refined by full-matrix least squares.

Special precautions were required to prevent loss of benzene from crystals of **1·4B** during data collection. The crystal was mounted by placing it inside a 0.5-mm Lindemann glass capillary, then drawing some benzene into the tube by capillary action, and finally sealing the two ends of the tube with epoxy cement. The crystal orientation shifted only once, prior to data collection, and remained stable during the data collection period. There was no apparent deterioration of the crystal during this period; although there was occasional ±5% variation in the intensity of individual reference reflections, the average of the five reference reflections remained constant within ±1%.

Sixteen reflections in **1** that were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indexes for **1** are $R = 0.051$ and $wR = 0.068$ for the remaining 1157 observed reflections; the final difference map has no peaks greater than ±0.2 e Å^{-3}. For **1·4B**, the final discrepancy indexes are $R = 0.086$ and $wR = 0.076$ for the 1363 observed reflections. The final difference map has no peaks greater than ±0.3 e Å^{-3} except for two peaks of 0.5 e Å^{-3}. Final atomic parameters for **1** and **1·4B** are given in Tables VI and VII, respectively (see paragraph at end of paper regarding supplementary material).

Acknowledgment. We thank the National Science Foundation (CHE-8009670), for support of this work, and Louis Todaro and David Witonsky for technical assistance.

Registry No. 1b, 6966-22-9; **1b**-benzene, 87656-13-1; **3**, 87681-12-7.

Supplementary Material Available: Final anisotropic thermal parameters and atomic parameters for hydrogen atoms in **1** and **1·4B**, distances less than 4 Å between the nonhydrogen atoms of the ester and carbon atoms of the neighboring benzene molecules in **1·4B** (Tables VIII–XII) (5 pages). Ordering information is given on any current masthead page.

^{13}C–^{1}H Coupling Constants in Carbocations. 4.[1] Conformations of Internal Cyclopropylcarbinyl Cations (Benzobicyclo[4.1.0]heptyl Cations) and Their Rearrangements to Naphthalenium Cations

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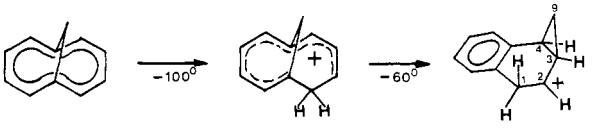
Contribution from the Department of Organic Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052. *Received May 12, 1983*

Abstract: Ionizations of 2-substituted 1,1-dimethyl-3,4-methano-1,2,3,4-tetrahydronaphthalen-2-ols (**8**) (3,3-dimethylbenzobicyclo[4.1.0]heptan-2-ols) in FSO_3H/SO_2ClF at −130 °C do not yield the corresponding 2-cations but benzylic (4-) cations **10** as a result of cyclopropylcarbinyl–cyclopropylcarbinyl rearrangements. At higher temperatures, **10a** and **10b** undergo a further series of rearrangements to yield ultimately dialkylnaphthalenium cations. Comparison of the $^{1}J_{C_\alpha H}$ values of the internal cyclopropylcarbinyl cations with those of model bicyclic ketones give ΔJ values of approximately 20 Hz, indicating that in all cases bisected cyclopropylcarbinyl geometries prevail. Conformations of these and related cations and of the bicyclic ketones are discussed.

Recently it has been reported that when 1,6-methano[10]-annulene is treated with FSO_3H/SO_2ClF at −100 °C, a monoprotonated cation is formed, which rearranges at −60 °C to a cyclopropylcarbinyl cation (**1**).[2] Observation of vicinal coupling



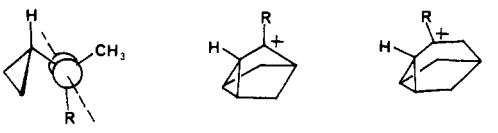
1

between H_2 and H_3 (7 Hz) but not between either of the protons at C_1 and H_2 led the authors to suggest that the structure of **1** may be "a more or less flat 'naphthalenium' skeleton" in which the cyclopropylcarbinyl moiety was not in the favored bisected arrangement, but one intermediate between that and the parallel conformation.[2] Support for such a structure was elicited from the calculations of Hehre and co-workers who showed the presence of two energy minima on either side of and 0.5 kcal higher than the most stable bisected conformation on the potential energy surface of the $C_4H_7^+$ species.[3]

We have developed a method for determining the conformations of carbocations, based on the difference, ΔJ, between the $^{1}J_{CH}$ value of the carbon adjacent to the cationic carbon in static classical cations and that in an appropriate model compound (ketone) according to eq 1, where A is the maximum inductive

$$\Delta J = A - B \cos^2 \theta \qquad (1)$$

enhancement of $J_{C_\alpha H}$ (22.5 Hz for trialkyl cations) and B is the maximum hyperconjugative diminution of $J_{C_\alpha H}$ (33.1 Hz for trialkylcations).[4] In the case of bisected cyclopropylcarbinyl cations **2–4**, the C_α–H bond is orthogonal to the vacant p orbital



	2	**3**	**4**
	ΔJ	ΔJ	ΔJ
a, R = H	27	22	22
b, R = CH_3	24	20	21

(1) Part 3: Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Hügel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539–3543.

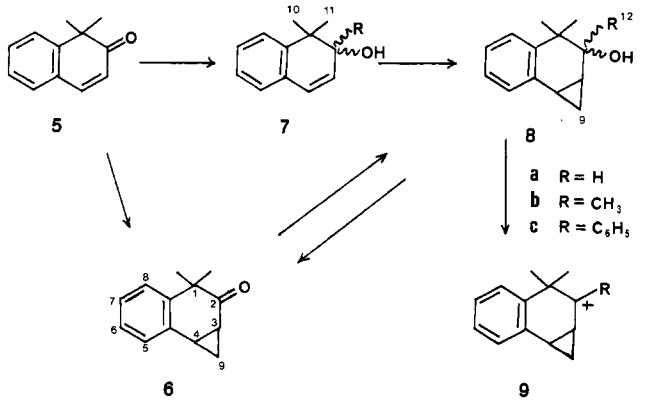
(2) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 4528–4529.

(3) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537–5539.

(4) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106–3111. Kelly, D. P.; Brown, H. C. *Ibid.* **1975**, *97*, 3897–3900.

0002-7863/84/1506-0687$01.50/0

Scheme I



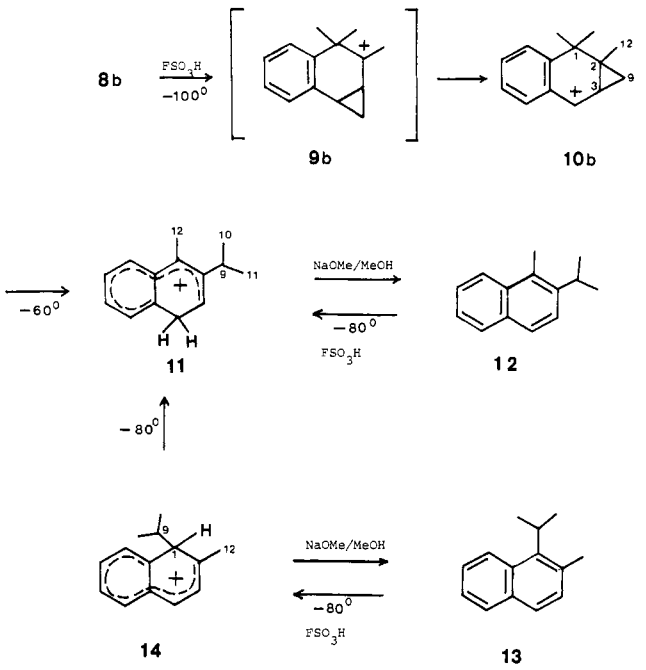
(θ = 90°) resulting in a maximum enhancement of J_{C_4H} over that for methyl cyclopropyl ketone,[4] nortricyclanone, and homonortricyclanone, respectively.[5] Reduction in the dihedral angle results in a reduced value of ΔJ such that when θ = 0°, the value is estimated as −10 Hz.[4] (Rapid 1,2-H shifts normally occur for this stereochemistry which prevents direct measurement of a static value for J_{C_4H}.[4]) It was thus of interest to see if the ΔJ criterion would provide additional support for the proposed structure of **1**.

The application of the ΔJ equation to this problem required the synthesis of an appropriate model ketone. 1,1-Dimethyl-3,4-methano-3,4-dihydronaphthalen-2(1*H*)-one (or 3,3-dimethyl-4,5-benzobicyclo[4.1.0]heptan-2-one) (**6**) was chosen since its synthesis was anticipated to be relatively facile from 2-naphthol via 1,1-dimethylnaphthalen-2(1*H*)-one (**5**)[6] and since it could be readily converted to a number of alcohols (**8a–c**) which in turn would serve as precursors for the internal cyclopropylcarbinyl cations **9a–c** (Scheme I). Ketone **6** would thus serve as the reference compound for the cations **9** as well as for **1**.

