SHORT PAPER

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Synthesis of diarylmethylamines via electrophilic trapping of tricarbonyl chromium complexed aryllithium intermediates with imines†

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Diarylmethylamine derivatives **4a–l** were synthesised in good yields via lithiation of the tricarbonyl (η^6-arene) chromium complexes **1**, followed by electrophilic trapping with imines **2** and decomplexation (sunlight and air).

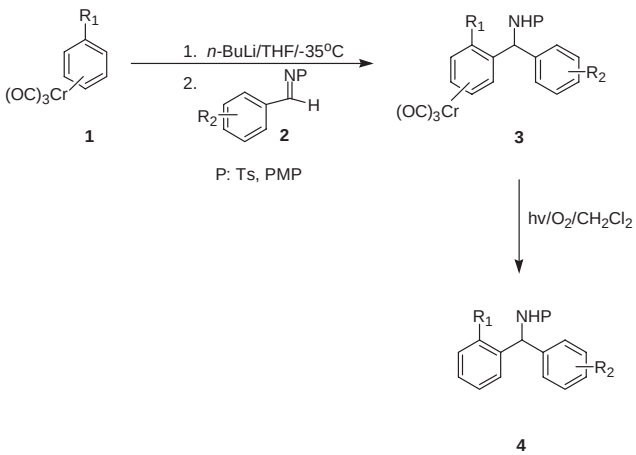
Keywords: diarylmethylamine, tricarbonyl (η^6-arene) chromium complex, lithiation, electrophilic trapping, imine

The diarylmethylamine moieties are present in a wide variety of pharmacologically interesting compounds,[1] for example, Cetirizine hydrochloride,[2] BW373U86 and SNC80.[1] Consequently, the biological and synthetic importance of diarylmethylamines has promoted the development of a multitude of methods for their synthesis. Among the numerous known synthetic methods, the reactions of organometallic reagents[1,3,4] such as Grignard reagents or phenyllithiums with various imines are often used, although the scope of their applications is rather restricted due to the limited functionality on the organometallic reagents. Despite the recent great achievements reached in the asymmetric synthesis[5] of diarylmethylamines, the ability to access efficiently certain specific substituted patterns, which may serve as new leads for the discovery,[1f] is limited and requires the design of new synthetic strategies, especially giving a number of unsolved aspects related to either the substrate availability or diversity.

It is also well documented that tricarbonyl (η^6-arene) chromium complexes are important reagents and intermediates in organic synthesis.[6] Tricarbonyl (η^6-arene) chromium complexes exhibit unique properties as compared to their parent free aromatic ligands. Changes of the reactivity, which arise upon the complexation of arene to the tricarbonylchromium fragment, allow a variety of transformations to be carried out that are inaccessible otherwise. In particular, the complexation of an aromatic ring to the tricarbonyl chromium moiety is known to enhance acidity of the arene ring proton and thus facilitate proton abstraction from the aromatic ring regioselectively.[7] In the presence of functional group, directed lithiation reactions, adjacent or remote, are achieved with ease, thus formed tricarbonyl (lithioarene) chromium complexes can react with various electrophiles such as iodine, methyl iodide, carbon dioxide and some carbonyl compounds.[8,9] Although many electrophiles have been used to trap tricarbonyl (lithioarene) chromium complexes,[8,10] to the best of our knowledge, imines as equivalent of carbonyl compounds have never been used as electrophiles in this reaction. It occured to us that instead of carbonyl compounds, the electrophilic trapping of tricarbonyl (lithioarene) chromium complexes intermediates with imines could provide an efficient approach to the diarylmethylamines with certain specific substituted patterns, which may not be easily accessed by the known methods. Herein we wish to report results on the synthesis of diarylmethylamines derivatives via lithiation reactions of tricarbonyl (η^6-arene) chromium complexes followed by electrophilic trapping with imines.

