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An orthomanganation route to 2-substituted derivatives of *N*-methyl-1, 8-naphthalimide

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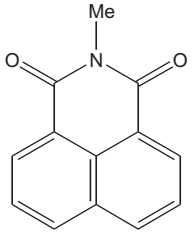
ABSTRACT

N-methyl naphthalimide can be readily cyclomanganated at the 2-position, directed by the adjacent amide O atom. Di-cyclomanganation also occurs readily to attach $Mn(CO)_4$ groups at both 2, 7 positions. An X-ray structure determination of the mono-substituted example confirmed the five-membered metallocyclic ring. Cleavage of the Mn–C bond by $HgCl_2$ or ICl generates 2-substituted HgCl or I derivatives respectively. Reaction of the mono-cyclomanganated *N*-methyl naphthalimide with phenylacetylene gives an (η^5-cyclohexadienyl)$Mn(CO)_3$ complex where the cyclohexadienyl ring has formed by two PhCCH adding in a formal [2 + 2 + 2] process across the C(1)–C(2) bond of the naphthalimide, breaking the aromaticity of the naphthalene ring as shown by a single crystal structure determination.

1. Introduction

The chemistry of *N*-alkyl-1,8-naphthalimides (for example the *N*-methyl compound **1**, also known as *N*-methyl-1,8-naphthalenedicarboximide) is well-developed. Derivatives find application as colorimetric and fluorescent sensors [1–3], and have promising chemotherapeutic properties [4,5]. Their photophysical properties are also of interest for electrochemical applications [6].

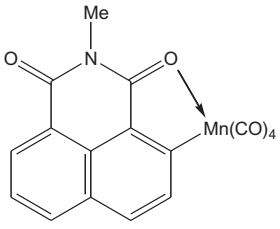


(1)

A very large number of papers (>10,000) discuss derivatives substituted at the 4-position, but in contrast there are very few 2-substituted examples (~100 papers) because of a paucity of synthetic routes. There are presently 41 structures reported for 4-substituted *N*-alkyl-1,8-naphthalimides, but none for 2-substituted analogues in the CCDC files [7].

Cyclometalation is a useful method of directing reactions at specific sites (for a recent review see Ref. [8]). We have previously reported extensively on the use of cyclomanganation of aryl ketones, amides, aldehydes, and other substrates as a means of specifically directing reactions at the ortho position of the aromatic ring [9–15], and as an extension of these studies have now examined **1** as a substrate.

We herein report the directed mono- and di-cyclomanganation of **1** at the 2-positions to give **2** and **3**, and demonstrate the use of the new complex **2** as an intermediate for preparing 2-halo- and 2-(chloromercurio)-*N*-alkyl-1,8-naphthalimides. The reaction of **2** with alkynes is also discussed, with PhCCH leading to dearomatisation of the naphthalene core.



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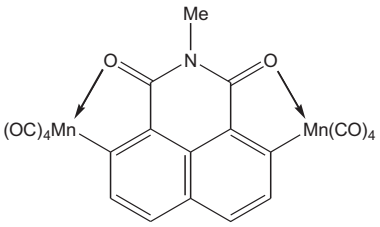

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2. Experimental details

2.1. General procedures

Spectroscopic data were obtained on a Perkin–Elmer Spectrum 100 FTIR and a Bruker BRX400 NMR, the latter with samples dissolved in $CDCl_3$. ESI-MS were from a Bruker MicrOTOF instrument, with solutions made up in methanol, operated under standard conditions. NaOMe was added to aid ionisation for the metal carbonyl samples [16]. $PhCH_2Mn(CO)_5$ was prepared by the literature method [17] and naphthalic anhydride and the alkynes were purchased from Aldrich. Chromatography was carried out on 20 × 20 cm silica gel plates. Petroleum spirit refers to a 60–80 °C fraction. Reactions were carried out under a nitrogen atmosphere in Schlenk equipment, but no precautions to exclude air were taken during work-up.

