Table V. HPLC Analysis of the Four Amide Products

amide	liquid phase	t_R, s	internal standard (t_R, s)
5	50 vol % CH_3OH-H_2O, 0.1 M NH_4NO_3	269	2-chloro-5-hydroxytoluene (798)
6	66 vol % CH_3OH-H_2O, 0.1 M NH_4NO_3	402	none used
7	20 vol % CH_3OH-H_2O, 0.1 M NH_4NO_3	685	p-$ClC_6H_4SO_3^-$ Na^+ (536)
8	H_2O, 0.1 M NH_4NO_3	319	butyramide (621)

of a Morrow stopped-flow apparatus equiped with a Beckman Model DU quartz spectrometer and a Type 549 storage oscilloscope. The spectrometer was set to read at 400 nm (p-nitrophenoxide ion). A recording of the transmittance vs time trace of the oscilloscope screen was photographed, and the initial rate (d(product)/dt) was determined from the initial slope of the p-nitrophenoxide concentration vs time. No correction had to be made for the absorbance of the ester or the amine at 400 nm, both reactants being transparent at this wavelength. A correction had to be made for the p-nitrophenoxide–p-nitrophenol equilibrium in the presence of the taurinate zwitterion in 95.3 mol % dioxane–water (see ref 1).

Product Analysis Runs. About 50 mg of the ester and an appropriate amount of the amine (same ratios of amine to ester as used in representative kinetic runs) in 50 mL of 95.3 mol % dioxane–water were allowed to stand (with stirring when necessary) at 25 °C for a length of time calculated to allow >99% reaction. The solvent was removed by vacuum distillation at room temperature, and the residue was analyzed by HPLC. Analyses were performed on a Waters Model 6000A chromatograph equiped with a reversed-phase Waters Microbondapak C_{18} column (30 cm × 3.9 cm i.d.). The flow rate was 1 mL/min at a pressure of approximately 1000 psi. The relevant parameters are listed in Table V. The yields ranged from 97% to 100%.

Acknowledgment. This work was supported in part by Grant number 13353 from the PSC-CUNY Research Award Program of the City University of New York.

Registry No. 1, 956-75-2; 2, 109686-78-4; 3, 100-46-9; 4, 91900-05-9; 5, 124563-44-6; 6, 6283-98-3; 7·Na, 124563-45-7; 8, 124563-46-8; $H_3C(CH_2)_4COCl$, 142-61-0; p-$NO_2C_6H_4OH$, 100-02-7; $EtOCO(CH_2)_3Cl$, 3153-36-4; $HO_2C(CH_2)_3N^+(Me)_3{\cdot}Cl^-$, 6249-56-5; p-$NO_2C_6H_4OCO(CH_2)_3N^+(Me)_3{\cdot}Cl^-$, 124563-42-4; $NH_2CH_2CH_2SO_3H$, 107-35-7; $EtOCO(CH_2)_3N^+(Me)_3{\cdot}Cl^-$, 51963-62-3; $NH_2CH_2CH_2SO_3^-{\cdot}Na^+$, 7347-25-3; γ-butyrolactone, 96-48-0.

Supplementary Material Available: NMR spectra for 4 and 6 (2 pages). Ordering information is given on any current masthead page.

Reactions of 2-Phenylethyl and 3-Phenylpropyl Carbinols with Fluorosulfuric Acid

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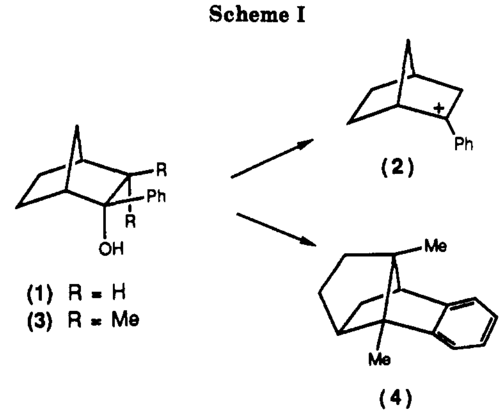
A series of 2-phenylethyl and 3-phenylpropyl carbinols have been reacted with HSO_3F at −78 °C, the solutions quenched, and the products isolated to give good yields of cyclization products. The 2-phenylethyl carbinols generally undergo rearrangement prior to cyclization, whereas the 3-phenylpropyl carbinols undergo direct cyclization of the initially formed carbocation, to give tetralins. The mechanisms and synthetic applications of these reactions are discussed.

Introduction

Carbocations are involved as reactive intermediates in numerous substitution, elimination, addition, and rearrangement reactions of synthetic, industrial, and biological importance.[1] Superacids,[2] such as fluorosulfuric acid, have been extensively employed for the generation and spectroscopic study of long-lived carbocations since the pioneering work in this area by Olah et al. Under these stable ion conditions carbocations can undergo complex rearrangements not accessible under less strongly acidic conditions. Such rearrangements are often highly sensitive to subtle changes in the structure of the precursors. For example we have long been interested in the study of aryl–norbornyl carbocations[3] whereas the parent 2-phenylnorbornanol 1 reacts with HSO_3F to produce the stable cation 2,[4] the 3,3-dimethyl analogue 3 undergoes rearrangement and cyclization to the tetracyclic product 4 (Scheme I).[5]

Scheme I

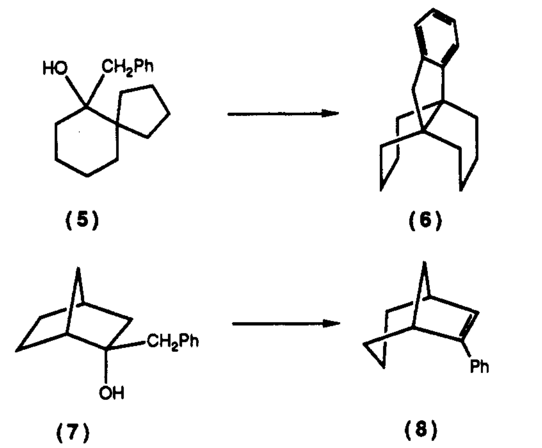


Such rearrangements can have useful applications in organic synthesis, and as a consequence superacids are being increasingly employed as reagents in organic synthesis.[6] In continuation of our studies[7] into the use of fluorosulfuric acid, we recently described[8] the reactions of

