CXXXIX.—*Imide Ring Closure in Derivatives of Diketosuccinic Acid Phenylosazone.*

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ALTHOUGH diketosuccinic anhydride phenylosazone has been long known, its properties have been little studied, the products of its reduction only having been described (J., 1927, 2133). In the present paper, the formation of derivatives containing the imide ring by the action of ammonia, primary amines, and α-hydrazines upon this anhydride is described.

Diketosuccinimide phenylosazone (I) is most readily prepared by fusing the anhydride with urea. It is very stable, being unchanged by prolonged boiling with hydrochloric acid, although it dissolves in boiling aqueous sodium hydroxide, liberating ammonia and forming sodium diketosuccinate phenylosazone (II), which is at once converted by acids into 4 : 5-diketo-1-phenylpyrazoline-3-carboxylic acid 4-phenylhydrazone (III).

Benzylamine combines at once with diketosuccinic anhydride phenylosazone if the latter is suspended in ether, the *benzylamine* salt of *diketosuccinobenzylamic acid phenylosazone* (IV) being formed. The base is readily removed and the anhydride re-formed by heating with acetic anhydride, and acidification causes the formation of the corresponding imide, diketosuccinobenzylimide phenylosazone (V). Dibenzylamine reacts in a similar manner, forming the *salt* of the diketosuccinodibenzylamic acid, from which acids liberate one molecule of the base, yielding *diketosuccinodibenzylamic acid phenylosazone*, imide formation not being here possible and the base preventing, as in the former case, the pyrazoline ring closure.

Aniline reacts with the anhydride to yield a mixture of *diketosuccinanilic acid phenylosazone* (VI) and *diketosuccinanil phenylosazone* (VII). By prolonged boiling with aniline, the former is converted into the latter, the yield of which consequently increases with the time of heating. Since, however, decomposition occurs during prolonged heating at this high temperature, it is advisable to boil for a short time only and to separate the mixture of anilic acid and anil. The former is converted by prolonged boiling with aqueous-alcoholic hydrochloric acid into the pyrazoline derivative (III).

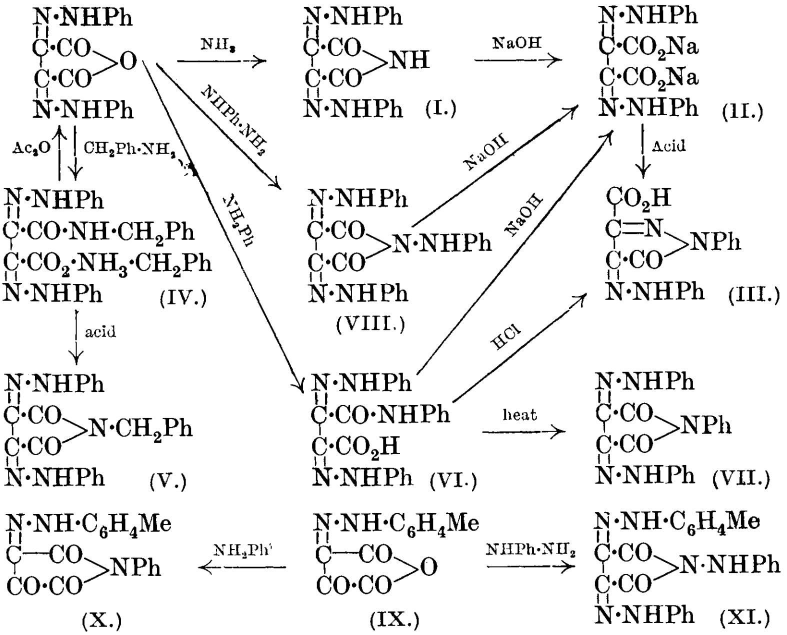
The anhydride is unaffected by prolonged fusion with tribenzylamine or with diphenylamine.

The anhydride reacts with phenylhydrazine in hot or cold acetic acid solution to yield a corresponding imide derivative, *diketosuccinophenylhydrazide phenylosazone* (VIII). *as*-Phenylmethylhydrazine acts similarly. No intermediate product could be isolated in either case and it therefore seems probable that both hydrazides are of the α-variety.

