LXX.—*Action of Hydrazine on Unsaturated γ -Diketones.*

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C. PAAL and HEINRICH SCHULZE (*Ber.*, 1900, **33**, 3796) have shown that the *cis*- and *trans*-forms of *s*-dibenzoyl ethylene,

may be readily distinguished from one another by the greater ease with which the *cis*-form interacts with hydrazine to form a 1 : 2-diazine.

We have employed this reaction to ascertain the configurations of some analogous unsaturated γ -diketones: $\alpha\beta$ -dibenzoylstyrene, dibenzoylstilbene, and α -benzoyl- β -trimethacetylstyrene. In the case of the last-mentioned compound, only one form is known; but the ease with which it forms a diazine shows that it has the *cis*-configuration. The result in the case of dibenzoylstyrene and dibenzoylstilbene has been to confirm the configurations assigned to the different modifications of these compounds by Japp and Klingemann (*Trans.*, 1890, **57**, 667):

	<i>cis</i> -Form.	<i>trans</i> -Form.
$\alpha\beta$ -Dibenzoylstyrene	m. p. 129°	m. p. 197—198°.
Dibenzoylstilbene	m. p. 220°	m. p. 232°.

The *cis*-forms of these compounds do not yield the corresponding diazines so readily as *cis-s*-dibenzoyl ethylene—doubtless owing to their

higher molecular weight and consequent greater inertness; and, for the same reason, their *trans*-forms do not interact with hydrazine at all, whereas *trans*-dibenzoylethylene differs from the *cis*-form, as already mentioned, only in the greater difficulty with which the formation of the diazine takes place. In the reactions which we are about to describe, a reducing action of the hydrazine sometimes accompanies the formation of the diazine, so that dibenzoylstyrene yields, at least when the reaction is allowed to take place in acetic acid solution, a mixture of the diazine with a dihydrodiazine; whilst, in the case of dibenzoylstilbene, a dihydrodiazine is the sole product. α -Benzoyl- β -trimethacetylstyrene, however, yields a diazine only.

EXPERIMENTAL.

Preparation of Dibenzoylstyrene, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{CO} \quad \text{CO} \cdot \text{C}_6\text{H}_5 \end{matrix}$.—The *cis*-form of this compound, melting at 129° , is readily obtained by the method described by Japp and Klingemann (*loc. cit.*, p. 672) of warming a mixture of benzil and acetophenone with alcoholic potassium hydroxide containing a little water. Johannes Wislicenus and Lehmann (*Annalen*, 1898, 302, 196), who had overlooked Japp and Klingemann's work, recommend the use of alcoholic sodium hydroxide (without the addition of water) as a condensing agent. This is quite the reverse of an improvement; for, according to the statements of these investigators, a further condensation of the dibenzoylstyrene with acetophenone to dibenzoyldiphenylbutadiene occurs under these conditions, and from the latter substance the dibenzoylstyrene has to be freed by recrystallisation.

We find that *isodibenzoylstyrene* (m. p. 197 — 198°), the *trans*-form—which was obtained by Japp and Klingemann only in quantity sufficient for analysis, and that, too, under conditions that could not always be depended upon to yield the compound—is present in small but fairly constant amount in the dark-coloured, aqueous-alcoholic, alkaline filtrate from the *cis*-dibenzoylstyrene obtained in the initial process of condensation. If this filtrate is diluted with water, the tarry precipitate steam-distilled to remove unaltered acetophenone, the non-volatile residue dissolved in alcohol, the solution boiled with animal charcoal, concentrated, and allowed to stand, a small quantity of *trans*-dibenzoylstyrene is deposited in slender colourless needles (m. p. 197 — 198°). The yield is, however, so unsatisfactory that we were obliged to prepare large quantities of the *cis*-compound in order to obtain about 2 grams of its *trans*-isomeride.

Action of Hydrazine on Dibenzoylstyrene.—Dibenzoylstyrene (m. p. 129°) was mixed with 1 mol. proportion of a 50 per cent. solution of

hydrazine hydrate and heated in glacial acetic acid solution in an open flask on the water-bath for 15 minutes.

