2,6-Dideoxy-2,6-imino-7-*O*-β-D-glucopyranosyl-D-*glycero*-L-*gulo*-heptitol (1). To a stirred slurry of compound **9** (575 g, 0.536 mol) in methanol (3.4 L) and cyclohexene (1.4 L) under argon was added a mixture of 5% Pd/C (58 g) in EtOH (50 mL). The resulting mixture was heated under gentle reflux for 16 h. After cooling, the slurry was filtered through Celite and concentrated to provide a solid, which was redissolved in CH_2Cl_2 (2.4 L) and washed with saturated $NaHCO_3$ solution (1.4 L) and brine (2 × 1.4 L). The organic solution was dried ($MgSO_4$) and concentrated to a foamy residue. To the residue was added methanol (3.8 L) and 25% NaOMe in methanol (10 mL). The mixture was stirred at room temperature for 16 h, and the crystalline solid that separated was collected by filtration, washed with 1:1 methanol–acetone (500 mL), and dried in vacuo to provide **1** as a colorless solid (177 g, 93%): mp 216–219 °C; IR (KBr) 3600–3100 cm^{-1} (OH and NH); ^1H NMR (D_2O) δ 2.89 (ddd, 1 H), 3.23 (dd, 1 H), 3.32 (dd, 1 H), 3.38 (dd, 1 H), 3.4–3.6 (m, 5 H), 3.7 (m, 2 H), 3.9–4.0 (m, 3 H), 4.13 (dd, 1 H), 4.49 (d, 1 H, $H_{1'}$, $J_{1',2'}$ = 7.9 Hz); MS (CI, CH_4) 356 (MH^+), 338 ($MH^+ - H_2O$), 324 ($MH^+ - CH_3OH$); $[\alpha]^{20}_D$ +27.5° (*c* 1.0, H_2O). Anal. Calcd for $C_{13}H_{25}NO_{10}\cdot H_2O$: C, 41.82; H, 7.29; N, 3.75; H_2O, 4.81. Found: C, 41.87; H, 7.44; N, 3.66; H_2O, 4.90 (Karl Fischer).

Acknowledgment. We thank Drs. Michael R. Whalon and Ed Huber for the measurement and interpretation of NMR spectra. We also thank Drs. Claude Judd and Jack Martin for helpful discussions.

Registry No. 1, 104343-33-1; 2, 81703-56-2; 3, 78821-34-8; 4, 120172-77-2; 5, 120172-78-3; 6, 120172-79-4; 7, 120172-80-7; 8, 120172-81-8; 9, 120204-12-8; 10, 119557-99-2; 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate, 74808-10-9.

Reactions of Benzyl Carbinols with Fluorosulfuric Acid

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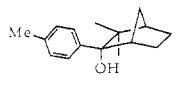
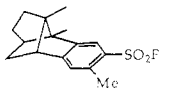
A series of benzyl carbinols have been reacted with HSO_3F at −78 °C, the solutions quenched, and the products isolated and identified. A variety of reaction modes occur including reduction (3-methyl- and 4-methyl-1-benzylcyclohexanol), rearrangement and cyclization (1-benzyl-2-methylcyclohexanol, 6-benzylspiro[4.5]decan-6-ol, 1-benzyl-*trans*-decalin-1-ol, 2-benzylcamphenilol, 2-benzylfenchol, 3-methyl-1-phenylbutan-2-ol, spiro[3-*exo*-benzylbicyclo[2.2.1]heptan-3-*endo*-ol-2,1′-cyclopentane]), and ring expansion (2-benzylnorbornanol). At higher temperatures fluorosulfonation of the product aryl ring can occur. The reaction mechanisms are discussed and that of the benzylnorbornyl ring expansion unambiguously determined by a series of deuterium labeling experiments.

Introduction

The reaction of 2-*p*-tolylcamphenilol (**1**) with HSO_3F to give 11-(fluorosulfonyl)-7,8,12-trimethyltetracyclo-[7.4.0.0^{2,7}0.^{4,8}]trideca-1(9),10,12-triene (**2**)[1] prompted our interest in the use of this super acid as a reagent in organic synthesis. A recent report[2] of the trifluoroacetic acid catalyzed cyclization of 5-aryl-1,1,1-trifluoropentan-2-ols (**3**) to 1-(trifluoromethyl)tetralins **4** requiring temperatures of 140–160 °C shows the difficulty of obtaining carbocation-induced intramolecular cyclization reactions with conventional acids. Reactions with such acids often give



1



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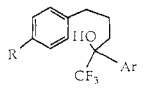

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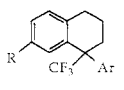
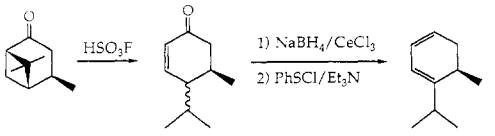


4

elimination and addition products without skeletal rearrangement. The ability of HSO_3F to generate carbocations in solution at low temperatures in the absence of good nucleophiles gives access to products from rearrangement and intramolecular cyclization not available with acids having counter anions capable of acting as bases and nucleophiles. Despite the fact that superacids have been extensively employed for the spectroscopic study of carbocations,[3] there have been few reports of the use of superacids as reagents in organic synthesis. Since the more complex rearrangements observed with fluorosulfuric acid often lead to synthetically useful structures,[4] we have been examining the use of fluorosulfuric acid as a reagent in organic synthesis. We have previously reported[4a] an application of the use of fluorosulfuric acid in the ring opening of pinanones which included an enantiospecific synthesis of the chiral diene **5** (Scheme I).

Scheme I



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Carbocations are involved in numerous substitution, elimination, addition, fragmentation, and rearrangement reactions of synthetic, industrial, and biological importance.[5] Rearrangements of carbocations are considered to occur for thermodynamic reasons, wherein an initially

(1) Coxon, J. M.; Pojer, P. M.; Robinson, W. T.; Steel, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 111.

(2) Bonnet-Delpon, D.; Cambillau, C.; Charpentier-Morize, M.; Jacquot, R.; Mesureur, D.; Ourevitch, M. *J. Org. Chem.* **1988**, *53*, 754.

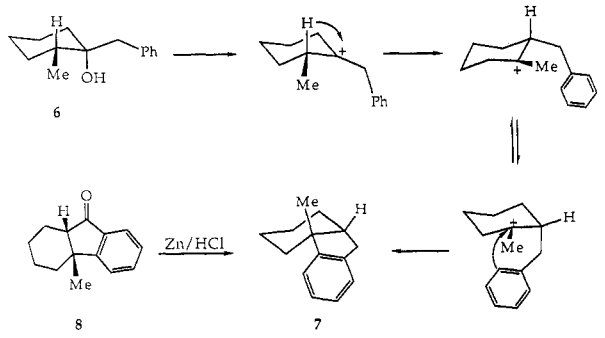
(3) (a) Olah, G. A.; Prakash, S. G. K.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985. (b) Gillespie, R. J. *Acc. Chem. Res.* **1968**, 202. (c) Brown, H. C.; Olah, G. A.; Hogeveen, H.; van Kruchten, E. M. G. A.; Kirmse, W. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1979; Vol 80.

(4) (a) Coxon, J. M.; Hydes, G. J.; Steel, P. J. *Tetrahedron* **1985**, *41*, 5213. (b) Dytnerski, D.; Ranganayakulu, K.; Singh, B. P.; Sorensen, T. S. *J. Org. Chem.* **1983**, *48*, 309.

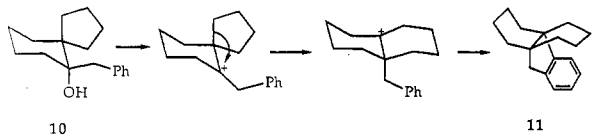
(5) Olah, G. A.; Schleyer, P. v. R. *Carbonium Ions*; John Wiley & Sons: New York, 1968–1976; Vols. 1–5.

0022-3263/89/1954-2542$01.50/0

Scheme II



Scheme III



generated carbocation rearranges to a thermodynamically more stable carbocation. In super acid media many reaction pathways have precedents[3a] including intramolecular cyclization, alkyl migration, hydride migration, ring expansion, ring contraction, and dimerization. The work described in this paper examines the reactions of benzyl carbinols with HSO_3F and is directed to the utilization of this reagent for synthesis of carbocyclics where intramolecular electrophilic ring closure can occur after molecular rearrangement.

