CONDENSATION OF ALDEHYDES AND KETONES

The Diketone Condensation of β-Aceto- and β-Propionaphthalenes with Furfural

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The alkaline condensation of β-aceto- and β-propionaphthalenes with furfural has given, respectively, 2-(α-furfuryl)-1, 3-di(β-naphthoyl)-propane and 3-(α-furyl)-2, 4-di(β-naphthoyl)pentane; both δ-diketones have also been obtained by the Michael condensation. Under more severe conditions, two molecules of furfural condense with three molecules of β-acetonaphthalene to form 2, 4-di(α-furyl)-1, 3, 5-tri(β-naphthoyl)pentane. Under similar conditions, benzaldehyde exhibits only a feeble capacity for triketone condensation with β-acetonaphthalene. The condensation of β-propionaphthalene with furfural has given the new compound furylidenepropionaphthalene. It has been shown that both under the conditions of the improved Chichibabin pyridine synthesis and under the conditions of the Leuckhardt reaction, 3-(α-furyl)-1, 3-di(β-naphthoyl)propane gives 4-(α-furyl)-2, 6-di(β-naphthyl)pyridine.

The diketone condensation of β-acetonaphthalene and β-propionaphthalene has been carried out previously with benzaldehyde and isobutyraldehyde in the case of the first reaction [1] and with formaldehyde in the case of the second [2]. In all cases, the reaction took place with a good yield of the corresponding 1,5-diketone.

In the present paper we describe the result of our attempts to effect the diketone condensation of both the ketones mentioned with furfural. It was found that when a solution of 2.5 moles of β-acetonapthalene and 1 mole of furfural in 0.2 N methanolic sodium hydroxide was boiled for one hour, ~40% of furylidenedi(β-acetonaphthalene)[2-(α-furyl)-1, 3-di(β-naphthoyl)-propane] (I) and 35% of furylidene-β-acetonaphthalene (II) were obtained. If, under the same conditions, the condensation were carried out in boiling 0.2 N ethanolic sodium hydroxide, a mixture was obtained consisting of the diketone I and a substance corresponding to a difuryltris(β-acetonaphthalene)[2, 4-di(α-furyl)-1, 3, 5-tri(β-naphthoyl)pentane] (III). In a 0.5 N ethanolic solution of sodium hydroxide, however, only the triketone III was obtained. Consequently, an increase in the "severity" of the condensation conditions leads to the formation of the triketone III. A similar pattern was found by Kostanecki et al. in the condensation of acetophenone with benzaldehyde [3] and with furfural [4]. The formation of a triketone takes place with the addition of the α,β-unsaturated ketone to the 1,5-diketone [5], in our case, obviously, as a result of the reaction I + II → III.

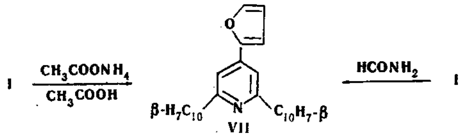
It is interesting that, under the same conditions, with benzaldehyde, β-acetonaphthalene gives mainly the 1,5-diketone, benzylidenedi(β-acetonaphthalene) [1] and only an extremely small amount of the triketone dibenzylidenetris(acetonaphthalene)[1, 3, 5-tri(β-naphthoyl)-2,4-diphenylpentane] (IV), the presence of which in the reaction products we have established for the first time.

The condensation of β-propionaphthalene with furfural under the influence of 2 N NaOH and ethanol leads mainly to furylidene-β-propionaphthalene (V) and a small amount of furylidenedi(β-propionaphthalene) [3-(α-furyl)-2,4-di(β-naphthoyl)pentane] (IV).

In order to confirm their structures, the diketones I and III were also obtained by the Michael condensation.

$$\mathrm{II} + \mathrm{CH_3COC_{10}H_7\text{-}\beta} \longrightarrow \mathrm{I}$$
$$\mathrm{V} + \mathrm{CH_3CH_2COC_{10}H_7\text{-}\beta} \longrightarrow \mathrm{VI}$$

Under the conditions of the Chichibabin pyridine synthesis [6], the diketone I gave a base corresponding to 4-(β-furyl)-2,6-di(β-naphthyl)pyridine (VII). When the diketone I was heated with formamide (Leuckhardt reaction) the same base VII was obtained.



