$^{13}C-^{1}H$ Coupling Constants in Carbocations. 8.[1] Application of the ΔJ Equation to Tertiary Dicyclopropylcarbinyl Cations: The Methyl Dicyclopropylcarbinyl, (1α,3β,5β,7α)-2-Methyltricyclo[5.1.0.0^{3,5}]octan-2-yl, (1α,3α,5α,7α)-2-Methyltricyclo[5.1.0.0^{3,5}]octan-2-yl, and 3-Methyltetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonan-3-yl (Triasteryl) Cations

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Received October 17, 1994[⊗]

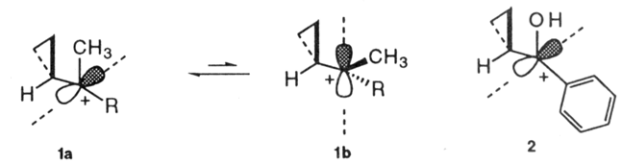
One-bond $^{13}C-^{1}H$ coupling constants have been determined for the title cations (**10**, **15**, **20**, and **25**) in superacids and the values for the carbons adjacent (α) to the cationic centers compared with those of the appropriate model ketones to obtain the ΔJ values. These values were found to be in the range 10−15 Hz, approximately one half that expected for a single cyclopropylcarbinyl cation. This has been interpreted in terms of delocalization of charge into the second cyclopropyl group in those cations which can adopt double bisected conformers, **10**, **20**, **25**, and in terms of averaging of the coupling constants as a result of two different dihedral angles in cation **15**. New methods for the synthesis of precursors to the 2-methyltricyclo[5.1.0.0^{3,5}]octan-2-yl cations, **15** and **20**, have been developed.

Introduction

The ΔJ equation (1), correlates the difference in one bond $^{13}C-^{1}H$ coupling constants of groups adjacent (α) to the cationic center and those in neutral model compounds (usually ketones) to the dihedral angle (θ) between the C−H bond and the vacant pπ orbital. This equation has been used in various studies concerned with determining the structure of acyclic, cyclic, bicyclic, and nonclassical cations.[2,3]

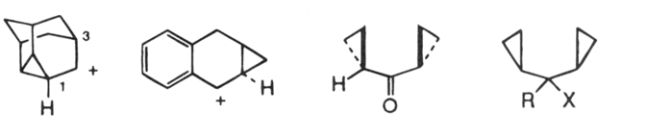
$$\Delta J = 22.5 - 33.1 \cos^2 \theta \qquad (1)$$

There is substantial evidence from theory,[4] and from solvolytic[5] and stable ion[6] studies, that the tertiary cyclopropylcarbinyl cation moiety c-$C_3H_5C^+R_2$ prefers a bisected conformation **1a** rather than a parallel conformation **1b**. For example, the dimethylcyclopropylcarbinyl cation **1** (R = CH_3) exhibits a markedly shielded (by 0.54 ppm) methyl proton resonance at δ 2.7 consistent with its position in the diamagnetic face of the cyclopropyl ring.[7] More recently, X-ray diffraction data[8] on the hexafluoroantimonate salt of protonated cyclopropyl phenyl ketone **2** established that in the solid state the cation adopts a conformation whereby the cyclopropyl group is in the bisected arrangement and the phenyl ring is fully conjugated with the pπ orbital. This illustrates the different conformations required to give maximum stabilization of the cation by the two different groups.



1a **1b** **2**

Internal cyclopropylcarbinyl cations, that is, those in which this moiety is embedded within a larger polycyclic framework, are either constrained to, as in **3**,[9] or preferentially adopt, as in **4**,[3d,f] the bisected arrangement. ΔJ values for the associated methine groups are typically 22 ± 2 Hz.[3a,d,f] The question then arises as to the conformation adopted by dicyclopropylcarbinyl cations, the parents of which (**9**, **10**) were first observed by Olah, Deno, and co-workers.[7]



3 **4** **5** **6** R=CH(CH$_3$)$_2$, X=OH; **7a** R=CH$_3$, X=OH; **7b** R=CH$_3$, X=OCH$_3$

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) Part 7: see Kelly, D. P.; Aherne, K.; Delgado, F.; Giansiracusa, J. J.; Jensen, W. A.; Karavokiros, K.; Mantello, R. A.; Reum, M. E. *J. Am. Chem. Soc.* **1993**, *115*, 12010−12015.

(2) For a review, see Kelly, D. P. *Advances in Carbocation Chemistry*; Coxon, J. M., Ed.; J.A.I. Press Inc.: Greenwich, CT; Vol. 2, in press.

(3) (a) Kelly, D. P.; Brown H. C. *J. Am. Chem. Soc.* **1975**, *97*, 3897−3900. (b) Kelly, D. P.; Underwood, G. R.; Barron, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 3106−3111. (c) Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Hugel, H. M.; Porter, A. M.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 3539−3543. (d) Kelly, D. P.; Leslie, D. R.; Smith, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 687−694. (e) Kelly, D. P.; Giansiracusa, J. J.; Leslie, D. R.; McKern, I. D.; Sinclair, G. C. *J. Org. Chem.* **1988**, *53*, 2497−2504. (f) Kelly, D. P.; Banwell, M. G.; Ireland, N. K.; Noel, A. L. *J. Org. Chem.* **1991**, *56*, 2040−2045.

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(6) For reviews, see: (a) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem Rev.* **1992**, 92, 69−95. (b) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley, New York, 1985; Ch. 3.

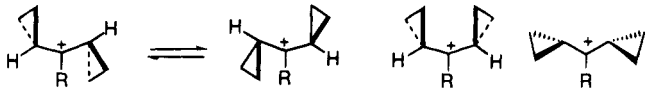
(7) (a) Pittman, C. U.; Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 2998−3000. (b) Deno, N. C.; Liu, J. S.; Turner, J. O.; Lincoln, D. N.; Fruit, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3000−3002.

(8) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692−1693.

