3, 5-DIKETOPYRAZOLIDINE DERIVATIVES. II.

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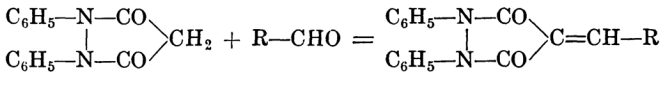
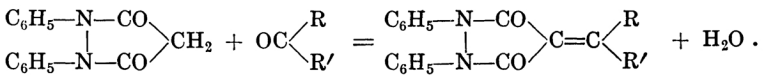
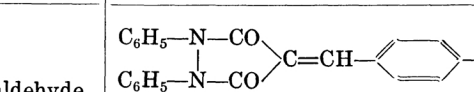
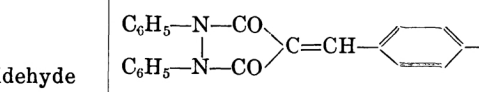
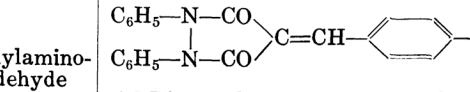
In the preceding paper,[1] it was reported as a property of 1, 2-diphenyl-3, 5-diketopyrazolidine that the compound condensed with aldehydes and ketones forming various coloured substances according to the following general formulae :—

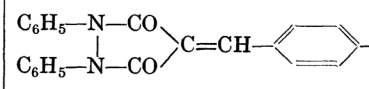
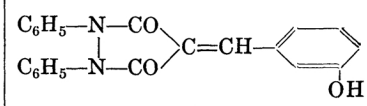
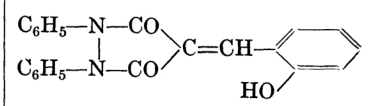
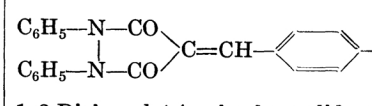
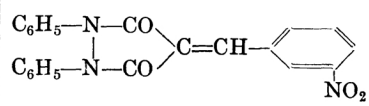
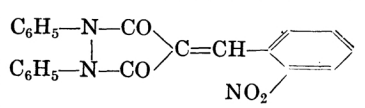
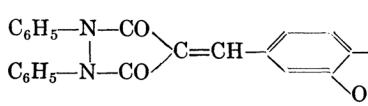


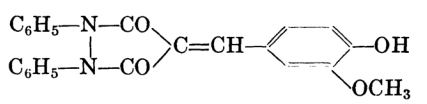
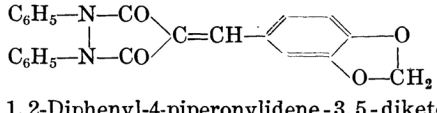
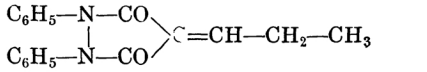


And six condensation products were synthesised in the previous experiment. In this paper, another thirteen condensation products with aldehydes are reported. Their colours and melting points are described in the following table.

Aldehyde	Condensation product	M.P., °C	Colour
p-Tolylaldehyde	 [1] 1, 2-Diphenyl-4-(*p*-methylbenzylidene)-3, 5-diketopyrpzolidine	175	Yellow
Anisaldehyde	 [2] 1, 2-Diphenyl-4-(*p*-methoxybenzylidene)-3, 5-diketopyrazolidine	199	Yellow
p-Dimethylamino-benzaldehyde	 [3] 1, 2-Diphenyl-4-(*p*-dimethylaminobenzylidene)-3, 5-diketopyrazolidine	256 (decomposed)	Vermilion

(1) This Bulletin, **6** (1931), 1.

Aldehyde	Condensation product	M.P., °C	Colour
p-Hydroxybenzaldehyde	 [4] 1,2-Diphenyl-4-(*p*-hydroxybenzylidene)-3, 5-diketopyrazolidine	231–232	Yellowish brown
m-Hydroxybenzaldehyde	 [5] 1, 2-Diphenyl-4-(*m*-hydroxybenzylidene)-3, 5-diketopyrazolidine	194	Reddish yellow
Salicylaldehyde	 [6] 1, 2-Diphenyl-4-(*o*-hydroxybenzylidene)-3, 5-diketopyrazolidine	193	Reddish yellow
p-Nitrobenzaldehyde	 [7] 1, 2-Diphenyl-4-(*p*-nitrobenzylidene)-3, 5-diketopyrazolidine	243	Reddish brown
m-Nitrobenzaldehyde	 [8] 1, 2-Diphenyl-4-(*m*-nitrobenzylidene)-3, 5-diketopyrazolidine	185	Russet
o-Nitrobenzaldehyde	 [9] 1, 2-Diphenyl-4-(*o*-nitrobenzylidene)-3, 5-diketopyrazolidine	174–176	Reddish yellow
Protocatechualdehyde	 [10] 1, 2-Diphenyl-4-(3′, 4′-dihydroxybenzylidene)-3, 5-diketopyrazolidine	255 (decomposed)	Yellow

Aldehyde	Condensation product	M.P., °C	Colour
Vanillin	 [11] 1, 2-Diphenyl-4-(3′-methoxy-4′-hydroxy-benzylidene)-3, 5-diketopyrazolidine	156–157	Yellow
Piperonal	 [12] 1, 2-Diphenyl-4-piperonylidene-3, 5-diketopyrazolidine	234–235	Yellow
Propionaldehyde	 [13] 1, 2-Diphenyl-4-propylidene-3, 5-diketopyrazolidine	260 (decomposed)	Yellow

The properties and the methods of formation of these compounds are as follows.

