SYNTHESIS OF NEW SPIROPYRROLIDINES AND MICHAEL ADDITION PRODUCTS USING PHASE TRANSFER CATALYZED ADDITION OF SCHIFF BASES TO 9-ARYLMETHYLENEFLUORENES

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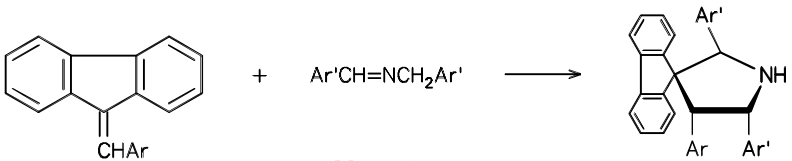
As a continuation of our previous studies concerned with the reactivity of benzylidene- and furfurylidenefluorenes in addition reactions[1,2], in the present work we have prepared a series of new spiropyrrolidines by reactions of 9-arylmethylenefluorenes *I* with aryl- (*II*) and furylazomethines (*IV*) and some Michael addition products by using diphenylmethyleneazomethines *VI* (refs[3 – 5]) and *VIII* (Scheme 1). The structure B was assigned to the furylspiropyrrolidines *Va* – *Vf* based on ^{1}H NMR data.

The reaction was carried out at room temperature with an excess of aqueous sodium hydroxide and a catalytic amount of triethylbenzylammonium chloride (TEBA).

An attempt at synthesis of an analogous reaction product by interaction of Schiff base *IV* with 1,1,2-triphenylethene has not been successful and the starting 1,1,2-triphenylethene was isolated unchanged.

EXPERIMENTAL

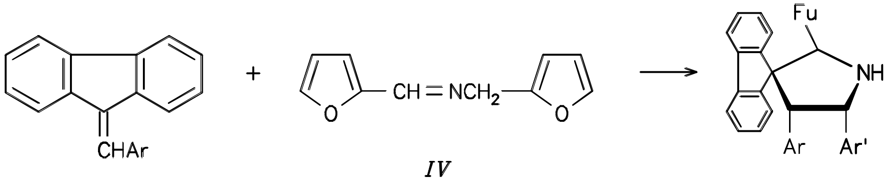
Melting points were determined on a Kofler hot stage apparatus and were not corrected. IR spectra were measured on a Specord 71 instrument (Zeiss, Jena). ^{1}H NMR spectra were recorded on a Tesla BS 487-C (80 MHz) spectrometer, using $CDCl_3$ solution and TMS as an internal standard. For thin layer chromatography (TLC), the solvent system used was hexane–acetone (4 : 1 v/v). The starting 9-arylmethylenefluorenes (*Ia* – *If*) were prepared from fluorene and the corresponding aromatic aldehydes. 4-Methyl-*N*-(4-methylbenzylidene)benzylamine (*IIb*) and 4-chloro-*N*-(4-chlorobenzylidene)benzylamine (*IIc*) were prepared as reported[6]. *N*-Furfurylidenefurfurylamine (*IV*) was obtained by reported procedure[7]. *N*-Diphenylmethylenebenzylamine (*VI*) was prepared from benzophenone and benzylamine[8], *N*-diphenylmethylene-(2-furfuryl)amine (*VIII*) was described previously[9].



Ia, Ib

II	Ar'
a	4-$CH_3C_6H_4$
b	4-ClC_6H_4

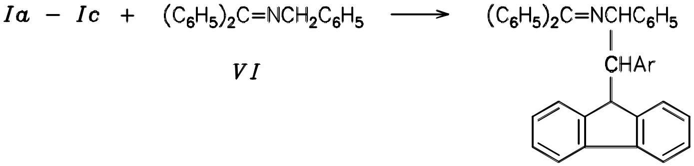
III	Ar	Ar'
a	C_6H_5	4-$CH_3C_6H_5$
b	C_6H_5	4-ClC_6H_5
c	4-$CH_3C_6H_5$	4-ClC_6H_5



IV

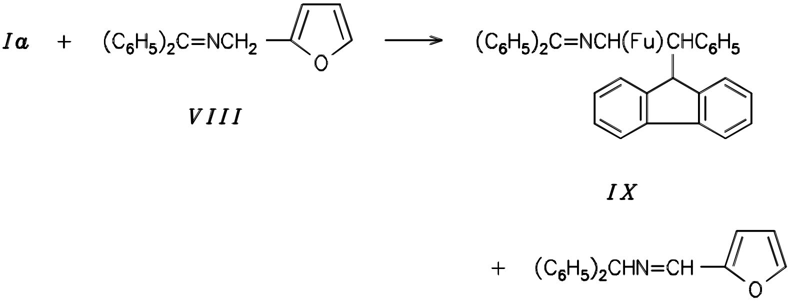
Ia – If

Va – Vf



VI

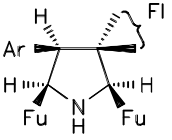
VIIa – VIIc



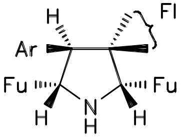
VIII

IX

X



A



B

Fl, 9-fluorenyl; Fu, 2-furyl

In formulae *I*, *V* and *VII*: *a*, Ar = C_6H_5
b, Ar = 4-$CH_3C_6H_4$
c, Ar = 4-ClC_6H_4
d, Ar = 4-$CH_3OC_6H_4$
e, Ar = 4-$(CH_3)_2NC_6H_4$
f, Ar = 2-furyl