Results and Discussion

The synthesis of **6** was accomplished by cyclopropanation of the enone **5** using dimethyloxosulfonium methylide.[7,8] The ^{13}C spectrum of **6** was assigned from consideration of the chemical shifts in 2-tetralone[9] and from the ^{13}C-H coupling constants. The cyclopropyl doublet at δ 23.3 was assigned to C_4 (rather than C_3) on the basis of the long-range coupling to H_5. Alcohol **8a** was prepared by two methods (Scheme I). Simmons–Smith cyclopropanation of the allylic alcohol **7a** generated from **5** with $NaBH_4/CeCl_3$[10] gave **8a** in low yield and was accompanied by a large amount of 1,2-dimethylnaphthalene,[11,12a,13] identified by its ^1H and ^{13}C NMR spectra.[14] The alcohol **8a** was readily oxidized to the target ketone **6** by treatment with pyridinium chlorochromate. Secondly, reduction of **6** with $NaBH_4$ proceeded in high yield to **8a**. Standard Grignard reactions of **6** with CH_3MgI and C_6H_5MgX gave the required alcohols **8b** and **8c**, respectively. However, attempted preparation of **8b** by the Simmons–Smith procedure using the methyl alcohol **7b** was unsuccessful. Since these alcohols were to be used to generate the corresponding cations, no attempt was made to determine the stereochemistry.[15]

Scheme II



Ionization of the methyl alcohol **8b** in FSO_3H/SO_2ClF at −100 °C gave a solution, the ^{13}C spectrum of which showed the presence of two cationic carbons as evidenced by signals at δ 200.2 and 210.0. On warming to −60 °C, the solution gave a spectrum of a single cation with δ C^+ 200.2 which was identified as the 1-methyl-2-isopropylnaphthalenium cation **11** from the following considerations. (a) The ^1H spectrum showed the presence of an isolated methyl group (δ 3.73), an isopropyl group (δ 1.76, 3.77), a two-proton singlet at δ 5.26 ppm, and deshielded aryl protons at 8.05–9.37 ppm. The values are similar to (but deshielded in comparison with) those reported for protonated 1,2-dimethylnaphthalene.[16] (b) Apart from the accidental magnetic equivalence of three methyl carbons, the ^{13}C spectrum is also very similar to that of the 1,2-dimethylnaphthalenium cation.[16] (c) When 1-methyl-2-isopropylnaphthalene (**12**) was protonated in FSO_3H at −80 °C, identical ^1H and ^{13}C spectra were obtained (Scheme II). (d) Quenching the ion solution obtained from **8b** after warming to −60 °C, gave **12**, identical with authentic material. (e) Protonation of 1-isopropyl-2-methylnaphthalene **13** under the same conditions gave a different naphthalenium cation, formulated as **14** where ipso protonation has occurred.[17,18] (f)

(5) (a) 3-Tricyclo[2.2.1.0^{2,6}]heptanone: ^{13}C δ (J_{CH}) $CDCl_3$ (67.8 MHz) 19.4 (d, 179, C_1), 17.3 (d, 183, C_2), 214.3, 37.8 (d, 155, C_4), 31.7 (t, 135, C_5, 19.4 (d, 179, C_6), 31.7 (t, 135, C_7). Cation **3**: δ ^{13}C (J_{CH}) (0.57 M in SbF_5/SO_2ClF, −60 °C, 15.1 MHz) 83.7 (d, 188, C_1, 6), 67.0 (d, 203, C_2), 292.5, 46.5 (d, 161, C_4), 43.1 (t, 141, C_5), 43.1 (t, 141, C_7). A value of 219 Hz was previously reported for $^1J_{C_2H}$: Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 3792–3794. The latter reference also gives $^1J_{C_2H}$ values of 205 and 208 Hz for **3** R = H and R = C_2H_5, respectively. (b) 3-Tricyclo-[3.2.1.0^{2,7}]octanone: ^{13}C δ (J_{CH}) ($CDCl_3$, 25 MHz) 23.1 (d, 170, C_1, C_7), 31.9 (d, 171, C_2), 209.0 (s, C_3), 44.6 (t, 128, C_4), 27.2 (d, 142, C_5), 31.4 (t, 132, C_6, 8). This ketone was prepared by K. Karavokiros according to Ficini, J.; Maujean, A. *Bull. Soc. Chim. Fr.* **1972**, 4395–4397. ^{13}C NMR data for cations **4** are reported in Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1976**, *98*, 7026–7033.

(6) (a) Wenkert, E.; Youssefych, R. D.; Lewis, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 4675–4680. (b) Brown, R. F. C.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2385–2391.

(7) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1363.

(8) Attempts to generate **6** via the Simmons–Smith procedure were unsuccessful: Limasset, J. C.; Amice, P.; Conia, J-M. *Bull. Soc. Chim. Fr.* **1969**, 3981–3990.

(9) Adcock, W.; Gupta, B. D.; Kitching, W. *J. Org. Chem.* **1976**, *41*, 1498–1504.

(10) Luche, J. *J. Am. Chem. Soc.* **1978**, *100*, 2226–2227.

(11) The 1,2-dimethylnaphthalene is presumably formed by Lewis acid (zinc iodide) promoted rearrangement in a similar fashion to the dienone–phenol rearrangement.[12,13] The yield of **8a** improved to 30% by using dimethoxyethane as solvent: (see ref 36).

(12) (a) Carlin, R. B.; Sivaramakrishnan, K. P. *J. Org. Chem.* **1970**, *35*, 3368–3372. (b) Duswalt, J. M.; Mayer, T. J. *Anal. Chem.* **1970**, *42*, 1789–1794.

(13) Arnold, R. T.; Buckley, J. S.; Richter, J. *J. Am. Chem. Soc.* **1947**, *69*, 2322–2325.

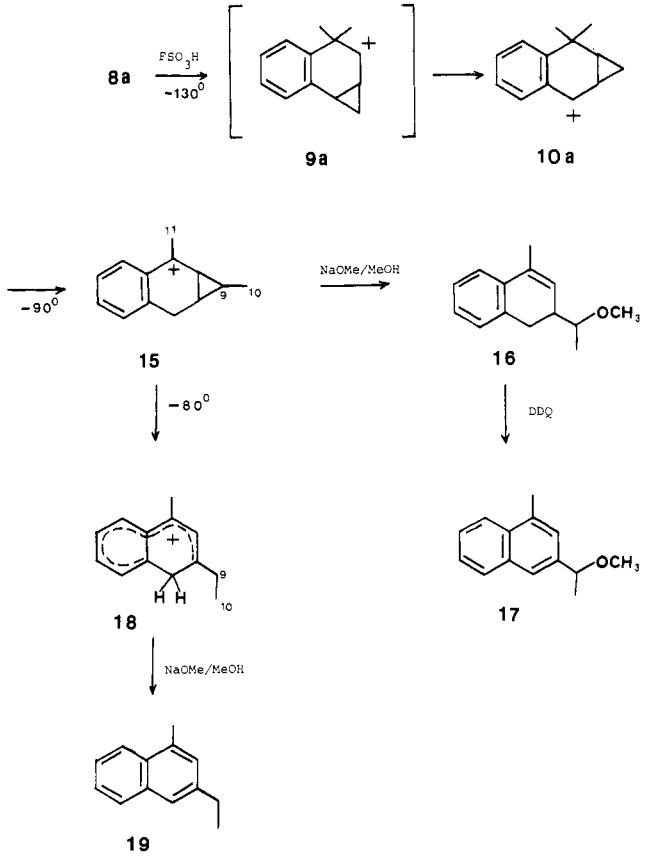
(14) Wilson, N. K., Stothers, J. B. *J. Magn. Reson.* **1974**, *15*, 31–39.

(15) For stereochemical studies of cyclopropylcarbinyl alcohols see: Poulter, C. D.; Boikess, R. S.; Brauman, J. I.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2291–2296.

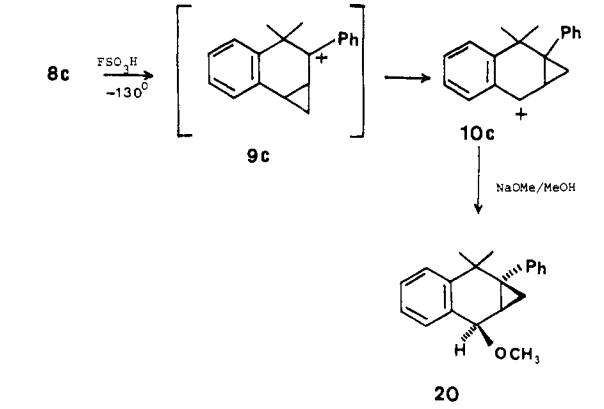
(16) Lammerstma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1979**, *101*, 3618–3624.

(17) Protonation at the ipso position rather than at C_4 may be due to reduction in steric compression between the peri proton (H_8) and the isopropyl group when C_1 is converted to tetrahedral carbon.

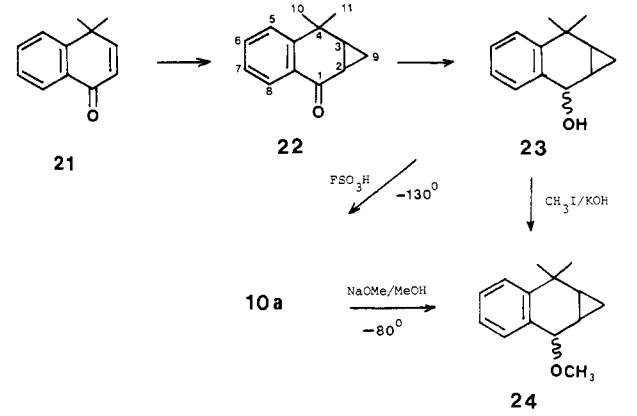
Scheme III



Scheme IV



Scheme V



Ionization of the deuterated alcohol **8** R = CD_3 at <−100 °C, warming to −60 °C, and quenching in methoxide/methanol yields an isopropylmethylnaphthalene in which the isopropyl group is half-deuterated. At this temperature the solution gave a ^{13}C spectrum identical with that of **11** except for the reduced intensity of the line at δ 22.2. The proton spectrum of the quenched ion showed that the CD_3 group was now part of the isopropyl moiety, since the ratio of the integrals for $CH:(CH_3)_2$ was 1:3 rather than 1:6 and since the methine absorption at δ 3.4 was a broad quartet rather than a sharp septet. In addition, decoupling at the deuterium frequency resulted in this quartet becoming quite sharp.

