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EXCEPTIONAL REACTIVITY OF THE AROMATIC RING IN 8-SUBSTITUTED 1-NAPHTHOL DERIVATIVES. READY REDUCTION TO TETRALINS.

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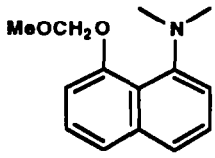
Abstract. *8-Lithio-1-methoxynaphthalene is acylated and alkylated to give 8-CO_2H, $COCH_3$ and $Me_2C(OH)$ derivatives in only poor yields. Methyl lithium does not add to the 8-acetyl compound, converting it instead to the lithium enolate. Compounds with secondary or tertiary alkyl peri-substituents undergo rapid protodealkylation, and are readily reduced to tetralins by H_2/Pd at atmospheric pressure.*

We have described the synthesis of the acetal **1**[1] and its hydrolysis to **2** in a reaction which involves exceptionally efficient intramolecular general acid catalysis by the Me_2NH^+ group.[2] We needed a similar acetal lacking the Me_2NH^+ group in order to estimate the efficiency of this catalysis, and prepared first the corresponding Me_3N^+ derivative.[1] However, N-demethylation of this compound proved faster than acetal hydrolysis. So we turned to what should be the more stable isopropyl derivative **3**, in which the Me_2NH^+ is replaced by the isosteric alkyl substituent. Remarkably, protodealkylation of **3** proved faster than the hydrolysis of the acetal function — just one of several remarkable reactions (Scheme) induced by *peri*-strain[1] in these systems.



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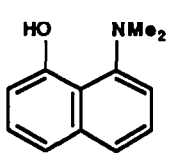

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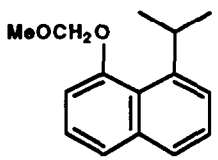

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Results and Discussion.

The introduction of a *peri*-substituent into 1-naphthol is not a trivial operation. Clearly electrophilic substitution and thermodynamic conditions must be avoided, but hetero-atom directed lithiation [3-5] appears to offer a simple solution. Both 2 and 8-lithium derivatives have been obtained from 1-methoxynaphthalene,[6] and recent calorimetric studies[7] show that the 8-Li isomer is the more stable, by 8kJ mol^{-1}. (Both are preferred to the 4-isomer.)

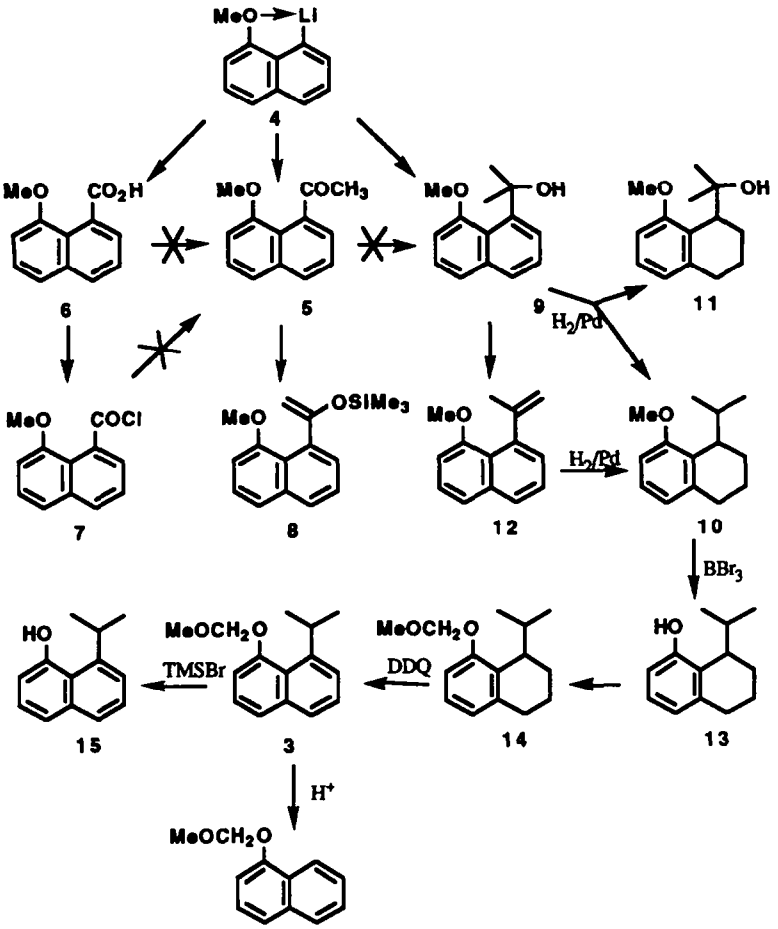
An attempt at direct coupling with 2-chloropropane, using copper(I) iodide,[8] failed even with 2-lithio-1-methoxynaphthalene. Only small amounts of the naphthalene dimer were obtained.[9] So we were obliged to introduce the isopropyl group indirectly.

