Synthesis of 1-Arylimino-4-methyl-4-trichloromethyl-2,5-cyclohexadienes

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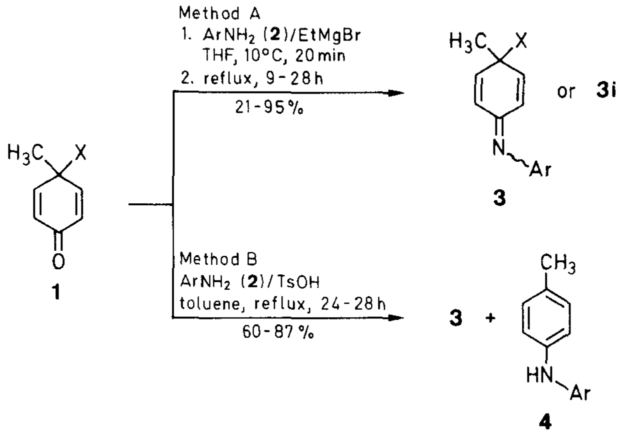
1-Arylimino-4-methyl-4-trichloromethyl-2,5-cyclohexadienes **3** were obtained in 21–95% yield by treating 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**1a**) with aryl amines **2**.

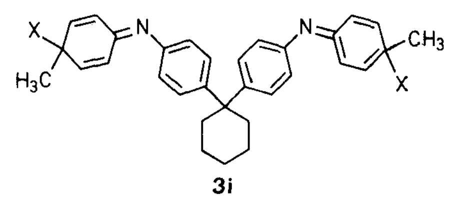
With the intention of synthesizing the diamine, 1,1-bis(4-di-*p*-tolylaminophenyl)cyclohexane (**5a**),[1] which is the hole-conduction and injection-agent in the electroluminescence, we carried out a direct *N*,*N'*-tetratolylation of 1,1-bis-(4-*p*-aminophenyl)cyclohexane (**2i**) with *p*-iodo- or bromotoluene by means of the Ullmann reaction. However, the yields were as low as 2%. Therefore, we intended to obtain **5a** via 1,1-bis(4-*p*-toluidinophenyl)cyclohexane (**4d**), because the conversion of **4d** to **5a** could be possible by the literature method.[2]

In order to prepare **4d**, first we carried out the reaction between 4-methyl-4-trichloro- and dichloromethyl-2,5-cyclohexadienone (**1a**[3] and **1b**, respectively) and the aryl amine **2i**, as in the reaction between secondary aliphatic amines and **1b**.[4] However, the reactions resulted only in the recovery of starting materials, **1a** or **1b**, and **2i**. This failure seemed to be attributed to the weak basisity of aryl amines. Therefore, some suitable reagent is necessary for activation of nitrogen atom in aryl amines. As a model reaction for the activation of **2i**, aniline (**2a**) and ethylmagnesium bromide were chosen leading to the *N*-magnesium bromide salt of aniline (organolithium reagent is not suitable for this purpose, because the *o*-position of aryl amines is much more subject to lithiation). The salts were treated with dienone **1a** in refluxing tetrahydrofuran to afford 1-phenylimino-4-methyl-4-trichloromethyl-2,5-cyclohexadiene (**3a**), which is a feasible synthetic intermediate for *N*-tolylaniline. Thus, several azomethine **3b–h** were prepared by this reaction between **1a** and the salt of corresponding aryl imines **2b–h** in moderate yields (Method A, Table 1.).

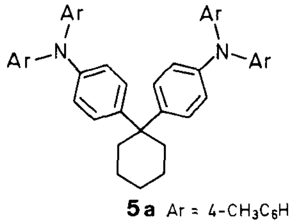
However, in the case of **2i** Method A did not give **3i**, since the *N*-magnesium salt of **2i** precipitated out in tetrahydrofuran to arrest the reaction progress. Secondly, in order to prepare **3i**, an acid catalyzed condensation between **2i** and the dienone **1a** was performed using *p*-toluenesulfonic acid in refluxing toluene to afford **3i**, which was contaminated with the product 1-{4-[1-(4'-*p*-toluidinophenyl)cyclohexyl]imino}-4-methyl-4-trichloromethyl-2,5-cyclohexadiene (**5b**). This acid catalyzed condensation was also applied for the aryl amines **2a–c** and **2g** to afford the corresponding azomethines **3a–c** and **3g** in almost the same yields as Method A (Method B, Table 2.). However, in this condensation, the azomethines **3a–c** were contaminated with small amounts of the corresponding *N*-tolylarylamines **4a–c**, respectively.