Careful ionization of this same alcohol at −120 °C produced a green solution, the ^{13}C spectrum at −100 °C of which showed a doublet (J = 167 Hz) at δ 210.5, and a cyclopropyl carbon doublet (J = 191 Hz) and triplet (J = 175 Hz) at δ 72.0 and 73.2, respectively, which is consistent with structure **10** but not **9**. Thus the initially formed (but unobserved) internal cyclopropylcarbinyl cation **9b** undergoes a very rapid cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement to **10b** followed by a slower reorganization involving the shift of one of the geminal methyl groups. This lack of stability of **9b** is in constrast to that reported for the secondary cation **1**.[2]

Ionization of the secondary alcohol **8a** in FSO_3H/SO_2ClF at −130 °C gave a yellow solution, the proton and carbon spectra of which showed the presence of a single cationic species. The ^{13}C spectrum exhibited a doublet at δ 221.7, two cyclopropyl doublets at δ 54.0 (J_{CH} = 173 Hz) and 51.7 (J_{CH} = 193 Hz), and a cyclopropyl triplet at δ 68.0 (J_{CH} = 175 Hz). The proton spectrum showed a doublet at δ 10.74 consistent with a benzylic cationic proton[19] rather than an alkyl cyclopropylcarbinyl proton.[20] Upon this information and the consistency of the NMR data with ions of unambiguous structure (see below) the ion was identified as **10a** and not the expected cation **9a** (Scheme III). When warmed to −90 °C, **10a** underwent a rapid rearrangement to another cation, the ^{13}C spectrum of which included a singlet at δ 233.8 and three cyclopropyl doublets at δ 49.6 (J_{CH} = 175 Hz), 63.5 (J_{CH} = 185 Hz), and 79.5 (J_{CH} = 171 Hz) (Table I). In addition the proton spectrum showed a three proton doublet at δ 2.22 and a deshielded three proton singlet at 3.70 ppm. The cation was thus identified as **15** which was confirmed by quenching the solution in methoxide/methanol, the only product isolated being the methyl ether **16** resulting from nucleophilic attack at C_9 with concomitant cyclopropyl ring opening. The identity of **16** was determined from its ^{13}C spectrum, its mass spectrum, and its ready dehydrogenation by dichlorodicyanobenzoquinone to the 1,3-disubstituted naphthalene **17**. Further warming of a solution of **15** to −80 °C for several hours resulted in a mixture of **15** and the 3-ethyl-1-methylnaphthalenium cation **18**, the latter identified by its similarity to other dialkylnaphthalenium cations.[16,21] When this solution is quenched in methoxide/methanol, the products obtained after preparative thin-layer chromatography were identified as 3-ethyl-1-methylnaphthalene (**19**) (and not 2-ethyl-1-methylnaphthalene), from its mass and proton spectra,[12] and the methyl ether **16**.

In a further attempt to observe a stable, internal cyclopropylcarbinyl cation similar to **1**, the phenyl alcohol **8c** was ionized in FSO_3H/SO_2ClF at −130 °C. Once again the spectrum of the resulting solution was consistent with **10c** and not with **9c** (Scheme IV). The benzylic, cationic methine group was identified by a proton doublet at δ 10.66 and a corresponding ^{13}C doublet at δ 217.9. The cyclopropyl group appeared as a singlet (δ 75.6), a doublet (δ 62.6, J_{CH} = 193 Hz), and a triplet (δ 73.6, J_{CH} = 174 Hz) (Table I). Quenching of the solution in methoxide/methanol afforded a methyl ether identified as **20** by its mass, proton,[22] and carbon spectra. These spectra were similar to those

(18) It is interesting to note that quenching of **14** after a few hours at −80 °C regenerates the naphthalene **13** but after two weeks at −80 °C the product isolated after quenching is the other isomer **12** (Scheme II).

(19) Olah, G. A.; Porter, R. D.; Kelly, D. P. *J. Am. Chem. Soc.* **1971**, *93*, 464–466. For the 1-phenylethyl cation, δ $^{1}HC^{+}$, 10.5 ppm.

(20) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146–156. For cation **2a** δ $^{1}HC^{+}$, 9.6 ppm.

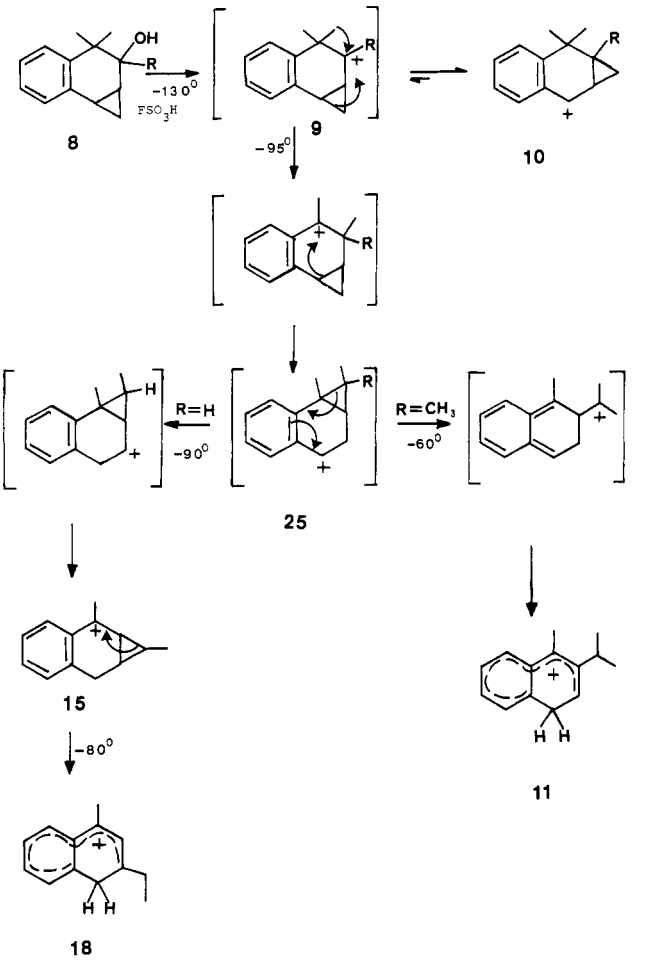
(21) Olah, G. A.; Mateescu, G. D.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 1865–1874.

Table I. ^{13}C NMR Parameters for Carbocations[a]

cation	position temp, °C	C_1	C_2	C_3	C_4	C_{4a}	C_5	C_6	C_7	C_8	C_{8a}	C_9	C_{10}	C_{11}	C_{12}
1[b]	−60	31.3 t, 132.4	221.2 d, 168	51.7 d, 191.6	43.7 d, 177	133.8	140.1 d, 169	130.8 d, 169	146.8 d, 165.4	132.2 d, 166.3	146.3	63.5 t, 172			
10a	−110	40.2 s	54.0 d, 173	51.7 d, 193	221.7 d, 169	131.9 s	141.6 d	128.0 d	148.0 d	130.5 d	155.6 s	68.0 t, 175	23.0 q	34.9 q	
10b	−100	46.2 s	91.5 s	72.0 d, 191	210.0 d, 167	131.0 s	136.8 d	130.1[c] d	143.5 d	128.0[c] d	153.8 s	73.2 t, 175	23.9 q	32.7 q	21.2[d] q
10c[e]	−80	45.6 s	75.6 s	62.6 d, 193	217.9 d, 169	131.9 s	140.4 s	128.9[e] d	147.2 d	130.5[e] d	155.5 s	73.6 t, 174	24.4 q, 130	33.1 q, 130	
11	−80	200.2 s	154.2 s	176.5 d, 166	43.9 t, 125	153.6 s	130.5 d	141.8 d, 166	131.5 d	133.9 d	135.1 s	30.8 d, 130	22.2[d] q, 130	22.2[d] q, 130	22.2 q, 130
14[f]	−70	65.9 d	217.6 s	133.8 d	176.6 d	133.9 s	140.4 d	131.2 d	140.7 d	130.8 d	157.0 s	46.4 d	15.4 q	23.3 q	29.7 q
15	−90	233.8 s	63.5 d, 185	79.5 d, 171	30.7 t, 133	143.9 s	130.4 d	143.2 d	131.5 d	133.9 d	133.9 s	49.6 d, 175	20.4 q, 131	30.4 q, 131	
18[g]	−80	196.9	135.2[h]	209.3	46.4	152.3	130.4[h]	141.4	130.4[h]	132.9	132[h]	35.4	13.1	26.1	
27b[i]	−80	65.5 d, 187	271.8	42.6	23 3		21.2	80.1 d, 177	53.5	37.1					
31	−80	65.0 d, 186	274.2 s	40.7 t, 127	34.2 t		33.6 s	88.2 d, 173	55.1 t, 170	36.8 q, 132		26.1[c] q	26.9[c] q		

[a] ±0.1 ppm from external (capillary) Me_4Si. $^1J_{CH}$ ± 1 Hz unless stated otherwise. [b] Data (from ref 2) are also consistent with structure **26**; see text; C_9, t, $J = 172 \pm 2$ Hz. [c] Assignments may be interchanged. [d] Signal reduced in intensity when cation prepared from **8b**-2-Cd_3. [e] Phenyl carbon resonances at δ 134.9 (ipso), 129.9, 131.2, 133.0. Signals at δ 128.9 and 130.5 tentatively assigned to C_6 and C_8, respectively. [f] Assignments of aryl carbons are based on those for dimethylnaphthalenium cations[16] and are tentative. [g] Observed in the presence of **15**. Assignments are based on those for 1,3-dimethylnaphthalenium cation.[16] [h] Overlapping resonances of **15** and **18**. [i] Data from ref 24 with a correction.[31]

Scheme VI



obtained for the analogous methyl ether **24**, prepared from an epimeric mixture of alcohols **23** which were in turn prepared by the sequence **21**–**23** (Scheme V). For example, the observation of a doublet at δ 80.4 in the ^{13}C spectrum of **20** corresponds well with that due to C_4 of **24** at δ 80.7.[23]

When a solution of **10c** was warmed to −80 °C, complete decomposition occurred. Thus the presence of a phenyl group destabilizes the adjacent cationic center in the first-formed cation (**9c**) unlike most other dialkyl cations. Olah and co-workers made a similar observation in the case of 2-substituted bicyclo[4.1.0]-heptyl cations where the phenyl derivative could not be prepared while the methyl and parent ions were relatively stable.[24]

The above results may be rationalized by the following rearrangement pathways (Scheme VI). All the alcohols **8** undergo ionization at −130 °C to give an unobserved ion **9** which is in unfavorable equilibrium with **10** produced by a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement, the driving force being the attainment of a benzylic cation.[25] In the case of the phenyl cation, no further rearrangement occurs, decomposition occurring at higher temperatures. However when the temperatures

(22) Ogawa, Y.; Matsusaki, H.; Hanaoka, K.; Ohkata, K.; Hanafusa, T. *J. Org. Chem.* **1978**, *43*, 849–855.