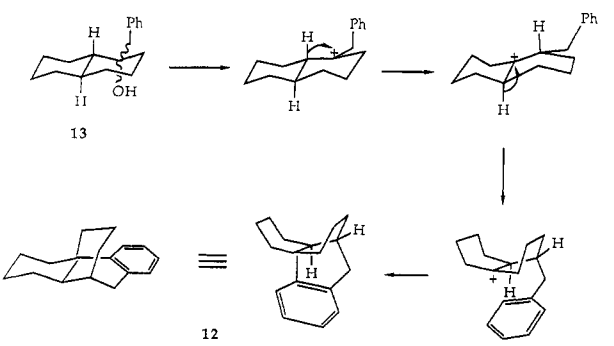
Results and Discussion

We now report the reactions of a number of benzyl carbinols with fluorosulfuric acid at −78 °C followed by quenching and product isolation. The initially formed carbocation from the ionization of a benzyl carbinol can rearrange to bring the stabilizing phenyl group into conjugation with the positive charge. However, in competition with benzylic cation formation, a variety of substrate-dependent reaction modes are shown to occur.

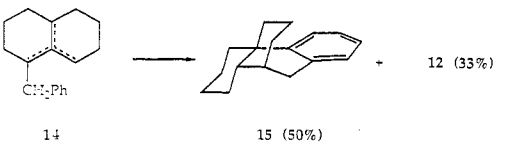
Reactions of Benzylcycloalkanols. Reaction of 1-benzyl-2-methylcyclohexanol (**6**) with HSO_3F at −78 °C followed by quenching and product extraction resulted in the formation of the cis stereoisomer of methylhexahydrofluorene **7** isolated in >85% yield (Scheme II). The cis stereochemistry was established from mutual NOE enhancements between the methyl protons and the tertiary proton and by comparison of the ^{13}C NMR with that of *cis*-8-methylhydrindan,[6] and the structure was confirmed by an independent preparation involving Clemmensen reduction of the known[7] 9-fluorenone **8**. The C2 methyl group of **6** facilitates a hydride shift to give a tertiary cation suitably disposed for ring closure at the ortho position of the phenyl ring. In the absence of the methyl group, reaction of 1-benzylcyclohexanol (**9**) with HSO_3F at −78 °C does not produce hexahydrofluorene but results in the formation of a complex mixture of hydrocarbons shown to be a mixture of dimers.[8]

The rearrangement and subsequent cyclization observed for 1-benzyl-2-methylcyclohexanol (**6**) was exploited in the synthesis of tetracyclo[7.4.4.0^{1,9}.0^{2,7}]heptadeca-2,4,6-triene (**11**). Thus reaction of 6-benzylspiro[4.5]decan-6-ol (**10**) with HSO_3F at −78 °C gives propellane **11** by a mechanism shown in Scheme III.[9] The C_s symmetry of **11** is supported by the ^1H and ^{13}C NMR spectra.[10]

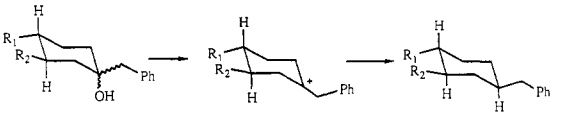
Scheme IV



Scheme V



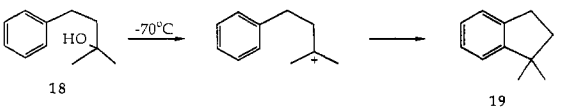
Scheme VI



9 R_1=R_2=H
16a R_1=H, R_2=Me
16b R_1=Me, R_2=H

17a R_1=H, R_2=Me
17b R_1=Me, R_2=H

Scheme VII

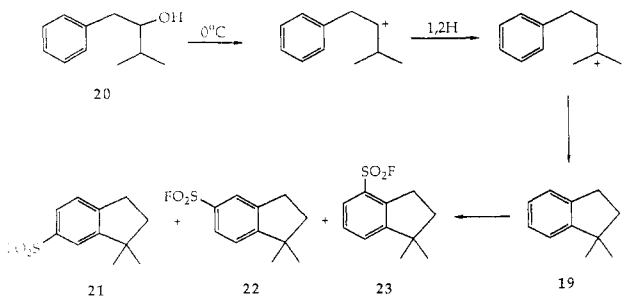


An analogous reaction to that producing **11** was utilized in the synthesis of (±)-9a-carba-14a-morphinan (**12**), which was isolated in ~90% yield from the reaction of the 1-benzyl-*trans*-decalin-1-ols (**13**) with HSO_3F (Scheme IV). Carbamorphinan **12** has been previously prepared[11] by cyclization (Scheme V) of an alkene mixture **14** to give isomer **15** (50%) in a mixture with (±)-9a-carba-14a-morphinan (**12**) (33%). In contrast the reaction of benzyl-9,10-*trans*-decalols **13** with fluorosulfuric acid resulted in the diastereoselective formation of **12**, consistent with the suprafacial nature of each hydride migration and absence of alkene intermediates in the reaction process.

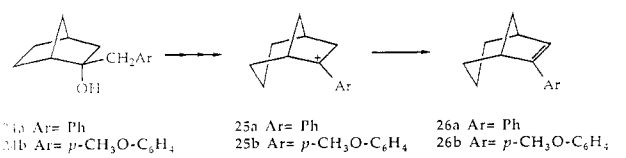
To allow cyclization to five-membered rings from the cations initially generated from benzyl carbinols, the precursor carbinols require structural features that facilitate rearrangement of an initially produced cation to a

(6) Gramain, J. C.; Quirion, J. C. *Magn. Reson. Chem.* **1986**, *24*, 938.
(7) Ng, K. S.; Roberts, J. L.; Rutledge, P. S.; Wilson, M. A.; Woodgate, P. D. *Aust. J. Chem.* **1976**, *29*, 2683.
(8) The formation of dimers has precedent in the reactions of alcohols in super acid media. (a) Butler, O.; Coxon, J. M.; Steel, P. J. *Aust. J. Chem.* **1983**, *36*, 955. (b) Heublein, G.; Barth, O. *Z. Chem.* **1972**, *12*, 19. (c) Taylor, A. R.; Keen, G. W.; Eisenbraun, E. J. *J. Org. Chem.* **1977**, *42*, 3477.
(9) A structurally related reaction has recently been reported for β-hydroxy acids containing a spiro ring to give propellane-like γ-lactones. Fujita, T.; Watanabe, S.; Sotoguchi, T.; Ogawa, K.; Sugahara, K. *Aust. J. Chem.* **1986**, *39*, 799.
(10) At room temperature substantial broadening of the cyclohexane ring signals in the high-field proton and carbon spectra (^1H, 300 MHz) are observed relative to those at lower field strengths indicating a relatively slow interconversion of the various cyclohexane ring conformers.
(11) Chakraborti, A. K.; Alam, S. K.; Chakraborti, P. C.; Dasgupta, R.; Chakravarty, J.; Ghatak, U. R.; Kabiraj, A.; Biswas, S. G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1243.

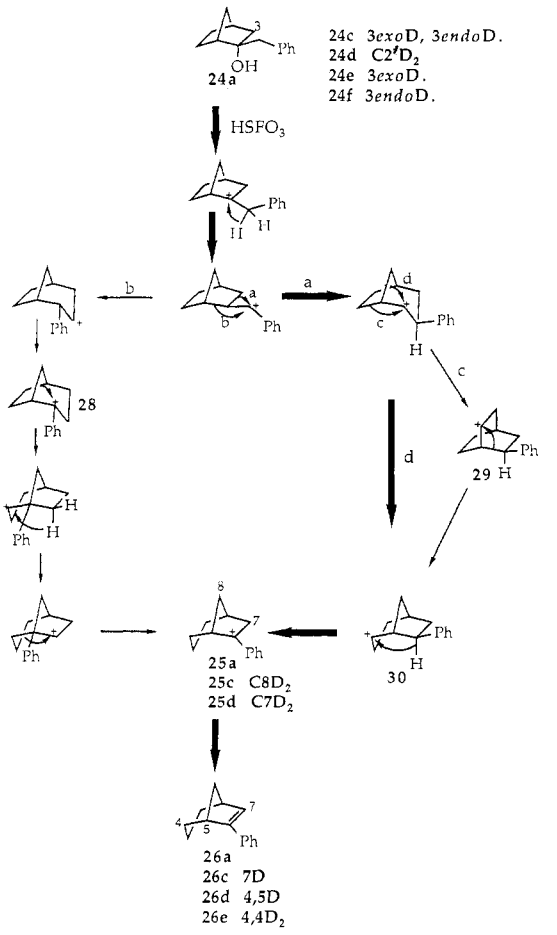
Scheme VIII



Scheme IX



Scheme X



position γ to the phenyl ring. Thus reaction of 1-benzyl-3-methylcyclohexanol (**16a**) and 1-benzyl-4-methylcyclohexanol (**16b**) (Scheme VI) with fluorosulfuric acid do not give bicyclic products but produce alkanes **17a** and **17b**, respectively (<50% yield). The structures of **17a** and **17b** were established from their NMR and mass spectra and by comparison with authentic samples prepared from alcohols **16a** and **16b** by dehydration and hydrogenation. The hydrogenation[12] of the alkenes from **16a** and **16b** gave mixtures of both cis and trans stereoisomers while the formation of **17a** and **17b** from the HSO_3F reaction is highly stereoselective. In the HSO_3F reactions the alkane products are considered to be formed by disproportionation of the initially formed carbocations in a process that has precedents.[8a,13] The formation of these reduced products is only observed for substrates that contain tertiary hydrogens reflecting the greater hydride donating ability of a tertiary relative to a secondary hydrogen.[14] The selectivity observed in these reactions with HSO_3F is such that both substrates give the thermodynamically preferred stereoisomer.

