

Reaction of 2'-Hydroxy[1,1';3',1'']terphenyl-5'-carbaldehyde with 2-Naphthylamine and 1,3-Diketones

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Abstract—The condensation of 2'-hydroxy[1,1';3',1'']terphenyl-5'-carbaldehyde with 2-naphthylamine and 1,3-cyclohexanedione or dimedone gave 7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-11-ones, while analogous three-component condensation with 1,3-indandione afforded azaindeno[1,2-*b*]phenanthren-12-one. In addition, hexahydro-2*H*-xanthene-1,8-diones and arylmethylenebisdiketones were isolated as by-products.

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We previously studied three-component condensations of 2-naphthylamine with 1,3-diketones and mono- or disubstituted benzaldehydes [1–3]. In the present work we involved in analogous condensation for the first time a trisubstituted benzaldehyde, 2'-hydroxy-[1,1';3',1'']terphenyl-5'-carbaldehyde (**I**). Derivatives of **I** are known as polymer stabilizers, dyes, medicines, and insecticides [4–6]. We examined reactions of aldehyde **I** with 2-naphthylamine (**II**) and a series of 1,3-diketones: 1,3-cyclohexanedione (**IIIa**), 5,5-dimethyl-1,3-cyclohexanedione (**IIIb**, dimedone), and 1,3-indandione (**IV**). The reactions of **I** with amine **II** and diones **IIIa** and **IIIb** were performed by heating equimolar amounts of the reactants in ethanol.

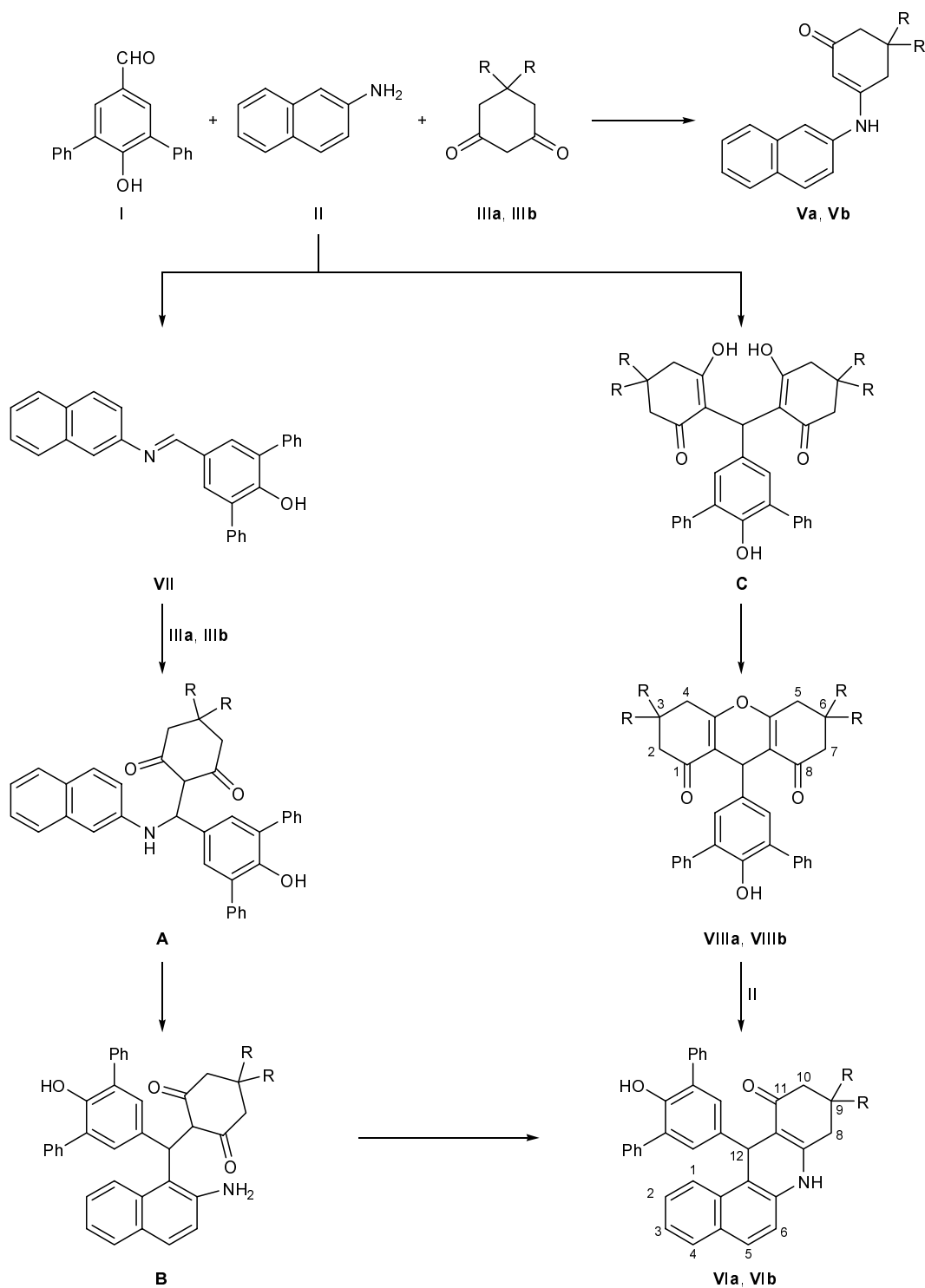
We found that the reaction direction is determined by the order of mixing of the reactants. When amine **II** was initially mixed with diketone **IIIa** or **IIIb**, the only product was the corresponding enamine **Va** or **Vb** which (after isolation) failed to react with aldehyde **I**. Mixing of amine **II** with aldehyde **I**, followed by addition of diketone **IIIa** or **IIIb**, selectively afforded benzo[*a*]acridin-11-one **VIa** or **VIb**. The condensation is likely to involve initial formation of amino ketone **A** which undergoes rearrangement into intermediate **B** according to the scheme proposed in [7]; dehydration of **B** is accompanied by intramolecular ring closure to give final products **VIa** and **VIb** (Scheme 1). Analogous compounds were obtained by condensation of preliminarily isolated Schiff base **VII** with diketones