The ketone **5** was prepared in variable but always low (5 - 10%) yields by reacting the 8-Li derivative **4** with acetic anhydride at -78°. Olah's conditions, involving transmetallation with $MgBr_2$ dietherate and quenching with N,N-dimethylacetamide,[10] gave no improvement. The acid **6** was obtained in somewhat higher yield (17%), but attempted conversion to **5** after Jorgenson[11], by treatment with MeLi in ether, gave a complex mixture which contained none of the desired ketone **5**, but small amounts of 1-methoxynaphthalene, the product of decarboxylation. Conversion of **6** to the acid chloride **7** ($SOCl_2$, reflux) and treatment with Me_2CuLi in THF at -78° , according to Posner[12] gave a similar result.

On treatment with MeLi in ether or THF at 0°C **5** enolised: quenching with chlorotrimethylsilane produced a quantitative yield of silyl enol ether **8**. These difficulties further illustrate the effects of the additional *peri*-strain arising when planar substituents become tetrahedral.[1] Eventually we found it simplest to introduce the three-carbon unit by reacting **4** with acetone: the alcohol **9** could be isolated in variable and at best modest yield (5 - 16%).[13]

Reductive cleavage of the benzylic C-O bond would give the desired isopropyl group directly, and should be accompanied by a modest decrease in *peri*-strain. Hydrogenolysis of such bonds is generally regarded as a reliable reaction. Thus Freifelder:[14] "An interesting point about palladium-on-carbon (and probably about palladium catalysts in general), is that even when a large amount of catalyst is used at low pressure and room temperature, ring reduction does not take place." Accordingly, **9** was exposed to hydrogen in ethanol in the presence of 5% palladium on carbon, as described by Mitsui *et al.*. [15] TLC showed the disappearance of **9** and the formation of two new compounds, identified as **10** and **11**, obtained in yields of 64 and 36%, respectively. Once more, relief of ground state strain resulting from non-bonded repulsion between the two *peri*-substituents must provide the driving force for the ready reduction of the aromatic system under such mild conditions.

We attempted to encourage C-O cleavage by incorporating the oxygen atom into a better leaving group.[16] Treatment of **9** with acetyl chloride in dichloromethane containing pyridine, or with acetic anhydride in the same solvent with DMAP and triethylamine [17,18] resulted in the recovery of unreacted starting material. However, when **9** was allowed to react with acetyl chloride in CH_2Cl_2 for 1h in the absence of base, and the mixture then treated with pyridine, the alkene **12** was isolated in quantitative yield. An acid-catalysed E1 reaction, favoured by the release of *peri*-strain, readily accounts for this reaction. Catalytic hydrogenation of **12** for 36h, under the conditions used for the reduction of **9**, gave a quantitative yield of **10**.



