Electron Paramagnetic Resonance Spectra of Substituted 1- and 2-Naphthylmethyl Radicals

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The EPR spectra of 7-*tert*-butyl-1-naphthylmethyl and 6-*tert*-butyl-2-naphthylmethyl radicals, prepared by photolysis of the hydrocarbon with *tert*-butyl peroxide at −40 °C, have been analysed by correlation methods: average α(C–H) coupling constants are 15.0 and 15.25 G respectively, in line with the expected relative stabilities of the two radicals and the recently reported stabilization energy for 1-naphthylmethyl.

Naphthylmethyl radicals have been prepared in a number of ways, including photolysis of 1- and 2-(halomethyl)-naphthalenes[1,2] and 1-(tributylstannylmethyl)naphthalene,[3] and by hydrogen abstraction from 1- and 2-methylnaphthalenes[2,4] for spectroscopic and reactivity studies, but no EPR studies on these radicals appear to have been carried out.

Electron parametric resonance spectra of 1- and 2-naphthylmethyl radicals would be of considerable value in comparisons of stability, reactivity and electron delocalization in benzylic radicals, but in practice, non-persistent radicals with more coupling constants than substituted benzyl radicals have proved difficult to analyse by conventional methods. We have found[5–8] that correlation methods are often valuable in analysis of weak and complex EPR spectra; here we report results for some substituted 1- and 2-naphthylmethyl radicals.

Results and Discussion

Radicals were prepared by UV photolysis of mixtures of *tert*-butyl peroxide and the appropriate methylnaphthalene in the cavity of an EPR spectrometer at −40 °C. Neither unsubstituted 1- nor 2-methylnaphthalene gave signals that could be unequivocally analysed, but we had greater success with *tert*-butyl substituted compounds, where one coupling had been removed with, hopefully, little effect on the other couplings in the radical. By using autocorrelation to establish possible coupling constants, followed by the use of MATCH, SEEK and MULTIPEAK[5,6] to evaluate coupling constants, the values for 7-*tert*-butyl-1-naphthylmethyl and 6-*tert*-butyl-2-naphthylmethyl radicals presented in Tables 1 and 2 were obtained, in spite of the low signal/noise in the spectra (see Fig. 1).

How can we be confident of our analysis? Firstly, for both radicals, in spite of the weakness of the spectra, concordant analyses were obtained from three separate spectra. Secondly, for each of the spectra, a search for extra couplings by either SEEK or MULTIPEAK indicated that none was present (a faulty analysis generally results in further couplings being found). Thirdly, the centres of the spectra, as determined by these analyses, agreed with the centres found by our direct centre-finding technique,[6] which does not depend on an analysis of the spectrum.

Further confirmation of our results, and the definite assignment of couplings to some positions, is provided by complete, partial or comparative analyses of other substituted naphthylmethyl radicals. In the 1-naphthylmethyl series, neither 3-*tert*-butyl- nor 4-D-substituents gave an unequivocal analysis. However by the autocorrelation difference method,[7] whereby the spectrum of a substituted radical is compared with that of an unsubstituted radical, individual coupling constants for the 2, 3, 4 and 7 positions were derived: these values and

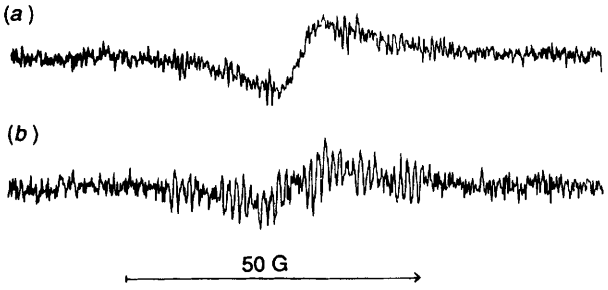

Fig. 1 EPR spectra of (*a*) 7-*tert*-butyl-1-naphthylmethyl and (*b*) 6-*tert*-butyl-2-naphthylmethyl radicals

the analysis of the 7-substituted compound were used as the starting point to provide the optimized values for the unsubstituted and 3-*tert*-butyl substituted radicals shown in Table 1. In the 2-naphthylmethyl series, the 1-bromo substituted radical was analysed unequivocally, and comparison of the autocorrelogram of the EPR spectrum of a mixture of the 6- and 7-*tert*-butyl with that of the pure 6-*tert*-butyl derivative identified the 6 and 7 couplings. These values were used as the starting point to provide the optimized coupling constants for the unsubstituted 2-naphthylmethyl radical shown in Table 2.

