

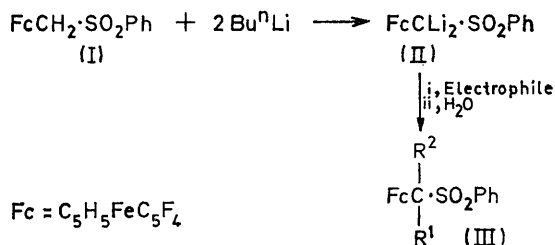
Organometallic Derivatives. Part IV.¹ The Lithiation of Ferrocenylmethyl Phenyl Sulphone and the Cleavage of Carbon-Sulphur Bonds by Aniline

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Ferrocenylmethyl phenyl sulphone was prepared by the reaction of dimethylaminomethylferrocene methiodide with sodium benzenesulphonate. This ferrocenylmethyl sulphone was dilithiated with *n*-butyl-lithium; condensation with methyl iodide then gave 1-ferrocenyl-1-methylethyl phenyl sulphone. The dilithioferrocene was also condensed with benzyl chloride, butyl bromide, and 1,2-dichloroethane, to give α -ferrocenylphenethyl phenyl sulphone, 1-ferrocenylpentyl phenyl sulphone, and 1-ferrocenylcyclopropyl phenyl sulphone respectively. The phenyl sulphinyl group was displaced from several α -substituted ferrocenylmethyl phenyl sulphones by aniline to give the corresponding α -substituted anilinomethylferrocenes.

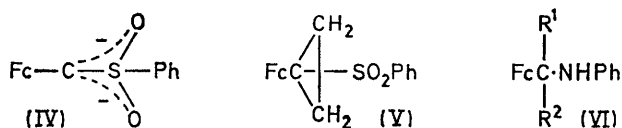
FERROCENYLMETHYL cations are unusually stable and have been extensively studied;² however the corresponding carbanions have received little attention. As part of a study of ferrocenylmethyl anions we recently reported the dilithiation of ferrocenylmethyl cyanide.³ The condensation of this lithiated intermediate with electrophiles gave $\alpha\alpha$ -disubstituted ferrocenylmethyl cyanides.

We now report the preparation and lithiation of ferrocenylmethyl phenyl sulphone (I). The sulphone (I) was prepared by nucleophilic displacement of



trimethylamine from dimethylaminomethylferrocene methiodide by benzenesulphonate. (A similar route to this compound was reported recently.⁴) The sulphone (I) was treated with 2 mol. equiv. of *n*-butyl-lithium; a

dilithiated intermediate (II) was shown to be present by quenching with deuterium oxide and analysis of the ¹H n.m.r. spectrum. The ease of formation of the intermediate (II) at room temperature indicated that the protons on the α -carbon atom are acidic. The dicarbanion was stabilized presumably by charge delocalization into the sulphur-oxygen bonds, assisted by the presence of the phenyl group [see (IV)], and into the ferrocenyl



group. The dilithio-derivative (II) was condensed with methyl iodide to give the sulphone (III; R¹ = R² = Me) in high yield. Similar reactions with *n*-butyl bromide and benzyl chloride gave the monobutylated (III; R¹ = Bu, R² = H) and monobenzylated (III; R¹ = CH₂Ph, R² = H) derivatives. Condensation with 1,2-dichloroethane gave the cyclopropane (V).

An attempt to prepare the $\alpha\alpha$ -disubstituted benzyl derivative (III; R¹ = R² = CH₂Ph) by extending the time of the reaction between benzyl chloride and the intermediate (II) was unsuccessful but a pair of isomeric

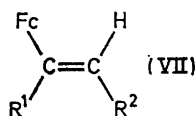
¹ Part III, G. Marr, B. W. Rockett, and A. Rushworth, *J. Chem. Soc. (C)*, 1971, 4000.

² M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

³ G. Marr and J. Ronayne, *Chem. Comm.*, 1970, 350.

⁴ M. Uher and S. Toma, *Coll. Czech. Chem. Comm.*, 1971, **36**, 3056.

olefins was produced, presumably the *cis*- and *trans*-forms of (VII; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{Ph}$).



Recently¹ we have displaced hydroxy-, dimethylamino-, phenoxy-, and piperidino-groups by aniline from the corresponding α -substituted ferrocenylmethanes. As aniline is a stronger nucleophile in some systems than *p*-nitrophenylsulphinate⁵ it was thought that the former might cleave the methylene-sulphur bond in the sulphone (I). This did in fact occur, to give the aminoferrocene (VI; $R^1 = R^2 = \text{H}$), and this displacement is of general utility in the preparation of α -substituted anilinoethylferrocenes. Thus the monobutyl, monobenzyl, and dimethyl sulphones (III; $R^1 = \text{Bu}$, $R^2 = \text{H}$), (III; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$), and (III; $R^1 = R^2 = \text{Me}$) gave the corresponding anilinoferrocenes (IV; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) (VI; $R^1 = \text{Bu}$, $R^2 = \text{H}$), and (VI; $R^1 = R^2 = \text{Me}$). The monobenzyl and the dimethyl sulphone also gave the olefins 1-ferrocenyl-2-phenylethylene (VII; $R^1 = \text{H}$, $R^2 = \text{Ph}$) and 2 ferrocenylpropene respectively.