Scheme

The reduced ring of **10** is now at least 'protected' against protodealkylation. O-demethylation of **10**, by the method of McOmie and West [9], proceeded smoothly in 92% yield. Subsequent treatment of the tetrahydronaphthol **13** with NaH in dimethylformamide, followed by methoxymethyl chloride, gave **14** (60%). Oxidation with DDQ in toluene [20] gave the desired acetal **3** in 70% yield. A small sample was cleaved to give 8-isopropyl-1-naphthol (**15**) in quantitative yield, using the conditions of Woodward *et al.*. [21]

In dilute acid **3** gave a complex mixture, including (by TLC) 1-naphthol and 1-methoxymethoxynaphthalene, and no **15** could be detected. Protodealkylation evidently occurs faster that the hydrolysis of the acetal group, and we never were able to use **3** as originally intended in our main kinetic studies.

Experimental

8-Lithio-1-methoxynaphthalene (4)

The anion was generated according to the method of Shirley and Cheng.[6] *t*-Butyllithium (0.65 ml of a 1.7M solution in pentane) was added to a stirred solution of 1-methoxynaphthalene (0.153 g) in cyclohexane (2 ml) under argon at room temperature and the mixture stirred for 24 hours; quenching procedures are described below.

8-Methoxy-1-acetonaphthone (5): (i). A solution of the anion (**4**, 40 mmol) was cooled to -78°C and acetic anhydride (6.12 g) added as an ethereal solution (30 ml). The mixture was allowed to warm to -20°C over 4 hours then quenched with saturated sodium hydrogen carbonate solution(50 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed with brine (50 ml) then evaporated under reduced pressure and the residue chromatographed, eluting initially with 10% ether-hexane to remove unreacted 1-methoxynaphthalene, then with 33% ether-hexane to afford the ketone (0.813 g, 10%), R_F (33% ether-hexane) 0.27, ν_{max} ($CHCl_3$) 1 690 cm^{-1}(C=O), δ_H ($CDCl_3$, 90 MHz) 7.75 (1H, dd, J 7 and 2 Hz), 7.50-7.25 (3H, m), 7.22 (1H, dd, 7 and 2 Hz), 6.75 (1H, dd, 6 and 3 Hz) 3.75 (3H, s) and 2.40 (3H, s). (Found: M^+, 200.0834. $C_{13}H_{12}O_2$ requires M^+, 200.0837), *m/z* 200 (80%, M^+), 185 (100, *M*-Me), 170 (70, *M*-CH_2O).

8-Methoxy-1-acetonaphthone (5): (ii). After the method of Olah *et al.*,[10a] stirred solution of the anion (**4**, 0.7 mmol) was cooled to -5°C and treated with magnesium dibromide etherate (1 ml of a 2M solution prepared by the action of magnesium metal on 1,2-dibromoethane). The mixture was allowed to warm to 0° C and N,N-dimethylacetamide (0.871 g) in ether (1 ml) added over 5 min. Stirring was continued for 1 hour at room temperature and the mixture poured into saturated sodium hydrogen carbonate solution (5 ml) and extracted with dichloromethane (3 x 5 ml). The combined organic extracts were dried ($MgSO_4$) and

evaporated under reduced pressure; the yield (< 5%) was assessed by NMR spectroscopy of the residue, integrating the O-Me resonances at 3.90 and 3.75 ppm.

8-Methoxy-1-naphthalenecarboxylic acid (6). After the method of Shirley and Cheng,[6] a solution of the anion (**4**, 34.3 mmol) was transferred via a double-ended needle into a slurry of solid carbon dioxide (50 g) in ether (250 ml) with mechanical stirring. Upon completion of the addition, the mixture was allowed to warm to room temperature and acidified with 3M hydrochloric acid to pH 3. The organic layer was separated and extracted with aqueous sodium hydrogen carbonate solution (3 x 200 ml). The combined aqueous extracts were acidified, extracted with dichloromethane (5 x 200 ml) and the combined organic extracts dried ($MgSO_4$). Chromatography of the residue with 10% methanol-chloroform as eluant (containing 1% triethylamine) afforded the acid (**6**, 1.23 g, 17%) which was dried *in vacuo* and used without further purification; *mp* 154-157°C (lit. [6] 157-159°), R_F (10% MeOH-$CHCl_3$ with 1% triethylamine) 0.23, $\nu_{max}(CHCl_3)$ 3 200-2 800 (O-H), and 1 700 cm^{-1}(C=O), $\delta_H(CDCl_3, 90\ MHz)$, 7.95 (1H, dd, J 9 and 2 Hz, H2), 7.75-7.40 (4H, m), 6.98 (1H, dd, 6 and 3 Hz, H7) and 4.05 (4H, s). (Found: M^+, 202.0639. $C_{12}H_{10}O_3$ requires 202.0630), *m/z* 202 (20%, M^+), 158 (65, M-CO_2,H^+).