Reactions of Acyclic Alcohols. Direct generation of a cation γ to a phenyl group as in the reaction of 2-methyl-4-phenylbutan-2-ol (**18**) with HSO_3F gives a high yield of dimethylindan (**19**) (Scheme VII). In contrast reaction of 3-methyl-1-phenylbutan-2-ol (**20**) with HSO_3F would require rearrangement to a γ cation before cyclization (Scheme VIII). In this case rearrangement can occur to give either a benzylic carbocation or the tertiary carbocation precursor of indane. At −70 °C reaction of **20** with HSO_3F gives a low yield of the indan **19** along with unreacted starting alcohol. Secondary alcohols are known to be resistant to ionisation in fluorosulfuric acid at low temperatures.[15] Reaction at 0 °C and at 25 °C resulted in the formation of three indan products, which were separated by preparative GLC and identified as the fluorosulfonated compounds **21** (45%), **22** (35%), and **23** (20%). The structure of the 4-fluorosulfonated isomer **23** followed from the coupling pattern of the three adjacent aromatic protons and the low-field position of the benzylic methylene protons deshielded by the fluorosulfonate group. The identity of **22** was established by means of difference NOE spectroscopy.[16] The ^{13}C NMR spectra of **21** along with **22** and **23** were assigned by two-dimensional heteronuclear correlation spectroscopy and are consistent with the known[17] substituent effects of the fluorosulfonate group. The same mixture of fluorosulfonated indans is obtained when the indan **19** is reacted with HSO_3F at room temperature. Formation of the indanes from **20** involves rearrangement to the tertiary cation followed by cyclization and fluorosulfonation, which is in contrast with the reaction of 2-*exo*-benzylnorbornanol (**24a**) discussed below.

Rearrangements of Benzylnorbornanols. As previously reported,[18] the reaction of 2-*exo*-benzylnorbornanol (**24a**) (Scheme IX) with HSO_3F could either undergo a Wagner–Meerwein shift to give a γ carbocation and cyclize or alternatively undergo a 1,2-hydride shift to give a benzylic cation. In contrast to the reaction of **20** reaction of **24a** with HSO_3F occurs via the benzylic cation **25a** to give 6-phenylbicyclo[3.2.1]oct-6-ene (**26a**). The identity of **26a** was established from the comparison of its ^1H and ^{13}C NMR spectra with those of related compounds.[19] At-

(12) (a) Anderson, J. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 10. (b) Augustine, R. L.; Yaghmaie, F. *J. Org. Chem.* **1987**, *52*, 1862.

(13) (a) Coxon, J. M.; Schuyt, H. A.; Steel, P. J. *Aust. J. Chem.* **1980**, *33*, 1863. (b) Coxon, J. M.; Robinson, W. T.; Steel, P. J. *Aust. J. Chem.* **1979**, *32*, 167.

(14) Sharma, R. B.; Sen Sharma, D. K.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747 and references therein.

(15) Olah, G. A.; Sommer, J.; Namanworth, E. *J. Am. Chem. Soc.* **1967**, *89*, 3576.

(16) Irradiation of the benzylic methylene triplet (2.99 ppm) resulted in enhancement of an aromatic singlet (7.81 ppm) and the adjacent methylene protons (2.02 ppm). Similarly irradiation of the methyl protons (1.30 ppm) resulted in enhancement of an aromatic doublet (7.34 ppm).

(17) Coxon, J. M.; Pojer, P. M.; Steel, P. J.; Rae, I. D.; Jones, A. J. *Aust. J. Chem.* **1978**, *31*, 1747.

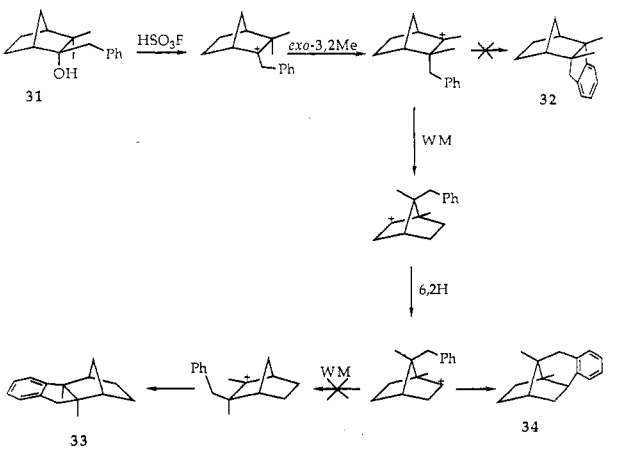
(18) Barrow, C. J.; Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1987**, *52*, 5300.

tempts to follow the course of the rearrangement by direct NMR observation of intermediate carbocations at temperatures between −90 °C and 0 °C resulted in only 6-phenylbicyclo[3.2.1]octan-6-yl cation (**25a**) being observed.[20a] The reaction of the 2-*exo*-(*p*-methoxybenzyl)-norbornanol (**24b**) with HSO_3F/SO_2ClF resulted in the formation of **26b**. At temperatures as low as −60 °C only the rearranged cation **25b**[20b] was observed in the NMR spectrum. Formation of **26a** and **26b** both require initial rearrangement to a benzylic cation and can result from migration of C3 (methylene migration) (path a, Scheme X) or C1 (bridgehead migration) (path b, Scheme X), both of which have precedent in the literature.[21] The latter path would give the 2-phenylbicyclo[3.2.1]octan-2-yl cation (**28**), derivatives of which are known[19e] to rearrange to derivatives of **25a**.[22]

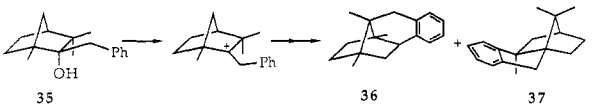
In order to establish the reaction pathway the 3,3-dideuterio alcohol **24c** (Scheme X) was reacted with HSO_3F and gave the 7-deuterioalkene **26c**. The absence of the olefinic proton signal at 6.25 ppm in the ^1H NMR spectrum indicated deuterium substitution at the vinyl C7-position and the existence of only one signal (6.3 ppm) in the ^2H NMR spectrum showed exclusive formation of **26c**. These results are consistent only with C3 (methylene) migration (path a) since the alternative pathway (path b) involving C1 bridgehead migration would give 4,4-dideuterio-**28** and hence rearrange[19e] to 8,8-dideuterio-6-phenylbicyclo[3.2.1]octan-6-yl cation (**25c**).

A further deuterium labeling experiment was undertaken to determine whether the reaction involved Wagner–Meerwein rearrangement by ethano bridge migration (path c) via **29** to **30** or methano bridge migration (path d) to **30**. Reaction of the dideuterio alcohol **24d** gave the 4,5-dideuterioalkene **26d**, the identity of which followed from the absence of a signal in the ^1H NMR spectrum at 2.97 ppm (C5H), the presence of two signals in the ^2H NMR spectrum at 2.99 ppm (D5) and 1.59 ppm (D4), and the one-bond coupling of C4, 24.6 ppm, and C5, 40.8 ppm, to deuterium in the ^{13}C NMR spectrum. Conversion of 2-(dideuteriobenzyl) alcohol **24d** to 4,5-dideuterio-6-phenylbicyclo[3.2.1]oct-6-ene (**26d**) occurs without loss of the deuterium label, thereby excluding the intermediacy of olefin or cyclopropyl intermediates in the reaction[19e,23] and is not consistent with ethano bridge migration (path c), which would give 4,4-dideuterio-6-phenylbicyclo-[3.2.1]oct-6-ene (**26e**). Formation of 6-phenylbicyclo-

Scheme XI



Scheme XII



Scheme XIII

[3.2.1]oct-6-ene (**26a**) from 2-*exo*-benzylnorbornanol (**24a**) therefore involves methano bridge migration (path d).[24]

The stereochemistry of proton (deuteron) loss in the formation of the alkene **26a** or **26c** from the benzylic cation **25a** or **25d** was examined by the reaction of the 3-*exo*- and 3-*endo*-monodeuterio alcohols **24e** and **24f**. In both cases the resulting alkene was a 50:50 mixture of **26a** or **26c**, which contained 50% (±5%) deuterium labeling at the vinylic carbon C7. The quenching process[4b] therefore does not distinguish between the diastereotopic protons in **25a** or **25d**.

