2-Lithiation of *NN*-Dimethyl Cyclopentadienyl Manganese Tricarbonyl Sulphonamide: a Route to 1,2-Disubstituted Cyclopentadienyl Manganese Tricarbonyl Derivatives

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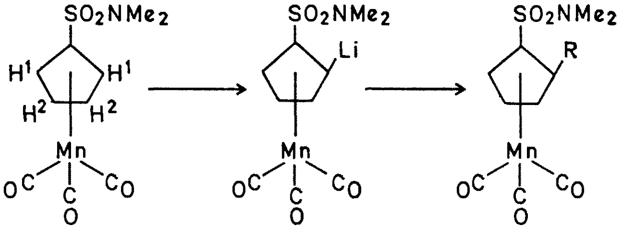
Summary The title compound (I) was metallated in the 2-position by methyl-lithium and the resulting 2-lithiosulphonamide (II) was condensed with D_2O, CO_2, and several carbonyl compounds to give the corresponding deuteriated compound, acid, and carbinols, respectively.

WE report the use of the 2-lithio-sulphonamide (II) as an intermediate in the synthesis of 1,2-disubstituted cyclopentadienyl manganese tricarbonyl derivatives. Previous attempts at the preparation of the 1,2-disubstituted cymantrenes have utilised electrophilic substitution of monosubstituted derivatives when mixtures of 1,2- and 1-3, disubstituted compounds have been obtained. These mixtures are very difficult to separate and, in any case, the 1,2-disubstituted isomer is the minor product. Compound (I),† m.p. 166—168°, was prepared in 50% yield from the corresponding sulphonyl chloride[1] and dimethylamine hydrochloride, and had m/e 311 (M^+) and the n.m.r. spectrum ($CDCl_3$) consisted of two triplets and a singlet at τ 7·25. One triplet was centred at 4·75 (J = 1 Hz) and the other at 5·20 (J = 1 Hz). This is an A_2B_2 pattern and comparison with the n.m.r. spectrum of the 2-deuteriated compound allows us to assign the resonance at 4·75 to H^1 and that at 5·20 to H^2. The resonance at 7·25 is associated with the *NN*-dimethyl group as confirmed by the integral ratio 1 : 1 : 3. The 2-lithio-sulphonamide (II) was generated using methyl-lithium as base in dry tetrahydrofuran at −70° under nitrogen. The anion was then quenched by addition of the agents listed in the Table. The reaction mixture was then worked up in a conventional manner and the product(s) isolated by chromatography on alumina.

TABLE

Reagent	Product (III)	M.p.	Yield %
	R		
D_2O	D	166—168°	44
CO_2	CO_2H	74° dec	53
Ph_2CO	Ph_2COH	184—185°	39
Me_2CO	Me_2COH	85—86°	38
PhCOMe	PhMeC(OH)	148—150°	30
PhCHO	PhCHOH	98—99°	50
FcCHO	FcCHOH	201—202°	14
FcCOMe	FcMeC(OH)	158—159°	14
CO_2-/CH_2N_2*	CO_2Me	121—123°	83

* In one experiment treatment with diazomethane gave a 25% yield of *N*-methyltoluene-*o*-sulphonamide but we have been unable to repeat this experiment.



(I) (II) (III)

These results parallel those of Hauser, Slocum, and their co-workers[2] which showed that *NN*-dimethylbenzenesulphonamide undergoes *ortho*-lithiation.

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† All new compounds have been fully characterised.

[1] M. Cais and J. Kozikowshi, *J. Amer. Chem. Soc.*, 1960, **82**, 5667.

[2] H. Watanabe, R. A. Achwarz, C. R. Hauser, J. Lewis, and D. W. Slocum, *Canad. J. Chem.*, 1969, **47**, 1543.