ACID INDUCED CATIONIC REARRANGEMENTS OF CARBOCYCLIC COMPOUNDS.

A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Canterbury by

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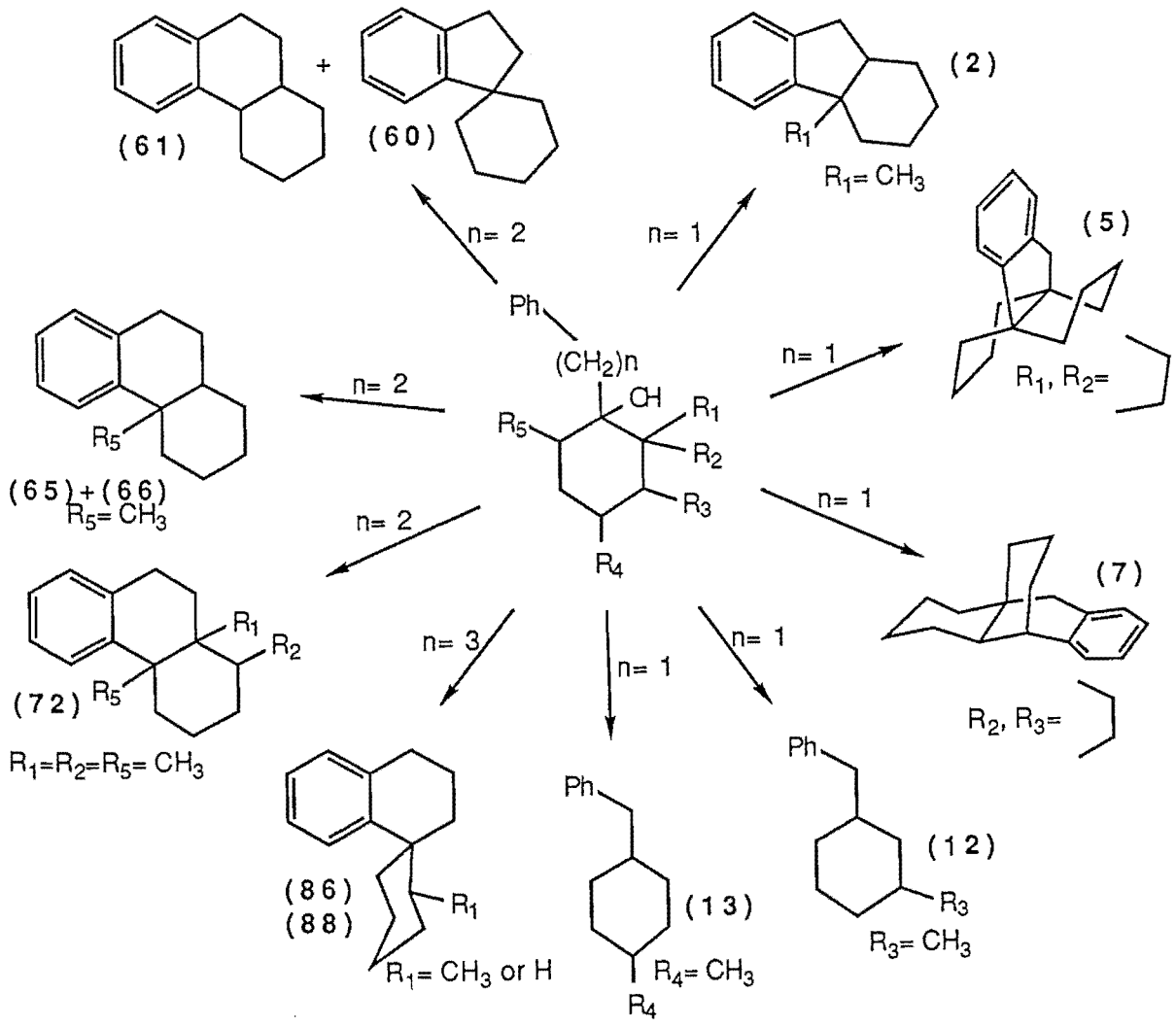
Abstract

This thesis examines fluorosulfonic acid as a reagent for use in organic synthesis. The acid strength of fluorosulfonic acid gives access to rearrangement products not available with weaker acids.

The reaction of a selected series of benzyl carbinols with HSO_3F are reported. Reaction of 1-benzyl-2-methylcyclohexanol **(1)** gave *cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrofluorene **(2)**, while 1-benzyl -3-methylcyclohexanol **(10)** and 1-benzyl-4-methylcyclohexanol **(11)** were reduced to *cis*-1-benzyl-3-methylcyclohexane **(12)** and *trans*-1-benzyl-4-methylcyclohexane **(13)** respectively.

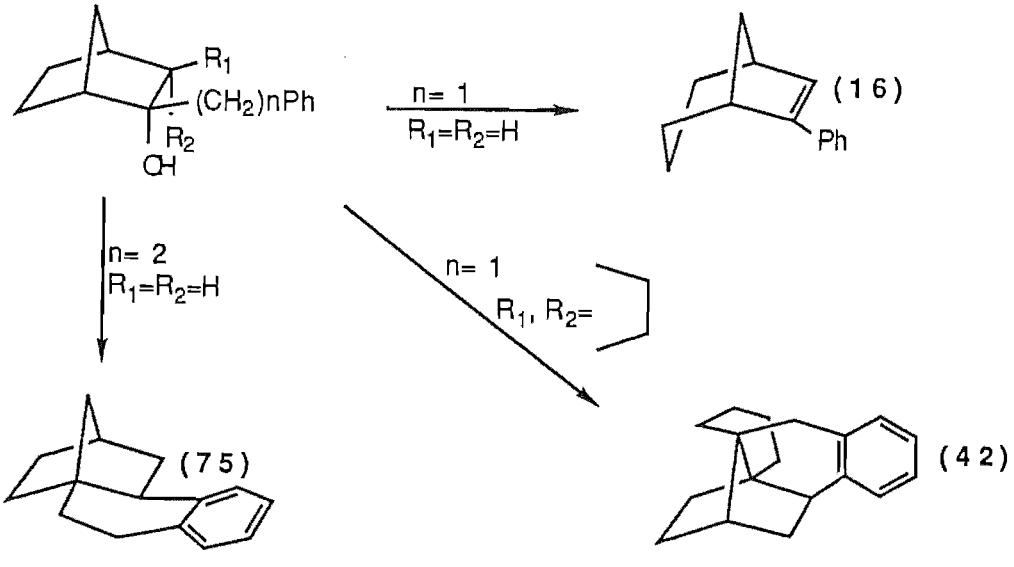


R= H unless otherwise indicated

6-Benzylspiro[4.5]decan-6-ol **(4)** underwent a ring expansion to give the propellane, tetracyclo[7.4.4.$0^{1,9}$.$0^{2,7}$]heptadeca-2,4,6-triene **(5)**. Reaction of 1-benzyl-*trans*-decalin-1-ol **(6)** with HSO_3F gave the natural product (±)-9a-carba-14α-morphinan **(7)**, while spiro[3-*exo*-benzylbicyclo[2,2,1]heptan-3-*endo*-ol-2,1'-cyclopentane] **(41)** gave pentacyclo[9.7.0.$0^{1,14}$.$0^{3,8}$.$0^{9,14}$]octadeca-3,5,7-triene **(42)**.

The mechanism of rearrangement of 2-*exo*-benzylbicyclo[2.2.1] heptan-2-*endo*-ol **(14)** to 6-phenylbicyclo[3.2.1]oct-6-ene **(16)** was elucidated by the use of deuterium labeled substrates.

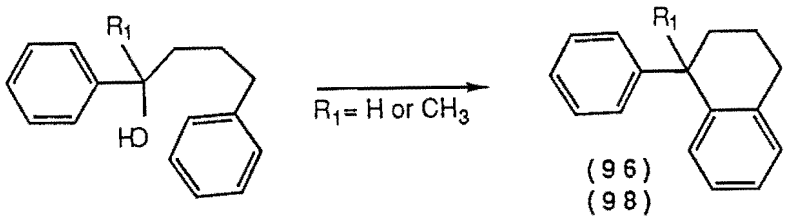
Reaction of phenylethyl carbinols with HSO_3F afforded a route to bicyclic systems, for example 1-(2-phenylethyl)cyclohexanol **(59)** gave *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(61)** and spiro[cyclohexane-1,1-indane] **(60)**, while 2-methyl-1-(2-phenylethyl)cyclohexanol **(64)** gave a mixture of *cis*- **(65)** and *trans*-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(66)**.

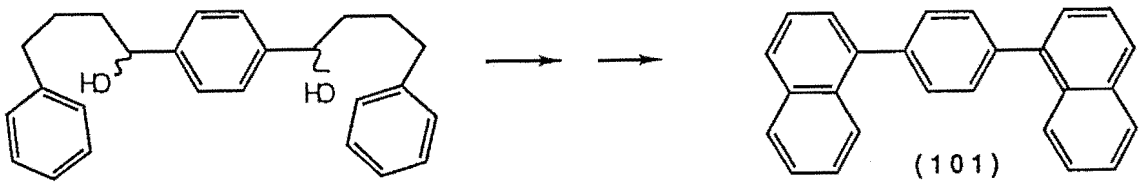


Reaction of 1-(2-phenylethyl)-2,2,6-trimethylcyclohexanol **(70)** gave predominantly 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-

octahydrophenanthrene **(72)** with a small amount of the 1α,4aβ, 10aβ-trimethyl-isomer **(73)** while reaction of 2-*exo*-(2-phenylethyl)bicyclo[2,2,1]heptan-2-*endo*-ol **(74)** gave tetracyclo[10.2.1.$0^{1,10}$.$0^{4,9}$]pentadeca-4,6,8-triene **(75)**.

Phenylpropyl carbinols provide an entry to spiro products. Reaction of 1-(3-phenylpropyl)cyclohexanol **(85)** gave spiro[cyclohexane-1,1-tetralin] **(86)**, while 2-methyl-1-(3-phenylpropyl)cyclohexanol **(87)** gave *trans*-2'-methyl-spiro[cyclohexane-1,1-tetralin] **(88)**.





1,4-Diphenylbutan-1-ol **(95)** afforded 1-phenyl-1,2,3,4-tetrahydronapthalene **(96)** and 2,5-diphenylpentan-2-ol **(97)** gave an analogous product **(98)**. 1,4-Di-(1-hydroxy-4-phenylbutan-1-yl)benzene **(99)** gave the two diastereoisomers of 1,4-di-(1,2,3,4-tetrahydronapth-1-yl)benzene **(100)**, which on oxidation gave 1,4-di-(1-naphthyl)benzene **(101)**.

Fluorosulfonic acid has been shown to be a synthetic reagent for the generation of several novel spiro, reduction, cyclisation and rearrangement products not accessible under weaker acid conditions.

CHAPTER 1

INTRODUCTION:

CARBOCATIONS AND FLUOROSULFONIC ACID.

Chapter 1: Introduction

Carbocations represent the most common and important class of reactive intermediates in organic reactions.[1] They are involved in numerous substitution, elimination, addition, and rearrangement reactions of synthetic, industrial and biological importance.

The suggestion that many acid-catalysed molecular rearrangements take place via carbocation intermediates, first proposed by Meerwein and Van Emster[2] in 1922, is now accepted as a basic tenet of chemical knowledge. Such rearrangements generally occur for thermodynamic reasons, wherein an initially generated less stable carbocation rearranges to a thermodynamically more stable carbocation by one of a variety of mechanisms. The ultimate fate of a carbocation depends on the specific reaction conditions, proton loss or reaction with a nucleophile being the most common.

Carbocations are involved in many synthetically important C-C bond formations. These Friedel-Crafts alkylations and acylations[3] involve the reaction of catalyst generated electron deficient carbon species with an electron rich source, generally in the form of a benzene ring. These reactions allow either intermolecular coupling of two carbon skeletons, useful in the construction of larger molecules, or intramolecular cyclisation to form fused-ring molecules. Carbocation rearrangements are often involved in the course of many Friedel-Crafts reactions.[3]

There is a large variety of catalysts used for the generation of carbocations in acid-catalysed rearrangement reactions and

Friedel-Crafts reactions. These range from weak Lewis acids, such as BF_3, through stronger protic acids such as polyphosphoric acid or H_2SO_4, to the more recently developed superacids, such as HSO_3F. These reagents act on a variety of substrates, most importantly alkyl halides, alcohols and alkenes. The various acids have differing advantages and limitations in their use.

Boron trifluoride is a weak Lewis acid and is used with reactive substrates to give greater control over the reaction than would be possible with a more aggressive reagent such as polyphosphoric acid. Polyphosphoric acid, a mixture of the polymers of H_3PO_4 produced from the action of P_2O_5 on H_3PO_4, is a reasonably good solvent for organic molecules and has strong dehydrating powers. However the reagent does not become mobile unless heated to above 60°C; below this temperature a gum or rigid glass may be formed. Furthermore the variation in the equilibrium distribution of the components of polyphosphoric acid makes reproducibility of reaction conditions difficult. In Friedel-Crafts reactions polyphosphoric acid has been widely used as a catalyst for the alkylation of aromatic substrates by alcohols.[4] One of the strongest of the Brønsted mineral acids used in Friedel-Crafts reactions is H_2SO_4. This widely used reagent has well understood properties. Its relatively high freezing point and viscosity place restrictions on the conditions available with this reagent. High concentrations of H_2SO_4 acid often result in polymerisation of organic substrates.

Since the early 1960's a number of acid media have been developed with higher acid strengths than H_2SO_4. These systems are called superacids. The widely accepted definition of a superacid is any

acid system with a strength greater than that of 100% H_2SO_4.[5] Such high-acidity non aqueous systems have given chemists access to carbocation rearrangements not available under 'normal' acid conditions.

Since pH as a measure of the acidity of a medium is only applicable to dilute aqueous systems a new scale for the determination of acidity for non-aqueous or concentrated systems is required. The real physical quantity describing the acidity of a medium is the activity of the proton.[5] Hammett and Deyrup in 1932[6] were the first to suggest a method to measure the protonation of a series of weak bases in an acid solution. This lead to the development of the acidity function which can be written as:

$$H_0 = pK_{BH^+} - \log[BH^+]/[B].$$

It is assumed that the nature of the indicator (B) does not effect the slope of H_0 plotted against $\log[BH^+]/[B]$. This assumption has been shown to be valid for only certain indicators, now known as the Hammett bases.

The H_0 values of 100% H_2SO_4 and HSO_3F are -12 and -15 respectively.[1,7] The chemical effect of this difference in H_0 values is that a substrate in a solution of HSO_3F is far more ionised than when in H_2SO_4. In media of low acidity very little of a reactant exists as a carbocation at any given time. Thus in the reaction of alcohols under 'normal' acid conditions the predominant species is either the protonated alcohol or an olefin. In contrast, however, spectroscopic studies of alcohols in superacid solutions show that under these conditions the predominant species are carbocations. Thus superacids allow the study of high concentrations of

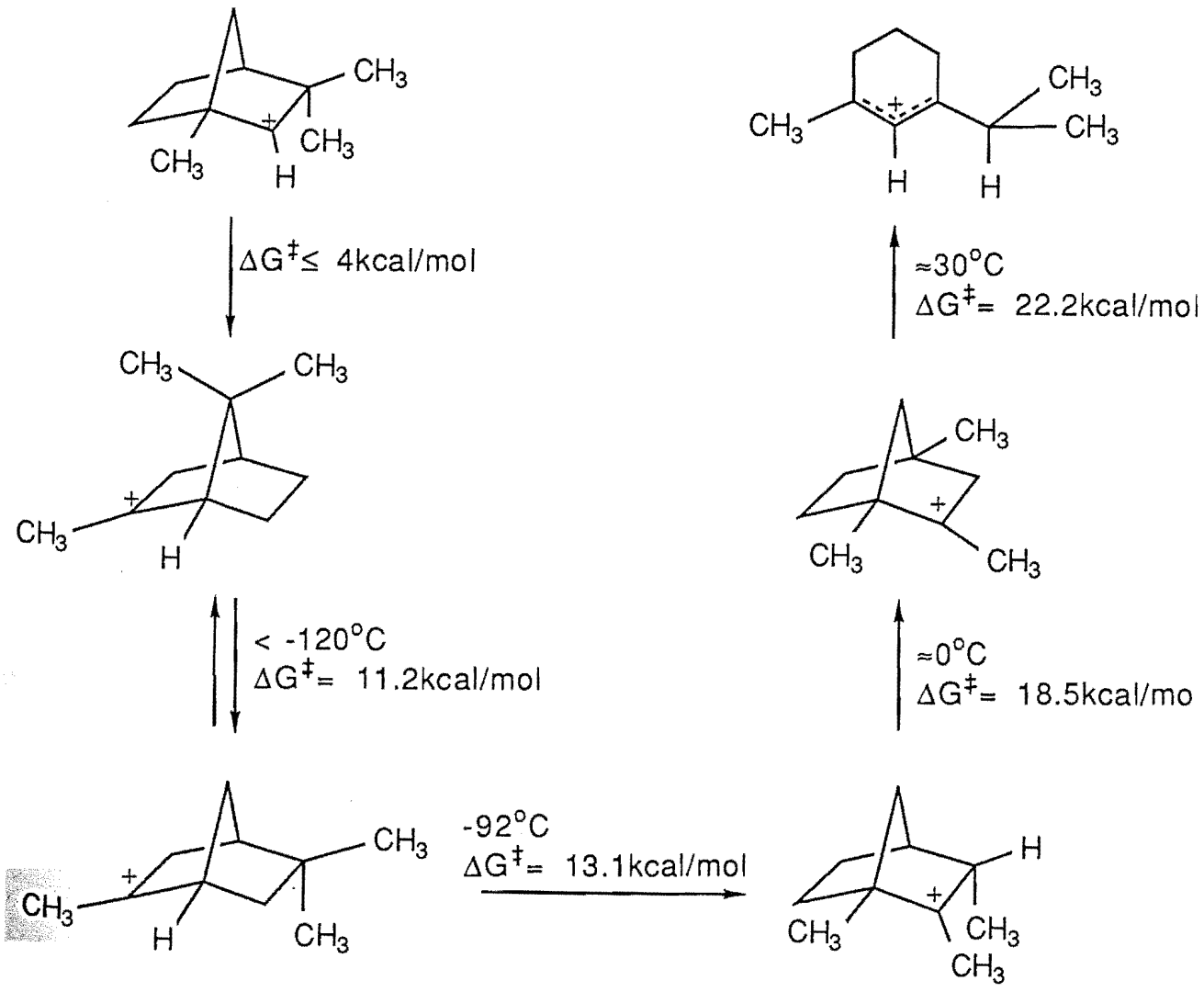
carbocations in a stable ion environment. Direct observation of carbocations by ^{1}H and ^{13}C NMR spectroscopy under stable ion conditions has greatly enhanced our understanding of the structure and chemistry of carbocations.[8]

The fate of a carbocation depends on the conditions under which it is produced. If the system contains a strongly nucleophilic counter-ion then this will react with the cation as it is formed ensuring the cation concentration remains low. If the system lacks a strongly nucleophilic species and the medium is of sufficiently high acidity to prevent deprotonation then the cation is said to experience stable ion conditions. Superacids satisfy these two requirements.[5]

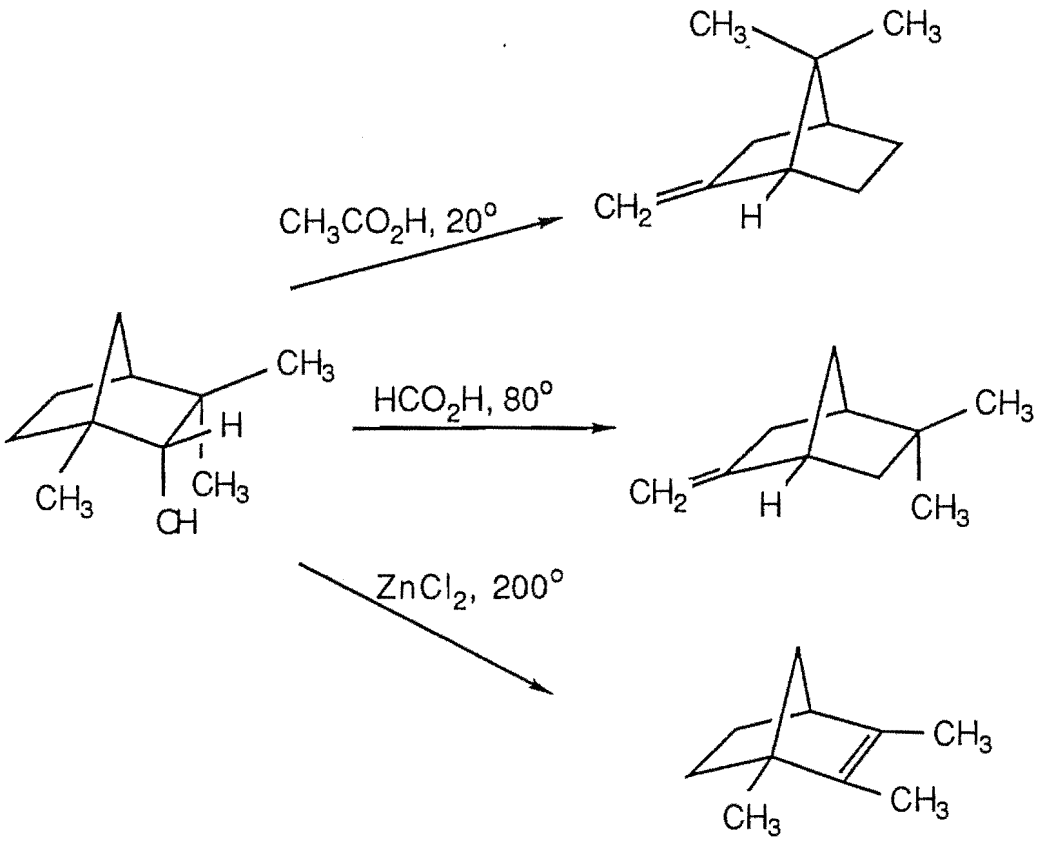
Thus reaction of an alcohol with a superacid produces a high concentration of the carbocation rather than the protonated alcohol. Since energy is no longer required for cleavage of the C-O bond then, at a given temperature, acid induced reactions involving cationic intermediates are more rapid with superacids than with acids of lower acidity. The much lower freezing points of superacid solutions relative to the common protic mineral acids facilitates their use over a much greater temperature range. By observing a solution of cations over a range of increasing temperatures the rearrangement sequence producing cations of increasing stability can be followed, and energy barriers of individual rearrangements measured. For example the sequence of rearrangements shown in Scheme 1 was deduced from variable temperature NMR studies[9] of cations derived from α-fenchol. Scheme 1 includes the activation energy barriers of the rearrangements involved. Clearly the superacid induced rearrangement sequence parallels that inferred from the previously

studied chemical reactions[9] summarised in Scheme 2. Upon warming the superacid solution Sorensen observed cationic rearrangements which do not have an acid catalysis equivalent, such as the ring opening to the monocyclic allylic cation which is observed at temperatures above 0°C. Under stable ion conditions carbocations frequently undergo rearrangements more complex than observed at the same temperature under 'normal' acid conditions. These rearrangements often produce products potentially worthy of investigation for synthetic use.

Scheme 1

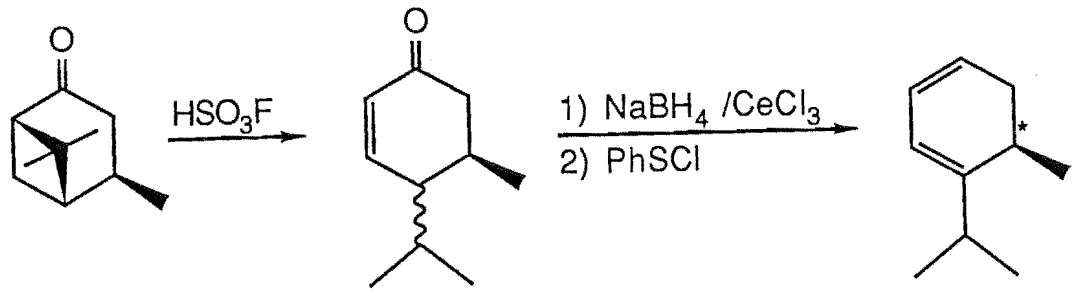


Scheme 2



Despite the fact that superacids have been extensively employed for the spectroscopic study of carbocations, there have been few reports of the use of superacids as reagents in organic synthesis. It has been the intent of his work to establish the usefulness of fluorosulfonic acid as a reagent in organic synthesis. In this department some investigations have been undertaken to utilise the cationic rearrangements accessible in superacid solutions for synthetic purposes. For example HSO_3F was shown[10] to be an efficient reagent for the ring opening of pinanones to give isopropylcyclohexanones. This rearrangement, observed only in superacids, was used[10] in a short synthesis of the chiral diene, o-methadiene (Scheme 3).

Scheme 3



The work described in this thesis continues this theme by examining the reactions of series of benzyl, 2-phenylethyl and 3-phenylpropyl carbinols with HSO_3F. It is expected that the initially formed carbocations will undergo rearrangement so as to bring the charge into conjugation with the stabilising influence of the aromatic ring.

Other reaction pathways which have precedence[5] in superacid media include intramolecular cyclisations, alkyl migrations, hydride migrations, ring expansions, ring contractions and dimerisations. The various competing cationic rearrangement mechanisms represent potentially useful pathways of interest to synthetic chemists. The purpose of this thesis was to explore the use of fluorosulfonic acid and to harness its acid strength to facilitate the synthesis of reaction products not otherwise accessible with weaker acids, thereby demonstrating its usefulness as a synthetic reagent.

CHAPTER 2

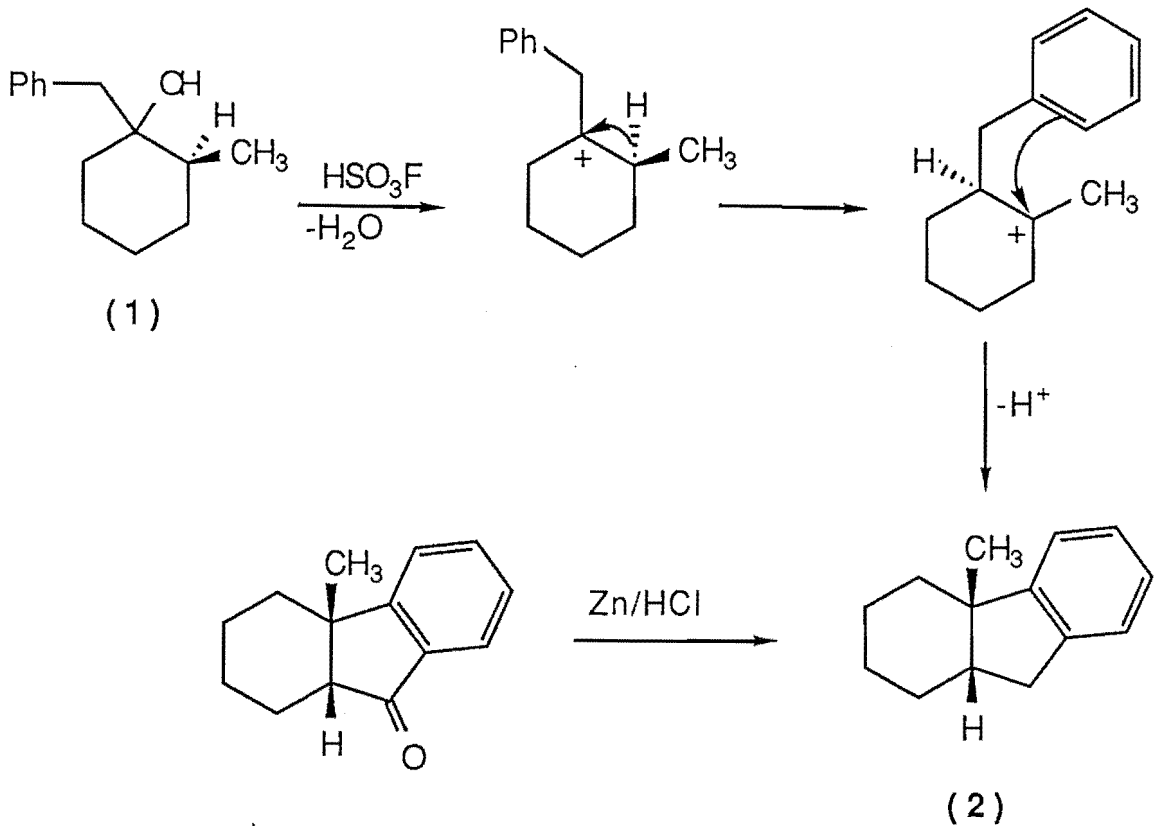
REACTIONS OF BENZYL CARBINOLS.

Chapter 2: Reactions of Benzyl Carbinols

Cycloalkanols.

Reaction of 1-benzyl-2-methylcyclohexanol **(1)** with HSO_3F at -78°C followed by quenching and product extraction resulted in the efficient conversion of the alcohol to a single stereoisomer of the methylhexahydrofluorene **(2)** in > 85% isolated yield (Scheme 4). The *cis*- stereochemistry was deduced from mutual NOE enhancements between the methyl protons and the tertiary proton and by comparison of the ^{13}C NMR with that of a related compound.[11] In addition, the structure was confirmed by an independent preparation involving Clemmensen reduction of the known[12] 9-fluorenone.