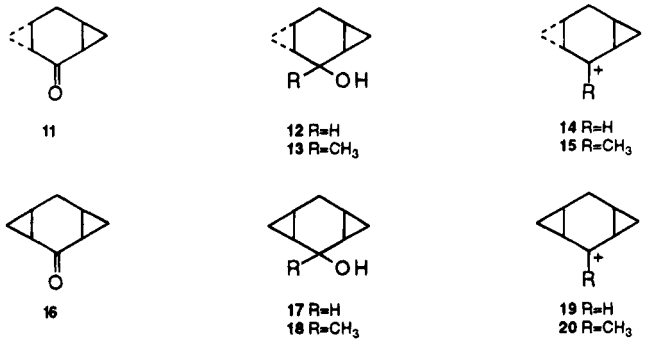
(9) Olah, G. A.; Liang, G.; Babiak, K. A.; Ford, T. M.; Goff, D. L.; Morgan, T. K.; Murray, R. K. *J. Am. Chem. Soc.* **1978**, *100*, 1494−1500.

0022-3263/95/1960-1651$09.00/0

Tertiary dicyclopropylcarbinyl derivatives (e.g. **6**, **7**) undergo solvolysis approximately 100-times faster than their monocyclopropylcarbinyl analogues[5,10] suggesting that both cyclopropyl groups may be in the favored bisected arrangement. The X-ray data of Childs *et al.*[8] shows that in the solid state, protonated dicyclopropyl ketone (5 → 8) has both groups bisected in a "sickle" conformation **8a**. ^{13}C NMR data of **8**, prepared in superacid by Olah and co-workers, was interpreted in favor of bisected cations although the exact conformation (**a**, **b**, or **c**) is uncertain.[7a,11]

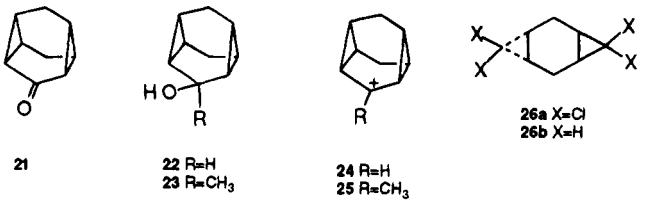


The conformationally constrained tricyclo[5.1.0.$0^{3,5}$]-octan-2-yl systems **14** and **19** have been examined by Lambert and co-workers[12] who, in so doing, prepared the *anti*- and *syn*-ketones, **11** and **16**, respectively, as well as the related secondary alcohols **12** and **17**. Solvolysis of the *p*-nitrobenzoate of **17** (β-OH) in dioxane/water proceeded 20–30 times faster than the equivalent reaction of the *p*-nitrobenzoate of **12** and gave a mixture of the epimeric alcohols **17**.[12] Lambert suggested that the intermediate cation **19** might have a face-to-face structure where both cyclopropyl groups "enjoy the bisected geometry" whereas the more flexible dicyclopropyl cation **9** "cannot attain the ideal geometry (of **19**) because of steric factors".



The triasteryl cations **24** and **25** provide the opportunity to examine a system in which the two cyclopropyl groups are locked in a face-to-face arrangement. Musso and co-workers have proposed the secondary cation **24** as the intermediate in a variety of reactions of the secondary alcohol **22** (prepared from **21**) and its esters.[13] Although solvolysis of the tosylate of **22** gave rearranged acetates and alcohols, azide ion captured the cation **24** intact. The cation **24** was observed in FSO_3H/SO_2ClF at −30 °C and it was concluded that both cyclopropyl groups provided stabilization of the cationic center.[13]

The stereochemical dependence of $^1J_{CH}$ provides a method to probe the conformations of the cations such as those described above.[3b] We now report our results for the tertiary dicyclopropylcarbinyl systems **10**, **15**, **20**, and **25** together with new methods of synthesis of the precursor alcohols **13** and **18**.



Results and Discussion

Synthesis. The preparation of the precursor **7a** to cation **10** was very straightforward and simply involved addition of methyllithium to commercially available dicyclopropyl ketone **5**. In contrast, the acquisition of precursors to the cations **15** and **20**, i.e. alcohols **13** and **18**, respectively, was much more demanding. Initial efforts focussed on preparing the related ketones **11** and **16**. Rather than using the procedure of exhaustive cyclopropanation of methyl cyclohexa-2,5-diene-1-carboxylate as performed by Lambert, Koeng, and Hamersma,[12] we developed alternative routes to the ketones **11** and **16**. Thus dichlorocarbene addition to cyclohexa-1,4-diene gave the known[14] bis-adduct **26a** which was subjected to reductive dehalogenation with sodium in ethanol.[15] The resulting hydrocarbon **26b**[14c] was treated with the chromium trioxide/3,5-dimethylpyrazole complex[16] thereby giving ketone **11** in 35% overall yield.

The *syn*-ketone **16** was obtained by two methods. The first involved solvolysis of the *p*-nitrobenzoate derivative[12] of the *syn*-alcohol **17** which afforded quantities of the alcohol itself. Pyridium chlorochromate-promoted oxidation of alcohol **17** then gave the previously reported[12] ketone **16**. The second and more direct route to compound **16** involved initial bis-cyclopropanation of cyclohexa-1,4-diene according to the procedure of Simmons and Smith.[17] Subjection of the resulting 6:1 mixture of (1α,3β,5β,7α)- and (1α,3α,5α,7α)-tricyclo[5.1.0.$0^{3,5}$]octanes to reaction with the chromium trioxide/3,5-dimethylpyrazole[16] complex then afforded a 5.5:1 mixture of ketones **11** and **16**. These two compounds could be separated from one another by high performance liquid chromatography (HPLC).

Independant subjection of ketones **11** and **16** to reaction with methyllithium resulted in formation of the corresponding cyclopropylcarbinols **13** and **18**. In the reaction involving formation of alcohol **18** a 6:1 mixture (as determined by ^1H NMR spectroscopy) of the two possible diastereoisomers was obtained. However, during attempted purification of this mixture it became apparent that the major diastereoisomer underwent preferential dehydration (to give the corresponding exocyclic alkene).

(10) (a) Hart, H.; Law, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 1957–1959. (b) Hart, H.; Sandri, J. M. *J. Am. Chem. Soc.* **1959**, *81*, 320–326.

(11) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548–3559.

(12) Lambert, J. B.; Koeng, F. R.; Hamersma, J. W. *J. Org. Chem.* **1971**, *36*, 2941–2947.

(13) (a) Biethan, V.; Fauth, W.; Musso, H. *Chem. Ber.* **1977**, *110*, 3636–3648. (b) Musso, H.; Biethan, V. *Chem. Ber.* **1967**, *100*, 119–131.

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(15) Lap, B. V.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979–4981.

