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G.A. Tolstikov on his 75th anniversary

Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: VIII.* Synthesis of *N*-(*o*-Cycloalkylphenyl) 2-Hydroxynaphthalene-1-carbaldehyde Imines

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Abstract—Substituted *o*-cycloalkylanilines reacted with 2-hydroxynaphthalene-1-carbaldehyde in methanol in the presence of formic acid to give the corresponding Schiff bases as ligands for the synthesis of titanium(IV) complexes.

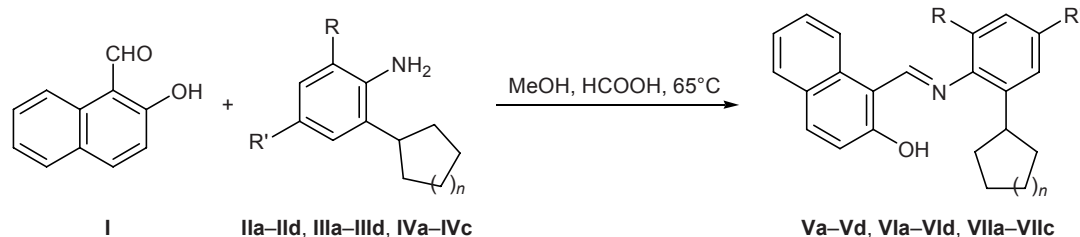
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Matsui et al. [2] showed that titanium and zirconium chelates with salicylaldehyde imine ligands exhibit a high catalytic activity in polymerization of olefins and revealed a strong dependence of their catalytic activity on the structure of the aldehyde and amine fragments. Variation of substituents in the ligand could change the polymerization mechanism so that a broad spectrum of polyolefins with versatile parameters could be obtained [3]. It should be noted that ligands for the above complexes were synthesized mainly from substituted salicylaldehydes. Complexes with ligands based on naphthalenecarbaldehydes having a hydroxy group in the *ortho* position with respect to the aldehyde group were described in patent [4], but no data on their catalytic activity were given.

While searching for new catalysts active at elevated temperature [5] we followed an approach based on introduction of a cycloalkyl group into the *ortho* position of an arene ring [6]. Such structural modification turned out to be successful for 2,6-bis(aryliminoalkyl)pyridine iron chloride complexes and 1,2-bis(arylimino)acenaphthene nickel bromide complexes. Catalysts on the basis of these complexes showed high efficiency over extended temperature range [7].

In the present work we applied the above approach to the synthesis of Schiff bases from 2-hydroxynaphthalene-1-carbaldehyde and substituted anilines having a cyclopentyl, cyclohexyl, or cyclooctyl group in the *ortho* position with a view to make such compounds

Scheme 1.



R = R' = H (a), Me (c); R = Me, R' = H (b); R = *cyclo*-C₄H₇(CH₂)_n, R' = H (d); II, V, n = 1; III, VI, n = 2; IV, VII, n = 4.

* For communication VII, see [1].

accessible for the preparation of the corresponding titanium and zirconium complexes. The synthetic procedure was analogous to that described in [4] for the reactions of 1-hydroxynaphthalene-2-carbaldehyde with aniline and 2,6-dimethylaniline. By heating 2-hydroxynaphthalene-1-carbaldehyde (**I**) with *o*-cycloalkylanilines **IIa–IIId**, **IIIa–IIIId**, and **IVa–IVc** in boiling methanol in the presence of a catalytic amount of formic acid we obtained in high yields (91–99%) the corresponding Schiff bases **V–VII** (Scheme 1).

The structure of compounds **V–VII** was confirmed by elemental analyses and spectral data. According to the ^1H NMR spectra, Schiff bases **V–VII** are individual *E* isomers. The spectra contained multiplet signals at δ 1.10–2.18 and 2.65–3.45 ppm from the methylene and CH protons in the cycloalkyl substituents, singlets from the N=CH protons at δ 9.06–9.37 ppm, and singlets from the hydroxy proton in the region δ 14.60–15.25 ppm. The downfield position of the OH signal is typical of compounds with intramolecular hydrogen bond. Signals from protons in the naphthalene ring were assigned by analogy with the data for 2-hydroxynaphthalene-1-carbaldehyde [8]. Compounds **V–VII** displayed in the IR spectra a strong absorption band in the region 1618–1625 cm^{-1} , which belongs to stretching vibrations of the azomethine bond. The mass spectra of **V–VII** contained strong molecular ion peaks.