Results and discussion

All tricarbonyl (η^6-arene) chromium complexes **1** used were conveniently prepared according to standard procedures.[11] As illustrated in Scheme 1, the lithiation reactions of **1** with *n*-butyllithium and subsequent reactions with imines **2** were performed. The reaction of anisole chromium complex **1a** with *N*-tosylbenzylideneimine **2a** that has high electrophilicity due to the electron-withdrawing sulfonyl group on the nitrogen atom, giving the corresponding alkylated complex **3a**, was first examined. The enhancement of acidity of the ring protons, depending on the coordination of an arene to the tricarbonylchromium fragment, makes deprotonation proceed easily at low temperature. **3a** was subjected to the decomplexation conditions and *N*-tosyldiarylmethylamine **4a** was obtained in 64% yield (Table 1, entry 1). It is deduced by ^{1}H and ^{13}CNMR of the product **4a** that the lithiation reaction of anisole chromium complex **1a** proceeds by *ortho*-selection. The regioselectivity is consistent with Card and Semmelhack's observation[7,8] that the strong *ortho*-directing effects of methoxy and fluoro groups are presented in the lithiation reaction of mono-substituted arene chromium complexes. In the course of the investigations, it was found that the reaction temperature plays a crucial role in making the reaction proceed smoothly. If the reaction temperature is lower than –35 °C, the reaction could slow down significantly, and the reaction could be complicated at temperature above –20 °C due to the instability of the tricarbonyl (lithioarene) chromium complex intermediates.



Scheme 1

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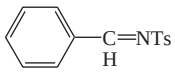
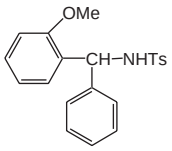
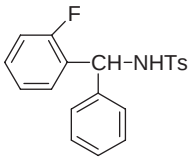
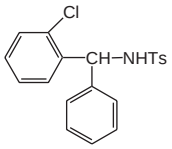
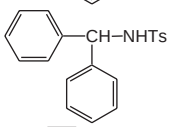
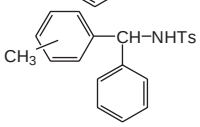
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Reactions of complexes **1** with imine **2a** via lithiation and decomplexation

Entry	R_1	Complex	Imine		Product		Yield[a]/%
1	OMe	**1a**		**2a**		**4a**	64
2	F	**1b**		**2a**		**4b**	68
3	Cl	**1c**		**2a**		**4c**	55
4	Br	**1d**		**2a**		**4d**	58
5	CH_3	**1e**		**2a**		**4e**	61
6	H	**1f**		**2a**		**4d**	60

[a]Isolated yield.

Based on the above results, the optimal reaction conditions were established to carry out the electrophilic trapping of tricarbonyl(lithioarene) chromium complexes with imine **2a**. As shown in Table 1, for several complexes with different substituents on the phenyl ring (**1a–f**), the lithiation reactions, and subsequent addition reactions to imine described above, prove to be applicable to the synthesis of the diarylmethylamine derivatives. It was also found that the substituents on phenyl ring such as MeO, F and Cl (Entries 1–3) had a strong *ortho*-directing effect. The addition reactions of chromium complex to imine, occurring at the *ortho*-position to the substituent, afforded the corresponding *ortho*-substituted diarylmethylamine derivatives that might not be easily accessed with present methods. However, for toluene complex (**1e**), the final products were a mixture of *meta*- and *para*-substituted *N*-tosyldiarylmethylamines **4e**, which could be detected by ^{1}H NMR and ^{13}CNMR, but were inseparable by flash chromatography (Entry 5). In no case was there any evidence of the formation of dialkylated products. One exception in the regioselectivity of lithiation reactions was when the complex **1d** with bromine as a substituent on the phenyl ring was subjected to the lithiation reaction conditions and trapped with imine **2a**. The product **4d** was obtained (Entry 4), simply because the bromine atom was removed from the phenyl ring of **1d** during the lithiation reaction. This chemistry is very similar to that of (benzene)-tricarbonylchromium **1f** and is consistent with the formation of a common intermediate, (phenyllithium)tricarbonyl chromium in these reactions (Entry 6).