Scheme 4



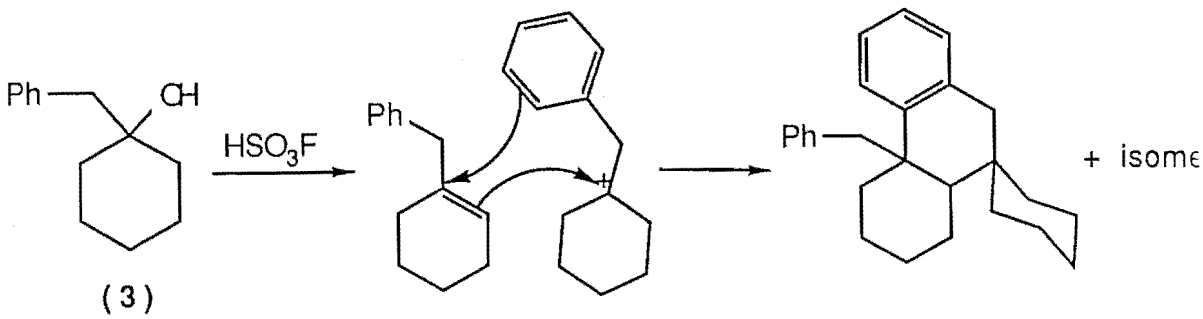
(1)

(2)

Cyclisation of **(1)** is a consequence of the presence of the methyl group which facilitates a hydride shift from C2 in the initially formed carbocation to produce another tertiary cationic centre which is suitably disposed to attack the *ortho* position of the phenyl ring. In the absence of the methyl group an analogous hydride shift would produce a secondary carbocation and therefore such a process might not occur.

Reaction of 1-benzylcyclohexanol **(3)** with HSO_3F at -78°C, which could have reacted analogously to **(1)**, resulted in the formation of a complex mixture of hydrocarbons. The mixture of hydrocarbons could only be partially separated but it was shown by mass spectrometry and NMR spectroscopy to contain mainly dimers of formula $C_{26}H_{32}$. The formation of dimeric products in reactions with super acids has precedent in the literature[13] and can result from reaction between a carbocation and an alkene with which it is in equilibrium, followed by cyclisation. Such a process, analogous to that observed by Butler *et al*, is shown in Scheme 5. Reaction of 1-benzylcyclopentanol gave a similarly complex mixture of dimeric products and no product analogous to that formed from **(1)** could be detected. In an attempt to resolve features of the NMR spectra of the products from the reaction of 1-benzylcyclopentanol the *para*-methyl analogue, 1-(*para*-methylbenzyl)cyclopentanol, was reacted with HSO_3F. A mixture of methyl substituted dimers was produced, but could not be separated and the NMR spectra did not allow identification of any products of the mixture.

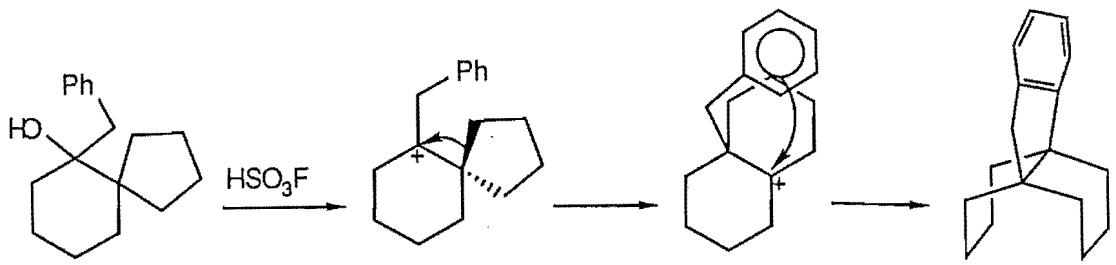
Scheme 5



(3)

A rearrangement analogous to that observed for 1-benzyl-2-methylcyclohexanol **(1)** was exploited in the synthesis of propellanes. Thus the 2-spiro alcohol **(4)** is smoothly converted to the propellane **(5)** by a mechanism shown in Scheme 6[14] involving ionisation, a Wagner-Meerwein shift[15] (W-M) and cyclisation.

Scheme 6

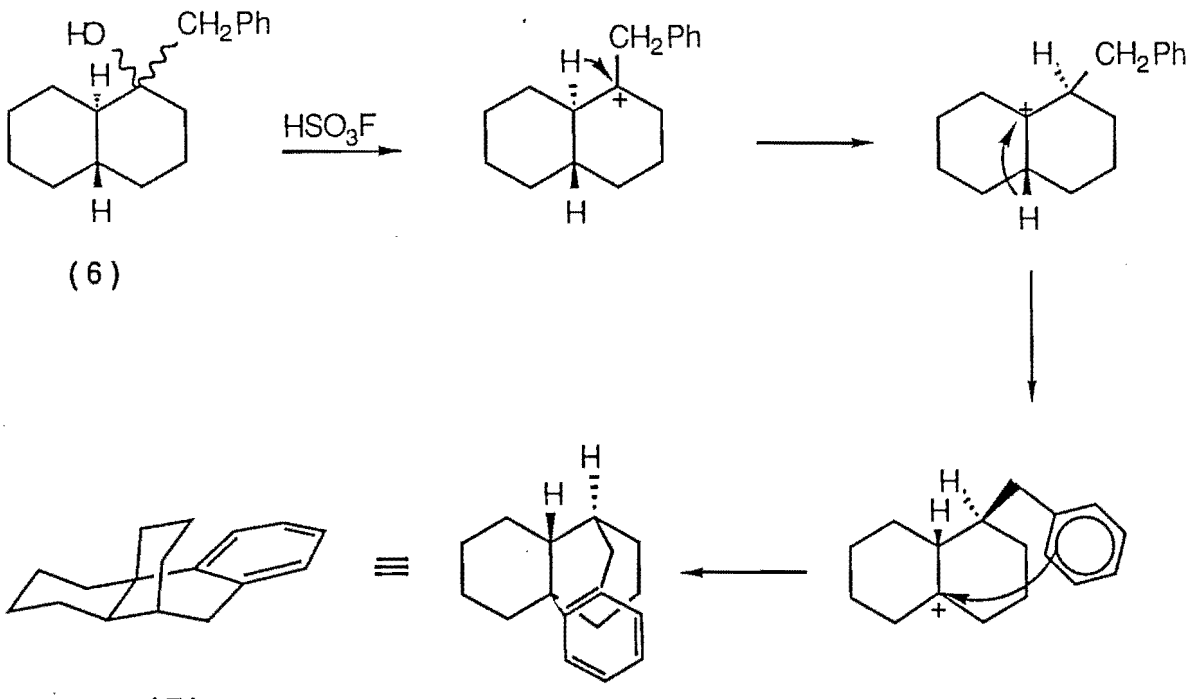


(4) (5) 80%

The C_s symmetry of **(5)** is supported by its ^1H and ^{13}C NMR spectra. 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.

As an example of a synthetic application of these reactions the decalols **(6)** were prepared and reacted with fluorosulfonic acid (Scheme 7) to give the known carbamorphinan **(7)** in ~ 90% isolated yield. Although **(7)** has been prepared[16] by a related cyclisation procedure (Scheme 8) the major product from reaction of the alkene mixture was the isomer **(9)** (50%) in preference to **(7)** (33%). By reacting the readily prepared *trans*-decalols **(6)** with fluorosulfonic acid the diastereoselective formation of **(7)** is ensured by the suprafacial nature of each hydride migration.

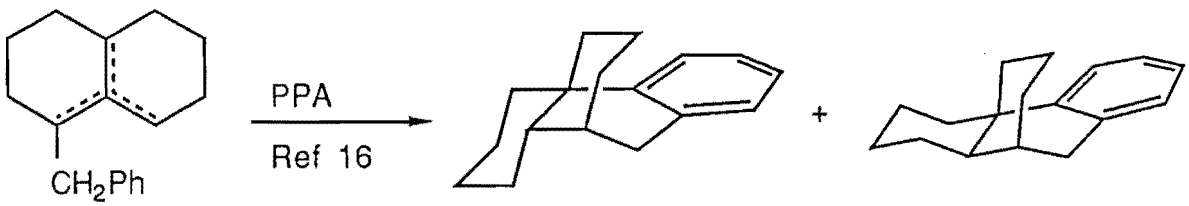
Scheme 7



(6)

(7)

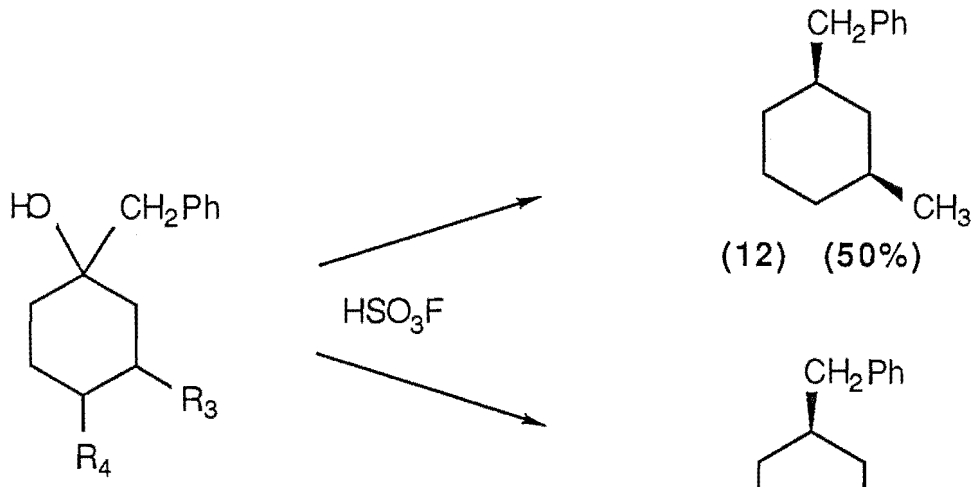
Scheme 8



(8) **(9)** **(50%)** **(7)** **(33%)**

Reaction of the 3- and 4-methyl alcohols **(10)** and **(11)** with fluorosulfonic acid resulted in a completely different mode of reaction (Scheme 9).

Scheme 9



(10) R_3= CH_3, R_4= H
(11) R_3= H, R_4= CH_3

(12) (50%)

(13) (30%)

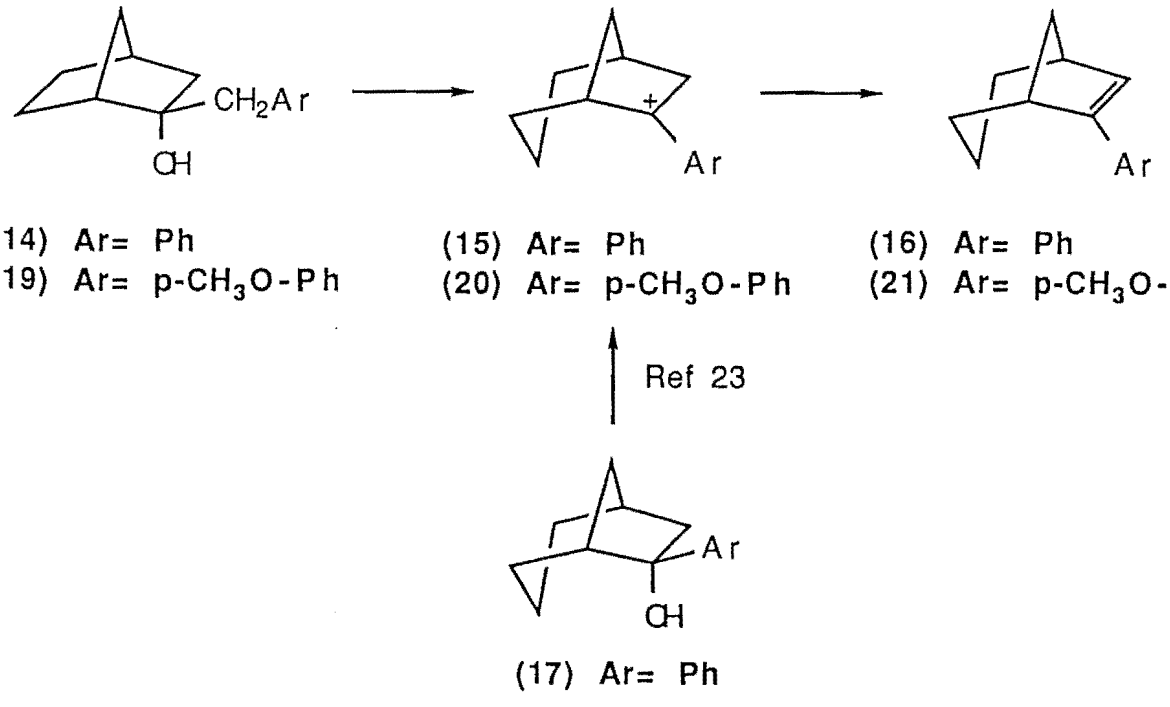
The only monomeric products isolated (in < 50% yield) were the reduced alkanes **(12)** and **(13)**, whose structures followed from their NMR and mass spectra and by comparison with authentic samples prepared from the starting alcohols by dehydration and hydrogenation. The alkanes are considered to be formed by disproportionation of the initially formed carbocations in a process which has precedent in the literature.[13a,17] The formation of these reduced products is only observed for substrates containing tertiary hydrogens because of the greater hydride donating ability of a tertiary relative to a secondary hydrogen.[18] It is also noteworthy that although the samples prepared by hydrogenation[19] are each mixtures of the two diastereoisomers the formation of **(12)** and

(13) from the HSO_3F reaction is highly diastereoselective. This selectivity is probably associated with the steric bulk of the hydride donor. Fluorosulfonation of the phenyl ring of the products is observed for reaction temperatures above 0°C.

Norbornanols.

The reactions of 2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol **(14)** and 2-*exo*-(*para*-methoxy-benzyl)bicyclo[2.2.1]heptan-2-*endo*-ol **(19)** with HSO_3F have been previously investigated in this department.[20] Preliminary studies had shown that the alcohols **(14)** and **(19)** underwent extensive rearrangement in super acid media (Scheme 10). The identity of the products **(16)** and **(21)** were determined by ^1H and ^{13}C NMR by comparison with the spectra of related compounds.[21,22]

Scheme 10



(14) Ar= Ph
(19) Ar= p-CH_3O-Ph

(15) Ar= Ph
(20) Ar= p-CH_3O-Ph

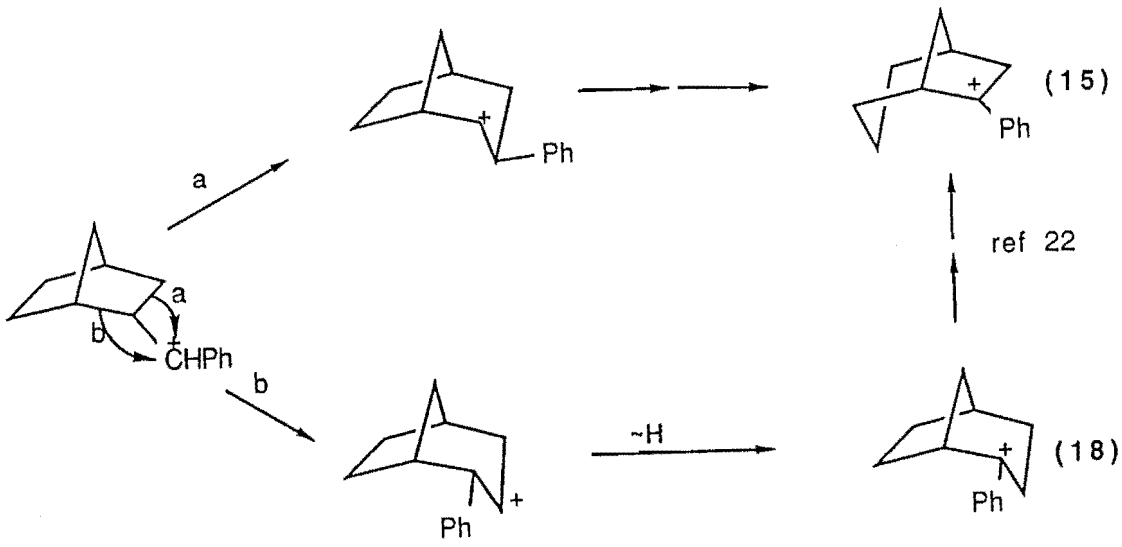
(16) Ar= Ph
(21) Ar= p-CH_3O-Ph

(17) Ar= Ph

This represents yet another mode of reaction of a benzyl carbinol, *viz* ring expansion. An attempt was made to follow the course of the conversion of **(14)** by direct NMR observation of the intermediate carbocations in HSO_3F/SO_2ClF at temperatures between -90°C and 0°C. However, the only species observed spectroscopically from reaction at -90°C was the rearranged 6-phenylbicyclo[3.2.1]octan-6-yl cation **(15)**, for which the ^{13}C NMR spectrum was identical to that previously reported.[23] The formation of this cation from alcohol **(14)** represents a more convenient method of preparation of this well-studied cation[22,23,24] than that previously reported[23] from the less readily prepared precursor **(17)**.

This rearrangement is of particular interest since several mechanisms are possible for the conversion of **(14)** to **(16)**. These can be subdivided according to whether the key ring expansion step occurs by migration of C3 (methylene migration) (Scheme 11, path a) or C1 (bridgehead migration) (Scheme 11, path b), both of which have ample precedent in the literature.[25]

Scheme 11



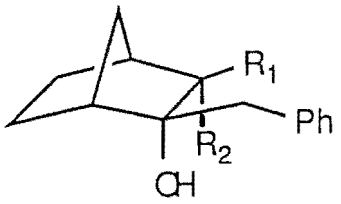
Initially the latter possibility was considered more likely since this would lead to the 2-phenylbicyclo[3.2.1]octan-2-yl cation **(18)**, derivatives of which are known[22] to rearrange to derivatives of **(15)**.

To test this hypothesis the reaction of the corresponding *para*-methoxy alcohol **(19)** with HSO_3F/SO_2ClF at low temperature was undertaken with the hope of stabilising intermediate cations sufficiently to allow direct observation of the rearrangement by NMR. The *para*-methoxy derivative of a cation **(18)** would be expected[26] to be considerably more stable than **(18)** and hence have a higher energy barrier to rearrangement. However, in the event, the only observed species even at -60°C was the rearranged cation **(20)**,[23] which on quenching gave alkene **(21)** (see Scheme 10).

The failure to detect the *para*-methoxy derivative of cation **(18)** represents only indirect evidence in favour of methylene migration in the ring expansion (Scheme 11, path a).

The validity of path a was unambiguously demonstrated by deuterium labelling at the 3-position of alcohol **(14)**. Thus reaction of the 3,3-dideuterio alcohol **(22)** with HSO_3F and quenching gave the 7-deuterio alkene **(25)**. The absence of the olefinic proton signal at 6.25 ppm in the ^1H NMR spectrum indicated > 90% deuterium substitution at the 7-position and the existence of only one signal (6.3 ppm) in the ^2H NMR spectrum showed exclusive formation of **(25)**. This result is consistent only with C3 (methylene) migration (i.e. Scheme 11, path a) since the alternative pathway would have

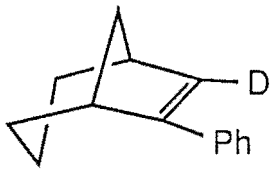
produced 4,4-dideuterio-(**18**) which would rearrange[22] to 8,8-dideuterio-(**15**).



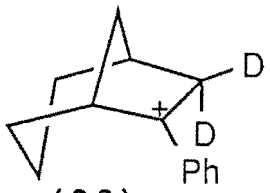
(**22**) R_1= R_2= D

(**23**) R_1= D, R_2= H

(**24**) R_1= H, R_2= D



(**25**)



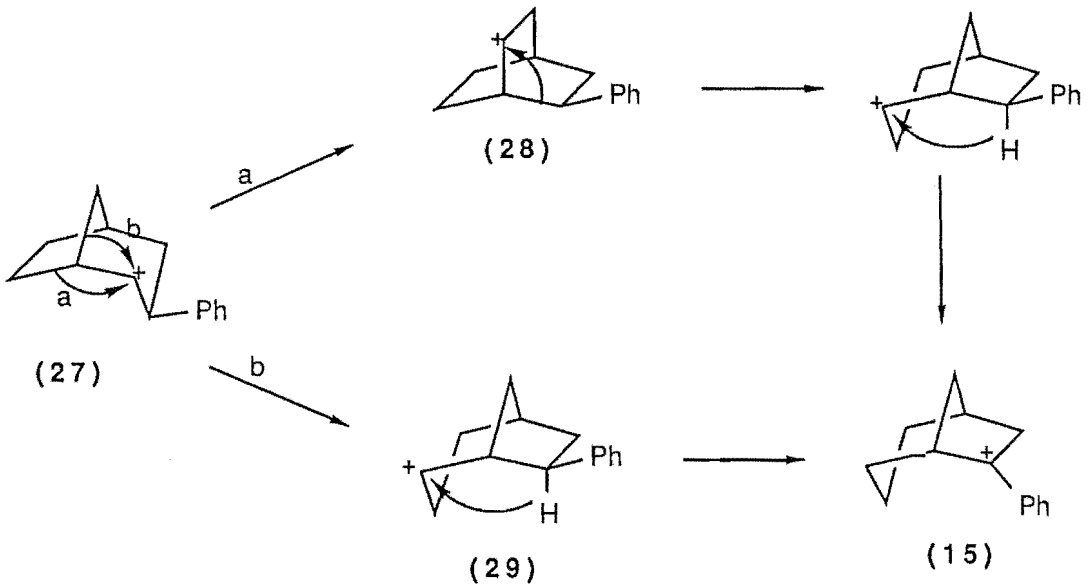
(**26**)

Since (**25**) must result from quenching of (**26**) it seemed of interest to determine whether there was any selectivity between *exo*-and *endo*- deuteron abstraction. Thus the selectively mono-deuterated alcohols (**23**) and (**24**) were prepared and reacted as above. The resulting products each contained approximately 50% (± 5%) deuterium labeling at C7, as measured by ^{1}H NMR and mass spectrometry; that is a *ca* 1:1 mixture of (**16**) and (**25**) was produced from both alcohols. Thus the rapid quenching process[27] does not distinguish between the diastereotopic deuterons in (**26**).

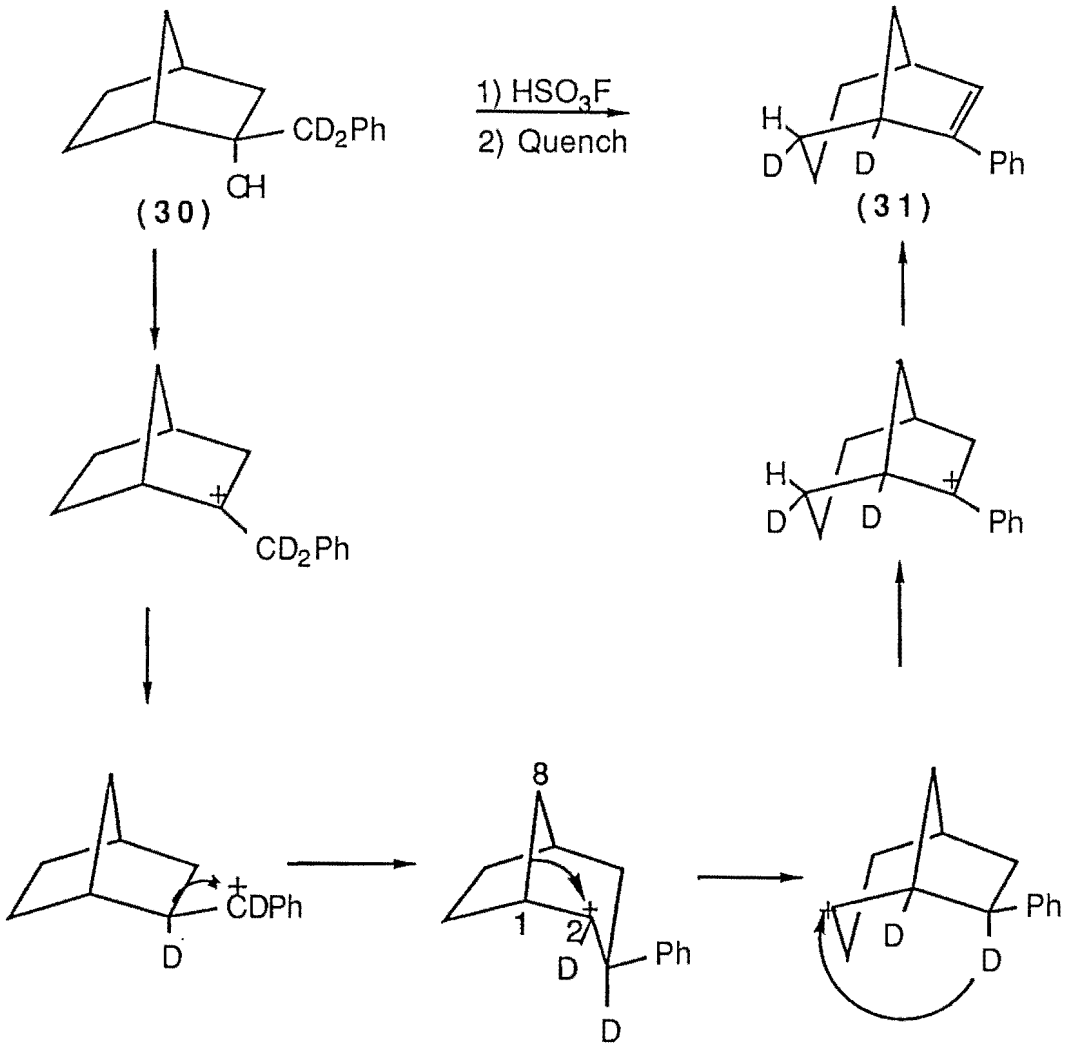
Although the mode of ring expansion was established there still remained an ambiguity concerning the precise mechanism for the rearrangement of the intermediate cation (**27**) to (**15**) (Scheme 12). In particular cation (**27**) could undergo a Wagner-Meerwein rearrangement by either ethano bridge migration (Scheme 12, path a) to give (**28**) or methano bridge migration (Scheme 12, path b) to (**29**) en route to (**15**).

These two possibilities were distinguished by deuterium labeling of the benzylic protons (Scheme 13).

Scheme 12



Scheme 13



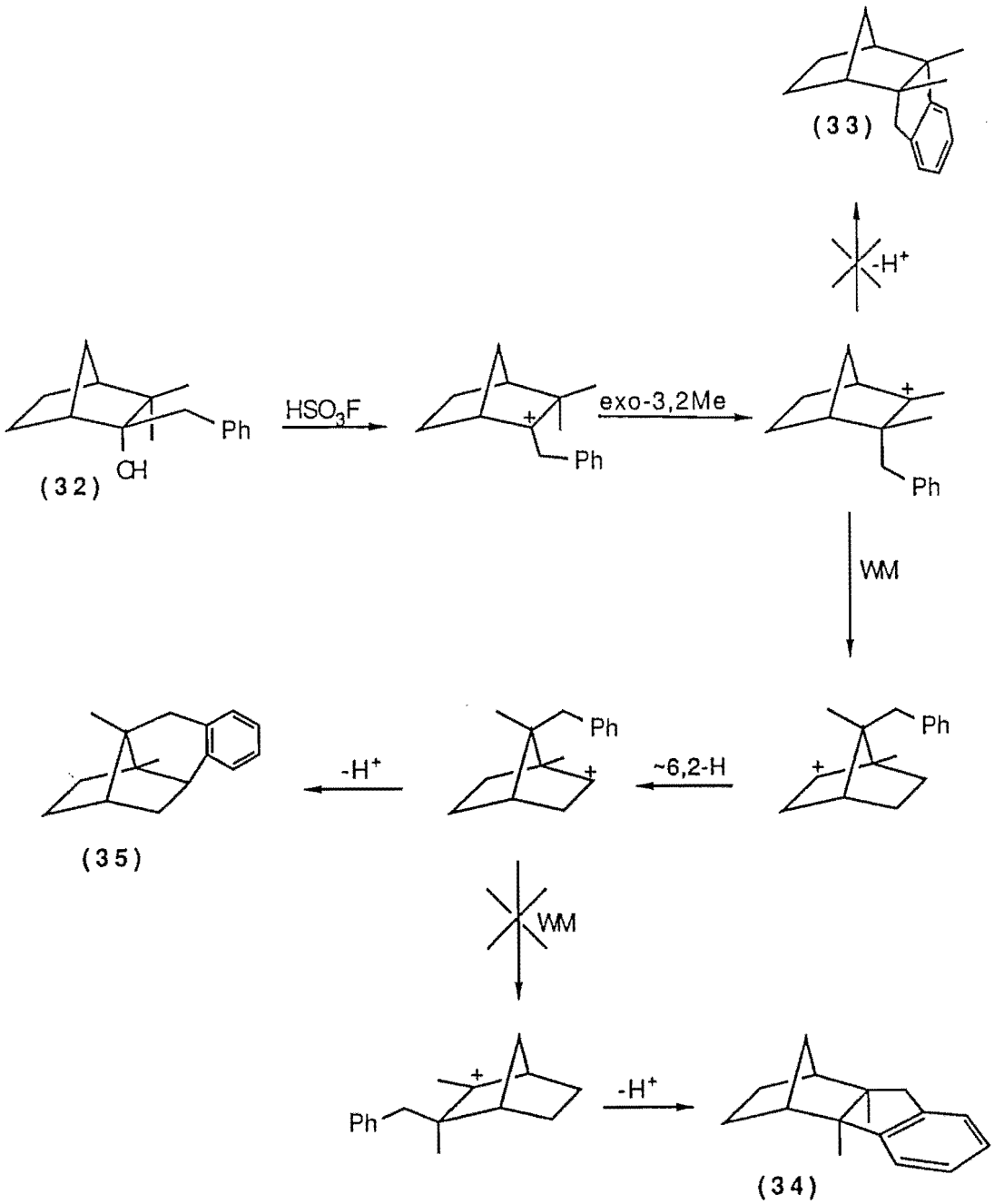
Thus reaction of the α,α-dideuterio alcohol **(30)**, as above, gave the 4,5-dideuterio alkene **(31)**. The identity of **(31)** followed from the absence of the signal in the ^{1}H NMR spectrum for the bridgehead proton H5 at 2.97 ppm, the existence of two signals in the ^{2}H NMR spectrum at 2.99 ppm (D5) and 1.59 ppm (D4), and the one-bond coupling of two carbons (C4, 24.6 ppm; C5, 40.8 ppm) to deuterium in the ^{13}C NMR spectrum. This result is not consistent with ethano bridge migration (Scheme 12, path a) since such a mechanism would have resulted in formation of the 4,4-dideuterio alkene.

