CC.—*Coumaranone Derivatives. Part III. Acylazo-derivatives of Coumaranonecarboxylic Acid.*

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THE first known acylazo-derivative was benzoylazobenzene, $C_6H_5 \cdot CO \cdot N:N \cdot C_6H_5$, which was prepared by Emil Fischer (*Annalen*, 1877, **190**, 67) by oxidising *s*-benzoylphenylhydrazine with yellow mercuric oxide. It was isolated as a dark red oil, which was decomposed by prolonged boiling with water. Benzoylazobenzene was re-examined by Hantzsch and Singer (*Ber.*, 1897, **30**, 319), who found that it combined with hydrogen chloride with the formation of benzoyl-*o*-chlorophenylhydrazine.

Fischer's compound remained an isolated example of the acylazo-class of compound until the year 1905, when the present author prepared benzeneazocarbonylcoumaranone,

and its phenylhydrazone (Part I., T., 1911, **99**, 914). These two substances and the corresponding tolyl derivatives have been subjected to more extended investigation.*

The orange azo-derivative still retains, in a greatly reduced

* Acylazo-derivatives have since been studied by Ponzio and Charrier (*Atti R. Accad. Sci. Torino*, 1909, **44**, 295), Gastaldi (*Gazzetta*, 1911, **41**, ii, 319) and Stollé (*Ber.*, 1912, **45**, 273).

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degree, the acidic properties of the parent ester. Its acetyl derivative is hydrolysed by cold alkalis, and a solution of the sodium salt is alkaline to phenolphthalein, showing that the acidic properties of the coumaranone ester have been greatly reduced by the introduction of the azo-group. The acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of ethyl acetocoumaranonecarboxylate and the mixture exposed to the oxidising action of the air. This method of preparation is of importance, as it proves that the coumaranone residue is still present in the azo-compound, which must therefore have the constitution assigned to it.

An alkaline solution of the azo-compound is reduced by zinc dust to benzenehydrazocarbonylcoumaranone,

which is also produced directly by adding phenylhydrazine to an alcoholic solution of ethyl coumaranonecarboxylate in an atmosphere of hydrogen. The colourless alcoholic solution of the hydrazo-derivative is rapidly oxidised by the air, with formation of the orange azo-derivative.

It is remarkable that the ester group of ethyl coumaranonecarboxylate is attacked by phenylhydrazine, and not by alkalis or ammonia. The resistance of the ester to the latter reagents was attributed to salt-formation. This factor is absent in the case of the hydrazine, as there is no evidence of salt-formation when phenylhydrazine is added to an alcoholic solution of the coumaranone ester.

On reducing the azo-compound with stannous chloride or with sodium hyposulphite, the azo-group is broken in the normal manner, with the formation of aniline.

All the above reactions agree with the formula already proposed for the orange substance, which classes it as an acylazo-compound, but, unlike Fischer's benzoylazobenzene, it is not acted on by dry hydrogen chloride or by boiling acids or alkalis. This marked resistance to hydrolysis may be attributed to the acidic character of the substance.

The properties of the red phenylhydrazone also agree with the formula proposed for it. This substance forms an acetyl derivative which is hydrolysed by cold alkalis, the formula of which must be either

Its colour is a much paler red than that of the phenylhydrazone itself; this points to a change of constitution, so that formula (I) is the more probable. An unstable, yellow sodium derivative is formed when an alcoholic solution of sodium ethoxide is added to a benzene solution of the azo-phenylhydrazone. The acidic properties of the red substance are, however, very weak, as it is insoluble in cold alkalis. When it is boiled with 50 per cent. potassium hydroxide a small amount dissolves, and on evaporating the mixture to dryness a yellow residue of the metallic derivative is left. On acidifying the residue practically the whole of the original red substance is recovered unchanged. This marked resistance of a phenylhydrazone to alkaline hydrolysis is not without analogy. For instance, Torrey and Brewster (*J. Amer. Chem. Soc.*, 1909, **31**, 1322) found that the phenylhydrazones of aceto- α -naphthol, and of pæonol, are insoluble in potassium hydroxide, and are not hydrolysed by boiling with this reagent.