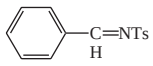
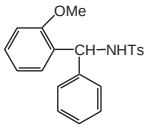
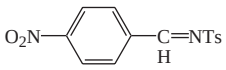
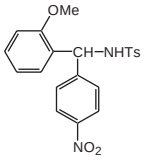
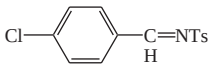
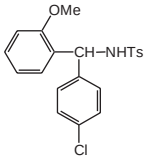
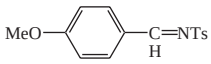
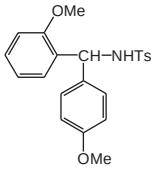
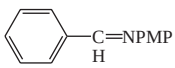
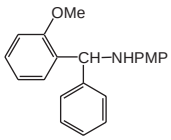
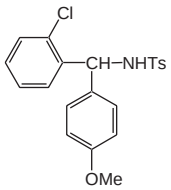
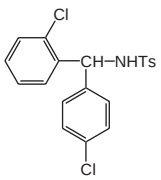
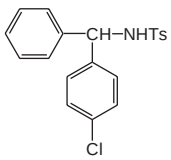
To further demonstrate the utility of this synthetic approach to the *N*-tosyldiarylmethylamines with certain specific substituted patterns, we then turned our attention to examine the structural diversity of the electrophilic trapping reagent imines **2a–d**. As shown in Table 2, *para*-substituted *N*-tosylbenzylideneimines with either elctron-withdrawing or donating function groups such as NO_2 (**2b**), Cl (**2c**), MeO (**2d**) also reacted with **1a** smoothly, affording the corresponding *N*-tosyldiarylmethylamines **4b-d** in good yield (60–74%) after the decomplexation reaction. Finally, *N*-*p*-methoxyphenyl-benzylideneimine **2e**, in which the PMP protecting group can be easily removed for the further transformation, also can react with **1a** to give the corresponding compound (**4i**) in 66% yield. Moreover, the results in Table 2 demonstrated that this novel approach provided a direct route to some diarylmethylamine derivatives that may not be accessible by the conventional methods. Note that although the reaction of *N*-tosylfurylideneimine with **1a** proceeded smoothly to afford the corresponding alkylated complex **3m** (R_1=OMe), under the same reaction conditions, no corresponding *N*-tosyldiarylmethylamines was obtained after decomplexation, probably because of the instability of the furyl ring to the decomplexation conditions.

In conclusion, we have developed a novel method for the synthesis of some diarylmethylamine derivatives. The synthesis becomes possible by regioselective lithiation of the tricarbonyl(η^6-arene)chromium complexes followed by electrophilic trapping with imines. This method may warrant further attention as a complement to the conventional methods for the synthesis of diarylmethylamine derivatives. In light of the recent progress on the selective lithiation of multi-substituted arene tricarbonylchromium complexes,[10] further studies focusing on the asymmetric version of this type of reaction will be investigated in our laboratory.

Experimental

IR spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DMX-300 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were recorded on a Bruker APEX-2 spectrometer using the FBA technique. All reactions were performed under an argon atmosphere.

Table 2 Reactions of Complexes **1** with Imines **2** via lithiation and decomplexation

Entry	R_1	Complex	Imine		Product		Yield[a]/%
1	OMe	**1a**		**2a**		**4a**	64
2	OMe	**1a**		**2b**		**4f**	71
3	OMe	**1a**		**2c**		**4g**	67
4	OMe	**1a**		**2d**		**4h**	74
5	OMe	**1a**		**2e**		**4i**	66
6	Cl	**1c**		**2d**		**4j**	64
7	Cl	**1c**		**2c**		**4k**	60
8	H	**1f**		**2c**		**4l**	66

[a]Isolated yield.

