Studies in the Cyclopropa-arene Series: Approaches to Cyclopropa[*a*]-naphthalene

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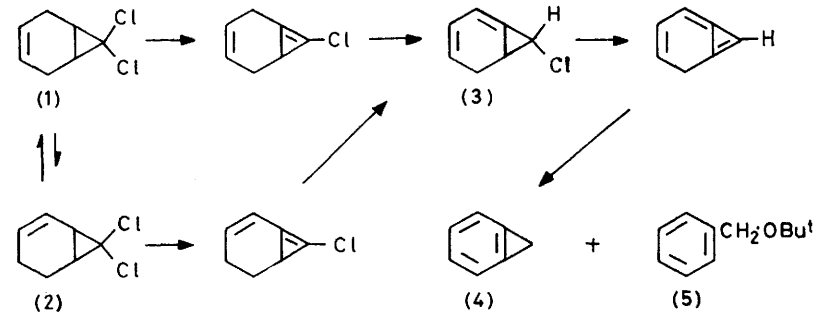
Whereas treatment of 7,7-dichlorobicyclo[4.1.0]hept-2-ene (2) with potassium t-butoxide yields cyclopropabenzene (4), analogous dehydrochlorination of the 2,3-benzo-analogue (6) does not afford cyclopropa[*a*]-naphthalene (9). Instead 1-chloromethylnaphthalene (10), 1-t-butoxymethylnaphthalene (11), and the elimination–addition product 1-chloromethylene-1,2,3,4-tetrahydro-2-t-butoxynaphthalene (12) are produced.

THE synthesis of cyclopropabenzene (4) by dehydrochlorination of 7,7-dichlorobicyclo[4.1.0]hept-3-ene (1) [1] has provided a general method for the preparation of linear cyclopropa-arenes, as demonstrated by the number of new ring systems synthesised in recent years.[2-4] Despite the interest that the method [1] has generated, the reports thus far published have been concerned with the dehydrochlorination of 7,7-dichlorobicyclo[4.1.0]heptenes either with a 3,4-double bond or with 3,4-benzo-annellation. Since the accepted route to cyclopropabenzene involves 1,2-elimination and prototropic shift (Scheme 1),[1,5,6] we have examined the dehydrochlorination of the bicyclohept-2-ene (2) in order to assess the significance of the double bond position, and to establish whether the route to linearly fused cyclopropa-arenes is adaptable to the synthesis of non-linear isomers such as cyclopropa[*a*]naphthalene (9).[7]

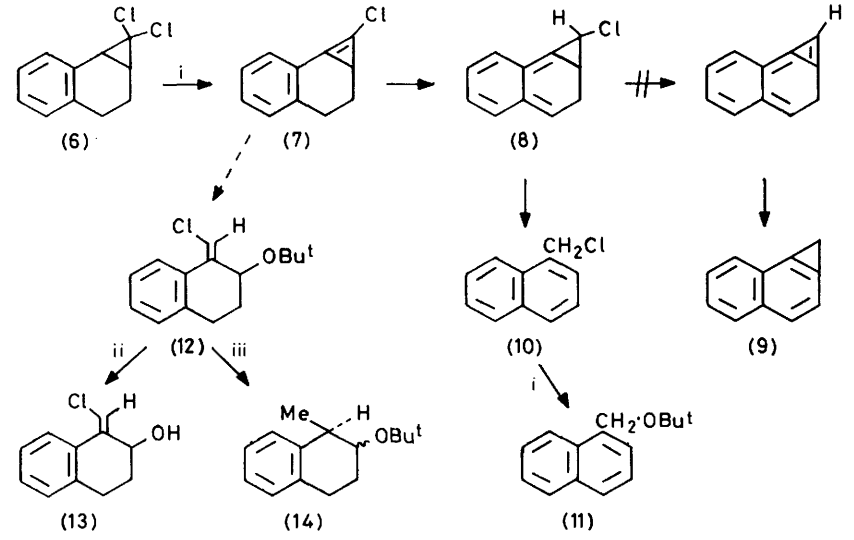
The dichlorobicyclohept-2-ene (2) [8] readily undergoes dehydrochlorination; by employing potassium t-butoxide (6.64 mol. equiv.) in dimethyl sulphoxide, cyclopropabenzene (4) is produced in essentially the same yield as can be obtained from the Δ^3-isomer (1). The reaction also leads to the same by-product, t-butoxymethylbenzene (5).[1,3] For comparison with the previously recorded data on the dehydrochlorination of compound (1),[3] the reaction of compound (2) with 4 mol. equiv. of base has been examined in detail by g.l.c. After 0.5, 1.5, 2.25, and 20.2 h the ratios of compounds (2), (4), and (5) were 42 : 48 : 3, 28 : 59 : 5, 14 : 72 : 6, and 7 : 79 : 7, respectively. For the dehydrochlorination of compound (1) under the same conditions, the ratios 5 : 82 : 9, 0 : 86 : 10, and 0 : 84 : 12 were obtained for compounds (1), (4), and (5), after 0.5, 1.5, and 18 h, respectively.[3] These data show that elimination from the bicyclohept-2-ene (2) proceeds less readily than from the bicyclohept-3-ene (1). Furthermore, the difference in the g.l.c. retention times of the olefins (1) and (2) is small and the shape of the g.l.c. peak for compound (2) from each of the reaction mixtures implies its partial isomerization to compound (1) during the reaction. Consistent with this is the known interconversion of norcar-2- and -3-ene with t-butoxide; the Δ^2-isomer undergoes isomerization three times faster than its Δ^3-counterpart.[9] Consequently, the route from 7,7-dichlorobicyclo[4.1.0]hept-2-ene (2) to cyclopropabenzene (4) is uncertain, since we are unable to differentiate between initial 1,2-elimination and [1,5] H shift to give the diene (3) in the same manifold as from the Δ^3-olefin (1), isomerization of (2) to (1) followed by elimination, or a combination of the two processes (Scheme 1). However, these results do exclude the route from compound (1) to cyclopropabenzene (4) *via* the olefin (2). The benzyl ether (5) (*ca.* 7%) found in the product mixture from compound (2) cannot arise from cyclopropabenzene (4) because of the known [3] reluctance of (4) to undergo ring cleavage under the reaction conditions.