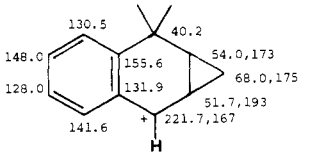
(23) The carbon spectrum of **24** shows two peaks at δ 80.7 and 75.5, intensity ratios ~1:6, which are probably due to the syn and anti ethers respectively. Ogawa and co-workers reported that $LiAlH_4$ reduction of the demethyl derivative of **22** yields exclusively the anti alcohol.[22] In our case the spectrum of **23** exhibited carbinol carbon peaks at δ 71.4 and 67.4, with intensity ratio ~1:5. Thus we assigned the higher intensity signals as arising from the anti isomers.

(24) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Org. Chem.* **1980**, *45*, 965–969.

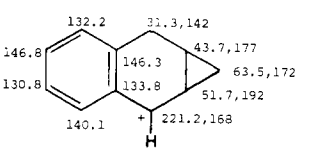
(25) 2-Methylbicyclo[4.1.0]heptan-2-ol ionizes cleanly at −130 °C to the expected tertiary cation and is stable up to 0 °C whereas 1-methylbicyclo-[4.1.0]heptan-2-ol affords a pair of rapidly equilibrating secondary cyclopropylcarbinyl cations.[24]

of **10a** and **10b** are raised rearrangement occurs (through **9**) by a 1,2-methyl shift[12,13] followed by bond migration[26] (C_3–C_4 to C_3–C_1) to give **25** (also not observed). In the case of the methyl cation (**10b**) ring opening followed by a series of rearrangements including two 1,2-hydride shifts yields the observed 1,2-disubstituted naphthalenium cation **11**. However, similar ring opening for **25** (R = H) is energetically less favorable, since it would produce a secondary alkyl cation. Thus, a 1,2-hydride shift followed by a cyclopropylcarbinyl rearrangement gives the observed benzylic cation **15**. Above −80 °C rearrangement occurs by ring opening and a 1,2-hydride shift to give the 3-ethyl-1-methylnaphthalenium cation (**18**).

The significant difference between the structures of these stable cations and that reported by Lammertsma and Cerfontain[2] for the demethyl derivative **1** deserves some comment. The structure of the latter cation was based on its NMR data and that of an ion derived from 2-methyl-1,6-methano[10]annulene, which was formulated as 4-methyl-**1** rather than 4-methyl-**10a** on the basis of a proton doublet at δ 9.98. We believe that the NMR data given for **1** are consistent with the alternative structure **26**, analogous to **10**, according to the following considerations. (a) The proton shift of the cationic methine group reported for **1** (δ 10.38) is similar to that of **10a**,**c** (δ 10.74, 10.66) and the 1-



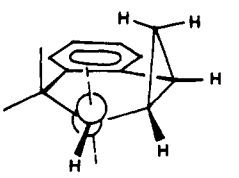
10a



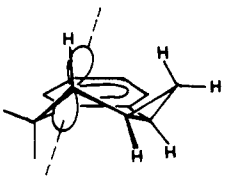
26

phenylethyl cation (δ 10.50[19]); that is, it is a benzylic cation. (b) The ^{13}C shift of the cationic carbon is almost identical with that of **10a**, similar to **10c** (δ 217.9), the 1-phenylethyl cation (δ 226), and the 1-cyclopropyl-1-phenylmethyl cation (δ 226.3),[27] but dissimilar to that for 1-cyclopropylethyl (δ 251.9)[20] and 2-bicyclo[4.1.0]heptyl (δ 238.9).[24] (c) The absence of vicinal proton coupling between the cationic methine proton (H_2) and either of H_1 protons of **1** may well be due to the absence of the adjacent methylene group, the cationic proton being coupled only to the adjacent cyclopropyl proton (**26**).[28] (d) Quenching of the cation yields 87% of the methyl ether corresponding to capture of **26** by methoxide ion. The only product isolated from quenching of **10c** was the analogous ether **20**. Similarly, ionization of **23** in FSO_3H produces the same cation **10a** as obtained from ionization of **8a**, the quenching in methoxide/methanol of which affords **24** identical with that obtained by methylation of **23** apart from differences in the ratio of syn:anti isomers (Scheme V). (e) Comparison of $J_{C_\alpha H}$ values given for **1** and those for the model ketone **6** indicates that **1** would exist in a pseudoboat conformation with the more favorable bisected arrangement of the cyclopropylcarbinyl moiety (see below). In this conformation, the cation should exhibit at least one non-zero vicinal coupling constant to the methylene group in its proton spectrum. We therefore conclude that, at the very least, the structure of the rearranged cation from 1,6-methano[10]annulene is not unequivocal.

Stereochemistry. If the structure of the rearranged cation from 1,6-methano[10]annulene were **1**, then comparison of $^{1}J_{C_\alpha H}$ (192 Hz)[2] with that for the model ketone **6** (171 Hz) indicates that **1** has the stable bisected arrangement of the internal cyclopropylcarbinyl moiety (ΔJ = 21 Hz, θ = 90°). Dreiding models of **1** suggest that there are two minimum energy conformations, a pseudoboat (A) in which the dihedral angle is ~90° and a pseudochair (B) in which the dihedral angle is ~0–10°. A flat cyclohexyl structure as has been proposed for **1** would have resulted in a ΔJ value intermediate between +22 and −10 Hz.[4] The ΔJ



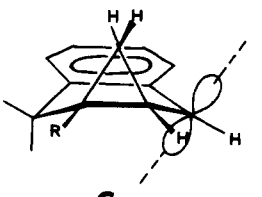
A



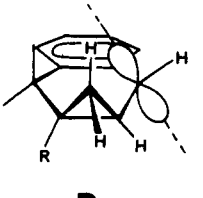
B

criterion thus supports conformation A but not B or a flat structure for **1**.[29] If in fact the cation is **26**, then it will have a similar conformation to **10a–c**.

The conformations of **10a–c** can be deduced from the comparison of their values of $^{1}J_{C_\alpha H}$ and that of the model ketone **22** and inspection of Dreiding models. The cyclohexyl moieties of **10** and **22** can exist in two minimum energy conformations, an anti-boat C and a syn-boat D. Conformation C has the bisected



C



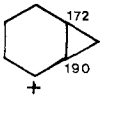
D

arrangement of the internal cyclopropylcarbinyl group (θ = 90°) and conformation D has a parallel arrangement (θ = 0–10°). Thus ΔJ should be a maximum for C and a minimum for D. The value of $J_{C_\alpha H}$ for **22** (168 Hz) yields values of 25, 23, and 25 Hz for ΔJ of **10a**, **10b**, and **10c**, respectively. Therefore these cations have the favored bisected arrangement of the cyclopropylcarbinyl group and exist in the anti-boat conformation C.

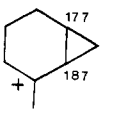
As indicated previously,[4] the ΔJ criterion is based on the assumption that the use of the analogous ketone as a reference removes all effects on ΔJ other than charge. The conformations of both **10** and **22** are thus assumed to be the same. In the case of the monomethyl analogoue of **22**, Julia and Bonnet have rationalized its rearrangement to a cycloheptadienone by alkoxide ion as proceeding via a conformation in which the extractable proton (H4) occupies an equatorial position.[30] For the *cis*-methyl ketone this corresponds to the syn-boat conformation D. The presence of the geminal dimethyl group in **22** may destabilize this conformer in favor of the anti-boat conformer (similar to C). In any event, differences in the conformations of the ketone are not expected to effect the ΔJ values significantly.[29]

Cation **26** has the same conformational possibilities as **10** and comparison of the appropriate $J_{C_\alpha H}$ values yields a value of 24 Hz for ΔJ, once gain confirming the bisected geometry of the cyclopropylcarbinyl residue and anti-boat stereochemistry.