Attempted preparation of the ketone (5) via the lithium salt of (6). After the method of House and Bashe,[20] methyllithium (7.1 ml of a 1.4M solution in ether) was added dropwise over 45 min to a vigorously stirred solution of the acid (**6**, 1.016 g) in ether (30 ml) at -10°C, the suspension allowed to warm to room temperature over 4 hours and stirred for 18 hours longer. It was then poured into ice (100 g), acidified with c.HCl and extracted with ether (3 x 30 ml). The combined organic extracts were washed with saturated sodium hydrogen carbonate solution (3 x 30 ml), then with brine (30 ml) and dried (Na_2SO_4). TLC analysis of the residue failed to show the presence of any of the desired product. The aqueous phase was acidified, extracted with ether (3 x 30 ml) and the combined organic extracts washed with brine (30 ml) and dried (Na_2SO_4). TLC analysis revealed only baseline material and a fast-running band. PTLC allowed the isolation of recovered starting material (**6**) and 1-methoxynaphthalene; the yields of these products were not determined.

Attempted preparation of the ketone (5) via the acid chloride (7).

8-Methoxy-1-naphthalenecarbonyl chloride was prepared by the action of thionyl chloride (4 ml) on the acid (**6**) (0.404 g) at reflux for 1 hour. Excess thionyl chloride was removed under reduced pressure and the residue dried *in vacuo* and used without further purification in a procedure described by Posner *et al.*. [12] Methyllithium (8.6 ml of a 1.4M solution in ether) was added to a solution of cuprous iodide (1.14 g) in ether (8 ml) at 0°C. After 5 min at -78°C, methanol (1 ml) was added and the mixture allowed to warm to room temperature, poured into an equal volume of saturated ammonium chloride solution , extracted with ether (3 x 20 ml) and the combined organic extracts dried ($MgSO_4$). TLC analysis of the residue revealed a

complex mixture of products from which the ketone was absent (by comparison with an authentic sample).

Attempted preparation of the alcohol (9) from the ketone (5).

Methylmagnesium iodide (0.77 ml of a 3M solution in ether) was added to a stirred solution of the ketone (**5**, 0.457 g) in ether (2 ml) at 0°C. The mixture was allowed to warm to room temperature after effervescence had ceased, and quenched with saturated sodium hydrogen carbonate solution (2 ml). Evaporation of the organic layer under reduced pressure afforded a residue shown by TLC and NMR analysis to be the unreacted ketone (**5**).

8-Methoxy-1-acetonaphthone trimethylsilyl enol ether (8). Methyllithium (0.85 ml of a 1.4M solution in ether) was added to a stirred solution of the ketone (**5**, 0.20 g) in ether (2 ml) at -78°C. The mixture was allowed to warm to room temperature, quenched with chlorotrimethylsilane (0.163 g), and the solvent removed under reduced pressure. The residue was taken up in dichloromethane (2 ml) and washed through a short column of Celite® ; evaporation of the eluant afforded the trimethylsilyl enol ether (**8**, 0.272 g, 100%) as the only product by TLC and NMR, R_F(33% ether-hexane) 0.74, $\nu_{max}(CHCl_3)$ 2 900, 1 620 and 1 590 cm^{-1}(C=O), $\delta_H(CDCl_3$, 90 MHz) 7.65 (1H, dd, J 6 and 3 Hz), 7.35-7.15 (4H, m), 6.75 (1H, dd, 6 and 3 Hz), 4.35 (1H, s), 4.25 (1H, s), 3.75 (3H, s) and 0.10 (9H, s). (Found: M^+, 272.1239. $C_{16}H_{20}SiO_2$ requires 272.1233), *m/z* 272 (54%, M^+), 257 (40, *M*-Me), 241 (50, *M*-OMe), 75 (40, $Me_2Si{=}OH^+$), 73 (100, Me_3Si^+).

