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SYNTHETIC APPROACHES TO LARGE DIAMONDOID HYDROCARBONS

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The elucidation of the structure of diamond represents one of the earliest triumphs of X-ray diffraction analysis,[1] providing a dramatic demonstration of the ability of C atoms to unite covalently in a giant crystalline array. Below the surface of the crystal each C atom is bonded to four others in the form of a tetrahedron. These internal bonds are broken only with great difficulty which explains the characteristic hardness of diamond. At the surface the covalency of carbon is satisfied by bonding to oxygen and these bonds can be broken quite easily by hydrogenolysis.

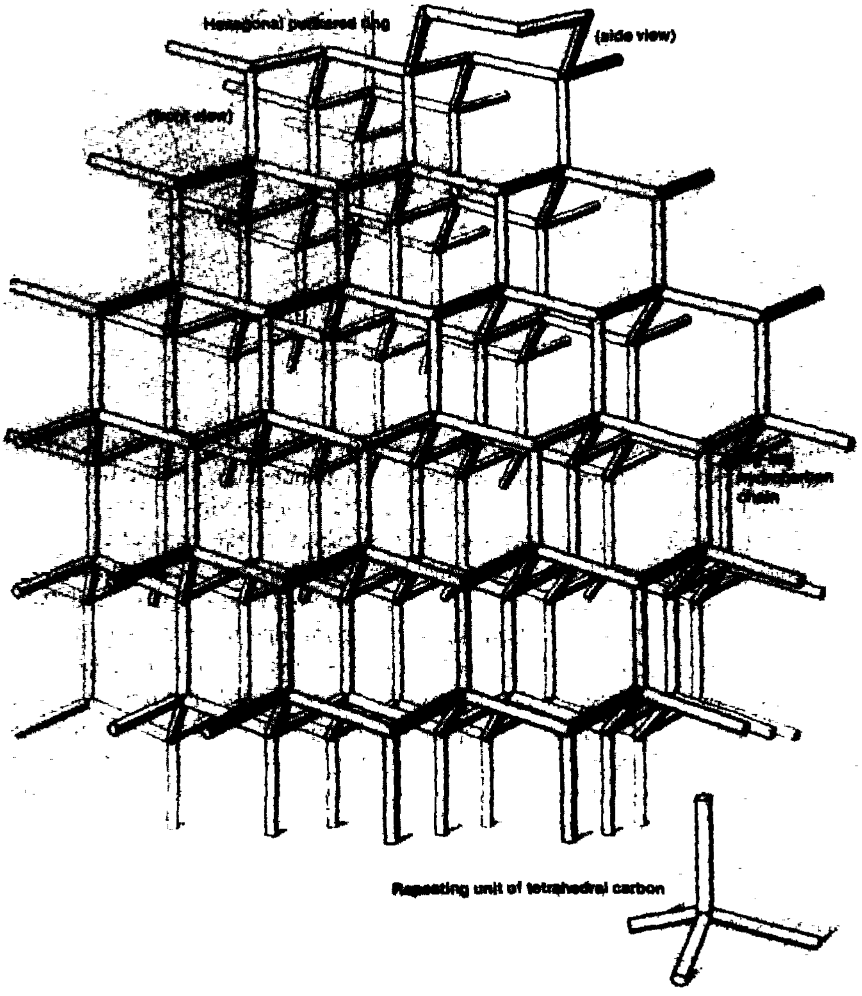

Fig. 1. The diamond lattice.

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Apart from the tetrahedron, numerous other symmetrical shapes are discernible in the diamond lattice: one recognises, for example, the zig-zag arrangement of C atoms found in normal alkanes; the ubiquitous hexagonal puckered ring; the *trans* : *anti* : *trans* geometry found in perhydroanthracenes; and a ten-carbon unit which represents the diamondoid form in miniature and whose cycloalkane counterpart is the $C_{10}H_{16}$ molecule, adamantane (1).

In fact, there exists an homology of bridged-ring cycloalkanes, of molecular formula $C_{4n+6}H_{4n+12}$ of which adamantane is the first member, whose topology is diamondoid in the sense that the arrangement of C atoms is such that each member is totally or largely superimposable on a fragment of the diamond lattice. It has been suggested that this homologous series be called the polymantanes.[2] Adamantane (1), diamantane (2) (formerly called congressane[3]), triamantane (3), and *anti*-tetramantane (4), the first four members of the series are known, and X-ray diffraction studies confirm the diamondoid arrangement in each. Adamantane and diamantane are in fact naturally occurring substances, having been isolated in 1933 and 1966, respectively, from petroleum fractions of the Hodonin oilfields in Czechoslovakia;[4,5] and although Prelog and Seiwerth[6] completed a rational synthesis of adamantane in 1941, the natural source was the only effective source until 1957.