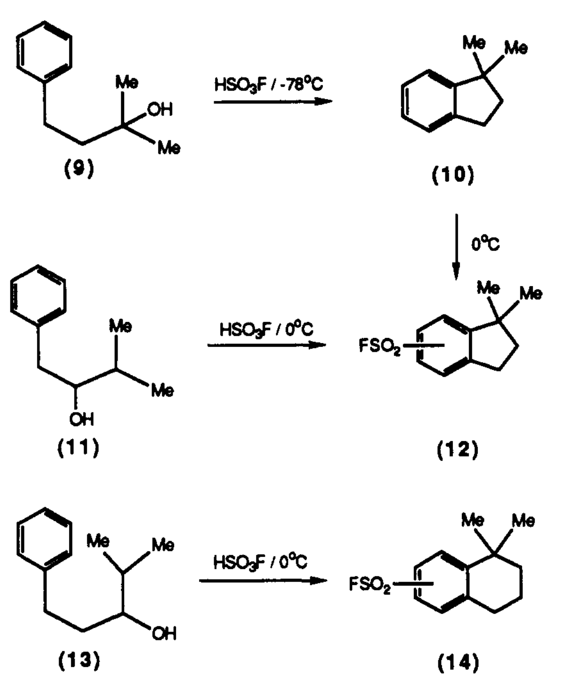
(1) Olah, G. A.; Schleyer, P. von R. *Carbonium Ions*; John Wiley & Sons: New York, 1968–1976; Vols 1–5.
(2) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985.
(3) Coxon, J. M.; Steel, P. J. *Aust. J. Chem.* **1980**, *33*, 2455 and references therein.
(4) Coxon, J. M.; Steel, P. J. *J. Chem. Soc., Chem. Commun.* **1984**, 344.
(5) Coxon, J. M.; Pojer, P. M.; Robinson, W. T.; Steel, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 111.
(6) For recent examples, see: (a) Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.* **1989**, *54*, 1452. (b) Olah, G. A.; Ernst, T. D. *J. Org. Chem.* **1989**, *54*, 1203. (c) Carr, G.; Dean, C.; Whittaker, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 351.
(7) Coxon, J. M.; Hydes, G. J.; Steel, P. J. *Tetrahedron* **1985**, *41*, 5213.

0022-3263/90/1955-1338$02.50/0

Scheme II



Scheme III



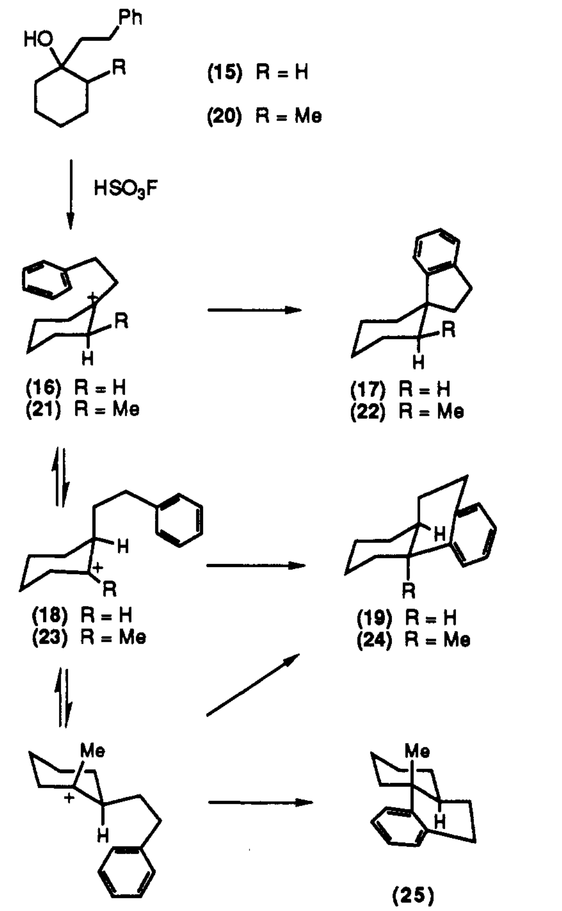
a series of benzyl carbinols with HSO_3F at −78 °C. A variety of reaction modes were observed to occur depending on the specific precursor. For example the spiro alcohol **5** underwent rearrangement and cyclization[8] to the propellane **6** whereas the norbornanol **7** was found to undergo an unusual ring expansion[9] and after quenching to give the alkene **8** (Scheme II). In the present paper we extend this study to investigate the reactions 2-phenylethyl and 3-phenylpropyl carbinols, wherein the additional methylene group(s) is expected to facilitate cyclization reactions in preference to other modes of reaction.

Results and Discussion

2-Phenylethyl Carbinols. Reaction of 2-methyl-4-phenylbutan-2-ol (**9**) with fluorosulfuric acid at −78 °C followed by quenching and product isolation gave 1,1-dimethylindan (**10**) in ca. 40% yield (Scheme III). This is a well-studied cyclialkylation reaction which can be effected by a variety of different acids.[10,11] The reaction

(8) Barrow, C. J.; Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1989**, *54*, 2542.
(9) Barrow, C. J., Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1987**, *52*, 5300.
(10) Roberts, R. M.; Khalaf, A. A. *Friedel-Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984.

Scheme IV

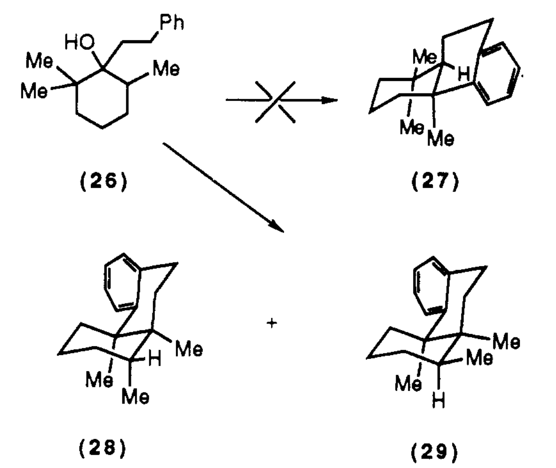


contrasts, however, with the previously reported[8] reaction of the isomeric benzyl carbinol **11**, which only reacts at higher temperatures to give a mixture of fluorosulfonated regioisomers **12**. Higher temperatures are required in the case of **11** since secondary alcohols are resistant to ionization in fluorosulfuric acid at low temperatures and accordingly fluorosulfonation of the indan ring occurs at 0 °C. Similarly the 2-phenylethyl analogue **13** failed to react at −78 °C but gave a mixture of three fluorosulfonated tetralins **14** at 0 °C. The formation of **14** results from ionization, a hydride shift, cyclization, and fluorosulfonation.