As shown in Scheme 12 the full mechanism for the conversion is unambiguously established and involves methano bridge migration (i.e. **(27)**→**(29)**). Although ethano bridge migration is greatly favoured over methano bridge migration in bicyclo[2.2.1]heptan-2-yl (norbornyl) cations, this is not the case for bicyclo[3.2.1]octan-2-yl cations in which there is increased overlap of the C1-C8 bond with the vacant orbital at C2. Also of interest is the fact that in the conversion of **(30)** to **(31)** both deuteride migration steps occur without loss of the deuterium label. This therefore excludes the intermediacy of olefin or cyclopropyl intermediates;[22,28] namely deprotonation followed by reprotonation.

In contrast to the ring expansion described above the corresponding 3,3-dimethyl (camphenilyl) alcohol **(32)** undergoes a completely different reaction course with HSO_3F (Scheme 14). Rearrangement and cyclisation occurs to give a hydrocarbon of formula $C_{16}H_{20}$ containing an *ortho* disubstituted benzene ring. Three structures were considered possible for this hydrocarbon (*viz* **(33)**-**(35)**). Rearrangement by a mechanism analogous to that of the 2-

substituted cyclohexanols described above and with preferential *exo*-3,2-methyl migration[29] would have resulted in formation of benzoisoalbene **(33)**. Alternatively a more complex rearrangement sequence (or *endo*-3,2-methyl migration) could have produced benzoalbene **(34)**. These two possibilities were eliminated by the existence of three benzylic protons in the hydrocarbon (as deduced by ^1H NMR) and by comparison of the NMR data with those of

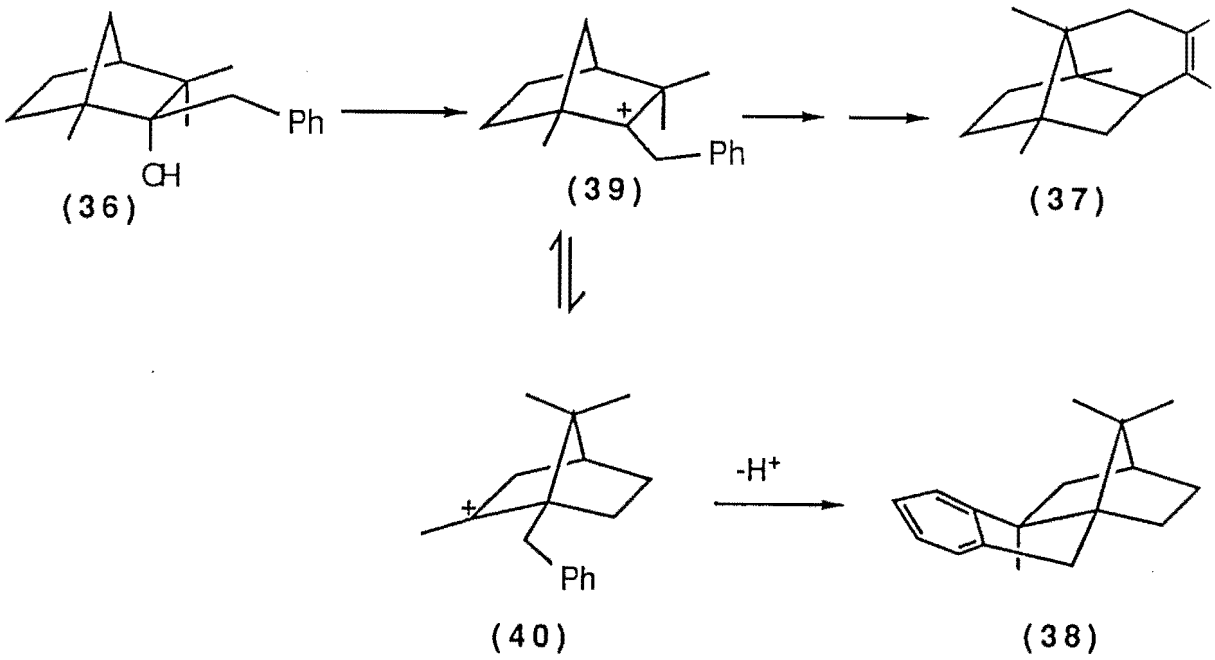
Scheme 14



naturally occurring albene,[30] its synthetic isomer isoalbene[31] and the demethylated analogues of **(33)** and **(34)**.[32] . The structure of the hydrocarbon product was deduced to be **(35)** by comparison of NMR spectral data with those of related compounds.[33,34] The mechanism of formation of **(35)**, shown in Scheme 14, is analogous to that for the reaction of the corresponding phenylcarbinol.[33] The preference for *exo*-3,2-methyl migration over *endo*- migration is well established[29] and hence formation of **(35)** is considered to involve *exo*-methyl migration and therefore require a 6,2-hydride shift prior to cyclisation.

Reaction of the related fenchol **(36)** produced two tetracyclic hydrocarbons (Scheme 15), the major product being **(37)** which is formed by a parallel mechanism to that for **(35)**.

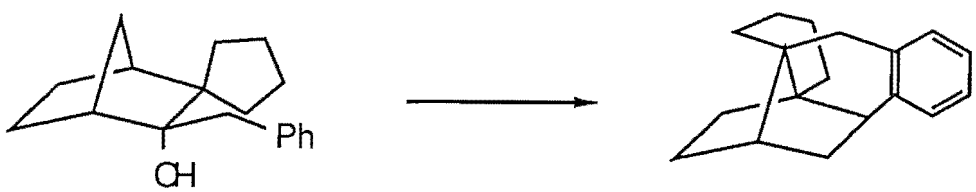
Scheme 15



In addition a minor product was tentatively identified as **(38)** on the basis of the highfield position of one of the *gem*-dimethyl proton signals (0.42 ppm) which molecular models show to lie over the shielding plane of the phenyl ring. A phenyl substituted derivative of **(38)** has previously been reported[35] with the corresponding methyl protons resonating at 0.39 ppm. The formation of **(38)** can result from Wagner-Meerwein rearrangement of the initially formed cation **(39)** to produce **(40)** which then cyclises to **(38)**. The formation of **(38)** from **(36)** but absence of an analogous product from **(32)** results from the presence of the C1 methyl group which is necessary for the W-M rearrangement to occur; i.e. the initially formed cation from **(32)** does not undergo W-M rearrangement as this would produce a secondary cation.

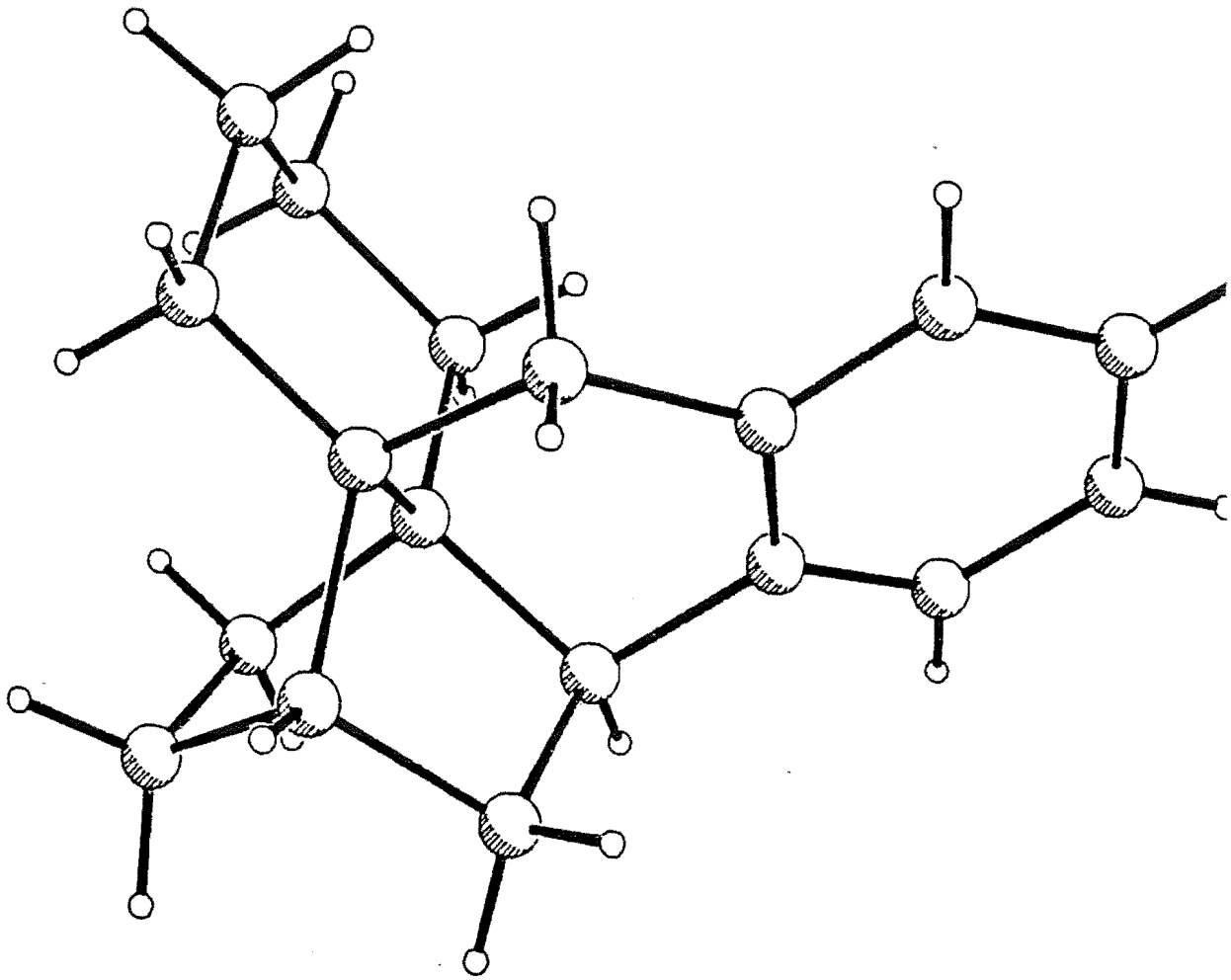
The spiro alcohol **(41)** was prepared and can be considered to represent a superposition of alcohols **(4)** and **(32)**. Reaction of **(41)** with HSO_3F follows an analogous pathway to that of **(32)** and results in formation of the pentacyclic hydrocarbon **(42)** (Scheme 16), the structure of which was determined spectroscopically and confirmed (Figure 1) by X-ray crystallography (see Experimental Part C).

Scheme 16



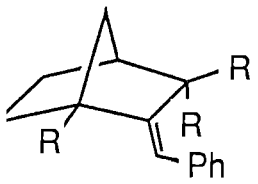
(41) **(42)**

Figure 1: Perspective view of the X-ray structure of (42)

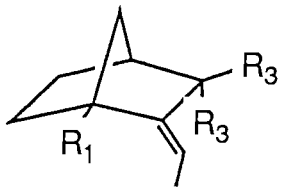


In the reactions of the benzylnorbornanols described above, fluorosulfonic acid induces substantial rearrangements of the carbon skeletons even at low temperature. This can be contrasted with the corresponding reactions under less strongly acidic conditions, wherein direct dehydration or only minor rearrangements occur. For example, the alcohols **(14)**, **(32)** and **(36)** have been previously reacted[20] with $AcOH/H_2SO_4$ at room temperature to give simple dehydration products. Thus **(14)** gave a 4:1 mixture of the

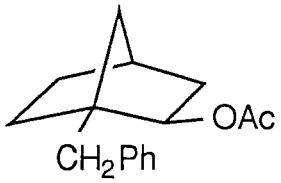
alkenes **(43)** and **(44)**, alcohol **(32)** produced a single alkene **(45)** and alcohol **(36)** gave a complex mixture of hydrocarbons which contained alkenes **(46)** and **(47)** as *ca* 5% of the mixture. Reaction of **(14)** at higher temperature (70°C) with $AcOH/H_2SO_4$ produced, in addition to a 1:1 mixture of alkenes **(43)/(44)**, the W-M rearranged acetate **(48)**. Alkene **(16)**, the exclusive product of reaction with HSO_3F, was not detected in the reaction mixture.



(43) R=H
(46) R=CH_3



(44) R_1= R_3= H
(45) R_1= H, R_3= CH_3
(47) R_1= R_3= CH_3



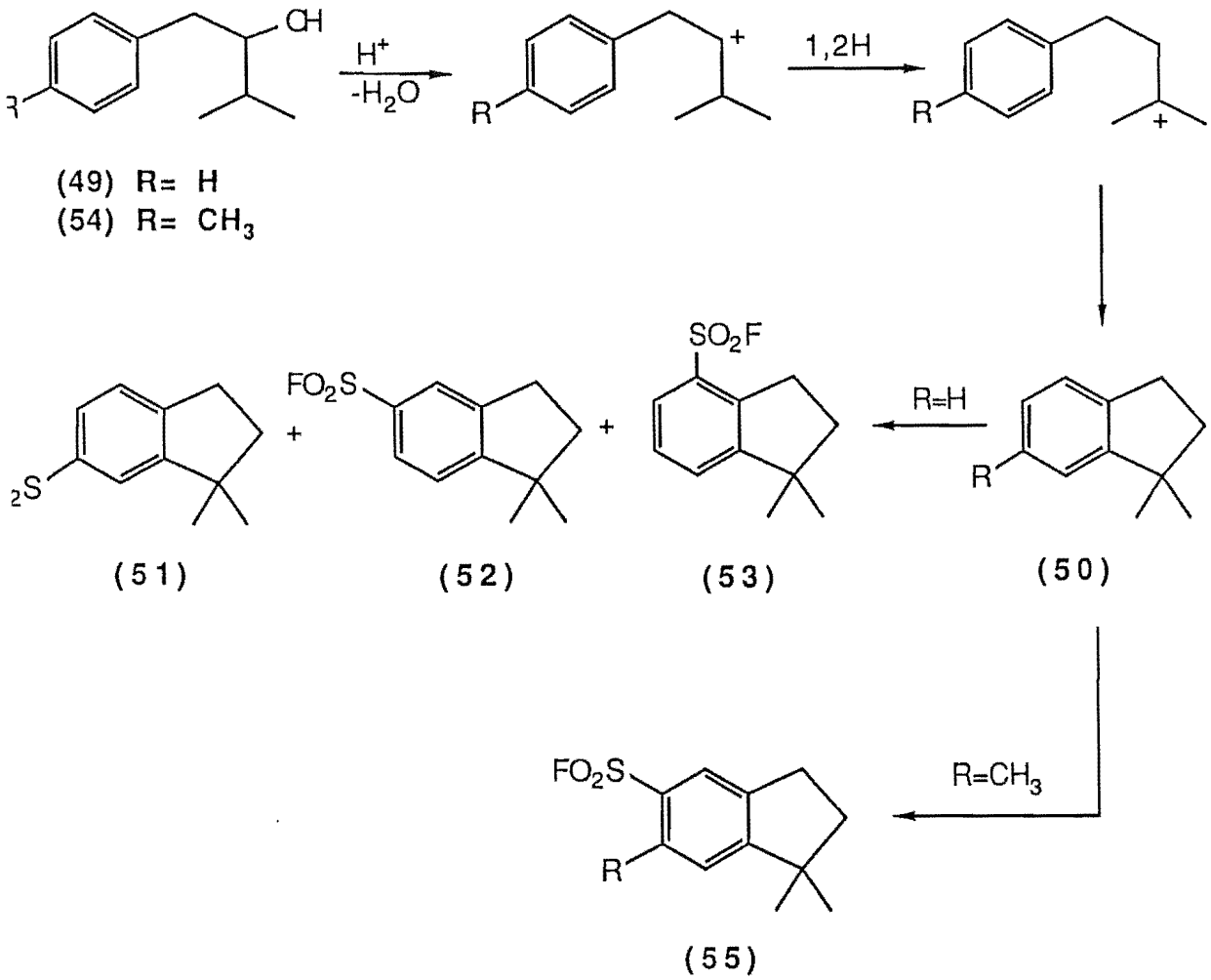
(48)

Acyclic Alcohols.

For comparison with the cyclic analogues discussed above a selection of acyclic benzylcarbinols were reacted with HSO_3F. In general, complex mixtures of products were formed. However, reaction of 3-methyl-1-phenylbutan-2-ol **(49)** at -70°C gave, after quenching, a small amount of the dimethyl indane **(50)** along with the unreacted starting alcohol. This is consistent with the known resistance of secondary alcohols to undergo ionisation in fluorosulfonic acid at low temperatures.[36] Reaction at 0°C and at 25°C resulted in the formation of three products which were separated by preparative GLC and identified by NMR as the fluorosulfonated compounds **(51)** (45%), **(52)** (35%) and **(53)** (20%) (Scheme 17).

The structure of the 4-fluorosulfonated isomer **(53)** followed from the coupling pattern of the aromatic protons (three adjacent protons) and the relatively low field position of the benzylic methylene protons (deshielded by the fluorosulfonate group).

Scheme 17



The 5- and 6-substituted isomers were distinguished by means of difference NOE spectroscopy. For one isomer irradiation of the benzylic methylene triplet (2.99 ppm) resulted in enhancements 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). These results identify this isomer at **(52)**. The ^{13}C NMR spectra of

(50)-(53) were assigned by two-dimensional heteronuclear correlation spectroscopy and provided confirmation of the structural assignments by comparison with the known[33b] substituent shifts of the fluorosulfonate group. Formation of the observed products is rationalised in Scheme 17. The initially formed secondary cation undergoes a hydride shift to produce a more stable tertiary cation which then undergoes cyclisation and fluorosulfonation. The same product mixture is obtained by reaction of authentic indane **(50)** with HSO_3F at room temperature. Further conformation of the structure of these products was obtained from the reaction of 1-(*para*-methylphenyl)-3-methylbutan-2-ol **(54)** in fluorosulfonic acid. The presence of the methyl group on the aromatic ring restricts the sites available for fluorosulfonation and further activates the 5 position towards fluorosulfonation. Thus the predominant product formed in the reaction of 1-(*para*-methylphenyl)-3-methylbutan-2-ol **(54)** is 1,1,6-trimethylindane-5-sulfonyl fluoride **(55)**.

CHAPTER 3

REACTIONS OF PHENYLETHYL CARBINOLS.

Chapter 3: Reactions of Phenylethyl Carbinols

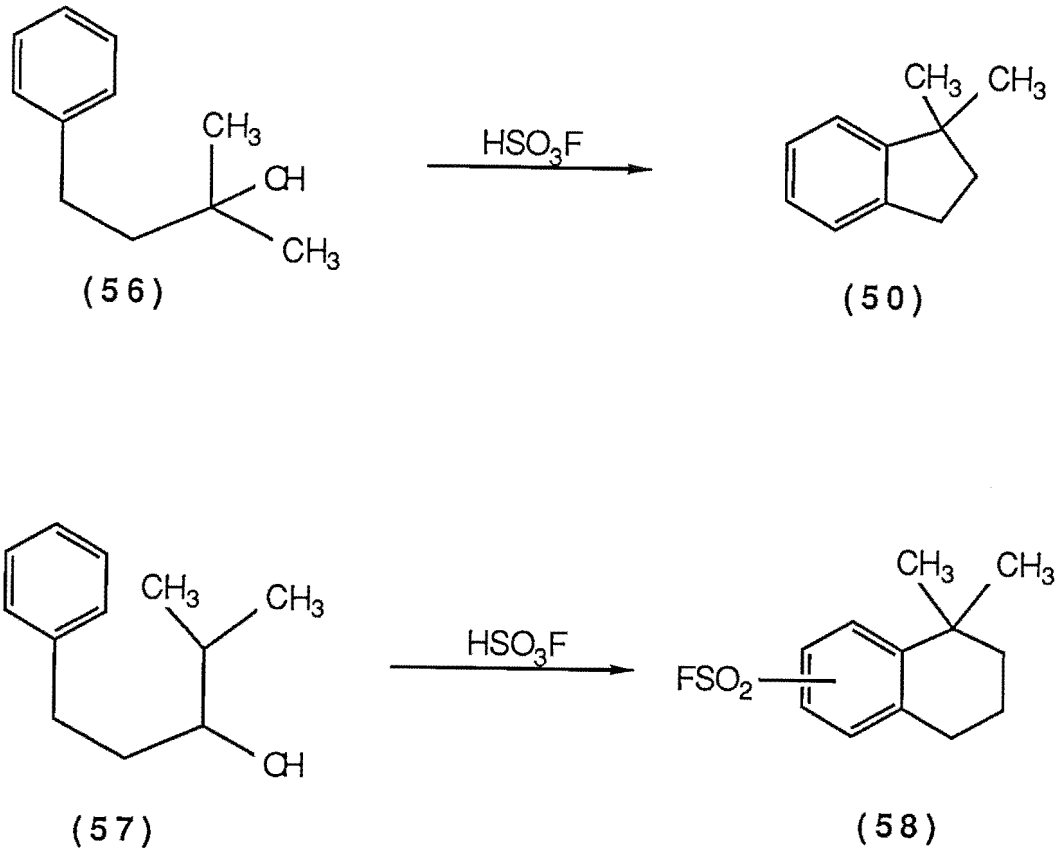
In chapter 2 the reactions of a variety of benzyl carbinols with HSO_3F were described. A number of different reaction modes were observed, dependent on the specific substrate. It seemed of interest therefore to examine the effect of introducing an additional methylene group between the phenyl ring and the cation bearing the initially generated positive charge. This chapter therefore describes the corresponding reactions of various 2-phenylethyl carbinols. The extra flexibility available in the presence of the additional carbon is expected to lead to a greater propensity for cyclisation over the other possible reaction modes.

Acyclic Alcohols.

Changing the position of the hydroxyl group from a secondary position in **(49)** to a tertiary position in **(56)** allowed the direct production of the tertiary carbocation in the acid media at low temperature. Thus rather than producing a mixture of fluoro-sulfonated products, as was the case with reaction of **(49)** at 0°C, reaction of **(56)** at -70°C resulted in a smooth conversion to a product identified by NMR as 1,1-dimethylindane **(50)** (Scheme 18). At this temperature there was no evidence of fluorosulfonation.

Alcohol **(57)** represents the methylene expanded analogue of **(49)**. When this was reacted with fluorosulfonic acid at -70°C the secondary alcohol was recovered, again consistent with the resistance of secondary alcohols to undergo ionisation at low temperatures.[36]

Scheme 18



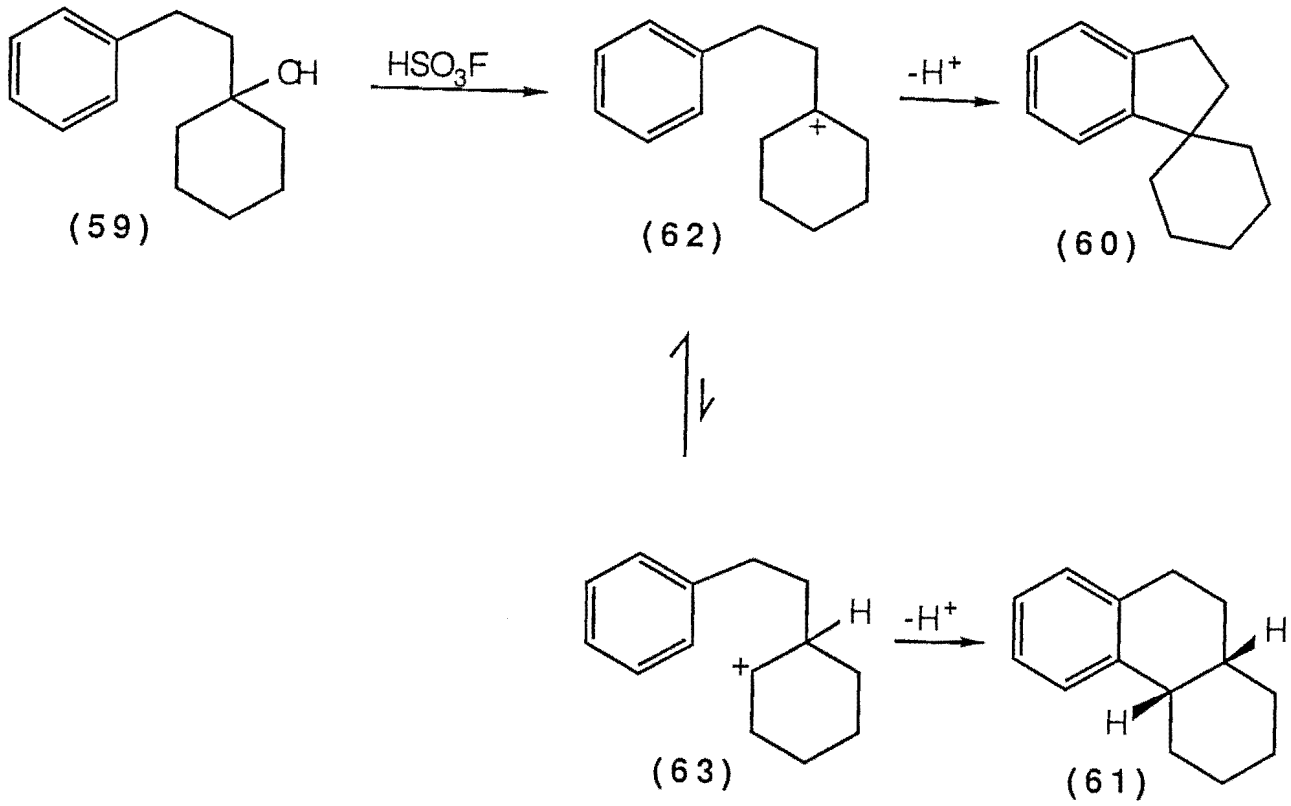
However when the reaction system was allowed to warm to 0°C the secondary carbocation was formed and rearranged via a hydride shift to give the more stable tertiary cation which then underwent cyclisation. As with previous reactions conducted at 0°C the aromatic ring then underwent fluorosulfonation to give a mixture of fluorosulfonated regioisomers **(58)**. Both the cyclisations shown in Scheme 18 have been previously effected with other acid catalysts.[37]

Phenylethylcycloalkanols.

In contrast to the reaction of 1-benzylcyclohexanol **(3)**, which predominantly underwent dimerisation (chapter 2), the added flexibility of the extra methylene group present in 1-(2-phenylethyl)cyclohexanol **(59)** reduces the activation energy barrier to cyclisation. Hence the reaction of **(59)** with HSO_3F at -70°C resulted in the production of two cyclised hydrocarbon products. The two hydrocarbons were formed in a 1:3 ratio and identified, by comparison with literature[38] ^1H and ^{13}C NMR data, as spiro[cyclohexane-1,1-indane] **(60)** and *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(61)** respectively. Inconsistencies[38,39] in some of the reported values for the NMR spectra of **(61)** were clarified by definitively assigning the NMR spectra through a combination of two dimensional techniques.

The formation of spiro[cyclohexane-1,1-indane] **(60)** occurs via an intramolecular cyclisation reaction of the initially formed tertiary cation **(62)** to form a five membered spiro ring (Scheme 19). This reaction is in competition with cyclisation onto the cyclohexane ring at the adjacent carbon to give *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(61)**. Although hydride transfer to produce a secondary carbocation **(63)** is thermodynamically unfavourable,[1] cyclisation of this cation is more favoured than cyclisation to give the spiro compound because of strain reasons. Thus although the equilibrium between the tertiary cation **(62)** and the secondary cation **(63)** will lie strongly in favour of **(62)**, kinetic trapping of the less stable cation **(63)** results in the preferential formation of *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(61)**.