The α-couplings in 7-*tert*-butyl-1-naphthylmethyl are slightly lower than those of 6-*tert*-butyl-2-naphthylmethyl, in line with the greater stabilization expected for the former radical, and in qualitative agreement with INDO calculated coupling constants. The general agreement between observed and calculated values is only moderate (about as good as in benzyl): further advances in theoretical methods are clearly needed to provide better comparisons with experimental results. Our value of $a(CH_2)$ for 2-naphthylmethyl also fits on a linear plot of a(CH) for a series of radicals ArĊHR against the muon hyperfine couplings for corresponding ArĊR–CH_2Mu radicals.[9]

There is some confusion over the relationship between α coupling constants and stabilization energies in benzylic radicals. Dust and Arnold[10] postulate a linear relationship between the two, and use the relationship to derive a Hammett-type $\sigma_\alpha^\bullet$ scale of substituent constants for radical reactions. On the other hand, Rossi, McMillen and Golden[11] argue on the basis of perturbation theory for a relationship between the non-bonding molecular orbital coefficient at the α position (approximately proportional to the square root of the coupling constant) and the stabilization energy. We have argued[12] that since even Hückel calculations show no simple relationship between a_α or the NBMO coefficient with the stabilization energy, the real-life situation is unlikely to be any simpler: any correlation sought should thus relate only to a series of very similar radicals. For the series: benzyl, 1-naphthylmethyl,

Table 1 Assignment of coupling constants in EPR spectra of 1-naphthylmethyl radicals

Substituent[a]	Coupling/G									Tests[b] C	S	M
H	15.2	15.2	7.5	5.6	2.0	1.8	1.6	1.0	0.0	×	×	×
3-Bu^t	15.2	14.9	7.5	5.4	1.8	—	1.5	0.9	0.0	×	×	×
7-Bu^t	15.1	14.9	7.6	5.2	2.2	2.1	—	0.8	0.0	√	√	√
4-D/H			7.4									
3-Bu^t/H						1.8						
7-Bu^t/H							1.7					
2-Br/H				6.0								
INDO[c]	15.8	15.3	7.8	8.4	3.3	4.5	2.95	3.0	2.5			
Assignment[d]	α	α	**4**	**2**	5	**3**	**7**	8	6			

[a] Where two substituents are given, the spectra of the two radicals have been compared directly[7] to give the coupling indicated. [b] C = Centre, S = Seek, M = Multipeak. See text. √ indicates successful test; × indicates unsuccessful test. [c] INDO calculations for the unsubstituted radical, using standard geometry (C–C = 1.40 Å, C–H = 1.09 Å). [d] Assignments in bold were made as described in the text. The remainder follow the INDO calculations.

Table 2 Assignment of coupling constants in EPR spectra of 2-naphthylmethyl radicals

Substituent[a]	Coupling/G									Tests[b] C	S	M
H	15.4	15.1	7.9	3.8	2.5	1.9	1.4	1.3	1.0	×	×	×
6-Bu^t	15.4	15.1	8.0	—	2.5	2.4	1.4	1.2	1.0	√	√	√
1-Br	14.8	14.6	—	3.1	2.4	1.5	1.4	1.2	0.9	√	√	√
1-Br/H			7.1									
(6 + 7)-Bu^t/6-Bu^t				3.4			1.6					
INDO[c]	16.6	16.5	9.3	3.4	5.3	4.2	3.4	3.9	3.2			
Assignment[d]	α	α	**1**	**6**	3	4	**7**	8	5			

[a] Where two substituents are given, the spectra of the two radicals have been compared directly[7] to give the coupling(s) indicated. [b] C = Centre, S = Seek, M = Multipeak. See text. √ indicates successful test; × indicates unsuccessful test. [c] INDO calculations for the unsubstituted radical, using standard geometry (C–C = 1.40 Å, C–H = 1.09 Å). [d] Assignments in bold were made as described in the text. The remainder follow the INDO calculations.