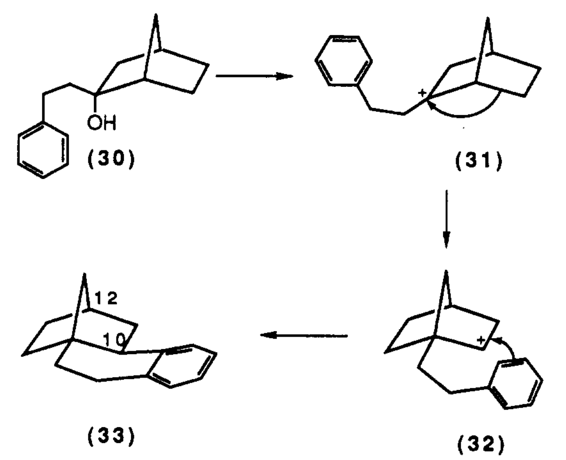
1-(2-Phenylethyl)cyclohexanol (**15**) reacted with HSO_3F at −78 °C to give a 1:3 mixture of spiro[cyclohexane-1,1′-indan] (**17**) and *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**19**).[12,13] The formation of spiro[cyclohexane-1,1′-indan] (**17**) results from intramolecular cyclization of the initially formed tertiary cation **16** (Scheme IV). Successfully competing with this process is a 1,2 hydride shift to give a secondary cation **18** and cyclization to give **19**. Thus although the equilibrium between the tertiary cation **16** and the secondary cation **18** will lie

(11) Sakhabutdinov, A. G.; Usmanova, A. G.; Frolov, P. A.; Kushnarev, D. F.; Schmidt, F. K. *Zh. Org. Khim.* **1988**, *24*, 1610.
(12) The mechanisms and reaction intermediates shown in the schemes account for the observed products, but have not necessarily been unambiguously established.
(13) Inconsistencies in some of the reported values for the ^{13}C NMR spectrum of **19** were clarified by definitive assignments (see Experimental Section) for both ^1H and ^{13}C NMR spectra through a combination of two dimensional techniques. (a) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (b) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245. (c) Zubenko, V. G.; Vorob'eva, N. S.; Zemskova, Z. K.; Pehk, T.; Petrov, A. A. *Neftekhimiya* **1981**, *21*, 323. (d) Bansal, R. C.; Browne, C. E.; Eisenbraun; Thomson, J. S. *J. Org. Chem.* **1988**, *53*, 452.

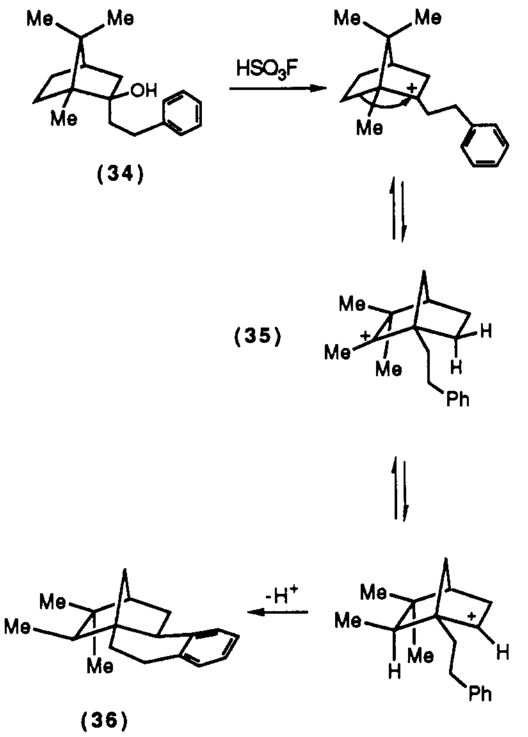
Scheme V



Scheme VI



Scheme VII



strongly in favor of **16**, trapping of the less stable cation **18** is competitive and results in the preferential formation of *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**19**). The stereoselective formation of the cis isomer **19** in preference to the more thermodynamically stable[14] trans stereoisomer reflects a kinetic preference for formation of the cis isomer. It is also noteworthy that the proportion of spiran **17** formed from reaction with HSO_3F is greater than that obtained from weaker acids,[10,13d] and that this phenylethyl carbinol reacts in a different manner to 1-benzylcyclohexanol which dimerizes in HSO_3F.[8]

Reaction of 2-methyl-1-(2-phenylethyl)cyclohexanol (**20**) gave a 3:1 mixture of *cis*- and *trans*-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**24** and **25**) (Scheme IV). The presence of the adjacent methyl in the initially formed tertiary carbocation **21** promotes hydride transfer to the carbocation **23**, and the formation of spirane **22** is no longer competitive with octahydrophenanthrene formation. As with the reaction of 1-(2-phenylethyl)-cyclohexanol (**15**), the cis isomer **24** is the kinetically favored product; however, a significant amount (25%) of the trans isomer **25** is also produced, which reflects the greater lifetime of the tertiary cation **23** relative to **18**, and this allows the conformational change required for formation of the trans stereoisomer.

The reaction of 2,2,6-trimethyl-1-(2-phenylethyl)cyclohexanol (**26**) with fluorosulfuric acid was examined as a potential route to the podocarpatrienes[15] (Scheme V). The carbocation initially produced at −78 °C might rearrange via a hydride shift analogous to that observed for **21**, and subsequent cyclization would then give cis-podocarpatriene (**27**).[16] In the event, however, the reaction afforded 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**28**) (85%) along with the 1α,4aβ,10aβ-trimethyl isomer 29 (15%). The formation of **28** and **29** results from methyl migration occurring in preference to hydride migration prior to cyclization.[17] The exclusive formation of cis-fused products parallels the results for reactions of (phenylethyl)cyclohexanols **15** and **20**.

2-*exo*-(2-Phenylethyl)norbornan-2-*endo*-ol (**30**) reacted with fluorosulfuric acid to give a single product in high yield and which was identified[18] as tetracyclo[10.2.1.0^{1,10}.0^{4,9}]pentadeca-4,6,8-triene (**33**) (Scheme VI). Thus whereas 2-*exo*-benzylnorbornan-2-*endo*-ol (**7**) underwent ring expansion in HSO_3F, the 2-phenylethyl analogue **30** undergoes ionization and Wagner–Meerwein rearrangement to **32** and cyclization from the more accessible and favored exo face to give **33**. Furthermore this bicyclic alcohol reacts in a different manner to the monocyclic 2-phenylethyl carbinols discussed above since neither direct cyclization nor hydride shifts are observed due to the availability of the alternative low-energy Wagner–Meerwein rearrangement pathway.[19]

(14) Supported by MMX calculations.

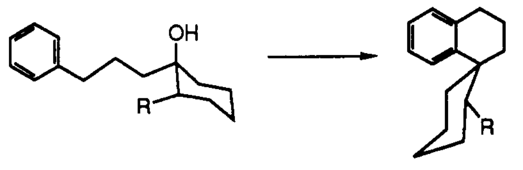
(15) Nasipuri, D.; De Dalal, I. *J. Chem. Soc., Perkin Trans. 1* **1976**, 19.

(16) Podocarpatrienes have recently been prepared from related alcohols, see: Banik, B. K.; Ghosh, S.; Ghatak, U. R. *Tetrahedron* **1988**, *22*, 6947.

(17) Rearrangements of closely related compounds have recently been discussed in detail, see: Davis, B. R.; Johnson, S. J.; Woodgate, P. D. *Aust. J. Chem.* **1987**, *40*, 1283.

(18) The structure of the hydrocarbon skeleton in **33** followed from the signals for an isolated CH_2CH_2 in the ^1H NMR spectrum, the multiplicity of the carbons in a DEPT spectrum and the magnitude of the ^1H–^1H coupling constants. The stereochemistry at C10 was deduced as follows. A ^1H–^{13}C heteronuclear two dimensional correlation spectrum located the positions of the bridgehead proton (H12) and the benzylic proton (H10). Irradiation of the C10 proton showed that it was strongly coupled to one of the C11 protons at 2.1 ppm. Irradiation of the bridgehead proton (H12) showed no apparent coupling to the proton at 2.1 ppm, demonstrating that the proton at 2.1 ppm, and hence the C10 proton, must both be endo. This is further supported by the existence of a small coupling between the C10 proton and the anti proton of the methylene bridge.