General procedure for synthesis of diarylmethylamines **4**: To a stirred solution of complex **1** (0.2 mmol) in THF (2 ml) at –35 °C was added *n*-butyllithium (0.13 ml, 1.6 M solution in hexane, 0.2 mmol) dropwise. After stirring for 0.5 h at –35 °C, a solution of imine **2** (0.1 mmol) in THF (2 ml) was added in one portion and the mixture was stirred for 5 h at the same temperature. A saturated aqueous solution of NaCl (5 ml) was then added. The mixture was warmed up to room temperature, followed by extraction with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by flash chromatography on neutral Al_2O_3 (eluent: petroleum ether/ethyl acetate=1:1) to give product **3**. Then a solution of complex **3** in CH_2Cl_2 (4 ml) at room temperature was exposed to air and sunlight until its colour disappeared (about 12 h). The mixture was filtered through celite and solvent was removed by evaporation under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) to give product **4**. Products **4a**, **4c** and **4l** are known compounds.[12]

4b: IR ν_{max}: 3274, 2956, 1594, 1490, 1325, 1159, 808, 759 cm^{-1}. δ_H 7.63 (2H, d, *J* = 8.1 Hz), 7.60–7.14 (9H, m), 7.04 (1H, t, *J* = 7.4 Hz), 6.91 (1H, t, *J* = 9.5 Hz), 5.81 (1H, d, *J* = 8.2 Hz), 5.38 (1H, d, *J* = 8.0 Hz), 2.38 (3H, s); δ_C 161.5, 158.2, 143.2, 139.5, 137.0, 129.0, 128.6, 127.7, 127.0, 126.8, 124.2, 115.8, 115.5, 56.4, 21.4. HRMS calcd for $C_{20}H_{18}FNO_2S$ ($M+H^+$): 356.1115; found: 356.1124.

4d: IR ν_{max}: 3251, 1599, 1495, 1162 cm^{-1}. δ_H 7.57 (2H, d, *J* = 8.1 Hz), 7.25–7.10 (12H, m), 5.57 (1H, d, *J* = 6.6 Hz), 4.96 (1H, d, *J* = 6.9 Hz), 1.50 (3H, s); δ_C 143.2, 140.6, 137.4, 129.4, 128.6, 127.6, 127.4, 127.2, 61.4, 21.5. HRMS calcd for $C_{20}H_{20}NO_2S$ ($M+H^+$): 398.1420; found: 398.1421.

4e: IR ν_{max}: 3264 cm^{-1}. δ_H 7.58 (2H, m), 7.26–7.19 (3H, m), 7.16–7.10 (5H, m), 6.99–6.96 (2H, m), 6.89 (1H, d, *J* = 9.9 Hz), 5.54 (1H, d, *J* = 7.0 Hz), 5.09 (1H, d, *J* = 6.1 Hz), 2.39 (3H, s), 2.21, 2.16* (3H, s), * two regioisomers (*m*/*p* = 2:3); δ_C 143.0, 140.5, 140.3, 138.1, 137.4, 129.3, 129.1, 128.5, 128.2, 128.0, 127.5, 127.4, 127.3, 127.28, 127.25, 127.2, 124.4, 77.3, 76.9, 76.6, 61.3, 61.1, 21.4, 21.2, 20.9. HRMS calcd for $C_{21}H_{21}NO_2SNa$ ($M+Na^+$): 374.1185; found: 374.1178.

4f: IR ν_{max}: 3283, 2925, 1600, 1519, 1346, 1161, 744 cm^{-1}. δ_H 8.09 (2H, d, *J* = 8.6 Hz), 7.54 (2H, d, *J* = 8.0 Hz), 7.41 (2H, d, *J* = 8.6 Hz), 7.23 (1H, t, *J* = 7.6 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 6.92 (1H, *J* = 7.6 Hz), 6.81 (1H, t, *J* = 7.5 Hz), 6.72 (1H, d, *J* = 8.3 Hz), 5.89 (1H, d, *J* = 9.2 Hz), 5.65 (1H, d, *J* = 9.2 Hz), 3.61 (3H, s), 2.36 (3H, s); δ_C 156.0, 148.1, 147.0, 143.3, 137.1, 129.7, 129.6, 129.2, 127.6, 126.9, 126.3, 123.3, 120.9, 111.2, 58.7, 55.2, 21.4. HRMS calcd for $C_{21}H_{21}N_2O_5S$ ($M+H^+$): 413.1165; found: 413.1162.