diphenylmethyl, stabilization energies have been established by very low pressure pyrolysis (VLPP) experiments[11,13] as 42, 54 and 59 or 61[14] kJ mol^{-1}; corresponding a_α values are 16.35,[5] 15.0*,[15] and 14.7 G[16] respectively. Plots of stabilization energy against either a_α or a_α^2 are both effectively linear over this range: these plots both predict* that the stabilization energy of the 2-naphthylmethyl radical is 52 kJ mol^{-1}. (*n.b.* There is an uncertainty of 6 kJ mol^{-1} in all the VLPP experimental results from which this estimate is derived.)

Experimental

Syntheses of the methylnaphthalene derivatives are described below. 360 MHz ^{1}H NMR spectra of the final products were recorded, and the resonances were assigned to particular protons by a combination of Nuclear Overhauser Effect (NOE) difference spectra, double resonance experiments, and by comparison with the chemical shift data of ref. 17 for a range of substituted naphthalenes. The naphthylmethyl radicals were produced by photolysis of the corresponding methylnaphthalenes in solution in *tert*-butyl peroxide (1:3) at −40 °C.

3-(p-tert-*Butylbenzoyl*)*propionic Acid*.—The general procedure of Wenham and Whitehurst[18] was followed. Aluminium trichloride powder (240 g, 1.80 mol) was added in portions to a stirred mixture of *tert*-butylbenzene (120 g, 0.90 mol), succinic anhydride (80 g, 0.80 mol) and 1,1,2,2-tetrachloroethane (300 cm^3). Much frothing occurred, and the mixture became hot. After all the aluminium chloride had been added, the mixture was poured into 1.5 dm^3 of ice and dilute HCl. The organic layer was then separated, washed with water, and steam distilled to remove the tetrachloroethane. The crude acid was dissolved in sodium carbonate solution, and precipitated with HCl. 3-(*p-tert*-Butylbenzoyl)propionic acid was recrystallized from benzene to form colourless crystals (119 g, 57%) [m.p. of semicarbazone 203–204 °C (lit.,[19] m.p. 204–205 °C)], δ(CDCl$_3$) 1.35 (9 H, s, Bu^t), 2.70 (2 H, t, CH$_2$), 3.30 (2 H, t, CH$_2$), 7.77 (4 H, AB quartet, *p*-Ar), 8.70 (1 H, diffuse, CO$_2$H).

4-(p-tert-*Butylphenyl*)*butyric Acid*.—The general method of Wenham and Whitehurst was used.[18] 3-(*p-tert*-Butylbenzoyl)-propionic acid (119 g, 0.51 mol), KOH (86 g), hydrazine hydrate (68 cm^3), and ethylene glycol (450 cm^3) were refluxed for 3 h, and then distilled until the temperature of the vapour had risen to 198 °C. After a further 12 h reflux, the mixture was allowed to cool slightly, and was then poured into cold water (300 cm^3); 200 cm^3 of cold water was used to rinse the flask and was then added to the remainder of the aqueous liquid. The product was precipitated by acidification with conc. HCl, and was then filtered, and recrystallized from light petroleum (100–120 °C), to form 4-(*p-tert*-butylphenyl)butyric acid (83 g, 74%), m.p. 57–59 °C (lit.,[19] m.p. 59–60 °C), δ(CDCl$_3$) 1.25 (9 H, s, Bu^t), 1.95 (2 H, m, CH$_2$), 2.60 (2 H, t, CH$_2$), 2.35 (2 H, t, CH$_2$), 7.20 (4 H, AB quartet, *p*-Ar), 10.50 (1 H, broad, CO$_2$H).

