A Convenient Synthesis of Some Arylated Phenylsulfonylacetonitriles and Ethyl Cyanoacetates Using Organo-iron Complexes

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A general method for the synthesis of some arylated phenylsulphonylacetonitriles **6a–g**, **10a**, **b** and **16** and ethyl cyanoacetates **7a–d** and **11a**, **b** is described. Nucleophilic substitution of the cyclopentadienyliron complexes of chloroarenes **1a–g** with phenylsulphonylacetonitrile **2** or ethyl cyanoacetate **3** in the presence of potassium carbonate in DMF, at room temperature under a nitrogen atmosphere gave cyclopentadienyliron complexes of arylated phenylsulphonylacetonitriles **4a–g**, **8a**, **b** and **15** and ethyl cyanoacetates **5a–d** and **9a**, **b** in very good yields (71–94%). Photolysis of these complexes liberated the arenes (70–91%). To demonstrate the versatility of this methodological approach, reactions of both carbon nucleophiles **2**, **3** with dimethyl chlorobenzene complexes **1h**, **j** gave the desired products **8a**, **9a**, **12** and **13** without significant steric effect. This synthesis is advantageous over all those previously reported and should be a practical route to a variety of alkanoic acid and heterocyclic precursors.

Arylated ethyl cyanoacetates and phenylsulphonylacetonitriles are valuable intermediates in the synthesis of some important heterocyclic compounds (*e.g.* azetinones, pyrimidines, as well as oxazaphosphorinane derivatives) and aryl alkanoic acids.[1–7] The latter are known to have pharmaceutical use as anti-inflammatory and antipyretic analgesics.[5–12] For example, one well known and widely studied alkanoic acid is 2-(*p*-isobutylphenyl)propionic acid (Ibuprofen). This compound is an anti-inflammatory analgesic which has been effectively used in the treatment of patients with rheumatoid arthritis, as well as in relieving general muscle pain and stiffness.[8–12] Its advantages over acetylsalicylic acid include greater potency with fewer side effects.[11]

Within the last two decades, extensive research has been carried out to develop better synthetic routes to these types of compounds.[5] In the synthetic scheme reported by Suzuki *et al.*, arylated phenylsulphonylacetonitriles were prepared *via* nucleophilic substitution of aryl iodide and phenylsulphonylacetonitrile using sodium hydride as a base and copper(I) iodide as a catalyst.[4] Subsequent alkylation, hydrogenation and hydrolysis produced the alkanoic acids. In this synthetic route, the most problematic step is the nucleophilic substitution. Sakamoto *et al.* modified this synthesis by the use of palladium(0) as a catalyst.[13] In spite of the harsh reaction conditions, mono- and *para*-disubstituted compounds were obtained in good yields. However, substituents placed at other positions on the aromatic ring resulted in a dramatic decrease in the alkanoic acid yield. It is also important to note that chlorobenzene fails to react under the conditions outlined above.[4]

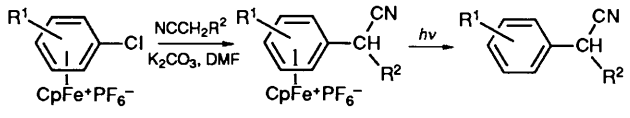
It has also been reported that the synthesis of ethyl arylcyanoacetates cannot be achieved directly through nucleophilic substitution of ethyl cyanoacetate anions with aryl halides. Previous methods of synthesis have involved the ethoxycarbonylation of arylacetonitrile[14] and the use of certain organometallic reagents or catalysts to promote nucleophilic substitution on the aromatic ring. Reagents and catalysts which have been used include copper(I) iodide,[15] PdX_2L_2,[16–18] aryllead(IV) triacetates[19] and $Cr(CO)_3$.[20]

In recent years, nucleophilic substitution of arenes complexed to a metal moiety with a variety of different nucleophiles have been investigated.[21–35] These metal moieties include tricarbonylchromium, tricarbonylmanganese and cyclopentadienyliron (Fecp). Due to the reactivity and relatively simple synthetic methods associated with arene(cyclopentadienyl)iron complexes, a large number of functionalized aromatic and biologically active compounds have been prepared using this methodology.[34–40] In a previous communication we reported the use of organo-iron complexes in the synthesis of isomeric ethyl tolylcyanoacetates.[36] This synthesis involved the arylation of ethyl cyanoacetate complexes followed by photochemical liberation of the free arenes.

Here we describe the synthesis of various substituted arylated cyanoacetates and phenylsulphonylacetonitriles *via* nucleophilic substitution. Ten different chloroarenes were treated with ethyl cyanoacetate or phenylsulphonylacetonitrile in the presence of potassium carbonate as a base in *N*,*N*-dimethylformamide (DMF).

Results and Discussion

Chloroarene complexes **1a–g** reacted with phenylsulphonylacetonitrile or ethyl cyanoacetate under very mild conditions. A mixture of the chloroarene complex **1a–g**, phenylsulphonylacetonitrile **2** or ethyl cyanoacetate **3** and potassium carbonate in DMF was stirred for 7 h at room temperature, under a nitrogen atmosphere. The reactions proceeded quite smoothly to give complexed arylated phenylsulphonylacetonitriles **4a–g** or ethyl cyanoacetates **5a–d** as yellow solids (yields 71–94%) (Scheme 1).



	R^1		R^2		R^2		R^2
1a	H	**2**	SO_2Ph	**4a–g**	SO_2Ph	**6a–g**	SO_2Ph
b	*o*-Me	**3**	CO_2Et	**5a–d**	CO_2Et	**7a–d**	CO_2Et
c	*m*-Me						
d	*p*-Me						
e	*o*-Cl						
f	*m*-Cl						
g	*p*-Cl						

Scheme 1

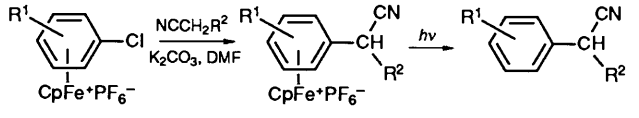
ortho-Substituents on the complexed aromatic ring caused no steric problems. ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis were used to characterize the prepared complexes **4a–g** and **5a–d**. In the ^1H NMR spectra of these complexes, a very distinctive singlet appeared around δ 5.22–5.47. This is characteristic of the cyclopentadienyl (cp) ring. For

complexes **4a–g**, in many cases the methine proton appeared at δ 6–7, overlapping with the arene protons. The assignment of some of these methine protons was based on the integration of the peaks in the region between δ 6–7 relative to other proton peaks in the spectra. The ^{13}C NMR was also in agreement with expectations, as is outlined in the Experimental section.