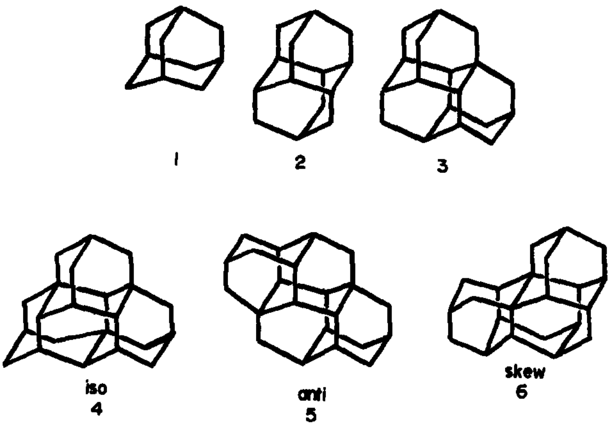
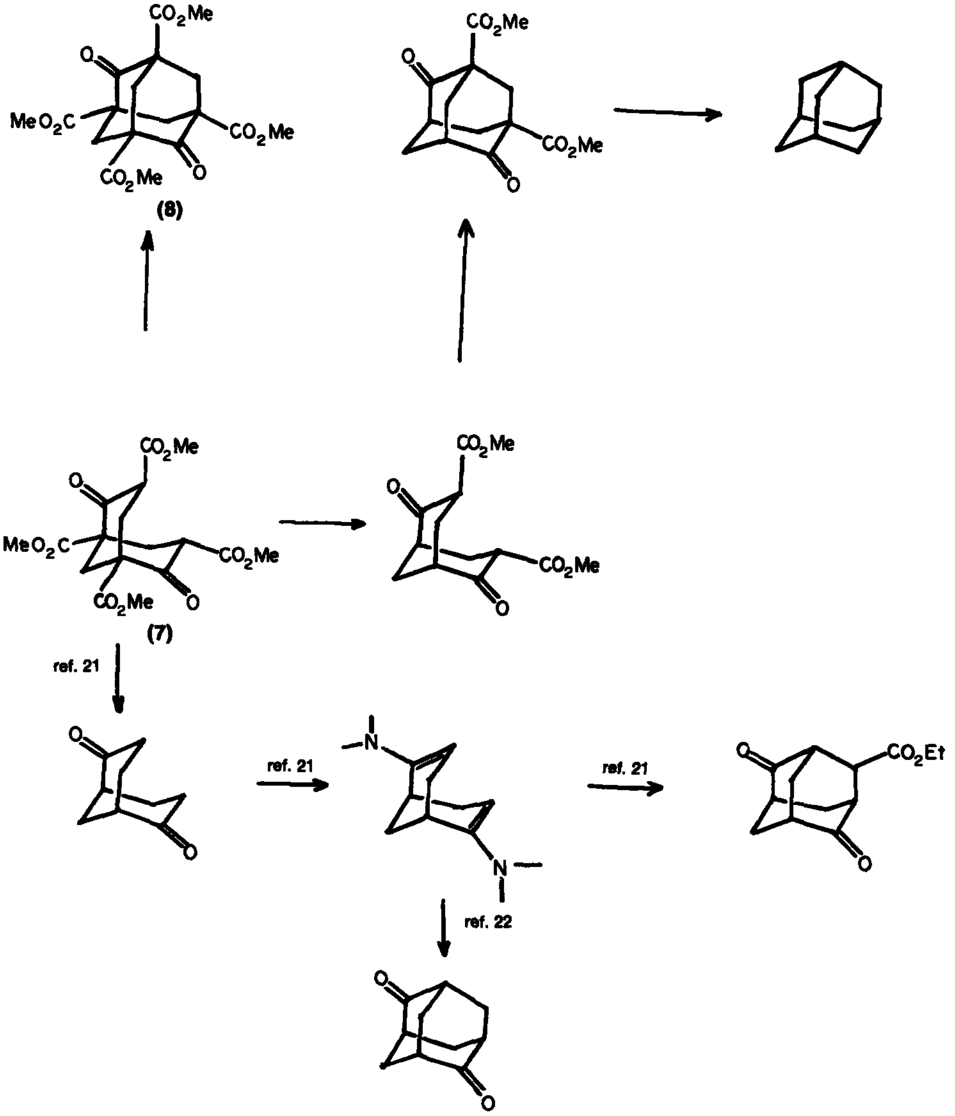


Fig. 2. The polymantanes.

The polymantane series bears a close formal similarity to the familiar aliphatic hydrocarbon series. Diamantane can be viewed as the union of two tetrahedral adamantane units in much the same way that ethane can be viewed as the union of two tetrahedral methane units (Fig. 2). This analogy extends to the number of possible isomeric forms of corresponding members of the two series. Just as the aliphatic hydrocarbon homology branches at butane so does the polymantanes at tetramantane, producing three possible isomers designated[7] isotetramantane, C_{3v}(4), *anti*-tetramantane, C_{2h}(5), and *skew*-tetramantane, C_2 (6), to emphasise their topological relationship to isobutane, and the *anti* and *skew* conformations of n-butane, respectively. One difference between the two series is the early emergence of quaternary C atoms in the polymantanes which gradually accumulate in the progression towards diamond itself. The number of possible isomeric forms increases rapidly for the higher polymantanes: there are 7 pentamantanes, 24 hexamantanes, and 88 heptamantanes.[2] Strict application of the von Baeyer nomenclature produces very unwieldy names (triamantane is heptacyclo$\{7.7.1.^{3,15}0^{1,12}.0^{2,7}.0^{4,13}.0^{6,11}\}$octadecane) and Balaban and Schleyer[2] have proposed a convenient alternative nomenclature for the higher polymantanes in anticipation of their eventual synthesis.

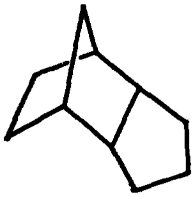
Apart from intrinsic interest, adamantane and diamantane have been particularly useful in research areas such as structure-reactivity relationships in carbocations and radicals;[8-10] the development of empirical force field (molecular mechanics) methods of calculating structures and energies of hydrocarbons;[11-14] and as model compounds for probing orientational disorder in molecular crystals.[15] Adamantane has also attracted much attention as a possible structural basis for some drugs,[8,16] and as a substrate for probing the limits of Bredt's rule.[17] There are several reviews of the chemistry of adamantane,[18] the latest being Fort's extensive monograph.[8] The emphasis in this report is on recent synthetic approaches to the larger members of the polymantane series.