2-(8-Methoxy-1-naphthyl)-propan-2-ol (9). A solution of the anion (**4**, 0.138 mol) was cooled to -78°C and a solution of acetone (17.4 g) in ether (100 ml) added over 1 hour. The mixture was allowed to warm to room temperature over 3 hours then quenched with methanol (20 ml) followed by sodium hydroxide solution (200 ml). After separation of the phases, the aqueous layer was extracted with dichloromethane (3 x 200 ml) and the combined organic extracts washed with brine (500 ml) and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure, the residue was chromatographed first with hexane as eluant to remove unreacted 1-methoxynaphthalene, then with 50% ether-hexane to yield the alcohol (**9**, 1.49 g, 5%), which was recrystallised from 25% ether-hexane to give prisms, *mp* 67-68°C. (Found: C, 77.9; H, 7.30. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.45%). R_F (33% ether-hexane.) 0.09, $\nu_{max}(CHCl_3)$ 3 450 (O-H) 2 950 (C-H) and 1 590 cm^{-1}(Ar-H), $\delta_H(CDCl_3$, 90 MHz) 7.80-7.30 (5H, m), 7.05 (1H, dd, J 7 and 2 Hz, H7), 6.10 (1H, br.s, exchanged with D_2O), 4.10 (3H, s) and 1.80 (6H, s). (Found: M^+, 216.1169. $C_{14}H_{16}O_2$ requires M^+, 216.1150), *m/z* 216 (30%, M^+), 201 (100, *M*-Me), 183 (50, *M*-CO), λ_{max}(cyclohexane) 233 and 292 nm (ε 17 000 and 4 400).

Reduction of the alcohol (9). A solution of the alcohol (**9**, 0.117 g) in absolute ethanol (2 ml) containing 5% palladium-on-carbon was exposed to an atmosphere of hydrogen (contained in a double-balloon) for 90 min. TLC analysis showed the presence of two new compounds. These were separated by PTLC with 33% ether-hexane as eluant, giving (i) **8-methoxy-1,2,3,4-tetrahydro-1-isopropylnaphthalene (10)** (0.040 g, 36%), R_F (33% ether-hexane.) 0.70, $\nu_{max}(CHCl_3)$ 2 950, 1 580 and 1 460 cm^{-1}, $\delta_H(CDCl_3)$ 7.05 (1H, t, J 8.6 Hz), 6.68 (1H, d, 8.6 Hz), 6.67 (1H, d, 8.6 Hz), 3.77 (3H, s), 3.04-2.97 (1H, m), 2.71-2.65 (2H, m), 2.08 (1H, septet, 6.5 Hz), 1.94-1.75 (2H, m), 1.70-1.51 (2H, m), 0.86 (3H, d, 6.5 Hz) and 0.79 (3H, d, 6.5 Hz) (Found: M^+, 204.1518. $C_{14}H_{20}O$ requires 204.1514), *m/z* 204 (9%, M^+), 161 (100, M-$C_3H_7^+$), λ_{max}(cyclohexane) 223 (ε 9 900), 228 (10 000), 272 (1 000) and 280 (1 000), and (ii) the alcohol **8-methoxy-1,2,3,4-tetrahydronaphthalenyl)-propan-2-ol (11)**, 0.076 g, 64%), m.p. 81-85°C, R_F (33% ether-hexane) 0.25, $\nu_{max}(CHCl_3)$ 3 450 (O-H), 2 900, 1 580 and 1 460 cm^{-1}, $\delta_H(CDCl_3)$ 7.11 (1H, t, J 7.8 Hz), 6.75 (2H, t, 7.8 Hz), 3.81 (1H, br.s exchanged with D_2O), 3.41 (1H, dd, 7.3 and 4 Hz), 2.74-2.69 (2H, m), 1.98-1.75 (3H, m), 1.54-1.46 (1H, m), 1.30 (1H, s) and 1.00 (3H, s), *m/z* 205 (5%, *M*-Me), 202 (1,M-H_2O), 187 (2, *M*-Me,H_2O), 162 (100, M-C_3H_6O) and 58 (50, C_3H_6O), λ_{max}(cyclohexane) 220 (ε 9 000), 272 (1 800) and 280 nm (1 800).