(16) Banwell, M. G.; Haddad, N.; Huglin, J. A.; Mackay, M. F.; Reum, M. E.; Ryan, J. H.; Turner, K. A. *J. Chem. Soc., Chem. Commun.* **1993**, 954–957.

(17) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347–1356.

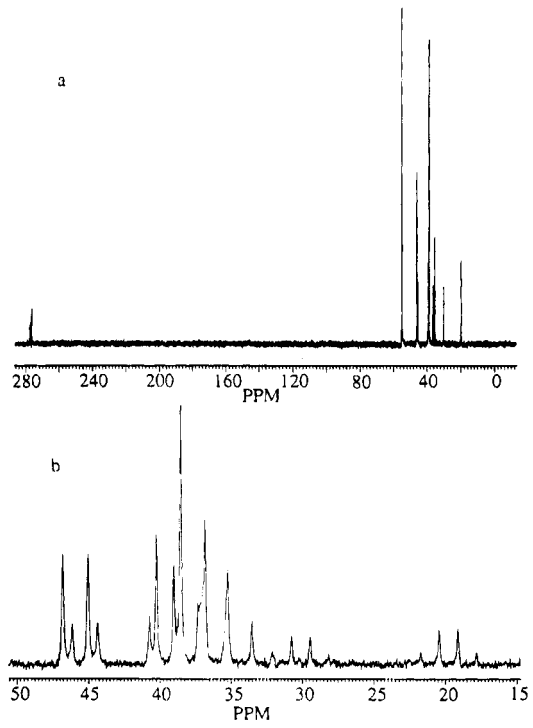


Figure 1. ^{13}C NMR spectra of cation **10** in $FSO_3H/CH_2Cl_2/SO_2ClF$ at −120 °C. (a) Proton decoupled (CH_2Cl_2 at δ 54.81). (b) Proton coupled.

Consequently, the material that was finally used in the cation generation studies consisted of a *ca.* 2:1 mixture of diastereoisomers with the same isomer still predominating.

The tertiary alcohol **23**, like its simpler congeners, was readily prepared by addition of methyllithium to the corresponding ketone **21** which had been provided to us by colleagues of the late Professor H. Musso.

Dicyclopropylcarbinyl Cation 10. When 1-methyldicyclopropylcarbinol (**7a**) was dissolved in FSO_3H/SO_2ClF at −78 °C, it produced a pale yellow solution, the ^{13}C NMR spectrum of which exhibited only three broadened signals at 277, 45, and 38 ppm as originally reported by Olah and co-workers.[7] However, preparation of the cation at −120 °C or cooling the ion solution from −78 °C, gave a clean, sharp 10-line ^{13}C NMR spectrum which indicated the presence of two very similar cations in a ratio of approximately >1:1 with δ_{C^+} 276.3 (major), 277.3 (minor) (Figure 1a). Warming to −80 °C reproduced the original three-line spectrum but with reduced intensity and a darker color. Successful ionization of **7a** to **10** at −120 °C was confirmed upon quenching of the ion solution in methoxide/methanol which yielded a methyl ether identical to authentic **7b** (prepared from **7a** by treatment with NaH/MeI).

The fully-coupled ^{13}C NMR spectrum of cation **10** allowed the identification of two sets of multiplets (Figure 1b). Within each set of multiplets the J_{CH} values were identical, 177 Hz for the methine carbons ($C_{1,3}$) at δ 45.9 and 45.2, 173 Hz for the methylene carbons ($C_{4,8}$) at δ 38.5 and 39.0, and 131 Hz for the methyl carbons at δ 19.7 (major) and 30.1 (minor) (Table 1).[18] The value of 177 Hz for $C_{1,3}$, together with that of **5** (165 Hz), gave $\Delta J = 12$ Hz. This is approximately one half of the value measured for monocyclopropylcarbinyl cations.

Three distinct situations may be envisaged which account for the observed value of 12 Hz for **10**. Firstly, both dihedral angles might be 56°, but this is unlikely given the overwhelming evidence for the stabilization provided by one bisected conformation. Secondly, the two dihedral angles are different, with one bisected conformation ($\theta = 90°$); the other angle would need to be ~30° (eq 1). Thirdly, both cyclopropyl groups may adopt bisected conformations, the second group delocalizing charge from the cationic center in a similar manner to a phenyl group. Indeed, the ΔJ equation has been modified for aryldialkyl cations so as to account for such delocalization, as shown by eq 2.[3c]

$$\Delta J = (1 + 0.6\sigma^+)(10.9 - 14.3\cos^2\theta) \qquad (2)$$

For phenyl cations, $\sigma^+ = 0$ and $\Delta J = 11$ Hz when $\theta = 90°$. If a cyclopropyl group has approximately the same capacity as a phenyl group at delocalizing adjacent positive charge in tertiary cations,[19] the observed value of 12 Hz for **10** is consistent with an all-bisected arrangement.

For the four possible doubly-bisected conformations of cation **10**, calculated steric energies increase in the order **a** = **a′** ≈ **c** < **b**, the face-to-face "U" conformer **b** being approximately 5 kcal higher. The "W" conformer **c** was favored by Olah from consideration of proton−proton coupling constants.[7a] The NMR results reported here are consistent with **10** existing as three conformers, two "sickle" conformers (**a**, **a′**), and a "W" conformer (**c**) (or less likely a "U" conformer) which interconvert rapidly at −70 °C. However, at −120 °C the interconversions, **10a** ⇌ **10a′** and **10a** ⇌ **10c** are both slow on the NMR time scale giving rise to two distinct cations, a "sickle" cation with nonequivalent cyclopropyl groups (6 lines) and a "W" cation (4 lines). Comparison of the ratio of the intensities of the peaks for the two cations **10a**,**a′**:**10c** (1:1.5) with that expected statistically (2:1) indicates that **10c** is the preferred conformer of the 1-methyl dicyclopropylcarbinyl cation.

In this context it is worth noting that Olah has previously reported[11] that protonation of dicyclopropyl ketone **5** occurs in $FSO_3H/SbF_5/SO_2ClF$ to give a spectrum exhibiting two methine and two methylene resonances, the asymmetry being ascribed to two conformers resulting from the orientation of the OH group. Protonated nortricyclanone **27a**, **27b**, in which the only conformational mobility is due to the OH group, also exhibits two sets of resonances.[20] However, values of $^1J_{C2H}$ are

(18) The multiplets corresponding to resonances at δ 35.2 and 36.2 are overlapped by other signals, but appear to be a triplet (J = ~173 Hz) and a doublet (no intensity at the chemical shift). These have been assigned to the methylene and methine carbons of one of the nonequivalent cyclopropyl groups of **10a**,**a′** (see Table 1).