Benzeneazocarbonylcoumaranonephenylhydrazone is quite stable towards boiling concentrated hydrochloric acid, but is readily hydrolysed by fuming hydrobromic acid with loss of phenylhydrazine and formation of benzeneazocarbonylcoumaranone. There is no doubt, therefore, that the red compound is the phenylhydrazone of the orange azo-compound.

The three tolylhydrazines react with ethyl coumaranonecarboxylate in the same way as phenylhydrazine, forming colourless hydrazo-compounds, orange azo-compounds, and red hydrazones of the latter substances, which have properties exactly similar to those of the corresponding compounds already discussed.

Absorption Spectra.

If the views expressed above are correct, the colourless hydrazo-compounds and the orange azo-compounds are derived from ethyl coumaranonecarboxylate by converting a carbethoxy-group into an acylhydrazo- and an acylazo-group respectively. The absorption curve of the coumaranone ester itself shows a deep band (Part II., preceding paper, Fig. 1), so that the effect produced by the above changes on the absorption curve might be somewhat obscured. In order to get a clearer idea of the effect of such substitutions, the absorption curves of benzoic acid, *s*-benzoylphenylhydrazine, and Fischer's benzoylazobenzene were compared. The benzoylazobenzene was prepared by Ponzio and Charrier's method (*loc. cit.*), and was obtained as a dark red solid, which forms orange solutions in alcohol. The three curves are drawn in Fig. 1. The curve for benzoic acid is reproduced from a paper by Hewitt, Pope, and Willett (T., 1912, **101**, 1772). This curve shows only general

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absorption. In the case of *s*-benzoylphenylhydrazine the general absorption is much greater, and a very shallow band appears at $1/\lambda$ 3700. The general absorption for benzoylazobenzene reaches the visible spectrum, and the shallow band is now at $1/\lambda$ 3400.

It is clear that an acylhydrazo- or an acylazo-group does not

FIG. 2.

FIG. 1.

- FIG. 1. ——— Benzoic acid in alcoholic solution (reproduced).
 - - - - *s*-Benzoylphenylhydrazine in alcoholic solution.
 Benzoylazobenzene in alcoholic solution.

- FIG. 2. ——— Benzeneazocarbonylcoumaranone in alcoholic solution.
 - - - - Acetyl derivative in alcoholic solution.
 Benzeneazocarbonylcoumaranone in alcohol + NaOH or NaOEt.

produce a well-marked band, so that any deep band present in the absorption curves of the compounds described in this communication must be due to the coumaranone residue present in the molecule.

The absorption curves of benzeneazocarbonylcoumaranone and of

its acetyl derivative are given in Fig. 2. The two curves are practically identical, which indicates that the azo-compound exists normally in the enolic form,

The addition of alkali to the parent ester fundamentally alters

FIG. 3.

FIG. 4.

- FIG. 3. ————— *p*-Toluenesazocarbonylcoumaranone in alcohol.
 - - - - - " " " + NaOH or NaOEt.
 Acetyl derivative of benzeneazocarbonylcoumaranonephenylhydrazide in alcohol.
- FIG. 4. ————— Benzenehydrazocarbonylcoumaranone in alcohol.
 - - - - - " " " + NaOH.
 Ethyl hydrazinocoumaranonecarboxylate in alcohol.

the character of its absorption curve (Part II., Fig. 1). In the case of the azo-derivative also, the addition of alkali to the solution greatly alters the character of the absorption curve. The same curve, drawn in Fig. 2, is produced by adding either aqueous sodium hydroxide solution or sodium ethoxide to the alcoholic

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solution of the azo-compound. The azo-derivative itself exists in the enolic form. Therefore the change in constitution, indicated by the change in the absorption spectrum, produced on adding alkali, might be explained according to the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (this vol., p. 415) by means of the formula:

The absorption curve of *p*-tolueneazocarbonylcoumaranone, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{C}(\text{OH}) \diagup \end{array} \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$, is given in Fig. 3, together with the alteration produced on adding sodium hydroxide or sodium ethoxide. The curves are almost exactly similar to those of the corresponding benzeneazocarbonylcoumaranone, except that the bands are slightly more persistent, and are displaced to a small extent towards the red end of the spectrum.