The earliest recorded attempt to synthesise an adamantane derivative was that of Meerwein[19] in 1922, predating by several years the isolation of the hydrocarbon as a natural product. Using the ester (7) which now bears his name, Meerwein sought first to remove the bridgehead carbomethoxy groups and then bring about the ring closure indicated (Scheme 1) using diiodomethane and sodium. Meerwein's synthesis was unsuccessful, though, interestingly, the second step was later to become the basis of several successful syntheses. Bottger[20] using dibromethane and Meerwein's ester directly obtained the adamantane derivative (8) and a short time later the first synthesis of the parent hydrocarbon was described by Prelog and Seiwert,[6] again using the Meerwein approach in the key step (Scheme 1). The overall yield was very low and although several improvements were introduced by Stetter[21] and Landa[22] and their respective co-workers (Scheme 1), only small amounts of the hydrocarbon were ever produced by conventional synthetic methods.



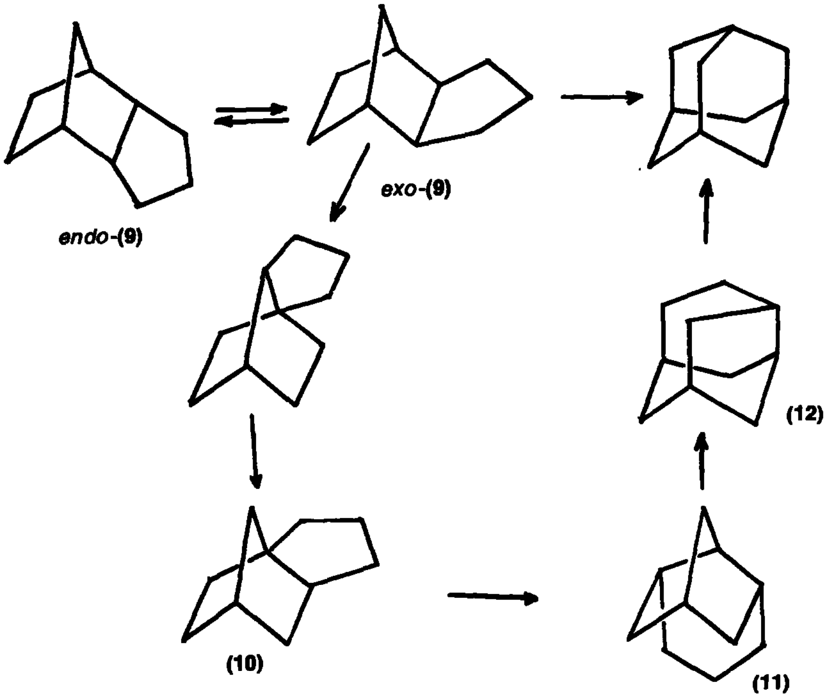
Scheme 1.

The picture changed dramatically in 1957 with the serendipitous discovery by Schleyer[23] that adamantane could be obtained from a very accessible isomeric hydrocarbon in a one-step operation. While studying the aluminium chloride-catalysed *endo*⇄*exo* isomerisation of tetrahydrodicyclopentadiene (9) (the hydrogenation product of cyclopentadiene dimer) Schleyer noted the formation of a third, crystalline substance which later proved to be adamantane. Not only did this discovery make



endo-(9)

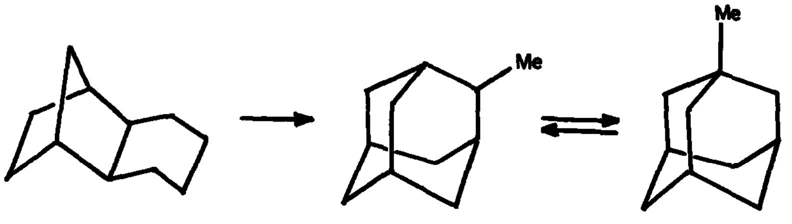
adamantane immediately available but it also established the pattern of much subsequent research in this area. In fact, Lewis acid-catalysed rearrangement is now the method of choice for the synthesis of the lower members of the polymantane series. The mechanism of the tetrahydrodicyclopentadiene → adamantane rearrangement, about which rather little is known on the experimental side, has been the subject of much speculation.[24] The process is thermodynamically controlled, success depending on the very high stability of adamantane relative to tetrahydrodicyclopentadiene (*vide infra*) and it is believed to involve carbocation intermediates which undergo multiple rearrangement via 1,2-bond and hydride shifts. Whitlock and Siefken[25] developed a general mathematical model for analysing the mechanism of the rearrangement, using as a basis set all the possible tricyclodecanes but excluding isomers with alkyl substituents or 3- or 4-membered rings, and found, by count, that of 2897 possible routes between precursor and product, that shown in Scheme 2 is the most direct, provided that intermediates interconvert via 1,2-bond shifts only and very high energy carbocations are excluded. The feasibility of at least a portion of this route has received some experimental support. Schleyer *et al.*[26] studied the rearrangement of tricycle **10** into adamantane and noted the transient formation of isomers **11** and **12**. However, no intermediates have ever been isolated or identified in the rearrangement of tetrahydrodicyclopentadiene itself, and although the short route of Whitlock and Siefken appears reasonable, it is quite possible that many other routes operate concomitantly. In fact, all known tricyclodecanes rearrange into adamantane under Lewis acid catalysis, emphasising that it is by far the most stable of the $C_{10}H_{16}$ manifold.



Scheme 2.