(19) There is no clear cut decision on which is the better group at delocalizing charge; the result depends on the criterion used and whether the cations under consideration are primary, secondary, or tertiary. (a) c-C_3H_5 > Ph > Me, refs 4, 4b and Brown H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1978**, *95*, 2400−2401. (b) ^{13}C NMR chemical shifts at cationic and *para*-carbons of tertiary cations; Ph > c-C_3H_5 > Me, ref 10 and Olah, G. A.; Westerman, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 7530−7531. (c) ^{19}F NMR shifts at *para*-position of phenyl cations; c-C_3H_5 > Ph > Me, Volz, H.; Shin, J.-U.; Streicher, H.-J. *Tetrahedron Lett.* **1975**, 1297−1300. (d) ^{19}F, ^{13}C, ^{1}H chemical shifts of C-6 of 1-(2-naphthyl)ethyl cations; c-C_3H_5 > Ph > Me, Kitching, W.; Adcock, W.; Aldous, G. *J. Org. Chem.* **1979**, *44*, 2652−2658. (e) ^{19}F of cyclopropylcarbinyl fluorides, Ph > c-C_3H_5 > vinyl, Noe, E. A.; Young, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 6218−6220. (f) Ion cyclotron resonance spectroscopy of isodesmic hydride transfer reactions, Wolf, J. F.; Harch, P. G.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 2902−2904, Ph > c-C_3H_5 > Me for primary and secondary cations, but Ph ~ c-C_3H_5 for tertiary cations.

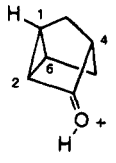
(20) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920−1927.

Table 1. ^{13}C NMR Parameters of Cations and Model Compounds[a]

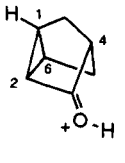
compound	temp, °C	position 1	2	3	4, 8	5, 7	6	CH_3
5[b]		20.5 (d, 165)	210.3 (s)	20.5 (d, 165)	10.4 (t, 165)			
8[b]	−70	29.3 (d, 180), 29.0 (d, 176)	234.0	26.7 (t, 171), 24.6 (t, 171)				
10[b]	−70	45	277	45	38			38
a, a'	−120	45.2 (d, 177)	277.3 (s)	36.2 (d)	35.2, 39.0 (t, 173, 173)			30.1 (q, 131)
c		45.9 (d, 177)	276.3 (s)	45.9 (d, 177)	38.5 (t, 173)			19.7 (q, 131)
11		20.2 (d, 169)	206.8 (s)	20.2 (d, 169)	12.3 (d, d, 161, 8)	11.2 (d, 165)	20.9 (t, 129)	
15	−110	42.8 (d, 180)	266.8 (s)	42.8 (d, 180)	43.2 (t, 174)	19.2 (d, 170)	23.1 (t, 133)	35.2 (q, 131)
16		23.7 (d, 164)	206.9 (s)	23.7 (d, 164)	15.7 (t, 162)	22.2 (d, 162)	18.0 (t, 128)	
20	−110	44.0 (d, 176)[c]	250.9 (s)	44.0 (d, 176)[c]	43.0 (t, 174)	80.9 (d, 172)	22.8 (t, 125)	35.9 (q, 134)
21		25.8[e] (d, 167)	28.2[f] (d, 172)	206.7 (s)	*e,f*	25.8 (d, 167)	17.2[g] (t, 130)	
25	−100	68.7[e] (d, 175)	50.2[f] (d, 182)	248.2 (s)	*e,f*	68.7 (d, 175)	19.9[g] (dd, 130, 135)	33.4 (q, 130)
27[d]	−80	41.2, 40.4 (d, 188)	28.5, 27.4 (d, 198)	247.4, 247.6 (s)	38.3, 39.4 (d, 161)	36.1, 36.6 (t, 141)		

[a] $^{13}C-^{1}H$ coupling constants, ±2 Hz unless otherwise specified, in parentheses. [b] Reference 11. Numbering scheme allows comparison with polycyclic systems. [c] ±4 Hz. [d] The first chemical shift given is that of the more intense signal (major isomer). [e] C1,5,6,8. [f] C2,4. [g] C7,9.

probably not sensitive to OH orientation since they are the same in **27** but different in **8** (Table 1).



27a



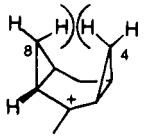
27b

Tricyclo[5.1.0.0]octanyl Cations 15 and 20. Very careful dissolution of alcohol **13** in FSO_3H/SO_2ClF at −120 °C also produced a pale yellow solution containing cation **15**, the coupled ^{13}C NMR spectrum of which was sufficiently clean to allow measurement of all couplings (Table 1). However, this cation could never be prepared without accompanying impurities and, furthermore, it was very sensitive to treatment with any of the superacids and to temperatures above −100 °C. Quenching of the solutions containing **15** with various nucleophiles only produced complex mixtures of products. Decomposition occurred steadily above −110 °C. From the $C_{1,3}$ couplings of **11** and **15**, ΔJ has been determined as 11 Hz.

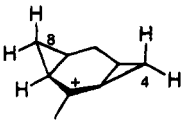
Examination of Dreiding models of cation **15** indicates that at any one time only one cyclopropyl ring can adopt the bisected conformation (θ = 90°), the other C−H dihedral angle being substantially less. The only conformational change available to the cation is a boat-to-boat interconversion, which merely swaps the orientation of the two cyclopropyl groups. Since the two α-carbons are equivalent, the value of J_{CH} must represent an average of the two $^{13}C-^{1}H$ interactions. As in the case of the dicyclopropylmethylcarbinyl cation **10** discussed above, application of the ΔJ equation yields a value of *ca.* 30° for the other dihedral angle if one is held at 90° in the bisected conformation (ΔJ = 22 Hz for 90°, *ca.* 0 Hz for 30°). These angles are consistent with those obtained from molecular models.

The observation of the same value of ΔJ for both cations **10** and **15** presents a problem, since in ion **10** rotation about the C^+-C_α bonds can provide four bisected conformations, **10a,a',b,c** whereas this is not possible in **15**. Therefore, either cation **10** has a similar conformational structure to **15** with two different dihedral angles of 90° and 35°, or it has a double-bisected conformation with greater charge delocalization into the second cyclopropyl ring. The marked difference in stability of the two cations supports the latter interpretation.

