LXXXI.—*Some Derivatives of Dibenzyl Ketone.*

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R. SCHIFF has shown (*Ber.*, 1898, 31, 205, 601, 1304, 1388; 1899, 32, 332), that benzalaniline forms additive products with acetoacetic ester and similar substances, giving, under certain conditions, three isomeric products. These, he considers, correspond with the ketonic, enolic, and keto-enolic forms of the original substance. When acetoacetic ester itself is used, equal molecules generally give rise to an additive product corresponding with different mixtures of the two desmotropic forms of the ester; the melting point lies between 95° and 100°, but in two cases was as high as 103—104°, pointing to the fact that the ester consisted of the pure enolic modification. When two molecules of the ester are mixed with one of benzalaniline, the resulting substance melts at 103°, and corresponds with the enolic form. A trace of piperidine introduced in the second case gives the third isomeride, melting at 78°, and corresponding with the ketonic modification of the ester. A trace of sodium ethylate changes this back to the enolic form, melting at 103°. That acetoacetic ester itself and the additive products melting at higher temperatures contain the enolic group is shown by the fact that they give reddish-blue colorations with ferric chloride. Dibenzyl ketone gives no colour reaction with this reagent; now, if the ferric chloride reaction for the enolic modification holds with such compounds, this might be taken as showing the absence of any such form in the original substance. When an alcoholic solution of the sodium salt is poured into dilute sulphuric acid at a temperature of -10°, the ketone that separates certainly gives a dark coloration with ferric chloride, which rapidly disappears, but the result is not sufficiently definite for any conclusions to be drawn.

Dibenzyl Ketone and Benzalaniline.

1. When equal molecules, or two molecules of the ketone to one of benzalaniline, are mixed together, a syrup is obtained which slowly solidifies; when this is dried on a porous plate and recrystallised from boiling benzene, the additive product separates out, on cooling, as a mass of silky needles, giving no reaction with ferric chloride, melting at 164·5°, and yielding the following data on analysis:

Found C = 86·31; H = 6·41; N = 3·82.

C₂₈H₂₅ON requires C = 85·93; H = 6·39; N = 3·58 per cent.

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A molecular weight determination by the boiling point method, using benzene as solvent, gave 413, the calculated value being 391.

2. When a trace of piperidine is added to either of the above mixtures, and, after solidification and drying, the mass is recrystallised from benzene, crystals melting at 174.5° are obtained. The same substance can also be produced by recrystallising the additive product melting at 164.5° from benzene containing a trace of piperidine. It gives no reaction with ferric chloride. On analysis, the following figures were obtained :

Found C = 86.14 ; H = 6.47.

$C_{28}H_{25}ON$ requires C = 85.93 ; H = 6.39 per cent.

A molecular weight determination by the boiling point method gave 403, the calculated value being 391.

3. When either of the mixtures of dibenzyl ketone and benzalaniline is treated with a trace of sodium ethylate, the additive product, after recrystallisation, melts at 164.5° , but if this form, or that melting at 174.5° , is recrystallised several times from benzene containing a trace of sodium ethylate, the third isomeride, melting at 182.5° , is obtained. This modification is similar to the others in appearance, and, like them, gives no colour reaction with ferric chloride. It gave the following data on analysis :

Found C = 86.27 ; H = 6.40.

$C_{28}H_{25}ON$ requires C = 85.93 ; H = 6.39 per cent.

Repeated crystallisation, and even fractional crystallisation, did not alter the melting points of the three modifications.