The absorption spectrum of the colourless benzenehydrazo-carbonylcoumaranone, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{C} \diagup \end{array} \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, is of a different type from that of the azo-derivative. The absorption curve, given in Fig. 4, shows two overlapping bands, and the addition of sodium hydroxide produces no marked change in the absorption spectrum, as was to be expected from the fact that the hydrazo-compound shows no acidic properties. It has, therefore, the ketonic constitution assigned to it above, which accounts for the great reduction in intensity, in its absorption curve, of the deep band present in the absorption curve of the enolic coumaranone ester.

The absorption curve of ethyl phenylhydrazinocoumaranonecarboxylate (Part II., *loc. cit.*), $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{C}(\text{NH} \cdot \text{NHPh}) \diagup \end{array} \text{C} \cdot \text{CO}_2\text{Et}$, drawn in Fig. 4, is exactly similar to that of benzenehydrazocarbonylcoumaranone. The heads of the overlapping bands are at the same oscillation frequencies in the two cases, although they appear at greater dilutions in the spectrum of the hydrazino-compound. A comparison of the two formulæ assigned to these compounds explains the similarity of the selective absorption. They each contain the group $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{NH} \cdot$, whilst neither contains an active enolic group. It is true that the coumaranone residue in the case of the hydrazino-compound has the same constitution as in the enolic compounds, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{C} \diagup \end{array} \text{C} -$, whilst in the hydrazo-derivative

it has the different constitution, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C}-$. This probably accounts for the greater intensities of the vibrations in the case of the former compound.

The absorption spectrum of benzeneazocarbonylcoumaranone-phenylhydrazone could not be examined owing to the small solubility of this compound in alcohol. The absorption curve of its acetyl derivative, which was sufficiently soluble to give a $M/2000$ -solution, is given in Fig. 3. The curve is different from what one might expect, as it is very similar to that of the parent azo-compound, although no enolic group is present in the coumaranone part of the molecule.

A comparison of the formulæ given to the two compounds might explain the similarity of the absorption curves. These formulæ are:

The change in constitution of the coumaranone residue is from $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C} \cdot$ to $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{C} :$, and this rearrangement has produced comparatively little change in the selective absorption.

EXPERIMENTAL.

Benzenehydrazocarbonylcoumaranone,

Ethyl coumaranonecarboxylate (1 mol.) and phenylhydrazine (1 mol.) were dissolved in alcohol (free from air), and the solutions mixed in a flask from which air had been displaced by hydrogen. The mixture became red, and after the lapse of a day a considerable quantity of colourless leaflets was deposited, which was collected and washed with dilute acetic acid. The substance was readily soluble in the usual organic solvents, but during the recrystallisation from alcohol it became slightly yellow, owing to oxidation. It was recrystallised from carbon tetrachloride in large quantity in order to minimise the risk of oxidation, and formed colourless leaflets, which melted at $140-141^\circ$. This substance is insoluble in dilute ammonia, and therefore does not possess acidic properties; it is slowly hydrolysed by boiling sodium hydroxide solution with the liberation of phenylhydrazine:

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0.1974 gave 0.4851 CO₂ and 0.0770 H₂O. C=67.0; H=4.3.

0.2473 „ 22.0 c.c. N₂ (moist) at 14° and 763 mm. N=10.6.

C₁₅H₁₂O₃N₂ requires C=67.2; H=4.5; N=10.4 per cent.

An alcoholic solution of this compound when exposed to the air yields benzeneazocarbonylcoumaranone, and when phenylhydrazine is simultaneously present the azophenylhydrazone (Part I., *loc. cit.*) is formed.

Derivatives of Benzeneazocarbonylcoumaranone,

The *sodium* derivative is an orange powder obtained by adding sodium ethoxide to an ethereal solution of the azo-compound:

0.2518 gave 0.0610 Na₂SO₄. Na=7.85.

C₁₅H₉O₃N₂ requires Na=8.0 per cent.