EXPERIMENTAL

The IR spectra were recorded on a Vector-22 spectrometer from samples prepared as KBr pellets or neat substances. The ^1H NMR spectra were measured on a Bruker WP-200 SY instrument at 200.13 MHz from solutions in carbon tetrachloride using hexamethyldisiloxane as internal reference. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using chloroform as eluent. Silica gel 5–40 μm was used for flash chromatography [9]; eluent chloroform–hexane, 1:3. The elemental compositions were determined from the high-resolution mass spectra which were run on a Finnigan MAT-8200 mass spectrometer. The melting points were determined by heating samples placed between glass plates at a rate of 1 deg/min.

2-Hydroxynaphthalene-1-carbaldehyde (**I**) and cycloalkylanilines **II–IV** were synthesized according to the procedures reported in [10, 11].

Schiff bases V–VII (general procedure). A mixture of 0.172 g (1 mmol) of 2-hydroxynaphthalene-1-carb-

aldehyde (**I**), 1 mmol of cycloalkylaniline **IIa–IIId**, **IIIa–IIIId**, or **IVa–IVc**, 10 ml of methanol, and 5 mg of anhydrous formic acid was heated for 10–12 h under reflux until the initial compounds disappeared according to the TLC data. The solvent was distilled off on a rotary evaporator under reduced pressure (water-jet pump) at a bath temperature of 45°C, and the residue was subjected to flash chromatography. The first bright yellow fraction was evaporated, and solid products were additionally purified by recrystallization from methanol.

1-(2-Cyclopentylphenyliminomethyl)naphthalen-2-ol (Va). Yield 94%, mp 113–114°C. IR spectrum: ν 1618 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.55–2.18 m (8H, CH_2), 3.45 m (1H, CH), 7.05–7.20 m (5H, 3-H, 3'-H, 4'-H, 5'-H, 6'-H), 7.27 t (1H, 6-H, $J = 8$ Hz), 7.40 t (1H, 7-H, $J = 8$ Hz), 7.64 d (1H, 5-H, $J = 8$ Hz), 7.73 d (1H, 4-H, $J = 8.5$ Hz), 8.11 d (1H, 8-H, $J = 8$ Hz), 9.31 s (1H, CH=N), 15.17 s (1H, OH). Found: $[M]^+$ 315.16236. $\text{C}_{22}\text{H}_{21}\text{NO}$. Calculated: M 315.16230.

1-(2-Cyclopentyl-6-methylphenyliminomethyl)naphthalen-2-ol (Vb). Yield 99%, mp 79–80°C. IR spectrum: ν 1624 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.51–2.04 m (8H, CH_2), 2.24 s (3H, CH_3), 3.45 m (1H, CH), 6.95–7.19 m (4H, 3-H, 3'-H, 4'-H, 5'-H), 7.25 t (1H, 6-H, $J = 8$ Hz), 7.40 t (1H, 7-H, $J = 8$ Hz), 7.69 d (1H, 5-H, $J = 8$ Hz), 7.78 d (1H, 4-H, $J = 8.5$ Hz), 7.98 d (1H, 8-H, $J = 8$ Hz), 9.12 s (1H, CH=N), 14.66 s (1H, OH). Found: $[M]^+$ 329.17747. $\text{C}_{23}\text{H}_{23}\text{NO}$. Calculated: M 329.17795.