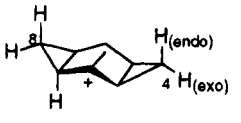
The *syn*-cation **20** was generated in a similar fashion (from precursors **18**) and gave an excellent spectrum at −110 °C from which the coupling constants were readily obtained; at 15 Hz the ΔJ value is slightly higher for this cation. In this *syn*-cation both dihedral angles are restricted to the same value. Nevertheless, different conformations are possible. In **20c** the nonbonding interactions of the *endo*-protons H_4, H_8 are minimized and the dihedral angles are *ca.* 30°. The double-bisected conformation ($\theta_1 = \theta_2 = 90°$) **20a** involves considerable nonbonding interaction between the *endo*-protons. The observed ΔJ value of 15 Hz for **20** is not consistent with **20c** (ΔJ predicted = 0 Hz) but is consistent with a more or less face-to-face arrangement similar to **a** but with lower angles, as shown in **20b**. Equation 1 gives an angle of 62° which would flatten the cyclohexyl ring and relieve the nonbonding interaction of the *endo* H_4, H_8 protons. Charge delocalization into the cyclopropyl rings, as proposed for **10** would be substantially reduced.



20a ($\theta_1 = \theta_2 = 90°$)



20b ($\theta_1 = \theta_2 = 62°$)



20c ($\theta_1 = \theta_2 = 30°$)

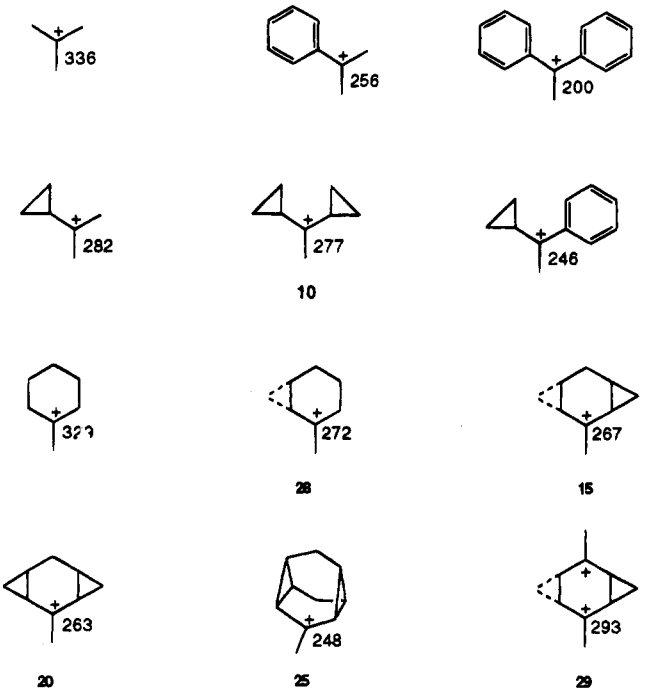
Tetracyclo[3.3.1.0.0]nonanyl Cation 25. Finally, the tertiary triasteryl alcohol **23** was ionized cleanly in FSO_3H/SO_2ClF at −120 °C to yield cation **25**, the ^{13}C spectrum of which exhibited five sharp peaks (Table 1). Use of $^{1}J_{C2H}$ of 182 Hz obtained from the coupled spectrum and that for triasterone **21** yielded a ΔJ value of 10 Hz. In cation **25**, conformational mobility is not possible with both dihedral angles fixed at 90°. The observed value of 10 Hz for ΔJ is consistent with this structure where charge delocalization into both cyclopropyl groups occurs and eq 2 applies.

Cationic Carbon Shifts. ^{13}C chemical shifts of cationic carbons have been used as a measure of charge density in closely related series of cations.[21,22] If charge delocalization occurs as a result of conformational changes as suggested above, then these changes should be reflected in the cationic carbon shifts.

Replacement of a methyl group in the *tert*-butyl cation by a phenyl group results in massive shielding of ap-

proximately 80 ppm of the cationic carbon.[23] Replacement of a second methyl group causes a somewhat smaller, but still significantly large change ($\Delta\delta \sim 56$ ppm). In the 1,1-diphenyl-1-ethyl cation, both phenyl groups can be almost planar with the cationic carbon thus providing close to maximum conjugative stabilization.[24]

Replacement of a methyl group in the *tert*-butyl cation



by a cyclopropyl moiety also causes a large shielding of the cationic carbon ($\Delta\delta \sim 54$ ppm)[25,26,3a] but a second cyclopropyl group (to give **10**) results in only a trivial change ($\Delta\delta \sim 5$ ppm). This result, together with that for the 1-cyclopropyl-1-phenylethyl cation, could be interpreted in terms of superiority of the phenyl group in the stabilization of charge or of a conformation in which only one cyclopropyl group is in the bisected orientation. However, consideration of the data for the internal cyclopropylcarbinyl cations provides an alternative explanation as outlined below.

The cationic carbon of **28**[27] is also shielded by *ca.* 57 ppm from that in 1-methylcyclohexyl[28] to a value not dissimilar to that for **10**, yet only has one cyclopropyl group. Addition of a second cyclopropyl group, as in **15**, which cannot attain the favored bisected arrangement, causes a trivial shift of 5 ppm. A similar shift in the isomeric *syn*-dicyclopropylcarbinyl cation **20**, may also be interpreted in terms of a conformation in which both cyclopropyl groups cannot adopt a completely bisected "U" (face-to-face) arrangement.

Cation **25**, where no other possibility but the face-to-face arrangement exists, has a very low cationic shift (*ca.* 248 ppm), which is substantially less than **10** (by 29 ppm), **15** (by 19 ppm), and **28** (by 24 ppm). As expected for a dication, **29** has a large value of δ_{C^+}, between that for 1-methylcyclohexyl and **1** (R = CH_3).[29]

The additional stabilization provided by enhanced delocalization of charge in **25**, and to a lesser extent in **20**, is also evidenced by the fact that the β-carbons are deshielded with respect to the α-carbons while the reverse applies in **10** and **15**.[30]

Conclusions

Within experimental error, the ΔJ values for all four cations (**10**, **15**, **20**, and **25**) are in a range of 10–15 Hz, approximately one-half of that estimated from the ΔJ equation for a bisected arrangement ($\theta = 90°$). The relatively low value of ΔJ for the conformationally mobile cation **10** may be due to its predominant conformers being either those with only a single bisected structure (with dihedral angles of 90° and 30° as proposed in case of **15**) or those with doubly bisected structures with additional charge delocalization in to the second cyclopropyl group. Comparison of cationic carbon shifts support the former interpretation, but calculations, X-ray, solvolysis, and other superacid studies support the latter. Neither ΔJ nor δ_{C^+} values are able to determine the precise conformation of this unconstrained cation.