With conventional aluminium chloride catalysis the yields of adamantane from tetrahydrodicyclopentadiene are low (15–20%) due to the formation of numerous by-products. Several attempts have been made to improve the efficiency and selectivity of the process by varying the Lewis acid catalyst and the operating conditions.[27] The most successful of these involved a switch from conventional batch operations in solution to a gas-phase flow system and a heterogeneous catalyst. Work in Belfast showed that by conducting the rearrangement of tetrahydrodicyclopentadiene in the gas phase using hydrogen and hydrogen chloride as the carrier gas and a solid catalyst composed of chlorinated platinum alumina, very substantial improvements in the conversion to adamantane could be realised.[28] This gas-phase procedure was further improved on by the Idemitsu Kosan Company of Japan to a point where hundreds of tons of admantane can be produced using a chlorinated-platinum–rhodium–alumina catalyst with an operating lifetime of several months.[29]

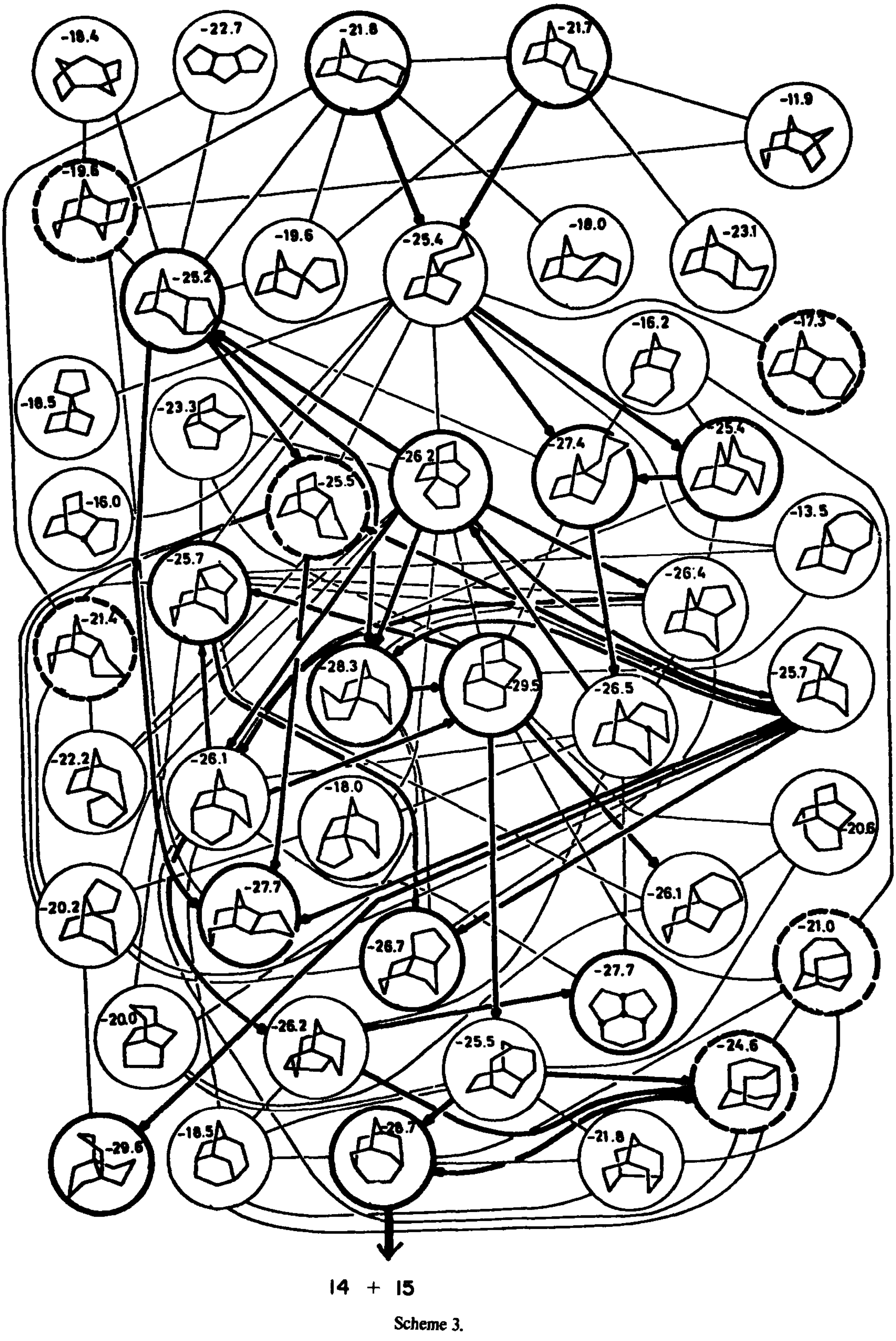
A very significant aspect of the rearrangement route to adamantane is the degree to which it is capable of extension to larger systems. Thus a Me group is readily added simply by carrying out the rearrangement with a tricycloundecane ($C_{11}H_{18}$) precursor. In rearrangements of this type alkyladamantanes are invariably preferred over nondiamondoid structures not possessing alkyl groups. Thus exposure of *cis,exo*-2,3-tetramethylenenorborane (**13**) to either aluminium chloride in solution or chlorinated platinum-alumina in the gas phase gives high yields of 1- and/or 2-methyladamantane (**14** and **15**), depending on the precise conditions.[30] The 1-Me isomer, thermodynamically the more stable of the two, appears to arise largely by isomerisation of the 2-Me isomer in a process which is slow relative to the rate of production of the latter. Using the gas-phase procedure it is possible to obtain almost pure 2-methyladamantane by conducting the rearrangement of **13** at very high flow rates.[31] In these circumstances the primary product is swept from the catalyst surface before any appreciable isomerisation to 1-methyladamantane occurs. The tricyclic $C_{11}H_{18}$ rearrangement energy surface is exceedingly complex—there are 434 isomers possible, though this is reduced to 69 if structures containing 3- or 4-membered rings are excluded. However, in contrast to the rearrangement of tetrahydrodicyclopentadiene→adamantane, several intermediates in rearrangements of various tricycloundecanes have been identified.[32] Osawa *et al.*[33] have conducted a comprehensive computer-assisted analysis of the formation of methyladamantanes from the various tricycloundecanes using the graphical presentation of Whitlock and Siefken. A glance at the resulting interconversion map (Scheme 3) gives some idea of the enormous concatentation of events, in terms of intermediates and pathways, which may occur before the methyladamantanes emerge in the security of thermodynamic stability. The very many alkyl and polyalkyladamantanes that have been obtained by rearrangements of this kind have been summarised in earlier reviews.[8,18]