4g: IR ν_{max}: 3258, 2925, 1600, 1492, 1165, 813, 752 cm^{-1}. δ_H 7.55 (2H, d, *J* = 8.3 Hz), 7.25–7.17 (m, 5H), 7.10 (2H, d, *J* = 8.0 Hz), 6.97 (1H, d, *J* = 7.4 Hz), 6.83 (1H, t, *J* = 7.3 Hz), 6.73 (1H, d, *J* = 8.3 Hz), 5.85 (1H, d, *J* = 9.1 Hz), 5.63 (1H, d, *J* = 9.1 Hz), 3.65 (3H, s), 3.61 (3H, s); δ_C 156.3, 143.0, 139.2, 137.4, 132.9, 129.5, 129.2, 129.1, 128.3, 128.2, 127.2, 126.9, 120.7, 111.2, 58.6, 55.3, 21.4. HRMS calcd for $C_{21}H_{21}ClNO_3S$ ($M+H^+$): 402.0925; found: 402.0928.

4h: IR ν_{max}: 3286, 2957, 1603, 1511, 1248, 1160, 815 cm^{-1}. δ_H 7.51 (2H, d, *J* = 8.1 Hz), 7.18–6.98 (6H, m), 6.81–6.74 (3H, m), 6.66 (1H, d, *J* = 8.2 Hz), 5.81 (1H, d, *J* = 9.0 Hz), 5.61 (1H, d, *J* = 9.0 Hz), 3.76 (3H, s), 3.61 (3H, s), 2.34 (3H, s); δ_C 158.6, 156.3, 142.7, 137.5, 132.6, 129.4, 128.9, 128.7, 128.0, 127.7, 126.9, 120.6, 113.4, 111.0, 58.4, 55.2, 21.3. HRMS calcd for $C_{22}H_{24}NO_4S$ ($M+H^+$): 398.1420; found: 398.1421.

4i: IR ν_{max}: 3404, 2935, 1599, 1242, 1029, 819 cm^{-1}. δ_H 7.41–7.22 (7H, m), 6.94 (2H, dd, *J* = 7.5, 8.2 Hz), 6.72 (2H, d, *J* = 8.8 Hz), 6.51 (2H, d, *J* = 8.8 Hz), 5.83 (1H, s), 3.80 (3H, s), 3.72 (3H, s); δ_C 156.7, 152.0, 143.1, 141.9, 131.1, 128.4, 128.2, 127.9, 127.4, 126.9, 120.8, 114.7, 114.5, 110.8, 57.3, 55.7, 55.4. HRMS calcd for $C_{21}H_{21}NO_2$: 319.1567; found: 319.1566.

4j: IR ν_{max}: 3271,2950, 1608, 1513, 1326, 1157, 1036 cm^{-1}. δ_H 7.63 (2H, d, *J* = 8.1 Hz), 7.40–7.37 (1H, m), 7.27–7.14 (5H, m), 6.96 (2H, d, *J* = 8.6 Hz), 6.78 (2H, d, *J* = 8.6 Hz), 5.86 (1H, d, *J* = 6.6 Hz), 5.11 (1H, d, *J* = 6.6 Hz), 3.77 (3H, s), 2.46 (3H, s); δ_C 158.9, 143.1, 137.6, 136.8, 132.5, 131.2, 129.6, 129.2, 128.9, 128.4, 128.3, 127.0, 126.7, 113.7, 57.8, 55.0, 21.3. HRMS calcd for $C_{21}H_{21}ClNO_3S$ ($M+H^+$): 402.0925; found: 402.0916.

4k: IR ν_{max}: 3273, 1597, 1491, 1333, 1161, 813 cm^{-1}. δ_H 7.60 (2H, d, *J* = 8.1 Hz), 7.27–7.17 (8H, m), 7.03 (2H, d, *J* = 8.5 Hz), 5.88 (1H, d, *J* = 7.1 Hz), 5.17 (1H, d, *J* = 7.1 Hz), 2.41 (3H, s); δ_C 143.6, 137.9, 137.1, 136.9, 133.8, 132.8, 130.1, 129.5, 129.3, 129.1, 128.8, 128.7, 127.2, 127.1, 58.1, 21.5. HRMS calcd for $C_{20}H_{18}Cl_2NO_2S$ ($M+H^+$): 406.0430; found: 406.0427.

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