7-tert-*Butyl*-1-*tetralone*.—The general procedure of Wenham and Whitehurst was followed.[18] 4-(*p-tert*-Butylphenyl)butyric acid (83 g, 0.38 mol) in benzene (200 cm^3) was added to phosphorus pentachloride (104 g, 1.78 mol) under benzene (200 cm^3). After 15 min, the solution was warmed on a boiling water

* It is assumed that 7- and 6-*tert*-butyl groups do not affect the α coupling constants in 1- and 2-naphthylmethyl radicals respectively.

bath for 5 min and was then cooled to 0 °C, at which point, anhydrous tin tetrachloride (250 g) was added rapidly to the well stirred solution. After 6 h stirring, the brown solution was poured onto ice/HCl, and the benzene layer was washed with HCl/water (1:1), water, dil. NaOH, and then water again, being finally dried over anhydrous magnesium sulfate. The benzene was evaporated, and the crude product was recrystallized from ethanol to yield 7-*tert*-butyl-1-tetralone (56 g, 73%), m.p. 100–102 °C (lit.,[19] m.p. 101–102.5 °C), $\delta(CDCl_3)$ 1.30 (9 H, s, Bu^t), 2.10 (2 H, m, CH_2), 2.60 (2 H, t, CH_2), 2.90 (2 H, t, CH_2), 7.20 (1 H, m, Ar), 7.50 (1 H, m, Ar), 8.05 (1 H, m, Ar).

7-tert-*Butyl*-1-*methyl*-1,2,3,4-*tetrahydro*-1-*naphthol*.—The general method of Kloetzel[20] was used. To a Grignard reagent prepared from methyl iodide (80 g, 0.56 mol) and magnesium turnings (16 g, 0.67 mol) and dry diethyl ether (200 cm^3) was added 7-*tert*-butyl-1-tetralone (56 g, 0.28 mol) in ether (200 cm^3) with stirring and cooling in ice, and the mixture was then refluxed for 30 min. The whole was then hydrolysed with ice/ammonium chloride solution while maintaining the ice-cooling. The ether layer was separated, and the aqueous layer was extracted with more ether; the ether layers were then combined and dried over anhydrous magnesium sulfate. The ether was then evaporated, and the product was recrystallized from light petroleum (40–60 °C) to yield 7-*tert*-butyl-1-methyl-1,2,3,4-tetrahydro-1-naphthol (19 g, 31%), m.p. 80–82 °C, $\delta(CDCl_3)$ 1.30 (9 H, s, Bu^t), 1.55 (3 H, s, Me), 1.85 (4 H, m, CH_2 groups), 2.70 (2 H, m, CH_2), 3.45 (1 H, s, OH), 7.15 (2 H, m, Ar), 7.65 (1 H, m, Ar), ν_{max}/cm^{-1} 3315 (OH), 1116 (C–O).

7-tert-*Butyl*-1-*methyl*-3,4-*dihydronaphthalene*.—Kloetzel's general method[20] was also used in this preparation. 7-*tert*-Butyl-1-methyl-1,2,3,4-tetrahydro-1-naphthol (19 g, 0.087 mol) was dissolved in anhydrous formic acid (80 cm^3). The crude product separated rapidly as an oil which was extracted with diethyl ether after the addition of 100 cm^3 of water. The ether extract was washed with sodium hydrogencarbonate solution, dried over anhydrous magnesium sulfate, and evaporated; the residue was then distilled under vacuum to yield 7-*tert*-butyl-1-methyl-3,4-dihydronaphthalene (14 g, 80%), b.p. 83 °C at 0.1 mmHg, $\delta(CDCl_3)$ 1.30 (9 H, s, Bu^t), 2.10 (5 H, methyl with other multiplet due to CH_2), 2.70 (2 H, m, CH_2), 5.80 (1 H, t, CH), 7.15 (3 H, m, Ar).

7-tert-*Butyl*-1-*methylnaphthalene*.—Kloetzel's aromatization method[20] was used. 7-*tert*-Butyl-1-methyl-3,4-dihydronaphthalene (10 g, 0.050 mol) was heated to 260–280 °C in a silicone oil bath with 1.0 g of 10% palladium/charcoal catalyst for 30 min; the temperature was then raised to 290 °C for 15 min to complete the dehydrogenation. The mixture was distilled under vacuum to yield 7-*tert*-butyl-1-methylnaphthalene (6.0 g, 61%), b.p. 75 °C at 0.07 mmHg (lit.,[21] b.p. 151–152 °C at 14 mmHg), purity >99% by GC, $\delta(CDCl_3)$ 1.39 (9 H, Bu^t), 2.62 (3 H, Me), 7.16 (2-H), 7.21 (3-H), 7.46 (6-H), 7.56 (4-H), 7.66 (5-H), 7.88 (8-H).