SCHEME 1

2′,4′,5′-Triarylfluorene-9-spiro-3′-pyrrolidines *IIIa* – *IIIc* and 4′-Aryl-2′,5′-bis(2-furyl)-fluorene-9-spiro-3′-pyrrolidines *Va* – *Vf*

Aqueous sodium hydroxide (50%, 3 ml) was added to a stirred solution of *II* (20 mmol), 9-arylmethylenefluorene *I* (10 mmol) and TEBA (0.23 g, 1 mmol) in dimethylsulfoxide (5 ml). The reaction mixture was green and was stirred at room temperature for 1 h. After 3 h, water (100 ml) was added. The solid was filtered, washed with water until neutral and recrystallized. Some physicochemical properties of the obtained products are summarized in Table I and their characteristic IR bands and ^{1}H NMR spectra are presented in Table II.

2-Aryl-2-fluorenyl-1-phenyl-*N*-(diphenylmethylene)ethylamines *VII* and *IX*

Aqueous sodium hydroxide (50%, 3 ml) was added to a stirred solution of *VI*, or *VIII* (10 mmol), respectively, 9-arylmethylenefluorene *I* (10 mmol) and TEBA (0.23 g, 1 mmol) in acetonitrile (5 ml). The reaction mixture was stirred for 10 min and water (100 ml) was added. After 24 h, the solid was filtered, washed with water and recrystallized from methanol–ethyl acetate. Characteristic data for the so obtained compounds are in Table I, their IR and ^{1}H NMR spectra are given in Table II.

TABLE I
Characteristic data for compounds *III*, *V*, *VII*, and *IX*

Compound	Formula (M.w.)	M.p., °C[a] (Yield, %)	Calculated/Found		
			% C	% H	% N
IIIa	$C_{36}H_{31}N$	174 – 176	90.52	6.54	2.93
	(447.6)	(44)	90.22	6.83	2.89
IIIb	$C_{34}H_{25}NCl_2$	171 – 173	78.83	4.83	2.70
	(518.4)	(60)	78.81	4.94	2.84
IIIc	$C_{35}H_{27}NCl_2$	173 – 175	78.97	5.07	2.63
	(523.3)	(54)	78.98	5.36	2.52
Va	$C_{30}H_{23}NO_2$	189 – 191	83.99	5.36	3.26
	(429.3)	(33)	84.25	5.10	3.36
Vb	$C_{31}H_{25}NO_2$	187 – 189	83.94	5.68	3.16
	(443.5)	(40)	84.22	5.95	3.14
Vc	$C_{30}H_{22}NO_2Cl$	189 – 190	77.69	4.74	3.02
	(463.8)	(46)	77.74	4.73	3.06
Vd	$C_{31}H_{25}NO_3$	196 – 198	81.02	5.48	3.05
	(459.5)	(47)	81.11	5.25	2.89
Ve	$C_{32}H_{28}N_2O_2$	179 – 181	81.33	5.97	5.93
	(472.6)	(61)	81.54	6.01	5.84
Vf	$C_{28}H_{21}NO_3$	149 – 150	80.17	5.05	3.34
	(419.5)	(50)	80.42	5.01	3.33
VIIa	$C_{40}H_{31}N$	178 – 179	91.39	5.94	2.66
	(525.7)	(47)	91.68	5.67	2.68
VIIb	$C_{41}H_{33}N$	189 – 191	91.24	6.16	2.60
	(539.7)	(42)	91.58	6.12	2.51
VIIc	$C_{40}H_{30}NCl$	151 – 152	85.80	5.36	2.50
	(560.2)	(48)	85.66	5.55	2.27
IX[b]	$C_{38}H_{29}NO$	195 – 196	88.51	5.67	2.72
	(515.6)	(23)	88.42	5.70	2.72

[a] Recrystallized from methanol–ethyl acetate. [b] A total of 10% of compound *X* (m.p. 94 – 95 °C, reported[5] m.p. 106 °C) was isolated from the mother liquor. IR (chloroform): $\nu(C=N) = 1\,630\ cm^{-1}$.