One of the most important steps in this synthetic strategy is the liberation of the desired arene ligands from the cyclopentadienyliron complexes. Photolysis is known to be an efficient route for the decomplexation of some (arene)cyclopentadienyliron complexes.[36,41–43] We successfully applied this technique to the liberation of the arylated phenylsulphonylacetonitriles and ethyl cyanoacetates. The samples were irradiated in an acetonitrile–dichloromethane mixture, using a xenon lamp as a source of radiation, under a nitrogen atmosphere for 2 h. Purification of the products by column chromatography resulted in isolation of the free aromatic ligands **6a–g** and **7a–d** in yields in the range 70–86%.

The identities of all products were confirmed by ^1H and ^{13}C NMR, IR and MS spectroscopy, m.p.s, and elemental analyses. The characterization of compounds **7b–d** have been reported in our previous communication.[36] The major differences in the ^1H and ^{13}C NMR spectra of these compounds **6a–g** and **7a–d** from those of the complexes were the absence of the cyclopentadienyl peak, the shift of the arene peaks downfield and a shift of the methine peak to a higher field. Compounds **6a–g** are the desired precursors for some alkanoic acid syntheses; compounds **7a–d** are some of the heterocyclic precursors. Our synthetic methodology was very versatile and efficient in the preparation of such precursors.

To further explore the versatility of this synthetic strategy, we carried out nucleophilic substitution of the 2,6-dimethylchlorobenzene and 2,5-dimethylchlorobenzene complexes **1h, i** with both phenylsulphonylacetonitrile and ethyl cyanoacetate. These reactions led to the formation of the desired products **8a, b** and **9a, b** in very high yields (Scheme 2). No steric effects were

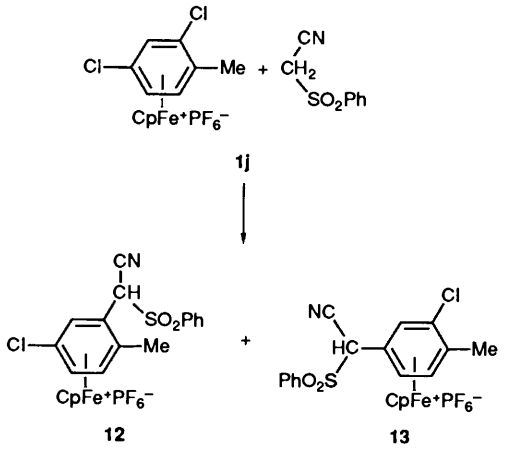


	R^1		R^2		R^2		R^2
1h	2,6-$(Me)_2$	**2**	SO_2Ph	**8a, b**	SO_2Ph	**10a, b**	SO_2Ph
i	2,5-$(Me)_2$	**3**	CO_2Et	**9a, b**	CO_2Et	**11a, b**	CO_2Et

Scheme 2

observed in these reactions, even in the case of two methyl groups *ortho* to the chlorine atom. It should also be noted that in the starting complex, **1h**, both the ^1H and ^{13}C NMR spectra exhibit a single peak for the two equivalent methyl groups on the aromatic ring. However, in both of the substituted complexes **8a** and **9a** the ^1H and ^{13}C NMR indicated the presence of two nonequivalent methyl groups. Following the nucleophilic substitution, photolysis of these products resulted in the liberation of the free aromatic ligands **10a, b** and **11a, b** in good yields.

We also carried out a nucleophilic substitution of the 2,4-dichlorotoluene complex **1j** with phenylsulphonylacetonitrile to give a mixture of two isomeric products (see Scheme 3). The structures of these products were established on the basis of their NMR spectra. The ^1H NMR spectra showed that the two isomers **12** and **13** were obtained in an almost equal ratio. Thus, even with two chlorine substituents on the aromatic ring, with a methyl group *ortho* to one of them, no steric effect was observed. This experiment further demonstrates that this type of nucleophilic substitution proceeds without significant steric effect.



Scheme 3

The change of the substituents on the aromatic ring from methyl to chloro could be achieved by nucleophilic substitution. As an example of this, we have carried out a reaction between a *p*-dichlorobenzene complex and 4-chlorophenol according to a previous procedure.[23] Work-up gave the η^4-bis-*p*-chlorophenyl ether-η^5-cyclopentadienyliron complex **14** (characterized by ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis). This complex reacted smoothly with phenylsulphonylacetonitrile to give the desired complex **15** in a good yield. Photolysis of the latter liberated the arene ligand **16** (Scheme 4). This approach also demonstrates the versatility of this methodology and facilitates the introduction of various functional groups to arylated phenylsulphonylacetonitriles and ethyl cyanoacetates.

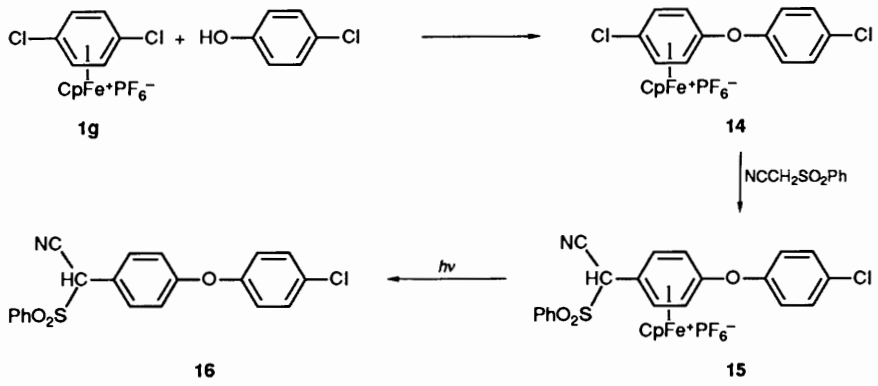
Experimental

^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz respectively, on a Gemini 200 NMR spectrometer, with chemical shifts calculated from the solvent signals. Coupling constants were calculated in Hz. MS spectra were obtained on a Hewlett-Packard 5970 Series Mass Selective Detector, by electron-impact (70 V). Signal positions are given in *m/z* units. IR were recorded (neat) on a Perkin-Elmer model 781 spectrophotometer. M.p.s. were measured in a capillary using a Mel-Temp II and are uncorrected. Elemental analyses were performed at the University of Saskatchewan.