[1] W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Comm.*, 1971, 1461; *Org. Synth.*, 1976, **55**, 12.
[2] W. E. Billups and W. Y. Chow, *J. Amer. Chem. Soc.*, 1973, **95**, 4099.
[3] A. R. Browne and B. Halton, *Tetrahedron*, 1977, **33**, 345.
[4] J. Ippen and E. Vogel, *Angew. Chem. Internat. Edn.*, 1974, **13**, 736; E. Vogel and J. Sombroek, *Tetrahedron Letters*, 1974, 1627; D. Davalian and P. J. Garratt, *J. Amer. Chem. Soc.*, 1975, **97**, 6883; *Tetrahedron Letters*, 1976, 2815; C. J. Saward and K. P. C. Vollhardt, *ibid.*, 1975, 4539; A. Kumar, S. R. Tayal, and D. Devaprabhakara, *ibid.*, 1976, 863; P. J. Garratt and W. Koller, *ibid.*, 1976, 4177; W. E. Billups, W. T. Chamberlain, and Y. A. Mehmet, *ibid.*, 1977, 571.
[5] J. Prestien and H. Günther, *Angew. Chem. Internat. Edn.*, 1974, **13**, 276.
[6] B. Halton, *Chem. Rev.*, 1973, **73**, 113.
[7] S. Tanimoto, R. Schäfer, J. Ippen, and E. Vogel, *Angew, Chem. Interna . Edn.*, 1976, **15**, 613.
[8] W. R. Grace and Co., B.P. 1,118,900 (*Chem. Abs.*, 1968, **69**, 43,516).
[9] O. Ya. Kovner, Yu. I. Ranneva, E. M. Mil'vitskaya, I. V. Shapiro, E. A. Kalmykova, A. I. Shatenshtein, and A. F. Plate, *Zhur. org. Khim.*, 1976, **12**, 998 (*Chem. Abs.*, 1976, **85**, 45,800).