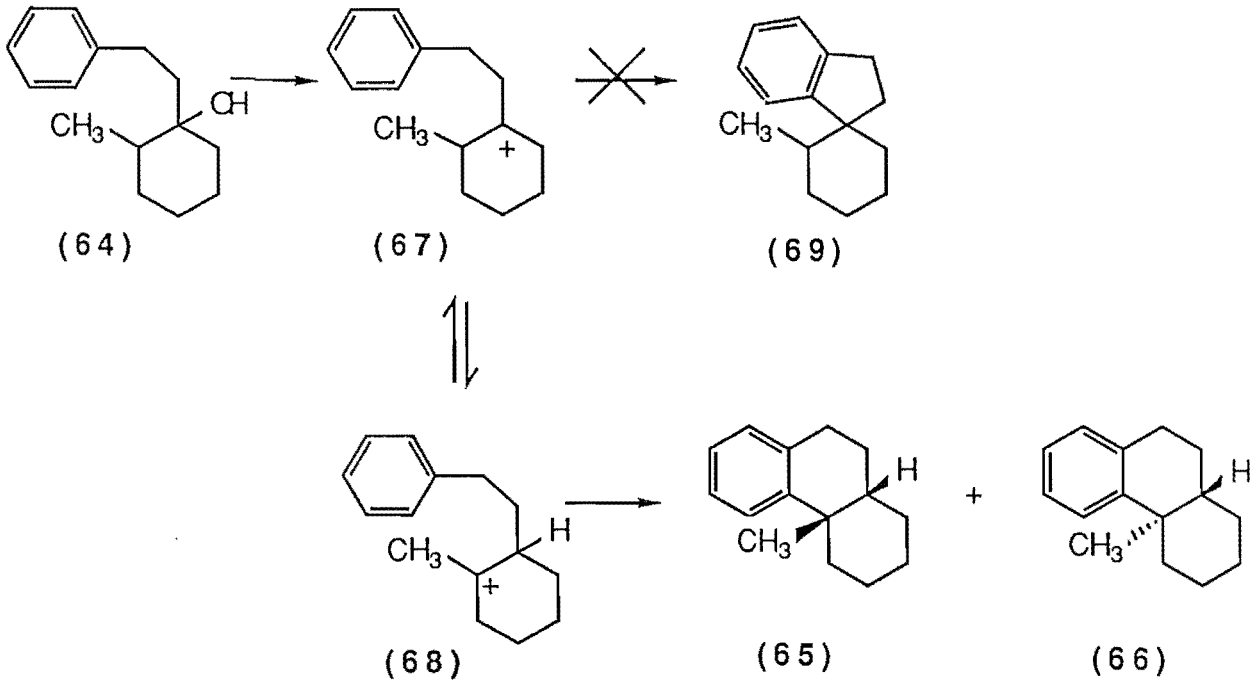
Scheme 19



The rapid cyclisation of the secondary cation **(63)** is also reflected in the stereoselective formation of the *cis*- isomer **(61)** in preference to the more stable *trans*- stereoisomer. This can be explained by consideration of the structure and conformation of the initially formed cation **(63)** wherein the phenyl ring is spatially orientated for the preferential formation of the *cis*- isomer.

Reaction of 2-methyl-1-(2-phenylethyl)cyclohexanol **(64)** gave a 3:1 mixture of *cis*- and *trans*- 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(65)** and **(66)** (Scheme 20) which were identified by comparison with literature[38] NMR data.

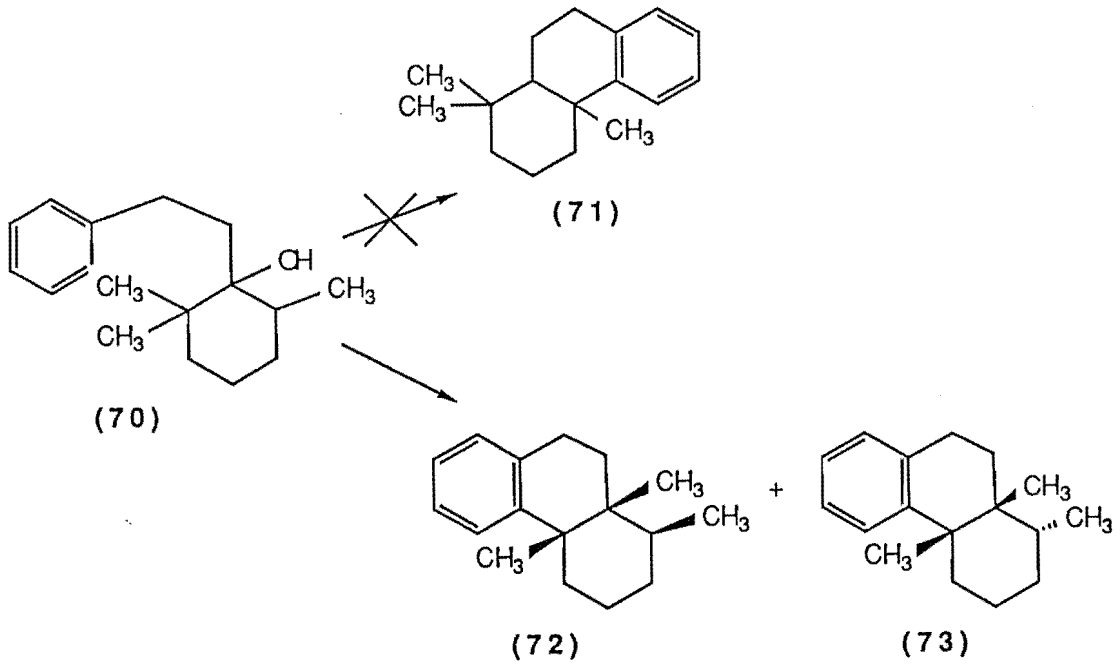
Scheme 20



The presence of the methyl group alpha to the initially formed tertiary carbocation **(67)** promotes the hydride transfer discussed in the previous reaction. This is due to the stabilising effect of the methyl group; the carbocation **(68)** formed from a hydride shift is tertiary, as opposed to the previous example where the analogous cation **(63)** was secondary. Thus the equilibrium between **(67)** and **(68)** becomes more equal and cyclisation of **(68)** becomes the favoured reaction pathway over formation of the analogous spiro product **(69)** which was not detected in the crude reaction mixture. As in the reaction of 1-(2-phenylethyl)cyclohexanol the orientation of the phenylethyl fragment favours formation of the *cis-* isomer **(65)**. However in the reaction of **(64)** a significant amount (25%) of the *trans-* isomer **(66)** is also produced. This can be explained by the longer lifetime of the tertiary cation **(68)** relative to **(63)**.

This in turn allows the cation to undergo the conformational movement required for the phenyl ring to attack the opposite face of the planar cationic carbon to form the *trans-* stereoisomer.

In an attempt to utilise these rearrangements in a synthetic application, 1-(2-phenylethyl)-2,2,6-trimethylcyclohexanol **(70)** was reacted with fluorosulfonic acid at -70°C. It was hoped that the carbocation initially formed would rearrange via a hydride shift in an analogous manner to 2-methyl-1-(2-phenylethyl)cyclohexanol **(64)**. Subsequent cyclisation would then produce the well-studied[40] hydrocarbon podocarpatriene **(71)**. In the event, however, reaction of **(70)** produced 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(72)** as the major product along with a small amount of the 1α,4aβ,10aβ-trimethyl isomer **(73)**.



The production of 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene involves the migration of a methyl group from C2 to C1 in preference to the hydride migration from C6 to C1.

This is then followed by cyclisation to give 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.

Rearrangements of closely related compounds have recently been discussed in detail in the literature.[41] The preference for methyl migration over hydride migration can be attributed to thermodynamic factors, in particular the presence of 1,3-diaxial interactions in podocarpatriene which are absent in the observed products 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(72)** and 1α,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **(73)**.

The formation of only *cis*- fused products parallels the results from reactions of other phenylethyl cyclohexanols discussed earlier. The ratio of the two observed products presumably reflects the relative migratory aptitudes of the two (non-equivalent) geminal methyl groups.

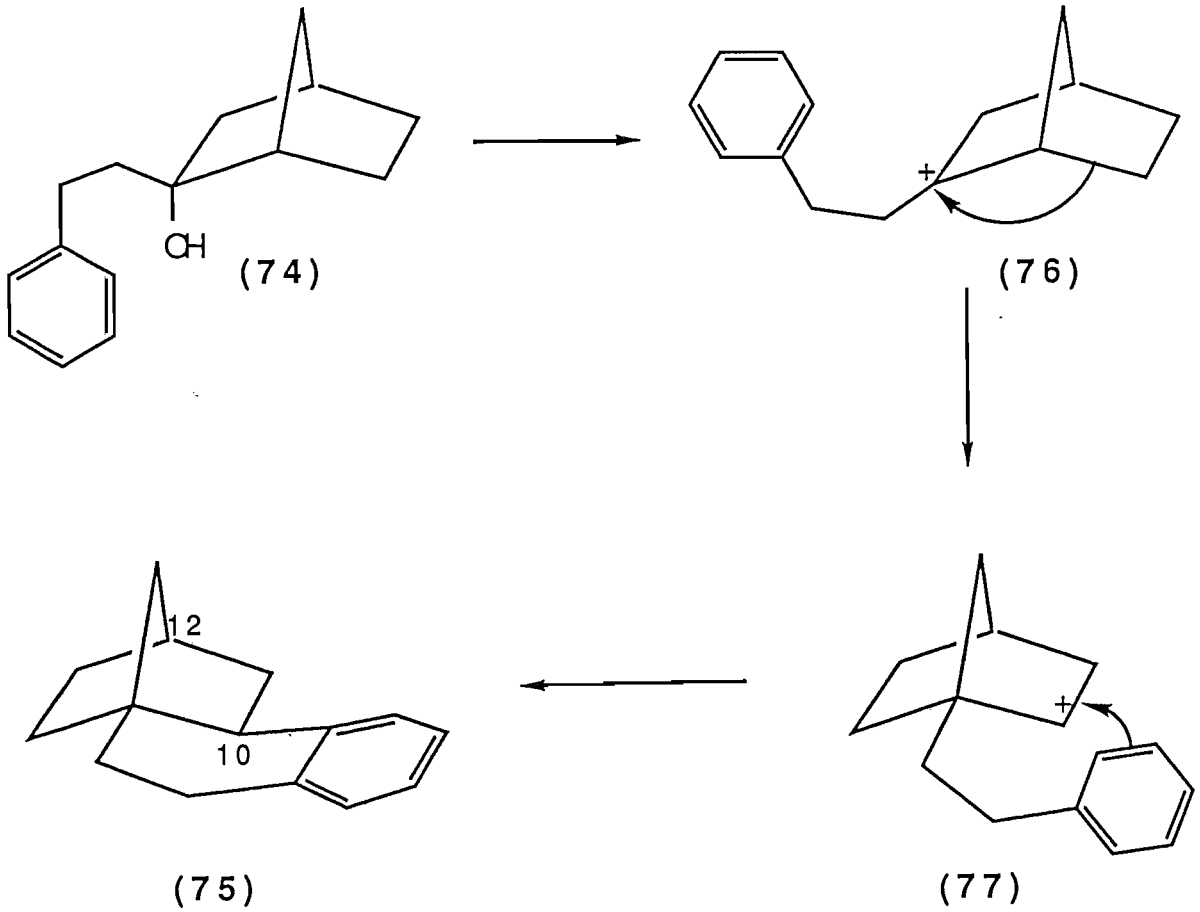
Norbornanols.

To extend the work described in chapter 2 on the norbornyl system 2-*exo*-(2-phenylethyl)bicyclo[2,2,1]heptan-2-*endo*-ol **(74)** was reacted with fluorosulfonic acid. This resulted in the smooth conversion to a single hydrocarbon which was identified by NMR experiments to be tetracyclo[10.2.1.$0^{1,10}$.$0^{4,9}$]pentadeca-4,6,8-triene **(75)**. The structure of the hydrocarbon skeleton in **(75)** followed from the existence of an isolated ethylene group in the ^{1}H NMR spectrum, the multiplicity of the carbons in a DEPT spectrum and the magnitude of the ^{1}H-^{1}H coupling constants. The stereochemistry at C10 was deduced as follows. A ^{1}H-^{13}C

heteronuclear two dimensional correlation spectrum located the positions of the bridgehead proton (H12) and the benzylic proton (H10). Irradiation of the H10 proton showed that it was strongly coupled to one of the C11 protons at 2.1 ppm. Irradiation of the bridgehead proton (H12) showed that it was not coupled to the proton at 2.1 ppm; therefore the proton at 2.1 ppm must be *endo*, and due to the large coupling between the H10 proton and the proton at 2.1 ppm, the H10 proton must also be *endo*. This is further supported by small couplings between the H10 proton (and the proton at 2.1 ppm) and the *anti-* proton of the methylene bridge.

Thus instead of the ring expansion which was observed for the 2-benzylnorbornyl system (chapter 2) the 2-phenylethyl analogue **(74)** undergoes a different rearrangement process (Scheme 21).

Scheme 21

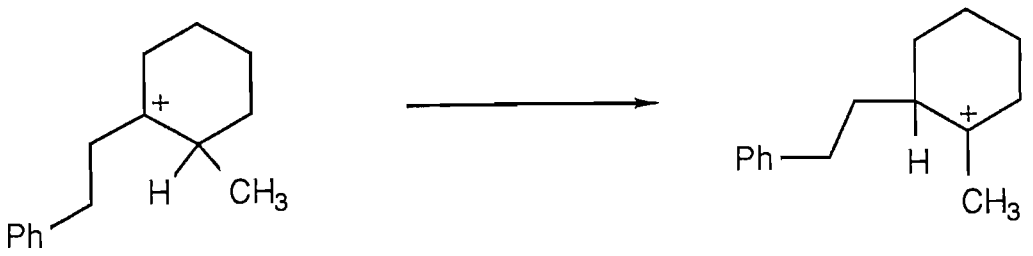


(74) **(76)** **(75)** **(77)**

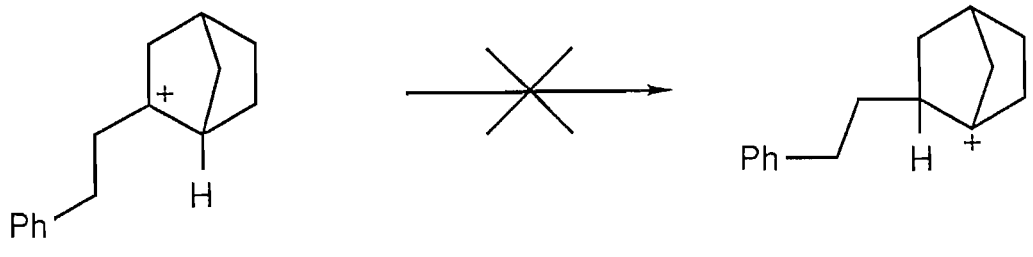
This process involves a Wagner-Meerwein rearrangement of the initially formed cation **(76)** to give **(77)** which then cyclises from the more accessible *exo*- face to give **(75)**.

Although the cation **(76)** might be considered to be structurally related to the 2-methylcyclohexyl cation **(67)**, the hydride shift observed in the latter case **(67 → 68)** is not possible in the case of **(76)** since this would produce an unstable[1] bridgehead carbocation **(78)** (Scheme 22).

Scheme 22



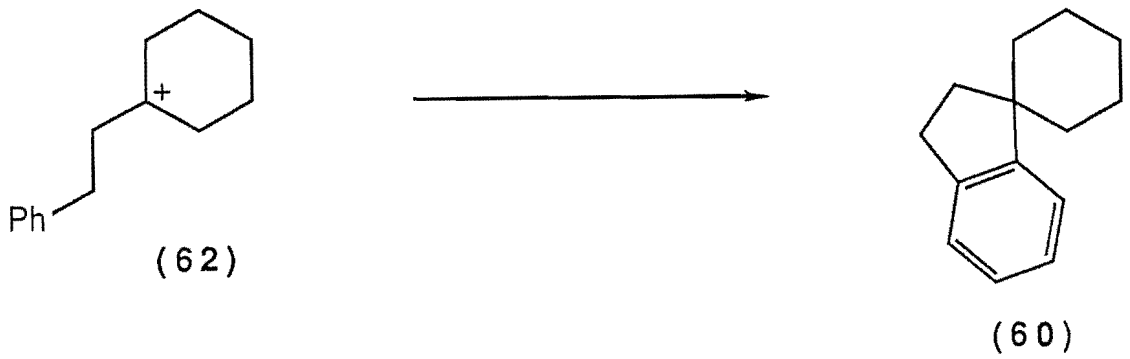
(67) **(68)**



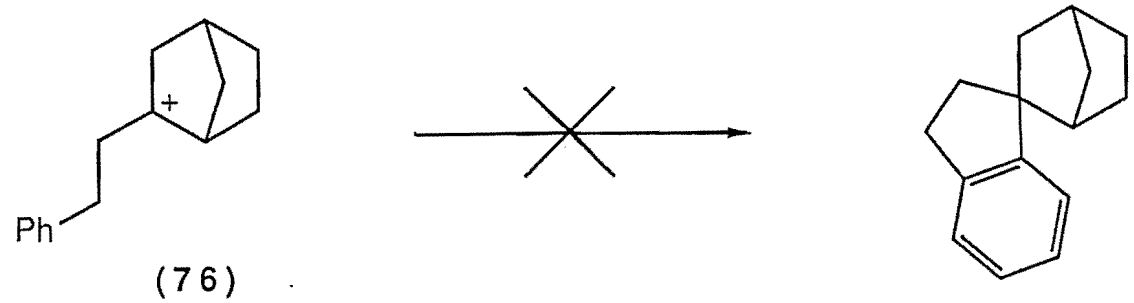
(76) **(78)**

Instead the Wagner Meerwein rearrangement, (76) → (77), occurs. This rearrangement has a lower activation energy than normal tertiary to secondary rearrangements, principally because secondary norbornyl cations have additional stability over normal (classical) secondary cations.[42] This latter fact is also responsible for the lack of formation of a spiro analogue as was observed in the case of the 1-(2-phenylethyl)cyclohexyl cation (62) which gave the spiro product (60). The analogous product (79) is not formed from (76) (Scheme 23) due to the lower activation energy of the Wagner-Meerwein rearrangement of (76) relative to the hydride shift involved in the conversion (62) → (60).

Scheme 23



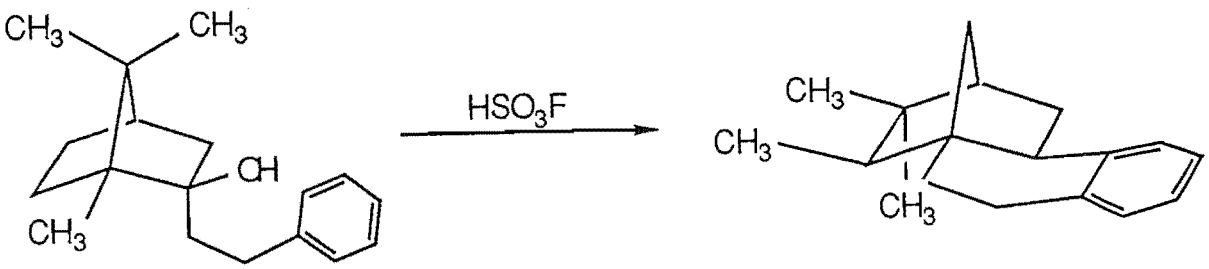
(62) (60)



(76) (79)

The fluorosulfonic acid reaction of 2-*endo*-(2-phenylethyl)-1,7,7-trimethylbicyclo[2,2,1]heptan-2-*exo*-ol (**80**) gave a hydrocarbon which was identified as 13,13,14-trimethyltetracyclo-[10.2.1.$0^{1,10}$.$0^{4,9}$]pentadeca-4,6,8-triene (**81**) (Scheme 24).

Scheme 24

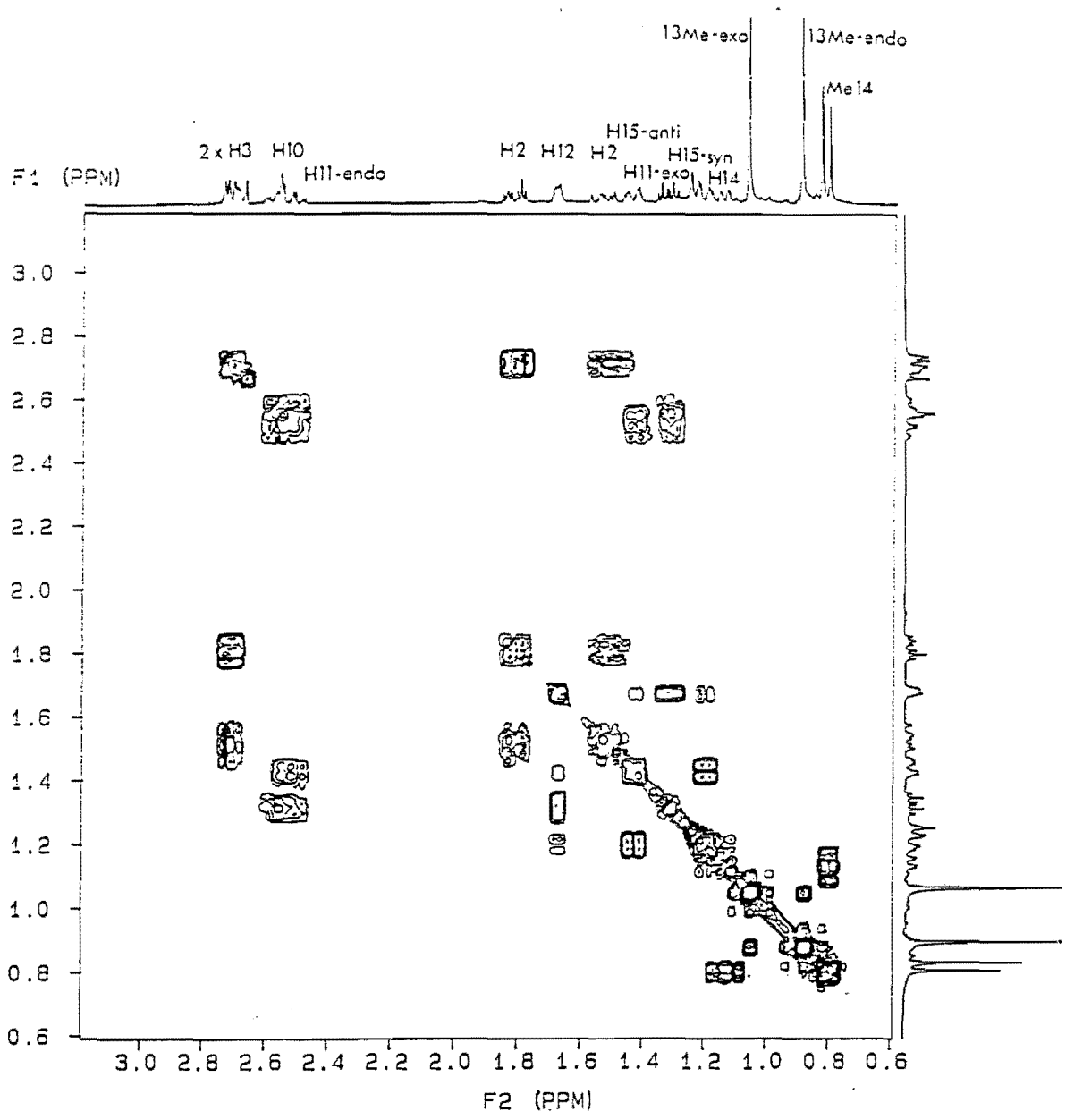


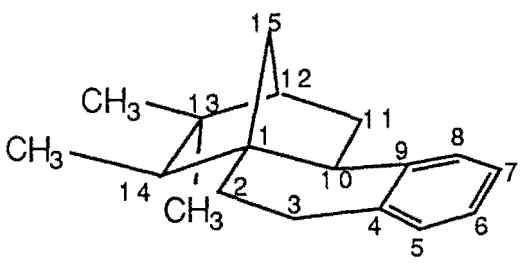
(80) (81)

The structure of (**81**) was determined by NMR. Figure 2 shows a ^{1}H-^{1}H homonuclear two-dimensional correlation spectrum for this compound along with the normal one-dimensional spectrum plotted along the axes. All signals for non-equivalent protons are well resolved in the one-dimensional spectrum, which greatly aids the structure determination. The three methyl groups are in different environments and one of them is coupled to a proton. Figure 2 indicates the presence of an isolated ethylene group with two benzylic protons. Thus there must be a tertiary carbon at the terminus of the ethylene chain attached to the aromatic ring.

Inspection of the coupling pattern for the protons showed typical values for an intact norbornyl group and the presence of only one protonated bridgehead position and that this proton was strongly coupled to only one other *exo*- proton.

Figure 2: ^{1}H-^{1}H homonuclear two-dimensional correlation spectrum of (81)





(81)

This suggested that the C1 bridgehead site is substituted with the ethylene chain. The other protonated bridgehead (H12) had only one *exo*- proton adjacent to it, with the C13-*exo*- position being occupied by a carbon atom, namely a methyl group.

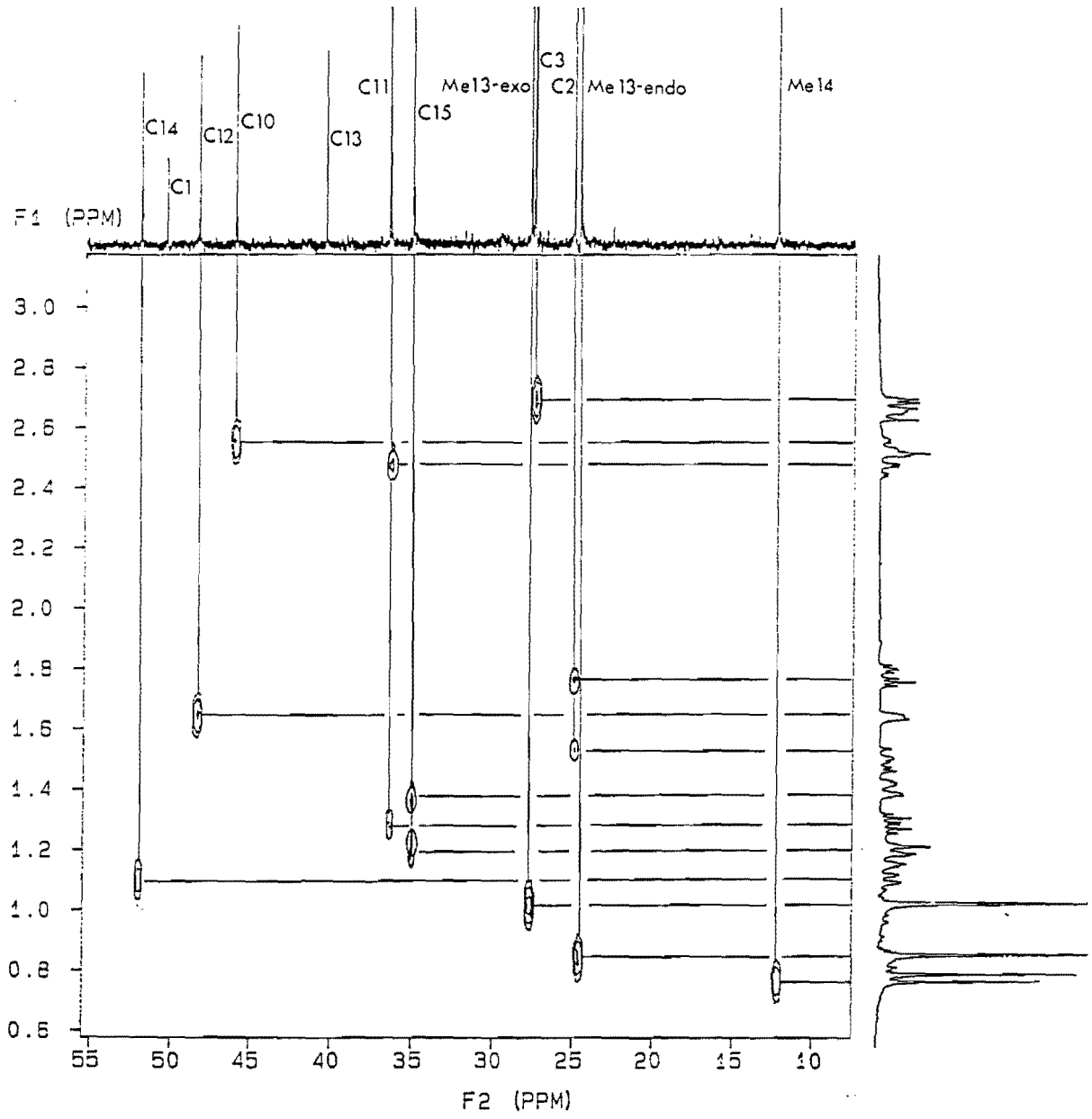
The C11-*exo*- proton coupled to the bridgehead (H12) proton had one other observable geminal coupling to the C11-*endo*- proton and there was no evidence of coupling to any adjacent *exo*- protons. This implied that the C11-*exo*- proton was one of a geminal pair and the *exo* position adjacent to the C11-*exo*- proton was occupied by a carbon atom.

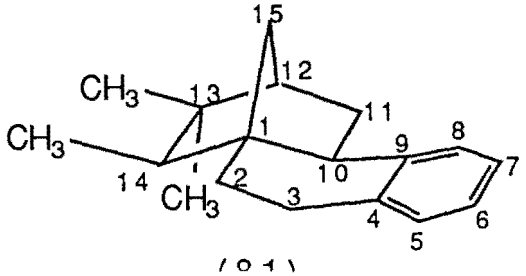
The two other downfield protons at *ca* 2.5 ppm in the ^{1}H NMR spectrum were coupled to each other. In addition to this coupling one proton was coupled to the H11-*exo*- proton and both were weakly coupled to a further proton (H15-*anti*), itself geminally coupled to another (H15-*syn*). Thus the bridge carbon was an unsubstituted methylene group and the aromatic ring was bonded to the norbornyl skeleton in the *exo*- position at C10.

Irradiation of the bridge *syn*- proton lead to the disappearance of a 2.0 Hertz coupling in the proton coupled to the doublet methyl group. This indicated the proton was in the *endo*- position, and therefore the methyl group was in the *exo*- position. There are two isomers **(81)** and **(82)** consistent with the above data and which can not be distinguished on the basis of the ^{1}H NMR spectrum.

Consideration of a ^{1}H-^{13}C two dimensional heteronuclear correlation spectrum (Figure 3), in addition to the information above, allowed complete assignment of the ^{13}C NMR spectrum.