In the conformationally constrained cation **20**, the low value is due to an intermediate conformation **20b** in which both dihedral angles are 62° (bisected), which is a compromise between **20c** and a doubly-bisected arrangement **20a** and its resulting (unfavorable) H_4-H_8 *endo* interactions. The latter is the only conformation available to the 3-methyltriasteryl cation **25**.

Thus, in the case of cation **25** (and probably **10**) the reduced value of ΔJ is due to charge delocalization into the two cyclopropyl groups (eq 2 applies), while in cation **20** it is due to reduced dihedral angles and in **15** it is due to two different dihedral angles, 90° and 30° (eq 1 applies).

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. Chromatographic filtrations were performed using thin layer chromatographic (TLC) grade silica gel (Merck Kieselgel GF_{254}) or alumina (aluminium oxide

(21) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089–2101. Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409–413 and references therein.

(22) This point has also been discussed in the papers cited in ref 19. In closely related series of aryldialkyl, diarylalkyl, and benzyhydryl cations, cationic carbon chemical shifts often correlate linearly with Hammett type substituent constants with some deviations occurring in some cations with strong electron-demanding substitents. Several research groups, including our own, have published extensively on "the tool of increasing election demand", for examples: (a) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org Chem.* **1983**, *48*, 2146–2151 and references therein. (b) Giansiracusa, J. J.; Jenkins, M. J.; Kelly, D. P. *Aust. J. Chem.* **1982**, *35*, 443–450 and references therein. (c) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089–2101 and references therein. (d) Forsyth, D. A.; Panyachotipun, C.; Pan, Y.; Moussa, A. M.; Youseff, A.-H. A. *J. Org. Chem.* **1990**, *55*, 5375–5386 and references therein.

(23) In order to overcome uncertainties in the use of individual ^{13}C shifts, Olah and Schleyer have proposed a classification scheme for cations based on the difference between total ^{13}C shifts of the cation and a neutral (model), Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683–691.

(24) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957–965.

(25) The fact that the $\Delta\delta$ value is less than that for replacement by phenyl was used to argue that the relative stability of phenyl was greater than cyclopropyl, ref 19b.

(26) Olah, G. A.; Liang, G.; Babiak, K. A.; Murray, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 6794–6796.

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

(28) Kirchen, R. P.; Sorensen, T. S. *J. Am Chem. Soc.* **1978**, *100*, 1487–1494.

(29) Prakash, G. K. S.; Fung, A. P.; Rawdah, T. N.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 2920–2923.

(30) Cation **15** exhibits significantly shielded β-carbons (19.2 ppm) compared with all the other cations (Table 1).

GF_{254}). Capillary gas liquid chromatographic (GLC) analyses were carried out using a Hewlett-Packard 5890A gas chromatograph fitted with a 15 m × 0.25 mm (i.d.) DB5 DURABOND 0.25 μm capillary column supplied by J&W Scientific. A nitrogen flow rate of 15 mL/min was used, and the chromatograph was interfaced with an HP3394A reporting integrator. High performance liquid chromatography (HPLC) was conducted using an ISCO Model 2350 pump, and peaks were detected using an ERMA ERC-7512 ultra-high sensitivity refractive index detector connected to a Spectra Physics reporting integrator. Infrared spectra were recorded as potassium bromide disks or as thin liquid films between sodium chloride plates by using a Perkin-Elmer 983G 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 nuclear magnetic resonance (NMR) spectra were recorded on JEOL FX-100, FX-90Q, or GX-400 spectrometers unless otherwise stated. Proton (±0.01 ppm) and carbon (±0.1 ppm) chemical shifts were measured from internal Me_4Si at probe temperature for solutions ($CDCl_3$) of neutral compounds and from external Me_4Si for cationic solutions. For the latter, field stabilization was provided by internal CD_2Cl_2, by a concentric capillary of acetone-d_6 containing Me_4Si, or by an external ^7Li lock. At temperatures below −100 °C, the GX-400 was run unlocked and signals were referenced to internal CH_2Cl_2 taken as δ 54.8 from TMS. Proton-coupled ^{13}C NMR spectra were obtained by the normal gated decoupling technique with a minimum 50% duty cycle. Coupling constants (±2 Hz) were measured by hand from expanded plots (18 Hz cm^{-1}). Assignments of ^1H and ^{13}C NMR spectra for alcohols **13** and **18** were made with the aid of normal 2D spectra, HH and CH COSY and DIFNOE experiments. Force field calculations were performed with PCMODEL (Serena Software) and CVFF (Discover, Biosym).

Synthesis. 1,1-Dicyclopropylethanol (7a). Dicyclopropyl ketone (**5**) was treated with methyllithium in diethyl ether to afford **7a** as a colorless oil (80%): bp = 74 °C (oven)/12 mmHg [lit.[31] bp = 56.6–60 °C/10 mmHg]; IR (film) 3580, 1018 cm^{-1}; ^{13}C NMR δ 69.8 (s), 25.6 (q, J = 127 Hz), 20.3 (d, J = 159 Hz), 0.45 (t, J = 159 Hz), 0.02 (t, J = 159 Hz).[32]

1,1-Dicyclopropyl-1-methoxyethane (7b). Treatment of alcohol **7a** with NaH and iodomethane in anhydrous THF under conditions specified elsewhere[33] gave, after workup, the title compound as a pale yellow oil: ^{13}C NMR δ 75.1 (s), 49.4 (q), 18.1 (q), 17.8 (d), 0.87 (t), 0.67 (t).[32]