In view of the success achieved in the dehydrochlorination of compound (2), analogous reactions have been performed with the dichlorotetrahydrocyclopropa[*a*]naphthalene (6) in an attempt to provide a more convenient synthesis of cyclopropa[*a*]naphthalene (9).[7] Compound (6) undergoes efficient dehydrochlorination with t-butoxide in tetrahydrofuran in direct analogy to its cyclopropa[*b*]-isomer.[2,3] However, unlike the behaviour of 1,1-dichloro-1a,2,7,7a-tetrahydrocyclopropa[*b*]naphthalene with t-butoxide (where the product distribution is markedly dependent on the quantity of base used),[3] the same products are generated from the dichlorotetrahydrocyclopropa[*a*]naphthalene (6) in essentially the same yields irrespective of the amount of base employed. Preparative t.l.c. afforded 1-chloromethylnaphthalene (10) (9%), 1-t-butoxymethylnaphthalene (11) (8%), (*E*)-1-chloromethylene-1,2,3,4-tetrahydro-2-t-butoxynaphthalene (12) (12%), and an inseparable mixture of solids (3%) identified as $C_{22}H_{16}Cl_2$ (major) and $C_{22}H_{17}Cl$ (minor) species by high resolution mass spectrometry. No evidence for the desired cyclopropa[*a*]naphthalene (9) was obtained.



SCHEME 1



SCHEME 2 Reagents: i, $KOBu^t$–$[CH_2]_4O$; ii, HCl–EtOH; iii, H_2–PtO_2

The naphthalene derivatives (10) and (11) were identical with authentic materials,[3] and the tetrahydronaphthalene (12) was identified by chemical and spectroscopic methods. Mass spectrometry showed the presence of a $C_{15}H_{19}ClO$ species, and the u.v. spectrum was consistent with a styrene-like chromophore. The ^1H n.m.r. spectrum showed one deshielded aromatic proton (δ 8.02), and a singlet for the t-butyl protons (δ 1.20). In addition, resonances at δ 1.98 (2 H, complex m), 2.93 (2 H, t, benzylic), and 4.23 (1 H, t), respectively, are assigned to $ArCH_2{\cdot}CH_2{\cdot}CH$– since irradiation at the frequency of the multiplet at δ 1.98 caused the benzylic and methine resonances to collapse to broad singlets. The methine proton also exhibits allylic coupling[10] (*J* 1.5 Hz) to a single vinylic proton (δ 6.43). Acid-catalysed cleavage of the ether (12) yielded the alcohol (13), thereby eliminating its alternative formulation as a vinyl ether. Hydrogenation of compound (12) gave an *E*–*Z*-mixture of the 1,2,3,4-tetrahydro-1-methyl-2-t-butoxynaphthalenes (14). The ^1H n.m.r. spectrum of this mixture showed two methyl doublets (δ 1.19 and 1.22) with the low field arm of the high field doublet obscured by the t-butoxy-proton singlet (δ 1.23), and signals for three benzylic protons (δ 2.7—3.1). The

[10] M. Barfield, R. J. Spear, and S. Sternhell, *Chem. Rev.*, 1976, **76**, 593.

formation of a methyl-containing product in this way is compatible only with the presence of an exocyclic double bond in the precursor. The formation of the tetrahydronaphthalenes (12) and (13) as *E*-isomers is consistent with the observed deshielding of the C-8 aromatic proton (δ *ca.* 8.05) and Dreiding models support this configuration as being sterically the more favoured.[11]

The failure to gain evidence for the desired cyclopropa[*a*]naphthalene (9) [7] is at first surprising, particularly in view of the successful synthesis of cyclopropabenzene (4) from the bicyclohept-2-ene (2). However, abstraction of the C-1 benzylic proton of compound (6) with base and chloride ion loss would afford the chloro-olefin (7) (Scheme 2) and, by subsequent [1,5] H shift, the high energy cyclopropanaphthalene (8) [*cf.* (1) ⟶ (3), Scheme 1] which can aromatize directly by hydrogen migration to the observed chloromethylnaphthalene (10) (Scheme 2). This last compound is known [3] to undergo nucleophilic substitution by t-butoxide under the reaction conditions to give the ether (11), thereby accounting for the major pathway in the dehydrochlorination of the tetrahydrocyclopropanaphthalene (6).

The formation of the exocyclic olefin (12) is more difficult to rationalise despite its formal derivation from compound (7) by addition of t-butyl alcohol to the 1,7a-bond. The production of small quantities of C_{22} species is thought to involve the intermediate (7) and/or (8) (Scheme 2), but the presence of these compounds, and also the ether (12), has no parallel in the dehydrochlorination of the cyclopropa[*b*]-analogue of compound (6).

The failure to obtain cyclopropa[*a*]naphthalene from compound (6), the benzo-analogue of (2), suggests that the dehydrochlorination method is inapplicable to the synthesis of non-linear cyclopropa-arenes, and we are currently exploring alternative routes to these compounds.