6-tert-*Butyl*-1,2,3,4-*tetrahydronaphthalene*.—Tetralin (200 g, 1.67 mol), *tert*-butyl chloride (47 g, 0.51 mol), and anhydrous zinc chloride (14 g) were heated under reflux in an oil bath at 75 °C, and the temperature was raised to 110 °C over 6 h. The zinc chloride was filtered off, and the filtrate distilled under vacuum. After the excess tetralin had been removed, a fraction distilled over to yield 6-*tert*-butyl-1,2,3,4-tetrahydronaphthalene (22 g, 23%), b.p. 82 °C at 0.12 mmHg (lit.,[19] b.p. 138–140 °C at 18 mmHg), purity 98% by GC, $\delta(CDCl_3)$ 1.30 (9 H, s, Bu^t), 1.70 (4 H, t, 2CH_2), 2.64 (4 H, t, 2 CH_2), 7.13 (3 H, m, Ar).

7-tert-*Butyl*-5-*chloromethyl*-1,2,3,4-*tetrahydronaphthalene*.—The general procedure of Grummitt and Buck[22] was followed. 6-*tert*-Butyl-1,2,3,4-tetrahydronaphthalene (20 g, 0.11 mol) was heated under reflux with paraformaldehyde (6 g), glacial acetic acid (15 cm^3), 85% *ortho*-phosphoric acid (10 cm^3), and conc. HCl (20 cm^3), with vigorous stirring for 6 h. After cooling, the mixture was washed twice with water, then with 10% potassium carbonate solution, and then with water again. Ether (20 cm^3) was added, and the solution was dried with magnesium sulfate followed by evaporation. The residue was distilled under vacuum to give 7-*tert*-butyl-5-chloromethyl-1,2,3,4-tetrahydronaphthalene (5.0 g, 20%), b.p. 106 °C at 0.12 mmHg, $\delta(CDCl_3)$ 1.25 (9 H, s, Bu^t), 1.75 (4 H, m, 2 CH_2), 2.75 (4 H, m, 2 CH_2), 4.60 (2 H, s, CH_2Cl), 7.15 (2 H, m, Ar).

7-tert-*Butyl*-5-*methyl*-1,2,3,4-*tetrahydronaphthalene*.—7-*tert*-Butyl-5-chloromethyl-1,2,3,4-tetrahydronaphthalene (5.0 g, 0.021 mol) was dissolved in dry tetrahydrofuran (20 cm^3), and added to a stirred solution of $LiAlH_4$ in THF (20 cm^3). The mixture was refluxed for 4 h, after which time it was cooled in ice, and water was carefully added, followed by dil. HCl. The THF layer was separated, dried and evaporated, and the residue was distilled under vacuum to give 7-*tert*-butyl-5-methyl-1,2,3,4-tetrahydronaphthalene (4.2 g, 98%), b.p. 82 °C at 0.1 mmHg, $\delta(CDCl_3)$ 1.20 (9 H, s, Bu^t), 1.70 (4 H, m, 2 CH_2), 2.10 (3 H, s, Me), 2.55 (4 H, m, 2 CH_2), 6.75 (2 H, m, Ar).

3-tert-*Butyl*-1-*methylnaphthalene*.—The aromatization method of Kloetzel,[20] using sulfur, was employed here. 7-*tert*-Butyl-5-methyl-1,2,3,4-tetrahydronaphthalene (4.2 g, 0.021 mol) was heated with sulfur (1.3 g, 0.041 mol) in a silicone oil bath at 230–240 °C for 1.5 h, with final heating to 270 °C for 5 min to complete the dehydrogenation. The product was distilled from the reaction mixture under vacuum to yield 3-*tert*-butyl-1-methylnaphthalene (3.1 g, 75%), b.p. 79 °C at 0.09 mmHg (lit.,[23] 138 °C at 5 mmHg), purity >99% by GC, $\delta(CDCl_3)$ 1.31 (9 H, Bu^t), 2.68 (3 H, Me), 7.30 (2 H), 7.32 (6-H, 7-H), 7.52 (4-H), 7.69 (5-H), 7.81 (8-H).

tert-*Butylation of* 2-*Methylnaphthalene*.—The literature preparation of Buu-Hoï *et al.*[24] was followed in an attempt to prepare 6-*tert*-butyl-2-methylnaphthalene; however, a mixture of the 6- and 7-*tert*-butyl derivatives resulted, as demonstrated by 360 MHz proton NMR spectroscopy.