EXPERIMENTAL

For general directions see Part I.⁶

Ferrocenylmethyl Phenyl Sulphone (I).—(Dimethylamino-methyl)ferrocene methiodide (20.0 g, 0.052 mol) and sodium benzenesulphinate (16.0 g, 0.08 mol) were added to water (100 ml) and the mixture was heated under reflux for 4 h. The sulphone (I) (15.9 g, 90%) was filtered off and crystallized from ether as yellow needles, m.p. 163–165° (lit.,⁴ 157–160°) (Found: C, 59.9; H, 4.7; Fe, 16.15. $\text{C}_{17}\text{H}_{16}\text{FeSO}_2$ requires C, 60.0; H, 5.0; Fe, 16.4%), τ [(CD_3)₂SO] 2.36 (5H, s, Ph), 5.64 (2H, s, CH_2), and 5.88 and 6.02 (9H, s and m, ferrocene).

Lithiation and Deuteration of the Ferrocenylmethyl Sulphone (I).—*n*-Butyl-lithium (0.0066 mol) was added to a solution of ferrocenylmethyl phenyl sulphone (1.0 g, 0.003

oil. The oil was chromatographed on alumina; ether eluted the deuterated sulphone (III; $R^1 = R^2 = \text{D}$) (0.95 g, 95%), τ [(CD_3)₂SO] 2.34 (5H, s, Ph) and 5.87–6.02 (9H, s and m, ferrocene).

1-Ferrocenyl-1-methylethyl Phenyl Sulphone (III; $R^1 = R^2 = \text{Me}$).—To the dilithioferrocene (III; $R^1 = R^2 = \text{Li}$) [from the ferrocenyl sulphone (I) (1 g, 0.003 mol)] a solution of methyl iodide (1.91 g, 0.0066 mol) in ether (10 ml) was added slowly. The mixture was heated under reflux for 30 min, hydrolysed, and extracted with ether, and the dried (MgSO_4) extracts were evaporated to leave a red oil. The oil was chromatographed on alumina; ether eluted the sulphone (III; $R^1 = R^2 = \text{Me}$) (0.775 g, 74%) which crystallised from ether-light petroleum as yellow needles, m.p. 149–150° (Found: C, 61.8; H, 5.5. $\text{C}_{19}\text{H}_{20}\text{FeSO}_2$ requires C, 61.95; H, 5.5%), τ (CCl_4) 2.68 (5H, s, Ph), 5.97 and 6.12 (9H, s and m, ferrocene), and 8.35 (6H, s, 2 \times Me).

1-Ferrocenylpentyl Phenyl Sulphone (III; $R^1 = \text{Bu}$, $R^2 = \text{H}$).—In a similar reaction *n*-butyl bromide (1.81 g, 0.0066 mol) was added to the dilithioferrocene (III; $R^1 = R^2 = \text{Li}$) (0.003 mol). Ether-light petroleum eluted the sulphone (III; $R^1 = \text{Bu}$, $R^2 = \text{H}$) (0.60 g, 63%) which formed orange crystals, m.p. 80–81° (from light petroleum) (Found: C, 64.1; H, 6.1; $\text{C}_{21}\text{H}_{24}\text{FeSO}_2$ requires C, 63.8; H, 6.1%), τ (CCl_4) 2.62 (5H, s, Ph), 5.98 (10H, s overlapping m, ferrocene and CH), and 8.48 (9H, m, Bu). Ether eluted the starting material (III; $R^1 = R^2 = \text{H}$) (0.185 g).

α -Ferrocenylphenethyl Phenyl Sulphone (III; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$).—In a similar reaction benzyl chloride (1.67 g, 0.0066 mol) was added to the lithioferrocene (III; $R^1 = R^2 = \text{Li}$) (0.003 mol). Ether eluted the sulphone (III; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) (0.89 g, 58%), which was deposited from ether as a yellow powder, m.p. 146–147° (Found: C, 66.7; H, 5.3. $\text{C}_{24}\text{H}_{22}\text{FeSO}_2$ requires C, 67.0; H, 5.15%; τ (CCl_4) 3.15 (10H, m, 2 \times Ph), 5.70 (1H, t, CH), 6.02 (9H, s, ferrocene), and 7.00 (2H, m, CH_2).