EXPERIMENTAL

Microanalyses were performed by Professor A. D. Campbell and his associates, Otago University, Dunedin. I.r. spectra were recorded for Nujol mulls or thin films with a Unicam SP 200 or SP 1000 spectrophotometer, unless otherwise stated, and u.v. spectra with a Shimadzu UV 200 instrument. N.m.r. spectra were recorded for solutions in deuteriochloroform (tetramethylsilane as internal standard) with a Hitachi–Perkin-Elmer R20 60 MHz instrument operating at 34 °C, and mass spectra with an A.E.I. MS 902 instrument. Merck Kieselgel GF_{254} was used for t.l.c.; preparative plates (1 m × 20 cm) were made to a thickness of 0.75 mm.

7,7-*Dichlorobicyclo*[4.1.0]*hept-2-ene* (2).—To a stirred solution of sodium methoxide (18.5 g, 0.345 mol) in pentane (130 cm³) containing cyclohexa-1,3-diene (10.0 g, 0.125 mol) at −10 to 0 °C, ethyl trichloroacetate (48.0 g, 0.250 mol) was added dropwise over 1 h. The solution was allowed to reach ambient temperature then stirred for 48 h, and water (150 cm³) was added; the organic phase was separated, washed with water (2 × 50 cm³), dried ($CaCl_2$), and concentrated under vacuum to a deep red mobile liquid. Fractional distillation gave 7,7-dichlorobicyclo[4.1.0]hept-2-ene (2) (13.5 g, 67%) as a colourless liquid, b.p. 52.5—53 °C at 1.25 mmHg (lit.,[8] 65 °C at 5.5 mmHg) (Found: C, 51.65; H, 5.2; Cl, 43.55. Calc. for $C_7H_8Cl_2$: C, 51.6; H, 4.95; Cl, 43.6%), $\nu_{max.}$ 3 025, 2 920, 1 642, 1 445, and 1 432 cm⁻¹, δ 1.96 (6 H, m) and 5.82 (2 H, m).

Cyclopropabenzene (4).—To a chilled (0 °C) and stirred solution of potassium t-butoxide (4.56 g, 40.7 mmol) in dimethyl sulphoxide (50 cm³), a solution of 7,7-dichlorobicyclo[4.1.0]hept-2-ene (2) (1.0 g, 6.13 mmol) in dimethyl sulphoxide (20 cm³) was added dropwise over 30 min. The mixture was stirred at ambient temperature for 17 h, diluted with water (100 cm³), and extracted with light petroleum (4 × 100 cm³). The combined extracts were washed with water (2 × 200 cm³), dried ($MgSO_4$), and concentrated under vacuum at 0 °C. The residual yellow oil (0.26 g, 40%) was shown by g.l.c.[3] to contain 93% of cyclopropabenzene (4), identical with a sample prepared from the dichlorobicyclohept-3-ene (1).[1,12] The reaction was repeated with compound (2) (1.89 g, 11.6 mmol) and t-butoxide (5.19 g, 46.4 mmol, 4 mol. equiv.). Samples (1 cm³) were withdrawn after 0.5, 1.5, 2.25, and 20.2 h, and shaken with water (3 cm³) and pentane (2 cm³). The compositions (%) of the pentane phases (analysed by g.l.c.[3]) are tabulated.

Compound	0.5 h	1.5 h	2.25 h	20.2 h
(2)	42	28	14	7
(4)	48	59	72	79
(5)	3	5	6	7
Unknown	7	8	8	7

1,1-*Dichloro*-1a,6,7,7a-*tetrahydrocyclopropa*[a]*naphthalene* (6).—To a stirred suspension of lithium aluminium hydride (1.6 g, 42 mmol) in ether (200 cm³) at 0 °C, a solution of α-tetralone (10.0 g, 68 mmol) in ether (75 cm³) was added dropwise over 30 min. The solution was refluxed for 45 min, cooled to 0 °C, and diluted cautiously with water. Aqueous sulphuric acid (10%; 50 cm³) was added and the ethereal layer was collected, washed with saturated sodium chloride solution (1 × 100 cm³), dried ($MgSO_4$), and concentrated in vacuum to give crude 1,2,3,4-tetrahydro-1-naphthol, which was used without further purification.