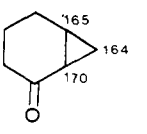
Comparison with other internal cyclopropylcarbinyl cations is instructive. Olah and co-workers reported $^{1}J_{CH}$ values for C_1 and C_6 of the bicyclo[4.1.0]hept-2-yl cations **27**.[31] When compared



27a



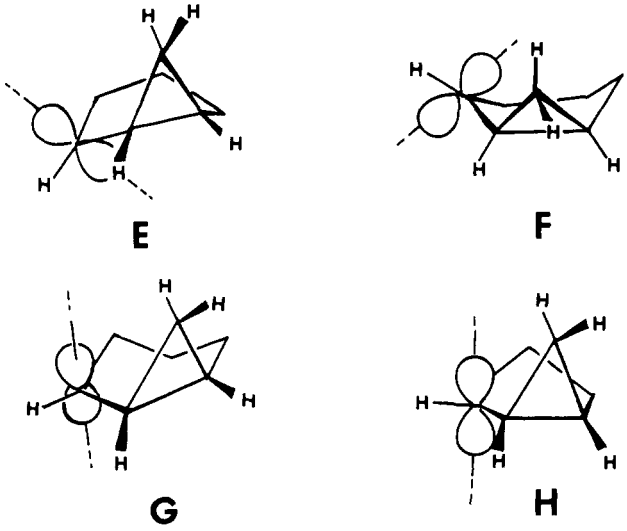
27b



28

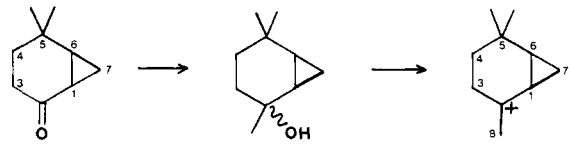
(26) We thank Professor L. Paquette for this suggestion.
(27) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666–2671.
(28) The NMR data for **1**[2] have been assigned to structure **26**.
(29) Although we cannot discount the possibility that a different model ketone, such as the non-methyl-substituted 3,4-methano-3,4-dihydronaphthalen-2(1*H*)-one may exist in a different conformation from **6**, the difference in $J_{C_\alpha H}$ between the two ketones would be insignificant in comparison with the large difference between ketone and cation.
(30) Julia, S.; Bonnet, Y. *Bull. Soc. Chim. Fr.* **1957**, 1347–1353.
(31) The assignments for C_1 and C_6 of **27b** in the original paper[24] should be reversed; Olah, G. A., personal communication. ^{13}C NMR data for **28** is as follows: δ ($CDCl_3$) 10.2 (t, J = 164 Hz, C_7), 17.4 (d, J = 161 Hz, C_6), 17.7 (t, J = 131 Hz, C_4), 21.2 (t, J = 131 Hz, C_5), 25.8 (d, J = 170 Hz, C_1), 36.7 (t, J = 129 Hz, C_3), 209.1 (s, C_2). The chemical shifts have been assigned previously by Grover, S. H.; Marr, D. H.; Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1975**, *53*, 1351–1361.

with $J_{C_\alpha H}$ for bicyclo[4.1.0]heptan-2-one **28** the data for **27** yield values of 20 Hz and 17 Hz for **27a** and **27b**, respectively. A Dreiding model of **27** indicates the possibility of two pseudoboat conformations, an anti-boat (E) with $\theta \simeq 80°$ and a syn-boat (F) with $\theta \simeq 0°$, and two pseudochair conformations, one with $\theta \simeq 80°$ (G) and one with $\theta \simeq 45°$ (H). Thus the relatively



high values of ΔJ suggest that the cations exist in either conformation E or G but not in F or H.

In order to evaluate the influence of the geminal dimethyl groups at C_5 of the bicyclo[4.1.0]hept-2-yl cations, the ketone **29** and methyl alcohol **30** were prepared. Upon ionization in FSO_3H/SbF_5 (1/1)/SO_2ClF at −130 °C, **30** gave the cation **31** which was stable at −80 °C.



29 30 31

Comparison of $J_{C_\alpha H}$ for **29** with **31** gives ΔJ = 17 Hz, identical with that obtained from **28** and **27b**, confirming a bisected arrangement for the cyclopropylcarbinyl moiety. Thus the geminal dimethyl group exerts no detectable influence upon the stereochemistry of these cations and all three non-benzylic cations, **27a**, **27b**, and **31**, exist in either conformation E or G.

Conclusions

The only benzobicyclo[4.1.0]heptyl cations observed are those with the positive charge in the benzylic position, although their formation requires intermediate cations with the positive charge further removed. Apart from the phenyl-substituted cation, the other cations rearrange on warming, eventually to highly resonance stabilized naphthalenium cations.

The application of the ΔJ equation to these benzobicyclo[4.1.0]heptyl cations shows that in all cases, the internal cyclopropylcarbinyl moiety exists in the bisected conformation which provides maximum stabilization of the positive charge. This situation also pertains to the previously observed bicyclo[4.1.0]heptyl cation whether it is structure **1** or **26**. The ΔJ equation has now been applied successfully to give conformations of acyclic trialkyl, dialkylaryl, and bicyclic carbocations.

Experimental Section

General Procedures. Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Microanalyses were carried out by AMDEL Microanalytical Service, Melbourne. Preparative and analytical thin-layer chromatography (TLC) were carried out using glass plates coated with silica gel (Merck Kieselgel GF_{254}) or alumina (aluminum oxide GF_{254}). The separated compounds were extracted with hot ethyl acetate. Infrared spectra were recorded as potassium bromide disks or as films between sodium chloride plates by using either a Perkin-Elmer 457 or a Perkin-Elmer 157C spectrophotometer. Mass spectra were recorded on a V.G. Micromass 70/70F high-resolution mass spectrometer at an ionizing potential of 70 eV. Generally only ions of intensity greater than 10% of the base peak are quoted. Proton and carbon magnetic resonance spectra were recorded on a JEOL FX-100 spectrometer unless otherwise stated. Proton (±0.01 ppm) and carbon (±0.1 ppm) chemical shifts were measured from internal Me_4Si at probe temperature for ($CDCl_3$) solutions of neutral compounds and at external Me_4Si for cationic solutions. For the latter, field stabilization was provided by a concentric capillary of acetone-d_6 containing Me_4Si or by an external ^7Li lock. Proton coupled ^{13}C spectra were obtained by the normal gated decoupling technique with a minimum 50% duty cycle, using 6000 Hz spectral width and either 16 384 or 8 192 data points. Coupling constants (±1 Hz) were measured by hand from spectra plotted at 14.3 Hz cm^{-1}. In the cases where accurate coupling constants could not be obtained from the coupled spectrum due to overlapping signals, selective excitation of each individual ^{13}C–H multiplet was used to provide accurate J_{CH} values. This excitation was achieved by using a DANTE sequence of 50 pulses of 2 μs duration with a repetition period calculated for the first sideband frequency. The decoupler was gated off during acquisition only.

Synthesis. 1,1-Dimethylnaphthalen-2(1*H*)-one (5). 2-Naphthol (80 g, 0.55 mol) was methylated according to the method of Wenkert et al.,[6] except for the use of NaOH rather than NaOMe and that the monomethyl intermediate was not purified but rather the naphthols were extracted (NaOH) and methylated to give **5** as a yellow oil (20.3 g, 21%): bp 90 °C (1 mm) [lit.[32] bp 146–150 °C (18 mm)]; IR (film) ν_{max} 1660, 1620 cm^{-1} (Lit.[6b] ν_{max} 1665, 1620 cm^{-1}); ^1H NMR δ 1.46 (s, 6 H, 2 × CH_3), 6.15 (d, 1 H, J = 10 Hz), 7.25–7.46 (m, 5 H, aryl H, H_1); ^{13}C NMR δ 27.7 (q, 2 × CH_3), 47.4 (s, C_1), 124.5 (d), 126.2 (d), 127.0 (d), 128.8 (s), 129.5 (d), 130.3 (d), 144.7 (d), 147.7 (s), 204.1 (s); MS (EI positive), m/z (relative intensity) 172 ($M^{+\cdot}$, 58), 144 (38), 129 (100), 128 (44), 127 (16) (Lit.[6b] m/z 172).

1,1-Dimethyl-3,4-methano-3,4-dihydronaphthalen-2(1*H*)-one (6). Method 1. The naphthalenone **5** (1.0 g, 5.8 mmol) was treated with dimethyloxosulfonium methylide as described by Corey and Chaykovsky.[7] The crude product was purified by column chromatography (silica gel, petroleum ether (40–60 °C): ethyl acetate 9:1) to give **6** as a white solid (0.96 g, 89%): mp 46.5–47 °C; 2,4-dinitrophenylhydrazone, orange needles from CCl_4, mp 209–209.5 °C; IR (KBr) 1670, 1490, 1380, 1345, 1040, 1030, 745, 735 cm^{-1}; ^1H NMR δ 1.06 (m, 1 H), 1.45 (s, 2 × CH_3), 1.65 (m, 1 H), 2.42 (m, 1 H), 2.60 (m, 1 H), 7.14–7.33 (m, 4 H, aryl); ^{13}C NMR δ 20.5 (d, d, m, J = 164, 167, 4 Hz, C_9), 23.3 (d, J = 168 Hz, C_4), 26.0 (d, J = 171 Hz, C_3), 29.2 (q, q, J = 129, 5 Hz), 31.4 (q, q, J = 129, 5 Hz), 45.2 (s, C_1), 126.1 (d), 126.5 (d), 127.3 (d), 127.7 (d), 134.4 (s), 140.9 (s), 211.3 (s, C=O); MS (EI) 186 ($M^{+\cdot}$, 8), 171 (18), 158 (25), 143 (100), 128 (37). Anal. ($C_{13}H_{14}O$) C, H.

Method 2. Alcohol **8a** was treated with pyridinium chlorochromate in dichloromethane according to Corey and Suggs[33] to give approximately a 50% yield of **6**.

1,1-Dimethyl-1,2-dihydronaphthalen-2-ol (7a). Naphthalenone **5** (3.6 g, 21 mmol) was reduced with $NaBH_4/CeCl_3$.[10] Recrystallization of the crude product (pentane) afforded a white solid (2.8 g, 76%): mp 59–61 °C (Lit.[34] 59–61 °C); IR (film) 3380, 1630, 1600, 1485, 1450, 1260, 1220, 1030, 790, 750 cm^{-1}; ^1H NMR δ 1.22 (s, CH_3), 1.35 (d, J = 8.3 Hz, OH), 1.40 (s, CH_3), 3.99 (d, d, J = 8.3, 4.6 Hz, H_2), 6.06 (d, d, J = 4.6, 9.7 Hz, 1 H), 6.50 (d, J = 9.7 Hz, 1 H), 7.07–7.38 (m, 4 H, aryl); ^{13}C NMR δ 21.8 (q, C_{10}), 27.0 (q, C_{11}), 39.2 (s, C_1), 74.0 (d, C_2), 125.0, 126.4, 127.2, 128.3, 128.6, 129.2, 131.4 (s), 142.9 (s); MS (CI *i*-C_4H_{10} positive), m/z 174 ($M^{+\cdot}$, 14), 158 (15), 157 (100), 156 (11), 131 (47).