1-(2-Cyclopentyl-4,6-dimethylphenyliminomethyl)naphthalen-2-ol (Vc). Yield 99%, mp 95–97°C. IR spectrum: ν 1624 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.53–2.05 m (8H, CH_2), 2.20 s and 2.30 s (3H each, CH_3), 3.06 m (1H, CH), 6.82 s and 6.90 s (1H each, 3'-H, 5'-H), 7.12 d (1H, 3-H, $J = 8.5$ Hz), 7.23 t (1H, 6-H, $J = 8$ Hz), 7.39 t (1H, 7-H, $J = 8$ Hz), 7.67 d (1H, 5-H, $J = 8$ Hz), 7.76 d (1H, 4-H, $J = 8.5$ Hz), 7.95 d (1H, 8-H, $J = 8$ Hz), 9.07 s (1H, CH=N), 14.60 s (1H, OH). Found: $[M]^+$ 343.19324. $\text{C}_{24}\text{H}_{25}\text{NO}$. Calculated: M 343.19360.

1-(2,6-Dicyclopentylphenyliminomethyl)naphthalen-2-ol (Vd). Yield 99%, mp 74–75°C. IR spectrum: ν 1623 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.55–2.08 m (16H, CH_2), 3.05 m (2H, CH), 7.01–7.19 m (4H, 3-H, 3'-H, 4'-H, 5'-H), 7.23 t (1H, 6-H, $J = 8$ Hz), 7.39 t (1H, 7-H, $J = 8$ Hz), 7.68 d (1H, 5-H, $J = 8$ Hz), 7.78 d (1H, 4-H, $J = 8.5$ Hz), 7.97 d (1H, 8-H, $J = 8$ Hz), 9.06 s (1H, CH=N), 14.70 s (1H, OH).

Found: $[M]^+$ 383.23522. $C_{27}H_{29}NO$. Calculated: M 383.23613.

1-(2-Cyclohexylphenyliminomethyl)naphthalen-2-ol (VIa). Yield 92%, mp 140–141°C. IR spectrum: ν 1621 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.40–1.97 m (10H, CH_2), 3.03 m (1H, CH), 7.06–7.20 m (5H, 3-H, 3'-H, 4'-H, 5'-H, 6'-H), 7.25 t (1H, 6-H, $J = 8$ Hz), 7.42 t (1H, 7-H, $J = 8$ Hz), 7.66 d (1H, 5-H, $J = 8$ Hz), 7.76 d (1H, 4-H, $J = 8.5$ Hz), 8.12 d (1H, 8-H, $J = 8$ Hz), 9.37 s (1H, CH=N), 15.21 s (1H, OH). Found: $[M]^+$ 329.17585. $C_{23}H_{23}NO$. Calculated: M 329.17795.

1-(2-Cyclohexyl-6-methylphenyliminomethyl)naphthalen-2-ol (VIb). Yield 98%, oily substance. IR spectrum: ν 1623 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.15–1.90 m (10H, CH_2), 2.26 s (3H, CH_3), 2.68 m (1H, CH), 6.97–7.21 m (4H, 3-H, 3'-H, 4'-H, 5'-H), 7.25 t (1H, 6-H, $J = 8$ Hz), 7.39 t (1H, 7-H, $J = 8$ Hz), 7.69 d (1H, 5-H, $J = 8$ Hz), 7.78 d (1H, 4-H, $J = 8.5$ Hz), 7.96 d (1H, 8-H, $J = 8$ Hz), 9.12 s (1H, CH=N), 14.65 s (1H, OH). Found: $[M]^+$ 343.19358. $C_{24}H_{25}NO$. Calculated: M 343.19360.

1-(2-Cyclohexyl-4,6-dimethylphenyliminomethyl)naphthalen-2-ol (VIc). Yield 95%, mp 144–145°C. IR spectrum: ν 1624 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.10–1.95 m (10H, CH_2), 2.22 s and 2.30 s (3H each, CH_3), 2.65 m (1H, CH), 6.82 s and 6.86 s (1H each, 3'-H, 5'-H), 7.13 d (1H, 3-H, $J = 8.5$ Hz), 7.22 t (1H, 6-H, $J = 8$ Hz), 7.37 t (1H, 7-H, $J = 8$ Hz), 7.67 d (1H, 5-H, $J = 8$ Hz), 7.76 d (1H, 4-H, $J = 8.5$ Hz), 7.93 d (1H, 8-H, $J = 8$ Hz), 9.08 s (1H, CH=N), 14.81 s (1H, OH). Found: $[M]^+$ 357.20885. $C_{25}H_{27}NO$. Calculated: M 357.20925.