A solution of the naphthol (5.0 g, 33.8 mmol) and sulphuric acid (0.3 g) in dry methanol (25 cm³) was heated under reflux for 6 h then diluted with water (100 cm³) and extracted with ether (2 × 70 cm³). The combined extracts were washed with water (70 cm³) and saturated sodium chloride solution (70 cm³), dried [$MgSO_4$ (25 g)], and concentrated under vacuum. Distillation afforded 1,2-dihydronaphthalene (2.5 g, 57%) as a liquid, b.p. 71—72 °C at 3 mmHg (lit.,[13] 77 °C at 5 mmHg).

To a stirred solution of 1,2-dihydronaphthalene (1.0 g, 7.7 mmol) and benzyltriethylammonium chloride (0.03 g) in chloroform (15 g) at 0 °C, sodium hydroxide solution (50%; 15 g) was added dropwise over 30 min. The mixture was stirred at ambient temperature for 18 h, diluted with chloroform (50 cm³), and poured on to water (200 cm³). The organic phase was separated, washed with

[11] For related systems see, *e.g.* W. S. Ang and B. Halton, *Austral. J. Chem.*, 1971, **24**, 851.

[12] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, 1965, 3625.

[13] I. I. Chizhevsksya and Z. B. Idel'chik, *Zhur. obshchei Khim.*, 1957, **27**, 83 (*Chem. Abs.*, 1957, **51**, 12,022d).

water (20 cm³) and saturated sodium chloride solution (20 cm³), dried [$MgSO_4$ (15 g)], and concentrated in vacuum. Distillation gave 1,1-*dichloro*-1a,6,7,7a-*tetrahydrocyclopropa*[a]*naphthalene* (6) (1.12 g, 68%) as a liquid, b.p. 109—110 °C at 13 mmHg (Found: C, 61.6; H, 4.7; Cl, 34.0. $C_{11}H_{10}Cl_2$ requires C, 62.0; H, 4.7; Cl, 33.3%), $\nu_{max.}$ 3 020, 3 000, 2 920, 1 572, 1 469, and 1 450 cm⁻¹, δ 1.90—2.80 (6 H, complex m) and 6.95—7.30 (4 H, complex m).

Dehydrochlorination of 1,1-*Dichloro*-1a,6,7,7a-*tetrahydrocyclopropa*[a]*naphthalene* (6).—To a chilled (0 °C) and stirred suspension of potassium t-butoxide (2.73 g, 24.4 mmol) in tetrahydrofuran (50 cm³), a solution of the tetrahydrocyclopropa[*a*]naphthalene (6) (1.30 g, 6.1 mmol) in tetrahydrofuran (20 cm³) was added dropwise over 1.5 h. The solution was stirred at ambient temperature for 18 h and the solvent removed under vacuum. The residue was extracted with benzene (150 cm³) and the extract washed with water (2 × 100 cm³), dried ($MgSO_4$), and concentrated under vacuum. Preparative t.l.c. [benzene–light petroleum (1 : 1)] of the resulting orange oil gave three bands (A—C), R_F 0.7—1.0, 0.6—0.7, and 0—0.5, respectively. The bands were extracted [chloroform (100 cm³)] and separately re-subjected to preparative t.l.c.

The material from band A (270 mg) (eluted from light petroleum) gave two overlapping bands, D and E (R_F 0.7 and 0.6, respectively), which were extracted with chloroform (100 cm³). Band D gave an inseparable mixture of two solids (*ca.* 50 mg, 3%) the major component of which was a $C_{22}H_{16}Cl_2$ species (*m/e* 350.062 700. Calc. for $C_{22}H_{16}{}^{35}Cl_2$: 350.062 891) and the minor component a $C_{22}H_{17}Cl$ compound (*m/e* 316.102 340. Calc. for $C_{22}H_{17}{}^{35}Cl$: 316.101 863). Band E afforded 1-chloromethylnaphthalene (10) (95 mg, 9%) as an oil, identical with a commercial sample.[3]