(1α,3β,5β,7α)-Tricyclo[5.1.0.0^{3,5}]octan-2-one (11). Chromium trioxide (37 g, 0.37 mol) was suspended in dichloromethane (315 mL) at −20 °C under nitrogen, and 3,5-dimethylpyrazole (35.6 g, 0.37 mol) was added in one portion. After the mixture had stirred for 15 min at −20 °C (1α,3β,5β,7α)-tricyclo[5.1.0.0^{3,5}]octane (**26b**)[14c] (2.0 g, 18.5 mmol) was then added. The reaction mixture was stirred for 3 h while maintaining an internal temperature of −15 to −20 °C. Aqueous NaOH (315 mL of a 5 M solution) and ether (630 mL) were added, and the mixture was stirred for 1 h in an ice–water bath. The phases were separated, the aqueous phase was extracted with ether (2 × 200 mL), the combined organic phases were washed with aqueous HCl (3 × 100 mL of a 2 M solution), water (2 × 100 mL), and brine (1 × 100 mL) and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light yellow oil. This crude product was distilled (bulb-to-bulb) to give the title ketone **11**[12,14c] as a colorless oil (1.2 g, 55%): bp = 120 °C (oven)/20 mmHg; ^1H NMR (400 MHz) δ 2.13 (m, 2H), 1.47 (m, 2H), 1.29 (m, 2H), 1.17 (m, 2H), 0.66 (m, 2H); ^{13}C NMR see Table 1.

(1α,3β,5β,7α)-2-Methyltricyclo[5.1.0.0^{3,5}]octan-2-ol (13). To a solution of ketone **11** (1.0 g, 8.2 mmol) in ether (45 mL) maintained at 0 °C under nitrogen was added methyllithium (6 mL of a 1.4 M solution in ether, 8.4 mmol) dropwise over 10 min with stirring. The reaction mixture was stirred for a further 0.5 h at 0 °C and then for 1 h at room temperature, before being transferred to a separating funnel with the aid of additional quantities of ether (10 mL). Ice–water (*ca.* 100 mL) was added, the phases were separated, and the aqueous phase was extracted with ether (1 × 50 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give an oil which was distilled (bulb-bulb) to give alcohol **13** as a colorless oil (1.0 g, 88%): bp = 100 °C (oven)/5 mmHg; IR (film) 3380, 3003 1125 cm^{-1}; ^1H NMR (400 MHz) δ 2.00 (ddd, J = 14.4, 7.3 and 3.2 Hz, 1H, H_{6endo}), 1.60 (dt, J = 14.4 and 4.4 Hz, 1H, H_{6exo}), 1.44 (s, 3H, CH_3), 1.36 (brs, 1H, OH), 0.85–0.90 (m, 1H, H3 or H1), 0.77–0.85 (m, 1H, H5 or H7), 0.68–0.76 (m, 1H, H7 or H5), 0.62–0.68 (m, 1H, H1 or H3), 0.55–0.61 (m, 1H, H_{8exo} or H_{4exo}), 0.48 (dt, J = 4.9 and 8.3 Hz, 1H, H_{4exo} or H_{8exo}), 0.30 (dt, J = 5.0 and 5.0 Hz 1H H_{8endo}), 0.24 (dt, J = 5.0 and 5.0 Hz 1H, H_{4endo}); ^{13}C NMR (100 MHz) δ 67.4 (s, C2), 32.3 (q, J = 128 Hz, CH_3), 21.5 (t, J = 128 Hz, C6), 20.1 [d, J = 179 Hz, C3(1)], 18.2 [d, J = 161 Hz, C1(3)], 8.1 [t, J = 160 Hz, C8(4)], 7.9 [d, J = 163 Hz, C7(5)], 6.4 [d, J = 163 Hz, C5(7)], 6.2 [t, J = 160 Hz C4-(8)]; MS (10 eV) m/z 138 ($M^{\bullet+}$, 1), 123 (100), 120 (10), 97 (35), 94 (20). Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 78.0; H, 10.3.

(1α,3α,5α,7α)-Tricyclo[5.1.0.0^{3,5}]octan-2-one (16). To a stirred solution of the alcohol **17**[12] (74 mg, 0.59 mmol) in dichloromethane (3.0 mL) were added pyridinium chlorochromate (320 mg, 1.50 mmol) and sodium acetate (122 mg, 1.50 mmol) in one portion. The reaction mixture was stirred under nitrogen at room temperature for 3 h and then diluted with ether (3 mL), and the resulting mixture was filtered through a 5 cm deep bed of TLC grade silica gel. The chromium salts were washed with 1:1 ether/dichloromethane (4 × 80 mL). The combined filtrates were then dried ($MgSO_4$) and carefully concentrated under reduced pressure to yield ketone **16**[12] (56 mg, 78%) as a pale yellow oil: R_f = 0.3 (CH_2Cl_2); IR (film) 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.20–2.35 (m, 2H, H_6), 1.75–1.83 (m, 4H, $H_{1,3,5,7}$), 1.20–1.25 (m, 2H, $H_{4,8exo}$), 0.93–0.98 (m, 2H, $H_{4,8endo}$); ^{13}C NMR see Table 1; MS (70 eV) m/z 122 ($M^{\bullet+}$, 35), 79 (46), 68 (46), 54 (100); HRMS [$M^{\bullet+}$], 122.0733; $C_8H_{10}O$ requires [$M^{\bullet+}$], 122.0732.

In the second method for the preparation of the title ketone, a 6:1 mixture of (1α,3β,5β,7α)-tricyclo[5.1.0.0^{3,5}]octane and (1α,3α,5α,7α)-tricyclo[5.1.0.0^{3,5}]octane[17] (433 mg, 4 mmol) was oxidized with the chromium trioxide/3,5-dimethylpyrazole complex[16] using the same procedure as detailed above for the preparation of (1α,3β,5β,7α)-tricyclo[5.1.0.0^{3,5}]octan-2-one (**11**). Capillary GLC analysis of the crude product showed that the *anti*-ketone **11** was produced at 75% conversion while the *syn*-ketone **16** was produced at >99% conversion. The crude product was subjected to HPLC [1:3 EtOAc/hexane elution, Waters μ-Porasil semipreparative column (P/N 84175), flow rate 2mL/min] which afforded two main fractions.

Concentration of the fractions containing the more mobile component (t_R = 17.9 min) afforded *anti*-ketone **11** (207 mg, 49% isolated yield or 66% at 75% conversion) which was identical in all respects to material obtained earlier.

Concentration of the fractions containing the less mobile component (t_R = 21.3 min) afforded ketone **16** (37 mg, 53% isolated yield or 53% at 100% conversion), identical in all respects with the material obtained earlier.

