ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 6, pp. 927–928. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © I.I. Oleinik, A.I. Kochnev, I.V. Oleinik, S.S. Ivanchev, G.A. Tolstikov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 6, pp. 934–935.

SHORT COMMUNICATIONS

Preparative Microwave-Assisted Synthesis of *N*-Salicylidene-4-triphenylmethylanilines

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Received November 6, 2007

DOI: 10.1134/S1070428008060249

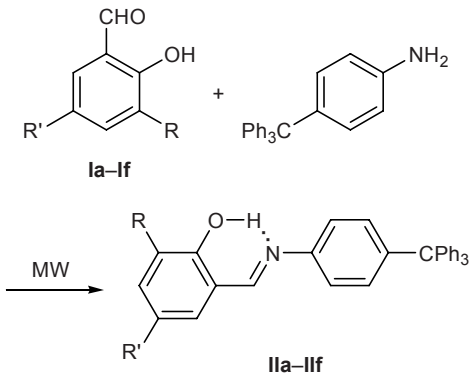
Chelate complexes derived from Group IV transition metals and salicylaldehyde imines showed a high catalytic activity in polymerization of olefins [1]. A synthetic approach to new complexes of this type is based on introduction into the ligand of various substituents, which leads to variation in the electron density distribution in the ligand and steric load of the active center in the complex [2].

In the present communication we describe preparation of new *N*-(2-hydroxyphenylmethylidene)aniline ligands by reaction of 4-triphenylmethylaniline with salicylaldehydes containing bulky substituents [*tert*-butyl, dimethyl(phenyl)methyl, and triphenylmethyl] in positions *3* and *5*. We previously showed [3] that substituted salicylaldehydes react with cyclohexylamine, aniline, cycloalkylanilines, and isobornylamine on heating in methanol in the presence of a catalytic amount of formic acid to give in high yield the corresponding salicylaldehyde imines; the condensation with less basic pentafluoroaniline can be performed in boiling benzene or toluene in the presence of anhydrous calcium sulfate and a catalytic amount of *p*-toluenesulfonic acid.

Under the above conditions, as well as on heating in a mixture of methanol with methylene chloride [4], the reactions of substituted salicylaldehydes **Ia**–**If** with 4-triphenylmethylaniline were slow, and the conversion was not complete because of very poor solubility of the amine. The yields of Schiff bases **IIa**–**IIf** did not exceed 25–30%.

There are numerous examples of successful application of microwave irradiation in organic synthesis. Microwave-assisted syntheses are characterized by short reaction time, enhanced selectivity, and high yield [5]. Using microwave activation, we succeeded in synthesizing Schiff bases **IIa**–**IIf** in 86–96% yield by condensation of aldehydes **Ia**–**If** with 4-triphenylmethylamine under solvent-free conditions and considerably shortening the reaction time.

The structure of Schiff bases **IIa**–**IIf** was confirmed by analytical and spectral data. The ^{1}H NMR spectra of **IIa**–**IIf** in carbon tetrachloride contained singlets from the N=CH protons in the region δ 8.33–8.52 ppm and downfield singlets from the hydroxy protons at δ 12.94–13.50 ppm; the position of the latter indicates formation of intramolecular hydrogen bond. Compounds **IIa**–**IIf** displayed in the IR spectra a strong absorption band at 1617–1620 cm^{-1}, corresponding to stretching vibrations of the C=N bond.



R = $PhMe_2C$, R′ = Me (**a**), *t*-Bu (**b**), $PhMe_2C$ (**c**), Ph_3C (**d**);
R = *t*-Bu, R′ = $PhMe_2C$ (**e**), Ph_3C (**f**).

Initial substituted salicylaldehydes **Ia–If** and 4-triphenylmethylaniline were synthesized according to the procedures described in [6, 7].

Substituted salicylaldehyde imines IIa–IIf (*general procedure*). A 5-ml ampule was charged with a mixture of 0.5 mmol of salicylaldehyde **Ia–If** and 0.17 g (0.5 mmol) of 4-triphenylmethylaniline. The ampule was sealed, placed into a hermetically closed Teflon container, and heated in an LG MS-1724W microwave oven over a period of 10 min at a power of 500 W. The solid products were purified by recrystallization from methanol.