The experiment was repeated, using 2 mol. proportions of hydrazine hydrate.

In both cases the product, precipitated by water and crystallised either from alcohol or from benzene, consisted of a mixture of flat prisms or plates, which formed the chief product, with a small quantity of slender needles, the larger proportion of hydrazine hydrate giving a slightly improved yield of the latter compound. The two substances were separated by levigation with the mother liquor, the lighter needles being readily floated off.

The flat prisms or plates were purified by recrystallisation from benzene or alcohol. From the former solvent the substance was deposited in tables, from the latter in scales, melting at 170° . It was identical with Alexander Smith's 3:4:6-triphenyl-1:2-diazine,

(m. p. 171° , Smith), obtained by the oxidation of 3:4:6-triphenyl-1:2-dihydro-1:2-diazine (*Annalen*, 1896, **289**, 319), as we found by comparing our specimen with one prepared by Smith's method.

0.3427 gave 28.8 c.c. moist nitrogen at 10° and 759 mm. $\text{N} = 9.00$.

$\text{C}_{22}\text{H}_{16}\text{N}_2$ requires $\text{N} = 9.09$ per cent.

The needles were purified by recrystallisation, first from boiling alcohol and afterwards from glacial acetic acid. They were redeposited in slender, colourless needles, with a satiny lustre and melting at 181.5 — 182.5° , with decomposition, when rapidly heated. The crystals turned yellow on exposure to light.

0.1609 gave 0.5017 CO_2 and 0.0894 H_2O . $\text{C} = 85.03$; $\text{H} = 6.17$.

0.1903 „ 14.50 c.c. moist nitrogen at 13° and 758 mm. $\text{N} = 8.98$.

$\text{C}_{22}\text{H}_{18}\text{N}_2$ requires $\text{C} = 85.16$; $\text{H} = 5.81$; $\text{N} = 9.03$ per cent.

This is the formula of a 3:4:6-triphenyldihydro-1:2-diazine. The position of the two additive hydrogen atoms remains for the present undetermined. The substance is not identical with Alexander Smith's 3:4:6-triphenyl-1:2-dihydro-1:2-diazine (m. p. 186 — 188° , when quickly heated) (*Annalen*, 1896, **289**, 316), obtained by the interaction of desylacetophenone with hydrazine, a specimen of which we prepared for comparison. Smith's compound is of a bright yellow

colour, and was oxidised to 3 : 4 : 6-triphenyl-1 : 2-diazine in an attempt which we made to acetylate it by means of acetic anhydride containing a little concentrated sulphuric acid ; in fact Smith had already oxidised it to this compound by treatment with chromium trioxide. Our isomeride, on the other hand, is colourless ; an attempt to acetylate it yielded only a resinous mass ; and we were quite unable to obtain the diazine from it by oxidation.

We afterwards found that by warming dibenzoylstyrene (m. p. 129°) with an excess of hydrazine in alcoholic (instead of acetic acid) solution on the water-bath for 15 minutes, an excellent yield of 3 : 4 : 6-triphenyl-1 : 2-diazine, without any admixture of the dihydro-compound, was obtained.

We also found that none of the dihydro-compound is formed when the diazine is boiled with hydrazine hydrate in acetic acid solution. In fact sodium in boiling alcohol has no action on the diazine. The reduction by hydrazine, to which the formation of the dihydro-compound is due, must, therefore, precede the condensation in which the diazine is formed.

The experiment was tried whether *isodibenzoylstyrene* (m. p. 197—198°) would interact with hydrazine. After boiling the mixture in alcoholic solution for 6 hours, the *iso*-compound was recovered unchanged. *iso*Dibenzoylstyrene is therefore the *trans*-modification.

Action of Hydrazine on Dibenzoylstilbene,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \cdot \text{CO} \quad \text{CO} \cdot \text{C}_6\text{H}_5 \end{array}$$

Dibenzoylstilbene (m. p. 220°), regarded by Japp and Klingemann (*loc. cit.*) as the *cis*-form, was obtained by Zinin by the oxidation of tetraphenylfurfuran ("lepiden") with nitric acid, and was termed by him "acicular oxylepiden." By heating it with alcoholic potassium hydroxide he converted it into the isomeric "octahedral oxylepiden" (m. p. 232°), which Japp and Klingemann formulate as *trans*-dibenzoylstilbene. That both these compounds are dibenzoylstilbenes is proved by the fact that, on reduction, they both yield tetraphenylfurfuran. The dibenzoylstilbenes used in the following experiments were prepared by Zinin's methods (Beilstein's *Handbuch*, 3rd ed., 3, 311 and 312).