Aluminium chloride (1.2 g) was added in small portions to a mixture of 2-methylnaphthalene (40 g, 0.28 mol) and *tert*-butyl chloride (27 g, 0.29 mol) with stirring. When the evolution of HCl had subsided, the mixture was poured onto ice, and the organic layer was dissolved in benzene. This was washed with dil. HCl and dried over anhydrous sodium sulfate, followed by evaporation of the benzene; the residue was fractionated under vacuum to yield 30 g of a mixture of the 6- and 7-*tert*-butyl derivatives of 2-methylnaphthalene (1:1), b.p. 92 °C at 0.2 mmHg.

p-tert-*Butylbenzyl Bromide*.—*p*-*tert*-Butyltoluene (75 g, 0.51 mol) was heated to 150 °C in a 250 cm^3 flask, and bromine (80 g, 1.00 mol) was added with stirring over 2 h. The evolved HBr was trapped under water.

After the addition, the mixture was poured into cold water, and the heavy oil which settled out was collected and distilled under vacuum to yield *p*-*tert*-butylbenzyl bromide (70 g, 61%), b.p. 88 °C at 0.9 mmHg (lit.,[25] 135–140 °C at 15 mmHg), $\delta(CDCl_3)$ 1.25 (9 H, s, Bu^t), 4.45 (2 H, s, CH_2), 7.35 (4 H, m, Ar).

6-tert-*Butyl*-2-*methylnaphthalene*.—The general method of Kochetkov *et al.*[26] was used in this preparation. The Grignard reagent was prepared from *p*-*tert*-butylbenzyl bromide (22 g, 0.097 mol) and magnesium turnings (2.7 g, 0.112 mol) using

diethyl ether (100 cm^3) as solvent. To this was added acetylacetaldehyde dimethyl acetal (10 g, 0.076 mol) in ether (20 cm^3) and the mixture was refluxed for 20 min. The whole was then hydrolysed with ammonium chloride solution, and the ether layer was separated, dried and evaporated. To the crude organic product was added a mixture of conc. sulfuric acid (18 g) and *ortho*-phosphoric acid (12 g), with cooling. The mixture was stirred for 15 min at room temperature, and then at 65 °C for 10 min; followed by dilution with water and addition of sodium hydroxide solution until the solution became alkaline.

The whole was then extracted with ether and the ether was evaporated; the residue was then distilled under vacuum to yield 6-*tert*-butyl-2-methylnaphthalene (5.5 g, 37%), b.p. 110 °C at 1.0 mmHg, purity >99% by GC, $\delta(CDCl_3)$ 1.19 (9 H, Bu^t), 2.22 (3 H, Me), 7.24 (3-H), 7.49 (7-H), 7.52 (1-H), 7.65 (8-H), 7.67 (4-H), 7.70 (5-H).

[α,α-$^2H_2$]-1-*Naphthylmethanol*.—1-Naphthoic acid (6.0 g, 0.035 mol) was dissolved in THF (25 cm^3) and added to $LiAlD_4$ (1.5 g, 0.036 mol) in THF (25 cm^3) with stirring. The mixture was refluxed for 4 h, and was then cooled in ice and hydrolysed with water, followed by dil. HCl.

The THF layer was dried with magnesium sulfate and evaporated; the residue was recrystallized from ether to form [α,α-$^2H_2$]-1-naphthylmethanol (4.9 g, 88%), m.p. 59–61 °C (lit.,[27] for protiated compound m.p. 60–62 °C).

[α,α-$^2H_2$]-1-*Naphthylmethyl Chloride*.—Thionyl chloride (7 g) was added dropwise, with stirring, to [α,α-$^2H_2$]-1-naphthylmethanol (4.9 g, 0.031 mol) in dry toluene (25 cm^3). The mixture was refluxed for 3 h, until no further evolution of gas occurred.

