LXV.—Condensation of Deoxybenzoin with Aromatic Aldehydes.

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THIS work was undertaken with the object of extending the analogy which exists between deoxybenzoin and 1:3-diketones, inasmuch as both these substances may be condensed with aryl aldehydes by Knoevenagel's reaction. In the case of deoxybenzoin, it is the negative phenyl group that influences the reactivity of the hydrogen atoms of the methylene group, and thus acts similarly to one of the carbonyl groups in the 1:3-diketones:

With this object in view, several aryl aldehydes, namely, salicylaldehyde, *p*-hydroxybenzaldehyde, 2-naphthol-1-aldehyde, cinnamaldehyde, vanillin, *o*-aminobenzaldehyde, *p*-dimethylaminobenzaldehyde, piperonal, and *o*- and *p*-nitrobenzaldehyde* were condensed with deoxybenzoin through the agency of hydrogen chloride, alcoholic potassium hydroxide, and diethylamine.

* It was subsequently found that deoxybenzoin had already been condensed with piperonal, and *o*- and *p*-nitrobenzaldehyde by Stobbe and Wilson (*Annalen*, 1910, 374, 237); these compounds are therefore omitted from this paper.

In the course of this work, it has been observed that different results are obtained by condensing deoxybenzoin and salicylaldehyde with hydrogen chloride at 0° and at 27° . At 0° , salicylidenedeoxybenzoin (I) is obtained, whilst at 27° pyranol formation takes place, as previously observed by Decker and von Fellenberg (*Annalen*, 1909, **364**, 1). These authors isolated the product in the form of the ferrichloride, but we isolated the hydrochloride (II) direct.

EXPERIMENTAL.

Salicylidenedeoxybenzoin (I).

0.8 Gram of salicylaldehyde was mixed with an alcoholic solution of 1 gram of deoxybenzoin. The mixture was cooled in ice and saturated with dry hydrogen chloride, when the colour of the solution changed to dark brown. The mixture was kept for two to three days, when an amorphous, brown precipitate formed, which was collected and crystallised twice from dilute alcohol. The substance darkens at 120° and melts at 160° . It is soluble in alcohol or acetic acid, but insoluble in water:

0.1850 gave 0.5686 CO_2 and 0.1042 H_2O . $\text{C} = 83.6$; $\text{H} = 6.0$.

$\text{C}_{21}\text{H}_{16}\text{O}_2$ requires $\text{C} = 84.0$; $\text{H} = 5.40$ per cent.

0.2 Gram of the substance was boiled under reflux with 10 c.c. of 50 per cent. alcoholic potassium hydroxide for two hours. The substance dissolved with change of colour. On cooling and acidifying with dilute hydrochloric acid, the original substance was precipitated.

Condensation of salicylaldehyde with deoxybenzoin could not be effected through the agency of potassium hydroxide, although various methods were tried.

2:3-Diphenylbenzopyryonium Chloride (II).

1.5 Grams of salicylaldehyde were mixed with 2 grams of deoxybenzoin dissolved in a small quantity of methyl alcohol. Dry hydrogen chloride was then passed through the mixture for two hours at 27° ; a very bright deep red coloration was developed, and the solution acquired a syrupy consistency. On keeping for two days, red, needle-shaped crystals separated. They were collected and recrystallised from dilute acetic acid containing a little hydrochloric acid, when they formed red needles melting at 100° . The substance is soluble in alcohol or acetic acid, but insoluble in water:

0.1550 gave 0.4582 CO_2 and 0.0700 H_2O . $\text{C}=80.6$; $\text{H}=5.0$.

$\text{C}_{21}\text{H}_{15}\text{OCl}$ requires $\text{C}=79.1$; $\text{H}=4.7$ per cent.

0.5 Gram of the above pyranol compound was dissolved in alcohol and boiled under reflux with 20 c.c. of 10 per cent. alcoholic potassium hydroxide for three hours. The solution was then diluted with water and acidified with dilute acetic acid. The brown precipitate was collected, dissolved in alcohol, and again precipitated by water. It was identified as the compound (I), darkening at 120° and melting at 160° . (Found: $\text{C}=83.5$; $\text{H}=6.0$. $\text{C}_{21}\text{H}_{16}\text{O}_2$ requires $\text{C}=84.0$; $\text{H}=5.4$ per cent.)

Two grams of deoxybenzoin and 1.6 grams of 2-naphthol-1-aldehyde were dissolved in methyl alcohol, and dry hydrogen chloride was passed into the solution for three hours at the ordinary temperature (25°). The solution gradually acquired a dark blue colour, and, after two to three days, dark blue needles separated. They were collected, washed with a little methyl alcohol, and recrystallised from dilute acetic acid, when they melted at $148-150^\circ$.