Three grams of dibenzoylstilbene (m. p. 220°) and 1·2 grams of a 50 per cent. solution of hydrazine hydrate were dissolved in absolute alcohol and boiled for 1½ hours. On cooling, the solution deposited yellow needles which, by repeated recrystallisation from boiling alcohol, were obtained with the constant melting point of 207—208°. The yellow colour was not removed by boiling the solution with animal charcoal. The compound is difficult to burn and the figures for carbon are somewhat low.

0.1752 gave 0.5544 CO_2 and 0.0934 H_2O . C = 86.30 ; H = 5.94.
 0.1774 „ 0.5594 CO_2 „ 0.0942 H_2O . C = 85.99 ; H = 5.90.
 0.1763 „ 0.5570 CO_2 „ 0.0934 H_2O . C = 86.16 ; H = 5.89.
 0.1722 „ 10.65 c.c. moist nitrogen at 11° and 757 mm. N = 7.34.
 $\text{C}_{28}\text{H}_{22}\text{N}_2$ requires C = 87.05 ; H = 5.70 ; N = 7.25 per cent.

This is the formula of a tetraphenyldihydrodiazine. The formula of a tetraphenyldiazine, $\text{C}_{28}\text{H}_{20}\text{N}_2$, on the other hand, would require C = 87.50 ; H = 5.21 ; N = 7.29 per cent., and for this the value found for hydrogen is much too high. A portion of the hydrazine has therefore exercised a reducing action as in the case already described.

The compound is a 3 : 4 : 5 : 6-tetraphenyldihydro-1 : 2-diazine,

in which the position of the two additive hydrogen atoms has not yet been determined.

Dibenzoylstilbene (m. p. 232°)—"octahedral oxylepiden"—was then boiled with excess of hydrazine hydrate in alcoholic solution for 9 hours, renewing the hydrazine hydrate. On allowing the solution to cool, practically the whole of the dibenzoylstilbene (m. p. 232°) crystallised out unchanged. No new product could be detected.

The dibenzoylstilbene melting at 220° is therefore the *cis*-form; that melting at 232° the *trans*-form.

Action of Hydrazine on α -Benzoyl- β -trimethacetylstyrene,

(m. p. 115°).— α -Benzoyl- β -trimethacetylstyrene was obtained by Japp and Maitland (Trans., 1904, **85**, 1496) by the condensation of benzil with methyl *tert*-butyl ketone under the influence of alcoholic potassium hydroxide.

A mixture of benzoyltrimethacetylstyrene with an excess of hydrazine hydrate was dissolved in alcohol and boiled for 15 minutes. On cooling, the solution deposited wedge-shaped crystals, which, after recrystallisation from alcohol, melted constantly at 185 — 186° . The yield was good.

0.1738 gave 0.5288 CO_2 and 0.1094 H_2O . C = 82.98 ; H = 6.99.
 0.1554 „ 12.97 c.c. moist nitrogen at 11° and 731 mm. N = 9.57.
 $\text{C}_{20}\text{H}_{20}\text{N}_2$ requires C = 83.33 ; H = 6.95 ; N = 9.72 per cent.

The compound is 3 : 4-*diphenyl*-6-*tert.*-*butyl*-1 : 2-*diazine*,

Neither in the foregoing experiment, nor in one in which boiling acetic acid was used as a solvent for the interacting substances, could any trace of the corresponding dihydrodiazine be detected. The experiment in which acetic acid was employed yielded a very resinous product.

The α -benzoyl- β -trimethacetylstyrene melting at 115° is the only known form of this substance ; but, as already mentioned, the ease with which it interacts with hydrazine to form a diazine leads us to assign to it the *cis*-configuration.

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