The question then arises, supposing these substances are analogous to those of Schiff, of assigning to them a constitution. Schiff states that "Spuren von Piperidin ketisiren die Enolformen, Spuren von Nahrumäthylat Enolisiren die Ketoformen." If such is the case, then presumably the second substance melting at 174.5° is the ketonic form, and that melting at 182° the enolic. That melting at 164.5° would then correspond with the mixed form, but there appears to be no evidence for this view, since the two forms melting at 182.5° and 174.5° , on being mixed and recrystallised, show an intermediate melting point. Moreover, if the original substance consisted of a mixture of the enolic and ketonic modifications, it might be supposed that a trace of sodium ethylate would have been sufficient to alter the equilibrium of the two forms, giving a preponderance of enolic molecules, which, in their turn, with benzalaniline, would have given the enolic compound melting at 182.5° , or at least have raised the melting point of the additive compound ; but the presence of sodium ethylate was shown to have no effect on the resulting compound, the substance

melting at 182.5° being only formed by the action of the ethylate on either of the other two.

On the other hand, if dibenzyl ketone consists of the pure ketonic modification, which appears highly probable from its reactions, the substance melting at 164.5° is the ketonic, and presumably that melting at 174.5° is the mixed, form; but here, again, if equal molecules of the lowest and highest melting points are recrystallised from boiling benzene and light petroleum, in which both are insoluble in the cold, the resulting crystals melt at $173.5-174^{\circ}$, but are easily decomposed into their components by further crystallisation from benzene, whereas the melting point of the substance obtained by the action of piperidine remained constant at 174.5° after repeated recrystallisation.

Deoxybenzoin and Benzalaniline.

Analogous substances are being investigated, in the hope of elucidating the problem. Deoxybenzoin, for instance, behaves in a very similar way to dibenzyl ketone. It gives no reaction with ferric chloride; an alcoholic solution of the sodium salt, poured into dilute sulphuric acid at -10° , regenerates the ketone, which has the same melting point, and also gives no reaction with ferric chloride. If this test is relied on, then the substance appears to consist only of the ketonic modification.

1. When equal molecules of deoxybenzoin and benzalaniline are mixed together and kept at a temperature slightly above their melting point, the additive compound slowly separates out, the mass becoming solid. On recrystallising from a mixture of benzene and light petroleum or of chloroform and light petroleum, small, colourless needles are formed melting at 154° . The following data were obtained on analysis:

Found C = 86.18; H = 6.05.

$C_{27}H_{23}NO$ requires C = 85.94; H = 6.10 per cent.

2. If a trace of piperidine is added to the above mixture, besides the second modification melting about 166° which separates, there is a certain quantity of a much less soluble substance crystallising from boiling toluene in needles exactly the same in appearance as the preceding substance melting at 188.5° . The quantity so far obtained was not sufficient for satisfactory purification, but an analysis of the fairly pure substance seemed to indicate that it had the same composition as the other modifications. The best method for obtaining the second isomeride is to dissolve the first, melting at 154° , in chloroform containing a trace of piperidine, and after some hours to precipitate the compound from solution by light petroleum; in this way, crystals

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showing a perfectly constant melting point of $164\text{--}165^\circ$ are obtained. The following figures were obtained on analysis.

Found C = 85.88 ; H = 6.09 .

$\text{C}_{27}\text{H}_{23}\text{NO}$ requires C = 85.94 ; H = 6.10 per cent.

3. The third isomeride is obtained by dissolving either of the preceding modifications in benzene, adding a trace of sodium ethylate, allowing to stand for 24 hours, and then precipitating by light petroleum. As in the case of dibenzyl ketone, it is not formed when sodium ethylate is added to equal molecules of the ketone and benzalaniline, either alone or in benzene solution. It forms needles similar in appearance to the others and melting at 172.5° , the melting point remaining constant on repeated recrystallisation.

An analysis gave the following data :

Found C = 85.29 ; H = 6.20 .

$\text{C}_{27}\text{H}_{23}\text{NO}$ requires C = 85.94 ; H = 6.10 per cent.

These substances are being further investigated and will form the subject of a future communication. It will be seen that the results are quite analogous to those obtained with dibenzyl ketone, except for the formation of the less soluble substance of higher melting point.

Dibenzyl Ketoxime.

The oxime prepared in the usual way showed a melting point of 125° instead of 119.5° as given by Rattner (*Ber.*, 1888, 21, 1316), a difference undoubtedly due to the greater purity of the ketone. On reduction with stannous chloride, it gives dibenzyl ketone.