Scheme VIII



(37) R = H (38) R = H
(39) R = Me (40) R = Me

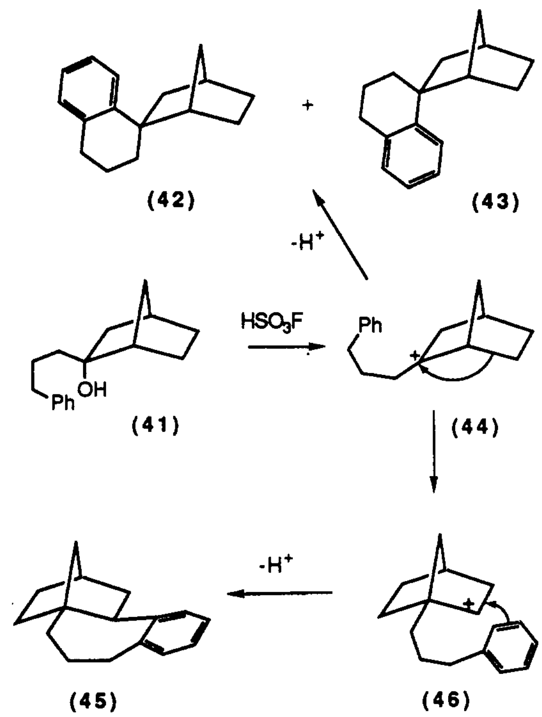
The reaction of 2-(2-phenylethyl)isoborneol (34) with fluorosulfuric acid gave 13,13,14-trimethyltetracyclo-[10.2.1.$0^{1,10}$.$0^{4,9}$]pentadeca-4,6,8-triene (36)[20] in good yield. The mechanism for formation of 36 is shown in Scheme VII and differs from that of the unsubstituted analogue 33 in requiring a 6,2 hydride shift prior to cyclization. The resistance of 35 to cyclization is considered steric in origin and is consistent with the known preference[21] for tertiary norbornyl cations to react with nucleophiles as their Wagner–Meerwein rearranged secondary cations.

3-Phenylpropyl Carbinols. In contrast to the previously reported reactions of benzyl carbinols, all the 2-phenylethyl carbinols described above undergo intramolecular cyclization, frequently with prior rearrangement. It seemed of interest therefore to examine the effect of introducing a further methylene group between the phenyl ring and the initially generated carbocation center which would allow cyclization with formation of a six-membered ring without prior rearrangement.

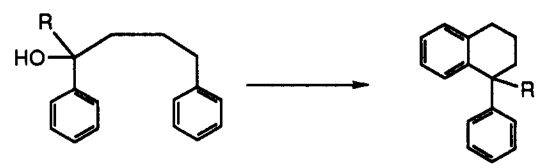
Indeed reaction of 1-(3-phenylpropyl)cyclohexanol (37) with fluorosulfuric acid gave, in 82% yield, spiro[cyclohexane-1,1′-tetralin] (38), formed by intramolecular cyclization without rearrangement (Scheme VIII). Thus whereas the 2-phenylethyl analogue 15 rearranges via a hydride shift to give 19 as the major product, the 3-phenylpropyl carbinol undergoes direct cyclization of the initially formed carbocation with formation of a six-membered spiran ring. Futhermore, introduction of an adjacent methyl group does not now induce a hydride shift as 2-methyl-1-(3-phenylpropyl)cyclohexanol (39) affords *trans*-2-methylspiro[cyclohexane-1,1′-tetralin] (40). It is notable that this latter reaction proceeds to give the thermodynamically more stable stereoisomer.

Reaction of 2-*exo*-(3-phenylpropyl)norbornan-2-*endo*-ol (41) with fluorosulfuric acid at −78 °C gave a mixture of three hydrocarbons in the ratio 2:1:1. These products were tentatively identified from the NMR spectra of the mixture as the two spiro hydrocarbons 42 and 43 and the tetracyclic product 45 (Scheme IX). The spiro products 42 and 43

Scheme IX

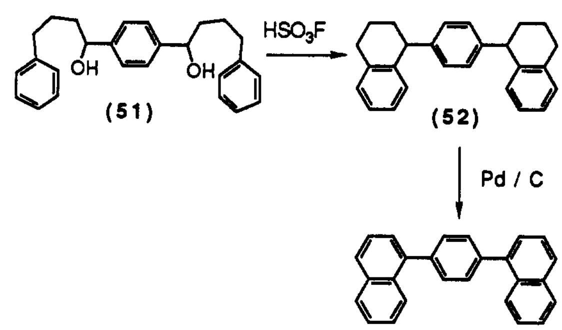


Scheme X

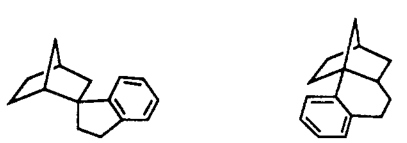


(47) R = H (49) R = H
(48) R = Me (50) R = Me

Scheme XI

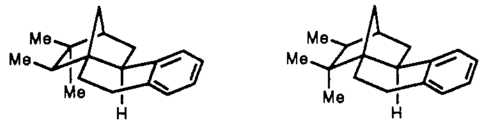


(19) Direct cyclization, as observed in the formation of 17, would produce spiran i, whereas a hydride shift, as occurs in the formation of 24 and which would produce ii, would require the intermediacy of an unstable bridgehead carbocation.



i ii

(20) The structure of 36 was determined by NMR spectroscopy. The aliphatic region of the ^{1}H NMR showed all protons well resolved at 300 MHz, and inspection of the coupling pattern indicated the existence of an intact norbornyl fragment and an isolated CH_2CH_2 with two of the protons benzylic. The three methyl groups are in different environments, one of which is coupled to a single proton. The only bridgehead proton was coupled to one adjacent exo-proton whose geminal partner was strongly coupled to the remaining benzylic proton. These latter two protons were weakly coupled to one proton of the methylene bridge. The other bridge proton showed a 2.0-Hz coupling to the proton coupled to the doublet methyl group, which implies that this methyl group is exo. The two isomers 36 and iii consistent with these data were distinguished by consideration of a ^{1}H–^{13}C two-dimensional heteronuclear correlation spectrum and the known ^{13}C two-dimensional heteronuclear corelation spectrum and the known ^{13}C NMR spectrum substituent effects for 2,2,3-*exo*-trimethyl substitution in a norbornyl ring; see: Brecknell, D. J.; Raymond, M. C.; Greenfield, K. L. *Aust. J. Chem.* **1984**, *37*, 1075. Copies of the ^{1}H–^{1}H homonuclear and ^{1}H–^{13}C heteronuclear two-dimensional spectra for 36 are available as supplementary material.