These azomethines **3a–i** and **5b** were converted to corresponding *N*-tolylarylamines **4a–i**, when they were subjected to reductive aromatization.[5] The diamine[1] **5a** was obtained from **4d** by literature procedure,[2] which will be reported elsewhere.

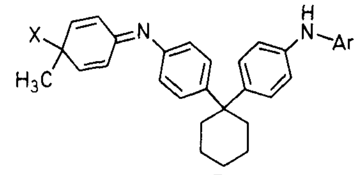




3i

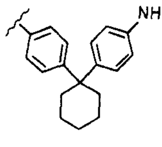


5a Ar = 4-CH$_3$C$_6$H$_4$



5b Ar = 4-CH$_3$C$_6$H$_4$

X = CCl$_3$

2, 3	Ar	2, 3	Ar
a	Ph	f	4-ClC$_6$H$_4$
b	4-MeC$_6$H$_4$	g	4-IC$_6$H$_4$
c	4-MeOC$_6$H$_4$	h	4-H$_2$NC$_6$H$_4$
d	4-EtOC$_6$H$_4$		
e	4-PhOC$_6$H$_4$	2i	 NH$_2$

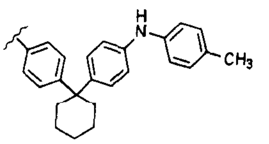
4	a	b	c	d
Ar	Ph	4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	 H N CH$_3$

Table 1. Azomethines **3a–h** Prepared (Method A)