Starting Materials.—Starting complexes **1a–h** were prepared by way of previously reported ligand exchange reactions.[22,44] Anhydrous aluminium chloride, aluminium powder, ferrocene, ethyl cyanoacetate, phenylsulphonylacetonitrile, 4-chlorophenol, ammonium hexafluorophosphate and chloroarenes are commercially available and were used without further purification. All solvents (reagent grade) were freshly distilled before use. Silica gel 60–100 mesh, was used in the column chromatographic purification of the liberated arenes.

Syntheses.—Cyclopentadienyl-(2,5-*dimethylchlorobenzene*)-*iron* **1i**, and -(2,4-*dichlorotoluene*)*iron* **1j**. These complexes were prepared through ligand exchange reactions, as reported for the corresponding 2,6-dimethylchlorobenzene complex.[34]

η^5-*Cyclopentadienyl*(η^6-2,5-*dimethylchlorobenzene*)*iron*(II) *hexafluorophosphate* **1i**. Yellow–green solid (8.29 g, 41%) (Found: C, 38.25; H, 3.6. $C_{13}H_{14}ClF_6FeP$ requires C, 38.4; H, 3.5%); $\delta_H(CD_3COCD_3)$ 2.59 (3 H, s, CH_3), 2.67 (3 H, s, CH_3), 5.21 (5 H, s, cp), 6.34 (1 H, d, *J* 6.2, complexed ArH), 6.56 (1 H, d, *J* 6.2, complexed ArH) and 6.81 (1 H, s, complexed ArH); $\delta_C(CD_3COCD_3)$ 18.52 (CH_3), 19.18 (CH_3), 79.89 (5 C, cp), 87.82, 88.68, 89.32 (3 C, ArC), 101.34, 103.69 and 107.82 (3 C, quaternary ArC).



Scheme 4

η⁵-*Cyclopentadienyl*(η⁶-2,4-*dichlorotoluene*)*iron*(II) *hexafluorophosphate* **1j**. Yellow–green solid (7.30 g, 34%) (Found: C, 33.65; H, 2.5. $C_{12}H_{11}Cl_2F_6FeP$ requires C, 33.8; H, 2.6%); $\delta_H(CD_3COCD_3)$ 2.65 (3 H, s, CH_3), 5.33 (5 H, s, cp) and 6.73–7.26 (3 H, m, complexed ArH); $\delta_C(CD_3COCD_3)$ 18.88 (CH_3), 82.24 (5 C, cp), 88.23, 89.14, 89.32 (3 C, ArC), 102.96, 106.58, 107.99 (3 C, quaternary ArC).

Nucleophilic Substitutions.—Reactions with phenylsulphonylacetonitrile. A mixture of starting cation **1a–i** (1 mmol), potassium carbonate (0.345 g, 2.5 mmol), phenylsulphonylacetonitrile (0.190 g, 1.05 mmol) and DMF (10 cm^3) was stirred at room temp. under a nitrogen atmosphere for *ca.* 7 h to give a red reaction mixture. This was rapidly filtered into 10% aqueous hydrochloric acid (10 cm^3). The reaction flask was then washed with ethanol and the latter added to the filtrate. The ethanol was removed under reduced pressure at 25 °C using a rotary evaporator (Buchi RE-111) and concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture which was then stirred for 15 min. The resulting yellow solid was filtered off and recrystallized from dichloromethane–diethyl ether.