Analogous derivatives of certain substituted phenylhydrazones and osazones of diketosuccinic anhydride have also been prepared. The tolylhydrazones (IX) (J., 1927, 2793) yield with aniline the corresponding *anils* (X), the ketonic group remaining unchanged. Phenylhydrazine acts upon the ketonic group as well as forming the *hydrazide* (XI). The 2 : 4-dichloro- and 2 : 4-dibromo-anhydrides (J., 1927, 1323) react with aniline less readily, the products consisting entirely of the corresponding *anils*.

All the above compounds which contain the succinimide ring are, like the parent substance, very stable towards acids, but are converted by boiling 10% sodium hydroxide solution into sodium diketosuccinate phenylosazones.

The following scheme represents the main reactions :



EXPERIMENTAL.

Diketosuccinimide phenylosazone (I) was prepared by fusing gently for 10 minutes a mixture of 5 g. of diketosuccinic anhydride phenylosazone and 50 g. of urea. The pasty, orange-yellow product, when cold, was powdered, extracted with hot water to remove urea and biuret, and crystallised from alcohol, in which it was rather sparingly soluble, separating in orange-yellow, long plates or thin prisms, m. p. 189° (Found: C, 62·5; H, 4·2; N, 22·8. $C_{16}H_{13}O_2N_5$ requires C, 62·8; H, 4·3; N, 22·8%).

The *benzylamine* salt of *diketosuccinobenzylamic acid phenylosazone* (IV) was prepared by adding 4 c.c. of benzylamine (excess) to a fine suspension of 3 g. of the anhydride in 30 c.c. of ether. The red anhydride was slowly converted into a yellow pulp of the *benzylamine* salt, which was filtered off and washed with ether. It crystallised from acetone, in which it was rather sparingly soluble, in light yellow, hair-like needles, m. p. 165° (decomp.) (Found: C, 68·8; H, 5·7; N, 15·95. $C_{30}H_{30}O_3N_6$ requires C, 68·9; H, 5·7; N, 16·1%).

Diketosuccinobenzylimide phenylosazone (V) was obtained from the above benzylamine salt by crystallisation from acetic acid, or by the addition of hydrochloric acid to its alcoholic solution. It crystallised from alcohol, in which it was rather sparingly soluble, in orange-yellow, rhombic plates, m. p. 179° (Found: N, 17·6. $C_{23}H_{19}O_2N_5$ requires N, 17·6%).

The *dibenzylamine* salt of *diketosuccinodibenzylamic acid phenylosazone*, $(CH_2Ph)_2N\cdot CO\cdot C(:N\cdot NHPh)\cdot C(:N\cdot NHPh)\cdot CO_2NH_2(CH_2Ph)_2$, was prepared in a similar manner to the corresponding benzylamine compound. It crystallised from alcohol, in which it was very soluble, in light yellow, hair-like needles, m. p. 161—162° (decomp.) (Found: N, 11·85. $C_{44}H_{42}O_3N_6$ requires N, 11·95%).

Diketosuccinodibenzylamic acid phenylosazone,

$$(CH_2Ph)_2N\cdot CO\cdot C(:N\cdot NHPh)\cdot C(:N\cdot NHPh)\cdot CO_2H,$$

was obtained from the above salt by the addition of hydrochloric acid to its alcoholic solution. It crystallised from alcohol, in which it was moderately easily soluble, in orange-yellow, flattened prisms, m. p. 180° (Found: N, 13·9. $C_{30}H_{27}O_3N_5$ requires N, 13·9%).

Diketosuccinanilic Acid Phenylosazone (VI).—When 2 g. of the anhydride were boiled for 10 minutes with 40 c.c. of aniline, a clear dark reddish-brown solution was obtained from which *diketosuccinanilic acid phenylosazone* separated on cooling. It was filtered off, washed with alcohol, and recrystallised from alcohol, in which it was rather sparingly soluble, separating in very small, orange-yellow, fine prisms, m. p. 201° (decomp.) (Found: C, 65·6; H, 4·6; N, 17·25. $C_{22}H_{19}O_3N_5$ requires C, 65·8; H, 4·7; N, 17·45%).