Figure 3: ^{1}H-^{13}C two dimensional heteronuclear correlation spectrum of (81)

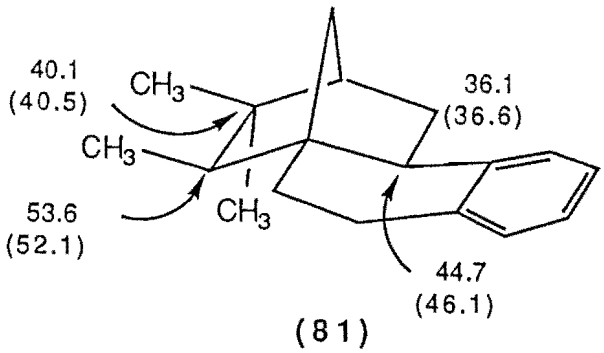




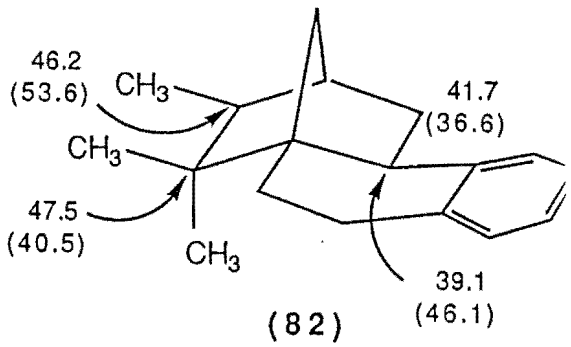
(81)

This in turn allowed a distinction between the structures **(81)** and **(82)** by applying the known[43] substitutent effects for 2,2,3-*exo*-trimethyl substitution in a norbornyl ring to the previously assigned ^{13}C NMR spectrum of the parent structure **(75)**. As shown in Figure 4 this leads to better agreement between calculated and observed chemical shifts for the 13,13,14-trimethyl isomer **(81)** than the alternative 13,14,14-trimethyl isomer **(82)**.

Figure 4: Calculated (and observed) ^{13}C NMR chemical shifts for (81) and (82).



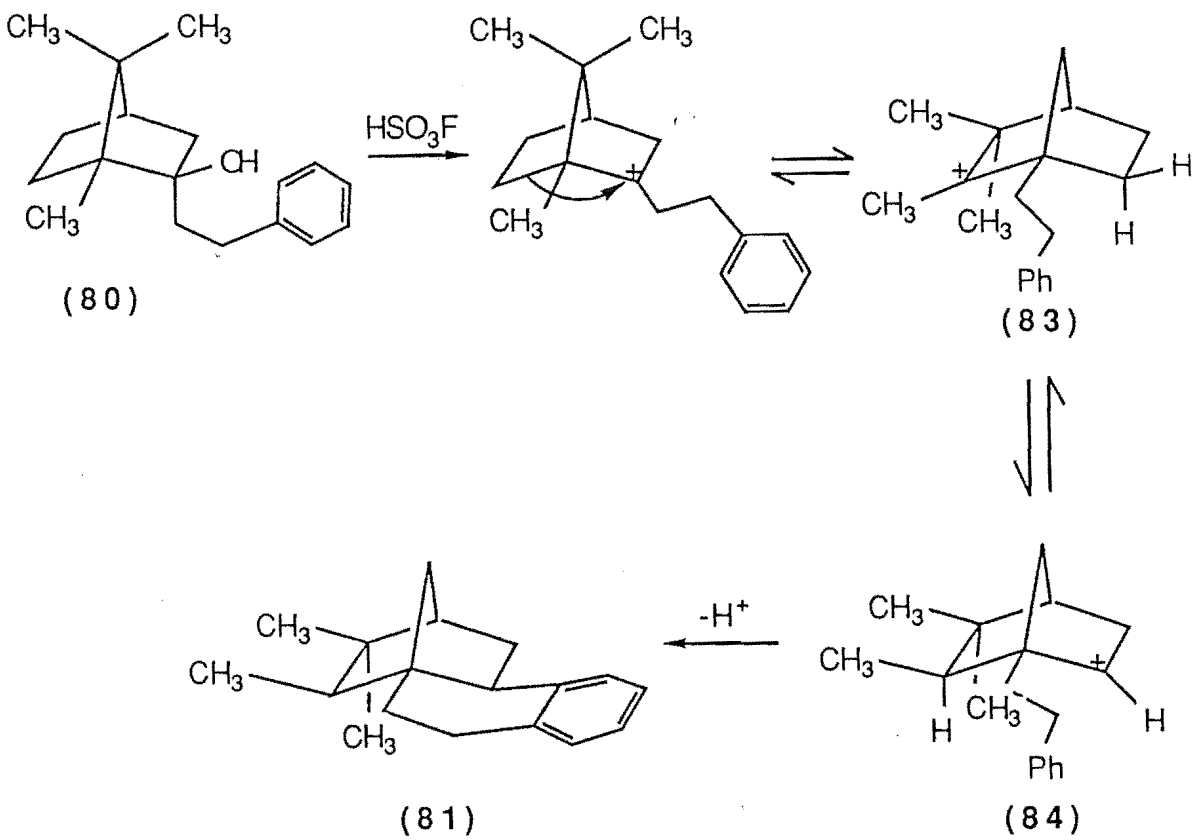
(81)



(82)

Furthermore, the formation of **(81)** is straightforwardly rationalised as shown in Scheme 25. The mechanism of formation of the trimethyl product **(81)** differs from that of the parent (unsubstituted) analogue **(75)** in that there is an additional step involved. In particular the Wagner-Meerwein rearranged cation **(83)** does not undergo cyclisation as was observed for **(77)**. Instead the tertiary cation **(83)** undergoes a facile[9] 6,2-hydride shift to give the secondary cation **(84)** which then cyclises to **(81)**.

Scheme 25



(80) (83) (84) (81)

The resistance of **(83)** towards cyclisation is steric in origin and consistent with the fact[44] that tertiary norbornyl cations react with nucleophiles preferentially as the secondary Wagner-Meerwein rearranged cations with which they are in equilibrium.

CHAPTER 4

REACTIONS OF PHENYLPROPYL CARBINOLS.

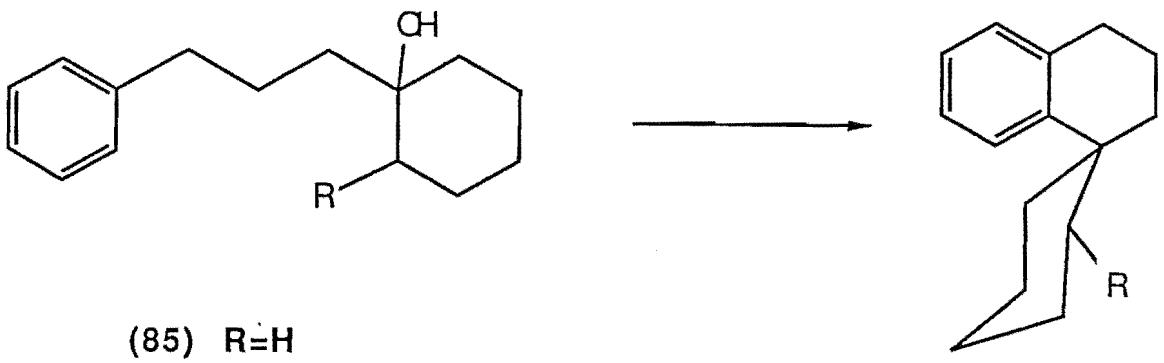
Chapter 4: Reactions of Phenylpropyl Carbinols

The reactions discussed above for benzyl carbinols (chapter 2) and phenylethyl carbinols (chapter 3) showed some important differences in the reaction course due to the presence of the extra methylene group. Thus it seemed of interest to examine the effect of the introduction of a further methylene group between the phenyl ring and the initially generated carbocationic centre. On the basis of the results described above it seemed likely that cyclisation would be the predominant reaction mode, given that the extra methylene group would allow cyclisation with the formation of a six membered ring without rearrangement. This chapter therefore describes the reactions of selected 3-phenylpropyl carbinols.

Phenylpropylcycloalkanols.

Reaction of 1-(3-phenylpropyl)cyclohexanol **(85)** with fluorosulfonic acid proceeded smoothly to give a single hydrocarbon in 82% yield (Scheme 26).

Scheme 26



(85) R=H
(87) R=CH_3

(86) R=H
(88) R=CH_3

The symmetry observed in the ^{13}C NMR spectrum immediately identified the product as the known[45] compound spiro[cyclohexane-1,1-tetralin] **(86)**, which is formed by cyclisation of the initially generated carbocation without rearrangement. In the reaction of 1-(2-phenylethyl)cyclohexanol strain energy factors provided a barrier to formation of the spiro compound which was sufficient to allow competitive reaction via a less favoured secondary carbocation. In the case of 1-(3-phenylpropyl)cyclohexanol **(85)** the formation of the six membered spiro ring is the lowest energy pathway available because it does not have the same strain energy barrier as in the reaction of 1-(2-phenylethyl)cyclohexanol. Thus whereas with 1-(2-phenylethyl)cyclohexanol there was a mixture of products observed, in the 1-(3-phenylpropyl)cyclohexanol case the spiro product is formed cleanly and in high yield.

In the fluorosulfonic acid reaction of 2-methyl-1-(3-phenylpropyl)cyclohexanol **(87)** introduction of a methyl group alpha to the position of initial carbocation formation does not result in formation of the seven membered ring product analogous to the product formed from 2-methyl-1-(2-phenylethyl)cyclohexanol. In fact the product formed, cleanly and in high yield, is *trans*-2-methyl-spiro[cyclohexane-1,1-tetralin] **(88)** which again results from cyclisation without rearrangement. It is notable that this reaction proceeds with exclusive diastereoselective formation of the single stereoisomer. Both the increase in the barrier for cyclisation to give a seven membered ring and the decrease in the energy barrier of formation of a six membered spiro ring over that for a five membered spiro ring interact in such a way that reaction via spiro ring formation is preferred over reaction via hydride mig-

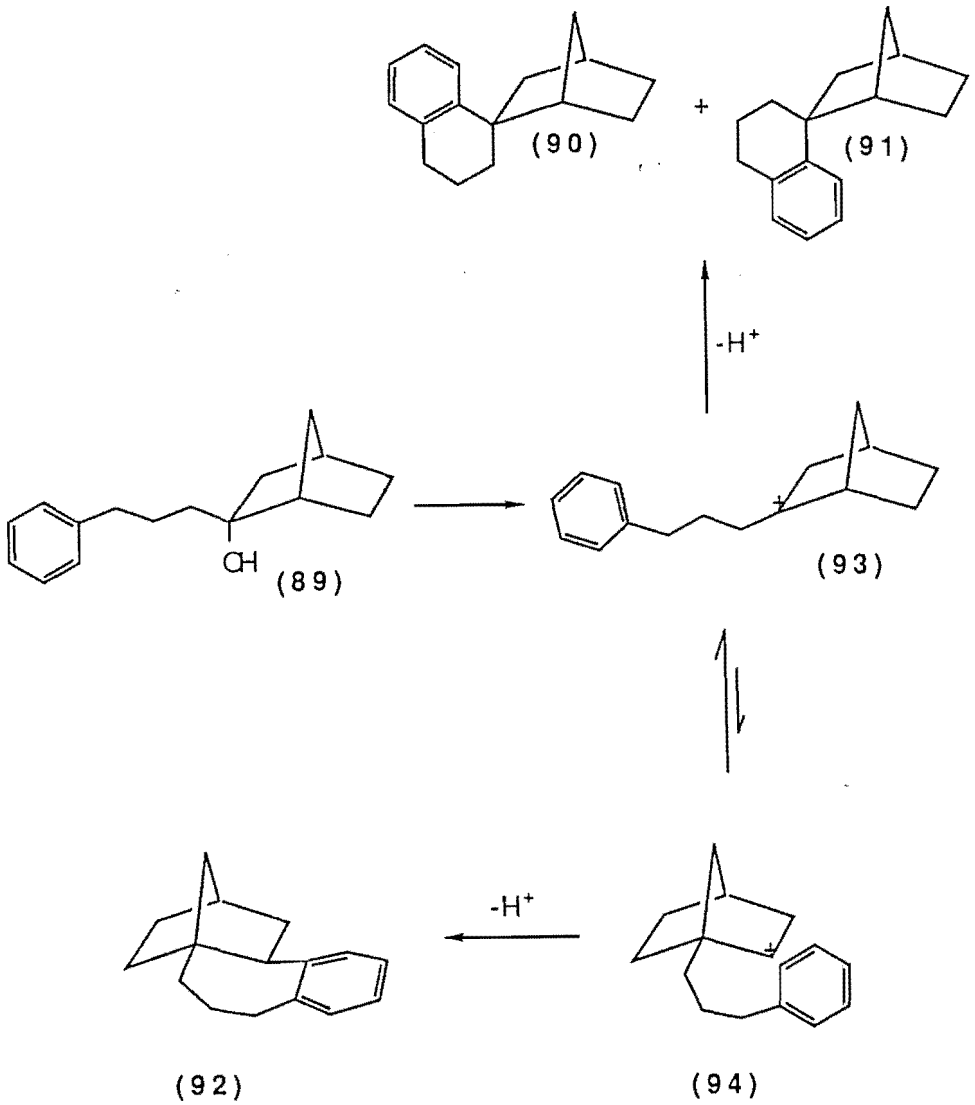
ration. Thus the 3-phenylpropyl carbinols **(85)** and **(87)** both react differently from the analogous benzyl and 2-phenylethyl carbinols.

Reaction of 2-*exo*-(3-phenylpropyl)bicyclo[2,2,1]heptan-2-*endo*-ol **(89)** with fluorosulfonic acid at -70°C gave a mixture of three hydrocarbons in a ratio of 2:1:1. Attempts to separate the mixture by a variety of methods were unsuccessful. However the products were tentatively identified on the basis of the NMR spectra of the mixture as the two spiro hydrocarbons, **(90)** and **(91)**, and the tetracyclic compound **(92)** (Scheme 27). The spiro products, **(90)** and **(91)**, would result from direct cyclisation without rearrangement, from the *exo*- and *endo*- faces respectively, of the tertiary norbornyl cation **(93)**, while **(92)** would result from cyclisation of the Wagner-Meerwein rearranged cation **(94)**. Spiro product formation from **(89)** but not from the 2-phenylethyl analogue **(74)** is again favoured by the formation of a six membered ring.

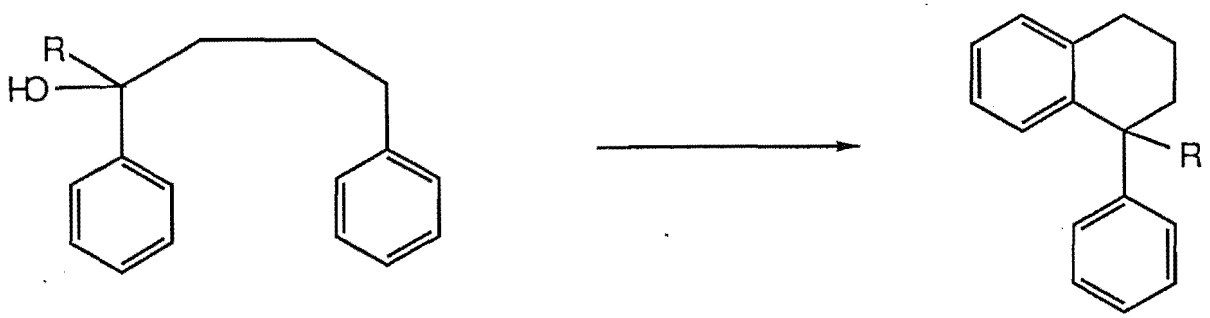
1,4 Diphenylbutanols.

Reaction of 1,4-diphenylbutan-1-ol **(95)** with fluorosulfonic acid gave 1-phenyl-1,2,3,4-tetrahydronapthalene **(96)** in a clean, high yielding reaction. Similarly reaction of 2,5-diphenylpentan-2-ol **(97)** gave an analogous product, namely 1-methyl-1-phenyl-1,2,3,4-tetrahydronapthalene **(98)** also in a clean and high yielding reaction (Scheme 28). Since in these cases the cations initially formed are stabilised by the aromatic ring no rearrangements are expected or observed and cyclisation occurs smoothly.

Scheme 27



Scheme 28

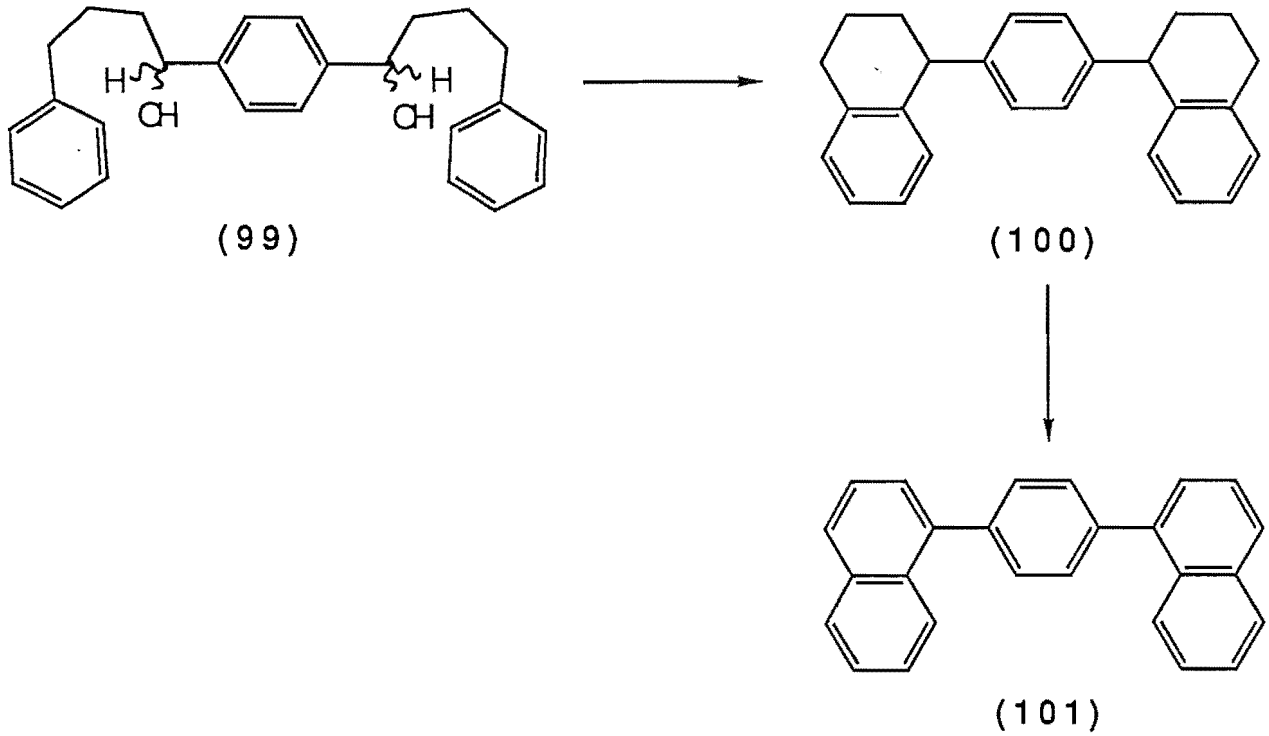


(95) R= H
(97) R= CH_3

(96) R=H
(98) R=CH_3

The high yields of the above reactions prompted an extension of these reactions to a short synthesis of 1,4-di-(1-naphthyl)benzene (**101**), as outlined in Scheme 29.

Scheme 29



(**99**) (**100**) (**101**)

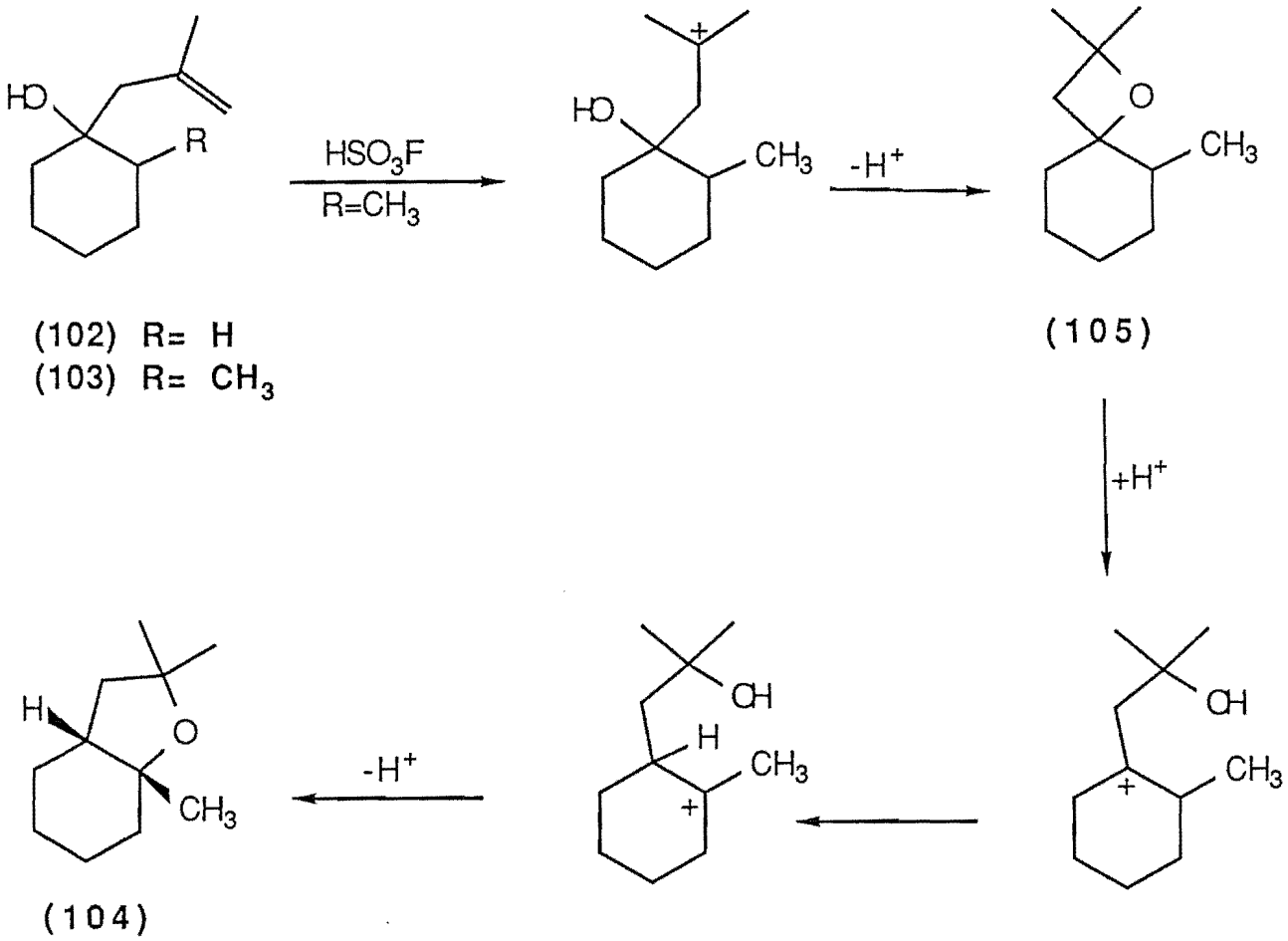
Thus reaction of 1,4-di-(1-hydroxy-4-phenylbutan-1-yl)benzene (**99**) gave a mixture of the two diastereoisomers of 1,4-di-(1,2,3,4-tetrahydronapth-1-yl)benzene (**100**) in high yield. This represents a double cyclisation analogous to that resulting from the reaction of (**95**). The partially saturated products (**100**) were then dehydrogenated over Pd/C to give 1,4-di-(1-naphthyl)benzene (**101**) in *ca* 36% yield. Although the yield of the aromatised product was not optimised, this represents a more convenient and efficient method of preparation of (**101**) than that previously reported,[46]

involving organometallic coupling of pre-formed aromatic precursors. Furthermore the construction of the naphthalene rings in Scheme 29 offers considerable versatility in the potential preparation of various substituted derivatives of **(101)**.

Methallyl Alcohols

Some exploratory experiments were conducted with a view to extending the above studies to substrates where the phenyl ring is replaced by a vinyl group. Thus the methallyl carbinols **(102)** and **(103)** (Scheme 30) were reacted with fluorosulfonic acid at -70°C (Scheme 30).

Scheme 30



While alcohol **(102)** underwent polymerisation 1-(2-methyl-2-propenyl)-2-methylcyclohexanol **(103)** gave a modest yield of a product which was identified as the tetrahydrofuran **(104)**. This product is considered to be formed via the intermediacy of an oxetan **(105)**. The only report of an analogous reaction with HSO_3F is that by Kelly *et al*[47] who observed the formation of 6a-methylhexahydro-2,6-methano-2H-cyclopenta[*b*]furan from 8-methyl-*endo*-tricyclo[3,2,1,$0^{2,4}$]octan-*syn*-8-ol.

The success of the reaction of **(103)** with HSO_3F suggests that this area of research could be productive and worthy of further investigation.

CHAPTER 5

CONCLUSIONS

Chapter 5: Conclusion

The reactions of a series of selected benzyl, 2-phenylethyl and 3-phenylethyl carbinols with fluorosulfonic acid have been studied.

The use of fluorosulfonic acid for reactions with aryl alcohols is restricted to temperatures below 0°C in order to avoid fluorosulfonation of the aryl ring. Thus use is limited to those alcohols which ionise below 0°C. The reaction solvent must be selected so that the reaction medium remains mobile at low temperature and the solvent is not susceptible to attack by either the acid or the cations generated in the reaction.

For the benzyl carbinols a variety of reaction pathways were found, including dimerisation, reduction, ring expansion and cyclisation. In contrast phenylethyl and phenylpropyl carbinols underwent cyclisation either with or without prior rearrangement. The reaction course for all substrates was dependent on both the nature of the aralkyl group and the carbon skeleton.

In a limited number of systems reaction with HSO_3F followed the same course as that induced by other acid reagents. Reactions of substrates with fluorosulfonic acid which parallel those observed for other acid reagents result when there are no alternative reaction pathways possible due to the simplicity of the substrate. For example the reaction of 3-methyl-1-phenylbutan-2-ol gave 1,1-dimethylindane with fluorosulfonic acid and with sulphuric acid. However at the reaction temperature required to effect rearrangement with HSO_3F the product underwent fluorosulfonation.

New reaction pathways were found, however, which establish fluorosulfonic acid as a reagent in selected synthetic applications. Several new reaction pathways were observed in the study of the benzyl carbinols where rearrangements other than cyclisation to form 5 and 6 membered rings structures occurred. For example the reaction of 1-benzyl-3-methylcyclohexanol with HSO_3F underwent reduction rather than cyclisation. The thermodynamic preference for cyclisation to produce a 6-membered ring compared with a 5-membered ring was synthetically utilised in the reaction of 1-benzyl-*trans*-decalin-1-ol to give the natural product (±)-9a-carba-14α-morphinan. An attempt to synthesise podocarpatriene from 1-(2-phenylethyl)-2,2,6-trimethylcyclohexanol was, however, not successful because, in this case, tertiary cation production via methyl migration is preferred over that via hydride migration and 1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene was formed.

The final synthetic study involved a system with two reactive centers. 1,4-Di-(1-hydroxy-4-phenylbutan-1-yl)benzene gave the two diastereoisomeric 1,4-di-(1,2,3,4-tetrahydronapth-1-yl)-benzenes in high yield. The ready oxidation of these products to give the aromatic 1,4-di-(1-naphthyl)benzene, provides an efficient route to such substrates.

The work described in this thesis demonstrates the usefulness of superacid induced rearrangements in synthesis.

EXPERIMENTAL SECTION A

ALCOHOL

PREPARATIONS.

Experimental Section

General.

Infrared spectra were recorded on a Shimadzu IR27G or Pye Unicam SP3-300 spectrophotometer. Mass spectra were recorded on an A.E.I. MS902 or Kratos MS80RFA spectrometer. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 $P.F._{254}$ 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 using the well established pulse sequence and phase cycling of Bax, Freeman and Morris.[48] Typically $128t_1$ increments were employed and after Fourier transformation the final 512x512 spectrum was symmetrised 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.[49] Some ^{13}C NMR spectral assignments were made by ^1H-^{13}C two-dimensional heteronuclear correlation spectroscopy which was recorded in the usual manner,[50] typically as a 128 x 1K matrix. 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 either benzylmagnesium chloride, 2-phenylethylmagnesium bromide or 3-phenylpropyl-magnesium chloride and the appropriate ketone in the usual manner. Purification of the alcohols were carried out by recrystallisation or column chromatography and reaction yields were typically 80%.

Reactions with Fluorosulfonic Acid.

To a vigorously stirred mixture of fluorosulfonic acid (2 ml) in dry dichloromethane (2 ml) at -78°C was added a solution of the alcohol (*ca* 2 mmole) in dichloromethane (2 ml) and the resulting mixture stirred at -78°C for 30 minutes, unless otherwise indicated. The mixture was then added cautiously to water (40 ml) neutralised with $NaHCO_3$ and the mixture then extracted repeatedly with diethyl ether. The combined ether extracts were washed with $NaHCO_3$, dried and concentrated to give a crude product which was purified by bulb-to-bulb distillation or by chromatography on alumina.

Experimental A
Preparation of Alcohols

Section 1 (Benzyl carbinols).