2-[Dimethyl(phenyl)methyl]-4-methyl-6-[(4-triphenylmethylphenylimino)methyl]phenol (IIa). Yield 91%, mp 175–177°C. IR spectrum: ν 1620 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.73 s (6H, Me), 2.35 s (3H, 4-CH_3), 6.85–7.28 m (26H, H_{arom}), 8.50 s (1H, CH=N), 12.97 s (1H, OH). Found: $[M]^+$ 571.28673. $C_{42}H_{37}NO$. Calculated: *M* 571.28750.

4-*tret*-Butyl-2-[dimethyl(phenyl)methyl]-6-[(4-triphenylmethylphenylimino)methyl]phenol (IIb). Yield 93%, mp 95–98°C. IR spectrum: ν 1619 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.31 s (9H, *t*-Bu), 1.73 s (6H, Me), 6.98–7.45 m (26H, H_{arom}), 8.52 s (1H, CH=N), 12.95 s (1H, OH). Found, %: C 87.58; H 7.09; N 2.18. $C_{45}H_{43}NO$. Calculated, %: C 88.05; H 7.06; N 2.28.

2,4-Bis[dimethyl(phenyl)methyl]-6-[(4-triphenylmethylphenylimino)methyl]phenol (IIc). Yield 96%, mp 109–111°C. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.66 s (12H, Me), 6.81–7.30 m (31H, H_{arom}), 8.43 s (1H, CH=N), 12.96 s (1H, OH). Found, %: C 88.76; H 7.03; N 1.92. $C_{50}H_{45}NO$. Calculated, %: C 88.85; H 6.71; N 2.07.

2-[Dimethyl(phenyl)methyl]-4-triphenylmethyl-6-[(4-triphenylmethylphenylimino)methyl]phenol (IId). Yield 75%, mp 122–124°C. IR spectrum: ν 1617 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.55 s (6H, Me), 6.90–7.27 m (41H, H_{arom}), 8.33 s (1H, CH=N), 13.15 s (1H, OH). Found, %: C 90.01; H 6.48; N 1.56. $C_{60}H_{49}NO$. Calculated, %: C 90.08; H 6.17; N 1.75.

2-*tert*-Butyl-4-[dimethyl(phenyl)methyl]-6-[(4-triphenylmethylphenylimino)methyl]phenol (IIe). Yield 86%, mp 153–155°C. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.37 s (9H, *t*-Bu), 1.64 s (6H, Me), 6.80–7.35 m (26H, H_{arom}), 8.47 s (1H, CH=N), 13.34 s (1H, OH). Found, %: C 87.80; H 7.16; N 2.34. $C_{45}H_{43}NO$. Calculated, %: C 88.05; H 7.06; N 2.28.

2-*tert*-Butyl-4-triphenylmethyl-6-[(4-triphenylmethylphenylimino)methyl]phenol (IIf). Yield 78%, mp 150–152°C. IR spectrum: ν 1618 cm^{-1} (N=CH). ^1H NMR spectrum, δ, ppm: 1.27 s (9H, *t*-Bu), 6.90–7.40 m (36H, H_{arom}), 8.35 s (1H, CH=N), 13.50 s (1H, OH). Found, %: C 89.20; H 6.52; N 1.73. $C_{55}H_{47}NO$. Calculated, %: C 89.51; H 6.42; N 1.90.

The IR spectra were recorded in KBr on a Bruker Vector 22 spectrometer. The ^1H NMR spectra were measured from solutions in CCl_4 on a Bruker WP-200 SY instrument at 200.13 MHz using hexamethyldisiloxane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. The elemental composition of compound **IIa** was determined from the high-resolution mass spectrum obtained on a Finnigan MAT-8200 mass spectrometer. The elemental compositions of **IIb–IIf** were determined using a Carlo Erba 1106 CHN analyzer.

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