = 1.0333$.

Hydrogen chloride, on being passed into a solution of the ethereal salt in dry ether, throws down a white, crystalline solid which does not melt sharply at 115° , dissolves in water with the greatest ease, and is insoluble in ether.

0.4067, dried in a vacuum, gave 0.1910 AgCl. $Cl = 11.61$.

$C_{14}H_{25}NO_4.HCl$ requires $Cl = 11.54$ per cent.

Ethylc Piperidyltricarballylate.

The union of piperidine with ethylic aconitate takes place to a small extent on mixing the two, and is accompanied by a slight evolution of

heat and a yellow coloration of the mixture. A satisfactory yield of the additive compound, however, is obtained by heating the mixture on the water bath for a day; it can be isolated by repeated distillation in a vacuum, and boils at 201—202° under a pressure of 10 mm.

The analysis corresponds with the formula for ethylic piperidyltricarallylate, $(\text{COOC}_2\text{H}_5 \cdot \text{CH}_2)_2\text{C}(\text{N} \cdot \text{C}_5\text{H}_{10}) \cdot \text{COOC}_2\text{H}_5$.

0.2479 gave 0.5435 CO_2 and 0.1880 H_2O . $\text{C} = 59.79$; $\text{H} = 8.45$.

0.2434 „ 0.5394 CO_2 „ 0.1840 H_2O . $\text{C} = 59.32$; $\text{H} = 8.40$.

0.2416 „ 0.5264 CO_2 „ 0.1849 H_2O . $\text{C} = 59.42$; $\text{H} = 8.45$.

0.2707 „ 10 c.c. nitrogen at 22° and 759 mm. $\text{N} = 4.17$.

$\text{C}_{17}\text{H}_{29}\text{NO}_6$ requires $\text{C} = 59.47$; $\text{H} = 8.45$; $\text{N} = 4.08$ per cent.

The additive compound is a pale yellow oil with green fluorescence, and on standing for some days becomes red; its density is $d_{20}^{20} = 1.084$.

Hydrogen chloride, on being passed into a solution of the ethereal salt in dry ether precipitates, as in the former cases, a salt in colourless needles which, dried in a vacuum over potash and sulphuric acid, melts, not sharply, at 110°.

A chlorine determination gave the following result.

0.3368 gave 0.1271 AgCl . $\text{Cl} = 9.34$.

$\text{C}_{17}\text{H}_{29}\text{NO}_6 \cdot \text{HCl}$ requires $\text{Cl} = 9.35$ per cent.

On adding potash to an aqueous solution of the hydrochloride, an oil is precipitated, which, on examination, was found to be unaltered ethylic piperidyltricarallylate; decomposition of the additive compound into piperidine and aconitic acid takes place, however, on boiling it with concentrated aqueous potash.

Ethylic Piperidylcinnamate, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{C}(\text{C}_5\text{NH}_{10}) \cdot \text{COOC}_2\text{H}_5$.

The addition of piperidine to ethylic phenylpropiolate, as already mentioned, is accompanied by great evolution of heat, and the dark-coloured product, on fractionation under diminished pressure, yields a viscous yellow oil which boils at 220—221° under a pressure of 11 mm., and has a density $d_{18}^{18} = 1.0730$.

0.2181 gave 0.5948 CO_2 and 0.1625 H_2O . $\text{C} = 74.37$; $\text{H} = 8.27$.

$\text{C}_{16}\text{H}_{21}\text{NO}_2$ requires $\text{C} = 74.13$; $\text{H} = 8.11$ per cent.

Ethylic piperidylcinnamate, like the other additive compounds, yields a hydrochloride; this separates as a yellow precipitate on passing hydrogen chloride into the ethereal solution of the oil, but on filtration becomes pasty.

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We are engaged in the study of the action of other organic bases on the ethereal salts of unsaturated acids, and hope to be able to publish the result in a short time.

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