1-Benzyl-2-methylcyclohexanol (1)[51] was prepared from 2-methylcyclohexanone and benzylmagnesium chloride. Purification was carried out by absorption of the product onto a radial chromatograph plate followed by elution with petroleum ether to give a single isomer of the alcohol as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.25 (5H, ArH), 3.00, 2.62 (AB, J= 14Hz, 2H, $ArCH_2$), 1.75-0.60 (m, 10H, CH_2's and H2), 1.05 (d, J= 5Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.5 (CH_3), 21.7 (C5), 25.5 (C4), 30.8 (C3), 36.3 (C6), 38.7 (C2), 46.6 ($Ar\underline{C}H_2$), 72.9 (C1), 126.2 (*para*), 128.0 (*meta*), 130.6 (*ortho*), 137.8 (*ipso*).

1-Benzylcyclohexanol (3)[52] was prepared from cyclohexanone and benzylmagnesium chloride to give the alcohol as a white crystalline solid. M.p. 58-59°C (Lit.[52] M.p. 61-62°C). ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.13 (s, 5H, ArH), 2.73 (s, 2H, $ArCH_2$), 1.53 (s, 10H, CH_2's), 1.23 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ_C 22.1 (2C, C3 and C5), 25.8 (C4), 37.3 (2C, C2 and C6), 48.8 ($Ar\underline{C}H_2$), 71.1 (C1), 126.3 (*para*), 128.0 (*meta*), 130.7 (*ortho*), 137.3 (*ipso*).

1-Benzylcyclopentanol[52] was prepared from cyclopentanone and benzylmagnesium chloride to give the alcohol as a white crystalline solid. M.p. 57-59°C (Lit.[52] M.p. 58-60°C). ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.23 (5H, ArH), 2.84 (s, 2H, $ArCH_2$), 1.63 (m, 8H, CH_2's), 1.40 (s, 1H, OH).

1-(*para*-Methylbenzyl)cyclopentanol was prepared from cyclopentanone and *para*-methylbenzylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with petroleum ether/ether (1:1) gave the alcohol as a pale yellow oil. $\upsilon_{max.}$ 3450, 1520, 1110, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.13 (s, 4H, ArH), 2.84 (s, 2H, $ArCH_2$), 2.33 (s, 3H, CH_3), 1.82-1.55 (m, 9H, CH_2's and OH). ^{13}C NMR ($CDCl_3$) δ_C 21.1 (CH_3), 23.6 (2C, C3 and C4), 39.4 (2C, C2 and C5), 46.7 ($Ar\underline{C}H_2$), 82.2 (C1), 128.9 (*meta*), 129.9 (*ortho*), 135.9 (*para*), 136.6 (*ipso*). Calc. for $C_{13}H_{18}O$: M^+, 190.1358. Found: M^+, 190.1357.

6-Benzylspiro[4.5]decan-6-ol (4) was prepared, in 50% yield, from benzylmagnesium chloride and spiro[4.5]decan-6-one[53] which had been prepared previously by a pinacol rearrangement. Purification was carried out by column chromatography on alumina. Elution with petroleum ether /ether (1:1) gave the alcohol as a clear oil. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.25 (m, 5H, ArH), 2.86 and 2.82 (dd, J_{AB}= 13.4 Hz, 2H, $ArCH_2$), 2.03 (m, 1H), 1.80 (m, 1H), 1.72-1.25 (m, 15H). ^{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*). Calc. for $C_{17}H_{24}O$: M^+, 244.1827. Found: M^+, 244.1811.

1-Benzyl-*trans*-decalin-1-ol (6) was prepared from *trans*-1-decalone and benzylmagnesium chloride 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. $\upsilon_{max.}$ 3525, 2950, 1510, 1460, 745, 715 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H 7.25 (m, 5H, ArH), 2.94 and 2.62 (dd, J= 13.2Hz, 2H, $ArCH_2$), 2.04 (m,

1H), 1.85 (m, 1H), 1.64 (m, 2H), 1.55-1.22 (m, 10H), 1.02-0.84 (m, 2H). ^{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*). Calc. for $C_{17}H_{24}O$: M^+-18, 226.1722. Found: M^+-18, 226.1725. Calc. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.0; H, 10.3.

1-Benzyl-3-methylcyclohexanol (10) was prepared from 3-methylcyclohexanone and benzylmagnesium chloride to give the alcohol as an oil, in 85% yield, which was a 1:4 mixture of *trans*:*cis* isomers. ^1H 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). ^{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. Calc. for $C_{14}H_{20}O$: C, 89.29; H, 10.71. Found: C, 88.57; H, 11.06.

1-Benzyl-4-methylcyclohexanol (11)[19a] was prepared from 4-methylcyclohexanone and benzylmagnesium chloride to give a mixture of the two diastereomeric alcohols as an oil. ^1H NMR ($CDCl_3$, 60 MHz) δ_H 2.80 ($ArCH_2$*cis*), 2.70 ($ArCH_2$*trans*).

2-*exo*-Benzylbicyclo[2.2.1]heptan-2-*endo*-ol (14)[54] was prepared from bicyclo[2,2,1]heptan-2-one and benzylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with petroleum ether gave the alcohol as a white crystalline solid. M.p. 64-65.5°C (Lit.[54] M.p. 61-63°C). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.23 (5H, ArH), 2.80 (2H, $ArCH_2$), 2.67-0.60 (11H, CH_2 and OH). ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 28.6 (C5), 37.4

(C4), 38.5 (C7), 45.6 (C3), 45.8 (C1), 47.9 (Ar$\underline{C}H_2$), 79.2 (C2), 126.4 (*para*), 128.2 (*meta*), 130.6 (*ortho*), 137.8 (*ipso*).

Deuterated alcohols (22-24) and (30).

Alcohols **(22)-(24)** were prepared by reaction of benzylmagnesium chloride with the appropriate deuterated norcamphor.[55] The extent of deuterium incorporation in the product alcohols was determined by mass spectrometry to be > 90% D_2 for **(22)**, > 95% D_1 for **(23)** and > 85% D_1 for **(24)**. The stereochemical location of the deuterium was determined by ^2H NMR spectroscopy by integration of the signals at 1.75 ppm (*exo*-D3) and 1.13 ppm (*endo*-D3) and shown to be > 95% stereochemically pure in each case. The ^1H and ^{13}C NMR spectra were consistent with these results. Alcohol **(30)** was prepared by reaction of norcamphor with the Grignard reagent prepared from α,α-dideuteriobenzyl chloride.[56] The mass spectrum and NMR spectra indicated > 95% D_2 incorporation.

3,3-Dideuteriobicyclo[2,2,1]heptan-2-one[55] was prepared by the literature method. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 2.66 (1H, H1), 2.58 (1H, H4), 2.06-2.00 (0.25H, H3-*exo*), 1.89-1.69 (3.25H, CH_2), 1.60-1.38 (3H, CH_2). ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 2.01 (0.75^2H, ^2H3-*exo*), 1.79 (0.75^2H, ^2H3-*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-*exo*-Benzyl-3,3-dideuteriobicyclo[2,2,1]heptan-2-*endo*-ol (22) was prepared from 3,3-dideuteriobicyclo[2,2,1]-heptan-2-one and benzylmagnesium chloride. Purification was carried out by column chromatography on 10% deactivated alumina. Elution with petroleum ether gave the alcohol as a white crystalline

solid. M.p. 60°-61°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.35-7.20 (5H, ArH), 2.88, 2.77 (AB, J= 13.5Hz, 2H, $ArCH_2$), 2.25 (1H, H1), 2.13 (1H, H4), 1.95-1.2 (7H, CH_2's and OH). ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 1.75 (1^2H, ^2H-*exo*), 1.11 (1^2H, ^2H-*endo*). ^{13}C NMR ($CDCl_3$) δ_C 22.2 (C6), 28.6 (C5), 37.4 (C4), 38.6 (C7), C3 not obs, 45.7 (C1), 47.9 (C8), 79.1 (C2), 126.4 (*para*), 128.2 (*meta*), 130.4 (*ortho*), 137.6 (*ipso*).

3-*exo*-Deuteriobicyclo[2,2,1]heptan-2-one was prepared in the following manner. To a solution of norcamphor (2g) in distilled dioxane (20ml) and D_2O (4ml), was carefully added Na chips (0.5g). After the sodium had all reacted the mixture was stirred for 20 hours at 48°C. The reaction mixture was then poured into a 1% solution of H_2SO_4 (50ml) and repeatedly extracted with ether. The organic layer was repeatedly washed with H_2O then dried over anhydrous magnesium sulphate after which the solvent was removed under reduced pressure to yield the ketone as a white crystalline solid (1.2g). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 2.65 (1H, H1), 2.58 (1H, H4), 1.88-1.65 (4H, CH_2), 1.61-1.35 (3H, CH_2). ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 2.05 (1^2H, ^2H3-*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).

2-Benzyl-3-*exo*-deuteriobicyclo[2,2,1]heptan-2-ol (23) was prepared from *exo*-3-deuteriobicyclo[2,2,1]heptan-2-one and benzylmagnesium chloride. Purification was carried out by column chromatography on 10% deactivated alumina. Elution with petroleum ether gave the alcohol as a white crystalline solid. M.p. 63-64°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.39-7.18 (5H, ArH), 2.88, 2.77 (AB, J= 13.5Hz, 2H, $ArCH_2$), 2.25 (1H, H1), 2.13 (1H, H4), 1.95-1.17 (7H,

CH_2's and OH), 1.12 (0.9H, H3). ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 1.55 (1^2H, $^2H3$-*exo*), 1.12 (0.08^2H, $^2H3$-*endo*). ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 28.6 (C5), 37.4 (C4), 38.6 (C7), 45.4 (t, C3), 45.7 (C1), 47.9 (C8), 79.2 (C2), 126.5 (*para*), 128.3 (*meta*), 130.6 (*ortho*), 137.7 (*ipso*).

3-*endo*-Deuteriobicyclo[2,2,1]heptan-2-one was prepared in the following manner. To a solution of 3,3-dideuteriobicyclo-[2,2,1]heptan-2-one (0.75g) in distilled dioxane (7ml) was added H_2O (15ml) and NaOH (15mg). The resulting mixture was stirred for 10 hours at room temperature. To the reaction mixture was added H_2O (25ml) and then it was extracted with ether (4x 75ml). The organic phase was washed with H_2O (4x 300ml) and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure to yield the ketone as a white crystalline solid (0.2g). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 2.65 (1H, H1), 2.58 (1H, H4), 2.10-1.98 (1.1H, H3), 1.88-1.66 (3H, CH_2), 1.59-1.36 (3H, CH_2). ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 1.86 (1^2H, $^2H3$-*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).

2-Benzyl-3-*endo*-deuteriobicyclo[2,2,1]heptan-2-ol (24) was prepared from *endo*-3-deuteriobicyclo[2,2,1]heptan-2-one and benzylmagnesium chloride. Purification was carried out by column chromatography on 10% deactivated alumina. Elution with petroleum ether gave the alcohol as a white crystalline solid M.p. 63-64°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.40-7.17 (5H, ArH), 2.88, 2.77 (AB, J= 13.5Hz, 2H, $ArCH_2$), 2.25 (1H, H1), 2.13 (1H, H4), 1.90-1.20 (8H, CH_2's and OH), ^2H NMR ($CHCl_3$, 46 MHz) δ_{2H} 1.15 (1^2H, ^2H-

endo), ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 28.6 (C5), 37.3 (C4), 38.6 (C7), 45.7 (C1), 47.9 (C8), 79.2 (C2), 126.5 (*para*), 128.3 (*meta*), 130.6 (*ortho*), 137.7 (*ipso*).

2-(α,α-Dideuteriobenzyl)bicyclo[2,2,1]heptan-2-ol (30) was prepared in the following manner. To a solution of $LiAlD_4$ (1gm) in dry ether (10 ml) was added a solution of ethyl benzoate (3.3 gm) in dry ether (30 ml). The resulting mixture was kept under reflux for five hours afterwhich any excess $LiAlD_4$ was destroyed by the addition of crystals of sodium sulphate decahydrate and the mixture was then diluted with sulphuric acid (1%). The solution was then extracted with ether and the organic layer was washed with H_2O. The organic layer was dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure. Purification was carried out by column chromatography on alumina. Elution with ether gave α,α-dideuteriobenzyl alcohol as a pale oil. The alcohol (0.5 gm) was then added to concentrated HCl (10 ml) and the mixture was stirred for seven days afterwhich H_2O (10 ml) was added and the solution was extracted several times with ether. The organic layer was washed with a $NaHCO_3$ solution, dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure. Purification was carried out on a short alumina filtration column to give α,α-dideuteriobenzyl chloride as a clear oil. The α,α-dideuteriobenzyl chloride was used to produce α,α-dideuteriobenzylmagnesium chloride which was reacted with bicyclo[2,2,1]heptan-2-one to give **2-(α,α-dideuteriobenzyl)-bicyclo[2,2,1]heptan-2-ol (30)** as a white crystalline solid. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.35-7.23 (m, 5H, ArH), 2.25 (m, 1H, H1), 2.13 (m, 1H, H4), 1.95-1.25 (m, 9H, 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 obs, 79.2 (C2), 126.5 (*para*), 128.3 (*meta*), 130.5 (*ortho*), 137.6 (*ipso*).

2-*exo*-Benzyl-3,3-dimethylbicyclo[2.2.1]heptan-2-*endo*-ol (32)[57] was available in this department. ^{1}H NMR (60 MHz, CCl_4) δ_H 7.71 (s, ArH), 2.75 (s, $ArCH_2$), 1.10 (s, $C3CH_3$), 0.97 (s, $C3CH_3$), 2.30-1.00 (m, 8H). ^{13}C NMR ($CDCl_3$) δ_C 21.1 (C6), 21.5 ($C3\underline{C}H_3$-*endo*), 24.2 (C5), 26.6 ($C3\underline{C}H_3$-*exo*), 34.5 (C7), 42.9 (C3), 43.2 ($Ar\underline{C}H_2$), 45.8 (C1), 50.4 (C4), 79.8 (C2), 126.3 (*para*), 128.2 (*meta*), 131.0 (*ortho*), 138.9 (*ipso*).

2-*exo*-Benzyl-1,3,3-trimethylbicyclo[2.2.1]heptan-2-*endo*-ol (36)[57] was available in this department. ^{1}H NMR (CCl_4, 60 MHz) δ_H 7.28 (m, 5H, ArH), 2.83 (s, 2H, $ArCH_2$), 1.07 (s, 3H, CH_3) 0.93 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 2.30-0.30 (m, 7H, CH_2's and CH). ^{13}C NMR ($CDCl_3$) δ_C 18.0 ($C1\underline{C}H_3$), 22.6 ($C3\underline{C}H_3$-*endo*), 25.1 (C5), 28.5 ($C3\underline{C}H_3$-*exo*), 30.7 (C6), 41.1 (C7), 42.1 ($Ar\underline{C}H_2$), 44.9 (C3), 50.3 (C4), 53.6 (C1), 81.8 (C2), 125.7 (*para*), 127.9 (*meta*), 130.5 (*ortho*), 140.4 (*ipso*).

Spiro[Bicyclo[2,2,1]heptan-3-one-2,1'-cyclopentane][58] was prepared in the following manner. To a stirred mixture of sodium amide (2g) in dry ether (10ml) was added dropwise a solution of bicyclo[2,2,1]heptan-2-one (1g) in dry ether (10ml). To this was carefully added a solution of 1,4 dibromobutane (2g) in dry ether (20ml). The reaction mixture was then stirred for 12 hours at room temperature. A mixture of ethanol (70ml) and H_2O (4ml) was added, the organic layer was then separated and the aqueous

layer was then extracted several times with ether. The organic layer was dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure. Purification was carried out by absorption onto a radial chromatograph plate followed by elution with petroleum ether to give the ketone in 80% yield. ^{13}C NMR ($CDCl_3$) δ_C 23.9, 26.8, 26.3, 25.4, 32.7, 36.0, 36.4, 46.5, 49.8. Mass Spectrum: 164 (24), 146 (11), 136 (26), 107 (9), 95 (100).

Spiro[3-*exo*-benzylbicyclo[2,2,1]heptan-3-*endo*-ol-2,1'-cyclopentane] (41) was prepared from spiro[bicyclo[2,2,1]heptan-3-one-2,1'cyclopentane][58] and benzylmagnesium chloride. Purification was carried out by absorption of the product onto a radial chromatograph plate followed by elution with petroleum ether to give the product as a yellow oil. (Yield 20%) $\upsilon_{max.}$ 3620, 1520, 1480, 720, 770 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz) δ_H 7.10 (s, 5H, ArH), 2.68 (s, 3H, $ArCH_2$), 2.16-0.80 (20H, CH_2). ^{13}C NMR ($CDCl_3$) δ_C 21.6 (C5), 23.2 (2C, 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*), Calc. for $C_{18}H_{24}O$: M^+, 256.1827. Found: M^+, 256.1822.

3-Methyl-1-phenylbutan-2-ol (49)[59] was prepared from 2-methylpropanal and benzylmagnesium chloride to give the alcohol as a pale yellow oil. $\upsilon_{max.}$ 3320, 750, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz) δ_H 7.13 (5H, ArH), 3.43 (m, 1H, H2), 2.69 (d, J= 4Hz, 2H, $ArCH_2$), 1.63 (m, 1H, H3), 0.98 (d, J= 6.5Hz, 3H, CH_3), 0.97 (d, J= 6.5Hz, 3H, CH_3).

1-(*para*-Methylphenyl)-3-methylbutan-2-ol (54) was prepared from 2-methylpropanal and *para*-methylbenzylmagnesium chloride to give the alcohol as a pale yellow oil. $\upsilon_{max.}$ 3420, 1525, 1045, 1000, 800cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.12 (s, 4H, ArH), 3.56 (m, 1H, H2), 2.83 (dd, J= 13.6, 3.6Hz, 1H, $ArCH_2$), 2.57 (dd, J= 13.6, 9.3, 1H, $ArCH_2$), 2.33 (s, 3H, $ArCH_3$), 1.75 (m, 1H, H3), 1.50 (br s, 1H, OH), 0.99 (d, J= 6.9Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 17.5, 19.0 (C4 and C3$\underline{C}H_3$), 21.0 (C3), 33.0 (Ar$\underline{C}H_3$), 40.3 (C1), 77.4 (C2), 128.3, 128.8, 129.1, 129.2 (*ortho* and *meta*), 135.8 (2C, *ipso* and *para*). Calc. for $C_{12}H_{18}O$: C, 80.85; H, 10.22. Found: C, 80.31; H, 10.22.

Section 2 (Phenylethyl carbinols).

2-Methyl-4-phenylbutan-2-ol (56)[60] was prepared from acetone and 2-phenylethylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with petroleum ether/ether (1:5) gave the alcohol as a clear oil in 75% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.23 (m, 5H, ArH), 2.71 (m, 2H, H4), 1.80 (m, 2H, H3), 1.29 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 29.4 (2C, CH_3), 30.8 (C3), 45.8 (C4), 70.9 (C2), 125.7 (*para*), 128.2 and 128.3 (2C, *meta* and *ortho*), 142.4 (*ipso*).

4-Methyl-1-phenylpentan-3-ol (57)[61] was prepared from 2-methyl-propanal and 2-phenylethylmagnesium bromide. Purification was carried out by column chromatography on alumina. Elution with ether gave the alcohol as a clear oil in 92% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.26 (m, 5H, ArH), 3.40 (m, 1H, H3), 2.84 (ddd, 1H, H1), 2.65 (ddd, 1H, H1), 1.74 (m, 3H, H2 and H4), 1.43 (br s, 1H, OH), 0.92 (d, J= 6.0Hz, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 17.3 and 18.9 (2xCH_3), 32.5 (C1), 33.8 (C4), 36.0 (C2), 76.2 (C3), 125.7 (*para*), 128.3 (2C, *meta* and *ortho*), 142.2 (*ipso*).

1-(2-Phenylethyl)cyclohexanol (59)[62] was prepared from cyclohexanone and 2-phenylethylmagnesium bromide. Purification was carried out by column chromatography on 10% deactivated alumina. Elution with ether gave the product as a white crystalline solid M.p. 50-54°C (Lit.[62] M.p. 57°C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.25 (m, 5H, ArH), 2.70 (m, 2H, $ArCH_2$), 1.76 (m, 2H, $ArCH_2C\underline{H_2}$), 1.70-1.15 (m, 11H, CH_2 and OH). ^{13}C NMR ($CDCl_3$) δ_C 22.3 (2C, C3 and C5), 25.9 (C4), 29.5 ($Ar\underline{C}H_2$), 37.6 (2C, C2 and C6), 44.4 ($ArCH_2\underline{C}H_2$), 71.4 (C1), 125.6 (*para*), 128.3 (4C, *ortho* and *meta*), 142.7 (*ipso*).

2-Methyl-1-(2-phenylethyl)cyclohexanol (64)[38] was prepared from 2-methylcyclohexanone and 2-phenylethylmagnesium bromide. Purification was carried out by absorption onto a radial chromatograph plate followed by elution with petroleum ether to give the alcohol as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.20 (m, 5H, ArH), 2.82-2.45 (m, 2H, $ArCH_2$), 2.00-1.20 (m, 12H), 0.93 (d, J= 6Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 14.9 (CH_3), 21.9 (C4), 25.7 (C5), 30.1 ($Ar\underline{C}H_2$), 30.6 (C6), 36.0 (C3), 38.4 (C2), 43.0 ($ArCH_2\underline{C}H_2$), 72.9 (C1), 125.7 (*para*), 128.3 and 128.4 (2C, *ortho* and *meta*), 142.8 (*ipso*).

1-(2-Phenylethyl)-2,2,6-trimethylcyclohexanol (70)[63] was prepared from 2,2,6-trimethylcyclohexanone and 2-phenylethyllithium. Purification was carried out by absorption onto a radial chromatograph plate followed by elution with ether to give the alcohol as an oil in 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.24 (m, 5H, ArH), 2.70 (m, 2H, $ArCH_2$), 1.91 (m, 1H), 1.85 (m, 2H, $ArCH_2C\underline{H}_2$), 1.70-1.10 (m, 7H), 1.02 (d, J= 7Hz, CH_3), 1.02 (s, CH_3), 0.99 (s, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 16.2, 20.4, 25.3, 30.9, 31.4, 33.1, 37.8 (C3), 76.8 (C1), 125.6 (*para*), 128.3 (4C, *ortho* and *meta*), 143.4 (*ipso*). Calc. for $C_{17}H_{26}O$: M^+, 246.1984. Found: M^+, 246.1996.

2-*exo*-(2-Phenylethyl)bicyclo[2,2,1]heptan-2-*endo*-ol (74)[64] was prepared from bicyclo[2,2,1]heptan-2-one and 2-phenylethylmagnesium bromide. Purification was carried out by column chromatography on 10% deactivated alumina. Elution with petroleum ether gave the alcohol as an oil (contaminated with a small amount of *endo*-norbornanol). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H

7.24 (m, 5H, ArH), 2.73 (m, 2H, $ArCH_2$), 2.21 (br s, 1H, H1), 2.14 (br s, 1H, H4), 2.05-1.10 (m, 11H, CH_2 and OH). ^{13}C NMR ($CDCl_3$) δ_C 22.2 (C6), 28.5 (C5), 29.9 ($Ar\underline{C}H_2$), 37.2 (C4), 38.8 (C7), 44.4 ($ArCH_2C\underline{H}_2$), 45.8 (C3), 46.8 (C1), 79.5 (C2), 125.6 (*para*), 128.2 (4C, *ortho* and *meta*), 142.7 (*ipso*). Calc. for $C_{15}H_{20}O$: M+-18, 198.1409. Found: M+-18, 198.1428.

2-*endo*-(2-phenylethynyl)-1,7,7-trimethylbicyclo-[2,2,1]heptan-2-*exo*-ol was prepared according to the literature method.[65] To a mixture of phenylacetylene (2g) in hexamethylphosphoric triamide (5ml) under nitrogen was added n-butyllithium (20ml,1M) and the resulting mixture was stirred for 15 minutes. To this was added 1,7,7-trimethylbicyclo[2,2,1]heptan-2-one (3g) in hexamethylphosphoric triamide (2ml) and the mixture was stirred for 3 hours at room temperature. The resulting mixture was purified by column chromatography on alumina. Elution with a 1:1 solution of petroleum ether and ether gave the alkynol as a white crystalline solid in 60% yield. M.p. 57-58°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.44-7.41 (m, 2H, *ortho*), 7.32-7.28 (m, 3H, *para* and *meta*), 2.33-2.27 (m, 1H, H3-*exo*), 2.05-1.94 (m, 1H, H6-*exo*), 1.97 (d, J= 13.4Hz, 1H, H3-*endo*), 1.82-1.75 (m, 1H, H4), 1.75-1.67 (m, 1H, H5-*exo*), 1.56-1.47 (m, 1H, H6-*endo*), 1.25-1.13 (m, 1H, H5-*endo*), 1.10 (s, 3H, C8$\underline{C}H_3$-*syn*), 1.01 (s, 3H, C1$\underline{C}H_3$), 0.90 (s, 3H, C8$\underline{C}H_3$-*anti*). ^{13}C NMR ($CDCl_3$) δ_C 10.5 (C1$\underline{C}H_3$), 21.1 (C8$\underline{C}H_3$-*syn*), 21.5 (C8$\underline{C}H_3$-*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*). Calc. for $C_{18}H_{22}O$: M+, 254.1672. Found: M+, 254.1681.

2-*endo*-(2-Phenylethyl)-1,7,7-trimethylbicyclo[2,2,1]-heptan-2-*exo*-ol (80) was prepared by shaking in a Parr apparatus overnight a mixture of 2-*endo*-(2-phenylethynyl)-1,7,7-trimethyl-bicyclo[2,2,1]heptan-2-exo-ol (0.2g) in ethyl acetate (5ml) and 5% palladium on carbon under a hydrogen atmosphere. The mixture was then filtered and purified by absorption onto a radial chromatograph plate followed by elution with a 1:3 solution of ether/petroleum ether to give the alcohol as a white crystalline solid in 60% yield. M.p. 40-42°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.32-7.18 (m, 5H, ArH), 2.88-2.77 (m, 1H, H2'), 2.73-2.63 (m, 1H, H2'), 2.03-1.80 (m, 1H), 1.92-1.83 (m, 1H), 1.79-1.65 (m, 3H), 1.68 (br s, 1H, OH), 1.49-1.40 (m, 3H), 1.26 (s, 1H), 1.13 (s, 3H, C1$\underline{C}H_3$), 0.89 (s, 3H, C7$\underline{C}H_3$-*anti*), 0.87 (s, 3H, C7$\underline{C}H_3$-*syn*). ^{13}C NMR ($CDCl_3$) δ_C 10.7 (C1$\underline{C}H_3$), 21.2 (C7$\underline{C}H_3$-*syn*), 21.6 (C7$\underline{C}H_3$-*anti*), 27.1 (C5), 30.5 (C6), 31.1 (C1'), 42.0 (C3), 45.1 (C4), 45.8 (C2'), 49.5 (C7), 52.5 (C1), 81.2 (C2), 125.6 (*para*), 128.3 (4C, *ortho* and *meta*), 143.0 (*ipso*). Calc. for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.26; H, 10.08.

Section 3 (Phenylpropyl carbinols)

1-(3-Phenylpropyl)cyclohexanol (85)[45] was prepared by the literature method and purified by column chromatography on alumina. Elution with petroleum ether/ether (1:9) gave the alcohol as a clear oil (85% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.31-7.13 (m, 5H, ArH), 2.62 (t, J= 7.6Hz, 2H, $ArCH_2$), 1.76-1.25 (m, 16H). ^{13}C NMR ($CDCl_3$) δ_C 22.2 (2C, C3 and C5), 24.8 (C4), 25.8 (C8), 36.4 (C9), 37.4 (2C, C2 and C6), 42.0 (C7), 71.4 (C1), 125.7 (*para*), 128.3 (*meta*), 128.4 (*ortho*), 142.5 (*ipso*).

2-Methyl-1-(3-phenylpropyl)cyclohexanol (87) was prepared from 2-methylcyclohexanone and 3-phenylpropylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with ether gave the alcohol as a clear oil (75% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.32-7.15 (m, 5H, ArH), 2.64-2.57 (m, 2H, $ArCH_2$), 1.66-1.12 (m, 14H), 0.83 (d, J= 6.3Hz, 3H, $C2\underline{C}H_3$). ^{13}C NMR ($CDCl_3$) δ_C 14.8 ($C2\underline{C}H_3$), 21.8 (C4), 25.6 (C5), 25.8 (C8), 30.5 (C3), 36.0 (C6), 36.5 (C9), 37.9 (C2), 40.6 (C7), 73.0 (C1), 125.7 (*para*), 128.3 (*ortho*), 128.4 (*meta*), 142.5 (*ipso*). Calc. for $C_{16}H_{24}O$: C, 82.72; H, 10.41; M^+-18, 214.1731. Found: C, 82.88; H, 10.27; M^+-18, 214.1732.

2-*exo*-(3-Phenylpropyl)bicyclo[2,2,1]heptan-2-*endo*-ol (89)[66] was prepared from bicyclo[2,2,1]heptan-2-one and 3-phenylpropylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with ether gave the alcohol as an oil. After standing a glassy solid formed. M.p. 38°C (Lit.[66] M.p. 37-41°C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.29 (m, 2H), 7.18 (m, 3H), 2.62 (t, J= 7.5Hz, 2H), 2.17 (m, 1H, H1), 2.06 (m, 1H, H4), 1.59 (m,

12H), 1.06 (dd, J= 12.8, 3.3Hz, 1H, H7-*syn*). ^{13}C NMR ($CDCl_3$) δ_C 22.1 (C6), 25.2 (C9), 28.5 (C5), 36.3 (C10), 37.1 (C4), 38.7 (C7), 41.9 (C8), 45.8 (C3), 46.7 (C1), 79.5 (C2), 125.7 (*para*), 128.3 (*ortho*), 128.4 (*meta*), 142.5 (*ipso*).