Dibenzyl Ketone Phenylhydrazone, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5$.

The phenylhydrazone is easily prepared by warming an alcoholic solution of phenylhydrazine and the ketone, when the condensation product separates out in well formed needles which are fairly soluble in boiling alcohol, soluble in cold ether, and melt at $128\text{--}129^\circ$. It is rapidly oxidised in contact with air, but may be kept unchanged in a vacuum even when exposed for months to bright sunlight.

Found N = 9.21 . $\text{C}_{21}\text{H}_{20}\text{N}_2$ requires N = 9.33 per cent.

Action of Sodium Ethylate on Dibenzyl Ketone.

When sodium ethylate acts on an alcoholic solution of the ketone, one of the hydrogen atoms appears to be replaced to a certain extent by the sodium, the resulting sodium compound giving some benzyl α -ethylbenzyl ketone on treatment with ethylic iodide. Dibenzyl ketone is

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recrystallised from dilute alcohol and ether, the substance separated out as glistening needles melting at 49°.

When ammonia acts on a cold alcoholic solution of the substance, and the resulting solution is treated with water, a semi-solid mass is obtained. If this is dissolved in a small quantity of hot alcohol, the imido-compound, $\text{NH}[\text{CH}(\text{C}_6\text{H}_5)\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5]_2$, crystallises out on cooling as white, silky needles. It is soluble in ether and benzene, but insoluble in light petroleum, and melts at 124°. It gave the following data on analysis:

Found C = 83.54; H = 6.28; N = 3.40.

$\text{C}_{30}\text{H}_{27}\text{N}$ requires C = 83.14; H = 6.23; N = 3.23 per cent.

On long standing, decomposition takes place, resulting in the formation of a yellow, insoluble substance possessing a high melting point. Its hydrochloride is obtained in the form of glistening needles by treating an alcoholic solution of the base with hydrochloric acid. It melts at 189° with decomposition, and is only slightly soluble in water.

If the alcoholic solution from which the above imido-compound has separated out is treated with a small quantity of water and the oil that separates is dissolved in ether, crystals of diphenyldibenzyl-dihydropyrazine, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{CH}(\text{C}_6\text{H}_5) \\ \text{CH}(\text{C}_6\text{H}_5)\cdot\text{N} \end{smallmatrix}\text{C}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, slowly separate in small quantity. These may be recrystallised from boiling alcohol or from glacial acetic acid, and is thus obtained in the form of small, white plates melting at 147°, which are almost insoluble in cold alcohol and slightly soluble in ether and benzene. A somewhat better yield is obtained by treating the bromide with a concentrated aqueous solution of ammonia and separating the mixture by the above means.

An analysis gave the following results:

Found C = 87.30; H = 6.16; N = 7.03.

$\text{C}_{30}\text{H}_{26}\text{N}_2$ requires C = 86.95; H = 6.28; N = 6.77 per cent.

Action of Aniline on Bromodibenzyl Ketone.

When aniline and the bromo-derivative are warmed together, an energetic reaction takes place, resulting in the formation of the corresponding dianilide, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NHC}_6\text{H}_5)\cdot\text{C}(\text{NC}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$. If the mass so obtained is washed with dilute acetic acid and water to get rid of the excess of aniline and then recrystallised from boiling alcohol, small needles separate out on cooling. They are only slightly soluble in cold alcohol, soluble in ether, carbon bisulphide, and benzene, and melt at 127.5°.

Found N = 7.60, $\text{C}_{27}\text{H}_{24}\text{N}_2$ requires N = 7.44 per cent.

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The hydrochloride, formed by warming an alcoholic solution with hydrochloric acid is almost insoluble in water and melts at 176°.

I have in conclusion to thank Professor S. Young for placing at my disposal some of the dibenzyl ketone prepared by his method (Trans., 1891, 59, 623).