1-(2,6-Dicyclohexylphenyliminomethyl)naphthalen-2-ol (VIId). Yield 92%, mp 93–94°C. IR spectrum: ν 1625 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.15–2.00 m (20H, CH_2), 2.65 m (2H, CH), 7.03–7.20 m (4H, 3-H, 3'-H, 4'-H, 5'-H), 7.25 t (1H, 6-H, $J = 8$ Hz), 7.39 t (1H, 7-H, $J = 8$ Hz), 7.70 d (1H, 5-H, $J = 8$ Hz), 7.80 d (1H, 4-H, $J = 8.5$ Hz), 7.93 d (1H, 8-H, $J = 8$ Hz), 9.06 s (1H, CH=N), 14.70 s (1H, OH). Found: $[M]^+$ 411.25704. $C_{29}H_{33}NO$. Calculated: M 411.25620.

1-(2-Cyclooctylphenyliminomethyl)naphthalen-2-ol (VIIa). Yield 96%, mp 75–76°C. IR spectrum: ν 1622 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.50–1.98 m (14H, CH_2), 3.34 m (1H, CH), 7.10–7.33 m (6H, 3-H, 6-H, 3'-H, 4'-H, 5'-H, 6'-H), 7.45 t (1H, 7-H, $J = 8$ Hz), 7.69 d (1H, 5-H, $J = 8$ Hz), 7.78 d (1H, 4-H, $J = 8.5$ Hz), 8.12 d (1H, 8-H, $J = 8$ Hz), 9.34 s (1H,

CH=N), 15.25 s (1H, OH). Found: $[M]^+$ 357.20921. $C_{25}H_{27}NO$. Calculated: M 357.20925.

1-(2-Cyclooctyl-6-methylphenyliminomethyl)naphthalen-2-ol (VIIb). Yield 98%, oily substance. IR spectrum: ν 1623 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.41–1.85 m (14H, CH_2), 2.25 s (3H, CH_3), 3.03 m (1H, CH), 7.01–7.12 m (3H, 3'-H, 4'-H, 5'-H), 7.16 d (1H, 3-H, $J = 8.5$ Hz), 7.27 t (1H, 6-H, $J = 8$ Hz), 7.42 t (1H, 7-H, $J = 8$ Hz), 7.70 d (1H, 5-H, $J = 8$ Hz), 7.80 d (1H, 4-H, $J = 8.5$ Hz), 7.97 d (1H, 8-H, $J = 8$ Hz), 9.11 s (1H, CH=N), 14.85 s (1H, OH). Found: $[M]^+$ 371.22309. $C_{26}H_{29}NO$. Calculated: M 371.22490.

1-(2-Cyclooctyl-4,6-dimethylphenyliminomethyl)naphthalen-2-ol (VIIc). Yield 98%, oily substance. IR spectrum: ν 1625 cm^{-1} (N=C). 1H NMR spectrum, δ , ppm: 1.45–1.85 m (14H, CH_2), 2.25 s and 2.33 s (3H each, CH_3), 3.01 m (1H, CH), 6.88 s and 6.91 s (1H each, 3'-H, 5'-H), 7.16 d (1H, 3-H, $J = 8.5$ Hz), 7.28 t (1H, 6-H, $J = 8$ Hz), 7.43 t (1H, 7-H, $J = 8$ Hz), 7.71 d (1H, 5-H, $J = 8$ Hz), 7.80 d (1H, 4-H, $J = 8.5$ Hz), 7.97 d (1H, 8-H, $J = 8$ Hz), 9.09 s (1H, CH=N), 14.95 s (1H, OH). Found: $[M]^+$ 385.24068. $C_{27}H_{31}NO$. Calculated: M 385.24055.

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