VII

The pyridine VII, like its phenyl analog, 2,6-di(β-naphthyl)-4-phenylpyridine, readily forms a picrate but it does not give a stable hydrochloride. Consequently, here again the naphthyl radicals greatly weaken the basicity of the base with respect to salt formation; the picrate is probably not a salt but a molecular compound of picric acid with the naphthalene nuclei.

EXPERIMENTAL

Furylidenedi(β-acetonaphthalene) (I).

a) Over 1 hr, 4.4 g of furfural in 10 ml of ethanol was added to a boiling solution of 18.7 g of β-acetonaphthalene in 100 ml of 0.2 N methanolic sodium hydroxide. After cooling, the mixture was neutralized with 50% acetic acid. The reaction product was separated off by decantation and was washed with water and ethanol. Yield 8 g, mp 121°–122° C (from ethanol–benzene, 1:1). Evaporation of the combined decantates and the ethanol used for washing gave 4 g of furylidene-β-acetonaphthalene, mp 90°–91° C [7]; a small amount of the initial β-acetonaphthalene, mp 50°–51° C, was isolated from the residue.

b) A mixture of 1.24 g of furylidene-β-acetonaphthalene [7], 1 g of β-acetonaphthalene, and 6 ml of 0.2 N sodium hydroxide in methanol was boiled in the water bath for 10 min and was left at room temperature for two days. 0.5 g of I crystallized out; mp 120°–121° C (from ethanol–benzene, 1:1). A mixture of the two samples (a and b) melted without depression.

Compound I has the form of colorless rods readily soluble in benzene, acetone, and dioxane and sparingly soluble in ethanol and gasoline. Found, %: C 82.92; 83.00; H 5.34; 5.63; Mol. wt. 408, 423. Calculated for $C_{29}H_{22}O_3$, %: C 83.25; H 5.26; Mol. wt. 418.

Dioxime—white needles, mp 192°–195° C (decomp., from methanol). Found, %: N 6.00, 6.26. Calculated for $C_{29}H_{24}N_2O_3$, %: N 6.25.

Difurylidenetris(β-acetonaphthalene) (III). Over 15 min, 0.9 g of furfural in 5 ml of ethanol was added to a boiling solution of 3.74 g of β-acetonaphthalene in 15 ml of 0.5 N ethanolic sodium hydroxide and the mixture was boiled for another 40 min. The subsequent working up was as described above in method (a). Yield 2.3 g, mp 226°–228° C (from benzene). White needles, sparingly soluble in all the usual organic solvents. Found, %: C 82.86; 82.61; H 5.56; 5.53; Mol. wt. 643, 667. Calculated for $C_{46}H_{34}O_5$, %: C 82.88; H 5.11; Mol. wt. 666.

Condensation under the influence of 0.2 N ethanolic NaOH. The reaction was carried out as described for I by method (a) (heating in the boiling water bath). By fractional crystallization, the reaction product yielded 2.2 g of the triketone (III), mp 226°–228° C and 1.4 g of the diketone I, mp 120°–121° C.

Furylidenedi(β-propionaphthalene) (VI).

a) Over 15 min, 1.2 g of furfural in 5 ml of ethanol was added to a boiling solution of 4.7 g of β-propionaphthalene in 30 ml of 2 N ethanolic sodium hydroxide. The mixture was boiled for another hour and was left at room temperature for a day. The oily layer that deposited partially crystallized and 0.8 g of VI with mp 129°–131° C (from ethanol) was filtered off. The oil was washed successively with 50% acetic acid, with water, and with ethanol, and was distilled. The following fractions were obtained: 1) 1.0 g, bp 155°–156° C (4 mm) and 2) 2.3 g, bp 223°–226° C (4 mm); Both fractions crystallized. The first corresponded to β-propionaphthalene, mp 60°–61° C (from gasoline), and the second to furylidene-β-propionaphthalene, mp 87°–89° C (from ethanol).