IIIa and **IIIb** under the same conditions, i.e., on heating in a boiling polar solvent.

Intermediate formation of arylmethylenebisdiketones **C** whose dehydration leads to xanthene-1,8-diones **VIIIa** and **VIIIb** is believed to be proved, for compounds **VIIIa** and **VIIIb** were isolated from the reaction mixture as concomitant products. Reaction of **VIIIa** and **VIIIb** with amine **II** gives benzoacridinones **VIa** and **VIb**. Xanthenediones **VIIIa** and **VIIIb** were also obtained by heating aldehyde **I** with 2 equiv of diketone **IIIa** or **IIIb** in boiling 1-butanol.

The reaction of aldehyde **I** with 2-naphthylamine (**II**) and 1,3-indandione (**IV**) was performed by heating equimolar amounts of the reactants in boiling 1-butanol. Our experimental and published [8] data suggest that the final product, 13-(2'-hydroxy[1,1';3',1'']terphenyl-5'-yl)-7-azaindeno[1,2-*b*]phenanthren-12-one (**IX**), is formed through intermediate amino ketone **D** which undergoes dehydration to intermediate **E** and oxidation of the latter. The use of 1-butanol as solvent allowed us to avoid isolation and dehydrogenation of intermediate product **E**, which were necessary when reactions of amine **II** with indandione **IV** and substituted benzaldehydes were carried out in ethanol [9]. We also found that the condensation of amine **II** with aldehyde **I** and diketone **IV** gives 2-(2'-hydroxy-[1,1';3',1'']terphenyl-5'-ylmethylidene)indan-1,3-dione (**X**). Therefore, we presumed that compound **IX** may be synthesized by reaction of indandione **X** with amine

Scheme 1.