1, 2-Diphenyl-4-(p-methylbenzylidene)-3, 5-diketopyrazolidine, [1]. When 0.8 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine and 1 gr. of *p*-tolylaldehyde were heated on the water-bath, a yellow mass was obtained. On recrystallization from alcohol, it gave yellow prismatic needles, which melts at 175° C. The yield was 1 gr.

Anal. Subst. = 0.0111 gr.; N_2 = 0.784 c.c. (25°C., 754 mm.) (Pregl's method).
Found: N = 7.93%. Calc. for $C_{23}H_{18}O_2N_2$: N = 7.91%.

1, 2-Diphenyl-4-(p-methoxybenzylidene)-3, 5-diketopyrazolidine, [2]. When 0.6 gr. of diphenyldiketopyrazolidine and 0.8 gr. of anis-aldehyde were heated on the water-bath under stirring, reddish yellow mass was obtained. On recrystallization from alcohol, it gave yellow long needles. It is sparingly soluble in cold alcohol. The yield was 0.5 gr. M.p.: 199° C.

Anal. Subst. = 0.0173 gr.; N_2 = 1.202 c.c. (26°C., 757 mm.) (Pregl's method).
Found: N = 7.80%. Calc. for $C_{23}H_{18}N_2O_3$: N = 7.57%.

1, 2-Diphenyl-4-(p-dimethylamino-benzylidene)-3, 5-diketopyrazolidine, [3]. When 0.8 gr. of diphenyldiketopyrazolidine and 1 gr. of *p*-dimethylaminobenzaldehyde were mixed and heated on a water-bath for a few minutes, the mixture solidified to a mass of vermilion colour. It was well

washed with hot alcohol, and the condensation product was left in an almost pure state. It is soluble in benzene, sparingly soluble in hot alcohol. It melts at 256° C. Before melting it seems to be somewhat decomposed. The yield was 1 gr.

Anal. Subst. = 0.0125 gr.; N_2 = 1.205 c.c. (26°C., 759 mm.) (Pregl's method).
Found: N = 10.86%. Calc. for $C_{24}H_{21}O_2N_3$: N = 10.97%.

1, 2-Diphenyl-4-(p-hydroxybenzylidene)-3, 5-diketopyrazolidine, [4]. When 1 gr. of *p*-hydroxybenzaldehyde and 0.8 gr. of diphenyldiketopyrazolidine were fused together on a wire gauze, the mixture solidified to a reddish brown mass. On recrystallization from alcohol it gave yellowish brown prisms, which melts at 231°–232° C. The yield was 0.8 gr. The compound is soluble in benzene, sparingly soluble in cold alcohol, but insoluble in water. It is soluble in alkali solution giving it red colour.

Anal. Subst. = 0.0116 gr.; N_2 = 0.790 c.c. (25°C., 757 mm.) (Pregl's method).
Found: N = 7.67%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(m-hydroxybenzylidene)-3, 5-diketopyrazolidine, [5]. When 0.5 gr. of *m*-hydroxybenzaldehyde and 0.5 gr. of diphenyl-diketopyrazolidine were heated on a wire gauze, a reddish brown viscous liquid was obtained, which on cooling solidified to a mass. On recrystallization from a small quantity of alcohol, it gave reddish yellow plates, which melts at 194° C. It is moderately soluble in alcohol. The yield was 0.4 gr.

Anal. Subst. = 0.0105 gr.; N_2 = 0.752 c.c. (28°C., 754 mm.) (Pregl's method).
Found: N = 7.96%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(o-hydroxybenzylidene)-3, 5-diketopyrazolidine, [8]. When 0.8 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine and 1.7 gr. of salicylaldehyde were heated on the water-bath for about five minutes, the former dissolved into the latter forming brownish yellow solution, which solidified on cooling to a mass. It was pressed on a porous plate to remove the excess of salicylaldehyde, and was recrystallized from ethyl alcohol. The yield was 0.5 gr. The compound forms reddish yellow prisms, which melts at 193° C., and is moderately soluble in ethyl alcohol.

Anal. Subst. = 0.0107 gr.; N_2 = 0.757 c.c. (26°C., 761 mm.) (Pregl's method).
Found: N = 7.99%. Calc. for $C_{22}H_{16}O_3N_2$: N = 7.87%.