Rearrangement of Methyl-Substituted Norbornyl Systems. In contrast to the reaction of 2-*exo*-benzylnorbornanol (**24a**), which undergoes a ring expansion to a benzylic cation, reaction of 2-benzylcamphenilol (**31**) produced a benzotricyclic hydrocarbon containing an ortho disubstituted benzene ring. Three structures were considered for this hydrocarbon (viz **32**–**34**, Scheme XI). If the rearrangement were analogous to that observed for the 2-substituted cyclohexanols, with *exo*-3,2-methyl migration,[25] the product formed would be benzoisoalbene (**32**). A more complex rearrangement (or *endo*-3,2-methyl migration) could give benzoalbene (**33**). The structures **32** and **33** are excluded by the presence of three benzylic protons and comparison of the NMR data with that of naturally occurring albene,[26] its synthetic isomer isoalbene,[27] and the demethylated analogues of **32** and **33**.[28] The

(19) (a) Bicyclo[3.2.1]oct-6-ene and bicyclo[3.2.1]oct-2-ene: Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1977**, *55*, 841. (b) 3-Phenylbicyclo-[3.2.1]oct-2-ene: Harris, A. R.; Mills, K.; Martin-Smith, M.; Murray-Rust, P.; Murray-Rust, J. *Can. J. Chem.* **1980**, *58*, 1847. (c) 2-Phenylbicyclo-[3.2.1]oct-2-ene: Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151. (d) Bicyclo[3.2.1]octan-6-one, bicyclo[3.2.1]octan-3-one, and bicyclo[3.2.1]octan-2-one: Grover, S. H.; Marr, D. H.; Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1975**, *53*, 1351. (e) 2-(*p*-Fluorophenyl)bicyclo-[3.2.1]oct-2-ene: Wolf, A. D.; Farnum, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 5175.

(20) (a) The ^{13}C NMR spectrum was identical with that previously reported from the less readily prepared precursor **27**: Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847. (b) The formation of cation **25a** from alcohol **24a** represents a more convenient method of preparation of this well-studied cation. Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089. Also see ref 19e and 20a.

27 Ar= Ph

(21) Krow, G. R. *Tetrahedron* **1987**, *43*, 3 and references therein.

(22) The failure to detect the *p*-methoxy analogue of cation **28** represents only indirect evidence in favour of methylene migration in the ring expansion (Scheme X, path a).

(23) Coxon, J. M.; Steel, P. J. *Aust. J. Chem.* **1979**, *32*, 2441.

(24) Although ethano bridge migration is favored over methano bridge migration in bicyclo[2.2.1]heptan-2-yl (norbornyl) cations, for bicyclo-[3.2.1]octan-2-yl cations there is more favorable overlap of the C1–C8 bond with the vacant orbital at C2.

(25) (a) Baldwin, J. E.; Barden, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6656. (b) Baldwin, J. E.; Barden, T. C. *J. Org. Chem.* **1983**, *48*, 625 and references therein.

(26) Kreiser, W.; Janitschke, L. *Chem. Ber.* **1979**, *112*, 408.

(27) Kreiser, W.; Janitschke, L.; Voss, W.; Ernst, L.; Sheldrick, W. S. *Chem. Ber.* **1979**, *112*, 397.

(28) Gutsche, C. D.; Bachman, G. L.; Udell, W.; Bäuerlein, S. *J. Am. Chem. Soc.* **1971**, *93*, 5172.

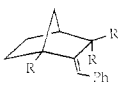
structure of the hydrocarbon product was established as **34** by comparison of NMR spectral data with that of related compounds.[29] Formation of this product involves rearrangement by methyl migration to give a carbocation γ to the phenyl group. Product is not observed from cyclization of this cation, and further rearrangement occurs before cyclization. The rearrangement involves *exo*-3,2-methyl migration, known[25] to be more favored than *endo*-3,2-methyl migration. The rearrangement is analogous to that of 2-*exo*-phenylcamphenilol.[1,17]

The related benzylfenchol **35** on reaction with HSO_3F gave **36** (Scheme XII) in a rearrangement analogous to that observed for **34**. A minor product was tentatively assigned as **37** on the basis of the highfield position of one of the *gem*-dimethyl proton signals (0.42 ppm), which lies over the shielding plane of the phenyl ring.[30]

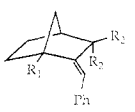
The spiro alcohol **39** is related to alcohols **10** and **31** and on reaction with HSO_3F follows an analogous pathway to that of **31** resulting in the formation of the pentacyclic hydrocarbon **40** (Scheme XIII), the structure of which was determined from its 2D NMR spectra and confirmed by X-ray crystallography.[31]

Conclusion

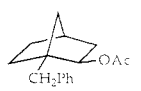
In the reactions of the benzylnorbornanols **24a**, **31**, **35**, and **39** described above, fluorosulfuric acid induces rearrangements of the carbon skeletons at low temperatures. This contrasts with the reactions of these and similar alcohols under milder acidic conditions at, or above, room temperature, where direct dehydration and less rearrangement occurs. For example, alcohols **24a**, **31**, and **35** react with $AcOH/H_2SO_4$ at room temperature to give simple dehydration products. Alcohol **31** gave alkene **41** and alcohol **35** gave alkenes **42** and **43** but in low yield. At room temperature alcohol **24a** gave a 4:1 mixture of the unrearranged alkenes **44** and **45**, while at higher temperatures **24a** gave the Wagner–Meerwein rearranged acetate **46** in addition to a 1:1 mixture of alkenes **44**/**45**. Alkene **26a**, the exclusive product of reaction with HSO_3F, was not detected in the reaction of **24a** with $AcOH/H_2SO_4$ at either room temperature or at 70 °C.



42 R=CH_3
44 R=H



41 R_1=H, R_2=CH_3
43 R_1=R_2=CH_3
45 R_1=R_2=H



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For systems where there are no alternative reaction pathways possible, the reaction with HSO_3F follows the same course as that induced by other acid reagents. For example the reaction of 3-methyl-1-phenylbutan-2-ol (**20**) gives 1,1-dimethylindan (**19**) with fluorosulfuric acid and with sulfuric acid.[32] In general the use of fluorosulfuric acid for reactions with aryl alcohols is restricted to temperatures below 0 °C in order to avoid fluorosulfonation of the aryl ring. The solvent for these reactions must be such that the reaction medium remains mobile at low temperature and the solvent is not attacked by either the acid or the cations generated in the reaction. We have found methylene chloride to be widely applicable.

The variety of novel reaction pathways induced by the action of fluorosulfuric acid on benzyl carbinols is illustrated by the ring expansion and rearrangement of **24a** to give **26a** and by the conversions involving cyclization of **10**, **13**, **31**, **35**, and **39** to give **11**, **12**, **34**, **36**, and **40**, respectively. These reactions demonstrate the usefulness of fluorosulfuric acid as a reagent in synthesis. The synthetic utility of such reactions is currently being extended to include an investigation of the reactions of (2-phenylethyl)- and (3-phenylpropyl)carbinols.

Experimental Section

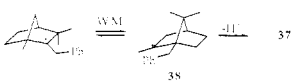
General. Infrared spectra were recorded on a Shimadzu IR27G or a Pye Unicam SP3-300 spectrophotometer. Mass spectra were recorded on an AEI MS902 or a Kratos MS80RFA spectrometer. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 PF_{254} silica gel. ^1H NMR spectra were recorded on a Varian T60 or XL-300 spectrometer and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer, for $CDCl_3$ solutions with $(CH_3)_4Si$ as an internal standard. Many of the ^1H NMR spectral assignments were made with the aid of homonuclear decoupling experiments, two-dimensional ^1H–^1H correlated spectra (COSY) and/or difference NOE spectra. COSY spectra were recorded in the normal fashion by using the well-established pulse sequence and phase cycling of Bax, Freeman, and Morris.[33] Typically $128t_1$ increments were employed, and after Fourier transformation the final 512 × 512 spectrum was symmetrized prior to contour plotting. Difference NOE spectra were obtained in an array experiment with the decoupler offset 10 000 Hz and then cycled over the multiplet peaks of the desired proton for irradiation, using a procedure based on that of Kinns and Saunders.[34] Some ^{13}C NMR spectral assignments were made by ^1H–^{13}C two-dimensional heteronuclear correlation spectroscopy, which was recorded in the usual manner,[35] typically as a 128 × 1K matrix. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected.

Preparation of Alcohols. Unless otherwise specified the alcohols used in this study were prepared by Grignard reactions between benzylmagnesium chloride and the appropriate ketone. Purification of the alcohols were carried out by recrystallization or column chromatography, and reaction yields were typically 80%. 1-Benzyl-2-methylcyclohexanol (**6**),[36] 1-benzylcyclohexanol (**9**),[37] 1-benzyl-4-methylcyclohexanol (**16b**),[12a] 2-methyl-4-phenylbutan-2-ol (**18**),[38] 3-methyl-1-phenylbutan-2-ol (**20**),[39] 2-*exo*-benzylnorbornanol (**24a**),[40] 2-benzylcamphenilol (**31**),[41] and 2-*exo*-benzylfenchol (**35**)[41] were prepared as previously reported.