(13) **(15)** **(14)**

The use of the rearrangement route to synthesise diamantane (**2**), the second member of the polymantane series, illustrates the extension of this approach to a more complex system. It also highlights one of its more important limitations: the problem of finding a suitable hydrocarbon to act as precursor. The choice of precursor is important: ideally, it should be isomeric with the desired diamondoid product; and it should possess a moderate degree of strain to ensure an adequate thermodynamic driving force for rearrangement. Precursors with excessive amounts of strain, such as that associated with molecules containing several small rings are generally unsatisfactory; in such systems relief of strain can often be achieved by indiscriminate fragmentation and disproportionation reactions. An additional important factor is that the rearrangement must be mechanistically feasible, i.e. carbocation intermediates must be energetically accessible and favourable bond alignments must be possible for the 1,2-alkyl shifts involved.

Initially, Schleyer *et al.*[34] used various stereoisomeric forms of the norbornene{2 + 2}photodimer (**16**) and obtained diamantane in 1–10% yield; the major product was that of rearrangement-disproportion, 1,2-tetramethyleneadamantane (**17**). Later work showed that diamantane could be obtained in 30% yield from pentacycle (**18**); however, this precursor is not readily available.[35] Much greater improvements were realised using the norbornadiene dimers (**19** and **20**).[36,37] These substances, known


-18.4
-22.7
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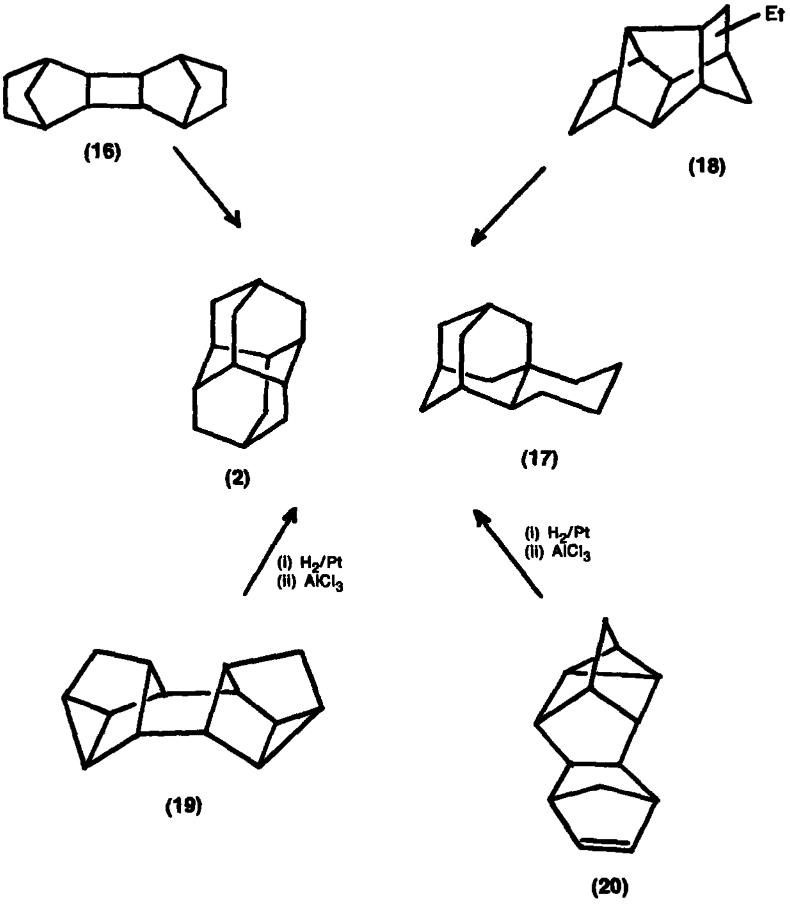
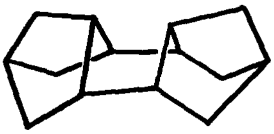
-20.0
-26.2
-25.5
-24.6
-29.6
-18.5
-28.7
-21.8
14 + 15

Scheme 3.

respectively as binor-S[38] and Katz dimer,[39] are not isomeric with diamantane but their tetrahydro derivatives are. Hydrogenolysis of the cyclopropane ring of Katz dimer is rather difficult (though the tetrahydro compound does give diamantane in good yield) and binor-S (19) is the preferred precursor. Binor-S is readily obtained by cobalt-catalysed {4 + 4} dimerisation of norbornadiene and hydrogenolysis using Adam's catalyst in acetic acid opens both cyclopropane rings, producing a single tetrahydro derivative for which there are three possible structures: (21, 22 and 23). Structure 21 has been eliminated on spectroscopic grounds,[40] the remaining uncertainty between 22 and 23 being of little importance since