1, 2-Diphenyl-4-(p-nitrobenzylidene)-3, 5-diketopyrazolidine, [7]. When 1 gr. of *p*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were heated at 110°C., a brownish black mass was obtained. It was purified by dissolving it in hot benzene and allowing it to stand after the addition of

ethyl alcohol. The compound crystallized out as reddish brown prisms. The yield was 0.8 gr. It melts at 243°C.; and is soluble in benzene and chloroform, and sparingly soluble in alcohol and ether.

Anal. Subst. = 0.0108 gr.; N_2 = 1.039 c.c. (25°C., 760 mm.) (Pregl's method).
Found: N = 10.88%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(m-nitrobenzylidene)-3, 5-diketopyrazolidine, [8]. One gram of *m*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were heated on the water-bath for a few minutes. On cooling the product solidified to a mass of red colour. It was dissolved in hot alcohol and this solution gave russet crystals when allowed to stand for one day. They were recrystallized once from alcohol. M.p.: 185°C. The yield was 0.6 gr.

Anal. Subst. = 0.0113 gr.; N_2 = 1.137 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 11.19%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(o-nitrobenzylidene)-3, 5-diketopyrazolidine, [9]. One gram of *o*-nitrobenzaldehyde and 1 gr. of diphenyldiketopyrazolidine were fused. The product solidified on cooling to a mass, which gave the prismatic needles of reddish yellow colour on recrystallization from alcohol. The yield was 0.7 gr. M.p.: 174°–176°C.

Anal. Subst. = 0.0111 gr.; N_2 = 1.106 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 11.09%. Calc. for $C_{22}H_{15}O_4N_3$: N = 10.91%.

1, 2-Diphenyl-4-(3', 4'-dihydroxybenzylidene)-3, 5-diketopyrazolidine, [10]. 1.2 Gr. of protocatechualdehyde and 1.2 gr. of 1, 2-diphenyl-3, 5-diketopyrazolidine were heated on a wire gauze above 150°C., and were kneaded into a mass. It was heated for a while with alcohol. The solution was coloured dark brown and the condensation product remained as a yellow precipitate. It was recrystallized from alcohol. The yield was 1.5 gr. M.p.: 255°C. Before melting it seems to be somewhat decomposed.

Anal. Subst. = 0.0116 gr.; N_2 = 0.811 c.c. (25°C., 749 mm.) (Pregl's method).
Found: N = 7.79%. Calc. for $C_{22}H_{16}O_4N_2$: N = 7.53%.

1, 2-Diphenyl-4-(3'-methoxy-4'-hydroxy-benzylidene)-3, 5-diketopyrazolidine, [11]. 1.2 Gr. of vanillin and 1.2 gr. of diphenyldiketopyrazolidine were fused on the water-bath and the product was dissolved in hot alcohol. This solution gave orange red crystals when allowed to stand for one day. On recrystallization from ligroin, the compound crystallized out as yellow crystals. It melts at 156°–157°C.; and the result of the analysis corresponds to the compound [11]. The yield was 1 gr.

Anal. Subst. = 0.0124 gr.; N_2 = 0.863 c.c. (27°C., 750 mm.) (Pregl's method).
Found: N = 7.72%. Calc. for $C_{23}H_{18}O_4N_2$: N = 7.25%.

1, 2-Diphenyl-4-piperonylidene-3, 5-diketopyrazolidine, [12]. When 1.2 gr. of piperonal and 1.2 gr. of diphenyldiketopyrazolidine were warmed on the water-bath under stirring, the whole changed into yellow powder. It was purified by dissolving it in hot chloroform and allowing it to stand after the addition of ethyl alcohol. The compound crystallized out as yellow needles. The yield was 1.6 gr. M.p.: 234°–235°C. It is soluble in ether, sparingly soluble in ethyl alcohol.

Anal. Subst. = 0.0152 gr.; N_2 = 1.029 c.c. (26°C., 760 mm.) (Pregl's method).
Found: N = 7.63%. Calc. for $C_{23}H_{16}O_4N_2$: N = 7.29%.

1, 2-Diphenyl-4-propylidene-3, 5-diketopyrazolidine, [13]. When 1 gr. of diphenyldiketopyrazolidine and 2 gr. of propionaldehyde were warmed on the water-bath for a while, the former dissolved into the latter forming brown solution. The excess of propionaldehyde was then evaporated off, and alcohol was added to the residue, and the solution was allowed to stand for one day. The condensation product deposited out as yellow crystals. It was filtered and washed with alcohol. The yield was 0.15 gr. It melts at 260°C. Before melting, it seems to be somewhat decomposed.

Anal. Subst. = 0.0107 gr.; N = 0.921 c.c. (28°C., 755 mm.) (Pregl's method).
Found: N = 9.58%. Calc. for $C_{18}H_{16}O_2N_2$: N = 9.59%.

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