1,1,2-Trimethyl-1,2-dihydronaphthalen-2-ol (7b). To a cooled solution (0 °C) of **5** (1.0 g, 5.8 mmol) in diethyl ether (8 cm^3) was added dropwise 14 cm^3 of ethereal methyllithium solution (0.5 M). The mixture was stirred for 8 h at 0 °C and warmed to room temperature. After hydrolysis with ammonium chloride, the organic layer was separated, washed, dried, evaporated, and distilled to give a colorless liquid (0.8 g, 73%): bp 68 °C (0.2 mm); n^{25}_D 1.5805; IR (film) 3440, 2980, 1630, 1600, 1450, 1360, 1090, 790, 755 cm^{-1}; ^1H NMR (60 MHz JEOL PMX-60) δ 1.25 (s, 2 × CH_3), 1.32 (s, CH_3), 1.60 (s, OH), 5.78 (d, J = 9 Hz, 1 H), 6.37 (d, J = 9 Hz, 1 H), 7.0–7.4 (m, 4 H), 7.6 (m, 1 H); ^{13}C NMR δ 21.8 (q), 22.1 (q), 22.5 (q), 41.8 (s, C_1), 74.3 (s, C_2), 123.9 (d), 125.4 (d), 125.7 (d), 126.2 (d), 127.4 (d), 130.9 (s), 135.9 (d), 144.1 (s); MS (EI), m/z 188 ($M^{+\cdot}$, 1), 186 (4), 172 (14), 171 (14), 170 (25), 169 (12), 158 (20), 157 (13), 156 (21), 155 (100), 129 (16), 128 (22), 115 (29). Anal. ($C_{13}H_{16}O$) C, H.

(32) Cromwell, N. H.; Campbell, R. D. *J. Org. Chem.* **1957**, *22*, 520–523.
(33) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647–2650.
(34) Oine, T.; Mukai, T. *Tetrahedron Lett.* **1969**, 157–160.

1,1-Dimethyl-3,4-methano-1,2,3,4-tetrahydronaphthalen-2-ol (8a). Method 1. Alcohol **7a** (1.0 g, 5.8 mmol) was treated with zinc–copper couple (prepared according to Le Goff[35]) in ether containing a molar equivalent of dimethoxyethane.[36] Column chromatography (silica gel, petroleum ether (40–60 °C):ethyl acetate (9:1)) afforded 1,2-dimethylnaphthalene (0.58 g, 64%) and *syn*-**8a** as a white solid (0.32 g, 29%): mp 88–89 °C; IR (KBr) 3350, 2965, 1490, 1360, 1045, 1030, 985, 740 cm^{-1}; ^{1}H NMR δ 0.82 (m, 1 H), 1.05 (m, 1 H), 1.17 (d, J = 7 Hz, OH), 1.29 (s, CH_3), 1.36 (s, CH_3), 1.7 (m, 1 H), 2.0 (m, 1 H), 4.12 (br t, (d, d), 1 H, H_2), 7.0–7.4 (m, 4 H); ^{13}C NMR δ 13.2 (t, C_9), 14.1 (d), 17.0 (d), 25.4 (q), 29.1 (q), 39.5 (s, C_1), 74.1 (d, C_2), 125.6 (d), 126.2 (d, 2 × C), 129.9 (d), 136.2 (s), 142.2 (s); MS (EI), m/z 188 ($M^{+\cdot}$, 57), 173 (67), 155 (31), 145 (100), 143 (62), 131 (50), 129 (61), 128 (55), 117 (50), 115 (52), 91 (53). Anal. ($C_{13}H_{16}O$) C, H.

Method 2. To a solution of **6** (1.0 g, 5.4 mmol) in methanol (10 cm^3) was slowly added $NaBH_4$ (0.2 g, 5.4 mmol) and the mixture was stirred for 10 min after which it was hydrolyzed with water, extracted, dried, evaporated, and recrystallized (pentane) to afford a mixture of *syn*- and *anti*-**8a** (0.95 g, 94%): ^{13}C NMR δ (COH, relative intensity) 74.1 (4), 77.9 (1).

1,1,2-Trimethyl-3,4-methano-1,2,3,4-tetrahydronaphthalen-2-ol (8b). Ketone **6** (1.0 g, 5.4 mmol) was added slowly to methylmagnesium iodide (or methyl-d_3-magnesium iodide) (10.8 mmol) in diethyl ether at room temperature and the mixture stirred for 4 h. Normal workup with saturated NH_4Cl solution yielded a crude product which was subjected to distillation to give **8b** as a colorless liquid (0.8 g, 73%): bp 115 °C (16 mm); n^{21}_D 1.5749; IR (KBr) 3500 br, 2970, 1585, 1360, 1040, 1030, 970, 745 cm^{-1}; ^{1}H NMR δ 0.73 (m, 1 H), 0.86 (br s, OH), 1.07 (m, 1 H), 1.27 (s, CH_3), 1.38 (s, CH_3), 1.43 (m, 1 H), 1.49 (s, CH_3), 1.97 (m, 1 H), 7.08–7.39 (m, 4 H, aryl); ^{13}C δ 13.3 (d, J = 164 Hz), 14.2 (t, J = 163 Hz, C_9), 21.0 (q, J = 128 Hz), 22.1 (d, J = 166 Hz), 25.7 (q, J = 128 Hz, C_{12} (CD_3)), 27.4 (q, J = 128 Hz), 43.1 (s, C_1), 73.4 (s, C_2), 125.2 (d), 126.1 (d), 126.3 (d), 130.3 (d), 136.2 (s), 144.1 (s); MS (EI), m/z 202 ($M^{+\cdot}$, 13), 187 (18), 159 (20), 144 (16), 143 (24), 132 (19), 129 (24), 128 (18), 117 (32), 115 (17), 104 (14), 91 (16), 71 (31), 43 (100). Anal. ($C_{14}H_{18}O$) C, H.

8b-2-CD_3: IR (KBr) 2225 cm^{-1}; ^{1}H NMR no singlet at δ 1.49; MS (EI), m/z 206/205 ($M^{+\cdot}$, 1.6/12), 190 (18), 159 (21), 144 (20), 143 (28), 132 (25), 129 (26), 128 (19), 117 (39), 115 (19), 104 (17), 91 (17), 74 (41), 46 (100).

1,1-Dimethyl-2-phenyl-3,4-methano-1,2,3,4-tetrahydronaphthalen-2-ol (8c). Ketone **6** (2.5 g, 13.5 mmol) was treated with freshly prepared phenylmagnesium bromide. The normal workup and recrystallization from pentane gave **8c** as a white solid (1.2 g, 34%): mp 98–99 °C; IR (KBr) 3595, 2975, 1600, 1480, 1445, 1360, 1180, 1040, 985, 745, 700, 575 cm^{-1}; ^{1}H NMR δ 0.99 (m, 2 H), 1.14 (s, CH_3), 1.22 (s, CH_3), 1.31 (s, OH), 2.20 (m, 2 H), 7.13–7.47 (m, 7 H), 7.65 (m, 2 H); ^{13}C NMR δ 14.33 (t), 14.45 (d), 22.8 (q), 23.2 (d), 27.8 (q), 43.8 (s, C_1), 77.0 (s, C_2), 125.3 (d), 126.1 (d), 126.4 (d), 126.7 (d), 127.3 (d, 4 × C), 130.1 (d), 135.9 (s), 144.4 (s), 145.7 (s); MS (EI), m/z 264 ($M^{+\cdot}$, 11), 144 (20), 133 (32), 129 (19), 128 (12), 115 (16), 105 (100), 91 (14), 77 (27), 55 (24). Anal. ($C_{19}H_{20}O$) C, H.

2-Isopropyl-1-methylnaphthalene (12). The six-step synthesis of **12** involved firstly the preparation of 2-(ethoxycarbonyl)-3,4-dihydronaphthalen-1(2*H*)-one from 3,4-dihydronaphthalen-1(2*H*)-one (α-tetralone).[37] Secondly, 2-isopropyl-3,4-dihydronaphthalen-1(2*H*)-one was obtained by a modification (isopropyl iodide) of the method of Adachi and Tanaka,[38] which, when the ketone was treated with methylmagnesium iodide in diethyl ether for 36 h followed by the usual workup and column chromatography (silica, petroleum ether (40–60 °C)), afforded 2-isopropyl-1-methyl-3,4-dihydronaphthalene as a colorless liquid: bp 100 °C (0.4 mm); n^{18}_D 1.5100; IR (film) 2960–2940, 2870, 1630, 1600, 1485, 1450, 755, 730 cm^{-1}; ^{1}H NMR δ 1.03 (d, J = 7 Hz, 2 × CH_3), 2.04 (s, CH_3), 2.14 (m, 2 H), 266 (m, 2 H), 3.08 (septet, J = 7 Hz, 1 H), 7.08–7.26 (m, 4 H); MS (EI), m/z 186 ($M^{+\cdot}$, 78), 171 (100), 143 (67), 129 (37), 128 (30), 115 (22).