b) A solution of 2.63 g of furylidene-β-propionaphthalene (mp 87°–89° C) and 1 g of β-propionaphthalene in 20 ml of 0.5 N ethanolic sodium hydroxide was left to stand at ~20° C. After 3 days, 0.6 g of crystals of VI with mp 129°–131° C (from ethanol) was separated off; a mixture with the sample obtained by method (a) melted without depression. Colorless rods, readily soluble in benzene, dioxane, and acetone, and less readily in ethanol. Found, %: C 83.82; 83.84; H 6.11; 5.96; Mol. wt. 411, 422.Calculated for $C_{31}H_{26}O_3$, %: C 83.40; H 5.84; Mol. wt. 446.

Dioxime—colorless needles, mp 195°–198° C (decomp from ethanol). Found, %: N 5.65, 5.55. Calculated for $C_{31}H_{28}N_2O_3$, %: N 5.58.

Furylidene-β-propionaphthalene (V). 1.84 g of β-propionaphthalene and 1 g of furfural were dissolved in 15 ml of 0.5 N ethanolic sodium hydroxide, and the solution immediately crystallized. This gave 2.4 g (91.6%) of yellowish crystals, mp 87°–89° C (from ethanol). Found, %: C 87.72; 87.76; H 5.60; 5.7; Mol. wt. 260. Calculated for $C_{18}H_{14}O_2$, %: C 82.44; H 5.34; Mol. wt. 262.

Oxime—colorless rods, mp 180°–184° C (decomp). Found, %: N 4.85, 5.25. Calculated for $C_{18}H_{15}NO_2$, %: N 5.05.

Dibenzylidenetris(β-acetonaphthalene) (IV). The condensation was carried out in just the same way as for the preparation of difurylidenetrisacetonaphthalene (III). Five grams of β-acetonaphthalene and 1.5 g of benzaldehyde yielded 3.6 g of benzylideneacetonaphthalene, mp 125°–127° C (from ethanol—acetone, 1:2) [1] and 0.5 g (~5%) of the triketone IV. The latter is very sparingly soluble in the mixture of ethanol and acetone mentioned and is therefore readily separated from the former compound. In the cold, IV is almost insoluble in all the usual organic solvents. Mp 227°–229° C (from benzene). Found, %: C 87.83; 87.53; H 5.59; 5.57; Mol. wt. 651, 696. Calculated for $C_{50}H_{38}O_3$, %: C 87.46; H 5.54; Mol. wt. 686.

4-(α-Furyl)-2, 6-di(β-naphthyl)pyridine (VII).

a) A mixture of 2.5 g of I, 5 g of ammonium acetate, and 30 ml of acetic acid was boiled for 2 hr. After the mixture had cooled, the crystals were filtered off, washed with water, and recrystallized from dioxane. Yield 1.5 g, mp 220°–221° C.

b) A mixture of 2 g of I and 30 g of formamide was boiled for 3 hr. On cooling, 1.5 g (79%) of crystals of VII with mp 219°–220° C (from dioxane) deposited. Their identity with the preceding sample was confirmed by a mixed melting point. Colorless rods, soluble in benzene and dioxane and sparingly soluble in ethanol, ether, and gasoline. Found, %: C 88.00; 87.56; H 4.38; 4.99; N 3.38; 3.46; Mol. wt. 388, 402. Calculated for $C_{29}H_{19}NO$, %: C 87.65; H 4.87; N 3.53%; Mol. wt. 397.

Picrate—yellow crystals, mp 250° C (from dioxane). Found, %: N 8.86, 8.85. Calculated for $C_{29}H_{19}NO \cdot C_6H_3N_3O_7$, %: N 8.94.

Hydrochloride. A solution of the base in benzene was saturated with dry hydrogen chloride. Yellow-green crystals deposited which, from the method of formation and form, must be regarded as the hydrochloride of the base. However, without recrystallization they melted at 217°–219° C. A mixture with the base gave no depression of the melting point. Obviously, on melting, the hydrogen chloride was split off completely and the initial base was regenerated.

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