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Original Scientific Paper

Non-degenerate Exchange of 1,2-Dialkyl Groups in Naphthalenium Cations*

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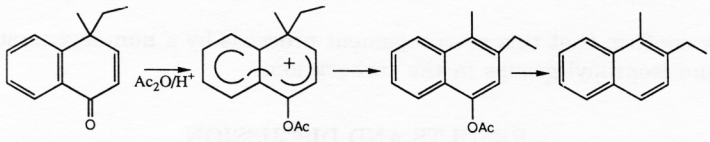
Protonation of 1-isopropyl-D_5(Me)-2-methylnaphthalene in FSO_3H/$/SO_2ClF$ leads initially to the *ipso* (C-1) protonated naphthalenium ion, which slowly rearranges irreversibly at –80 °C to the C4-protonated 2-isopropyl-D_5(Me)-1-methylnaphthalenium cation, the two alkyl groups having thus *exchanged* positions. A similar exchange does not occur in the case of 1-ethyl-2-methyl-naphthalenium cation. A possible mechanism for this unique rearrangement is discussed.

INTRODUCTION

The relative migratory aptitude of alkyl groups in protonated alkyl aromatic hydrocarbons is well established to be Me < Et < *i*-Pr < *t*-Bu.[1] The dienone-phenol rearrangement[1,2] has been used to create competitive migration of one of the two alkyl groups of a geminal, 1,2-dialkylnaphthalenone to the vicinal carbon.[3] Thus treatment of **1** with acetic anhydride/sulfuric acid gave the rearranged acetate **2** exclusively, as shown by NMR spectroscopy and by reduction to the known 1-methyl-2-ethylnaphthalene (**3**)[3,4] (Scheme 1).



1 2 3

Scheme 1

In a more recent study of cyclopropa[a]naphthalenium cations it was shown that treatment of the alcohol **4** with FSO_3H at –100 °C gave the rearranged cation **5** which underwent further rearrangement on warming to yield the 2-isopropyl-1-methylnaph-

* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
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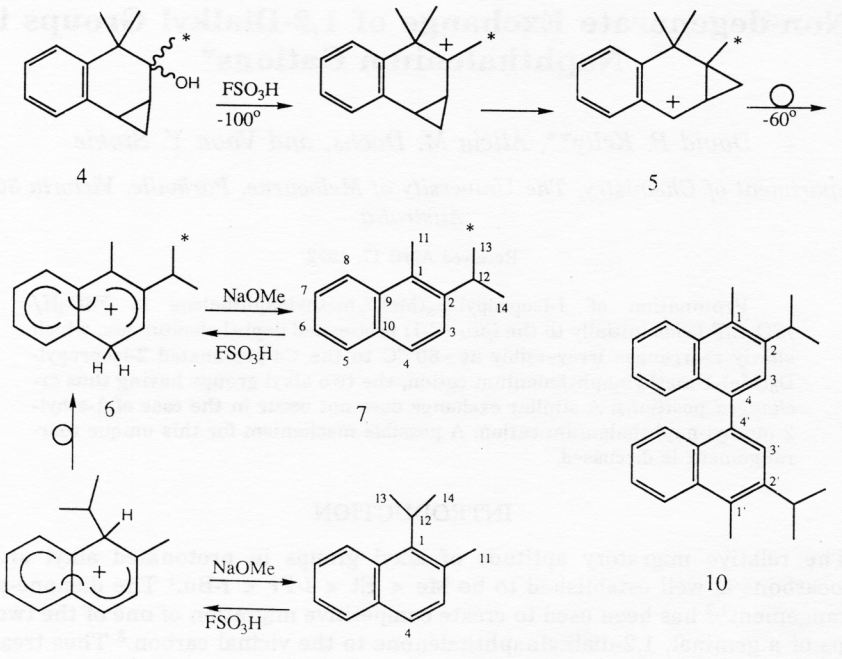
thalenium cation (**6**)[5] (Scheme 2). The later was identified by similarity of its ^{13}C NMR spectrum to that of protonated 1,2-dimethylnaphthalene,[6] by isolation of 2-isopropyl-1-methylnaphthalene upon quenching in methoxide/methanol,[5] by its generation from authentic hydrocarbon **7** and by isolation of 2-isopropyl-D_3(Me)-1-methylnaphthalene (**7**)-D_3 from the quenched cation derived from **4**-2-D_3(Me).[5] A surprising result was that protonation of the regioisomer 1-isopropyl-2-methylnaphthalene (**8**) yielded the ipso,[7,8] protonated species **9** but on quenching in methoxide/methanol after storage for one week at –80 °C, the product isolated was the hydrocarbon **7**, not **8**[5] (Scheme 2).