A solution of the above dihydronaphthalene (0.5 g, 2.7 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (excess) in dry benzene was heated under reflux for 2 h. The mixture was filtered, evaporated, and distilled (bulb-to-bulb) to give **12** as a colorless liquid (0.29 g, 60%): bp 140 °C (oven) (4 mm) [Lit.[38] bp 126–127 °C (5 mm)]; ^{13}C NMR[39] δ 13.7 (q), 23.5 (q, 2 × CH_3), 29.7 (d), 123.6 (d, C_8), 124.1 (d, C_6), 124.5 (d, C_4), 125.7 (d, C_7), 126.2 (d, C_5), 128.3 (d, C_3), 129.3 (s), 132.0 (s), 132.9 (s), 143.2 (s, C_2); MS (EI), m/z 184 ($M^{+\cdot}$, 67), 169 (100), 154 (20), 153 (12), 141 (18); MS (CI, i-C_4H_{10}), m/z 184 ($M^{+\cdot}$, 63), 169 (100).

1-Isopropyl-2-methylnaphthalene (13). This hydrocarbon was prepared in four steps from 2-methylnaphthalene according to the method of Mannschreck and Ernst:[40] bp 110 °C (1.0 mm) [Lit.[40] bp 88–89 °C (0.4 mm)]; ^{13}C NMR[39] δ 21.5 (q, CH_3), 21.7 (q, 2 × CH_3), 29.1 (d), 124.1 (d, C_8), 124.9 (d, C_4), 126.2 (d, C_7), 128.9 (d, C_5), 129.9 (d, C_3), 131.7 (s), 132.4 (s), 133.4 (s), 140.8 (s, C_1); MS (EI), m/z 184 ($M^{+\cdot}$, 67), 169 (100), 154 (20), 153 (12), 141 (18), 115 (10).

4,4-Dimethylnaphthalen-1(4*H*)-one (21). This compound was prepared according to the literature:[13] mp 68–70 °C (Lit.[13] (69.5–70 °C); IR (KBr) 1665, 1600, 1305, 770 cm^{-1}; ^{13}C NMR δ 29.4 (q, 2 × CH_3), 37.3 (s, C_4), 126.1, 126.3, 126.5 (d, 4 × CH), 130.3 (s, C_{8a}), 132.6 (d, C_2), 149.6 (s, C_{4a}), 157.5 (d, J = 161 Hz, C_3), 184.6 (s, C=O); MS (EI), m/z 173 ($M^{+\cdot}$ + 1, 75), 172 ($M^{+\cdot}$, 100), 157 (51), 129 (85), 128 (70), 127 (20).

4,4-Dimethyl-2,3-methano-2,3-dihydronaphthalen-1(4*H*)-one (22). Ketone **21** (1.09 g, 5.8 mmol) was treated with dimethyloxosulfonium methylide as above.[7] The crude product was purified by column chromatography (silica, petroleum ether:ethyl acetate 9:1) to yield **22** as a colorless liquid (0.9 g, 83%): bp 113 °C (1.0 mm); n^{18}_D 1.5618; 2,4-dinitrophenylhydrazone, red needles from CCl_4/EtOH, mp 190–190.5 °C; IR (film) 3065 (w), 2960, 1670, 1600, 1465, 1350, 1275, 1030, 970, 915, 765, 725 cm^{-1}; ^{1}H NMR δ 0.71 (m, 1 H), 1.28 (s, CH_3), 1.28 (m, overlapping, 1 H), 1.57 (s, CH_3), 1.77 (m, 1 H), 2.17 (m, 1 H), 7.22–7.51 (m, 3 H), 7.84 (br d, J = 8 Hz, H_8); ^{13}C NMR δ 14.2 (t, J = 164 Hz, C_9), 25.8 (d, J = 168 Hz, C_2), 26.6 (q, J = 128 Hz, C_{10}), 28.5 (d, J = 164 Hz, C_3), 34.6 (s, C_4), 35.0 (q, J = 128 Hz, C_{11}), 125.5 (d, C_7), 126.6 (d, C_8), 127.1 (d, C_5), 129.6 (s, C_{8a}), 133.3 (d, C_6), 147.4 (s, C_{4a}); MS (EI), m/z 186 ($M^{+\cdot}$, 29), 171 (100), 144 (19), 143 (24), 128 (31), 115 (16). Anal. ($C_{13}H_{14}O$) C, H.

4,4-Dimethyl-2,3-methano-1,2,3,4-tetrahydro-*syn*- and *anti*-naphthalen-1-ols (23). To a solution of **22** (0.135 g, 0.726 mmol) in sodium-dried diethyl ether (2 cm^3) under nitrogen was added $LiAlH_4$ (0.2 mmol, 0.2 cm^3 of 1.0 M solution in tetrahydrofuran) and the reaction was stirred for 20 min, after which it was hydrolyzed with water, extracted, dried, and evaporated to yield **23** (0.136 g, 100%) as an oil: ^{13}C NMR δ 2.3 (t, C_9), 18.1 (d), 24.0 (d), 27.8 (q), 32.9 (q), 35.0 (s), 67.4 (d, COH, presumably[35] anti, relative intensity 5), 71.4 (d, COH, presumably syn, relative intensity 1), 124.7 (d), 125.8 (d), 126.2 (d), 127.5 (d), 135.6 (s), 141.6 (s); MS (EI), m/z 188 ($M^{+\cdot}$, 62), 173 (81), 155 (100), 145 (41), 143 (43), 129 (42), 128 (41), 115 (36); exact mass calcd for $C_{13}H_{16}O$, 188.1201; found, 188.1200.

4,4-Dimethyl-2,3-methano-*syn*- and *anti*-1-methoxy-1,2,3,4-tetrahydronaphthalenes (24). Alcohols **23** (90 mg, 0.48 mmol) were methylated according to Johnstone and Rose[41] to give **24** as an oil (90 mg, 93%): ^{13}C NMR (major isomer) δ 3.4 (t, C_9), 13.5 (d), 23.2 (d), 27.9 (q), 32.9 (q), 35.2 (s), 55.6 (q), 75.5 (d, COMe, presumably anti, relative intensity 6), [80.7 (d, COMe, presumably syn, relative intensity 1)], 125.0 (d), 125.8 (d), 126.1 (d), 127.4 (d), 129.1 (s), 142.1 (s); MS (EI), m/z 202 ($M^{+\cdot}$, 66), 187 (78), 171 (50), 155 (100), 143 (44), 141 (34), 129 (85), 128 (56), 115 (46), 45 (94); exact mass calcd for $C_{14}H_{18}O$, 202.1357; found, 202.1355.

5,5-Dimethylbicyclo[4.1.0]heptan-2-one (29). Treatment of 4,4-dimethylcyclohex-2-en-1-one (3.90 g, 31.5 mmol)[42] with dimethyloxosulfonium methylide as above,[7] afforded an oil which was distilled to give **29** as a colorless liquid (1.5 g, 34%). Redistillation of the forerun on a spinning-band column gave a further 1.1 g (total, 60%): bp 50–51 °C (1.0 mm); n^{23}_D 1.4778; 2,4-dinitrophenylhydrazone, orange needles from EtOAc/petroleum ether, mp 134.5-135.5 °C; IR (film) 2960, 2880, 1690, 1475, 1365, 1350 cm^{-1}; ^{1}H NMR δ 0.83–1.91 (m, 6 H), 1.12 (s, 6 H), 2.13–2.28 (m, 2 H); ^{13}C NMR δ 10.2 (t, J = 164 Hz, C_7), 26.6 (d, J = 169 Hz, C_5), 27.2 (q, J = 126 Hz, CH_3), 28.7 (d, d, J (av) = 121 Hz, C_3), 30.0 (q, J = 124 Hz, CH_3), 30.4 (d, J = 164 Hz, C_1), 30.4 (t, J = 127 Hz, C_4), 33.2 (s, C_2), 209.0 (s, C_5); MS (EI), m/z 138 ($M^{+\cdot}$, 36), 123 (35), 96 (77), 95 (76), 81 (82), 67 (82), 55 (98), 55 (86), 41 (100), 39 (87), 27 (77). Anal. ($C_9H_{14}O$) C, H.

2,5,5-Trimethylbicyclo[4.1.0]heptan-2-ol (30). Ketone **29** (0.87 g, 6.3 mmol) was added slowly to methylmagnesium iodide (10.0 mmol) in diethyl ether at room temperature and the mixture stirred for 2 h. Normal workup with saturated NH_4Cl solution and column chromatography (neutral aluminum oxide, diethyl ether) afforded a mixture of *syn*- and *anti*-**30** (0.34 g, 35%): bp 165–167 °C dec; IR (film) 3370,

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2960, 2870, 1470, 1370, 1360, 1170, 1090, 1070, 925, 890 cm^{-1}, ^1H NMR (major isomer) δ −0.10 (q, 1 H, J = 5.4 Hz), 0.5 (m, 1 H), 0.68–1.42 (m, 6 H), 0.90 (s, 3 H), 1.14 (s, 3 H), 1.28 (s, 3 H), 1.91 (br, s, 1 H, OH); ^{13}C NMR δ 6.9 (t, C_7), 23.5 (d), 24.1 (d), 26.7 (s, C_2), 29.0 (q), 29.9 (q), 32.5 (t), 32.8 (t), 32.9 (q), 69.1 (s, C_5); MS (EI), m/z 136 ($M^{+\cdot} - H_2O$, 36), 121 (55), 107 (38), 105 (24), 93 (100), 91 (40), 79 (47), 77 (32), 55 (30), 43 (30), 41 (54), 39 (45). Anal. ($C_{10}H_{18}O$) C, H.

Preparation of Cations. The cations were prepared by adding the appropriate alcohol or hydrocarbon (150–200 mg) in small amounts, either as solids or solutions in SO_2ClF or $CFCl_3$, to precooled solutions of FSO_3H/SO_2ClF (final volume ~1.5 cm^3, 1:2 v/v $FSO_3H:SO_2ClF$) at −130 °C (pentane/liquid N_2 slush) or −80 °C (acetone/CO_2) in 10-mm NMR tubes and stirred vigorously (vortex mixer) under nitrogen. Proton NMR samples were prepared similarly in 5-mm tubes.