Product	Reaction Time (h)	Yield[a] (%)	mp (°C)	Molecular Formula[b]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ, *J*(Hz)	^{13}C-NMR (CDCl$_3$/TMS)[c,d] δ	MS (30 eV) *m/z* (%)
3a	28	73	82–84	$C_{14}H_{12}NCl_3$ (300.6)	1578, 1484, 906, 839, 794, 786, 759, 734, 697, 687	1.63 (s, 3H), 6.50 (dd, 1H, *J* = 10.38, 1.22), 6.59 (dd, 1H, *J* = 10.38, 1.22), 6.66 (dd, 1H, *J* = 9.93, 1.22), 6.71 (dd, 1H, *J* = 9.93, 2.44), 6.83 (d, 2H, *J* = 7.33), 7.11 (t, 1H, *J* = 7.33), 7.33 (t, 2H, *J* = 7.94)	23.96 (s), 56.13 (s), 105.18 (s), 120.45 (d), 122.54 (d), 124.19 (s), 128.87 (d), 132.27 (d), 138.80 (d), 140.65 (d), 149.96 (s), 155.95 (s)	303 (1.4), 302 (1), 301 (1.5), 300 (0.7), 299 (M^+, 4.4), 231 (1.4), 230 (1.0), 229 (3), 228 (2), 214 (1), 183 (20), 182 (100), 167 (45)
3b	28	72	143–144	$C_{15}H_{14}NCl_3$ (314.6)	1583, 1449, 1221, 1114, 909, 844, 826, 795, 761, 678	1.63 (s, 3H), 2.34 (s, 3H), 6.55 (m, 2H), 6.76 (m, 2H), 6.75 (d, 2H, *J* = 8.25), 7.14 (d, 2H, *J* = 8.25)	20.91 (q), 23.99 (q), 56.13 (s), 105.26 (s), 1290.54 (d), 122.58 (s), 129.47 (d), 132.39 (d), 133.82 (s), 138.51 (d), 140.32 (d), 147.32 (s), 155.95 (s)	315 (5), 313 (M^+, 5), 213 (4), 197 (20), 196 (100), 181 (41), 180 (14)
3c	9	74	119–120	$C_{15}H_{14}NOCl_3$ (330.6)	1500, 1286, 1240, 1281, 1032, 909, 841, 836, 791, 756	1.63 (s, 3H), 3.81 (s, 3H), 6.57 (d, 1H, *J* = 10.37), 6.60 (d, 1H, *J* = 10.37), 6.66 (d, 1H, *J* = 10.37), 6.81 (d, 2H, *J* = 8.85), 6.89 (d, 2H, *J* = 8.85)	24.02 (q), 55.47 (s), 56.14 (s), 105.32 (s), 114.19 (d), 122.03 (d), 122.58 (d), 132.49 (d), 138.26 (d), 140.17 (d), 143.06 (s), 155.95 (s), 156.84 (s)	331 (5), 329 (M^+, 5), 259 (5), 212 (100), 213 (20), 198 (8), 197 (25), 182 (8), 181 (10), 133 (15)
3d	24	95	76–77	$C_{16}H_{16}NOCl_3$ (344.7)	1602, 1505, 1473, 1393, 1248, 1249, 1120, 1048, 849, 830, 802, 796, 790, 757, 676	1.42 (t, 3H, *J* = 6.96), 1.63 (s, 3H), 4.03 (q, 2H, *J* = 7), 6.56 (d, 1H, *J* = 10.4), 6.61 (d, 1H, *J* = 10.4), 6.66 (s, 2H), 6.80 (d, 2H, *J* = 8.9), 6.88 (d, 2H, *J* = 8.9)	14.91 (q), 24.05 (q), 56.16 (q), 63.72 (t), 105.35 (s), 114.82 (d), 122.06 (d), 122.63 (d), 132.54 (d), 138.20 (d), 140.11 (d), 142.96 (s), 155.89 (s), 155.89 (s), 156.22 (s)	345 (6), 343 (M^+, 5), 273 (3), 227 (20), 226 (100), 199 (8), 198 (50), 197 (6), 183 (3), 119 (8)
3e	24	87	99–100	$C_{20}H_{16}NOCl_3$ (392.7)	1589, 1489, 1237, 1241, 1166, 827, 794, 748	1.60 (s, 3H), 6.59 (d, 1H, *J* = 8), 6.22 (d, 1H, *J* = 8), 6.66 (d, 1H, *J* = 8), 6.70 (dd, 1H, *J* = 8, 1.83), 6.83 (d, 2H, *J* = 8.55), 7.00 (d, 2H, *J* = 8.55), 7.02 (d, 2H, *J* = 7.33), 7.09 (t, 2H), 7.33 (t, 2H, *J* = 7.94)	23.98 (q), 56.17 (s), 105.18 (s), 118.50 (d), 119.59 (d), 122.00 (d), 122.47 (d), 123.05 (d), 129.73 (d), 132.33 (d), 138.72 (d), 140.69 (d), 145.47 (s), 153.90 (s), 156.22 (s), 157.60 (s)	393 (5), 391 (M^+, 5), 321 (4), 275 (37), 274 (100), 181 (46), 180 (30)
3f	24	70	139–140	$C_{14}H_{11}NCl_4$ (335.1)	1659, 1608, 1480, 1454, 1227, 1218, 1116, 1098, 1087, 1068, 1011, 910, 846, 839, 792, 761, 682	1.64 (s, 3H), 6.47 (dd, 1H, *J* = 10.37, 1.83), 6.63 (dd, 1H, *J* = 10.37, 3.05), 6.65 (dd, 1H, *J* = 10.37, 1.83), 6.73 (dd, 1H, *J* = 10.37, 3.05), 6.77 (d, 2H, *J* = 8.54), 7.30 (d, 2H, *J* = 8.54)	23.90 (q), 56.19 (s), 104.98 (s), 121.84 (d), 122.20 (d), 129.00 (d), 129.60 (s), 132.04 (d), 139.31 (d), 141.35 (d), 148.44 (s), 156.40 (s)	337 (3), 335 (M^+, 7), 333 (5), 265 (3), 263 (3), 218 (35), 217 (20), 216 (100), 201 (20), 182 (10), 181 (55), 180 (25)
3g	70	21	144–145	$C_{14}H_{11}NCl_3I$ (426.5)	1655, 1606, 1585, 1465, 1451, 1391, 1220, 1117, 1060, 1003, 908, 873, 794, 776, 765, 757, 680, 471	1.63 (s, 3H), 6.46 (dd, 1H, *J* = 10.38, 1.83), 6.60 (d, 2H, *J* = 8.54), 6.63 (dd, 1H, *J* = 10.38, 2.75), 6.64 (dd, 1H, *J* = 10.07, 1.83), 6.73 (dd, 1H, *J* = 10.07, 2.75), 7.63 (d, 2H, *J* = 8.54)	23.90 (q), 56.22 (s), 87.92 (s), 104.97 (s), 122.20 (d), 122.66 (d), 132.01 (d), 137.92 (d), 139.41 (d), 141.45 (d), 149.61 (s), 156.27 (s)	427 (3), 425 (M^+, 3), 357 (2), 355 (4), 309 (15), 308 (66), 182 (18), 181 (100), 180 (40)
3h	24	47	170–190	$C_{22}H_{18}N_2Cl_6$ (523.1)	1652, 1606, 1583, 1490, 1451, 1257, 1218, 1116, 1062, 912, 859, 833, 828, 792, 758, 675	1.64 (s, 6H), 6.62 (s, 4H), 6.67 (d, 2H, *J* = 9.77), 6.71 (d, *J* = 10.38), 6.85 (s, 4H)	24.01 (q), 56.20 (s), 105.23 (s), 121.36 (d), 122.58 (d), 132.37 (m), 138.70 (d), 140.64 (d), 146.45 (s), 159.09 (s)	524 (2), 522 (M^+, 2), 405 (12), 403 (12), 287 (22), 286 (100)