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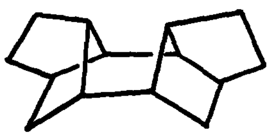

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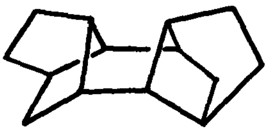


(23)

they may well be interconvertible in the presence of a Lewis acid. In any event, with aluminium chloride in hot cyclohexane or dichloromethane tetrahydrobinor-S is transformed into diamantane in 70–80% yield.[36,37]

It has been estimated[40] that tetrahydrobinor-S and diamantane are but two of a least 40,000 pentacyclotetradecanes: to involve even a small fraction of that number in a mechanistic analysis using all possible 1,2-bond shifts would produce a rearrangement graph of the type in Scheme 3 of unmanageable complexity unless assumptions reducing the number of isomers and pathways are made. In fact, Schleyer *et al.*[40] were able to use a number of simplifying assumptions, following the discovery that when the rearrangement is allowed to proceed under very mild conditions transient intermediates can be observed. At 0°, at least two major (max concentration 20% each) and at least five minor (less than

1% total) intermediates can be detected by glc analysis. At the end of the reaction, however, only diamantane and the disproportionation product (**17**) remain. The initial intermediate (as yet unidentified) rearranges to the major intermediate (**25**) (identified by ^{13}C NMR) which then slowly rearranges to diamantane.

Starting with tetrahydrobinor-S Schleyer *et al.*[40] generated a graph using 1,2-bond shifts but excluded the intervention of isomers containing quaternary C atoms. Molecular mechanics calculations were used to estimate the heats of formation of the various isomers, thereby providing an indication of the exothermicity or endothermicity of each bond shift. This preliminary treatment produced 13 tetrahydrobinor-S isomers, but it did not lead to diamantane. Interestingly, however, the isomer which the calculations predicted to be of lowest energy turned out to be the isomer **25** identified in the low temperature rearrangement. The several most likely exothermic pathways for interconversion of tetrahydrobinor-S and **25** are shown in Scheme 4; at least two intermediates must be involved but several isomers of comparable enthalpy may intervene. Since this treatment did not lead directly to diamantane it follows that at least one tetrasubstituted isomer must be involved after **25** and that this isomer must be of higher enthalpy since **25** is isolable. The extension of graph generation beyond **25** requires tetrasubstituted intermediates; however, generating a full graph was highly impracticable because of the number of isomers possible. A simplifying approach involved consideration of all the possibilities but generating only those portions of the graph which were energetically favourable. Starting with **25** new isomers were generated by 1,2-bond shifts and the strain energy calculations for the generated isomer then revealed the best candidate for the next intermediate. From the various possibilities the isomer lowest in strain energy (i.e. most negative ΔH_f° value) was processed further and the same procedure was continued until diamantane was reached. Thus **25** generated three new isomers with quaternary C atoms, (**26**, **27** and **28**), of which **28** was lowest in strain energy. Similarly **28** gave four new isomers, the least strained of which was **29**. In the same manner **28** led, via **30**, to diamantane. The proposed route from **25** to diamantane is:

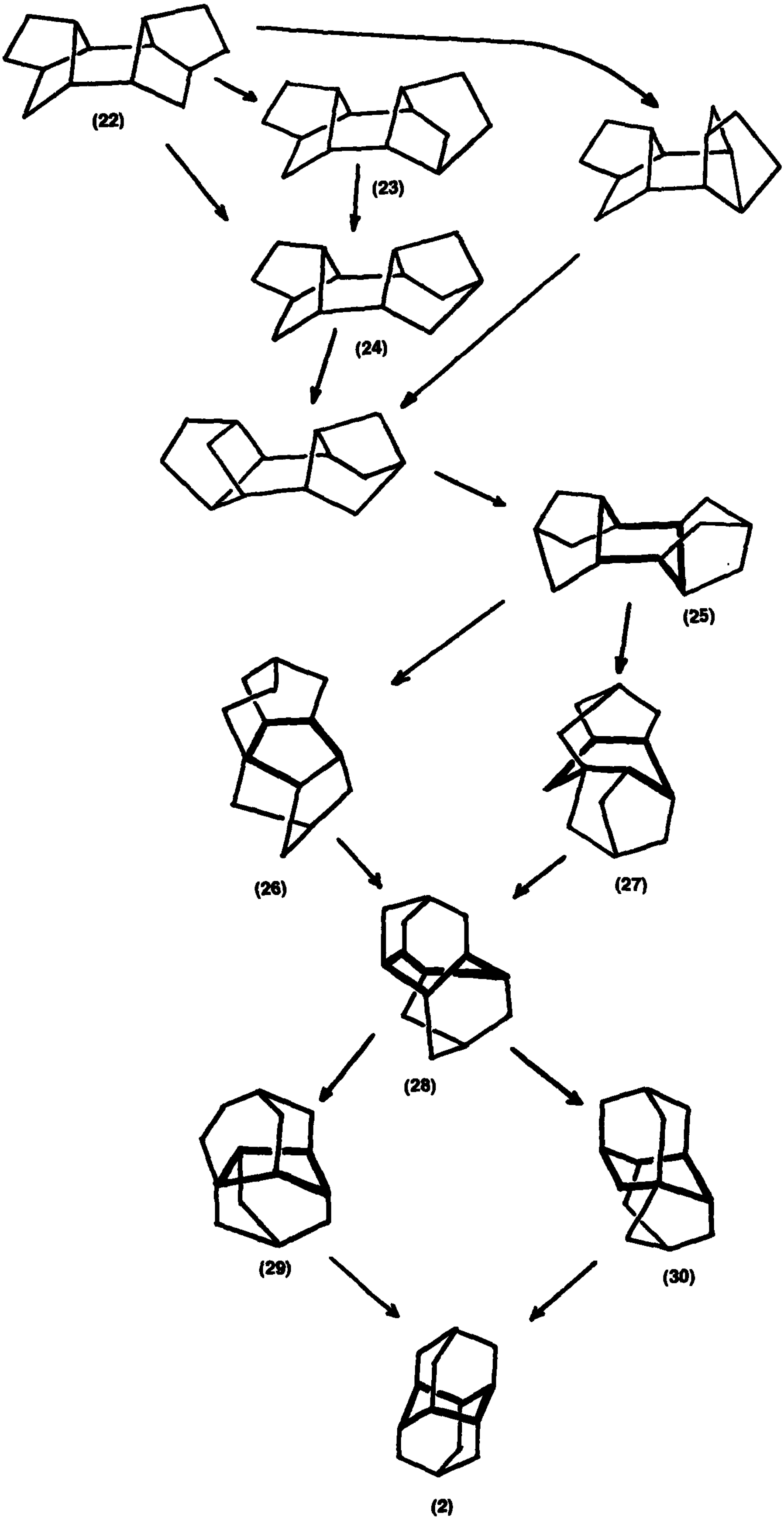
	25	→	**26**	→	**28**	→	**29**	→	**2**
ΔH_f° kcal/mole	−13.21		−8.37		−20.06		−18.12		−37.37