R = H (a), Me (b).

II. In fact, we synthesized dione **X** by reaction of **IV** with aldehyde **I**, and the condensation of **X** with amine **II** under analogous conditions led to formation of fused polycyclic product **IX** (Scheme 2).

The structure of compounds **Va, Vb, VIa, VIb, VII, VIIIa, VIIIb, IX**, and **X** was confirmed by the analytical data and ^1H NMR and IR spectra. The IR spectra of **Va, Vb, VIa**, and **VIb** contained bands

2'-Hydroxy[1,1';3',1'']terphenyl-5'-carbaldehyde (**I**) was synthesized from [1,1';3',1'']terphenyl-2'-carbaldehyde and hexamethylenetetraamine in the presence of trifluoroacetic acid, following the procedure reported in [13], mp 168–169°C.

3-(2-Naphthylamino)-2-cyclohexenone (Va). Diketone **IIIa**, 1.12 g (0.01 mol), was added to a solution of 1.43 g (0.01 mol) of 2-naphthylamine (**II**) in 30 ml of ethanol, and the mixture was heated for 3 h under reflux. The solvent was distilled off, and the crystalline residue was recrystallized from ethanol–benzene (1:3). Yield 1.25 g (53%). Yellow crystals, mp 176°C. IR spectrum, ν , cm^{-1} : 3430, 3250, 3210, 2925, 1620, 1597, 1499, 1464, 1364, 1305, 1247, 1186, 1136, 811, 754, 473. ^1H NMR spectrum, δ , ppm: 1.85–1.90 m (2H, CH_2), 2.20–2.30 m (2H, CH_2), 2.38–2.42 m (2H, CH_2), 5.70 s (1H, CH), 7.20–7.70 m (7H, H_{arom}), 8.80 s (1H, NH). Found, %: C 81.03; H 6.35; N 5.92. $\text{C}_{16}\text{H}_{15}\text{NO}$. Calculated, %: C 81.01; H 6.33; N 5.90.

5,5-Dimethyl-3-(2-naphthylamino)-2-cyclohexenone (Vb) was synthesized in a similar way using dimedone (**IIIb**). Yield 1.59 g (60%). Yellow crystals, mp 185°C. IR spectrum, ν , cm^{-1} : 3448, 3260, 3229, 3024, 2954, 2926, 1640, 1581, 1534, 1504, 1464, 1365, 1308, 1276, 1246, 1149, 1120, 868, 819, 774, 761, 605, 551, 468. ^1H NMR spectrum, δ , ppm: 1.10 s (6H, CH_3), 2.10 s (2H, CH_2), 2.40 s (2H, CH_2), 5.49 s (1H, CH), 7.30–7.90 m (7H, H_{arom}), 8.90 s (1H, NH). Found, %: C 81.53; H 7.14; N 5.26. $\text{C}_{18}\text{H}_{19}\text{NO}$. Calculated, %: C 81.51; H 7.17; N 5.28.

12-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-yl)-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-11-one (VIa). Aldehyde **I**, 2.74 g (0.01 mol), was added to a solution of 1.43 g (0.01 mol) of amine **II** in 50 ml of ethanol, the mixture was heated for 15 min under reflux, 1.12 g (0.01 mol) of 1,3-cyclohexanedione (**IIIa**) was added, and the mixture was heated for 5 h under reflux. After cooling, the precipitate was filtered off, washed with hot methanol, and recrystallized from benzene. Yield 3.73 g (89%), colorless crystals, mp 320°C. IR spectrum, ν , cm^{-1} : 3537, 3264, 3193, 2933, 1650, 1609, 1582, 1518, 1492, 1465, 1420, 1395, 1317, 1279, 1235, 1190, 1135, 1116, 1029, 958, 819, 773, 759, 703, 638, 598. ^1H NMR spectrum, δ , ppm: 1.85–2.05 m (2H, CH_2), 2.20–2.35 m (2H, CH_2), 2.60–2.70 m (2H, CH_2), 5.85 s (1H, CH), 7.08 s (2H, H_{arom}), 7.20–7.45 m (13H, H_{arom} , 1H, OH), 7.65 d (1H, H_{arom}), 7.74 d (1H, H_{arom}), 8.05 d (1H, H_{arom}), 9.35 s (1H, NH). Found, %: C 85.17; H 5.51; N 2.86. $\text{C}_{35}\text{H}_{27}\text{NO}_2$. Calculated, %: C 85.20; H 5.48; N 2.84.