36 iii

(21) Kleinfelter, D. C.; Schleyer, P. v. R. *J. Org. Chem.* **1961**, *26*, 3740.

would result from direct cyclization of the initially formed cation **44** from the exo and endo faces, respectively, while **45** would result from cyclization of the Wagner–Meerwein rearranged cation **46**.

Cyclization without rearrangement was also observed in the fluorosulfuric acid reactions of 1,4-diphenylbutan-1-ol (**47**) and 2,5-diphenylpentan-2-ol (**48**), which gave 1-phentyltetralin (**49**) and 1-methyl-1-phenyltetralin (**50**), respectively, in high yields (Scheme X). In these cases the initially formed cation is stabilized by conjugation with a phenyl ring.[22] This fact was also exploited in a short new synthesis of 1,4-di(1-naphthyl)benzene (**53**) (Scheme XI). Thus reaction of 1,4-bis(1-hydroxy-4-phenylbutan-1-yl)benzene (**51**) with fluorosulfuric acid gave a 1:1 mixture of the two diastereoisomers of the double cyclization product **52**, which was then dehydrogenated over Pd/C to give **53**.

Conclusion

Reactions of alcohols with fluorosulfuric acid at low temperature continue to provide access to interesting carbocyclic compounds in high yields. Such reactions must be conducted at low temperatures in order to avoid fluorosulfonation of the aromatic products. In our earlier study[8] of the reactions of benzyl carbinols various modes of reaction were observed, including dimerization, reduction, ring expansion, and rearrangement/cyclization. In contrast, all the carbinols examined in the present study undergo cyclization reactions. The 2-phenylethyl carbinols generally undero rearrangement prior to cyclization, whereas the 3-phenylpropyl carbinols undergo direct cyclization without rearrangement.

Experimental Section

General. ^{1}H 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 ^{1}H NMR spectral assignments were made with the aid of homonuclear decoupling experiments, two-dimensional ^{1}H–^{1}H correlated spectra (COSY) and/or difference NOE spectra. Some ^{13}C NMR spectral assignments were made by ^{1}H–^{13}C two-dimensional heteronuclear correlation spectroscopy. In all cases standard Varian software (version 5.2 or 6.1) was used. Mass spectra were recorded on an AEI MS902 or Kratos MS80RFA spectrometer. Melting points were determined using 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 (2-phenylethyl)magnesium bromide or (3-phenylpropyl)magnesium chloride and the appropriate ketone. Purification of the alcohols was carried out by recrystallization or column chromatography, and reaction yields were typically >80%. 2-Methyl-4-phenylbutan-2-ol (**9**),[23] 4-methyl-1-phenylpentan-3-ol (**13**),[24] 1-(2-phenylethyl)cyclohexanol (**15**),[25] 2-methyl-1-(2-phenylethyl)cyclohexanol (**20**),[13c] 2,2,6-trimethyl-1-(2-phenylethyl)cyclohexanol (**26**),[26] 2-*exo*-(2-phenylethyl)norbornan-2-*endo*-ol (**30**),[27] 1-(3-phenylpropyl)cyclohexanol (**37**),[28] 2-*exo*-(3-phenylpropyl)norbornan-2-*endo*-ol (**41**),[29] 1,4-diphenylbutan-1-ol (**47**),[30] and 2,5-diphenylpentan-2-ol (**48**),[31] were prepared by literature methods.

2-(2-Phenylethyl)isoborneol (34) was prepared by a two-step sequence previously used for the preparation of other hindered 2-phenylethyl carbinols.[32] Addition of lithium phenylacetylide to camphor in HMPT under nitrogen, followed by chromatography on alumina, gave 2-(phenylethynyl)isoborneol as a white crystalline solid in 60% yield: mp 57–58 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.44–7.41 (m, 2 H, ortho), 7.32–7.28 (m, 3 H, para and meta), 2.33–2.27 (m, 1 H, H3-exo), 2.05–1.94 (m, 1 H, H6-exo), 1.97 (d, J = 13.4 Hz, 1 H, H3-endo), 1.82–1.75 (m, 1 H, H4), 1.75–1.67 (m, 1 H, H5-exo), 1.56–1.47 (m, 1 H, H6-endo), 1.25–1.13 (m, 1 H, H5-endo), 1.10 (s, 3 H, C7-CH_3-syn), 1.01 (s, 3 H, C1-CH_3), 0.90 (s, 3 H, C7-CH_3-anti); ^{13}C NMR ($CDCl_3$) δ_C 10.5 (C1-CH_3), 21.1 (C7-CH_3-syn), 21.5 (C7-CH_3-anti), 27.0 (C5), 32.7 (C6), 45.5 (C4), 48.0 (C7), 48.3 (C3), 53.9 (C1), 78.4 (C2), 83.5 (C1′), 93.4 (C2′), 123.1 (ipso), 128.0 (para), 128.2 (meta), 131.5 (ortho); calcd for $C_{18}H_{22}O$ (M^+) 254.1672, found (M^+) 254.1681. The alkynol in ethyl acetate was hydrogenated over 5% palladium on carbon in a Parr apparatus, and the product was purified by radical chromatography to give the alcohol **34** as a white crystalline solid in 60% yield: mp 40–42 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.32–7.18 (m, 5 H, ArH), 2.88–2.77 (m, 1 H, H2′), 2.73–2.63 (m, 1 H, H2′), 2.03–1.80 (m, 1 H), 1.92–1.83 (m, 1 H), 1.79–1.65 (m, 3 H), 1.68 (br s, 1 H, OH), 1.49–1.40 (m, 3 H), 1.26 (s, 1 H), 1.13 (s, 3 H, C1-CH_3), 0.89 (s, 3 H, C7-CH_3-anti), 0.87 (s, 3 H, C7-CH_3-syn); ^{13}C NMR ($CDCl_3$) δ_C 10.7 (C1-CH_3), 21.2 (C7-CH_3-syn), 21.6 (C7-CH_3-anti), 27.1 (C5), 30.5 (C6), 31.1 (C2″), 42.0 (C3), 45.1 (C4), 45.8 (C2′), 49.5 (C7), 52.5 (C1), 81.2 (C2), 125.6 (para) 128.3 (4 C, ortho and meta), 143.0 (ipso). Anal. Calcd for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.26; H, 10.08.

2-Methyl-1-(3-phenylpropyl)cyclohexanol (39) was prepared from 2-mehylcyclohexanone and (3-phenylpropyl)magnesium chloride and purified by column chromatography on alumina, which gave the alcohol as a clear oil (75% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.32–7.15 (m, 5 H, ArH), 2.64–2.57 (m, 2 H, $ArCH_2$), 1.66–1.12 (m, 14 H), 0.83 (d, J = 6.3 Hz, 3 H, C2-CH_3); ^{13}C NMR ($CDCl_3$) δ_C 14.8 (C2-CH_3), 21.8 (C4), 25.6 (C5), 25.8 (C1″), 30.5 (C3), 36.0 (C6), 36.5 (C1‴), 37.9 (C2), 40.6 (C1′), 73.0 (C1), 125.7 (para), 128.3 (ortho), 128.4 (meta), 142.5 (ipso). Anal. Calcd for $C_{16}H_{24}O$: C, 82.72; H, 10.41; ($M^+ - H_2O$) 214.1731. Found: C, 82.88; H, 10.27; ($M^+ - H_2O$) 214.1732.