The *acetyl* derivative, prepared by the aid of sodium acetate and acetic anhydride, crystallises from alcohol in brownish-yellow needles melting at 187°. It is more readily soluble in alcohol or benzene than the parent compound, and is easily hydrolysed by cold alkalis. This acetyl derivative is also formed when phenylhydrazine is added to an alcoholic solution of the acetyl derivative of ethyl coumaranonecarboxylate and the mixture left exposed to the air:

0.2065 gave 0.4996 CO₂ and 0.0765 H₂O. C=65.9; H=4.1.

0.2136 „ 16.5 c.c. N₂ (moist) at 14° and 759 mm. N=9.3.

C₁₇H₁₂O₄N₂ requires C=66.2; H=3.9; N=9.1 per cent.

The acetyl group was estimated by Herzig's method (*Monatsh.*, 1884, 5, 90):

0.2357 gave 0.0882 BaSO₄, corresponding with 0.0453 acetic acid.

One acetyl group would give 0.0459 acetic acid.

Reduction of Benzeneazocarbonylcoumaranone.

The azo-compound behaves towards reducing agents in the same way as azobenzene.

(a) Zinc dust was added to the hot alcoholic sodium hydroxide solution of the azo-compound until the orange-red solution became colourless. The hydrazo-derivative (*loc. cit.*) was recovered in a pure condition from this solution.

(b) On reducing the azo-compound with boiling hydrochloric acid and stannous chloride, or with sodium hyposulphite in sodium hydroxide solution, the azo-group was broken, with the formation of aniline. The other product of reduction was isolated as orange needles, which melted at 261° and sublimed without decomposition.

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The substance contains nitrogen, and dissolves in concentrated sulphuric acid with the formation of a bright red solution:

0.0674 gave 0.1746 CO_2 and 0.0248 H_2O . $\text{C}=70.7$; $\text{H}=4.1$.

No simple formula can be deduced from these figures, and more of the substance is being accumulated for a complete investigation.

Derivatives of Benzeneazocarbonylcoumaranonephenylhydrazone.

The *sodium* derivative is an orange powder obtained by adding sodium ethoxide to the benzene solution of the azophenylhydrazone:

0.3157 gave 0.0620 Na_2SO_4 . $\text{Na}=6.35$.

$\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_4\text{Na}$ requires $\text{Na}=6.1$ per cent.

The *acetyl* derivative forms orange-red needles melting at 139° , and is sparingly soluble in the usual organic solvents. It is readily hydrolysed by cold alkalis:

0.1938 gave 0.4927 CO_2 and 0.0802 H_2O . $\text{C}=69.3$; $\text{H}=4.6$.

0.2059 „ 23.90 N_2 (moist) at 14° and 759 mm. $\text{N}=13.8$.

$\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}_4$ requires $\text{C}=69.3$; $\text{H}=4.5$; $\text{N}=14.1$ per cent.

The acetyl was estimated by Herzig's method (*loc. cit.*):

0.3523 gave 0.1017 BaSO_4 , corresponding with 0.0523 acetic acid.

A monoacetyl derivative would give 0.0532 acetic acid.

Hydrolysis of Benzeneazocarbonylcoumaranonephenylhydrazone.

This phenylhydrazone is very resistant to hydrolytic agents. It was boiled for a day with concentrated hydrochloric acid without any hydrolytic action taking place. A large quantity was boiled with excess of 50 per cent. potassium hydroxide; the red substance gradually dissolved, and on evaporating the solution to dryness an orange-coloured residue of the potassium derivative of the red azophenylhydrazone was obtained. Hydrochloric acid was added to this residue, which was converted, apparently, entirely into the unchanged red compound; but a minute proportion of it was now soluble in dilute ammonia. The ammoniacal solution was acidified with dilute acid, and a small quantity of benzeneazocarbonylcoumaranone separated out. It was found during this work that fuming hydrobromic acid was a very powerful hydrolytic agent, and this acid readily decomposed the phenylhydrazone.

Fuming hydrobromic acid was added to the boiling alcoholic solution of the red phenylhydrazone, and the mixture boiled for twenty minutes. The alcohol was evaporated off, the residue made alkaline with sodium hydroxide, and steam blown through the mixture. Phenylhydrazine could be detected in the distillate, and the orange azo-compound was precipitated on acidifying the residue.