12-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-yl)-9,9-dimethyl-7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-11-one (VIb) was synthesized in a similar way using dimedone (**IIIb**). Yield 3.55 g (80%), colorless crystals, mp 279–280°C. IR spectrum, ν , cm^{-1} : 3534, 3266, 3197, 2943, 1648, 1610, 1582, 1519, 1494, 1467, 1422, 1393, 1339, 1318, 1280, 1236, 1182, 1149, 1118, 1075, 1030, 1013, 958, 904, 880, 820, 770, 760, 748, 703, 698, 632, 597, 586. ^1H NMR spectrum, δ , ppm: 1.08 s (3H, CH_3), 1.10 s (3H, CH_3), 2.10–2.13 m (2H, CH_2), 2.15–2.20 m (2H, CH_2), 5.80 s (1H, CH), 7.10 s (2H, H_{arom}), 7.20–7.49 m (13H, H_{arom} , 1H, OH), 7.70 d (1H, H_{arom}), 7.78 d (1H, H_{arom}), 8.10 d (1H, H_{arom}), 9.30 s (1H, NH). Found, %: C 85.18; H 5.96; N 2.71. $\text{C}_{37}\text{H}_{31}\text{NO}_2$. Calculated, %: C 85.22; H 5.95; N 2.69.

5'-(2-Naphthyliminomethyl)[1,1';3',1'']terphenyl-2'-ol (VII). A solution of 2.74 g (0.01 mol) of aldehyde **I** in 10 ml of 1-butanol was added to a solution of 1.43 g (0.01 mol) of amine **II** in 20 ml of ethanol, and the mixture was heated for 15 min under reflux. The mixture was cooled, and the precipitate was filtered off and recrystallized from ethanol. Yield 2.95 g (85%). Yellow crystals, mp 138–139°C. IR spectrum, ν , cm^{-1} : 3311, 3056, 2916, 2847, 1676, 1583, 1462, 1427, 1321, 1228, 1163, 1116, 1026, 892, 784, 748, 699, 578, 504. ^1H NMR spectrum, δ , ppm: 7.20–7.50 m (10H, H_{arom}), 7.59–7.90 m (9H, H_{arom} , 1H, OH), 8.50 s (1H, CH). Found, %: C 87.20; H 5.23; N 3.52. $\text{C}_{29}\text{H}_{21}\text{NO}$. Calculated, %: C 87.22; H 5.26; N 3.51.

9-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-yl)-2,3,4,5,6,7,8,9-octahydro-1*H*-xanthene-1,8-dione (VIIIa). A solution of 2.74 g of aldehyde **I** and 2.24 g (0.02 mol) of 1,3-cyclohexanedione (**IIIa**) in 50 ml of ethanol was heated for 6 h under reflux. The precipitate was filtered off, washed with diethyl ether, dried, and recrystallized from methanol. Yield 1.95 g (42%), colorless crystals, mp 201°C. IR spectrum, ν , cm^{-1} : 3520, 3180, 2957, 2863, 1595, 1463, 1428, 1372, 1300, 1211, 1160, 775, 700, 673. ^1H NMR spectrum, δ , ppm: 1.90–2.05 m (2H, CH_2), 2.10–2.24 m (2H, CH_2), 2.30–2.40 m (2H, CH_2), 4.65 s (1H, CH), 7.00 s (2H, H_{arom}), 7.20–7.70 m (10H, H_{arom} , 1H, OH). Found, %: C 80.50; H 5.65. $\text{C}_{31}\text{H}_{26}\text{O}_4$. Calculated, %: C 80.52; H 5.63.