1,4-Bis(1-hydroxy-4-phenylbutan-1-yl)benzene (37) was prepared from terephthalaldehyde and (3-phenylpropyl)magnesium chloride using dry tetrahydrofuran as the reaction solvent. The alcohol was purified by column chromatography on alumina to give the alcohol as a white crytalline solid in 85% yield: mp 77–78 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.37–7.13 (m, 14 H, ArH), 4.68 (m, 2 H, H1′), 2.63 (t, $J_{3',4'}$ = 7.3 Hz, 4 H, H4′), 1.90–1.60 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ_C 27.5 (C3′), 35.7 (C4′), 38.6 (C2′), 74.3 (C1′), 125.7 (C4′-para), 126.0 (4 C, C2,3,5,6), 128.3 (C4′-ortho), 128.4 (C4′-meta), 142.2 (C4′-ipso), 144.0 (C1,4). Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.09; H, 8.11.

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) 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.

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1,1-Dimethylindan (10). Reaction of 2-methyl-4-phenylbutan-2-ol (9) with HSO_3F as above gave 10[23] in 41% yield: ^1H 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); ^{13}C NMR ($CDCl_3$) δ_C 28.7 (2 C, CH_3), 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).

Fluorosulfonated 1,1-Dimethyltetralins (14). Reaction of 4-methyl-1-phenylpentan-3-ol (13) with HSO_3F at 0 °C gave a mixture of isomers of 1,1-dimethyltetralinsulfonyl fluoride, which were not separated but identified by NMR comparison with related fluorosulfonyl indans[8] as 1,1-dimethyltetralin-6-sulfonyl fluoride (60%) [^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.94 (d, H5), (dd, H7), 7.27 (d, H8), 2.86 (m, 2 H, H4), 1.85 (m, 2 H, H3), 1.70 (m, 2 H, H2), 1.32 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ_C 18.9 (C3), 30.9 (C4), 31.5 (2 C, CH_3), 34.3 (C1), 38.3 (C2), 124.8 (C6), 126.9 (C8), 130.5 (C5)], 1,1-dimethyltetralin-5-sulfonyl fluoride (25%) [^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.89 (d, H6), 7.73 (d, H7), 7.34 (t, H8), 3.14 (t, 2 H, H4), 1.85 (m, 2 H, H3), 1.70 (m, 2 H, H2), 1.32 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ_C 18.7 (C3), 30.6 (C4), 31.9 (2 C, CH_3), 34.6 (C1), 37.9 (C2), 126.1 (C6), 128.1 (C7), 134.4 (C8)], and 1,1-dimethyltetralin-7-sulfonyl fluoride (15%) [^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.70 (d, H6), 7.68 (s, H8), 7.55 (d, H5), 2.86 (m, 2 H, H4), 1.85 (m, 2 H, H3), 1.70 (m, 2 H, H2), 1.32 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ_C 19.1 (C3), 27.4 (C4), 31.4 (2 C, CH_3), 34.6 (C1), 37.9 (C2), 125.4 (C8), 127.9 (C7), 129.1 (C5)].

Spiro[cyclohexane-1,1′-indan] (17) and *cis*-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (19). Reaction of 1-(2-phenylethyl)cyclohexanol (15) with HSO_3F as above gave, in 40% yield, a 3:1 mixture of 19[13d] [^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.08 (m, ArH), 2.85 (m, H9), 2.73 (m, H4a), 2.03 (m, H10), 1.78–1.25 (m, CH_2's and CH); ^{13}C NMR ($CDCl_3$) δ_C 21.5 (C2), 23.8 (C10), 26.3 (C3), 29.6 (C9), 31.4 (C4), 31.8 (C1), 33.8 (C10a), 40.2 (C4a), 125.2 (2 C, C6 and C7), 128.5 and 128.7 (C5 and C8), 136.0 (C8a), 142.1 (C4b)] and 17[28] [^{13}C NMR ($CDCl_3$) δ_C 23.5 (2C, C3 and C5), 26.1 (C4, 30.0 (C3′), 35.2 (C2′), 37.2 (2 C, C2 and C6), 122.2 (C7′), 124.3 (C4′), 126.0, 126.1 (C5′ and C6′).

***cis*- and *trans*-4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (24 and 25).** Reaction of 2-methyl-1-(2-phenylethyl)cyclohexanol (20) with HSO_3F as above gave, in 80% yield, a 3:1 mixture of 24[13c,33] [^1H NMR ($CDCl_3$, 60 MHz) δ_H 1.23 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 22.9 (C2), 24.4 (C3), 25.1 (C10), 27.1 (C1), 28.1 (C9), 31.8 (C4a-CH_3), 37.5 (C4a), 38.2 (C10a), 41.3 (C4), 125.1 (C5), 125.8 (2 C, C6 and C7), 129.3 (C8), 135.8 (C8a), 144.3 (C4b)] and 25[33] [^1H NMR ($CDCl_3$, 60 MHz) δ_H 1.07 (s, CH_3)].

1β,4aβ,10aβ- and 1α,4aβ,10aβ-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrenes (28 and 29). Reaction of 2,2,6-trimethyl-1-(2-phenylethyl)cyclohexanol (26) with HSO_3F as above give, in 90% yield, a 5:1 mixture of 28,[17] [^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.33 (d, J = 7.7 Hz, 1 H), 7.14–7.04 (m, 3 H, ArH), 2.93–2.63 (m, 2 H, H9), 1.86–1.15 (m, 9 H), 1.09 (s, 3 H, C4a–CH_3), 0.93 (s, 3 H, C10a–CH_3), 0.82 (d, J = 6.8 Hz, 3 H, C1-CH_3); ^{13}C NMR ($CDCl_3$) δ_C 16.2 (C1-CH_3), 16.4 (C10a-CH_3), 22.8 (C3), 25.8 (C9), 28.4 (C10), 30.0 (C4a-CH_3), 30.9 (C2), 32.1 (C4), 33.2 (C1), 41.3 (C4a), 124.7, 125.8, 126.1 (C5, C6, C7), 129.7 (C8), 136.3 (C8a), 144.3 (C4b)] and 29[17] [^{13}C NMR ($CDCl_3$) δ_C 16.4 (C1-CH_3), 20.4 (C4a–CH_3), 21.4 (C10a–CH_3)].