2.2. Preparation of N-methyl-1,8-naphthalimide (**1**)

1,8-Naphthalic anhydride (2.0 g, 0.01 mol) was dissolved in absolute ethanol (150 mL) and 5 mL of 25% $MeNH_2$(aq) was added. The solution was stirred at room temperature for 3 d, and the solid product which had crystallised from the reaction mixture was filtered and dried to give *N*-methyl-1,8-naphthalimide (2.2 g, 100%), pure by IR (KBr disc, $\nu_{C=O}$ 1701 m, 1668 vs cm^{-1}), ^1H NMR [δ 3.55 s ($-CH_3$), 7.74 apparent t (dd), 8.19 dd, 8.58 dd ($-C-H$)], ^{13}C NMR [δ 27.0 ($-CH_3$), 126.9, 131.2, 133.9 (all $-C-H$), 122.6, 128.1, 131.6 (quart *C*), 164.5 (*C*=O)] and ESI-MS [*m*/*z* 212.068 $[M + H]^+$ (calc 212.071), *m*/*z* 234.047 $[M + Na]^+$ (calc 234.052)].

2.3. Cyclomanganation of N-methyl-1,8-naphthalimide

A mixture of $PhCH_2Mn(CO)_5$ (0.51 g, 1.78 mmol) and *N*-methyl-*1,8*-naphthalimide(0.43 g, 2.04 mmol) in heptane (50 mL) was heated under gentle reflux for 2 h, by which time an IR spectrum of an aliquot of the reaction mixture showed ν_{CO} bands from $PhCH_2Mn(CO)_5$ were absent. The mixture was evaporated to dryness and the residue was chromatographed on silica, with CH_2Cl_2/petroleum spirits (2:9) as eluent. Two yellow bands were resolved.

The slower moving band (R_f 0.15) was removed and recrystallized from CH_2Cl_2/petroleum spirits at −20 °C to give orange crystals of orthomanganated *N*-methyl-1,8-naphthalimide (**2**) (0.27 g, 40%). Anal.: Calc for $C_{17}H_8MnNO_6$: C 54.13; H 2.14; N 3.71%. Found C 54.44; H 2.21; N 3.66%. IR: ν(CO) cm^{-1} (CH_2Cl_2) 2086 m, 1999 vs, 1942 s; (KBr disc) 2083 s, 1995 vs, 1940 s, 1690 m, 1621 m, 1575 s, 1533 m. NMR ($CDCl_3$) ^1H: δ 3.55 s ($-CH_3$), 7.66 apparent t (dd),8.00 d, 8.23 d, 8.39 d, 8.48 d (all C–*H*). ^{13}C: δ 28.3 ($-CH_3$), 126.6, 132.1, 132.9, 136.3, 140.6 (all *C*–H), 120.3, 128.8, 130.4 (quart. *C*). ESI-MS (−ve ion, NaOMe added [16]): *m*/*z* 408.027, ($[M + OMe]^-$ calc. 407.991); (+ve ion): *m*/*z* 399.966 $[M + Na]^+$ calc. 399.962; *m*/*z* 776.936 $[2M + Na]^+$ calc. 776.936.

The faster moving band (R_f 0.60) was removed to give an orange powder of di-manganated *N*-methyl-1,8-naphthalimide (**3**) (0.05 g, 10%). Anal.: Calc for $C_{21}H_7Mn_2NO_{10}$ C 46.44; H 1.30; N 2.58%. Found C 47.98; H 1.84; N 2.54%. IR: ν(CO) cm^{-1} (CH_2Cl_2) 2084 m, 2002 vs, 1942 s; (KBr disc) 2086 s, 2012 w,sh, 1993 s, 1965 s, 1943 vs, 1613 s, 1606 sh. NMR ($CDCl_3$) ^1H: δ 3.56 s ($-CH_3$), 8.05 d, 8.32 d (both C–*H*). ^{13}C: δ 27.2 ($-CH_3$), 133.1, 137.9 (both *C*–H), 125.9, 126.8, 127.5 (quart. *C*) 176.4 (*C*=O), 204.0 (Mn–C), 210.5, 212.6, 220.9 (Mn–*C*O). ESI-MS (−ve ion, NaOMe added [16]): *m*/*z* 573.967, ($[M + OMe]^-$ calc 573.901).

2.4. Preparation of 2-(chloromercurio)-N-methyl-1,8-naphthalimide (**4**)

Cyclomanganated *N*-methyl-1,8-naphthalimide (0.030 g, 0.08 mmol) and $HgCl_2$ (0.033 g, 0.12 mmol) were dissolved in MeOH (10 mL) and heated to reflux for 75 min. The mixture was cooled and the precipitate was collected by filtration and washed with MeOH to give an off-white powder of 2-(chloromercurio)-*N*-methyl-1,8-naphthalimide (**4**) (0.030 g, 61%). Anal.: Calc for $C_{13}H_8ClHgNO_{12}$ C 34.99; H 1.81; N 3.14%. Found C 34.68; H 1.85; N 3.04%. IR: (KBr disk, cm^{-1}) 1698 m, 1643 vs, 1612 w, 1577 m. The compound was too insoluble for NMR spectra.