(1α,2α,3α,5α,7α)- and (1α,2β,3α,5α,7α)-2-Methyltricyclo-[5.1.0.0^{3,5}]octan-2-ol (18). Methyllithium (0.5 mL of a 1.0 M solution in ether) was added dropwise to a stirred solution of ketone **16** (48 mg, 0.39 mmol) in ether (2.0 mL) maintained at 0 °C under nitrogen. The resulting solution was allowed to stir at 0 °C for 30 min, and then at room temperature for a further 1 h. The reaction mixture was transferred to a separating funnel with the use of additional ether (10 mL), and ice (*ca.* 50 mL) was added slowly. The resulting solution

(31) Nishida, S.; Fujioka, T.; Shimizu, N. *J. Organomet. Chem.* **1978**, *156*, 37–44.

(32) Both the alcohol **7a** and its methyl ether **7b** exhibit nonequivalent methylene carbon signals presumably due to symmetry considerations (C2 prochiral center), Jennings W. B.; *Chem. Rev.* **1975**, *75*, 307. The integrity of the cyclopropyl ring was confirmed by INADEQUATE experiments which showed the connectivity of the methine and the two methylene carbons.

(33) Banwell, M. G.; Collis, M. P.; Mackay, M. F.; Richards, S. L. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1913–1920.

was washed with ether (2 × 50 mL), and the combined organic phases were dried ($MgSO_4$), before being concentrated under reduced pressure to yield a *ca.* 6:1 mixture of the title compounds **18** (28 mg, 52%) as a pale yellow oil: $R_f = 0.2$ (CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ (major isomer) 2.12 (dt, J = 14.6 and 6.1 Hz, 1H, H_{6exo}), 2.02 (dt, J = 14.6 and 1.2 Hz, 1H, H_{6endo}), 1.56 (s, 3H), 1.26 (br s, 1H, OH), 1.03–1.13 (m, 2H, $H_{5,7}$), 1.06 (dt, J = 5.4 and 9.0 Hz, 2H, $H_{1,3}$), 0.34 (dt, J = 5.4 and 9.0 Hz, 2H, $H_{4,8exo}$), 0.22 (dt, J = 5.4 and 5.4 Hz, 2H, $H_{4,8endo}$); ^{13}C NMR (100 MHz, d_6-acetone) δ (major isomer) 67.0 (s, C2), 34.7 (q, J = 125 Hz, CH_3), 23.7 (d, J = 161 Hz, $C_{5,7}$), 19.3 (t, J = 127 Hz, C6), 14.2 (d, J = 161 Hz, $C_{1,3}$), 9.3 (t, J = 157 Hz, $C_{4,8}$); MS m/z (70 eV) 123 [($M^{\bullet+}$ – CH_3), 26], 120 (19), 105 (52), 97 (88), 95 (29), 91 (74), 79 (92), 77 (53), 43 (100); HRMS [$M^{\bullet+}$ – CH_3], 123.0809; $C_9H_{14}O$ requires [$M^{\bullet+}$ – CH_3], 123.0810.

3-Methyltetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonan-3-ol (23). Methyllithium (1.1 mL of a 1.5 M solution in ether) was added dropwise at 0 °C to a solution of ketone **21**[13] (108 mg, 0.8 mmol) in anhydrous ether (5 mL). The mixture was stirred for 3 h and then worked up as described above for the preparation of compound **18**. The resulting solid was recrystallized (pentane) to give alcohol **23** (830 mg, 70%) as colorless plates: mp = 59–61 °C; IR (KBr) 3312, 1126, 1106, 941 cm^{-1}; ^1H NMR (400 MHz) δ 2.16–2.22 (m, 3H), 1.98 (br d, 1H), 1.8 (vbr s, IH, OH), 1.41 (s, 3H, CH_3), 0.86–0.92 (m, 6H); ^{13}C NMR (100 MHz) δ 69.6 (s, C3), 30.8 (q, J = 126 Hz, CH_3), 21.7 (d, J = 163 Hz, C2, 4), 16.6 (t, J = 128 Hz), 16.0 (t, J = 128 Hz), 13.2 (d, J = 161 Hz), 11.3 (d, J = 163 Hz); MS (70 eV) m/z 135 [($M^{\bullet+}$ – CH_3), 100], 132 (71), 117 (78), 91 (40); HRMS [$M^{\bullet+}$ – CH_3], 135.0809; $C_{10}H_{14}O$ requires [$M^{\bullet+}$ – CH_3], 135.0810.

Generation of Cations. Method A. Approximately 20 mg of the appropriate alcohol contained in a 5 mm NMR tube was dissolved in CH_2Cl_2 or CD_2Cl_2 (0.1 mL) and the resulting solution cooled to −120 °C (N_2/pentane slush). Precooled (−80 °C) FSO_3H:SO_2ClF (1:1) solution was added (*ca.* 0.4 mL) and the tube cooled to −120 °C. The components were made homogenous by rapid vortex mixing while maintaining the temperature at *ca.* −120 °C. Clear yellow solutions resulted except in the case of **15**, where a darker red-brown solution was obtained.

Method B. The precursor alcohol was dissolved in SO_2ClF and added dropwise at <0 °C to the FSO_3H/SO_2ClF (1:1) mixture at −120 °C with rapid vortex mixing.

In the case of cation **10**, the ion solution was quenched by addition to a rapidly stirred solution of NaOMe in MeOH at −78 °C. Neutralization, extraction with pentane, drying, evaporation and radial chromatography (dichloromethane: ether, 1:9) afforded 1,1-dicyclopropyl-1-methoxyethane **7b**, identical to authentic material.

Acknowledgment. We thank Ms. Voon Stokie for the preparation of **7a**, Dr. A. M. Dachs for the preparation of **23**, Professor J. B. Lambert and Dr. F. Koeng of Northwestern University for a sample of the *p*-nitrobenzoate derivative of **17**, Mr. N. Lui and (the late) Professor H. Musso of Karlsruhe University for a sample of triasterone (**21**), and Dr. K. H. Ang and Dr. J. M. White for assistance with NMR experiments (K.H.A.) and calculations (K.H.A., J.M.W.). This work was supported by the Research Grants Committee of the Australian Research Council. J.H.R. is the grateful recipient of an Australian Post-Graduate Research Award and J.R.P. thanks the University of Melbourne for a MUPS award. We acknowledge several helpful suggestions of a referee.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds **7a**, **7b**, **13**, **18**, and **23** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9417434