Scheme 2

We now confirm that this rearrangement proceeds by a non-degenerate *exchange* of methyl and isopropyl groups in the carbocation.

RESULTS AND DISCUSSION

1-Isopropyl-D_5-2-methylnaphthalene (**8**), in which the isopropyl group was labelled (CD_3CHCD_2H), was prepared by hydrogenation of 1-isopropenyl-D_5-2-methylnaphthalene from acetone-D_6 and 1-bromo-2-methylnaphthalene.[9] Treatment of **8**-D_5 with FSO_3H/SO_2ClF at –80 °C gave a red-brown solution, the ^{13}C NMR spectrum of which was identical to that previously recorded for **9**, except for the low intensity multiplets at 15.4 (CD_3) and 23.3 (CD_2H) ppm[5] (Figure 1A). After storage for one week at –80 °C, the solution was considerably darker and gave a ^{13}C NMR spectrum consistent with a mixture (~ 1:1) of the two cations **9** and **6** (δ Cl of **6** at 200.1, δ Cl of **9** at 65.9 ppm)[5] (Figure 1B). After four weeks storage the solution was dark green and showed no sig-

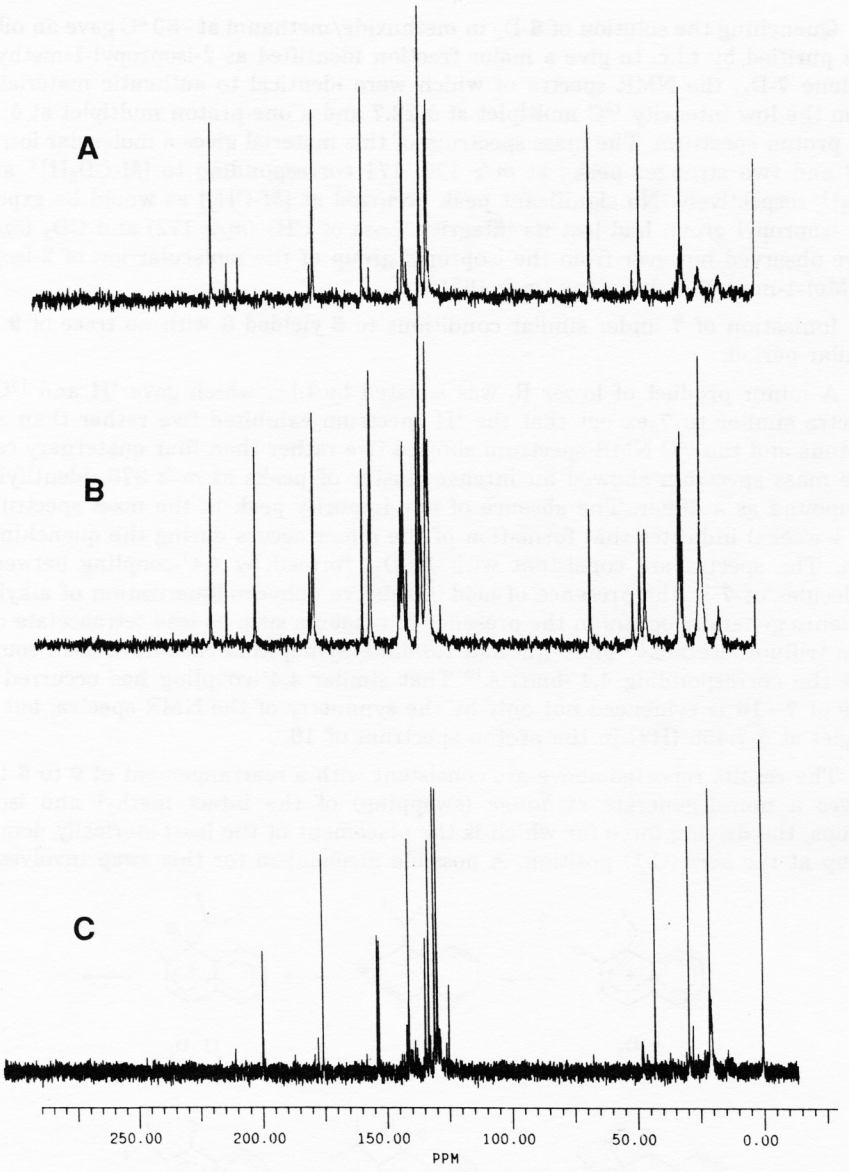


Figure 1. ^{13}C NMR spectra of the rearrangement process **9** $\xrightarrow{0}$ **6** at –80 °C: A, **9**-D_5; B, after 1 week; C, after 4 weeks, **6**-D_5.

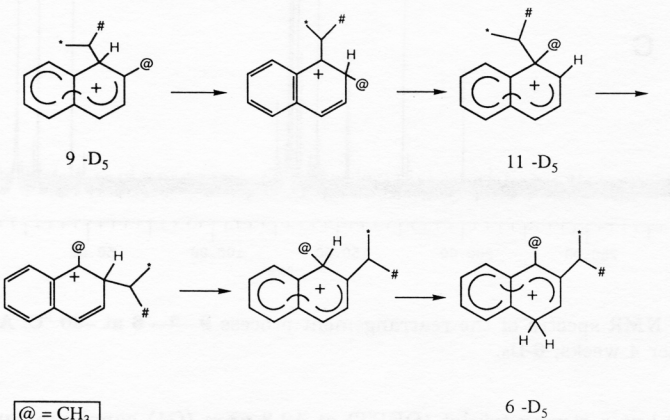
nal at δ 65.9 but a strong triplet (DEPT) at 42.8 ppm (C4) consistent only with **6**. In addition, only one low intensity multiplet was observed at 21 ppm, consistent with the equivalent methyl resonances, C11, 13, 14 previously observed for **6**. The resonance of the C11 methyl group had moved from δ 29.6 to 22.0 ppm (Figure 1C).