η⁵-*Cyclopentadienyl*[η⁶-*phenyl*(*phenylsulphonyl*)*acetonitrile*]-*iron*(II) *hexafluorophosphate* **4a**. (0.414 g, 79%) (Found: C, 43.9; H, 3.1; N, 2.65. $C_{19}H_{16}F_6FeNO_2PS$ requires C, 43.6; H, 3.1; N, 2.7%); ν_{max}(neat)/cm^{-1} 2320 (CN) and 1335 and 1165 (SO_2); $\delta_H(CD_3COCD_3)$ 5.32 (5 H, s, cp), 6.46–6.70 (6 H, m, complexed ArH and CH), 7.71–7.80 (2 H, m, $SO_2C_6H_5$), 7.85–7.99 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3COCD_3)$ 61.96 (CH), 79.41 (5 C, cp), 87.68, 89.78, 89.82, 90.31, 91.47 (5 C, ArC), 92.20 (quaternary ArC), 113.13 (CN), 130.81 (2 C, $SO_2C_6H_5$), 130.91 (2 C, $SO_2C_6H_5$) and 137.29 (quaternary $SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(o-*tolyl*)*phenylsulphonlylacetonitrile*]*iron*(II) *hexafluorophosphate* **4b**. (0.380 g, 71%) (Found: C, 44.9; H, 3.4; N, 2.65. $C_{20}H_{18}F_6FeNO_2PS$ requires C, 44.7; H, 3.4; N, 2.6%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1340 and 1160 (SO_2); $\delta_H(CD_3COCD_3)$ 2.68 (3 H, s, CH_3), 5.30 (5 H, s, cp), 6.50 (1 H, s, CH), 6.64–6.68 (4 H, m, complexed ArH), 7.77–7.85 (2 H, m, $SO_2C_6H_5$), 7.94–8.00 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3SOCD_3)$ 18.21 (CH_3), 59.27 (CH), 78.40 (5 C, cp), 86.69, 87.59, 88.99 (3 C, ArC), 89.16 (quaternary ArC), 90.00 (ArC), 104.36 (quaternary ArC), 113.28 (CN), 129.68 (2 C, $SO_2C_6H_5$), 130.29 (2 C, $SO_2C_6H_5$), 133.87 (quaternary $SO_2C_6H_5$) and 137.16 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(m-*tolyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **4c**. (0.475, 88%) (Found: C, 44.8; H, 3.6; N, 2.65. $C_{20}H_{18}F_6FeNO_2PS$ requires C, 44.7; H, 3.4; N, 2.6%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1346 and 1162 (SO_2); $\delta_H(CD_3COCD_3)$ 2.60 (3 H, s, CH_3), 5.27 (5 H, s, cp), 6.30–6.62 (5 H, complexed ArH and CH), 7.72–7.80 (2 H, m, $SO_2C_6H_5$), 7.87–8.04 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3COCD_3)$ 20.35 (CH_3), 61.73 (CH), 79.55 (5 C, cp), 85.76, 87.41, 88.94, 90.50 (4 C, ArC), 91.40 (quaternary ArC), 105.79 (quarternary ArC), 112.91 (CN), 130.74 (4 C, $SO_2C_6H_5$), 134.77 (quarternary $SO_2C_6H_5$) and 137.15 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(*p-tolyl*)*phenylsulphonylacetonitrile*]-*iron*(II) *hexafluorophosphate* **4d**. (0.419, 79%) (Found: C, 44.6; H, 3.4; N, 2.5. $C_{20}H_{18}F_6FeNO_2PS$ requires C, 44.7; H, 3.4; N, 2.6%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1342 and 1140 (SO_2); $\delta_H(CD_3COCD_3)$ 2.61 (3 H, s, CH_3), 5.26 (5 H, s, cp), 6.37–6.58 (m, 5 H, complexed ArH and CH), 7.70–7.77 (2 H, m, $SO_2C_6H_5$) and 7.85–7.93 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3COCD_3)$ 20.52 (CH_3), 61.59 (CH), 79.57 (5 C, cp), 86.86, 89.23, 89.93 (3 C, ArC), 90.38 (quaternary ArC), 90.63 (ArC), 106.43 (quaternary ArC), 113.05 (CN), 130.71 (2 C, $SO_2C_6H_5$), 130.80 (2 C, $SO_2C_6H_5$), 134.82 (quaternary ArC) and 137.16 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(o-*chlorophenyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **4e**. (0.527 g, 94%) (Found: C, 40.7; H, 2.5; N, 2.3. $C_{19}H_{15}ClF_6FeNO_2PS$ requires C, 40.9; H, 2.7; N, 2.5%); ν_{max}(neat)/cm^{-1} 2300 (CN) and 1338 and 1163 (SO_2); $\delta_H(CD_3COCD_3)$ 5.46 (5 H, s, cp), 6.71–7.08 (5 H, s, complexed ArH and CH), 7.76–7.83 (2 H, m, $SO_2C_6H_5$), 7.93–8.02 (3 H, m, $SO_2C_6H_5$); $\delta_C(CH_3COCD_3)$ 60.25 (CH), 81.86 (5 C, cp), 89.40 (quaternary ArC), 88.10, 89.61, 90.96, 91.09 (4 C, ArC), 109.50 (quaternary ArC), 113.41 (CN), 130.93 (2 C, $SO_2C_6H_5$), 131.23 (2 C, $SO_2C_6H_5$), 135.41 (quaternary $SO_2C_6H_5$) and 137.63 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(m-*chlorophenyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **4f**. (0.451 g, 81%) (Found: C, 40.8; H, 2.9; N, 2.5. $C_{19}H_{15}ClF_6FeNO_2PS$ requires C, 40.9; H, 2.7; N, 2.5%); ν_{max}(neat)/cm^{-1} 2280 (CN) and 1345 and 1162 (SO_2); $\delta_H(CH_3COCD_3)$ 5.47 (5 H, s, cp), 6.40–7.06 (5 H, m, complexed ArH and CH), 7.75–7.85 (2 H, m, $SO_2C_6H_5$), 7.90–8.05 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3COCD_3)$ 61.38 (CH), 81.77 (5 C, cp), 86.57, 87.24, 89.61, 90.85 (4 C, ArC), 92.95 (quaternary ArC), 108.44 (quaternary ArC), 112.71 (CN), 130.93 (4 C, $SO_2C_6H_5$), 135.17 (quaternary $SO_2C_6H_5$) and 137.40 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(p-*chlorophenyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **4g**. (0.428 g, 77%) (Found: C, 41.0; H, 3.0; N, 2.4. $C_{19}H_{15}ClF_6FeNO_2PS$ requires C, 40.9; H, 2.7; N, 2.5%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1348 and 1142 (SO_2); $\delta_H(CH_3COCD_3)$ 5.44 (5 H, s, cp), 6.55–6.77 (3 H, m, complexed ArH and CH), 7.02 (2 H, d, *J* 6.2, complexed ArH), 7.72–7.81 (2 H, m, $SO_2C_6H_5$), 7.89–7.98 (3 H, m, $SO_2C_6H_5$); $\delta_C(CD_3COCD_3)$ 61.12 (CH), 81.73 (5 C, cp), 87.40, 90.04, 90.07, 91.15 (4 C, ArC), 91.51 (quaternary ArC), 109.09 (quaternary ArC), 112.93 (CN), 130.80 (2 C, $SO_2C_6H_5$), 130.91 (2 C, $SO_2C_6H_5$), 134.70 (quaternary $SO_2C_6H_5$), and 137.32 ($SO_2C_6H_5$).

η⁵-*Cyclopentadienyl*[η⁶-(2,6-*dimethylphenyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **8a**. (0.500 g, 91%)

(Found: C, 46.0; H, 3.6; N, 2.4. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.8; H, 3.7; N, 2.5%); ν_{max}(neat)/cm^{-1} 2315 (CN) and 1340 and 1160 (SO_2); δ_H(CH_3COCD_3) 2.70 (3 H, s, CH_3), 2.89 (3 H, s, CD_3), 5.25 (5 H, s, cp), 6.57–6.64 (4 H, m, complexed ArH and CH), 7.81–7.89 (2 H, m, $SO_2C_6H_5$), 7.97–8.12 (3 H, m, $SO_2C_6H_5$); δ_C(CH_3COCD_3) 20.18 (CH_3), 20.22 (CH_3), 58.66 (CH), 79.74 (5 C, cp), 89.47 (ArC), 90.39 (quaternary ArC), 90.57, 91.08 (2 C, ArC), 104.31 (quaternary ArC), 105.52 (quarternary ArC), 113.82 (CN), 130.45 (2 C, $SO_2C_6H_5$), 131.21 (2 C, $SO_2C_6H_5$), 136.79 (quaternary $SO_2C_6H_5$), and 137.35 ($SO_2C_6H_5$).

η^5-*Cyclopentadienyl*[η^6-(2,5-*dimethylphenyl*)*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **8b**. (0.506 g, 92%) (Found: C, 46.0; H, 3.7; N, 2.6. $C_{21}H_{20}F_6FeNO_2PS$ requires C, 45.8; H, 3.7; N, 2.5%); ν_{max}(neat)/cm^{-1} 2315 (CN) and 1336 and 1160 (SO_2); δ_H(CD_3COCD_3) 2.61 (3 H, s, CH_3), 2.62 (3 H, s, CH_3), 5.23 (5 H, s, cp), 6.22 (1 H, s, CH), 6.56–6.59 (3 H, m, complexed ArH), 7.78–7.85 (2 H, m, $SO_2C_6H_5$), 7.92–8.04 (3 H, m, $SO_2C_6H_5$); δ_C(CD_3COCD_3) 18.61 (CH_3), 19.97 (CH_3), 59.96 (CH), 79.91 (5 C, cp), 87.55, 90.43, 90.50 (3 C, ArC), 90.60 (quaternary ArC), 103.82 (quaternary ArC), 104.86 (quaternary ArC), 113.73 (CN), 130.93 (2 C, $SO_2C_6H_5$), 130.99 (2 C, $SO_2C_6H_5$), 135.20 (quaternary $SO_2C_6H_5$), and 137.39 ($SO_2C_6H_5$).