This compound crystallises from acetic acid, in which it is very soluble, in glistening, orange-yellow, long plates, containing one molecule of acetic acid, which melt between 135° and 200° according to the rate of heating. The crystals must be dried on a porous glass filter in a current of air; they lose acetic acid slowly on heating below 100°, and on being washed with alcohol or ether they fall to a fine powder of the pure compound (m. p. 201°, decomp.) (Found: loss after heating at 130°, 13·1. $C_{22}H_{19}O_3N_5,C_2H_4O_2$ requires loss, 13·0%).

Diketosuccinanil phenylosazone (VII) slowly separated as a felted mass of orange-red, slender prisms when the aniline mother-liquor from the above preparation was diluted with about 150 c.c. of alcohol. It crystallised from acetic acid, in which it was moderately easily soluble, in orange-red, long, slender prisms, m. p. 252° (decomp.) (Found: C, 69·1; H, 4·5; N, 18·1. $C_{22}H_{17}O_2N_5$ requires C, 68·9; H, 4·4; N, 18·3%).

Diketosuccinophenylhydrazide phenylosazone (VIII) was formed by the action of phenylhydrazine upon the anhydride in acetic acid suspension, slowly in the cold but almost instantaneously on heating. The *hydrazide*, which separated in felted, fine prisms on cooling, crystallised from acetic acid, in which it was moderately easily soluble, in orange-yellow, thin prisms, m. p. 270° (decomp.) (Found : C, 66·1; H, 4·55; N, 21·1. $C_{22}H_{18}O_2N_6$ requires C, 66·3; H, 4·5; N, 21·1%).

Diketosuccinophenylmethylhydrazide phenylosazone (formula as VIII) was prepared in the same manner by the action of phenylmethylhydrazine upon the anhydride. It crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, fine prisms, m. p. 243·5° (decomp.) (Found : N, 20·5. $C_{23}H_{20}O_2N_6$ requires N, 20·4%).

Diketosuccinanil p-*tolylhydrazone* (X) was obtained by boiling 2 g. of diketosuccinic anhydride *p*-tolylhydrazone (IX) with 10 c.c. of aniline for a minute. A very dark red solution was obtained which, after being cooled and diluted with 40 c.c. of ether, slowly deposited the *anil.* This crystallised from alcohol, in which it was sparingly soluble, in yellow, rhombic plates, m. p. 199° (decomp.) (Found : C, 66·6; H, 4·5; N, 13·7. $C_{17}H_{13}O_3N_3$ requires C, 66·4; H, 4·2; N, 13·8%).

Diketosuccinophenylhydrazide o-*tolylphenylosazone* (XI) was prepared by heating 2 g. of diketosuccinic anhydride *o*-tolylhydrazone with 3 g. of phenylhydrazine in acetic acid solution. It crystallised from acetic acid, in which it was moderately easily soluble, in orange-yellow, fine prisms, m. p. 250° (decomp.) (Found : N, 20·5. $C_{23}H_{20}O_2N_6$ requires N, 20·4%).

Diketosuccinanil 2 : 4-*dichlorophenylosazone* (formula as VII) was prepared by boiling the corresponding anhydride with aniline. It crystallised from acetic acid, in which it was sparingly soluble, in orange-yellow, hair-like needles, m. p. 308° (decomp.) (Found : Cl, 27·1. $C_{22}H_{13}O_2N_5Cl_4$ requires Cl, 27·25%).

Diketosuccinanil 2 : 4-*dibromophenylosazone*, prepared in the same manner, crystallised from acetic acid, in which it was sparingly soluble, in orange, hair-like needles, m. p. 309° (decomp.) (Found : Br, 45·8. $C_{22}H_{13}O_2N_5Br_4$ requires Br, 45·8%).

Diketosuccinophenylhydrazide 2 : 4-*dichlorophenylosazone* (formula as VIII) was prepared in the same manner as the unsubstituted compound from the corresponding anhydride. It crystallised from acetic acid, in which it was sparingly soluble, in deep yellow, hair-like needles, m. p. 280° (decomp.) (Found : Cl, 26·6. $C_{22}H_{14}O_2N_6Cl_4$ requires Cl, 26·5%).

Diketosuccinophenylhydrazide 2 : 4-*dibromophenylosazone*, which was similarly prepared, crystallised from acetic acid, in which it was sparingly soluble, in orange-yellow, hair-like needles, m. p. 295° (decomp.) (Found : Br, 44·8. $C_{22}H_{14}O_2N_6Br_4$ requires Br, 44·8%).

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