Quenching the solution of **6**-D_5 in methoxide/methanol at –80 °C gave an oil which was purified by t.l.c. to give a major fraction identified as 2-isopropyl-1-methylnaphthalene **7**-D_5, the NMR spectra of which were identical to authentic material, apart from the low intensity ^{13}C multiplet at δ 22.7 and a one-proton multiplet at δ 1.26 in the proton spectrum. The mass spectrum of this material gives a molecular ion at *m/z* 189 and two stronger peaks at *m/z* 172, 171 corresponding to $[M\text{-}CD_2H]^+$ and $[M\text{-}CD_3]^+$ respectively. No significant peak occurred at $[M\text{-}CH_3]$ as would be expected if the isopropyl group had lost its integrity. Loss of CH_3 (*m/z* 172) and CD_3 (*m/z* 169) were observed however from the isopropyl group of the molecular ion of 2-isopropyl-D_3(Me)-1-methylnaphthalene (*m/z* 187).[5]

Ionisation of **7** under similar conditions to **8** yielded **6** with no trace of **9** after a similar period.

A minor product of lower R_f was isolated by t.l.c. which gave ^1H and ^{13}C NMR spectra similar to **7** except that the ^1H spectrum exhibited five rather than six aryl protons and the ^{13}C NMR spectrum showed five rather than four quaternary carbons. The mass spectrum showed an intense cluster of peaks at *m/z* 376, identifying the compound as a dimer. The absence of any impurity peak in the mass spectrum of **6** (at 4 weeks) indicates that formation of the dimer occurs during the quenching reaction. The spectra are consistent with **10**-D_{10} formed by 4,4′-coupling between two molecules of **7** in the presence of acid. Oxidative dehydrodimerization of alkyl naphthalenes generally occurs in the presence of reagents such as lead tetraacetate or thallium trifluoroacetate.[10] Thus 1,2- and 1,8-dimethylnaphthalenes have been coupled to give the corresponding 4,4′-biaryls.[10] That similar 4,4′-coupling has occurred in the case of **7**→**10** is evidenced not only by the symmetry of the NMR spectra, but by the singlet at δ 7.456 (H3) in the proton spectrum of **10**.