9-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-yl)-3,3,6,6-tetramethyl-2,3,4,5,6,7,8,9-octahydro-1*H*-xanthene-1,8-dione (VIIIb) was synthesized as described for compounds **VIIIa** using dimedone (**IIIb**). Yield 1.89 g (45%), colorless crystals, mp 211–212°C. IR spectrum, ν , cm^{-1} : 3525, 3034, 2959, 2927, 2887, 2869, 1591,

1467, 1426, 1373, 1306, 1249, 1218, 1165, 880, 777, 702, 679. ^1H NMR spectrum, δ , ppm: 1.00 s (3H, CH_3), 1.10 s (3H, CH_3), 2.20–2.30 m (2H, CH_2), 2.40–2.50 m (2H, CH_2), 4.57 s (1H, CH), 6.90 s (2H, H_{arom}), 7.15–7.70 m (10H, H_{arom} , 1H, OH). Found, %: C 81.04; H 6.53. $\text{C}_{35}\text{H}_{34}\text{O}_4$. Calculated, %: C 81.08; H 6.56.

13-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-yl)-7-azaindeno[1,2-b]phenanthren-12-one (IX). A solution of 1.43 g (0.01 mol) of amine **II** in 10 ml of 1-butanol and a solution of 1.46 g (0.01 mol) of 1,3-indandione (**IV**) in 10 ml of 1-butanol were added to a solution of 2.74 g (0.01 mol) of aldehyde **I** in 20 ml of 1-butanol, and the mixture was heated for 4 h under reflux. The mixture was cooled, and the precipitate was filtered off and washed with three portions of hot acetone. Yield 3.36 g (64%). Yellow crystalline substance, mp 315°C. IR spectrum, ν , cm^{-1} : 3383, 3076, 2917, 1679, 1561, 1468, 1417, 1320, 1221, 1195, 1184, 1151, 1091, 991, 735, 699. ^1H NMR spectrum, δ , ppm: 7.40–7.70 m (15H, H_{arom}), 7.75–7.95 m (4H, H_{arom}), 8.20 d (1H, H_{arom}), 8.50 s (2H, H_{arom}), 9.48 br.s (1H, OH). Found, %: C 86.84; H 4.40; N 2.63. $\text{C}_{38}\text{H}_{23}\text{NO}_2$. Calculated, %: C 86.86; H 4.38; N 2.66.

2-(2'-Hydroxy[1,1';3',1'']terphenyl-5'-ylmethylen)indan-1,3-dione (X). A solution of 2.74 g (0.01 mol) of aldehyde **I** and 1.46 g (0.01 mol) of 1,3-indandione (**IV**) in 30 ml of 1-butanol was heated for 30 min under reflux. The precipitate was filtered off, washed with diethyl ether, and recrystallized from acetone. Yield 2.80 g (70%). Yellow crystals, mp 246°C. IR spectrum, ν , cm^{-1} : 3460, 2923, 1681, 1567, 1468, 1418, 1326, 1282, 1219, 1193, 1153, 1086, 995, 960, 926, 880, 779, 733, 704, 691, 601, 526. ^1H NMR spectrum, δ , ppm: 7.35–7.45 m (3H, H_{arom}), 7.47–7.50 m (6H, H_{arom}), 7.60–7.68 m (2H, H_{arom}), 7.80–7.96 m

(5H, H_{arom}), 8.50 s (1H, CH), 9.25 br.s (1H, OH). Found, %: C 83.60; H 4.49. $\text{C}_{28}\text{H}_{18}\text{O}_3$. Calculated, %: C 83.58; H 4.48.

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