Reactions with Ethyl Cyanoacetate.—A mixture of the starting cation **1h, i** (1 mmol), potassium carbonate (0.345 g, 2.5 mmol) and ethyl cyanoacetate (0.119 g, 1.05 mmol) in DMF (10 cm^3) was stirred at room temp., under a nitrogen atmosphere for *ca.* 7 h. The resulting dark red reaction mixture was filtered into 10% aqueous hydrochloric acid (10 cm^3). Concentrated aqueous ammonium hexafluorophosphate was added to the reaction mixture and the product was extracted with dichloromethane (3 × 50 cm^3). The combined extract was washed with water (4 × 40 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure at 25 °C. The residual yellow–brown oil was washed with diethyl ether (3 × 20 cm^3) and then dissolved in CH_2Cl_2 and precipitated by diethyl ether.

η^5-*Cyclopentadienyl*[η^6-*ethyl phenyl*(*cyano*)*acetate*]*iron*(II) *hexafluorophosphate* **5a**. (0.362 g, 80%) (Found: C, 42.4; H, 3.7; N, 3.0. $C_{16}H_{16}F_6FeNO_2P$ requires C, 42.2; H, 3.5; N, 3.1%); ν_{max}(neat)/cm^{-1} 2260 (CN) and 1755 (CO); δ_H(CH_3COCD_3) 1.24 (3 H, t, *J* 7.1, CH_3), 4.24 (2 H, q, *J* 6.7, CH_2), 5.31 (5 H, s, cp), 5.72 (1 H, s, CH) and 6.63 (5 H, br s, ArH); δ_C(CD_3COCD_3) 13.86 (CH_3), 43.11 (CH), 64.55 (CH_2), 78.83 (5 C, cp), 86.98, 89.09, 89.19, 89.37, 90.21 (5 C, ArC), 96.93 (quaternary ArC), 115.33 (CN) and 163.70 (CO).

η^5-*Cyclopentadienyl*[η^6-*ethyl* 2,6-*dimethylphenyl*(*cyano*)*acetate*]*iron*(II) *hexafluorophosphate* **9a**. (0.371 g, 77%) (Found: C, 44.9; H, 4.4; N, 2.8. $C_{18}H_{20}F_6FeNO_2P$ requires C, 44.75; H, 4.2; N, 2.9%); ν_{max}(neat)/cm^{-1} 2315 (CN) and 1755 (CO); δ_H(CD_3COCD_3) 1.21 (3 H, t, *J* 7.1, CH_2CH_3), 2.63 (3 H, s, $ArCH_3$), 2.73 (3 H, s, $ArCH_3$), 4.29 (2 H, m, CH_2CH_3), 5.24 (5 H, s, cp), 5.97 (1 H, s, CH), 6.48–6.50 (br s, 3 H, ArH); δ_C(CD_3COCD_3) 13.94 (CH_2CH_3), 18.93 ($ArCH_3$), 20.00 ($ArCH_3$), 39.13 (CH), 67.40 (CH_2CH_3), 79.40 (5 C, cp), 88.29, 89.48, 89.58 (3 C, ArC), 95.81, 102.86, 104.02 (3 C, quaternary ArC), 115.97 (CN) and 163.92 (CO).

(η^5-*Cyclopentadienyl*)[η^6-*ethyl* 2,5-*dimethylphenyl*(*cyano*)*acetate*]*iron*(II) *hexafluorophosphate* **9b**. (0.368 g, 76%) (Found: C, 44.5; H, 4.1; N, 2.7. $C_{18}H_{20}F_6FeNO_2P$ requires C, 44.75; H, 4.2; N, 2.9%); ν_{max}(neat)/cm^{-1} 2255 (CN) and 1756 (CO); δ_H(CH_3COCD_3) 1.23 (3 H, t, *J* 7.1, CH_2CH_3), 2.60 (3 H, s, $ArCH_3$), 2.63 (3 H, s, $ArCH_3$), 4.20 (2 H, m, CH_2CH_3), 5.22 (5 H, s, cp), 5.94 (1 H, s, CH), 6.48 (3 H, br s, ArH); δ_C(CD_3COCD_3) 13.95 (CH_2CH_3), 18.40 ($ArCH_3$), 20.05 ($ArCH_3$), 41.28 (CH), 64.68 (CH_2), 79.40 (5 C, cp), 86.73, 89.53, 90.01 (3 C, ArC), 95.16, 102.68, 104.14 (3 C, quaternary ArC), 115.60 (CN) and 163.69 (CO).

Reaction of Complex **1d** *with 4-Chlorophenol under High Dilution Conditions.*—To a stirred mixture of complex **1g** (0.824 g, 2 mmol), potassium carbonate (0.690 g, 5.0 mmol) and dichloromethane (100 cm^3) in 500 cm^3 round-bottom flask fitted with a 125 cm^3 pressure-equalized dropping funnel was added dropwise 4-chlorophenol (0.264 g, 2.05 mmol) in dichloromethane (10 cm^3) over a 5 h period. The resulting material was filtered into 10% aqueous hydrochloric acid (10 cm^3) after which a solution of ammonium hexafluorophosphate (0.326 g, 2 mmol) in water (40 cm^3) was added. The product was extracted with dichloromethane (4 × 70 cm^3), and the extract washed with water (2 × 50 cm^3) and dried ($MgSO_4$). The residue was washed with diethyl ether (2 × 15 cm^3) and recrystallized from acetone–ether to give the monosubstituted complex as yellow–brown crystals.

η^5-*Cyclopentadienyl*[η^6-*bis*(4-*chlorophenyl*)*ether*]*iron*(II) *hexafluorophosphate* **14**. (0.840 g, 83%) (Found: C, 40.5; H, 2.4. $C_{17}H_{13}Cl_2F_6FeOP$ requires C, 40.4; H, 2.6%); ν_{max}(neat)/cm^{-1} 1280–1230 and 1090 (C–O); δ_H(CH_3COCD_3) 5.37 (5 H, s, cp), 6.52 (2 H, d, *J* 6.9, complexed ArH), 6.80 (2 H, d, *J* 6.9, complexed ArH), 7.39 (2 H, d, *J* 8.9, uncomplexed ArH) and 7.57 (2 H, d, *J* 8.7, uncomplexed ArH); δ_C(CD_3COCD_3) 77.51 (2 C, complexed ArC), 80.59 (5 C, cp), 82.25 (quaternary complexed ArC), 87.90 (2 C, complexed ArC), 89.42 (quaternary complexed ArC), 123.40, 131.64 (4 C, uncomplexed ArC) and 132.35, 133.40 (2 C, quaternary uncomplexed ArC).