6-Benzylspiro[4.5]decan-6-ol (10) was prepared, in 50% yield,

(29) 11-(Fluorosulfonyl)-7,8,12-trimethyltetracyclo[7.4.0.0^{2,7}.0^{4,8}]trideca-1(9),10,12-triene,[17] 7,8-dimethyltetracyclo[7.4.0.0^{2,7}.0^{4,8}]trideca-1(9),10,12-triene,[1] and 1,6,7-trimethyltricyclo[4.3.0.0^{3,7}]nonan-2-one: Jäger, V.; Kuhn, W.; Buddrus, J. *Tetrahedron Lett.* **1986**, *27*, 2587.

(30) 14,14-Dimethyl-2-phenyltetracyclo[9.2.1.0^{1,9}.0^{3,8}]tetradeca-3,5,7-triene, a phenyl-substituted derivative of **37**, has been reported with the corresponding methyl protons resonating at 0.39 ppm: Hixson, S. S.; Day, R. O.; Franke, L. A.; Rao, R. V. *J. Am. Chem. Soc.* **1980**, *102*, 412. The formation of **37** can result from Wagner–Meerwein rearrangement of the initially formed cation to produce **38**, which then undergoes cyclization (below). The formation of **37** from **35** but absence of an analogous product from **31** is considered a consequence of the C1 methyl group, which allows the WM rearrangement to be competitive with *exo*-3,2-methyl migration.



(31) Bright, S. T.; Coxon, J. M.; Steel, P. J. Unpublished results.

(32) At the temperatures required for the ionisation of the secondary alcohol in HSO_3F the dimethylindan undergoes fluorosulfonation.

(33) Bax, A.; Freeman, R.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 164.

(34) Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

(35) Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501.

(36) Sisti, A. J.; Rusch, G. M. *J. Org. Chem.* **1974**, *39*, 1182.

(37) Newkome, G. R.; Allen, J. W.; Anderson, G. M. *J. Chem. Ed.* **1973**, *50*, 372.

(38) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1966**, *31*, 89.

(39) Vigneron, J. P.; Dhaenens, M.; Horeau, A. *Tetrahedron* **1977**, *33*, 507.

(40) Lapalme, R.; Borschberg, H. J.; Soucy, P.; Deslongchamps, P. *Can. J. Chem.* **1979**, *57*, 3272.

(41) Sisti, A. J.; Rusch, G. M.; Sukhon, H. K. *J. Org. Chem.* **1971**, *36*, 2030.

from spiro[4.5]decan-6-one,[42] which had been prepared by a pinacol rearrangement. Purification of the alcohol was carried out by column chromatography on alumina. Elution with petroleum ether/ether (1:1) gave the alcohol as a clear oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.25 (m, 5 H, ArH), 2.86 and 2.82 (dd, J_{AB} = 13.4 Hz, 2 H, ArCH_2), 2.03 (m, 1 H), 1.80 (m, 1 H), 1.72–1.25 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ_C 22.1, 22.4, 26.1, 26.3, 33.5, 33.9, 34.3, 35.8, 40.7 (C10), 50.5 (C5a), 75.1 (C1), 126.2 (para), 128.0 (meta), 130.9 (ortho), 137.7 (ipso). Anal. Calcd for $C_{17}H_{24}O$: (M^+) 244.1827. Found: (M^+) 244.1811.

1-Benzyl-*trans*-decalin-1-ol (13) was prepared from *trans*-1-decalone in 65% yield. Purification was carried out by column chromatography on alumina. Elution with petroleum ether/ether (1:1) gave the alcohol as a clear oil: ν_{max} 3525, 2950, 1510, 1460, 745, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ_H 7.25 (m, 5 H, ArH), 2.94 and 2.62 (dd, J = 13.2 Hz, 2 H, ArCH_2), 2.04 (m, 1 H), 1.85 (m, 1 H), 1.64 (m, 2 H), 1.55–1.22 (m, 10 H), 1.02–0.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ_C 21.1, 25.6, 26.4, 26.9, 34.1, 34.8, 37.2, 37.6, 46.3, 49.4, 73.0, 126.1 (para), 127.9 (meta), 130.5 (ortho), 137.9 (ipso). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90; (M^+ – 18) 226.1722. Found: C, 83.0; H, 10.3; (M^+ – 18) 226.1725.

1-Benzyl-3-methylcyclohexanol (16a) was prepared from 3-methylcyclohexanone in 85% yield as an oil, which was a 1:4 mixture of trans:cis isomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.25 (m, ArH), 2.80 (ArCH_2-*cis*), 2.71 (s, ArCH_2-*trans*), 1.67 (m, CH_2), 1.55 (m, CH_2), 1.30 (m, CH), 0.85 (d, J = 6.5 Hz, CH_3); cis, ^{13}C NMR ($CDCl_3$) δ_C 21.6, 22.6, 27.8, 34.7, 36.7, 45.8, 50.6, 71.6, 126.3, 128.0, 130.5, 137.0. Anal. Calcd for $C_{14}H_{20}O$: C, 89.29; H, 10.71. Found: C, 88.57; H, 11.06.

2-*exo*-(*p*-Methoxybenzyl)norbornanol (24b) was prepared from norcamphor and (*p*-methoxybenzyl)magnesium chloride in 85% yield: bp 230–240 °C (8 mm); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.16 (d, J = 8.6 Hz, ortho), 6.85 (d, J = 8.6 Hz, meta), 3.97 (s, OCH_3), 2.80 and 2.70 (dd, J = 13.6 Hz, ArCH_2), 2.23 (m, H4), 2.12 (m, H1), 1.88 (m, 1 H), 1.73–1.49 (m, 4 H), 1.33–1.21 (m, 3 H), 1.09 (dd, J = 12.9, 3.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 28.7 (C5), 37.4 (C4), 38.6 (C7), 45.7 (2 C, C1 and C3), 47.0 (ArCH_2), 55.2 (OCH_3), 79.2 (C2), 113.8 (meta), 129.8 (ipso), 131.5 (ortho), 158.4 (para). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; (M^+) 232.1463. Found: C, 78.0; H, 8.8; (M^+) 232.1456.

Deuterated Alcohols 24c, 24d, 24e, and 24f. Alcohols **24c, 24e,** and **24f** were prepared from the appropriate deuterated norcamphors,[43] the spectral data of which are given below.

(a) 3-*exo*-Deuteronorcamphor: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.65 (1 H, H1), 2.58 (1 H, H4), 1.88–1.65 (4 H, CH_2's), 1.61–1.35 (3 H, CH_2 and CH); ^{2}H NMR ($CHCl_3$, 46 MHz) δ_{2H} 2.05 (1 ^{2}H, ^{2}H3-*exo*); ^{13}C NMR ($CDCl_3$) δ_C 24.2 (C6), 27.2 (C5), 35.3 (C4), 37.7 (C7), 45.1 (t, C3), 49.9 (C1), 217.7 (C2).

(b) 3-*endo*-Deuteronorcamphor: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.65 (1 H, H1), 2.58 (1 H, H4), 2.10–1.98 (1.1 H, H3), 1.88–1.66 (3 H, CH_2 and CH), 1.59–1.36 (3 H, CH_2 and CH); ^{2}H NMR ($CHCl_3$, 46 MHz) δ_{2H} 1.86 (1 ^{2}H, ^{2}H3-*endo*); ^{13}C NMR ($CDCl_3$) δ_C 24.2 (C6), 27.2 (C5), 35.2 (C4), 37.7 (C7), 45.2 (t, C3), 49.9 (C1), 217.7 (C2).

(c) 3,3-Dideuteronorcamphor: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.66 (1 H, H1), 2.58 (1 H, H4), 2.06–2.00 (0.25 H, H3-*exo*), 1.89–1.69 (3.25 H, CH_2), 1.60–1.38 (3 H, CH_2); ^{2}H NMR ($CHCl_3$, 46 MHz) δ_{2H} 2.01 (0.75 ^{2}H, ^{2}H3-*exo*), 1.79 (0.75 ^{2}H, ^{2}H3-*endo*); ^{13}C NMR ($CDCl_3$) δ_C 24.2 (C6), 27.2 (C5), 35.3 (C4), 37.7 (C7), 45.1 (t, C3), 49.9 (C1), 217.7 (C2).

2-(α,α-Dideuteriobenzyl)norbornanol (24d) was prepared from norcamphor and the magnesium Grignard of α,α-dideuteriobenzyl chloride[44] in 85% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.35–7.23 (m, 5 H, ArH), 2.25 (m, 1 H, H1), 2.13 (m, 1 H, H4), 1.95–1.25 (m, 9 H, CH_2's and OH); ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 28.7 (C5), 37.4 (C4), 38.6 (C7), 45.6 (C3), 45.8 (C1), C8 not obsd, 79.2 (C2), 126.5 (para), 128.3 (meta), 130.5 (ortho), 137.6 (ipso).

