

## Addition of Fluorene to Schiff Bases†

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Kostadinka Popandova-Yambolieva

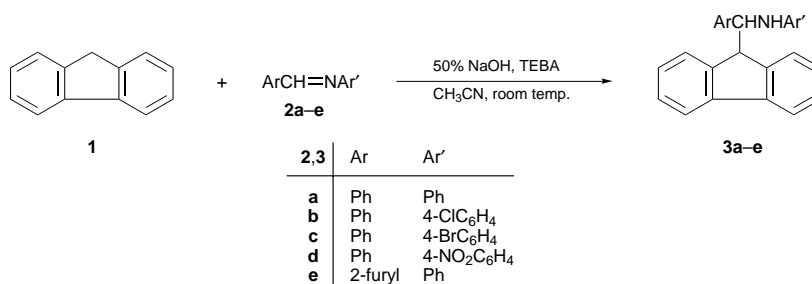
Department of Chemistry, University of Sofia, 1 J.Bourchier Avenue, 1126 Sofia, Bulgaria

Addition of fluorene to *N*-arylmethylideneanilines under conditions of phase-transfer catalysis gives *N*-aryl-*N*-[9*H*-fluoren-9-yl(aryl)methyl]amines **3a–e**.

It is known that indene and fluorene have acidic properties, but their application in the Michael addition has been little described. The addition of fluorene to some  $\alpha,\beta$ -unsaturated ketones,<sup>1</sup> nitriles and esters<sup>2</sup> has been realized under various conditions. Some years ago we reported our preliminary results on the Michael addition of fluorene to some  $\alpha,\beta$ -unsaturated ketones, esters and nitriles under conditions of phase-transfer catalysis (PTC) in acetonitrile.<sup>3</sup> Later a similar addition was realized with other  $\alpha,\beta$ -unsaturated ketones and nitriles under PTC conditions in benzene.<sup>4</sup> There is no report in the literature on the addition of fluorene to Schiff bases. Having in mind that some fluorenyl derivatives of aminobenzoic acids are anti-inflammatory agents,<sup>5</sup> we decided to study the behaviour of fluorene (**1**) towards *N*-arylmethylideneanilines (**2**). We now present the results of our studies on the reaction of **1** with **2** under PTC conditions. The expected compounds **3a–e** were obtained (Scheme 1).

The reaction was carried out at room temperature with an excess of aqueous sodium hydroxide, a catalytic amount of

mmol) in acetonitrile (10 cm<sup>3</sup>). The reaction mixture was stirred at room temperature for 1 h. Water (100 cm<sup>3</sup>) was added and the solid was filtered off, washed until neutral and recrystallized from methanol–ethyl acetate. The following products were obtained: *N*-[9*H*-fluoren-9-yl(phenyl)methyl]-*N*-phenylamine (**3a**) (1.48 g, 43%), mp 152–153 °C;  $\nu_{\max}/\text{cm}^{-1}$  (CHCl<sub>3</sub>) 3430 (NH) (Found: C, 89.78; H, 6.3; N, 3.9. C<sub>26</sub>H<sub>21</sub>N requires C, 89.9; H, 6.05; N, 4.0%);  $\delta_{\text{H}}$  3.18 (1 H, br s, NH), 4.48 (1 H, d, *J* 4.5 Hz), 5.18 (1 H, d, *J* 4.5 Hz), 6.15–7.80 (18 H, m, aromatic); *N*-(4-chlorophenyl)-*N*-[9*H*-fluoren-9-yl(phenyl)methyl]amine (**3b**) (0.8 g, 22%), mp 162–164 °C;  $\nu_{\max}/\text{cm}^{-1}$  (CDCl<sub>3</sub>) 3430 (NH) (Found: C, 81.6; H, 5.3; N, 3.6. C<sub>26</sub>H<sub>20</sub>ClN requires C, 81.7; H, 5.2; N, 3.7%);  $\delta_{\text{H}}$  3.44 (1 H, br s, NH), 4.45 (1 H, d, *J* 4.1 Hz), 5.08 (1 H, d, *J* 4.1 Hz), 6.08–7.80 (17 H, aromatic); *N*-(4-bromophenyl)-*N*-[9*H*-fluoren-9-yl(phenyl)methyl]amine (**3c**) (0.7 g, 17%), mp 170–172 °C;  $\nu_{\max}/\text{cm}^{-1}$  (CHCl<sub>3</sub>) 3420 (NH) (Found: C, 73.1; H, 4.7; N, 3.4. C<sub>26</sub>H<sub>20</sub>BrN requires C, 73.2; H, 4.7; N, 3.3%);  $\delta_{\text{H}}$  3.36 (1 H, br s, NH), 4.40 (1 H, d, *J* 4.0 Hz), 5.11 (1 H, d, *J* 4.0 Hz), 6.10–7.80 (17 H, m, aromatic); *N*-[9*H*-fluoren-9-yl(phenyl)methyl]-*N*-(4-nitrophenyl)amine (**3d**) (0.8 g, 20%, mp 127–128 °C;  $\nu_{\max}/\text{cm}^{-1}$  (CHCl<sub>3</sub>) 3370



Scheme 1

TEBA (triethylbenzylammonium chloride) and acetonitrile as solvent. For 4-methoxy- and 4-dimethylamino-benzylideneanilines only the starting Schiff bases were recovered. Also, owing to steric hindrance, there was no reaction with either *N*-phenylbenzophenone imine or with *N*-benzylidene-*tert*-butylamine.

The structures of the new compounds **3a–e** were assigned by IR and <sup>1</sup>H NMR spectroscopy and by elemental analysis.

## Experimental

Melting points were determined by a Boetius micropoint apparatus and are uncorrected. IR spectra were recorded on a Specord 71 spectrophotometer (Carl Zeiss, Iena). <sup>1</sup>H NMR spectra were measured with a TESLA BS 487-C spectrometer (80 MHz) using CDCl<sub>3</sub> solutions and Me<sub>4</sub>Si as internal standard. The starting *N*-arylmethylideneanilines were prepared by reported procedures.

**Typical Procedure.**—Aqueous sodium hydroxide (50% w/v; 3 cm<sup>3</sup>) was added to a stirred solution of fluorene (1.66 g, 10 mmol), the corresponding Schiff base **2** (10 mmol) and TEBA (0.23 g, 1

(NH), 1590 (NO<sub>2</sub>) (Found: C, 79.3; H, 5.1; N, 6.9. C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> requires C, 79.5; H, 5.1; N, 7.1%); *N*-[9*H*-fluoren-9-yl(2-furyl)methyl]-*N*-phenylamine (**3e**) (0.95 g, 29%), mp 178–180 °C;  $\nu_{\max}/\text{cm}^{-1}$  (CDCl<sub>3</sub>) 3430 (NH) (Found: C, 85.5; H, 5.7; N, 3.9. C<sub>24</sub>H<sub>19</sub>NO requires C, 85.4; H, 5.7; N, 4.1%).  $\delta_{\text{H}}$  3.46 (1 H, br s, NH), 4.68 (1 H, d, *J* 4.1 Hz), 5.26 (1 H, d, *J* 4.1 Hz), 6.04 and 6.30 (2 H, 2 d, *J* 6; *J* 6 Hz), 6.62 (1 H, d, *J* 14 Hz), 6.90–7.75 (13 H, m, aromatic).

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\*To receive any correspondence.

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