Tetracyclo[10.2.1.0^{1,10}.0^{4,9}]pentadeca-4,6,8-triene (33). Reaction of 2-*exo*-(2-phenylethyl)norbornan-2-*endo*-ol (30) with HSO_3F as above gave 33 in 82% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.16–7.10 (m, 1 H, H8), 7.05–7.03 (m, 3 H, H6, H7, and H8), 2.87–2.71 (m, 2 H, H3), 2.66–2.60 (m, 1 H, H10), 2.25–2.22 (m, 1 H, H12), 2.15–2.07 (m, 1 H, H11-endo), 1.86–1.81 (m, 2 H, H2), 1.74–1.64 (m, 1 H, H13-exo), 1.60–1.27 (m, 5 H, H15-syn, H13-endo, H14 and H11-exo), 1.02–0.98 (m, 1 H, H15-anti); ^{13}C NMR ($CDCl_3$) δ_C 28.1 (C2), 28.3 (C3), 29.9 (C13), 37.0 (C12), 37.3 (C14), 38.8 (C15), 41.6 (C11), 44.6 (C10), 46.5 (C1), 124.7 (C5), 126.1 (C8), 128.4 (C6), 128.5 (C7), 135.4 (C4), 143.4 (C9); calcd for $C_{15}H_{18}$ (M^+) 198.1397, found (M^+) 198.1396.

13,13,14-Trimethyltetracyclo[10.2.1.0^{1,10}.0^{4,9}]pentadeca-4,6,8-triene (36). Reaction of 2-(2-phenylethyl)isoborneol (34) with HSO_3F as above gave 36 in 76% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.15–7.03 (m, 1 H), 6.98–6.95 (m, 3 H), 2.67–2.63 (m, 2 H, H3), 2.50–2.42 (m, 2 H, H10 and H11-endo), 1.78–1.72 (m, 1 H, H2), 1.62 (br s, 1 H, H12), 1.51–1.43 (m, 1 H, H2), 1.40–1.35 (m, 1 H, H15-anti), 1.29–1.23 (m, 1 H, H11-exo), 1.18–1.11 (m, 1 H, H15-syn), 1.09–1.06 (m, 1 H, H14), 0.99 (s, 3 H, C13-CH_3-exo), 0.82 (s, 3 H, C13-CH_3-endo), 0.75 (d, J = 7.3 Hz, 3 H, C14-CH3); ^{13}C NMR ($CDCl_3$) δ_C 12.5 (C14-CH_3), 24.8 (C13-CH_3-endo), 25.2 (C2), 27.7 (C3), 27.9 (C13-CH_3-exo), 35.2 (C15), 36.6 (C11), 40.5 (C13), 46.1 (C10), 48.5 (C12), 50.5 (C1), 52.1 (C14), 124.6 (C5), 126.2 (C8), 128.2 (C6), 128.5 (C7), 135.1 (C4), 143.5 (C9); calcd for $C_{18}H_{24}$ (M^+) 240.1879, found (M^+) 240.1874.

Spiro[cyclohexane-1,1′-tetralin] (38). Reaction of 1-(3-phenylpropyl)cyclohexanol (37) with HSO_3F as above gave 38[28] in 82% yield: ^1H NMR ($CDCl_3$, 30 MHz) δ_H 7.41 (d, J = 7.6 Hz, 1 H, H8′), 7.18–7.13 (m, 1 H), 7.09–7.03 (m, 2 H), 2.75 (t, J = 6.2 Hz, 2 H, H4′), 1.84–1.23 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ_C 19.2 (C4), 22.0 (2 C, C3 and C5), 26.2 (C3′), 31.0 (C4′), 37.0 (C1), 38.7 (2 C, C2 and C6), 125.1 (C6′), 125.7 (C7′), 126.7 (C8′), 129.0 (C5′), 137.1 (C4a′), 146.6 (C8a′); calcd for $C_{15}H_{20}$: C, 89.92; H, 10.07; Found: C, 89.81; H, 10.27.

***trans*-2-Methylspiro[cyclohexane-1,1′-tetralin] (40).** Reaction of 2-methyl-1-(3-phenylpropyl)cyclohexanol (39) with HSO_3F as above gave 40: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.37 (d, J = 8 Hz, 1 H, H8′), 7.25–7.12 (m, 1 H), 7.08–7.03 (m, 2 H), 2.72–2.68 (m, 2 H, H4′), 2.15–2.05 (m, 1 H), 1.94–1.25 (m, 12 H), 0.58 (d, J = 6.9 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ_C 17.0 (C2-CH_3), 19.6 (C4), 22.0 (C5), 24.4 (C2′), 26.8 (C3′), 30.1 (C3), 31.1 (C4′), 40.3 (C6), 40.6 (C1), 40.7 (C2), 124.8 (C6′), 125.8 (C7′), 126.1 (C8′), 128.8 (C5′), 138.1 (C4a′), 145.4 (C8a′). Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35; (M^+) 214.1721. Found: C, 89.47; H, 10.22; (M^+) 214.1722.

Hydrocarbons from 41. Reaction of 2-*exo*-(3-phenylpropyl)norbornan-2-*endo*-ol (41) with HSO_3F at −78 °C gave a mixture of three hydrocarbons in the ratio 2:1:1 and tentatively assigned the structures[29] **42**, **43**, and **45**. The major isomer is characterized by the following: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.22 (m, 4 H), 2.93 (m, 2 H), 2.64 (m, 1 H), 2.21 (m, 2 H), 1.99–0.85 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ_C 21.3, 29.1, 29.8, 31.2, 33.5, 34.8, 35.6, 42.9, 45.8, 125.5, 125.6, 128.0, 128.4, 139.7, 141.1. The minor isomers are characterized by the following: ^{13}C NMR ($CDCl_3$) δ_C 19.6, 24.4, 24.8, 28.5, 29.1, 29.2, 33.7, 35.9, 36.0, 36.8, 37.1, 37.2, 38.9, 44.8, 44.9, 46.2, 49.1, 123.5, 124.6, 125.1, 125.2, 127.8, 127.9, 128.2, 128.9, 136.7, 137.7, 142.4, 142.6.

1-Phenyl-1,2,3,4-tetrahydronaphthalene (49). Reaction of 1,4-diphenylbutan-1-ol (47) with HSO_3F as above gave 49[34] in 89% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.30–7.00 (m, 8 H, ArH), 6.84 (d, $J_{7,8}$ = 8 Hz, 1 H, H8), 4.12 (t, $J_{1,2}$ = 6.4 Hz, 1 H, H1), 2.92–2.81 (m, 2 H, H4), 2.21–2.12 (m, 1 H, H2), 1.93–1.70 (m, 3 H, H3 and H2); ^{13}C NMR ($CDCl_3$) δ_C 21.0 (C3), 29.8 (C2), 33.3 (C4), 45.6 (C1), 125.6 (C6), 125.9 (2C, C7 and para), 128.2 (ortho), 128.8 (meta), 128.9 (C8), 130.2 (C5), 137.6 (C4a), 139.4 (ipso), 147.4 (C8a).