TABLE II
IR and ^{1}H NMR spectra for compounds *III*, *V*, *VII*, and *IX*

Compound	ν_{max}, cm$^{-1\,a}$	δ, ppm^b
IIIa	3 340 (NH)	2.12 and 2.31 2 s, 6 H (2 $\times$ Me); 2.58 brs 1 H (NH); 4.09 d, 1 H (H-4, J = 11); 5.09 s, 1 H (H-2); 5.23 d 1 H (H-5, J = 11); 6.50 – 8.08 m, 21 H (arom.)
IIIb	3 370 (NH)	2.58 brs, 1 H (NH); 3.93 d, 1 H (H-4, J = 10.5); 4.98 s, 1 H (H-2); 5.14 d, 1 H (H-5, J = 10.5); 6.45 – 7.60 m 21 H (arom.)
IIIc	3 360 (NH)	2.09 s, 3 H (Me); 2.54 brs, 1 H (NH); 3.94 d, 1 H (H-4, J = 10); 5.05 s, 1 H (H-2); 5.19 d, 1 H (H-5, J = 10); 6.50 – 7.65 m, 20 H (arom.)
Va	3 380 (NH)	2.84 brs, 1 H (NH); 4.54 d, 1 H (H-4, J = 10); 5.21 s, 1 H (H-2); 5.37 d, 1 H (H-5, J = 10); 5.58, 5.92, 6.34 and 6.44 4 d, 4 H (β-furyl); 6.51 – 7.80 m, 15 H (arom. and α-furyl)
Vb	3 375 (NH)	1.92 s, 3 H (Me); 2.91 brs, 1 H (NH); 4.40 d, 1 H (H-4, J = 10.5); 5.09 s, 1 H (H-2); 5.24 d, 1 H (H-5, J = 10.5); 5.49 and 5.81 2 d, 2 H (β-furyl); 6.15 – 6.50 m, 4 H (β-furyl and α-furyl); 6.77 – 7.63 m, 12 H (arom.)
Vc	3 380 (NH)	2.95 brs, 1 H (NH); 4.38 d, 1 H (H-4, J = 10); 5.11 s, 1 H (H-2); 5.24 d, 1 H (H-5, J = 10); 5.52 and 5.84 2 d, 2 H (β-furyl); 6.24 m, 2 H (β-furyl); 6.52 d, 2 H (α-furyl); 6.79 – 7.63 m, 12 H (arom.)
Vd	3 380 (NH)	2.65 brs, 1 H (NH); 3.35 s, 3 H (MeO); 4.29 d, 1 H (H-4, J = 10.5); 4.66 s, 1 H (H-2); 5.13 d, 1 H (H-5, J = 10.5) 6.20 m, 6 H (β-furyl and α-furyl); 6.50 – 7.78 m, 12 H (arom.)
Ve	3 400 (NH)	2.59 s, 7 H (2 $\times$ Me and NH); 4.23 d, 1 H (H-4, J = 10.5); 4.66 s, 1 H (H-2); 5.14 d, 1 H (H-5, J = 10.5); 5.97 – 6.30 m, 6 H (β-furyl and α-furyl); 6.75 – 7.81 m, 12 H (arom.)
Vf	3 400 (NH)	2.71 brs, 1 H (NH); 4.38 d, 1 H (H-4, J = 10); 4.78 s, 1 H (H-2); 5.12 d, 1 H (H-5, J = 10); 5.45, 5.96 and 6.23 3 d, 6 H (β-furyl); 6.75 – 7.62 m, 11 H (arom. and α-furyl)
VIIa	1 630 (C=N)	4.43 dd, 1 H (H-2, J = 11/4); 4.85 d, 1 H (H-1, J = 3); 5.26 d, 1 H (Fl–**H**, J = 11); 6.40 – 7.90 m, 28 H (arom.)
VIIb	1 630 (C=N)	1.84 s, 3 H (Me); 4.35 dd, 1 H (H-2, J = 10/3); 4.78 d, 1 H (H-1, J = 3); 5.20 d, 1 H (Fl–**H**, J = 10); 6.25 – 7.70 m, 27 H (arom.)
VIIc	1 620 (C=N)	3.86 d, 1 H (H-4, J = 4); 4.20 dd, 1 H (H-2, J = 10/3); 5.20 d, 1 H (Fl–**H**, J = 10); 6.24 – 7.60 m, 27 H (arom.)
IX	1 625 (C=N)	4.09 d, 1 H (H-1, J = 4); 4.56 dd, 1 H (H-2, J = 10/4); 5.60 d, 1 H (Fl–**H**, J = 10); 6.50 m, 2 H (β-furyl); 6.75 – 7.70 m, 24 H (arom. and α-furyl)

[a] In Nujol. [b] $CDCl_3$ solutions, tetramethylsilane used as an internal standard.

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