It is energetically favourable and efficient, involving only four bond shifts two of which are mildly endothermic and two which are very exothermic.

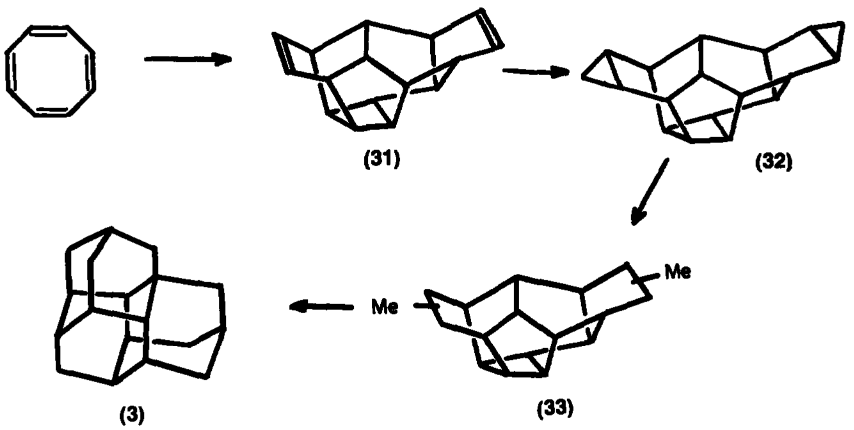
In this proposed route, the chair cyclohexane ring (heavy lines in **25**) becomes the medial or zonal chair cyclohexane ring of diamantane. Throughout the rearrangement alternation takes place between 5- and 6-membered rings, but the middle C atoms need not become scrambled. The rearrangement of methylene attachments around the central cyclohexane ring in **25**, **29** and **2** can be envisaged as occurring most easily by tetrasubstituted intermediates. In **25** the middle cyclohexane ring carries attachments on one face at positions {1,2,3} and on the other face at positions {4,5,6}; in diamantane these attachments alternate at {1,3,5} on one face and {2,4,6} on the other.

The history of triamantane (**3**), the third member of the polymantane series, is rather similar to that of diamantane, beginning with the development of a rather inefficient precursor followed by the discovery of a much more effective precursor. Initially, Schleyer *et al.*[41] used the cyclooctatetraene dimer (**31**) as a structural basis (Scheme 5), bringing it up to the required carbon level in **32** via Simmons–Smith cyclopropanation of the double bonds and thence to the desired hydrogen level in **33** by catalytic hydrogenolysis of the cyclopropane rings. Polycycle **33** did indeed give triamantane on aluminium bromide treatment, but the yield (~1%) did not encourage the routine preparation and study of this interesting molecule. Work in Belfast in the 1970s was directed towards the realisation of much more efficient routes to triamantane.[42] We were struck by the remarkable ease with which tetrahydrobinor-S can be changed into diamantane and we considered the possibility of modifying the binor-S structure so as to make it a structural basis for triamantane also.

The elaboration of binor-S into a triamantane precursor requires the addition of four C atoms. However, to preserve the isomeric relationship between precursor and product this addition must be brought about without an increase in the total number of rings since binor-S and triamantane are both heptacycles. Ideally, we wished to rearrange binor-S into a hexacyclic olefin which could be raised to the C_{18} heptacyclic level by {4+2} cycloaddition with butadiene and thence to the required $C_{18}H_{24}$ level by hydrogenation. Binor-S is a highly strained, reactive molecule, formally consisting of two nortricyclyl



Scheme 4.