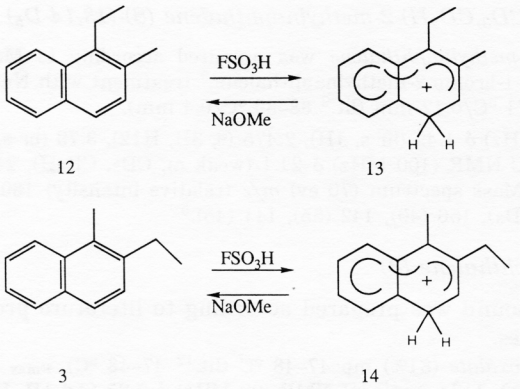
The results reported above are consistent with a rearrangement of **9** to **6** that involves a non-degenerate *exchange* (swapping) of the intact methyl and isopropyl groups, the driving force for which is the placement of the least sterically demanding group at the *peri* (C-1) position. A possible mechanism for this swap involves a 1,2-



Scheme 3

hydride shift, a 1,2-methyl migration to generate a 1,1-dialkylnaphthalenium system **11** as in the dienone-phenol rearrangement (Scheme 1), followed by migration of the isopropyl group to the vacant 2-position. Subsequent 1,2-H and 1,4-H shifts then afford **6**-D_5 (Scheme 3). (We cannot exclude, at this stage, the possibility that the isopropyl group migrates first to give a 2,2-dialkylnaphthalenium system, which is then followed by the methyl migration.).

In order to explore the generality of this rearrangement 1-ethyl-2-methylnaphthalene (**12**) was subjected to similar conditions as **8** but unlike **8** the ^{13}C NMR spectrum of the cation produced at –80 °C showed peaks consistent with protonation at C4 only (triplet at δ 43.7), cation **13**. After two weeks at –80 °C the spectrum was unchanged. Warming of the solution to –40 °C resulted in no change of the spectrum. Protonation of the isomeric 2-ethyl-1-methylnaphthalene (**3**) occurs also at C4 (triplet at δ 43.5) in a similar manner to **7**, to yield cation **14**. Quenching of the cations **13** and **14** regenerates the hydrocarbons **12** and **3** respectively (Scheme 4).

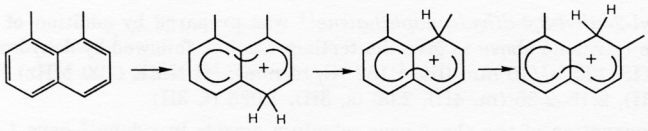


12 13

3 14

Scheme 4

It is obvious that the 1,8 (peri) interaction is sufficiently large in the case of H and *i*-Pr to favour rearrangement. Initial relief of strain occurs with the formation of a tetrahedral centre by protonation at C1 to give **9**, followed by migration of the isopropyl group. Rearrangement has also been reported in the case of 1,8-dimethylnaphthalene, where the initially formed C4-protonated cation **15** rearranges *via* the C1-protonated cation **16** to the 1,7-dimethylnaphthalenium cation (**17**) (Scheme 5).[6] However, the steric interaction between H and Et is obviously less than both H/*i*-Pr and Me/Me, the cations being stable and relatively unaffected by temperature increases. Estimates



15 16 17

Scheme 5

of the steric strain may be elicited from the kinetics of hydrogenation of 1-alkyl- and 1,8-dialkylnaphthalenes, the relative rates being 4.9, 6.8, 6.2 and 59 for 1-Me, 1-Et, 1-*i*-Pr and 1,8-Me_2 respectively.[11] Although there is little difference between the rates for Et and *i*-Pr, the greater *peri* strain in the latter case is shown by the preference for hydrogenation of the substituted ring over that of the unsubstituted ring.[11]

EXPERIMENTAL

The hydrocarbons were prepared by literature procedures from commercially available starting materials. Melting points are uncorrected. NMR spectra were recorded of $CDCl_3$ (hydrocarbons) or SO_2ClF (cations) solution on JEOL FX-90, FX-100 or GX-400 spectrometers. Chemical shifts of the cation solutions were referenced to external Me_4Si (capillary of Me_4Si and acetone-D6) and those of $CDCl_3$-solutions to internal Me_4Si or to the solvent taken as δ 7.26 (^1H) or 77.0 (^{13}C). Mass spectra were recorded on a Micromass VG 70/70 F spectrometer in positive ion, electron impact (70 eV) mode. Infrared spectra were recorded as films (NaCl) on a Perkin Elmer 983 spectrometer.