Reaction of η^5-*Cyclopentadienyl*[η^6-*bis*(4-*chlorophenyl*)*ether*]*iron*(II) *Hexafluorophosphate* **1j** *with Phenylsulphonylacetonitrile.*—A mixture of **14** (0.505 g, 1.0 mmol), potassium carbonate (0.345 g, 2.5 mmol) and phenylsulphonylacetonitrile (0.190g, 1.05 mmol) in DMF (10 cm^3) was stirred for 7 h to give a red solution. This was worked up as described in the general procedure for reactions with phenylsulphonylacetonitrile to yield a pale yellow precipitate.

η^5-*Cyclopentadienyl*[η^6-*bis*(4-*chlorophenyl*)*ether*)]*phenylsulphonylacetonitrile*]*iron*(II) *hexafluorophosphate* **15** (0.552 g, 85%) (Found: C, 46.1; H, 2.8; N, 2.3. $C_{25}H_{19}ClF_6FeNO_3PS$ requires C, 46.2; H, 2.95; N, 2.2%); ν_{max}(neat)/cm^{-1} 2305 (CN), 1342, 1140 (SO_2) and 1080 (C–O); δ_H(CD_3COCD_3) 5.38 (5 H, s, cp), 6.42 (2 H, d, *J* 8.9, complexed ArH), 6.64 (3 H, m, complexed ArH and CH), 7.51 (2 H, d, *J* 8.6, uncomplexed ArH), 7.64 (2 H, d, *J* 8.8, uncomplexed ArH), 7.75–7.84 (2 H, m, $SO_2C_6H_5$), 7.90–7.98 (3 H, m, $SO_2C_6H_5$); δ_C(CH_3COCD_3) 61.14 (CH), 79.85 (5 C, cp), 86.14 (2 C, complexed ArC), 88.96 (quaternary complexed ArC), 89.96 (2 C, complexed ArC), 112.93 (CN), 123.54 (2 C, uncomplexed ArC), 130.74 (2 C, $SO_2C_6H_5$), 130.80 (2 C, $SO_2C_6H_5$), 131.62 (2 C, uncomplexed ArC), 132.40, 134.78 (2 C, quaternary uncomplexed ArC), 135.90 (quaternary $SO_2C_6H_5$), 137.19 ($SO_2C_6H_5$), and 152.37 (quaternary ArC).

Reaction of 2,4-*Dichlorotoluene*(*cyclopentadienyliron*) *with Phenylsulphonylacetonitrile.*—A mixture of the complex **1j** (0.427 g, 1 mmol), potassium carbonate (0.690 g, 2.5 mmol), phenylsulphonylacetonitrile (0.190 g, 1.05 mmol) and DMF (10 cm^3) was stirred at room temp. for 5 h to give a red reaction mixture. This was filtered into 10% aqueous hydrochloric acid (10 cm^3). The ethanol was removed by a rotary evaporation and to the concentrated acid solution was added ammonium hexafluorophosphate (0.163 g, 1 mmol) in water (75 cm^3). After the mixture had been stirred for 10 min the yellow precipitate was filtered off to provide a 1:1 mixture of the products **12** and **13**. The ratio of these two isomers was determined from the cyclopentadienyl peaks in the ^{1}H NMR spectrum.

Demetallations.—General procedure for photolysis. Each of the complexes **4a–g, 8h, i, 9h, i** and **15** was separately dissolved in a mixture of CH_2Cl_2–CH_3CN (30 cm^3/10 cm^3) in a Pyrex tube.

The solution was deoxgenated by bubbling nitrogen through it after which the reaction tube was fitted into a photochemical apparatus equipped with a Xenon lamp (lower limit of 290 nm), and irradiated at room temp. for 2 h. The solvent was concentrated to a volume of 1–2 cm^3 using rotary evaporation. The residue was applied to a silica gel column which was then washed with hexane and eluted with chloroform. Removal of the solvent from the eluate gave the expected liberated arene, with the following yields and spectral data.

Phenyl phenylsulphonylacetonitrile **6a**. A yellowish solid (0.103 g, 80%) (Found: C, 65.1; H, 4.5; N, 5.2. $C_{14}H_{11}NO_2S$ requires C, 65.35; H, 4.3; N, 5.4%); m.p. 147–148 °C; ν_{max}(neat)/cm^{-1} 2310 (CN) and 1370 and 1160 (SO_2); δ_H($CDCl_3$) 5.15 (1 H, s, CH) and 7.25–7.74 (10 H, m, 2 Ph); δ_C($CDCl_3$) 63.00 (CH), 113.37 (CN), 125.34 (quaternary ArC), 128.98 (2 C, $SO_2C_6H_5$), 129.14 (2 C, $SO_2C_6H_5$), 129.68 (2 C, ArC), 130.01 (2 C, ArC), 130.45 (1 C, ArC), 134.29 (quaternary $SO_2C_6H_5$) and 135.19 ($SO_2C_6H_5$); *m/z* 257 (M^+, 15%), 141 (16), 116 (100) and 77 (26).

o-*Tolyl(phenylsulphonyl)acetonitrile* **6b**. A white solid (0.096 g, 71%) (Found: C, 66.4; H, 4.8; N, 5.1. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%); m.p. 133–134 °C; ν_{max}(neat)/cm^{-1} 2305 (CN) and 1335 and 1160 (SO_2); δ_H($CDCl_3$) 2.43 (3 H, s, CH_3), 5.44 (1 H, s, CH), 7.17–7.38 (4 H, m, ArH), 7.56–7.64 (2 H, m, $SO_2C_6H_5$), 7.75–7.86 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 19.44 (CH_3), 59.60 (CH), 113.92 (CN), 124.07 (quaternary ArC), 126.52, 129.17 (2 C, ArC), 129.92, 130.07 (4 C, $SO_2C_6H_5$), 130.52, 131.19 (2 C, ArC), 134.79 (quaternary $SO_2C_6H_5$), 135.16 ($SO_2C_6H_5$) and 138.12 (quaternary ArC); *m/z* 271 (M^+, 10%), 130 (100), 103 (34) and 77 (26).