1,4-Diphenylbutan-1-ol (95)[67] was prepared from benzaldehyde and 3-phenylpropylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with methanol gave the alcohol as a white crystalline solid which was recrystallised from pentane. M.p. 45°C (Lit.[67] M.p. 47°C). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.39-7.14 (m, 10H, ArH), 4.69 (m, 1H, H1), 2.63 (t, J=7.2Hz, 2H, H4), 1.91-1.55 (m, 5H). ^{13}C NMR ($CDCl_3$) δ_C 27.6 (C3), 35.7 (C4), 38.6 (C2), 74.5 (C1), 125.7 (4-*para*), 125.9 (1-*ortho*), 127.6 (1-*para*), 128.3 (4-*ortho*), 128.4 (4-*meta*), 128.5 (1-*meta*), 142.2 (4-*ipso*), 144.7 (1-*ipso*).

2,5-Diphenylpentan-2-ol (97)[68] was prepared from acetophenone and 3-phenylpropylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with methanol gave the alcohol as a clear oil. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.41-7.09 (m, 10H, ArH), 2.55 (t, $J_{4,5}$= 8Hz, 2H, H5), 1.88-1.45 (m, 5H, CH_2 and OH), 1.54 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 25.7 (C4), 30.3 (C1), 36.0 (C5), 43.8 (C3), 74.6 (C2), 124.7 (2-*ortho*), 125.7 (5-*para*), 126.5 (2-*para*), 128.1 (4C, 5-*ortho* and 2-*meta*), 128.4 (5-*meta*), 142.2 (5-*ipso*), 147.8 (2-*ipso*).

1,4-Di-(1-hydroxy-4-phenylbutan-1-yl)benzene (99) was prepared from terephthalaldehyde and 3-phenylpropylmagnesium chloride using dry tetrahydrofuran as the reaction solvent. The

alcohol was purified by column chromatography on alumina. Elution with methanol/ether (1:9) gave the alcohol as a white crystalline solid in 85% yield. M.p. 77-78°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.37-7.13 (m, 14H, ArH), 4.68 (m, 2H, H1'), 2.63 (t, $J_{3',4'}$= 7.3Hz, 4H, H4'), 1.90-1.60 (m, 10H). ^{13}C NMR ($CDCl_3$) δ_C 27.5 (C3'), 35.7 (C4'), 38.6 (C2'), 74.3 (C1'), 125.7 (4'-*para*), 126.0 (4C, C2,3,5,6), 128.3 (4'-*ortho*), 128.4 (4'-*meta*), 142.2 (4'-*ipso*), 144.0 (C1,4). Calc. for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.09; H, 8.11.

1-(2-Methyl-2-propenyl)cyclohexanol[69] **(102)** was prepared from cyclohexanone and 2-methylpropenylmagnesium chloride. Purification was carried out by column chromatography on alumina. Elution with petroleum ether /ether (1:1) gave the alcohol as a clear oil in 40% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 4.94 (m,1H), 4.75 (m,1H, C=CH_2), 2.18 (s, 2H, CH_2), 1.84 (s, 3H, CH_3), 1.80-1.20 (11H, CH_2 and OH). ^{13}C NMR ($CDCl_3$) δ_C 22.3 (2C, C2 and C6), 25.3 (C4), 25.7 (2C, C3 and C5), 37.9 (CH_3), 49.8 (C7), 71.0 (C1), 114.6 (C9), 142.6 (C8).

1-(2-Methyl-2-propenyl)-2-methylcyclohexanol (103) was prepared from 2-methylcyclohexanone and 2-methylpropeneyl-magnesium chloride. Purification was carried out by column chromatography on alumina. Elution with petroleum ether /ether (1:1) gave the alcohol as a 3:7 mixture of the *cis*- and *trans*-isomers in 40% yield. The mixture: $\upsilon_{max.}$ 3550, 1715, 1650, 1450, 1380 cm^{-1}. The major isomer was characterised by: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 4.90 and 4.72 (2H, H9), 2.39 and 2.07 (d, J= 12Hz, 2H, CH_2), 1.83 (3H, C=$\underline{C}H_3$), 1.80-1.10 (10H, CH_2's and OH), 0.93 (d, J= 7Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.3 (CH_3), 22.0 (C6), 25.2, 25.6,

30.9, 36.5, 39.6, 48.26 (C7), 72.7 (C1), 114.4 (C9), 142.8 (C8). The minor isomer was characterised by: ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 4.93 and 4.77, 2H, H9), 2.25 and 2.12 (d, J= 12Hz, 2H, CH_2), 1.85 (3H, $C=CCH_3$), 1.80-1.10 (10H, CH_2 and OH), 0.94 (d, J= 7Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.3 (CH_3), 22.0 (C2), 23.6, 24.4, 31.3, 36.6, 40.8, 41.9, 73.7 (C1), 114.7 (C9), 142.8 (C8).

EXPERIMENTAL SECTION B

ACID REACTIONS

AND THEIR PRODUCTS.

Experimental B
Acid Products

Section 1 (Benzyl carbinol reactions)

Reaction of 1-benzyl-2-methylcyclohexanol (1) with HSO_3F as above gave ***cis*-4a-methyl-1,2,3,4,4a,9a-hexahydrofluorene (2)** in > 85% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.31-7.08 (m, 4H), 2.89 (dd, J= 15.4, 7.0 Hz, 1H), 2.66 (dd, J= 15.4, 7.2 Hz, 1H), 2.08 (m, 1H), 1.51-1.28 (m, 6H), 1.66 (m, 2H), 1.23 (s, 3H). ^{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. Calc. for $C_{14}H_{18}$: M^+, 186.1408. Found: M^+, 186.1418. An authentic sample of 4a-methyl-1,2,3,4,4a,9a - hexahydrofluorenone was prepared in the following manner. Sodium borohydride reduction of 2-methylcyclohexanone was carried out by the usual method to give 2-methylcyclohexanol. The alcohol was then converted to the benzoate ester according to the literature[12] method. 4a-Methyl-1,2,3,4,4a,9a-hexahydrofluoren-9-one was prepared from the ester according to the literature[12] method. Purification was carried out by absorption onto a radial chromatograph plate followed by elution with benzene to give the ketone as a white crystalline solid. ^{13}C NMR ($CDCl_3$) δ_C 21.2, 21.6, 22.3, 24.5 (C2, C3, C4, C4a$\underline{C}H_3$), 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[12] with $Zn/HgCl_2/HCl$ gave **(2)** in 90% yield which was identical in all respects with the hydrocarbon produced from the HSO_3F reaction. ^1H NMR ($CDCl_3$, 60 MHz) δ_H 7.60-7.00 (4H, ArH), 2.79 (t, J= 6Hz, 1H, H9a), 2.60-0.80 (13H, CH_2). ^{13}C NMR ($CDCl_3$) δ_C 22.2, 22.9, 25.8, 26.8, 35.4, 35.6, 45.3, 46.3, 121.6,

125.2, 125.9, 126.1, 142.3, 152.6. Calc. for $C_{14}H_{18}$: M^+, 186.1408. Found: M^+,186.1418.

Reaction of 1-benzylcyclohexanol (3) with HSO_3F as above gave a complex mixture of hydrocarbons which was 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.

Reaction of 1-benzylcyclopentanol with HSO_3F as above gave a complex mixture of hydrocarbons which was shown by mass spectrometry to consist mainly of dimers of formula $C_{24}H_{28}$. Attempts to separate and identify the components were not successful.

Reaction of 1-(*para*-methylbenzyl)cyclopentanol with HSO_3F as above gave a complex mixture of hydrocarbons. Attempts to separate and identify the components were unsuccessful.

Reaction of 6-benzylspiro[4.5]decan-6-ol (4) with HSO_3F as above gave **tetracyclo[7.4.4.0^{1,9}.0^{2,7}]-heptadeca-2,4,6-triene (5)** in 80% yield. M.p. 41-42.5°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.22 (d, J= 7Hz, 1H), 7.16 (t, J= 7Hz, 1H), 7.11 (t, J= 7Hz, 1H), 7.07 (d, J= 7.5Hz, 1H), 2.69 (s, 2H), 1.62-1.40 (m, 12H), 1.31 (m, 4H). ^{13}C NMR ($CDCl_3$) δ_C 22.3 (2C), 22.5 (2C), 33.1 (4C), 41.7, 44.9, 48.3, 121.3, 125.6, 125.8, 142.0, 152.2. Calc. for $C_{17}H_{22}$: M^+, 226.1721; C, 90.20; H, 9.80. Found: M^+, 226.1721; C, 89.94; H, 9.96.

Reaction of 1-benzyl-*trans*-decalin-1-ol (6) with HSO_3F as above gave **(±)-9a-carba-14α-morphinan (7)**[16] in 90% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.20 (d, J= 6.5Hz, 2H), 7.09 (m, 3H), 3.24 (dd, J= 17.5, 7.1 Hz, 1H), 2.70 (d, J= 17.5 Hz, 1H), 2.15 (m, 2H), 1.92-0.94 (m, 14H). ^{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. Calc. for $C_{17}H_{22}$: M^+, 226.1722. Found: M^+, 226.1728.

Reaction of 1-benzyl-3-methylcyclohexanol (10) with HSO_3F at -78°C gave, in addition to polymeric products, ***cis*-1-benzyl-3-methylcyclohexane (12)** in ~ 50% yield after chromatography on alumina. B.p. 120°C at 12 mm. ^1H 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 ($C3\underline{C}H_3$), 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 thus obtained 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 **(10)** by H_3PO_4 dehydration followed by hydrogenation over 5% Pd/C.

Reaction of 1-benzyl-4-methylcyclohexanol (11) was similar to that for **(10)** and gave ***trans*-1-benzyl-4-methylcyclohexane (13)**[19a] in ~ 30% yield. An authentic sample of a mixture of *cis*- and *trans*- isomers was prepared by dehydration of **(11)** followed by hydration as described below.

1-Benzyl-4-methylcyclohexene (11) was prepared by heating phosphoric acid and 1-benzyl-4-methylcyclohexanol on a steam bath for 1/2 an hour. H_2O was added and the mixture was

repeatedly extracted with ether. The organic extract was dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure to yield 1-benzyl-4-methylcyclohexene as a pale oil (2.2g). ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.17 (5H, ArH), 5.42 (br s, 1H, H2), 3.22 (2H, $ArCH_2$), 2.63-1.00 (7H, CH_2 and CH), 0.90 (d, J= 5Hz, 3H, CH_3).

1-Benzyl-4-methylcyclohexane was prepared by reaction of 1-benzyl-4-methylcyclohexene in ethyl acetate and 5% palladium on carbon under hydrogen for 12 hours. The reaction mixture was extracted several times with ether. The organic phase was dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure to yield the alkane as a mixture of the *cis* and *trans* isomers:

Trans-: ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.15 (5H, ArH), 2.57 (d, J= 6Hz, 2H, $ArCH_2$). ^{13}C NMR ($CDCl_3$) δ_C 22.7 (C4$\underline{C}H_3$), 32.8 (C4), 33.2 (2C, C2 and C6), 35.3 (2C, 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 (5H, ArH), 2.45 (d, J= 6Hz, 2H, $ArCH_2$). ^{13}C NMR ($CDCl_3$) δ_C 20.2 (C4CH_3), 28.4 (C2 and C6), 30.1 (C4), 30.8 (2C, 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 in an analogous method to that for 1-benzyl-4-methylcyclohexene. ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 7.20 (5H, ArH), 5.45 (1H, H2), 3.20 (2H, $ArCH_2$), 2.4-0.8 (10H, CH_2 and CH_3).

1-Benzyl-3-methylcyclohexane was prepared in an analogous method to that for 1-benzyl-4-methylcyclohexane. The alkane was present as a mixture of the *cis*- and *trans*- isomers: *Trans*: ^{1}H NMR ($CDCl_3$, 60 MHz) δ_H 2.55 (d, J= 7Hz, 2H, $ArCH_2$), 0.9 (d, J= 3Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 20.7 (C3$\underline{C}H_3$), 20.9 (C5), 27.3 (C3), 31.2 (C6), 33.9 (C4), 34.7 (C1), 38.9 (C2), 41.3 (Ar$\underline{C}H_2$), 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= 7Hz, 2H, $ArCH_2$), 0.85 (d, J= 3Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 22.9 (C3$\underline{C}H_3$), 26.3 (C5), 32.8 (2C, 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*). Calc. for $C_{14}H_20$: C, 89.4; H, 10.6. Found: C, 88.53; H, 11.08.

Reaction of 2-*exo*-benzylbicyclo[2.2.1]heptan-2-*endo*-ol (14) with HSO_3F as above gave **6-phenylbicyclo[3.2.1]oct-6-ene (16)** in 72% yield. B.p. 115-125°C at 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, 7H). ^{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). Calc. for $C_{14}H_{16}$: M^+, 184.1252; C, 91.25; H, 8.75. Found: M^+, 184.1250; C, 91.39; H, 9.01.

Direct Observation of 15.

A HSO_3F/SO_2ClF solution of **(14)** was prepared in an NMR tube at low temperature by a previously described procedure.[28] The only observed species between -90°C and -20°C was the 6-phenyl-

bicyclo[3.2.1]octan-6-yl cation **(15)**.[23] ^{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 (22)-(24) and (30) each gave a product with identical physical properties to **(16)**, but which included deuterium labeling. Thus **(22)** produced 7-deuterio-6-phenylbicyclo[3.2.1]oct-6-ene **(25)** for which the ^1H NMR showed > 90% reduction of the olefinic signal at 6.25 ppm and the ^2H NMR a single signal at ~ 6.3 ppm. Similarly **(23)** and **(24)** each gave a 1:1 mixture of **(16)** and **(25)**, that is ~ 50% deuterium labeling of H7. Alcohol **(30)** gave 4,5-dideuterio-6-phenylbicyclo[3.2.1]oct-6-ene **(31)**, lacking two ^1H NMR signals at 2.97 and ~1.6 ppm exhibited by the undeuterated analogue. ^2H NMR showed only two signals at 2.99 and 1.59 ppm. Mass spectra and ^{13}C NMR spectra were in accord with these structures.

Reaction of 2-*exo*-benzyl-3,3-dimethylbicyclo[2.2.1]-heptan-2-*endo*-ol (32) with HSO_3F as above gave **7,8-dimethyl-tetracyclo[8.4.0.0^{2,7}.0^{4,8}]tetradeca-1(10),11,13-triene (35)** in 92% yield. B.p. 140-150°C at 14 mm. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.28 and 7.05 (m, 4H), 2.97 and 2.62 (dd, J= 18.4 Hz, 9-CH_2), 2.43 (dd, J= 8.2, 2.2 Hz, H2), 1.90-1.15 (m, 7H), 0.97 (s, C9CH_3), 0.57 (s, C8CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.1 (C7$\underline{C}H_3$), 19.0 (C8$\underline{C}H_3$), 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 (2C) and 127.7 (C11-C14), 136.9 (C10), 147.2 (C1). Calc. for $C_{16}H_{20}$: M^+, 186.1408. Found: M^+ 146.1403.

Reaction of 2-*exo*-benzyl-1,3,3-trimethylbicyclo[2.2.1]-heptan-2-*endo*-ol (36) with HSO_3F as above gave a mixture of two hydrocarbons which were not separated but which were identified by NMR as **4,7,8-trimethyltetracyclo-[8.4.0.0^{2,7}.0^{4,8}]tetradeca-1(10)11,13-triene** (37) (60%). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.05 (m, 3H), 6.88 (d, J= 6.7 Hz, 1H), 2.87 and 2.45 (dd, J= 18.5 Hz, 9-CH_2) 2.39 (dd, J= 8.3, 2.2 Hz, H2), 1.88-1.15 (m, 6H), 0.92 (s, C7CH_3), 0.82 (s, C4CH_3), 0.61 (s, C8CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.7, 16.0, 16.8 (C4$\underline{C}H_3$, C7$\underline{C}H_3$, C8$\underline{C}H_3$), 34.0, 35.2, 37.1 (C5, C6, C9), 47.7, 48.3 (C2, C3), 124.6, 125.0 (2C), 127.7 (C11-C14), 136.8 (C10), 147.0 (C1), and **9,14,14-trimethyl-tetracyclo[9.2.1.0^{1,9}.0^{3,8}]tetradeca-3,5,7-triene (38)** (30%). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 3.00 and 2.66 (dd, J= 18.5 Hz, 2-CH_2), 1.36, 1.00, 0.42 (3xCH_3). ^{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.

Reaction of spiro[3-*exo*-benzylbicyclo[2,2,1]heptan-3-*endo*-ol-2,1'cyclopentane] (41) with HSO_3F as above gave **pentacyclo[9.7.0.0^{1,14}.0^{3,8}.0^{9,14}]octadeca-3,5,7-triene (42)** in 86% yield. M.p. 48-49°C. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.00 (m, ArH), 2.76 (s, 2-CH_2), 2.46 (dd, J= 8, 2 Hz, H9), 1.98 (m, 16-CH_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). Calc. for $C_{18}H_{22}$: M^+, 238.1721. Found: M^+, 238.1716.

Reaction of 3-methyl-1-phenylbutan-2-ol (49) with HSO_3F at -70°C as above gave the starting alcohol **(49)** (70%) plus **1,1-dimethylindane (50)** (20%), identical with an authentic sample prepared by literature methods.[60,70] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.15 (m, 4H, ArH), 2.89 (t, $J_{2,3}$= 7.2Hz, 2H, H3), 1.92 (t, $J_{2,3}$= 7.2Hz, 2H, H2), 1.26 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 28.7 (2C, 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). Reaction of **(49)** at 0°C and 25°C and reaction of **(50)** at 25°C all gave similar mixtures of three fluorosulfonated isomers, samples of which were separated by preparative GLC and identified as **1,1-dimethylindane-6-sulfonyl fluoride (51)** (45%) ^1H 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, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 28.4 (2C, CH_3), 30.5 (C3), 41.1 (C2), 44.3 (C1), 122.2 (C7), 125.6 (C4), 126.9 (C5); **1,1-dimethylindane-5-sulfonyl fluoride (52)** (35%) ^1H 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, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 28.1 (2C, CH_3), 29.8 (C3), 41.0 (C2), 44.5 (C1), 122.9 (C7), 124.4 (C4), 127.1 (C6); **1,1-dimethylindane-4-sulfonyl fluoride (53)** (20%) ^1H 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, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 28.6 (2C, CH_3), 30.0 (C2), 40.6 (C3), 44.3 (C1), 127.0 (C5), 127.7 (C6), 129.5 (C7).

Reaction of 1-(*para*-methylphenyl)-3-methylbutan-2-ol (54) with HSO_3F as above with subsequent warming to 0°C prior to

quenching gave predominantly **1,1,6-trimethylindane-5-sulfonyl fluoride (55) (40%)**. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.84 (s, 1H, H4), 7.13 (s, 1H, H7), 2.93 (t, J= 7.3Hz, 2H, $ArCH_2$), 2.66 (s, 3H, $C6CH_3$), 1.98 (t, J= 7.5Hz, 2H, H2), 1.28 (s, $2xCH_3$). ^{13}C NMR ($CDCl_3$) δ_C 28.2 ($2xC1\underline{C}H_3$), 28.4 ($C6\underline{C}H_3$), 29.5 (C2), 41.2 (C3), 44.5 (C1), 126.1, 126.4 (C4 and C7), 140.6, 141.4 (C3a and C6), 158.3 (C7a).

Section 2 (Phenylethyl carbinols reactions)

Reaction of 2-methyl-4-phenylbutan-2-ol (56) with HSO_3F gave **1,1-dimethylindane (50)**[60,70] in 41% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.15 (m, 4H, ArH), 2.89 (t, $J_{2,3}$= 7.2Hz, 2H, $ArCH_2$), 1.92 (t, $J_{2,3}$= 7.2Hz, 2H, H2), 1.26 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 28.7 (2C, 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).

Reaction of 4-methyl-1-phenylpentan-3-ol (57) with HSO_3F at 0°C gave a mixture of fluorosulfonated isomers (**58**) of 1,1-dimethyltetralin. The isomers were identified by NMR spectroscopy as **1,1-dimethyltetralin-6-sulfonyl fluoride** (60%) ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.94 (d, H5), 7.67 (dd, H7), 7.27 (d H8), 2.86 (m, $ArCH_2$), 1.85 (m, 3-CH_2), 1.70 (m, 2-CH_2), 1.32 (s, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 18.9 (C3), 30.9 (C4), 31.5 (2C, 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, $ArCH_2$), 1.85 (m, 3-CH_2), 1.70 (m, 2-CH_2), 1.32 (s, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 18.7 (C3), 30.6 (C4), 31.9 (2C, CH_3), 34.6 (C1), 37.9 (C2), 126.1 (C6), 128.1 (C7), 134.4 (C8); **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, $ArCH_2$), 1.85 (m, 3-CH_2), 1.70 (m, 2-CH_2), 1.32 (s, 2xCH_3). ^{13}C NMR ($CDCl_3$) δ_C 19.1 (C3), 27.4 (C4), 31.4 (2C, CH_3), 34.6 (C1), 37.9 (C2), 125.4 (C8), 127.9 (C7), 129.1 (C5).

Reaction of 1-(2-phenylethyl)cyclohexanol (59) with HSO_3F gave, in 40% yield, a (3:1) mixture of two hydrocarbons which were identified by comparison with literature NMR[38,39] as

***cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (61)**, ^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 (2C, C6 and C7), 128.5, 128.7 (C5 and C8), 136.0 (C8a), 142.1 (C4b); and **spiro[cyclohexane-1,1-indane] (60)**, ^{13}C NMR ($CDCl_3$) δ_C 23.5 (2C, C3' and C5'), 26.1 (C4'), 30.0 (C3), 35.2 (C2), 37.2 (2C, C2' and C6'), 122.2 (C7), 124.3 (C4), 126.0, 126.1 (C5 and C6).

Reaction of 2-methyl-1-(2-phenylethyl)cyclohexanol (64) with HSO_3F gave a 3:1 mixture of ***cis*- (65)** and ***trans*- 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (66)** in 80% yield. The isomers were identified by comparison with literature NMR data.[38,71] Mixture: ^1H NMR ($CDCl_3$, 60 MHz) δ_H 7.10 (m, ArH), 2.80 (m, $ArCH_2$), 2.50-1.00 (m, CH_2's and CH), 1.23 (s, 3H, CH_3-*cis*), 1.07 (s, 0.9H, CH_3-*trans*). *Cis*-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene ^{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$\underline{C}H_3$), 37.5 (C4a), 38.2 (C10a), 41.3 (C4), 125.1 (C5), 125.8 (2C, C6 and C7), 129.3 (C8), 135.8 (C8a), 144.3 (C4b).

Reaction of 1-(2-phenylethyl)-2,2,6-trimethylcyclohexanol (70) with HSO_3F gave as the major product **1β,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (72)**[41] in 90% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.33 (d, J= 7.7Hz, 1H), 7.14-7.04 (m, 3H, ArH), 2.93-2.63 (m, 2H, H9), 1.86-1.15 (m, 9H), 1.09 (s, 3H, 4aCH_3), 0.93 (s, 3H, 10aCH_3), 0.82 (d, J= 6.8Hz, 3H, C1CH_3). ^{13}C NMR ($CDCl_3$) δ_C 16.2 (C1$\underline{C}H_3$), 16.4 (C10a$\underline{C}H_3$), 22.8 (C3),

25.8 (C9), 28.4 (C10), 30.0 (C4a$\underline{C}H_3$), 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). The isolated product was contaminated by *ca* 15% of **1α,4aβ,10aβ-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (73)**[41] ^{13}C NMR ($CDCl_3$) δ_C 16.4 (C1$\underline{C}H_3$), 20.4 (C4a$\underline{C}H_3$), 21.4 (C10a$\underline{C}H_3$).

Reaction of 2-*exo*-(2-phenylethyl)bicyclo[2,2,1]heptan-2-*endo*-ol (74) with HSO_3F gave **tetracyclo[10.2.1.0^{1,10}.0^{4,9}]-pentadeca-4,6,8-triene (75)** in 82% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.16-7.10 (m, 1H, H8), 7.05-7.03 (m, 3H, H6, H7 and H8), 2.87-2.71 (m, 2H, H3), 2.66-2.60 (m, 1H, H10), 2.25-2.22 (m, 1H, H12), 2.15-2.07 (m, 1H, H11-*endo*), 1.86-1.81 (m, 2H, H2), 1.74-1.64 (m, 1H, H13-*exo*), 1.60-1.27 (m, 5H, H15-*syn*, H13-*endo*, H14 and H11-*exo*), 1.02-0.98 (m, 1H, 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). Calc. for $C_{15}H_{18}$:M^+,198.1397. Found: M^+,198.1396.

Reaction of 2-*endo*-(2-phenylethyl)-1,7,7-trimethylbicyclo[2,2,1]heptan-2-*exo*-ol (80) with HSO_3F gave **13,13,14-trimethyltetracyclo[10.2.1.0^{1,10}.0^{4,9}]pentadeca-4,6,8-triene (81)** (76% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.15-7.03 (m, 1H), 6.98-6.95 (m, 3H), 2.67-2.63 (m, 2H, H3), 2.50-2.42 (m, 2H, H10 and H11-*endo*), 1.78-1.72 (m, 1H, H2), 1.62 (br s, 1H, H12), 1.51-1.43 (m, 1H, H2), 1.40-1.35 (m, 1H, H15-*anti*), 1.29-1.23 (m, 1H, H11-*exo*), 1.18-1.11 (m, 1H, H15-*syn*), 1.09-1.06 (m, 1H, H14), 0.99 (s, 3H, C13CH_3-*exo*), 0.82 (s, 3H, C13CH_3-*endo*), 0.75 (d,

J= 7.3Hz, 3H, C14CH_3). ^{13}C NMR ($CDCl_3$) δ_C 12.5 (C14$\underline{C}H_3$), 24.8 (C13$\underline{C}H_3$-*endo*), 25.2 (C2), 27.7 (C3), 27.9 (C13$\underline{C}H_3$-*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). Calc. for $C_{18}H_{24}$: M^+, 240.1879. Found: M^+, 240.1874.

Section 3 (Phenylpropyl carbinol reactions)

Reaction of 1-(3-phenylpropyl)cyclohexanol (85) with HSO_3F gave a hydrocarbon in 82% yield which was identified by NMR spectroscopy as **spiro[cyclohexane-1,1-tetralin] (86)**. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.41 (d, J= 7.6Hz, 1H, H8), 7.18-7.13 (m, 1H), 7.09-7.03 (m, 2H), 2.75 (t, J= 6.2Hz, 2H, H4), 1.84-1.23 (m, 14H). ^{13}C NMR ($CDCl_3$) δ_C 19.2 (C4'), 22.0 (2C, C3' and C5'), 26.2 (C3), 31.0 (C4), 37.0 (C1), 38.7 (2C, C2' and C6'), 125.1 (C6), 125.7 (C7), 126.7 (C8), 129.0 (C5), 137.1 (C4a), 146.6 (C8a). Calc. for $C_{15}H_{20}$: C, 89.92; H, 10.07. Found: C, 89.81; H, 10.27.

Reaction of 2-methyl-1-(3-phenylpropyl)cyclohexanol (87) with HSO_3F gave a hydrocarbon in 83% yield which was identified by NMR spectroscopy as ***trans*-2'-methyl-spiro-[cyclohexane-1,1-tetralin] (88)**. ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.37 (d, J= 8Hz, 1H, H8), 7.25-7.12 (m, 1H), 7.08-7.03 (m, 2H), 2.72-2.68 (m, 2H, H4), 2.15-2.05 (m, 1H), 1.94-1.25 (m, 12H), 0.58 (d, J= 6.9Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 17.0 (C2'$\underline{C}H_3$), 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). Calc. for $C_{16}H_{22}$: C, 89.65; H, 10.35; M^+, 214.1721. Found: C, 89.47; H, 10.22; M^+, 214.1722.

Reaction of 2-*exo*-(3-phenylpropyl)bicyclo[2,2,1]heptan-2-*endo*-ol (89) with HSO_3F gave, in 75% yield, a mixture of hydrocarbons in a ratio of 2:1:1. The major isomer is characterised by: ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.22 (m, 4H), 2.93 (m, 2H), 2.64 (m, 1H), 2.21 (m, 2H), 1.99-0.85 (m, 11H); ^{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 characterised by ^{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.

Reaction of 1,4-diphenylbutan-1-ol (95) with HSO_3F gave a hydrocarbon in 89% yield which was identified by NMR spectroscopy as **1-phenyl-1,2,3,4-tetrahydronapthalene (96).**[72] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.30-7.00 (m, 8H, ArH), 6.84 (d, $J_{7,8}$= 8Hz, 1H, H8), 4.12 (t, $J_{1,2}$= 6.4Hz, 1H, H1), 2.92-2.81 (m, 2H, H4), 2.21-2.12 (m, 1H, H2), 1.93-1.70 (m, 3H, 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).