2.5. Preparation of 2-iodo-N-methyl-1,8-naphthalimide (**5**)

A solution of ICl (0.023 g, 0.14 mmol) in CCl_4 (1 mL) was added to **2** (0.05 g, 0.13 mmol) in CCl_4 (2 mL). The mixture was left for 2 h. Solvent was removed and the residue chromatographed on silica plates, eluting with CH_2Cl_2:petroleum spirits (1:1). A yellow band at R_f 0.3 was unreacted **2**, while a pale yellow band at R_f 0.1 was removed and shown to be the mono-iodinated product **5**, (4 mg, 9%). NMR ($CDCl_3$) ^1H: δ 3.61 s ($-CH_3$), 7.80 apparent t (dd), (J = 8 Hz), 7.80 d (J = 9 Hz), 8.21 dd (J = 8, 1 Hz), 8.38 d (J = 9 Hz), 8.69 dd (J = 7, 1 Hz) (all C–*H*); ^{13}C: 29.7 ($-CH_3$), 101.5, 126.9, 127.2, 131.2, 131.3, 131.5, 133.3, 133.9, 134.1, 141.7 (aryl *C*–H), 162.3, 163.2 (*C*=O). IR: (KBr disk, cm^{-1}) 1697 m, 1657 vs, 1646 sh, 1583 m. ESI-MS: *m*/*z* 359.952 $[M + Na]^+$, calc. 359.949; *m*/*z* 696.915 $[2M + Na]^+$, calc. 696.909. The structure of **5** was also determined by X-ray crystallography (see below).

2.6. Reaction of cyclomanganated N-methy-1,8-naphthalimide with phenylacetylene to give **6**

Cyclomanganated naphthalimide **2**, (0.040 g, 0.11 mmol) was dissolved in benzene (15 mL). PhCCH (0.1 mL, excess) was added and the stirred mixture was brought to reflux in an oil bath at 100 °C. After 90 min, a small sample removed for solution IR analysis showed all starting material was consumed. The solvent and excess alkyne were removed under vacuum and the residue chromatographed on silica plates, eluting with 1:1 CH_2Cl_2/pet spirits. This gave one major yellow band. This was removed and recrystallised from a mixture of CH_2Cl_2 and pet spirits to give orange crystals of **6** (0.044 g, 73%). Anal.: Calc for $C_{32}H_{20}MnNO_5$ C 69.45; H 3.64; N 2.52%. Found C 69.42; H 3.73; N 2.53%. IR: (CH_2Cl_2, cm^{-1}) 2019 s, 1954 s,br. NMR ($CDCl_3$) ^1H: δ 3.03 s ($-CH_3$), 5.60 s, 5.89 s (C–*H* of cyclohexadienyl ring), 5.94 d, 6.38 d (C–*H* of de-aromatised ring), 7.0–7.8 m, (aromatic C–*H*). ESI-MS: *m*/*z* 576.064 $[M + Na]^+$, calc. 576.061; *m*/*z* 1129.136 $[2M + Na]^+$, calc 1129.134.

2.7. X-ray crystal structures

Crystals of **2** and **5** were from CH_2Cl_2/Et_2O, while those of **6** were from CH_2Cl_2/petroleum spirits. Intensity data were obtained on a Bruker SMART diffractometer with Mo-Kα X-rays, and were corrected for absorption using a multi-scan procedure. The structures were solved by direct methods and developed and refined on F_o^2. For compound **2**, after the main part of the structure had been revealed it became clear there was disorder involving a 180° rotation of the planar naphthalimide rings relative to the $Mn(CO)_4$ group, giving an alternative orientation. This disordered component was resolved for all of the naphthalimide atoms and also for the Mn atom, and these were refined with isotropic temperature factors. The relative site occupancies were refined to give a major/minor orientation of 78%/22%. There was also concomitant disorder for the CO ligands but this was not resolved. H atoms were included in calculated positions for the major component but were omitted for the minor one. The structure of the main component is shown in Fig. 1a, with the disorder illustrated in Fig. 1b.

The crystal structure of **2** also appeared to have a minor (*ca* 3%) orientational disorder for one of the two independent molecules,