m-*Tolyl(phenylsulphonyl)acetonitrile* **6c**. A yellowish oil (0.117 g, 86%) (Found: C, 66.3; H, 5.0; N, 5.0. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%); ν_{max}(neat)/cm^{-1} 2250 (CN) and 1335 and 1160 (SO_2); δ_H($CDCl_3$) 2.30 (3 H, s, CH_3), 5.07 (1 H, s, CH), 7.04–7.07 (2 H, m, ArH), 7.21–7.24 (2 H, m, ArH), 7.48–7.57 (2 H, m, $SO_2C_6H_5$), 7.67–7.74 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 21.14 (CH_3), 63.02 (CH), 113.45 (CN), 125.15 (quaternary ArC), 126.82, 128.81 (2 C, ArC), 129.07, 130.05 (4 C, $SO_2C_6H_5$), 130.26, 131.21 (2 C, ArC), 134.41 (quaternary $SO_2C_6H_5$), 135.12 ($SO_2C_6H_5$) and 138.98 (quaternary ArC); *m/z* 271 (M^+, 13%), 130 (100), 103 (18) and 77 (24).

p-*Tolyl(phenylsulphonyl)acetonitrile* **6d**. A white solid (0.109 g, 80%) (Found: C, 64.7; H, 5.1; N, 5.4. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%); m.p. 116–117 °C; ν_{max}(neat)/cm^{-1} 2303 (CN) and 1333 and 1158 (SO_2); δ_H($CDCl_3$) 2.36 (3 H, s, CH_3), 5.08 (1 H, s, CH), 7.16 (4 H, br s, ArH), 7.51–7.56 (2 H, m, $SO_2C_6H_5$), 7.68–7.75 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 21.19 (CH_3), 62.81 (CH), 113.45 (CN), 122.22 (quaternary ArC), 129.10 (2 C, ArC), 129.55, 129.66 (4 C, $SO_2C_6H_5$), 130.03 (2 C, ArC), 134.43 (quaternary $SO_2C_6H_5$), 135.09 ($SO_2C_6H_5$) and 140.82 (quaternary ArC); *m/z* 271 (M^+, 4.3%), 130 (100), 103 (13) and 77 (19).

o-*Chlorophenyl(phenylsulphonyl)acetonitrile* **6e**. A white solid (0.108 g, 74%) (Found: C, 57.9; H, 3.7; N, 4.8. $C_{14}H_{10}ClNO_2S$ requires C, 57.6; H, 3.45; N, 4.8%; m.p. 120–121 °C; ν_{max}(neat)/cm^{-1} 2305 (CN) and 1340 and 1165 (SO_2); δ_H($CDCl_3$) 5.81 (1 H, s, CH), 7.34–7.63 (4 H, m, ArH), 7.74–7.85 (2 H, m, $SO_2C_6H_5$), 7.84–7.89 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 58.94 (CH), 113.26 (CN), 124.08 (quaternary ArC), 127.70 (ArC), 129.50 (2 C, $SO_2C_6H_5$), 130.00 (2 C, $SO_2C_6H_5$), 130.19, 131.26 and 132.04 (3 C, ArC), 135.30 (quaternary $SO_2C_6H_5$), 135.45 ($SO_2C_6H_5$) and 135.60 (quaternary ArC); *m/z* 293 [(^{37}Cl), 7], 291 [(^{35}Cl), 20], 150 (100) and 77 (74).

m-*Chlorophenyl(phenylsulphonyl)acetonitrile* **6f**. A yellowish oil (0.102 g, 70%) (Found: C, 57.5; H, 3.5; N, 4.65. $C_{14}H_{10}ClNO_2S$ requires C, 57.6; H, 3.45; N, 4.8%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1340 and 1162 (SO_2); δ_H($CDCl_3$) 5.12 (1 H, s, CH) and 7.18–7.46 (4 H, m, ArH), 7.52–7.62 (2 H, m, $SO_2C_6H_5$) and 7.72–7.80 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 62.16 (CH), 112.90 (CN), 127.09 (quaternary ArC), 127.82 (ArC), 129.22 (2 C, $SO_2C_6H_5$), 129.62 (ArC), 129.87 (2 C, $SO_2C_6H_5$), 130.14, 130.60 (2 C, ArC), 133.99 (quarternary $SO_2C_6H_5$), 134.84 (quaternary Arc) and 135.40 ($SO_2C_6H_5$); *m/z* 293 [(^{37}Cl), 4], 291[(^{35}Cl), 14], 141 (91), 77 (100).

p-*Chlorophenyl(phenylsulphonyl)acetonitrile* **6g**. A yellowish oil (0.109 g, 75%) (Found: C, 57.6; H, 3.7; N, 4.6. $C_{14}H_{10}ClNO_2S$ requires C, 57.6; H, 3.45; N, 4.8%); ν_{max}(neat)/cm^{-1} 2305 (CN) and 1338 and 1160 (SO_2); δ_H($CDCl_3$) 5.12 (1 H, s, CH), 7.21 (2 H, d, *J* 8.4, ArH), 7.34 (2 H, d, *J* 8.4, ArH), 7.51–7.65 (2 H, m, $SO_2C_6H_5$), 7.75–7.81 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 60.08 (CH), 113.07 (CN), 123.82 (quaternary ArC), 129.25 (4 C, $SO_2C_6H_5$), 129.91, 130.94 (4 C, ArC), 134.13 (quaternary $SO_2C_6H_5$), 135.35 ($SO_2C_6H_5$) and 136.90 (quaternary ArC); *m/z* 293 [(^{37}Cl), 3], 291 [(^{35}Cl), 8], 150 (100), 141 (11) and 77 (28).

Ethyl phenyl(cyano)acetate **7a**. A colourless oil (0.076 g, 80%) (Found: C, 69.8; H, 5.7; N, 7.3. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.85; N, 7.4%); ν_{max}(neat)/cm^{-1} 2220 (CN) and 1750 (CO); δ_H($CDCl_3$) 1.26 (3 H, t, *J* 7.1, CH_3), 4.23 (2 H, q, *J* 7.2, CH_2), 4.70 (1 H, s, CH) and 7.38–7.46 (5 H, br s, ArH); δ_C($CDCl_3$) 13.87 (CH_3), 43.76 (CH), 63.29 (CH_2), 115.60 (CN), 123.05 (quaternary ArC), 127.89, 129.20, 129.32 (5 C, ArC) and 164.50 (CO); *m/z* 189 (M^+, 3%), 145 (5), 117 (100) and 89 (24).