The product was distilled under vacuum to yield [α,α-$^2H_2$]-1-naphthylmethyl chloride (3.8 g, 67%), b.p. 96 °C at 0.2 mmHg.

[α-^{2}H]-1-*Methylnaphthalene*.—1-Naphthylmethyl chloride (18 g, 0.102 mol) was converted to the Grignard reagent using magnesium turnings (2.6 g, 0.108 mol) and 50 cm^3 of diethyl ether as solvent. Most of the ether was distilled off, and the residue was quenched with D_2O (3 cm^3), while cooling the flask in a dry-ice/acetone mixture. The contents of the flask were then poured off, and the solid residue was washed with ether; the combined ether washings were evaporated and the residue was fractionated to yield [α-^{2}H]-1-methylnaphthalene (5.2 g, 36%), b.p. 28 °C at 0.03 mmHg, purity >97% by GC, NMR spectroscopy shows an incompletely resolved 1:1:1 triplet at δ 2.6 (2 H), and a seven-proton aromatic multiplet.

[4-^{2}H]-1-*Methylnaphthalene*.—The Grignard reagent was prepared from 4-bromo-1-methylnaphthalene (22 g, 0.010 mol) and magnesium turnings (2.5 g, 0.104 mol) using diethyl ether (50 cm^3) as solvent. The procedure of the last preparation was then followed, giving [4-^{2}H]-1-methylnaphthalene (5.7 g, 40%), b.p. 52 °C at 0.7 mmHg, purity 96% by GC. (R_t on OV1 identical with 1-methylnaphthalene.)

1-*Methylindene*.—1-Indanone (25 g, 0.19 mol) was dissolved in dry diethyl ether (100 cm^3) and added slowly, with stirring, to the Grignard reagent from methyl iodide (36 g, 0.25 mol) and magnesium turnings (8.5 g, 0.35 mol). After refluxing for 30 min, ice (300 cm^3) and 20% sulfuric acid (100 cm^3) were cautiously added. The ether layer was dried and evaporated, and 20% sulfuric acid (100 cm^3) was added to the residue. The mixture was refluxed for 15 min, followed by steam distillation; the aqueous distillate was then extracted with ether, and the ether layer was separated, dried and distilled under vacuum, giving 1-methylindene (13.9 g, 57%), b.p. 48 °C at 1.0 mmHg (lit.,[28] b.p. 76–78 °C at 11 mmHg), $\delta(CDCl_3)$ 2.10 (3 H, s, Me), 3.20 (2 H, s, CH_2), 6.05 (1 H, s, CH), 7.45 (4 H, m, Ar).

2-*Bromo*-1-*methylnaphthalene*.—To a solution of potassium *tert*-butoxide in *tert*-butyl alcohol, prepared from potassium metal (0.6 g, 0.015 mol) and *tert*-butyl alcohol (25 cm^3), was added 1-methylindene (13.9 g, 0.107 mol) with stirring. Bromoform (3.9 g, 0.015 mol) was added to the dark-coloured mixture, over 5 min, and the whole was stirred for a further 3 h. Ice (20 g) and water (40 cm^3) were then added, followed by 3 mol dm^{-3} sodium carbonate solution (50 cm^3), and the mixture was steam distilled. The distillate was extracted with light petroleum (30–40 °C), and, after drying, the petrol was evaporated and the residue was distilled under vacuum to remove unreacted 1-methylindene. The residue from this distillation was dissolved in ethanol (15 cm^3) and refluxed with KOH (0.2 g) for 30 min, after which time the ethanol was evaporated. The dark-brown, oily residue was extracted twice with boiling light petroleum (60–80 °C), and the combined extracts were chromatographed on alumina, using light petroleum (60–80 °C) to elute the compound.

The 2-bromo-1-methylnaphthalene was finally obtained by crystallization from light petroleum (60–80 °C) after standing overnight in a refrigerator (1.3 g, 6%), m.p. 32–34 °C (lit.,[28] m.p. 31–33 °C), purity 98% by GC, $\delta(CDCl_3)$ 2.71 (3 H, Me), 7.43 (6-H, 7-H), 7.44 (4-H), 7.53 (3-H), 7.71 (5-H), 7.92 (8-H).

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