1-Methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (50). Reaction of 2,5-diphenylpentan-2-ol (48) with HSO_3F as above gave 50[31] in 70% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.26–7.07 (m, 8 H, ArH), 7.00 (d, $J_{7,8}$ = 7 Hz, 1 H, H8), 2.84 (t, $J_{3,4}$ = 6.5 Hz, 2 H, H4), 2.12–2.02 (m, 1 H, H2), 1.92–1.65 (m, 3 H, H3 and H2), 1.72 (s, 3 H, C1-CH_3); ^{13}C NMR ($CDCl_3$) δ_C 19.5 (C3), 30.0 (C1-CH_3), 30.3 (C4), 41.5 (C2), 42.9 (C1), 125.4 (para), 125.7 (C6), 125.8 (C7), 127.4 (ortho), 127.8 (meta), 129.0 (C8), 129.2 (C5), 137.0 (C5a), 144.4 (ipso), 151.6 (C8a).

1,4-Di(1-naphthyl)benzene (53). Reaction of 1,4-bis(1-hydroxy-4-phenylbutan-1-yl)benzene (51) with HSO_3F as above gave a mixture of the two diastereoisomers of 1,4-bis(1,2,3,4-tetrahydronaphth-1-yl)benzene (52) in 83% yield: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.15–6.85 (m, 12 H, ArH), 4.08 (br t, $J_{1',2'}$ = 6 Hz, 2 H, H1′), 2.94–2.76 (m, 4 H, H4′), 2.21–1.68 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ_C 20.94/20.90 (C3′), 29.76 (2 C, C2′), 33.14/33.17 (C4′), 45.15/45.18 (C1′), 125.5 (2 C, C6′), 125.8 (2 C, C7′), 128.6 (4 C, C2,3,5,6), 128.9 (2 C, C8′), 130.2 (2 C, C5′), 137.6 (2 C, C4a′), 139.52/139.57 (C1,4), 144.88/144.91 (C8a′). A sample of 52 was heated over 10% palladium on carbon at 250 °C for 2 h. Extraction with ether gave 53[35] in 36% yield: ^1H NMR

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($CDCl_3$, 300 MHz) δ_H 8.09 (d, J = 7 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 2 H), 7.90 (d, J = 8.5 Hz, 2 H), 7.63 (s, 4 H), 7.63–7.47 (m, 8 H); ^{13}C NMR ($CDCl_3$ δ_C 125.4, 125.8, 126.08, 126.11, 127.1, 127.7, 128.3, 130.0, 131.7, 133.9, 139.7, 140.0.

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Registry No. **9**, 103-05-9; **10**, 4912-92-9; **13**, 68426-07-3; **14** 5-sulfonyl fluoride, 124620-37-7; **14** 6-sulfonyl fluoride, 124620-32-2; **14** 7-sulfonyl fluoride, 124620-38-8; **15**, 124620-30-0; **17**, 380-18-7; **19**, 20480-66-4; **20**, 79235-09-9; **24**, 79297-74-8; **25**, 70561-39-6; **26**, 101740-77-6; **28**, 124620-39-9; **29**, 124620-40-2; **30**, 67476-28-2; **33**, 124620-33-3; **34**, 124620-28-6; **36**, 124620-34-4; **37**, 101100-11-2; **38**, 109445-09-2; **39**, 124620-29-7; **40**, 124620-35-5; **41**, 38229-94-6; **42**, 124751-28-6; **43**, 124751-29-7; **45**, 124620-36-6; **47**, 30078-89-8; **48**, 58978-27-1; **49**, 3018-20-0; **50**, 52376-43-9; **51**, 124620-31-1; **52** (isomer 1), 124620-41-3; **52** (isomer 2), 124620-42-4; **53**, 64065-97-0; lithium phenylacetylide, 4440-01-1; camphor, 76-22-2; 2-(phenylethynyl)isoborneol, 124620-27-5; 2-methylcyclohexanone, 583-59-5; (3-phenylpropyl)magnesium chloride, 54812-94-1; terephthalaldehyde, 623-27-8; fluorosulfuric acid, 7789-21-1.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compound **36** (2 pages). Ordering information is given on any current masthead page.

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trans-Bis(5-acetoxy-1,2,3-η^3-cyclohexenyl)palladium Complexes by Palladium(II)-Promoted Addition of Acetate to 1,4-Cyclohexadienes[1]

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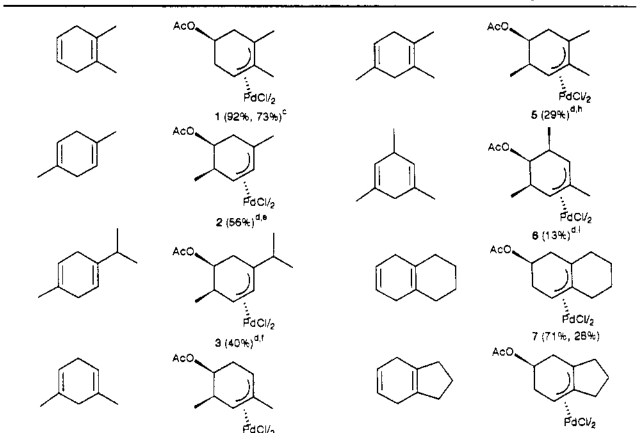
Acetate adds to alkyl-substituted 1,4-cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride to yield the corresponding *trans*-bis(5-acetoxy-1,2,3-η^3-cyclohexenyl)palladium complexes. This highly stereoselective and regioselective palladium(II)-promoted distal addition is achieved in either acetic acid or acetonitrile solvents.

(η^3-Allyl)palladium complexes have become useful synthons in organic synthesis.[2,3] Standard preparation procedures include insertion of palladium(0) into the carbon–heteroatom bond of allylic systems,[4] direct substitution of the allylic hydrogen of alkenes by palladium(II),[5] and palladium(II)-promoted addition of nucleophiles and palladium across 1,3-dienes.[6] Both Larock's group with acyclic nonconjugated dienes[7] and this group with 1,4-cyclohexadienes[1,8] demonstrated that nonconjugated dienes afford (η^3-allyl)palladium complexes via the initial addition

Table I. Palladium(II)-Promoted Addition of Acetate[a]

1,4-cyclohexadiene	product (% yield)[b]	1,4-cyclohexadiene	product (% yield)[b]



[a] Details in the Experimental Section. [b] The first isolated yield is in acetic acid; a second is in acetonitrile. [c] See ref 9. [d] Hydride–addition complex formation was avoided by slowly adding (2 h, syringe pump) the diene to the mixture. [e] Similar results (53–54%) were obtained by adding (15 min, syringe or addition funnel) the diene to a mixture containing $CuCl_2$. [f] *p*-Cymene was also formed (7%). [g] *m*-Xylene was also formed (23%). [h] 1,2,4-Trimethylbenzene was also formed (53%). [i] 1,3,5-Trimethylbenzene was also formed (33%).

(1) (a) 1,4-Diene-Derived (η^3-Allyl)palladium Complexes. 5. Part 4: Åkermark, B.; Söderberg, B. C.; Hall, S. S. *J. Org. Chem.* **1989**, *54*, 1110–1116. (b) Taken in part from the Ph.D. (Teknisk Doktor) Dissertation of B.C.S., The Royal Institute of Technology, Dec 1987. (c) Initially disclosed at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988, paper ORGN 197.

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