Quenching of Cations. 11. A solution of cation **11** (~2 cm^3, ~0.5 M) from dissolution of alcohol **8b** in FSO_3H/SO_2ClF at −100 °C was warmed to −60 °C [^1H NMR δ (−60 °C) 1.76 (d, J = 7 Hz, 2 × CH_3), 3.77 (m, 1 H), 3.73 (s, CH_3), 5.26 (br s, 2 H), 8.05–8.65 (m, 3 H), 9.10 (m, 1 H), 9.37 (br s, 1 H)] and poured into a solution of NaOMe (3.5 g) in MeOH (60 cm^3) at −110 °C with vigorous stirring. After warming to room temperature, the colorless solution was diluted with water (60 cm^3), extracted with petroleum ether (40–60 °C), washed with H_2O (3 × 30 cm^3), dried, and evaporated. The product was purified by preparative TLC (silica, petroleum ether) to afford 2-isopropyl-1-methylnaphthalene (**12**), identical with independently synthesized material (see above). Similarly, a solution of **8b**–*2-methyl-d_3* was warmed to −60 °C for 15 min, quenched, and purified by TLC (petroleum ether:ethyl acetate 15:1) to yield 2-(isopropyl-d_3)-1-methylnaphthalene: ^1H NMR δ 1.28 (d, J = 7 Hz, 1 × CH_3), 2.65 (s, CH_3), 3.47 (br q, 1 H), 7.19–8.09 (m, 6 H); ^{13}C NMR δ 23.5 (q, m, CH_3, CD_3); MS (EI), m/z 187 ($(M + 3)^{+\cdot}$, 100), 172 ($(M + 3)^{+\cdot} - CH_3$, 96), 169 ($(M + 3)^{+\cdot} - CD_3$, 86).

14. Naphthalene **13** (0.18 g, 0.98 mmol) dissolved in SO_2ClF at ~0 °C was added dropwise to a solution of FSO_3H/SO_2ClF (1:2 v/v) at −110 °C under nitrogen with rapid vortex mixing to give a deep red solution (1:3 $FSO_3H:SO_2ClF$, 1.5 cm^3, 0.65 M) of **14**: ^1H NMR δ (−80 °C), 0.47 (d, J = 6 Hz, CH_3), 1.76 (d, J = 6 Hz, CH_3) , 1.76 (m, overlapping, 1 H), 3.28 (s, CH_3), 5.14 (br s, H_1), 7.75–8.60 (m, 5 H), 9.40 (d, J = 8 Hz, H_4); ^{13}C NMR see Table I.

The solution of **14** was quenched immediately after recording of the NMR spectra and worked up in the usual way. The product was identified (^1H NMR) as **13**. A solution of **14**, stored at −80 °C for 14 days was quenched in the same way, but the product isolated was **12**, identical (^1H NMR) with authentic material.

15. A solution of **10a**, prepared by ionization of **8a** in FSO_3H/SO_2ClF at −130 °C was warmed to −95 °C for 15 min, after which time the solution contained only **15**. This was poured into NaOMe/MeOH at −110 °C and worked up in the usual way. Preparative TLC (silica, petroleum ether:ethyl acetate 9:1) afforded slightly impure methyl ether **16** as a colorless oil: ^1H NMR δ 1.15 (d, J = 6 Hz, CH_3), 2.07 (dd, $J \simeq J$ = 1.4 Hz, $CH_3C{=}C$), 2.4 (m, 1 H), 2.77 (m, 2 H), 3.2 (m, 1 H), 3.32 (s, CH_3O), 5.73 (m, 1 H), 7.13–7.26 (m, 4 H); ^{13}C NMR δ 16.6 (q), 19.4 (q), 30.5 (t, C_4), 39.5 (d, C_3), 56.4 (q, CH_3O), 78.3 (d, C_9), 122.7 (d, C_2), 126.2 (d), 126.5 (d), 126.8 (d), 127.7 (d), 128.8 (s), 132.9 (s), 135.6 (s); MS (EI), m/z 202 ($M^{+\cdot}$, 32), 200 (39), 187 (19), 185 (22), 171 (94), 169 (33), 143 (78), 142 (95), 141 (24), 115 (19), 59 (100).

1-Methyl-3-(1-methoxyethyl)naphthalene (17). Compound **16** (18.2 mg, 0.09 mmol) was treated with DDQ (20.5 mg, 0.09 mmol) in benzene at 20 °C for 1 h. The mixture was passed through a short column of aluminum oxide using diethyl ether as eluent and evporated to give slightly impure **17** (17 mg, 94%) as a colorless oil: ^1H NMR δ 1.50 (d, J = 6 Hz, CH_3), 2.70 (s, CH_3), 3.26 (s, CH_3), 4.42 (q, J = 6 Hz, 1 H), 7.1–7.3 (m, 2 H), 7.43–7.59 (m, 2 H), 7.78–7.93 (m, 2 H); MS (EI), m/z 200 ($M^{+\cdot}$, 19), 185 ($M^{+\cdot} - CH_3$, 63), 168 ($M^{+\cdot} - CH_3OH$, 100), 167 (44), 165 (24), 153 (28), 152 (29), 141 (37), 115 (31); exact mass calcd for $C_{14}H_{16}O$, 200.1201; found, 200.1198.

18. When a solution of **10a** was warmed to −80 °C, the ^{13}C NMR spectrum indicated the presence of two cations **15** and **18**. Quenching of this solution in the usual manner, followed by preparative TLC (silica, petroleum ether:ethyl acetate 15.1) yielded the methyl ether **16** and 3-ethyl-1-methylnaphthalene (**19**) as a colorless oil: ^1H NMR[12] δ 1.31 (t, J = 7 Hz, CH_3), 2.67 (s, CH_3), 2.77 (q, J = 7 Hz, 2 H), 7.20 (br s, 1 H), 7.39–7.49 (m, 3 H), 7.74–8.0 (m, 2 H); MS (EI), m/z 170 ($M^{+\cdot}$, 100), 155 (83), 141 (17), 128 (19), 115 (22).

10a. Solutions of **10a**, prepared both from **8a** and from **23**, were poured into solutions of NaOMe/MeOH at −110 °C with stirring and worked up in the usual way, to give a colorless oil, **24**, as a mixture of syn and anti isomers (~5:1): ^{13}C NMR (syn) δ 4.6 (t), 15.6 (d), 22.8 (d), 28.8 (q), 33.5 (q), 35.2 (s), 55.9 (q), 80.8 (d), 125.6 (d), 126.1 (d), 129.1 (d), 130.2 (s), 131.1 (d), 144.1 (s); MS (EI), m/z 202 ($M^{+\cdot}$, 22), 187 (72), 171 (34), 157 (57), 155 (100), 143 (39), 142 (41), 141 (32), 129 (60), 128 (48), 115 (40), 59 (30), 45 (39).

10c. A solution of **10c** [(^1H NMR δ (−90°), 1.51 (s, CH_3), 2.20 (s, CH_3), 2.74 (br s, 1 H), 4.39 (m, 1 H), 4.96 (m, 1 H), 7.50–8.45 (m, 4 H), 10.66 (d, J = 8 Hz, 1 H)] prepared from **8c** was poured into NaOMe/MeOH at −110 °C and the resulting mixture worked up in the usual way. TLC of the product (silica, petroleum ether:ethyl acetate 9:1) afforded the methyl ether **20** as a colorless oil: ^1H NMR δ 0.39 (t, J = 5 Hz, 1 H), 0.83 (d, d, J = 3, 9 Hz, 1 H), 1.25 (s, CH_3), 1.41 (s, CH_3), 1.82 (m, 1 H), 3.41 (s, OCH_3), 4.60 (d, J = 3 Hz, 1 H), 7.1–7.5 (m, 9 H); ^{13}C NMR δ 13.2 (t), 24.6 (d), 25.6 (q), 31.4 (q), 33.8 (s), 38.8 (s), 56.0 (q, OCH_3), 80.4 (d, C_4), 125.7 (d), 126.1 (d), 126.4 (d), 127.4 (d, 2 × C), 128.5 (s), 129.0 (d), 130.9 (d), 133.0 (d, 2 × C), 143.7 (s), 145.3 (s); MS (EI), m/z 278 ($M^{+\cdot}$, 100), 246 (47), 231 (70), 216 (24), 215 (27), 173 (17), 119 (16), 105 (16), 91 (20); exact mass calcd for $C_{20}H_{22}O$, 278.1670; found, 278.1668.

Acknowledgment. We are grateful to A. Smrdel for preparing one sample of **5**, to Professor T. A. O'Donnell for preparing $CeCl_3$, and to A. S. Wedgwood for the mass measurements. This work was supported by the Australian Research Grants Scheme.

Registry No. 5, 23230-52-6; **6**, 80816-93-9; **7a**, 22303-18-0; **7b**, 34599-69-4; *syn*-**8a**, 88105-34-4; *anti*-**8a**, 88195-40-8; **8b**, 88105-35-5; **8c**, 88105-36-6; **10a**, 88105-37-7; **10b**, 88105-38-8; **10c**, 88105-39-9; **11**, 88083-68-5; **12**, 61994-26-1; **13**, 32114-79-7; **14**, 88083-67-4; **15**, 88105-40-2; **16**, 88105-41-3; **17**, 88105-42-4; **18**, 88105-47-9; **19**, 17179-41-8; **21**, 16020-16-9; **22**, 61463-22-7; *anti*-**23**, 88195-41-9; *syn*-**23**, 61463-23-8; *anti*-**24**, 88105-43-5; *syn*-**24**, 88195-42-0; **29**, 88105-44-6; *anti*-**30**, 88105-45-7; *syn*-**30**, 88195-43-1; **31**, 88105-46-8.