The compound is soluble in acetic acid, alcohol, or ether, but insoluble in water:

0.1255 gave 0.3738 CO_2 and 0.0566 H_2O . $\text{C}=81.16$; $\text{H}=5.01$.

$\text{C}_{25}\text{H}_{17}\text{OCl}$ requires $\text{C}=81.41$; $\text{H}=4.61$ per cent.

This substance decomposes gradually on keeping. It has been isolated in the form of the ferrichloride by Decker and von Fellenberg (*loc. cit.*).

Two grams of deoxybenzoin and 1.6 grams of anthranilic acid were mixed together, powdered, and heated in an oil-bath at $130-150^\circ$ for three days. The product was then rendered alkaline with dilute sodium hydroxide solution and extracted with ether. The aqueous portion was acidified with dilute acetic acid and again extracted with ether. A solid gradually separated from

the aqueous solution. This was collected, washed, and crystallised from alcohol, when colourless, rectangular cubes melting at above 300° were obtained. The compound is insoluble in water, soluble in acetic acid or ether, and sparingly so in aqueous sodium hydroxide or alcohol:

0.1357 gave 5.8 c.c. N_2 at 32° and 762 mm. $N=4.8$.

$C_{21}H_{16}ON$ requires $N=4.53$ per cent.

p-Hydroxybenzaldehyde and deoxybenzoin in molecular proportion were dissolved in a small quantity of ethyl alcohol, and the solution was cooled in ice and saturated with dry hydrogen chloride, when a change of colour took place at once. On allowing the mixture to remain for two to three days, a precipitate gradually formed, which was collected and crystallised from dilute acetic acid, separating in red needles melting at 155° . The substance is soluble in alcohol or acetic acid, but insoluble in water. It does not contain chlorine:

0.1460 gave 0.4465 CO_2 and 0.0722 H_2O . $C=83.4$; $H=5.5$.

$C_{21}H_{16}O_2$ requires $C=84.0$; $H=5.4$ per cent.

Vanillin and deoxybenzoin in molecular proportion were condensed as above, when an oil was obtained which solidified in three to four days. This separated from hot alcohol as an amorphous, reddish mass melting at 146 — 148° . It is soluble in acetic acid, alcohol, or ether, but insoluble in water. It does not contain chlorine:

0.1274 gave 0.3755 CO_2 and 0.0596 H_2O . $C=80.4$; $H=5.3$.

$C_{22}H_{18}O_3$ requires $C=80.0$; $H=5.4$ per cent.

Cinnamylidenedeoxybenzoin hydrochloride,

Deoxybenzoin and cinnamaldehyde in molecular proportion were condensed as above, and there was obtained a solid which separated from hot alcohol as an amorphous mass melting at 100° .

DEOXYBENZOIN WITH AROMATIC ALDEHYDES. 825

It is soluble in alcohol, acetic acid, or ether, but insoluble in water. The substance contains chlorine:

0.1238 gave 0.3609 CO_2 and 0.0657 H_2O . $\text{C}=79.5$; $\text{H}=5.9$.
 $\text{C}_{23}\text{H}_{19}\text{OCl}$ requires $\text{C}=79.7$; $\text{H}=5.5$ per cent.

Deoxybenzoin and cinnamaldehyde in molecular proportion were dissolved in a little alcohol, and the mixture was cooled in ice, a few drops of diethylamine being added. A crystalline precipitate formed within an hour, which separated from hot glacial acetic acid in snow-white needles melting at 145° . The yield was almost theoretical.

It is insoluble in water and sparingly soluble in ethyl alcohol or acetic acid:

0.1095 gave 0.3558 CO_2 and 0.0601 H_2O . $\text{C}=88.6$; $\text{H}=6.1$.
 $\text{C}_{23}\text{H}_{18}\text{O}$ requires $\text{C}=89.0$; $\text{H}=5.8$ per cent.

p-Dimethylaminobenzaldehyde and deoxybenzoin in molecular proportion were condensed in the usual manner, and a solid was obtained which crystallised from dilute acetic acid in colourless needles melting at 98° . It is very readily soluble in ethyl alcohol or acetic acid, but insoluble in water:

0.1159 gave 4.6 c.c. N_2 at 28° and 761 mm. $\text{N}=4.6$.
 $\text{C}_{23}\text{H}_{21}\text{ON}$ requires $\text{N}=4.3$ per cent.

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