The material from band B (270 mg) [eluted with benzene–light petroleum (1 : 4)] gave band F (R_F 0.6), which was extracted with chloroform (100 cm³) to yield (E)-1-*chloromethylene*-1,2,3,4-*tetrahydro*-2-*t*-*butoxynaphthalene* (12) (180 mg, 12%) as an oil (Found: M^+, 250.112 870. $C_{15}H_{19}{}^{35}ClO$ requires M, 250.112 429), $\nu_{max.}$ 3 080, 2 985, 2 940, 2 880, 1 625, 1 605, 1 490, 1 465, and 1 400 cm⁻¹, $\lambda_{max.}$ 250 (log ε 3.87), 280sh (2.94), and 290sh nm (2.81), δ 1.20 (9 H, s), 1.98 (2 H, m), 2.93 (2 H, t of d, J 6.5 and 2 Hz), 4.23 (1 H, t of d, $J_{2,3}$ 6.5, $J_{2,11}$ 1.5 Hz), 6.43 (1 H, d, $J_{11,2}$ 1.5 Hz), 7.11 (3 H, m), and 8.02 (1 H, m). Irradiation at δ 4.23 caused collapse of the doublet at δ 6.43 to a singlet and of the multiplet at δ 1.98 to a pair of overlapping triplets. Irradiation at δ 2.93 caused collapse of the multiplet at δ 1.98, but had no effect on the signals at δ 4.23 and 6.43. Irradiation at δ 1.98 caused collapse of the triplets at δ 2.93 and 4.23 to broadened singlets.

The material from band C [eluted with benzene–light petroleum (2 : 3)] gave band G (R_F 0.7), which was extracted with chloroform (100 cm³) to yield 1-t-butoxymethylnaphthalene (11) (110 mg, 8%) as an oil identical with a sample independently prepared from 1-chloromethylnaphthalene (10).[3]

On repeating the reaction with 8, 16, and 32 mol. equiv. of base, the same products were obtained with yields as recorded above ±1.5%.

(E)-1-*Chloromethylene*-1,2,3,4-*tetrahydro*-2-*naphthol* (13).—A solution of (*E*)-1-chloromethylene-1,2,3,4-tetrahydro-2-t-butoxynaphthalene (12) (180 mg, 0.72 mmol) in ethanol (10 cm³) acidified with hydrochloric acid (1 cm³; 2M) was heated under reflux for 5 h, cooled, and extracted with chloroform–water (1 : 1; 100 cm³). The separated organic phase was washed with water (2 × 20 cm³), dried (Na_2SO_4), and concentrated in vacuum to a syrup which on preparative t.l.c. [benzene–light petroleum (1 : 1)] gave three bands (A—C); these were extracted with chloroform (100 cm³). Band A (R_F 0.8) afforded unchanged (12) (23 mg, 13% recovery). Band B (R_F 0.6) gave traces of unidentified material (10 mg). Band C (R_F 0.1) yielded a crystalline solid identified as (E)-1-*chloromethylene*-1,2,3,4-*tetrahydro*-2-*naphthol* (13) (70 mg, 50%), m.p. 59—61° (Found: M^+, 194.049 510. $C_{11}H_{11}{}^{35}ClO$ requires M, 194.049 835), $\nu_{max.}$ 3 350, 3 060, 2 930, 1 620, 1 600, and 1 485 cm⁻¹, δ 2.08 (2 H, m), 2.10 (1 H, s, exchangeable), 2.97 (2 H, m), 4.45 (1 H, slightly broadened t, $J_{2,3}$ 5 Hz), 6.37 (1 H, slightly broadened s), 7.15 (3 H, m), and 8.11 (1 H, m).

(E)- *and* (Z)-1,2,3,4-*Tetrahydro*-1-*methyl*-2-*t*-*butoxynaphthalene* (14).—A solution of (*E*)-1-chloromethylene-1,2,3,4-tetrahydro-2-t-butoxynaphthalene (12) (100 mg, 0.4 mmol) in ethanol (5 cm³) was hydrogenated over Adams catalyst. After uptake ceased, the solution was filtered and concentrated in vacuum to an oily solid. Preparative t.l.c. [benzene–light petroleum (1 : 4)] gave a single band (R_F 0.6) which was extracted with chloroform (100 cm³) to yield a mixture of (E)- and (Z)-1,2,3,4-*tetrahydro*-1-*methyl*-2-*t*-*butoxynaphthalene* (14) (51 mg, 59%) as an oil (Found: M^+, 218.167 380. $C_{15}H_{22}O$ requires M, 218.167 051), $\nu_{max.}$ 3 060, 3 020, 2 985, 1 535, 1 505, 1 430, and 1 410 cm⁻¹, δ 1.19 and 1.22 (3 H, two d, J 7 Hz), 1.23 (9 H, s), 1.55—2.2 (2 H, complex m), 2.70—3.10 (3 H, m), 3.50—3.8 and 3.7—4.06 (1 H, two m), and 7.10 (4 H, s).

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