The extent of deuterium incorporation in the product alcohols was determined by mass spectrometry to be >90% D_2 for 2-*exo*-benzyl-3,3-dideuterionorbornanol (**24c**), >95% D_2 for 2-(α,α-dideuteriobenzyl)norbornanol (**24d**), >95% D_1 for 2-benzyl-3-*exo*-deuterionorbornanol (**24e**), and >85% D_1 for 2-benzyl-3-*endo*-deuterionorbornanol (**24f**). The stereochemical location of the deuterium was determined by ^{2}H NMR spectroscopy by integration of the signals at 1.75 ppm (*exo*-D3) and 1.13 ppm (*endo*-D3), and the products were shown to be >95% stereochemically pure in each case. The ^{1}H and ^{13}C NMR spectra were consistent with these results.

Spiro[3-*exo*-benzylbicyclo[2.2.1]heptan-3-*endo*-ol-2,1′-cyclopentane] (39) was prepared from spiro[bicyclo[2.2.1]heptan-3-one-2,1′-cyclopentane].[45] Purification was carried out by radial chromatography, and elution with petroleum ether gave **39** as a yellow oil (yield 20%): ν_{max} 3620, 1520, 1480, 720, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.10 (s, 5 H, ArH), 2.68 (s, 3 H, ArCH_2 and CH), 2.16–0.80 (20 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ_C 21.6 (C5), 23.2 (2 C, C3′ and C4′), 24.0 (C6), 30.5 (C5′), 34.4 (C7), 35.1 (C2′), 43.7 (C8), 45.3 (C4), 46.3 (C1), 56.8 (C2), 79.7 (C3), 126.3 (para), 128.1 (meta), 130.7 (ortho), 138.8 (ipso). Anal. Calcd for $C_{18}H_{24}O$: (M^+) 256.1827. Found: (M^+) 256.1822.

Reactions with Fluorosulfuric Acid. To a vigorously stirred mixture of fluorosulfuric acid (2 mL) in dry dichloromethane (2 mL) at –78 °C was added a solution of the alcohol (ca. 2 mmol) in dichloromethane (2 mL), and the resulting mixture was stirred at –78 °C for 30 min, unless otherwise indicated. The mixture was then added cautiously to water (40 mL) and neutralized with $NaHCO_3$, and the mixture was extracted repeatedly with diethyl ether. The combined ether extracts were washed with $NaHCO_3$, dried, and, after removal of solvent, gave a crude product which was purified by bulb-to-bulb distillation or by chromatography on alumina.

(i) 1-Benzyl-2-methylcyclohexanol (6) with HSO_3F as above gave *cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrofluorene (**7**) in >85% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.31–7.08 (m, 4 H), 2.89 (dd, J = 15.4, 7.0 Hz, 1 H), 2.66 (dd, J = 15.4, 7.2 Hz, 1 H), 2.08 (m, 1 H), 1.66 (m, 2 H), 1.51–1.28 (m, 6 H), 1.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 22.2, 22.8, 25.7, 26.8, 35.3, 35.6, 45.2, 46.2, 121.4, 125.0, 125.7, 125.9, 142.1, 152.4. Anal. Calcd for $C_{14}H_{18}$: (M^+) 186.1408. Found: (M^+) 186.1418. An authentic sample of *cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrofluoren-9-one (**8**) was prepared from the benzoate ester of 2-methylcyclohexanol according to the literature[7] method. Purification was carried out by radial chromatography and elution with benzene: ^{13}C NMR ($CDCl_3$) δ_C 21.2, 21.6, 22.3, 24.5 (C2, C3, C4, C4a-CH_3), 39.3 (C1), 41.4 (C4a), 56.0 (C9a), 122.7 (C7), 123.7 (C5), 127.2 (C6), 134.4 (C8), 134.8 (C4b), 163.0 (C8a), 185.54 (C9). Clemmensen reduction of *cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrofluoren-9-one (**8**)[7] with $Zn/HgCl_2/HCl$ gave (**7**) in 90% yield, which was identical in all respects with the hydrocarbon produced from the HSO_3F reaction.

(ii) 1-Benzylcyclohexanol (9) with HSO_3F as above gave a complex mixture of hydrocarbons shown by mass spectrometry to consist mainly of dimers of formula $C_{26}H_{32}$. Attempts to separate and identify the components were not successful.

(iii) 6-Benzylspiro[4.5]decan-6-ol (10) with HSO_3F as above gave tetracyclo[7.4.4.$0^{1,9}$.$0^{2,7}$]heptadeca-2,4,6-triene (**11**) in 80% yield: mp 41–42.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.22 (d, J = 7 Hz, 1 H), 7.16 (t, J = 7 Hz, 1 H), 7.11 (t, J = 7 Hz, 1 H), 7.07 (d, J = 7.5 Hz, 1 H), 2.69 (s, 2 H), 1.62–1.40 (m, 12 H), 1.31 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ_C 22.3 (2 C), 22.5 (2 C), 33.1 (4 C), 41.7, 44.9, 48.3, 121.3, 125.6, 125.8, 142.0, 152.2. Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80; (M^+) 226.1721. Found: C, 89.94; H, 9.96; (M^+) 226.1721.

(iv) 1-Benzyl-*trans*-decalin-1-ol (13) with HSO_3F as above gave (±)-9a-carba-14a-morphinan (**12**)[11] in 90% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.20 (d, J = 6.5 Hz, 2 H), 7.09 (m, 3 H), 3.24 (dd, J = 17.5, 7.1 Hz, 1 H), 2.70 (d, J = 17.5 Hz, 1 H), 2.15 (m, 2 H), 1.92–0.94 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ_C 19.8, 22.7, 26.7, 27.4, 27.9, 31.2, 33.5, 37.0, 37.9, 41.6, 124.0, 125.0, 125.3, 127.8, 138.3, 146.7. Anal. Calcd for $C_{17}H_{22}$: (M^+) 226.1722. Found: (M^+) 226.1728.

(v) 1-Benzyl-3-methylcyclohexanol (16a) with HSO_3F at –78 °C gave, in addition to polymeric products, *cis*-1-benzyl-3-methylcyclohexane (**17a**) in ~50% yield after chromatography on alumina: bp 120 °C (12 mm); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.48 (d, J = 6.5 Hz, ArCH_2); ^{13}C NMR ($CDCl_3$) δ_C 22.9 (C3-CH_3),

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26.2 (C5), 32.7 (C6), 32.8 (C3), 35.3 (C4), 39.8 (C1), 42.0 (C2), 44.3 (CH_2), 125.6 (para), 128.0 (meta), 129.1 (ortho), 141.3 (ipso). The sample was shown by NMR to contain <5% of the trans isomer. An authentic sample of a mixture of the cis and trans isomers (ca. 1:1) was prepared from **16a** by dehydration with H_3PO_4 followed by hydrogenation over 5% Pd/C.

(vi) 1-Benzyl-4-methylcyclohexanol (16b) was reacted in a manner similar to that for **16a** to give *trans*-1-benzyl-4-methylcyclohexane (**17b**)[12a] in ~30% yield. An authentic sample of a mixture of cis and trans isomers was prepared by dehydration of **16** followed by hydrogenation as described below.

1-Benzyl-4-methylcyclohexene was prepared by heating phosphoric acid and 1-benzyl-4-methylcyclohexanol (**16b**) on a steam bath for 30 min. Water was added, and the mixture was repeatedly extracted with ether and dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to give 1-benzyl-4-methylcyclohexene as a pale oil (2.2 g): ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.17 (5 H, ArH), 5.42 (br s, 1 H, H2), 3.22 (2 H, ArCH_2), 2.63–1.00 (7 H, CH_2's and CH), 0.90 (d, J = 5 Hz, 3 H, CH_3).

1-Benzyl-4-methylcyclohexane was prepared from 1-benzyl-4-methylcyclohexene in ethyl acetate by reaction with 5% palladium on carbon in a hydrogen atmosphere for 12 h to give the alkane as a mixture of cis and trans isomers: (trans) ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.15 (5 H, ArH), 2.57 (d, J = 6 Hz, 2 H, ArCH_2); ^{13}C NMR ($CDCl_3$) δ_C 22.7 (C4-CH_3), 32.8 (C4), 33.2 (2 C, C2 and C6), 35.3 (2 C, C3 and C5), 39.6 (C1), 44.1 (C7), 125.6 (para), 128.1 (meta), 129.1 (ortho), 141.3 and 141.7 (ipso); (cis) ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.15 (5 H, ArH), 2.45 (d, J = 6 Hz, 2 H, ArCH_2); ^{13}C NMR ($CDCl_3$) δ_C 20.2 (C4-CH_3), 28.4 (2 C, C2 and C6), 30.1 (C4), 30.8 (2 C, C3 and C5), 37.5 (C1), 40.9 (C7), 125.6 (para), 128.1 (meta), 129.1 (ortho), 141.3 and 141.7 (ipso).