This experiment was repeated but the reaction mixture was heated under reflux for 6 h. Ether-light petroleum eluted an isomer of the ferrocenyl olefin (VII; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{Ph}$) (0.75 g, 34%) which crystallised from light petroleum as dark red *prisms*, m.p. 94–96° (Found: C, 78.9; H, 5.9; Fe, 14.8%; M^+ , 378. $\text{C}_{25}\text{H}_{22}\text{Fe}$ requires C, 78.4; H, 5.9; Fe, 14.8%; M , 378), τ (CCl_4) 2.76 and 2.92 (10H, s and s, 2 \times Ph), 3.77 (1H, s, CH), and 6.01 (11H, s overlapping m, ferrocene and CH_2). Ether-light petroleum

Products from the reactions of ferrocenylmethyl sulphones with aniline

| Compound | Yield (%) | M.p. (°C) | C | Found (%) | | | Fe | Formula | | | Calc. (%) | | | Fe |
|--|-----------|-----------|------|-----------|-----|--|------|--|------|-----|-----------|--|--|------|
| | | | | H | N | | | C | H | N | | | | |
| (VI; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) | 69 | 58–59 | 75.8 | 6.0 | 3.8 | | | $\text{C}_{24}\text{H}_{23}\text{FeN}$ | 75.6 | 6.1 | 3.7 | | | |
| (VI; $R^1 = R^2 = \text{Me}$) | 83 | 168–169 | 71.4 | 6.8 | 4.5 | | | $\text{C}_{19}\text{H}_{21}\text{FeN}$ | 71.5 | 6.6 | 4.4 | | | |
| (VI; $R^1 = \text{Bu}$, $R^2 = \text{H}$) | 37 | 53–54 | 72.5 | 7.5 | 3.6 | | | $\text{C}_{21}\text{H}_{26}\text{FeN}$ | 72.4 | 7.5 | 4.0 | | | |
| (VII; $R^1 = \text{H}$, $R^2 = \text{Ph}$) | 17 | 112–113* | 74.7 | 5.8 | | | 19.1 | $\text{C}_{18}\text{H}_{16}\text{Fe}$ | 75.0 | 5.6 | | | | 19.4 |

* Lit., 120–122° (P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990).

mol) in tetrahydrofuran (20 ml) and ether (80 ml). The mixture was stirred at room temperature for 30 min, then quenched with deuterium oxide and extracted with ether. The dried (MgSO_4) extracts were evaporated to leave a red

⁵ A. J. Parker, in 'Organic Sulphur Compounds,' by N. Kharsch, Pergamon, Oxford, 1961, p. 105.

⁶ G. Marr and T. M. White, *J. Chem. Soc. (C)*, 1970, 1789.

next eluted another isomer of the olefin (VII; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{Ph}$) (0.89 g, 40%), which crystallised from light petroleum as dark red *granules*, m.p. 96–98° (Found: C, 79.4; H, 6.0%; M^+ , 378. $\text{C}_{25}\text{H}_{22}\text{Fe}$ requires C, 78.4; H, 5.9; M , 378), τ (CCl_4) 2.82 and 3.02 (11H, d and s, Ph and CH), 5.76 (2H, t, substituted cyclopentadiene ring), and 6.01 (9H, t overlapping s, ferrocene and CH_2).

1-Ferrocenylcyclopropyl Phenyl Sulphone (V).—1,2-Dichloroethane (2.61 g, 0.013 mol) was added to the dilithioferrocene (III; $R^1 = R^2 = \text{Li}$) (0.003 mol) and the mixture was heated under reflux for 6 h. Ether eluted the *sulphone* (V) (1.21 g, 89%) which formed orange-yellow crystals, m.p. 131–132° (from light petroleum) (Found: C, 61.8; H, 5.0. $\text{C}_{19}\text{H}_{18}\text{FeSO}_2$ requires C, 62.3; H, 4.95%), τ (CCl_4) 2.62 (5H, s, Ph), 6.04 and 6.10 (9H, s and m, ferrocene), and 8.30 and 8.71 (4H, m and m, $[\text{CH}_2]_2$). Ether eluted the starting material (III; $R^1 = R^2 = \text{H}$) (0.73 g).

Reaction of Aniline with Ferrocenylmethyl Phenyl Sulphone.—The sulphone (I) (1 g, 0.003 mol) and aniline (1.5 g, 0.006 mol) were added to water (50 ml). The mixture was heated under reflux for 18 h, cooled, and extracted with ether. The dried (MgSO_4) extracts were evaporated to leave a red

oil which was chromatographed on alumina. Ether–light petroleum eluted *N*-(ferrocenylmethyl)aniline (0.34 g, 85%), identical (m.p. and i.r. spectrum) with an authentic sample.⁷

Reactions of the Sulphones (III; $R^1 = \text{Bu}$, $R^2 = \text{H}$), (III; $R^1 = \text{CH}_2\text{Ph}$, $R^2 = \text{H}$) and (III; $R^1 = R^2 = \text{Me}$) with Aniline.—These reactions were carried out similarly; analyses and m.p.s are given in the Table.

We thank Dr. B. W. Rockett for discussions and the P.C.M.U. for recording the mass spectra.

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⁷ I. K. Barben, *J. Chem. Soc.*, 1961, 1827.