*1-Isopropyl-(13,14-CD_3,CD_2H)-2-methylnaphthalene (**8**)-(13,14-D_5)*

1-Isopropyl-D_5-2-methylnaphthalene was prepared according to Mannschreck and Ernst from acetone-D_6 and 1-bromo-2-methylnaphthalene;[9] treatment with $NaBH_4$ in diglyme yielded **9**-D_5, (57%) b.p. 70–71 °C/0.12 mm (lit.[9] 88–89 °C/0.4 mm).

^1H NMR (400 MHz) δ 1.49 (br s, 1H), 2.475 (s, 3H, H12), 3.79 (br s, 1H, H9), 7.20–7.8 (m, 5H), 8.23 (d, 1H); ^{13}C NMR (100 MHz) δ 21.1 (weak m, CD_3, CD_2H), 21.57 (s, C12), 28.76 (br s, C9) plus aryl C.[5] Mass spectrum (70 ev) *m/z* (relative intensity) 189 (56, *M*), 172 (100, *M*-CD_2H), 171 (87, *M*-CD_3), 156 (40), 142 (55), 141 (45).[5]

*1-Methyl-2-ethylnaphthalene (**3**)*

The title compound was prepared according to literature procedures *via* the following intermediates.

1-Tetralone-2-glyoxalate (81%) mp 47–48 °C (lit.[12] 47–48 °C), ν_{max} (film) 3400 (br), 1718, 1614, 1591, 1282, 1293, 1174 cm^{-1}; ^1H NMR (90 MHz) δ 7.95 (d,d 1H, H8), 7.15–7.55 (m, 3H), 4.30 (q 2H), 2.85 (br s, 4H), 1.35 (t, 3H); ^{13}C NMR (22.5 MHz) δ 186.4 (C1), 170.2 (C2′), 162.8 (C1′-enol), 142.3 (s), 133.4 (d), 131.1 (s), 127.8 (d), 126.9 (d), 126.8 (d), 108.4 (s, C2), 61.9 (t), 27.9 (t), 22.3 (t), 13.9 (q).

2-Ethoxycarbonyl-1-tetralone[12,13] b.p. 92–94 °C/0.05 mm (lit.[11] 116–120 °C/0.2 mm), recrystallised (–10 °C) from petroleum ether (40–60 °C), m.p. 34–35°, ν_{max} (film) 1740, 1690, 1640, 1610 cm^{-1}; ^1H NMR (90 MHz) δ 7.8 (m, H8), 7.1–7.35 (m, 3H), 4.25 (q, 2H), 2.45–2.90 (m, 5H), 1.35 (t, 3H); ^{13}C NMR (22.5 MHz) δ 172.7 (C1), 165.0 (C1′), 139.3 (s), 130.4 (d), 130.0 (s), 127.3 (d), 126.5 (d), 124.2 (d), 96.9 (d, C2), 60.4 (t), 27.7 (t), 20.5 (t), 14.2 (q); mass spectrum (70 eV) *m/z* (%) 218 (*M*, 60), 172 (65), 144 (100), 118 (68), 115 (57), 90 (55).

2-Ethyl-1-tetralone[12,14,15] b.p. 72–76 °C/1 mm (lit.[14] 168–180 °C/4 mm) ν_{max} (film) 1681 cm^{-1}; ^1H NMR (60 MHz) δ 8.0 (m, 1H, H8), 7.2–7.6 (m, 3H), 3.0 (m, 1H) 1.4–2.65 (m, 6H), 1.0 (t, 3H).

1-Methyl-2-ethyl-3,4-dihydronaphthalene[14] was prepared by addition of methyl magnesium iodide to the tetralone above to give the tertiary alcohol, followed by dehydration with $KHSO_4$,[14] (74%) b.p. 118–120 °C/10 mm (lit.[14] 132 °C/14 mm); ^1H NMR (400 MHz) δ 7.03–7.21 (m, 4H), 2.668 (m, 2H), 2.15–2.25 (m, 4H), 2.00 (s, 3H), 1.025 (t, 3H).