1-Benzyl-3-methylcyclohexene was prepared by an analogous method to that for 1-benzyl-4-methylcyclohexene: ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.20 (5 H, ArH), 5.45 (1 H, H2), 3.20 (2 H, ArCH_2), 2.4–0.8 (10 H, CH_2's and CH_3).

1-Benzyl-3-methylcyclohexane was prepared by an analogous method to that above to give the alkane as a mixture of the cis and trans isomers: (trans) ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 2.55 (d, J = 7 Hz, 2 H, ArCH_2), 0.9 (d, J = 3 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 20.7 (C3-CH_3), 20.9 (C5), 27.3 (C3), 31.2 (C6), 33.9 (C4), 34.7 (C1), 38.9 (C2), 41.3 (ArCH_2), 125.6 (para), 128.0 (meta), 129.0 and 129.1 (ortho), 141.2 and 141.6 (ipso); (cis) ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 2.45 (d, J = 7 Hz, 2 H, ArCH_2), 0.85 (d, J = 3 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 22.9 (C3-CH_3), 26.3 (C5), 32.8 (2 C, C6 and C3), 35.4 (C4), 39.9 (C1), 42.1 (C2), 44.4 (C7), 125.6 (para), 128.0 (meta), 129.0 and 129.1 (ortho), 141.2 and 141.6 (ipso).

(vii) 2-Methyl-4-phenylbutan-2-ol (18) with HSO_3F gave 1,1-dimethylindan (**19**)[38,46] in 41% yield: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.15 (m, 4 H, ArH), 2.89 (t, $J_{2,3}$ = 7.2 Hz, 2 H, ArCH_2), 1.92 (t, $J_{2,3}$ = 7.2 Hz, 2 H, H2), 1.26 (s, 6 H, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 28.7 (2 C, CH_3's), 30.1 (C3), 41.4 (C2), 44.0 (C1), 121.9 (C7), 124.4 (C4), 126.1, 126.2 (C5 and C6), 142.6 (C3a), 152.4 (C7a).

(viii) 3-Methyl-1-phenylbutan-2-ol (20) with HSO_3F at −70 °C as above gave the starting alcohol (**20**) (70%) plus 1,1-dimethylindan (**19**) (20%), identical with an authentic sample prepared by literature methods:[38,46] ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.15 (m, 4 H, ArH), 2.89 (t, $J_{2,3}$ = 7.2 Hz, 2 H, H3), 1.92 (t, $J_{2,3}$ = 7.2 Hz, 2 H, H2), 1.26 (s, 6 H, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 28.7 (2 C, CH_3's), 30.1 (C3), 41.4 (C2), 44.0 (C1), 121.9 (C7), 124.4 (C4), 126.1, 126.2 (C5 and C6), 142.6 (C3a), 152.4 (C7a). Reaction of **20** at 0 °C and 25 °C and reaction of **19** at 25 °C all gave similar mixtures of three fluorosulfonated isomers, which were separated by preparative GLC and identified as follows. 1,1-Dimethylindan-6-sulfonyl fluoride (**21**) (45%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.79 (dd, J = 8.0, 1.8 Hz, H5), 7.72 (d, J = 1.8 Hz, H7), 7.41 (d, J = 8.0 Hz, H4), 3.00 (t, J = 7.3 Hz, ArCH_2), 2.02 (t, J = 7.3 Hz, CH_2), 1.31 (s, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 28.4 (2 C, CH_3's), 30.5 (C3), 41.1 (C2), 44.3 (C1), 122.2 (C7), 125.6 (C4), 126.9 (C5). 1,1-Dimethylindan-5-sulfonyl fluoride (**22**): (35%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.83 (dd, J = 7.6, 2.0 Hz, H6), 7.81 (s, H4), 7.34 (d, J = 7.6 Hz, H7), 2.99 (t, J = 7.3 Hz, ArCH_2), 2.02 (t, J = 7.3 Hz, CH_2), 1.30 (s, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 28.1 (2 C, CH_3's), 29.8 (C3), 41.0 (C2), 44.5 (C1), 122.9 (C7), 124.4 (C4), 127.1 (C6). 1,1-Dimethylindan-4-sulfonyl fluoride (**23**) (20%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.80 (d, J = 7.5 Hz, H5), 7.49 (d, J = 6.9 Hz, H7), 7.40 (dd, J = 7.5, 6.9 Hz, H6), 3.27 (t, J = 7.3 Hz, ArCH_2), 2.04 (t, J = 7.3 Hz, CH_2), 1.30 (s, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 28.6 (2 C, CH_3's), 30.0 (C2), 40.6 (C3), 44.3 (C1), 127.0 (C5), 127.7 (C6), 129.5 (C7).

(ix) 2-*exo*-Benzylnorbornanol (24a) with HSO_3F as above gave 6-phenylbicyclo[3.2.1]oct-6-ene (**26a**) in 72% yield: bp 115–125 °C (12 mm); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.46 (d, ortho), 7.31 (t, meta), 7.20 (t, para), 6.25 (dd, J = 3.0, 0.9 Hz, H7), 2.97 (m, H5), 2.69 (m, H1), 2.13 (m, H8-*anti*), 1.60-1.35 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ_C 19.0 (C3), 25.1 (C4), 25.3 (C2), 40.4 (C1), 40.8 (C5), 45.1 (C8), 125.5 (ortho), 126.7 (para), 127.0 (C7), 128.4 (meta), 136.0 (ipso), 143.6 (C6). Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75; (M^+) 184.1252. Found: C, 91.39; H, 9.01; (M^+) 184.1250.

NMR Observation of 6-Phenylbicyclo[3.2.1]octan-6-yl Cation. A HSO_3F/SO_2ClF solution of 2-*exo*-benzylnorbornanol (**24a**) was prepared in an NMR tube at low temperature by a previously described procedure.[23] The only observed species between −90 °C and −20 °C was the 6-phenylbicyclo[3.2.1]octan-6-yl cation (**25a**):[20a] ^{13}C NMR ($CDCl_3$) δ_C 19.4 (C3), 27.0 (C2), 35.9 (C1), 39.6 (C4), 42.5 (C8), 49.5 (C7), 55.5 (C5), 133.1 (meta), 135.5 (ipso), 142.5 (ortho), 155.0 (para), 268.8 (C6).

Reactions of alcohols 24c, 24d, 24e, and 24f with HSO_3F each gave a product with physical properties identical with those of **26a**, but with deuterium incorporated. Thus **24c** gave 7-deuterio-6-phenylbicyclo[3.2.1]oct-6-ene (**26c**) for which the ^{1}H NMR showed >90% reduction of the olefinic signal at 6.25 ppm and the ^{2}H NMR exhibited a single signal at 6.3 ppm. Similarly **24e** and **24f** each gave a 1:1 mixture of **26a** and **26c**, i.e. 50 ± 5% deuterium labeling of H7. Alcohol **24d** gave 4,5-dideuterio-6-phenylbicyclo[3.2.1]oct-6-ene (**26d**), lacking the two ^{1}H NMR signals at 2.97 and 1.6 ppm exhibited by the undeuterated analogue. The ^{2}H NMR showed only two signals at 2.99 and 1.59 ppm.

(x) 2-*exo*-(*p*-Methoxybenzyl)norbornanol (24b) with HSO_3F gave 6-(*p*-methoxyphenyl)bicyclo[3.2.1]oct-6-ene (**26b**): bp 190–205 °C (12 mm); ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.27 (d, J = 8.5 Hz, ortho), 6.73 (d, J = 8.5 Hz, meta), 6.02 (d, J = 3 Hz, H7), 3.75 (s, OCH_3), 2.92 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ_C 19.0 (C3), 25.1 (C4), 25.4 (C2), 40.3 (C1), 40.9 (C5), 45.1 (C8), 55.2 (OCH_3), 113.8 (meta), 124.7 (C7), 126.7 (ortho), 128.8 (ipso), 142.9 (C6), 158.6 (para). Anal. Calcd for $C_{15}H_{18}O$: (M^+) 214.1357. Found: (M^+) 214.1347.

(xi) 2-*exo*-Benzylcamphenilol (31) with HSO_3F gave 7,8-dimethyltetracyclo[8.4.0.0^{2,7}.0^{4,8}]tetradeca-1(10),11,13-triene (**34**) in 92% yield: bp 140–150 °C (14 mm); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.28 and 7.05 (m, 4 H), 2.97 and 2.62 (dd, J = 18.4 Hz, C9-H_2), 2.43 (dd, J = 8.2, 2.2 Hz, H2), 1.90–1.15 (m, 7 H), 0.97 (s, C9-CH_3), 0.57 (s, C8-CH_3); ^{13}C NMR ($CDCl_3$) δ_C 15.1 (C7-CH_3), 19.0 (C8-CH_3), 29.8 (C5), 34.5 (C6), 38.2 (C3), 40.1 (C9), 45.5 (C7), 47.0 (C8), 48.0 (C4), 50.9 (C2), 124.6, 125.1 (2 C) and 127.7 (C11–C14), 136.9 (C10), 147.2 (C1). Anal. Calcd for $C_{16}H_{20}$: (M^+) 212.1565. Found: (M^+) 212.1558.