Reaction of 2,5-diphenylpentan-2-ol (97) with HSO_3F gave a hydrocarbon in 70% yield which was identified by NMR spectroscopy as **1-methyl-1-phenyl-1,2,3,4-tetrahydronapthalene (98).**[68] ^1H NMR ($CDCl_3$, 300 MHz) δ_H 7.26-7.07 (m, 8H, ArH), 7.00 (d, $J_{7,8}$= 7Hz, 1H, H8), 2.84 (t, $J_{3,4}$= 6.5Hz, 2H, H4), 2.12-2.02 (m, 1H, H2), 1.92-1.65 (m, 3H, H3 and H2), 1.72 (s, 3H, C1CH_3). ^{13}C NMR ($CDCl_3$) δ_C 19.5 (C3), 30.0 (C1$\underline{C}H_3$), 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).

Reaction of 1,4-di-(1-hydroxy-4-phenylbutan-1-yl)-benzene (99) with HSO_3F gave a hydrocarbon in 83% yield which was identified by NMR spectroscopy as a mixture of the two diastereoisomers of **1,4-di-(1,2,3,4-tetrahydronapth-1-yl)-**

benzene (100). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.15-6.85 (m, 14H), ArH, 4.08 (t, $J_{1',2'}$= 6Hz, 2H, H1'), 2.94-2.76 (m, 4H, H4'), 2.21-1.68 (m, 8H). ^{13}C NMR ($CDCl_3$) δ_C 20.9 (C3'), 29.8 (C2'), 33.1 and 33.2 (C4'), 45.2 (C1'), 125.5 (C6'), 125.8 (C7'), 128.6 (4C, C2,3,5,6), 128.9 (C8'), 130.2 (C5'), 137.6 (C4a'), 139.6 (C1,4), 144.9 (C8a').

Dehydrogenation of 1,4-di-(1,2,3,4-tetrahydronapth-1-yl)benzene (100).

A sample of 1,4-di(1,2,3,4-tetrahydronapth-1-yl)benzene **(100)** was heated over 10% palladium on carbon at 250°C for 2 hours afterwhich the sample was cooled, extracted with ether and the organic layer filtered from the catalyst. Removal of the solvent gave the aromatised product **1,4-di-(1-naphthyl)benzene (101)**[46] in 36% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.09 (d, J= 7Hz, 2H), 7.93 (d, J= 7.2Hz, 2H), 7.90 (d, J= 8.5Hz, 2H), 7.63 (s, 4H), 7.63-7.47 (m, 8H). ^{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.

Reaction of 1-(2-methyl-2-propenyl)cyclohexanol (102) with HSO_3F gave a complex mixture of hydrocarbons. Attempts to separate and identify the components were unsuccessful.

Reaction of 1-(2-methyl-2-propenyl)-2-methylcyclohexanol (103) with HSO_3F gave **2,2,7-trimethyl-2,3,3a,4,5,6,7,7a-octahydrobenzo[*b*]furan (104)** in 30% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.19 (m, H3a), 2.00 (t, J= 12.5 Hz, H3), 1.68 (m, H3), 1.58 (m, CH_2), 1.55 (m, H7), 1.41 (m, CH_2), 1.34 (s, 2-CH_3), 1.27 (s, 7a-CH_3), 1.20 (s, 2-CH_3). ^{13}C NMR ($CDCl_3$) δ_C 20.9,

24.1, 25.3 (C4, C5, C6), 26.4 (C7a$\underline{C}H_3$), 30.8, 31.2 (C2$\underline{C}H_3$), 36.4 (C7), 42.5 (C3), 43.6 (C3a), 78.6 (C2), 81.2 (C7a).

EXPERIMENTAL SECTION C

X-RAY

CRYSTALLOGRAPHY.

Experimental C
Crystallography.

Structure Solution and Refinement.

Table 1 lists crystal data and X-ray experimental details for **(42)**. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatised Mo Kα radiation (λ 0.7107 Å). Cell parameters were determined by least squares refinement, the setting angles of 25 accurately centred reflections (2θ >20°) being used. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities a were corrected for Lorentz and polarisation effects but no correction was made for absorption. Reflections with intensities $I > 2\sigma(I)$ were used for structure solution and refinement.

The structure was solved by direct methods and refined by blocked cascade least-squares procedures. All carbon atoms were refined with isotropic thermal parameters. Hydrogen atoms were included in calculated positions. The function minimised was $\Sigma w (|F_o|-|F_c|)^2$, with $w= [\sigma^2(F_o) + .001F_o^2]^{-1}$. The magnitude of residual electron density in final Fourier syntheses was < 0.3 $eÅ^{-3}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL.[73]

Discussion of the Structure.

Figure **5** shows a perspective view and atom labeling of the X-ray crystal structure of **(42)**. Tables 2-4 list the atomic coordinates, bond lengths and bond angles respectively, with standard deviations in parentheses. The structure of the product is

thus confirmed as **(42)**, as was proposed on the basis of the spectroscopic data. The crystal structure is unusual in that it contains four independent molecules in the asymmetric unit. All four molecules exist in a similar conformation and have similar bonding geometries. No unusual geometry or intermolecular contacts exist (Figure 6).

Figure 5: Perspective view with atom labeling of the X-ray structure of (42)

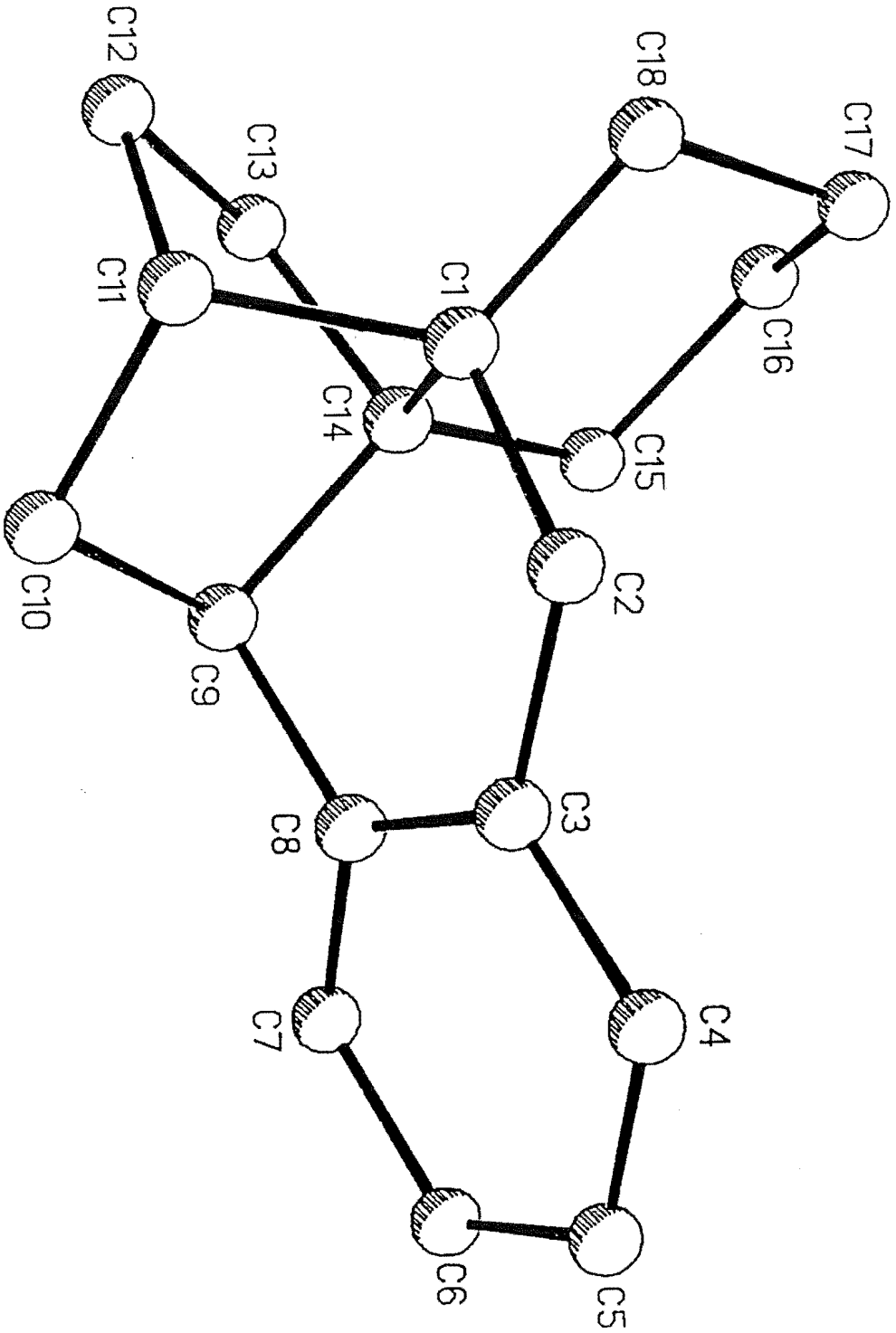


Figure 6: Packing diagram for (42)

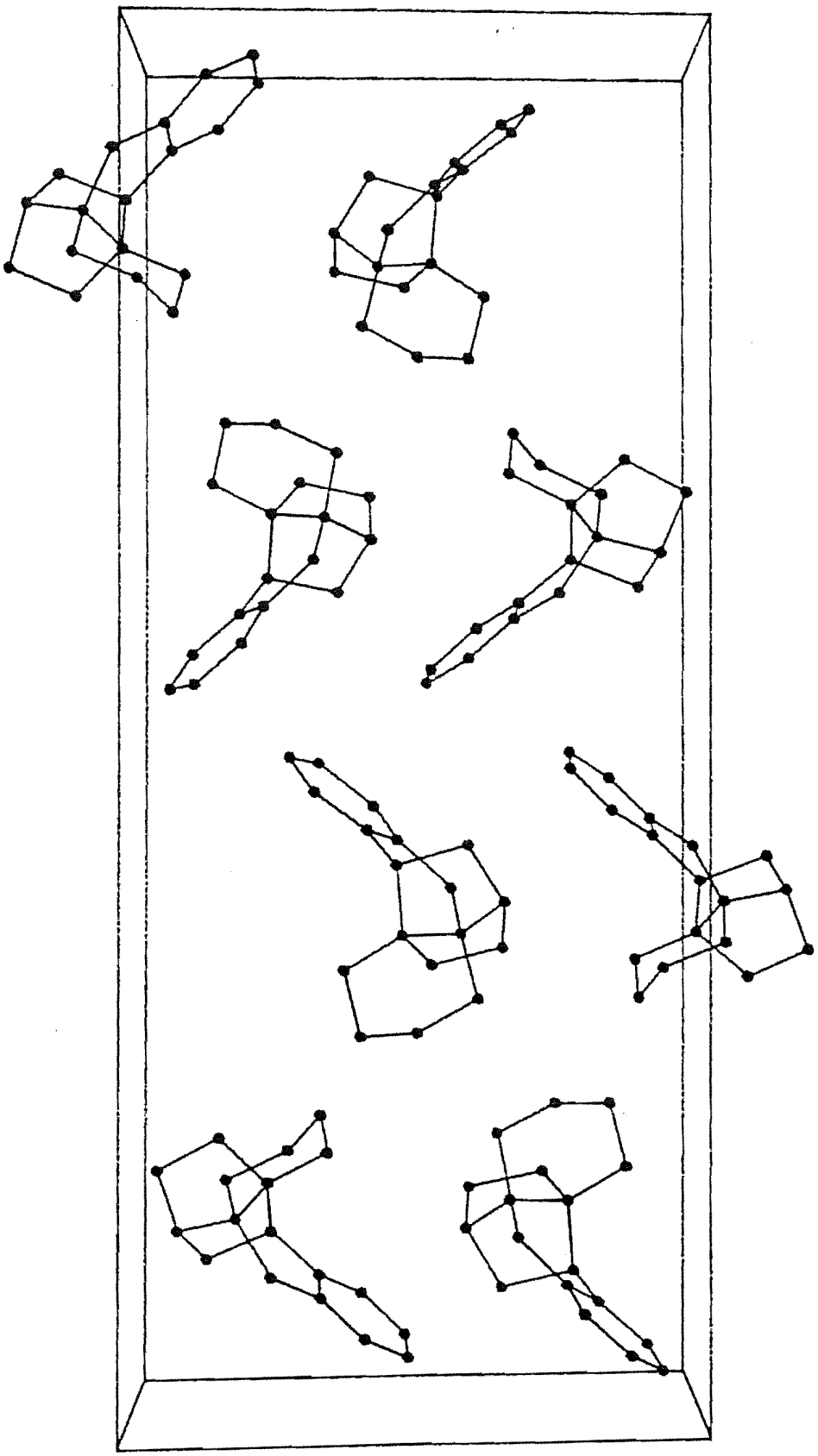


Table 1. Crystal Data and X-Ray Experimental Details.

Formula	$C_{18}H_{22}$
Molecular Weight	238.4
Crystal System	monoclinic
Space Group	$P2_1$
a (Å)	7.105(2)
b (Å)	30.616(12)
c (Å)	12.133(4)
β (degrees)	94.02(3)
V (Å^3)	2633(2)
Dc (g cm^{-3})	1.203
Z	8
F (000)	1040
μ (cm^{-1})	0.63
Radiation	MoKα
Wavelength (Å)	0.7107
Temperature (°C)	-125
Crystal Dimensions (mm)	0.52 x 0.27 x 0.05
Scan mode	ω
2θ range (degrees)	3-45
Unique reflections	3719
Observed Reflections (I>2σ(I))	1802
Number of parameters	288
R (%)	5.98
wR (%)	6.72

Table 2. Atomic coordinates ($x10^4$) and isotropic thermal parameters ($Å^2x10^3$) for (42).

	x	y	z	U
C(1)	198(13)	1459	4263(7)	23(3)
C(2)	-1402(14)	1118(3)	4448(8)	27(3)
C(3)	-1036(13)	786(3)	5346(7)	22(2)
C(4)	-2498(15)	544(3)	5734(8)	32(3)
C(5)	-2186(15)	251(3)	6620(8)	32(3)
C(6)	-399(13)	214(3)	7127(8)	24(3)
C(7)	1097(14)	463(3)	6748(8)	26(3)
C(8)	763(13)	734(3)	5851(7)	20(2)
C(9)	2293(13)	996(3)	5365(7)	20(2)
C(10)	2473(14)	856(3)	4126(7)	30(3)
C(11)	1625(14)	1257(3)	3479(8)	26(3)
C(12)	3199(14)	1607(4)	3511(8)	32(3)
C(13)	3361(14)	1726(3)	4759(7)	32(3)
C(14)	1687(13)	1489(3)	5259(7)	22(2)
C(15)	1025(14)	1719(3)	6248(7)	28(3)
C(16)	75(15)	2162(3)	5953(8)	32(3)
C(17)	-1395(13)	2115(3)	5002(7)	26(3)
C(18)	-666(14)	1897(3)	3973(7)	24(3)
C(21)	4010(13)	3447(3)	3340(7)	19(2)
C(22)	5547(13)	3784(3)	3170(7)	22(2)
C(23)	5117(13)	4120(3)	2290(7)	22(2)
C(24)	6536(14)	4399(3)	1948(7)	25(3)
C(25)	6137(15)	4694(4)	1104(8)	32(3)
C(26)	4318(14)	4725(3)	615(8)	33(3)
C(27)	2925(14)	4464(3)	962(7)	28(3)
C(28)	3289(13)	4163(3)	1811(7)	24(3)
C(29)	1828(14)	3881(3)	2282(8)	25(3)
C(30)	1703(14)	3987(3)	3537(7)	26(3)
C(31)	2560(13)	3595(3)	4156(8)	22(3)
C(32)	1047(16)	3250(4)	4111(8)	38(3)
C(33)	856(14)	3139(3)	2847(7)	27(3)
C(34)	2462(13)	3401(3)	2366(7)	20(2)
C(35)	3169(13)	3190(3)	1328(7)	23(2)
C(36)	4122(13)	2755(3)	1596(8)	21(3)
C(37)	5664(13)	2796(3)	2514(7)	26(3)
C(38)	4921(14)	2990(3)	3573(8)	30(3)
C(41)	-1529(14)	1352(3)	-703(8)	19(3)
C(42)	-689(14)	932(3)	-157(8)	28(3)
C(43)	-1838(13)	711(3)	694(7)	22(2)
C(44)	-1068(16)	404(4)	1436(9)	38(3)
C(45)	-2134(15)	206(4)	2195(9)	31(3)

Table 2 Continued

C(46)	-4024(15)	323(3)	2229(9)	41(3)
C(47)	-4802(15)	627(3)	1505(8)	33(3)
C(48)	-3762(14)	824(3)	724(8)	26(3)
C(49)	-4485(14)	1157(3)	-106(8)	21(3)
C(50)	-4377(14)	979(4)	-1300(8)	28(3)
C(51)	-2787(14)	1253(3)	-1761(8)	26(3)
C(52)	-3663(14)	1691(3)	-2110(8)	30(3)
C(53)	-4097(14)	1878(3)	-977(7)	27(3)
C(54)	-3190(13)	1558(3)	-94(7)	22(2)
C(55)	-2592(13)	1767(3)	1012(7)	25(3)
C(56)	-986(14)	2087(3)	874(9)	35(3)
C(57)	657(14)	1891(3)	336(7)	32(3)
C(58)	32(13)	1689(3)	-810(8)	30(3)
C(61)	5732(13)	3618(3)	8209(8)	18(3)
C(62)	4907(15)	4022(3)	7557(8)	30(3)
C(63)	6103(13)	4226(3)	6714(7)	24(2)
C(64)	5330(14)	4509(3)	5910(8)	23(3)
C(65)	6510(16)	4696(4)	5154(9)	36(3)
C(66)	8380(14)	4606(3)	5226(8)	29(3)
C(67)	9170(14)	4319(3)	6015(7)	25(3)
C(68)	8012(13)	4128(3)	6769(7)	21(2)
C(69)	8743(15)	3827(3)	7654(8)	29(3)
C(70)	8511(16)	4019(4)	8823(9)	36(3)
C(71)	6902(13)	3749(3)	9288(8)	26(3)
C(72)	7821(14)	3326(3)	9701(8)	32(3)
C(73)	8353(15)	3106(4)	8593(8)	32(3)
C(74)	7467(13)	3412(3)	7679(7)	18(2)
C(75)	6956(14)	3181(3)	6613(8)	33(3)
C(76)	5346(13)	2853(3)	6710(8)	30(3)
C(77)	3628(15)	3052(4)	7238(8)	40(3)
C(78)	4182(14)	3281(3)	8331(7)	26(3)

Table 3. Bond Lengths (Å) for (42).

C(1)-C(2)	1.571(12)	C(1)-C(11)	1.566(13)
C(1)-C(14)	1.552(12)	C(1)-C(18)	1.507(10)
C(2)-C(3)	1.499(13)	C(3)-C(4)	1.385(14)
C(3)-C(8)	1.388(12)	C(4)-C(5)	1.407(14)
C(5)-C(6)	1.376(14)	C(6)-C(7)	1.411(14)
C(7)-C(8)	1.376(13)	C(8)-C(9)	1.504(13)
C(9)-C(10)	1.577(13)	C(9)-C(14)	1.574(13)
C(10)-C(11)	1.555(13)	C(11)-C(12)	1.549(14)
C(12)-C(13)	1.554(13)	C(13)-C(14)	1.552(14)
C(14)-C(15)	1.495(13)	C(15)-C(16)	1.546(14)
C(16)-C(17)	1.508(13)	C(17)-C(18)	1.536(13)
C(21)-C(22)	1.526(13)	C(21)-C(31)	1.546(13)
C(21)-C(34)	1.563(12)	C(21)-C(38)	1.559(13)
C(22)-C(23)	1.500(13)	C(23)-C(24)	1.405(13)
C(23)-C(28)	1.392(13)	C(24)-C(25)	1.381(14)
C(25)-C(26)	1.387(14)	C(26)-C(27)	1.361(14)
C(27)-C(28)	1.394(13)	C(28)-C(29)	1.495(14)
C(29)-C(30)	1.566(13)	C(29)-C(34)	1.536(13)
C(30)-C(31)	1.521(13)	C(31)-C(32)	1.504(14)
C(32)-C(33)	1.568(13)	C(33)-C(34)	1.542(13)
C(34)-C(35)	1.532(13)	C(35)-C(36)	1.516(13)
C(36)-C(37)	1.512(13)	C(37)-C(38)	1.543(13)
C(41)-C(42)	1.547(13)	C(41)-C(51)	1.543(13)
C(41)-C(54)	1.567(14)	C(41)-C(58)	1.527(14)
C(42)-C(43)	1.521(14)	C(43)-C(44)	1.387(14)
C(43)-C(48)	1.413(14)	C(44)-C(45)	1.373(16)
C(45)-C(46)	1.393(15)	C(46)-C(47)	1.369(14)
C(47)-C(48)	1.380(14)	C(48)-C(49)	1.498(13)
C(49)-C(50)	1.555(14)	C(49)-C(54)	1.534(13)
C(50)-C(51)	1.543(14)	C(51)-C(52)	1.527(13)
C(52)-C(53)	1.539(14)	C(53)-C(54)	1.556(13)
C(54)-C(55)	1.521(13)	C(55)-C(56)	1.523(14)
C(56)-C(57)	1.502(14)	C(57)-C(58)	1.557(13)
C(61)-C(62)	1.559(14)	C(61)-C(71)	1.554(13)
C(61)-C(74)	1.563(13)	C(61)-C(78)	1.524(13)
C(62)-C(63)	1.511(14)	C(63)-C(64)	1.389(13)
C(63)-C(68)	1.386(13)	C(64)-C(65)	1.406(15)
C(65)-C(66)	1.354(15)	C(66)-C(67)	1.388(13)
C(67)-C(68)	1.400(13)	C(68)-C(69)	1.482(13)
C(69)-C(70)	1.554(15)	C(69)-C(74)	1.563(14)
C(70)-C(71)	1.549(15)	C(71)-C(72)	1.520(13)
C(72)-C(73)	1.572(14)	C(73)-C(74)	1.551(13)
C(74)-C(75)	1.496(13)	C(75)-C(76)	1.534(14)
C(76)-C(77)	1.544(14)	C(77)-C(78)	1.527(13)

Table 4. Bond Angles (degrees) for (42).

C(2)-C(1)-C(11)	109.2(5)	C(2)-C(1)-C(14)	112.9(7)
C(11)-C(1)-C(14)	93.5(7)	C(2)-C(1)-C(18)	109.8(7)
C(11)-C(1)-C(18)	118.7(7)	C(14)-C(1)-C(18)	111.9(6)
C(1)-C(2)-C(3)	117.6(8)	C(2)-C(3)-C(4)	120.9(8)
C(2)-C(3)-C(8)	120.4(8)	C(4)-C(3)-C(8)	118.5(8)
C(3)-C(4)-C(5)	121.3(9)	C(4)-C(5)-C(6)	119.0(9)
C(5)-C(6)-C(7)	120.2(9)	C(6)-C(7)-C(8)	119.4(9)
C(3)-C(8)-C(7)	121.4(9)	C(3)-C(8)-C(9)	115.7(8)
C(7)-C(8)-C(9)	122.8(8)	C(8)-C(9)-C(10)	109.8(7)
C(8)-C(9)-C(14)	110.0(8)	C(10)-C(9)-C(14)	102.8(7)
C(9)-C(10)-C(11)	102.3(7)	C(1)-C(11)-C(10)	104.5(7)
C(1)-C(11)-C(12)	102.0(7)	C(10)-C(11)-C(12)	106.3(8)
C(11)-C(12)-C(13)	100.9(8)	C(12)-C(13)-C(14)	105.4(8)
C(1)-C(14)-C(9)	100.0(6)	C(1)-C(14)-C(13)	102.9(7)
C(9)-C(14)-C(13)	105.5(7)	C(1)-C(14)-C(15)	114.6(8)
C(9)-C(14)-C(15)	119.1(8)	C(13)-C(14)-C(15)	112.8(8)
C(14)-C(15)-C(16)	112.6(8)	C(15)-C(16)-C(17)	111.2(8)
C(16)-C(17)-C(18)	114.1(8)	C(1)-C(18)-C(17)	110.5(7)
C(22)-C(21)-C(31)	113.8(7)	C(22)-C(21)-C(34)	115.5(7)
C(31)-C(21)-C(34)	92.6(7)	C(22)-C(21)-C(38)	109.8(7)
C(31)-C(21)-C(38)	115.7(7)	C(34)-C(21)-C(38)	108.6(7)
C(21)-C(22)-C(23)	116.6(7)	C(22)-C(23)-C(24)	120.9(8)
C(22)-C(23)-C(28)	119.9(8)	C(24)-C(23)-C(28)	119.2(8)
C(23)-C(24)-C(25)	120.1(9)	C(24)-C(25)-C(26)	120.0(10)
C(25)-C(26)-C(27)	120.2(9)	C(26)-C(27)-C(28)	121.1(9)
C(23)-C(28)-C(27)	119.4(9)	C(23)-C(28)-C(29)	116.0(8)
C(27)-C(28)-C(29)	124.6(8)	C(28)-C(29)-C(30)	109.9(8)
C(28)-C(29)-C(34)	111.6(8)	C(30)-C(29)-C(34)	99.9(7)
C(29)-C(30)-C(31)	105.5(8)	C(21)-C(31)-C(30)	100.2(7)
C(21)-C(31)-C(32)	106.2(8)	C(30)-C(31)-C(32)	106.0(8)
C(31)-C(32)-C(33)	101.6(8)	C(32)-C(33)-C(34)	103.9(8)
C(21)-C(34)-C(29)	98.8(7)	C(21)-C(34)-C(33)	105.1(7)
C(29)-C(34)-C(33)	107.5(8)	C(21)-C(34)-C(35)	113.9(7)
C(29)-C(34)-C(35)	117.5(7)	C(33)-C(34)-C(35)	112.6(7)
C(34)-C(35)-C(36)	111.3(7)	C(35)-C(36)-C(37)	112.0(8)
C(36)-C(37)-C(38)	111.9(8)	C(21)-C(38)-C(37)	110.9(7)
C(42)-C(41)-C(51)	112.0(8)	C(42)-C(41)-C(54)	114.4(8)
C(51)-C(41)-C(54)	93.4(7)	C(42)-C(41)-C(58)	109.7(8)
C(51)-C(41)-C(58)	116.4(8)	C(54)-C(41)-C(58)	110.1(8)
C(41)-C(42)-C(43)	116.9(8)	C(42)-C(43)-C(44)	122.4(9)
C(42)-C(43)-C(48)	118.3(8)	C(44)-C(43)-C(48)	119.3(9)
C(43)-C(44)-C(45)	121.5(10)	C(44)-C(45)-C(46)	119.0(10)
C(45)-C(46)-C(47)	120.2(10)	C(46)-C(47)-C(48)	121.7(10)
C(43)-C(48)-C(47)	118.4(9)	C(43)-C(48)-C(49)	115.9(8)
C(47)-C(48)-C(49)	125.7(9)	C(48)-C(49)-C(50)	110.5(8)

Table 4 Continued

C(48)-C(49)-C(54)	111.2(8)	C(50)-C(49)-C(54)	102.7(8)
C(49)-C(50)-C(51)	103.4(8)	C(41)-C(51)-C(50)	101.7(7)
C(41)-C(51)-C(52)	105.0(8)	C(50)-C(51)-C(52)	106.5(8)
C(51)-C(52)-C(53)	100.5(7)	C(52)-C(53)-C(54)	106.4(8)
C(41)-C(54)-C(49)	98.3(7)	C(41)-C(54)-C(53)	102.6(7)
C(49)-C(54)-C(53)	106.1(7)	C(41)-C(54)-C(55)	114.3(7)
C(49)-C(54)-C(55)	118.3(8)	C(53)-C(54)-C(55)	114.8(8)
C(54)-C(55)-C(56)	109.8(8)	C(55)-C(56)-C(57)	113.7(8)
C(56)-C(57)-C(58)	111.4(8)	C(41)-C(58)-C(57)	110.8(8)
C(62)-C(61)-C(71)	112.5(8)	C(62)-C(61)-C(74)	113.0(8)
C(71)-C(61)-C(74)	93.4(7)	C(62)-C(61)-C(78)	109.8(8)
C(71)-C(61)-C(78)	116.1(8)	C(74)-C(61)-C(78)	111.2(8)
C(61)-C(62)-C(63)	117.5(9)	C(62)-C(63)-C(64)	121.4(9)
C(62)-C(63)-C(68)	118.3(8)	C(64)-C(63)-C(68)	120.4(9)
C(63)-C(64)-C(65)	119.2(9)	C(64)-C(65)-C(66)	120.2(10)
C(65)-C(66)-C(67)	121.4(10)	C(66)-C(67)-C(68)	119.1(9)
C(63)-C(68)-C(67)	119.8(8)	C(63)-C(68)-C(69)	117.5(9)
C(67)-C(68)-C(69)	122.7(9)	C(68)-C(69)-C(70)	111.8(8)
C(68)-C(69)-C(74)	110.2(8)	C(70)-C(69)-C(74)	101.1(8)
C(69)-C(70)-C(71)	105.0(8)	C(61)-C(71)-C(70)	101.3(8)
C(61)-C(71)-C(72)	104.4(7)	C(70)-C(71)-C(72)	105.3(8)
C(71)-C(72)-C(73)	101.9(8)	C(72)-C(73)-C(74)	104.1(8)
C(61)-C(74)-C(69)	98.9(7)	C(61)-C(74)-C(73)	104.0(7)
C(69)-C(74)-C(73)	107.3(7)	C(61)-C(74)-C(75)	113.3(7)
C(69)-C(74)-C(75)	118.3(8)	C(73)-C(74)-C(75)	113.3(8)
C(74)-C(75)-C(76)	112.3(8)	C(75)-C(76)-C(77)	112.8(8)
C(76)-C(77)-C(78)	112.3(8)	C(61)-C(78)-C(77)	111.7(8)

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