2,6-*Dimethylphenyl(phenylsulphonyl)acetonitrile* **10a**. A white solid (0.130 g, 91%) (Found: C, 67.1; H, 5.4; N, 4.8. $C_{16}H_{15}NO_2S$ requires C, 67.35; H, 5.3; N, 4.9%); m.p. 140–142 °C; ν_{max}(neat)/cm^{-1} 2302 (CN) and 1338 and 1160 (SO_2); δ_H($CDCl_3$) 2.37 (3 H, s, CH_3), 2.64 (3 H, s, CH_3), 5.59 (1 H, s, CH), 7.11–7.31 (3 H, m, ArH), 7.60–7.69 (2 H, m, $SO_2C_6H_5$), 7.78 (1 H, tt, *J* 7.4, 2.3, $SO_2C_6H_5$) and 7.95–8.01 (2 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 20.78 (2 $ArCH_3$), 57.88 (CH), 112.94 (CN), 121.99 (quaternary ArC), 129.07 (ArC), 129.34, 129.56 (4 C, $SO_2C_6H_5$), 130.23, 130.69 (2 C, ArC), 135.15 ($SO_2C_6H_5$), 136.79 (quaternary $SO_2C_6H_5$), 139.17 (quaternary ArC) and 139.82 (quaternary ArC); *m/z* 285 (M^+, 10%), 144 (100), 117 (25) and 77 (12).

2,5-*Dimethylphenyl(phenylsulphonyl)acetonitrile* **10b**. A white solid (0.123 g, 86%) (Found: C, 67.7; H, 5.1; N, 4.7. $C_{16}H_{15}NO_2S$ requires C, 67.35; H, 5.3; N, 4.9%); m.p. 166 167 °C; ν_{max}(neat)/cm^{-1} 2305 (CN) and 1335 and 1160 (SO_2); δ_H($CDCl_3$) 2.20 (3 H, s, CH_3), 2.33 (3 H, s, CH_3), 5.36 (1 H, s, CH), 6.88 and 7.11 (3 H, br s, ArH), 7.51–7.60 (2 H, m, $SO_2C_6H_5$), 7.70–7.80 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 19.01, 20.69 (2 C, $ArCH_3$), 59.67 (CH), 114,13 (CN), 123.80 (quaternary ArC), 129.15, 130.20 (4 C, $SO_2C_6H_5$), 130.53, 131.11, 131.34 (3 C, ArC), 134.98 (quaternary $SO_2C_6H_5$), 135.16 ($SO_2C_6H_5$), 135.26 and 136.32 (2 C, quaternary ArC); *m/z* 285 (M^+, 10%), 144 (100), 117 (24) and 77 (13).

Ethyl 2,6-*dimethylphenylcyanoacetate* **11a**. A colourless oil (0.098 g, 90%) (Found: C, 71.5; H, 6.9; N, 6.3. $C_{13}H_{15}NO_2$ requires C, 71.8; H, 7.0; N, 6.45%); ν_{max}(neat)/cm^{-1} 2255 (CN) and 1750 (CO); δ_H($CDCl_3$) 1.28 (3 H, t, *J* 7.12, CH_3), 2.42 (6 h, s, $ArCH_3$), 4.2–4.4 (2 H, m, CH_2), 5.18 (1 H, s, CH), and 7.07–7.17 (3 H, m, ArH); δ_C($CDCl_3$) 13.86 (CH_3), 20.20 (2 C, $ArCH_3$), 38.04 (CH), 63.03 (CH_2), 115.19 (CN), 128.93, 129.23 (3 C, ArC), and 128.59 and 137.01 (quaternary ArC) and 165.19 (CO); *m/z* 217 (M^+, 34%), 171 (8), 144 (100) and 118 (61).

Ethyl 2,5-*dimethylphenylcyanoacetate* **11b**. A colourless oil (0.0760 g, 70%) (Found: C, 71.5; H, 7.0; N, 6.2. $C_{13}H_{15}NO_2$ requires C, 71.8; H, 7.0; N, 6.45%); ν_{max}(neat)/cm^{-1} 2250 (CN) and 1750 (CO); δ_H($CDCl_3$) 1.26 (3 H, t, *J* 7.1, CH_3), 2.31 (3 H, s, $ArCH_3$), 2.32 (3 H, s, $ArCH_3$), 4.16–4.28 (2 H, q, *J* 7.1, CH_2), 4.82 (1 H, s, CH), 7.08 (2 H, br s, ArH) and 7.23 (1 H, br s, ArH); δ_C($CDCl_3$) 13.86 (CH_3), 18.85 (2 C, $ArCH_3$), 40.96 (CH), 63.11 (CH_2), 115.93 (CN), 128.62 (quaternary ArC), 129.10, 130.00, 131.05 (3 C, ArC), 132.95, 136.70 (2 C, quaternary ArC) and 165.50 (CO); *m/z* (217 (M^+, 24%), 144 (100) and 118 (43).

p-(p-*Chlorphenoxy*)*phenyl*(*phenylsulphonyl*)*acetonitrile* **16**. A colourless oil (0.139 g, 72%) (Found: C, 62.45, H, 3.5; N, 3.5. $C_{20}H_{14}ClNO_3S$ requires C, 62.6; H, 3.7; N, 3.65%); ν_{max}(neat)/cm^{-1} 2300 (CN) and 1333 and 1155 (SO_2); δ_H($CDCl_3$) 5.13 (1 H, s, CH), 6.95–7.06 (4 H, m, ArH), 7.26–7.42 (4 H, m, ArH), 7.55–7.66 (2 H, m, $SO_2C_6H_5$), 7.73–7.83 (3 H, m, $SO_2C_6H_5$); δ_C($CDCl_3$) 62.37 (CH), 113.39 (CN), 118.50 (ArC), 119.67 (quaternary ArC), 121.00 (2 C, ArC), 129.30 (2 C, ArC), 130.08, 130.10 (4 C, $SO_2C_6H_5$), 131.01, 131.52 (4 C, ArC), 134.55 (quaternary $SO_2C_6H_5$), 135.32 ($SO_2C_6H_5$), 154.47, 159.34 (2 C, quaternary ArC); *m*/*z* 385 [(^{37}Cl), 16], 383 [(^{35}Cl), 44], 330 (100), 243 (8), 219 (9) and 78 (63).

Acknowledgements

Financial support given by the University of Winnipeg is gratefully acknowledged.

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Paper 2/03917F
Received 22*nd July* 1992
Accepted 15*th September* 1992