[a] Yield of isolated product based on **2**.
[b] Satisfactory microanalyses obtained: C ±0.13, H ±0.12, N ±0.22.
[c] Center peak of CDCl$_3$ referred to TMS as standard, $\delta = 77.10$.
[d] Off-resonance spectra.

Table 2. Azomethines **3a–c**, **g**, **5b** and Tolylarylamines **4a–c** Prepared

Substrate Arylamine	Products[a]	Yield[b] (%)	mp (°C)	Molecular Formula[c] or Lit. mp (°C)	IR (KBr) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ, J(Hz)	^{13}C-NMR (CDCl$_3$/TMS)[d,e] δ
2a	**3a**	86	–	–	–	–	–
	4a	12	87.1–87.8	89[6]	3396, 3014, 2915, 1597, 1500, 1486, 1469, 1463, 1441, 1309, 1241, 1228, 1153, 1110, 1078, 810, 694, 506	–	–
2b	**3b**	60	–	–	–	–	–
	4b	4	80.1–80.6	80.5[7]	3420, 3411, 3025, 2914, 1321, 807, 506, 475	–	–
2c	**3c**	87	–	–	–	–	–
	4c	4	84–85	$C_{14}H_{15}N$ (197.3)	3415, 2952, 2910, 2836, 1516, 1251, 1034, 814, 517	2.27 (s, 3H), 3.78 (s, 3H), 5.30–5.45 (br, 1H), 6.83 (d, 2H, J = 6.11), 6.84 (d, 2H, J = 7.32), 7.10 (d, 2H, J = 6.11), 7.03 (d, 2H, J = 7.32)	20.55 (q), 55.63 (q), 114.73 (d), 116.64 (d), 121.15 (d), 129.35 (s), 129.82 (d), 136.72 (s), 142.46 (s), 154.87 (s)
2g	**3g**	78	–	–	–	–	–
	4g	0	–	–	–	–	–
2i	**3i**	60	glass	$C_{34}H_{32}N_2Cl_6$ (681.4)	2935, 2858, 1658, 1653, 1607, 1583, 1498, 1452, 1263, 1226, 1178, 1116, 1065, 1012, 910, 833, 795, 755, 682	1.50–1.55 (br, 2H), 1.55–1.62 (br, 4H), 1.62 (s, 6H), 2.25–2.30 (br, 4H), 6.56 (s, 4H), 6.66 (s, 4H), 6.76 (d, 4H, J = 8.25), 7.24 (d, 4H, J = 8.25)	22.98 (t), 23.99 (q), 26.46 (t), 37.35 (t), 45.74 (s), 56.13 (s), 105.32 (s), 120.47 (d), 127.65 (d), 127.65 (d), 132.45 (d), 138.46 (d), 140.27 (d), 144.78 (s), 147.19 (s), 155.90 (s)
	4d	0	–	–	–	–	–
	5b	12	glass	$C_{33}H_{33}N_2Cl_3$ (564.0)	2935, 2858, 1668, 1656, 1607, 1579, 1515, 1467, 1451, 1314, 1225, 1181, 1117, 1110, 910, 834, 798, 755, 733, 501	1.46 (br, 2H), 1.53–1.60 (br, 4H), 1.61 (s, 3H), 2.20–2.27 (br, 4H), 2.28 (s, 3H), 5.49–5.59 (br, 1H), 6.55 (s, 2H), 6.65 (s, 2H), 6.75 (d, 2H, J = 8.86), 6.93 (d, 2H, J = 7.94), 6.96 (d, 2H, J = 7.94), 7.14 (d, 2H, J = 8.55), 7.23 (d, 2H, J = 8.86)	20.65 (q), 22.98 (t), 23.96 (q), 26.47 (t), 37.35 (t), 45.45 (s), 56.12 (s), 105.32 (s), 116.89 (d), 118.48 (d), 120.47 (d), 122.79 (d), 127.75 (d), 128.01 (d), 129.79 (d), 130.46 (s), 132.40 (d), 138.46 (d), 140.24 (d), 140.64 (s), 140.71 (s), 141.25 (s), 145.18 (s), 147.00 (s), 155.90 (s)