Dehydrogenation of the above over selenium dioxide in xylene[16] gave *1-methyl-2-ethylnaphthalene (**3**)* (48%) b.p. 125 °C/(oven)/0.5 mm (lit. 140–145 °C/11 mm,[14] 155 °C/30 mm[15]); ^1H NMR (90 MHz) δ 7.13–7.49 (m, 6H), 2.71 (q, 2H), 2.49 (s, 3H), 1.16 (t, 3H); ^{13}C NMR (22.5 MHz) δ 139.1 (s), 133.1 (s), 132.2 (s), 130.1 (s), 128.3 (d), 127.6 (d), 126.0 (d), 125.6 (d), 124.4 (d), 123.8 (d), 27.4, 15.3, 13.8.

1-Ethyl-2-methylnaphthalene (12)

1-Ethyl-2-methylnaphthalene (12) was prepared in a manner similar to **3** *via* 2-methyl-1-tetralone, b.p. 100–102 °C/4 mm (lit.[14] 136–138 °C/16 mm); ^{1}H NMR (90 MHz). δ 8.05 (d,d, 1H, H8), 7.1–7.5 (m, 3H), 2.85–3.10 (m, 2H), 1.7–2.7 (m, 3H), 1.25 (d, J = 7 Hz, 3H); ^{13}C NMR. δ 200.4 (s), 143.9 (s), 132.9 (d), 132.2 (s), 128.5 (d), 127.1 (d), 126.3 (d), 42.4 (d), 31.2 (t), 28.6 (t), 15.2 (q).

2-Ethyl-1-methyl-3,4-dihydronaphthalene, b.p.. 122–124 °C/8 mm (lit.[14] 132 °C/14 mm); ^{1}H NMR (60 MHz) δ 7.0–7.3 (m, 4H), 2.0–2.8 (m, 6H), 1.82 (s, 3H), 1.05 (t, 3H); ^{13}C NMR (22.5 MHz) δ 135.8 (s), 131.7 (s), 131.4 (s), 127.2 (d), 126.2 (d), 125.9 (s), 125.4 (d), 122.2 (d), 30.6, 28.6, 21.0, 19.9, 13.6.

Dehydrogenation as above[16] gave 1-ethyl-2-methylnaphthalene (**12**) b.p. 100–104 °C/6 mm (lit. 133–135 °C/15 mm[14], 153 °C/30 mm[15]); ^{1}H NMR (90 MHz) δ 7.2–7.05 (m, 6H), 3.05 (q, J = 8 Hz, 2H), 2.44 (s, 3H), 1.22 (t, J = 8 Hz, 3H); ^{13}C NMR (22.5 MHz) δ 137.2 (s), 132.6 (s), 132.3 (s), 131.8 (s), 129.2 (d), 128.5 (d), 125.7 (d × 2), 124.3 (d), 123.5 (d), 21.6 (t), 19.9 (q), 14.2 (q).

Generation and quenching of cations. The cation solutions were prepared as described previously,[5] by slow addition of the hydrocarbon dissolved in cold SO_2ClF to the rapidly stirred (vortex) mixture of FSO_3H/SO_2ClF (1:1 pbv) at –78 °C. The solutions were quenched by their slow addition to excess sodium methoxide in methanol at –78 °C with rapid stirring. The mixtures were allowed to warm to room temperature, diluted with water until clear, extracted with pentane, dried and evaporated to yield yellow oils. Compounds **7**-D_5 and **10**-D_{10} were isolated from the oil by preparative thin layer chromatography.

1-Isopropyl-13,14-CD_3CD_2H)-2-methylnaphthalenium (9)-D_5, 0.5 M; ^{13}C NMR δ (25. MHz, –80 °C)[5] 217.9, 176.7, 157.0, 140.7, 140.4, 133.8, 131.1, 130.8, 65.8, 45.9 (C12), 29.6, (C11), 23.3 (br m, C13), 15.4 (br m, C14).