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Similar colourless hydrazo-derivatives, orange azo-derivatives, and red azo-hydrazones were prepared by treating ethyl coumaranonecarboxylate with the three tolylhydrazines, in exactly the same way as already described in the case of phenylhydrazine.

p-Toluenehydrazocarbonylcoumaranone forms clusters of fine, colourless needles melting at 153° . It is hydrolysed by sodium hydroxide solution with the liberation of *p*-tolylhydrazine, and its alcoholic solution is oxidised by the air with the formation of the orange azo-compound:

0.1736 gave 0.4324 CO_2 and 0.0796 H_2O . $\text{C}=68.0$; $\text{H}=5.1$.

0.2253 „ 18.6 c.c. N_2 (moist) at 15° and 759 mm. $\text{N}=9.7$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{C}=68.1$; $\text{H}=5.0$; $\text{N}=9.9$ per cent.

o-Toluenehydrazocarbonylcoumaranone forms long, colourless needles melting at 182° :

0.2573 gave 21.5 c.c. N_2 (moist) at 18° and 770 mm. $\text{N}=9.9$.

$\text{C}_{16}\text{H}_{14}\text{O}_3\text{N}_2$ requires $\text{N}=9.9$ per cent.

p-Tolueneazocarbonylcoumaranone crystallises in deep orange needles, melting at 187° :

0.1096 gave 0.2756 CO_2 and 0.0420 H_2O . $\text{C}=68.6$; $\text{H}=4.3$.

0.2315 „ 20.1 c.c. N_2 (moist) at 20° and 769 mm. $\text{N}=10.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

The *silver* derivative is a brick-red powder; the *sodium* derivative is an orange powder.

The *acetyl* derivative forms brown needles melting at 187° :

0.2418 gave 18.4 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=8.8$.

$\text{C}_{18}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{N}=8.7$ per cent.

m-Tolueneazocarbonylcoumaranone melts at 162° , and forms a brick-red *silver* derivative, an orange *sodium* derivative, and a brown *acetyl* derivative:

0.1875 gave 0.4697 CO_2 and 0.0742 H_2O . $\text{C}=68.4$; $\text{H}=4.4$.

0.2316 „ 19.6 c.c. N_2 (moist) at 19° and 761 mm. $\text{N}=9.8$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

o-Tolueneazocarbonylcoumaranone forms deep orange needles melting at 193° :

0.1532 gave 0.3859 CO_2 and 0.0621 H_2O . $\text{C}=68.6$; $\text{H}=4.5$.

0.2436 „ 21 c.c. N_2 (moist) at 17° and 757 mm. $\text{N}=10.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_2$ requires $\text{C}=68.6$; $\text{H}=4.3$; $\text{N}=10.0$ per cent.

The *silver* derivative is a brick-red powder:

0.2736 gave 0.0779 Ag. $\text{Ag}=28.5$.

$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_2\text{Ag}$ requires $\text{Ag}=28.7$ per cent.

The above azo-compounds, when reduced with zinc dust and sodium hydroxide, or hydrochloric acid and stannous chloride, or

sodium hyposulphite, behave in the same way as benzeneazocarbonylcoumaranone.

p-Tolueneazocarbonylcoumaranone-p-tolylhydrazone crystallises in ruby-red needles melting at 204° :

0.2145 gave 0.5671 CO_2 and 0.1041 H_2O . $\text{C}=72.0$; $\text{H}=5.4$.

0.2518 „ 31.2 c.c. N_2 (moist) at 14° and 763 mm. $\text{N}=14.7$.

$\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_4$ requires $\text{C}=72.0$; $\text{H}=5.2$; $\text{N}=14.6$ per cent.

o-Tolueneazocarbonylcoumaranone-o-tolylhydrazone forms deep red needles melting at 173° :

0.2037 gave 0.5345 CO_2 and 0.0970 H_2O . $\text{C}=71.8$; $\text{H}=5.3$.

0.1835 „ 22.4 c.c. N_2 (moist) at 16° and 762 mm. $\text{N}=14.4$.

$\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_4$ requires $\text{C}=72.0$; $\text{H}=5.2$; $\text{N}=14.6$ per cent.

The above azohydrazones are extremely resistant to hydrolytic agents, but are hydrolysed when boiled with fuming hydrobromic acid.

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