(xii) 2-*exo*-Benzylfenchol (35) with HSO_3F as above gave a mixture of two hydrocarbons, which were not separated but which were identified by NMR as follows. 4,7,8-Trimethyltetracyclo[8.4.0.0^{2,7}.0^{4,8}]tetradeca-1(10),11,13-triene (**36**) (60%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.05 (m, 3 H), 6.88 (d, J = 6.7 Hz, 1 H), 2.87 and 2.45 (dd, J = 18.5 Hz, C9-H_2) 2.39 (dd, J = 8.3, 2.2 Hz, H2), 1.88–1.15 (m, 6 H), 0.92 (s, C7-CH_3), 0.82 (s, C4-CH_3), 0.61 (s, C8-CH_3); ^{13}C NMR ($CDCl_3$) δ_C 15.7, 16.0, 16.8 (C4-CH_3, C7-CH_3, C8-CH_3), 34.0, 35.2, 37.1 (C5, C6, C9), 47.7, 48.3 (C2, C3), 124.6, 125.0 (2 C), 127.7 (C11–C14), 136.8 (C10), 147.0 (C1). 9,14,14-Trimethyltetracyclo[9.2.1.0^{1,9}.0^{3,8}]tetradeca-3,5,7-triene (**37**) (30%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 3.00 and 2.66 (dd, J = 18.5 Hz, C2-H_2), 1.36, 1.00, 0.42 (CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 12.8, 17.9, 19.8, 29.5, 29.7, 30.4, 38.4, 48.2, 50.0, 121.8, 124.5, 124.7, 127.6.

(xii) Spiro[3-*exo*-benzylbicyclo[2.2.1]heptan-3-*endo*-ol-2,1′-cyclopentane] (39) with HSO_3F as above gave pentacyclo[9.7.0.0^{1,14}.0^{3,8}.0^{9,14}]octadeca-3,5,7-triene (**40**) in 86% yield: mp 48–49 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.00 (m, ArH), 2.76 (s,

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C2-H_2), 2.46 (dd, J = 8, 2 Hz, H9), 1.98 (m, C16-H_2), 1.84 (m, H11), 1.72 (dd, J = 12.8, 2 Hz, H10-*endo*), 1.52 (m, H10-*exo*), 1.37 (m, CH_2's), 1.22 (m, CH_2's), 1.16 (m, H15), 0.72 (m, H15); ^{13}C NMR ($CDCl_3$) δ_C 20.9 (C16), 21.4, 25.6 (C15), 28.6, 29.1, 29.8, 35.4 (C2), 39.9 (C10), 45.5, 46.0 (C1, C14), 47.7 (C11), 50.0 (C9), 124.7 (C7), 125.1, 125.2 (C5 and C6), 127.5 (C4), 137.1 (C3), 146.3 (C8). Anal. Calcd for $C_{18}H_{22}$: (M^+) 238.1721. Found: (M^+) 238.1716.

Reactions of 24a, 31, and 35 with Acetic Acid/Sulfuric Acid. The alcohol (2 mmol) was dissolved in glacial acid (30 mL), concentrated sulfuric acid (1 mL) was added, and the mixture was stirred for 20 h. Water (50 mL) was added, and the mixture was extracted with ether (3 × 100 mL). The combined ether extracts were washed until neutral and dried, and the solvent was removed in vacuo to give products that were purified by distillation or chromatography on alumina.

(a) Reaction of 2-*exo*-benzylnorbornanol (24a) at 25 °C gave in 95% yield a 4:1 mixture of the known[40] *E* and *Z* alkenes 2-benzylidenenorbornane (**44** and **45**). **44**: ^1H NMR (CCl_4, 60 MHz) δ_H 7.10 (br s, ArH), 6.17 (t, J = 2.5 Hz, C=C*H*Ar), 3.20 (br s, H1), 2.80 (br s, H4); ^{13}C NMR ($CDCl_3$) δ_C 28.5 (C6), 29.7 (C5), 37.3 (C4), 38.9, 39.1 (C3, C7), 47.8 (C1), 118.0 (C=CHAr), 125.6 (para), 127.7 (ortho), 128.3 (meta), 138.9 (ipso), 149.7 (C2). **45**: ^1H NMR (CCl_4, 60 MHz) δ_H 6.00 (br s, C=C*H*Ph); ^{13}C NMR ($CDCl_3$) δ_C 28.4, 28.8, 35.8, 38.8, 40.4, 41.4, 118.9, 125.7, 127.9, 128.2; bp (for the mixture) 125-135 °C (6 mm). Anal. Calcd for $C_{14}H_{16}$: (M^+) 184.1252. Found: (M^+) 184.1252.

(b) Reaction of 2-*exo*-benzylnorbornanol (24a) at 70 °C gave the above alkenes (50%) and 1-benzylnorbornyl acetate (**46**): ^1H NMR ($CDCl_3$, 60 MHz) δ_H 7.13 (br s, ArH), 4.50 (d, J = 6.5 Hz, H2), 2.83 (s, ArCH_2), 2.06 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 21.3 (CH_3), 29.2, 29.6 (C5, C6), 35.4 (C4), 36.7 (ArCH_2), 39.8 (C7), 41.6 (C3), 51.0 (C1), 78.6 (C2), 125.9 (para), 128.0 (meta), 129.9 (ortho), 139.5 (ipso), 170.5 (C=O).

(c) Reaction of 2-*exo*-benzylcamphenilol (31) as above gave (*E*)-2-benzylidenecamphenilol (**41**) in 85% yield: bp 126-135 °C (10 mm); ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.00 (m, ArH), 6.01 (s, C=C*H*Ar), 3.27 (d, H1), 1.96 (br s, H4), 1.13 (s, CH_3's); ^{13}C NMR ($CDCl_3$) δ_C 23.8 (C5), 26.3 (*endo*-CH_3), 27.9 (C6), 29.1 (*exo*-CH_3), 38.0 (C7), 42.5 (C1), 43.3 (C4), 116.3 (C=CHAr), 125.5 (para), 128.0, 128.1 (ortho, meta), 139.0 (ipso), 159.2 (C2).

(d) Reaction of 2-*exo*-benzylfenchol (35) as above at 25 °C gave a complex mixture of hydrocarbons, which was not separated but which was shown by ^{13}C NMR to contain alkenes **42** (C=*C*HAr δ_C 116.6) and **43** (δ_C 117.1) as ca. 50% of the mixture.

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The Triplex Diels-Alder Reaction of 1,3-Dienes with Enol, Alkene, and Acetylenic Dienophiles: Scope and Utility

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The [4 + 2] cycloaddition of an electron-rich diene to an electron-rich dienophile may be catalyzed by irradiation of a cyanoarene. This reaction is shown to proceed through an intermediate ternary excited state complex (triplex) and is therefore called the triplex Diels-Alder reaction. The triplex Diels-Alder reactions of a series of cyclic and acyclic 1,3-dienes with alkenyl benzene, enol ether, and alkynylbenzene dienophiles was investigated. This procedure works extremely well in some cases but poorly in others. A mechanistic hypothesis for the scope and limitations of the triplex Diels-Alder reaction based on these findings is advanced.

Introduction

The Diels-Alder reaction is a convenient, predictable route for the thermal cycloaddition of an electron-deficient dienophile to an electron-rich diene.[1] This reaction often occurs rapidly under mild conditions and has been employed inumerable times for the synthesis of complex materials. In general, however, the Diels-Alder reaction is unsuccessful when both diene and dienophile components are electron-rich compounds. Of the many procedures that have been devised to accelerate the Diels-Alder reaction, none work well for this case. The removal of this restriction seemed imminent in 1981 when Bauld and coworkers discovered that triarylaminium salts initiated the Diels-Alder-like dimerization of 1,3-cyclohexadiene (CHD) and other electron-rich dienes.[2] They proposed a radical cation chain reaction mechanism for this process,[3] and subsequent examinations have supported this path with a few important exceptions.[4,5] However, the aminium salt catalyzed Diels-Alder reaction is often restricted to the dimerization of dienes because of lack of selectivity; the "crossed" cycloadditions that have been reported require very large excesses of the dienophile. Additional complications with this procedure arise when the aminium salt initiates the isomerization or polymerization of the dienophile.[4]

In 1983, Jones and co-workers[6] described a photosensitized dimerization of CHD under conditions where the radical cation chain reaction mechanism is thermodynamically impossible. Our investigation and extension of this discovery led to its generalization as the triplex Diels-Alder reaction.[7] According to this proposal, an exciplex formed

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