2-Isopropyl-(13,14-CD_3CD_2H)-1-methylnaphthalenium (6)-D_5. From rearrangement of **9**-D_5; ^{13}C NMR (100 MHz, –60 °C) δ 43.8 (t, DEPT, C4), 30.3 (C12), 22.0 (C11), 20.5 (br m, C13,14), plus 10 aryl carbons.[5]

Quenching of **6**-D_5 and chromatography of the resulting oil gave **7**-D_5 and **10**-D_{10}: *2-isopropyl-(13,14-D_5)-1-methylnaphthalene*[5] (**7**)-D_5, R_f 0.9; ^{1}H NMR (400 MHz) δ 8.050 (dd, J = 7.8, 1.0 Hz, 1H), 7.786 (dd, J = 8.0, 1.5 Hz, 1H), 7.696 (d, J = 8.7 Hz, 1H), 7.485 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.436 (d, J = 8.7 Hz, 1H), 7.409 (ddd, J = 7.8, 6.8, 1.0 Hz, 1H), 3.444 (d, J = 6.6 Hz, H12), 2.656 (s, 3H, H11), 1.267 (br d, J = 6.6 Hz, 1H, H13). ^{13}C NMR (100 MHz) δ 143.2, 132.9, 131.9, 129.4, 128.3, 126.2, 125.7, 124.6, 124.2, 123.6, 29,33, 22.7 (m, CD_3CD_2H) 13.7; mass spectrum *m/z* (%) 190 (15, *M* + 1), 189 (73, *M*), 188 (9), 173 (18), 172 (100, *M*-CD_2H),171 (88, *M*-CD_3), 157 (19), 156 (29), 155 (20), 143 (13), 142 (38), 141 (27).

2,2′-Di (isopropyl-D_5-1,1′-dimethyl-4,4′-binaphthalene (**10**)-D_{10}, R_f 0.8, colourless prisms from ethanol, m.p. 141–143 °C; ^{1}H NMR (400 MHz, »100%« $CDCl_3$) δ 8.155 (ddd, J = 8.5, 1.0, 0.7 Hz, 2H, H8,8′), 7.483 (ddd, J = 8.5, 6.8, 1.2 Hz, 2H), 7.456 (s, 2H, H3,3′), 7.456 (s, 2H, H3,3′), 7.416 (d m, J = 8.2, 0.7 Hz, 2H, H5,5′), 7.223 (ddd, J = 8.2, 6.8, 1.2 Hz, 2H), 3.535 (br d, J = 6.8 Hz, 2H, H12,12′), 2.770 (s, 6H), 1.263 (br m, 2H, CD_2H × 2). ^{13}C NMR (100 MHz) δ 142.7 (s), 137.1 (s), 132.9 (s), 131.5 (s), 129.1 (s), 127.1, 125.9, 125,6, 124.6, 124.3, 29.46, 22.7 (br m), 13.89. Mass spectrum *m/z* (%) 378 (*M*+2, 7), 377 (*M*+1, 37), 376 (*M*, 100), 375 (*M*-1, 22), 359 (*M*-CD_2H, 17) 358 (*M*-CD_3, 15), Found: M^+, 376.2975. $C_{28}H_{20}D_{10}$ requires 376.2975.

1-Ethyl-1-methylnaphthalenium (13). ^{13}C NMR (25, MHz, –80 °C) δ 204.8 (s, C1), 179.7 (d, C3), 154.6 (s), 143.7 (s), 141.7 (d), 133.5 (s), 133.3 (d), 131.5 (d), 130.7 (d), 43.7 (t, C4), 29.3 (t), 19.8 (1), 15.8 (q).

2-Ethyl-1-methylnaphthalenium (14). ^{13}C NMR (25 MHz, –80 °C) δ 200.8 (s, C1), 176.6 (d, C3), 153.8 (s), 149.2 (s), 141.8 (d), 134.7 (s), 133.6 (d), 131.4 (d), 130.4 (d), 43.5 (t, C4), 26.7 (t), 22.4 (q), 12.4 (q).

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SAŽETAK

Nedegenerirana izmjena 1,2-dialkilnih skupina u naftalenijevu kationu

David P. Kelly, Alicia Dachs i Voon Y. Stokie

Protoniranjem 1-izopropil-D_5(Me)-2-metilnaftalena u FSO_3H/SO_2ClF na –80 °C generiran je *ipso* (C-1) protonirani naftalenijev ion i ^{13}C NMR spektrometrijom praćena njegova ireverzibilna pregradnja u C-4 protonirani 2-izopropil-D_5(Me)-1-metilnaftalenijev kation. Diskutira se o mehanizmu pregradnje.