8-Methoxy-1-isopropenylnaphthalene (12).

Acetyl chloride (0.246 g) was added to a stirred solution of the alcohol (**9**, 0.620 g) in dichloromethane (20 ml) under nitrogen, followed after 1 hour by pyridine (0.476 g). After stirring for 12 hours, the mixture was evaporated onto silica (2 g), and flash chromatographed with 50% ether-hexane as eluant to yield the alkene (**12**, 0.567 g, 100%) as an oil, R_F (50% ether-hexane) 0.91, $\nu_{max}(CHCl_3)$ 2 900, 1 630, 1 620 and 1 560 cm^{-1}(C=C), $\delta_H(CDCl_3$, 90 MHz) 7.80 (1H, dd, J 9 and 2 Hz), 7.60-7.30 (3H, m), 7.25 (1H, dd, 7 and 3 Hz), 6.90 (1H, dd, 7 and 3 Hz), 5.10-5.00 (1H, m), 4.88-4.76 (1H, m), 3.90 (3H, s) and 2.10 (3H, br.s) , (Found: M^+, 198.1045. $C_{14}H_{14}O$ requires 198.1045), *m/z* 198 (100%, M^+), 183 (65, *M*-Me), and 167 (70, *M*-OMe), λ_{max}(cyclohexane), 223 (ε–11 400), 233 (10 900) and 298 nm (2 500).

Reduction of the alkene (12).

A stirred solution of the alkene (**12**, 0.533 g) in absolute ethanol (10 ml) containing 5% palladium-on-carbon (1 g) was exposed to an atmosphere of hydrogen (contained in a double balloon) for 36 hours. Filtration through Celite® and evaporation of the solvent under reduced pressure afforded (**10**, 0.503 g, 92%) as the only product by NMR and TLC analysis.

8-Isopropyl-5,6,7,8-tetrahydro-1-naphthol (13).

Boron tribromide (0.93 ml of a 2.1M solution in hexane) was added in one portion to a stirred solution of the hydrocarbon (**10**, 0.398 g) in dichloromethane (5 ml) at -78°C, after the

method of McOmie and West.[19] The mixture was allowed to warm to room temperature over 3 hours and stirred for 20 hours in the dark. Aqueous sodium hydroxide (5 ml of a 1M solution) was added and the mixture extracted with dichloromethane (3 x 10 ml), the combined organic extracts washed with brine (20 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue flash chromatographed with 33% ether-hexane as eluant to afford the tetrahydronaphthol (**13**, 0.341 g, 92%) as a pale yellow oil, R_F (33% ether-hexane.) 0.54, ν_{max} (film) 3 650-3 100 (broad, O-H) cm^{-1}, $\delta_H(CDCl_3)$ 6.96 (1H, t, J 7.7 Hz), 6.67 (1H, d, 7.5 Hz), 6.57 (1H, d, 8 Hz), 4.57 (1H, br.s, exchanged with D_2O, O-H), 2.91-2.84 (1H, m), 2.71-2.66 (2H, m), 2.13 (1H, septet, 7 Hz), 1.93-1.52 (4H, m), 0.94 (3H, d, 7 Hz) and 0.83 (3H, d, 7 Hz). (Found:M^+, 190.1362. $C_{13}H_{18}O$ requires 190.1358), *m/z* 190 (30%, M^+) and 147 (100, M-$C_3H_7^+$).