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[a] For data of products **3a–c**, **g**, see Table 1.

[b] Yield of isolated products based on **2**.

[c] Satisfactory microanalyses obtained: C, H, N ±0.30.

[d] Center peak of CDCl$_3$ referred to TMS as standard, δ = 77.1.

[e] Off-resonance spectra.

Melting points were measured with a Yanagimoto Micro-MP apparatus and are uncorrected. The following instruments were used for recording the spectra. IR: Nicolex-5ZDX spectrophotometer, ^{1}H-NMR: Jeol-GX 400 spectrometer, ^{13}C-NMR: Jeol-FX 100 spectrometer, MS: Jeol-D 300 spectrometer.

1-Arylimino-4-methyl-4-trichloromethyl-2,5-cyclohexadienes 3a–h; General Procedures:

Method A: To a stirred solution of EtMgBr [generated from EtBr (0.6 mL, 8.1 mmol) and Mg turnings (0.165 g, 6.75 mmol)] in dry THF (1.5 mL) is added a solution of arylamine **2**, (8.1 mmol) in anhydrous THF (10 mL) at 0 °C. After 20 min, a solution of **1**[3] (1.506 g, 6.67 mmol) in anhydrous THF (30 mL) is added under Ar atmosphere. The mixture is refluxed for 9–28 h, and THF is removed under reduced pressure. The residue is dissolved in aq NH_4Cl (40 mL), extracted with $CHCl_3$ (3 × 40 mL), washed with brine, and dried (Na_2SO_4). The solvent is removed *in vacuo* and the residue is purified by chromatography on silica gel [Et_2O/hexane = 1 : 8] to afford azomethines **3** as crystals (except in the case of **3i**). Analytical samples are obtained by recrystallization from hexane.

Method B: A solution of **1a** (1.96 g, 9.8 mmol), an appropriate aryl amine **2** (8.7 mmol), and TsOH (0.01 g, 0.07 mmol) in toluene (30 mL) is refluxed for 24–28 h using a Dean–Stark apparatus, the side tube of which is packed with $MgClO_4$ (2 g). Toluene is then evaporated under reduced pressure. The residue is triturated with water (30 mL) and extracted with $CHCl_3$ (3 x 30 mL). The combined $CHCl_3$ extracts are washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The products are separated by chromatography on silica gel (Et_2O/hexane = 1 : 8). The first eluate is the *N*-tolylaryl amine **4** followed by azomethines **3** as crystals (except in the case of **3i**). Analytical samples is are obtained by recrystallization from hexane.

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