8-Isopropyl-5,6,7,8-tetrahydro-1-methoxymethoxynaphthalene (14).

A solution of the naphthol (**13**, 312mg) in DMF was added to a suspension of sodium hydride (0.075 g of a 60% dispersion in mineral oil) in DMF (5 ml) at 0°C. After warming to room temperature and stirring for 30 min, chloromethyl methyl ether (*caution*: *carcinogen*, 0.197 g) was added and the mixture stirred for 1 hour further. A solution of sodium hydrogen carbonate (20 ml) was added, the mixture extracted with ether (3 x 25 ml), the combined organic extracts dried (K_2CO_3) and evaporated under reduced pressure. PTLC of the residue with 33% ether-hexane as eluant afforded recovered starting material (0.070 g, 22%) and the acetal (**14**, 0.231 g, 60%) as an oil, R_F (33% ether-hexane) 0.67, ν_{max}(film) 2 900, 1 605, 1 580 and 1 460 cm^{-1}, $\delta_H(CDCl_3)$ 7.04 (1H, t, J 8 Hz), 6.90 (1H, d, 8 Hz), 6.75 (1H, d, 8 Hz), 5.17 (2H, s), 3.49 (3H, s), 3.08-3.01 (1H, m), 2.73-2.68 (2H, m), 2.16-2.08 (1H, septet, 6.8 Hz), 1.95-1.81 (2H, m), 1.79-1.54 (2H, m), 0.91 (3H, d) and 0.83 (3H, d, 6.8 Hz). (Found: M^+, 234.1629. $C_{15}H_{22}O_2$ requires 234.1620), *m/z* 234 (20%, M^+) and 191 (100, M-$C_3H_7^+$).

8-Isopropyl-1-methoxymethoxynaphthalene (3).

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.322 g) was added to a solution of the acetal (**14**, 0.166 g) in toluene (7 ml), the dark red solution refluxed for 4 hours and then poured onto a column of alumina (UG1), eluting with toluene until the eluant ceased to contain UV-active compounds. Removal of the solvent under reduced pressure yielded an oil which was submitted to PTLC with 33% diethyl ether hexane as eluant to afford the acetal (**4**, 0.100 g, 61%), R_F (33% ether hexane.) 0.55, ν_{max}(film) 2 950, 1 580 cm^{-1}, $\delta_H(CDCl_3$, 90 MHz) 7.65 (1H, dd, J 7 and 3 Hz), 7.45-7.08 (5H, m), 5.20 (2H, s), 4.52 (1H, spt, 7Hz), 3.50 (3H, s) and 1.32 (6H, d, 7Hz).

8-Isopropyl-1-naphthol (15).

Chlorotrimethylsilane (0.0043 g) was added to a stirred solution of the acetal (**3**, 0.010 g) in dichloromethane-d_2 (0.3 ml) containing tetra-n-butylammonium bromide (0.014 g) at 0°C. After 1 hour the mixture was allowed to warm to room temperature and stirred for a further 30 min. NMR and TLC analysis of the mixture showed that starting material was absent. PTLC of the reaction mixture with 33% ether-hexane as eluant afforded the naphthol (8 mg, 100%) as an air sensitive oil, R_F (33% ether-hexane) 0.42, $\nu_{max}(CHCl_3)$ 3 650-3 100 cm^{-1}(O-H), $\delta_H(CDCl_3$, 90 MHz) 7.70-7.13 (5H, m), 6.70 (1H, dd, 6.5 and 2.2 Hz), 5.20 (1H, br.s, exchanged with D_2O, O-H), 4.54 (1H, spt, 7 Hz) and 1.37 (6H, d, 7 Hz), (Found: M^+, 186.1039. $C_{13}H_{14}O$ requires 186.1045), *m/z* 186 (30%, M^+), 171 (100, *M*-Me), 169 (25, *M*-OH).

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