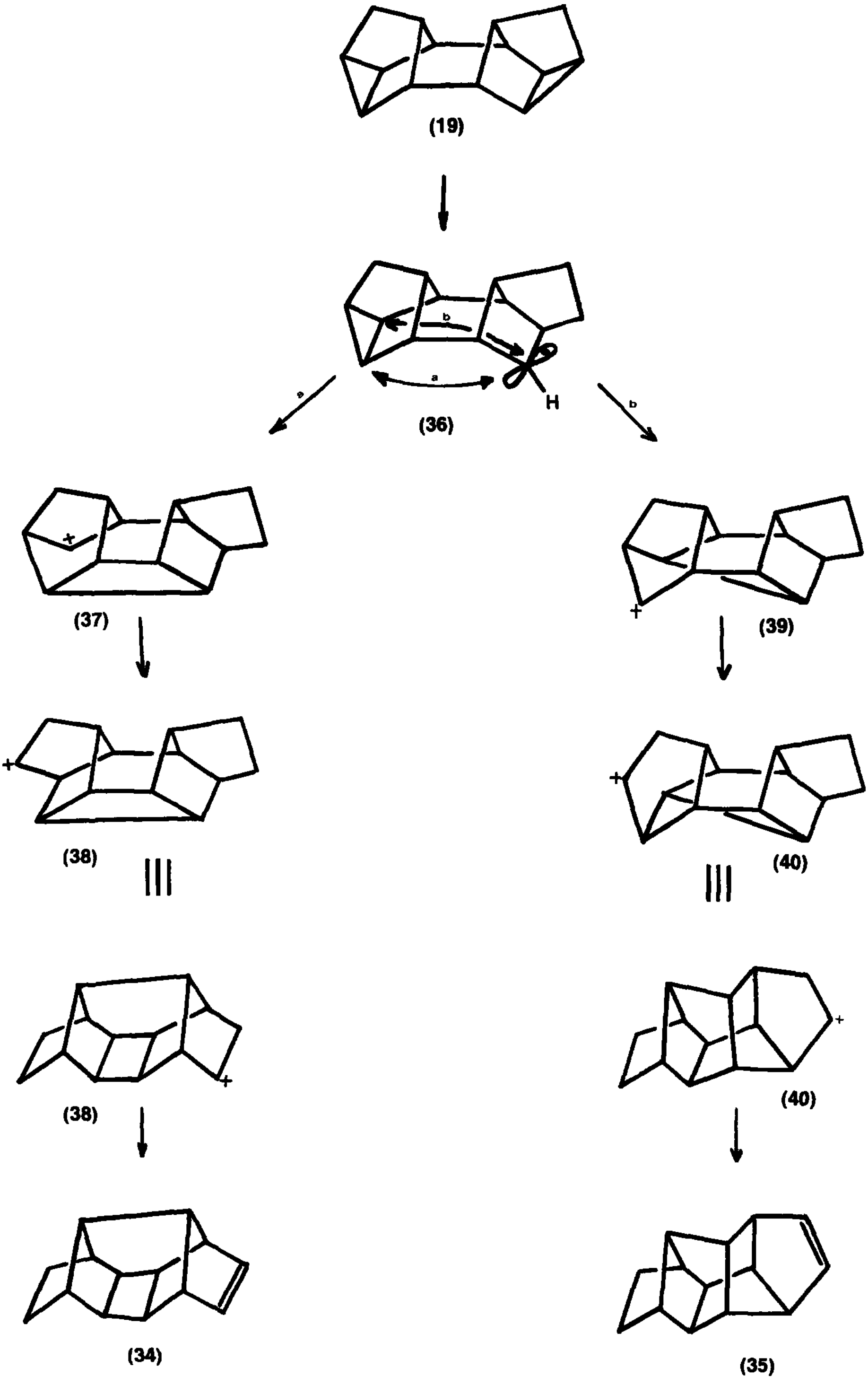


Scheme 5.

units conjoined in such a manner that the central cyclohexane ring is in a boat conformation.[43] One consequence of this molecular arrangement which is pertinent to its eventual use in triamantane synthesis is the *syn* geometry of the two C_7 units. This geometry holds the inside edges of the cyclopropane rings in close proximity, offering the possibility of opening one with concomitant involvement of the other in a transannular process. This type of change can in fact be brought about in the gas phase and in solution. When binor-S is vapourised in nitrogen and passed over a platinum-silica catalyst a 1:1 mixture of the hexacyclic olefins (**34** and **35**) is obtained in good yield (Scheme 6). Solution studies reveal that binor-S in benzene containing silver perchlorate behaves in exactly the same way, furnishing these olefins in 60% yield. It was believed originally that the respective use of platinum metal and silver ion were essential to the success of these two methods for preparing **34** and **35**. However, the role of the metals was questioned when it was discovered that perchloric acid in benzene also promoted olefin formation (though less efficiently than silver perchlorate) as did silica gel alone in either the gas phase or as a suspension in boiling decalin. It appears, in fact, that the conversion of binor-S into olefins (**34** and **35**) is a proton initiated process; that silver perchlorate in benzene gives better yields than perchloric acid in benzene is probably due to the fact that the olefins form particularly stable adducts with silver ion which precipitate from solution as they are formed; in perchloric acid the olefins are free to react further with the solvent giving products of alkylation which can be detected.

The binor-S rearrangement is probably initiated by protonation of one of the cyclopropane rings, producing cation **36** (Scheme 6) the vacant orbital of which should be favourably disposed in distance and dihedral angle towards interaction with the inside edge of the second cyclopropane ring. Cyclopropyl participitation in **36** along pathway *a* produces cation **37** which cannot easily eliminate a proton but which can undergo a 1,2-bond shift to cation **38**. Proton loss from **38** produces olefin **34**. There is a second, equally accessible pathway for cyclopropyl participation in cation **36** along direction *b*, leading to a comparable set of cationic intermediates **39** and **40**, and terminating after proton loss in olefin **35**.

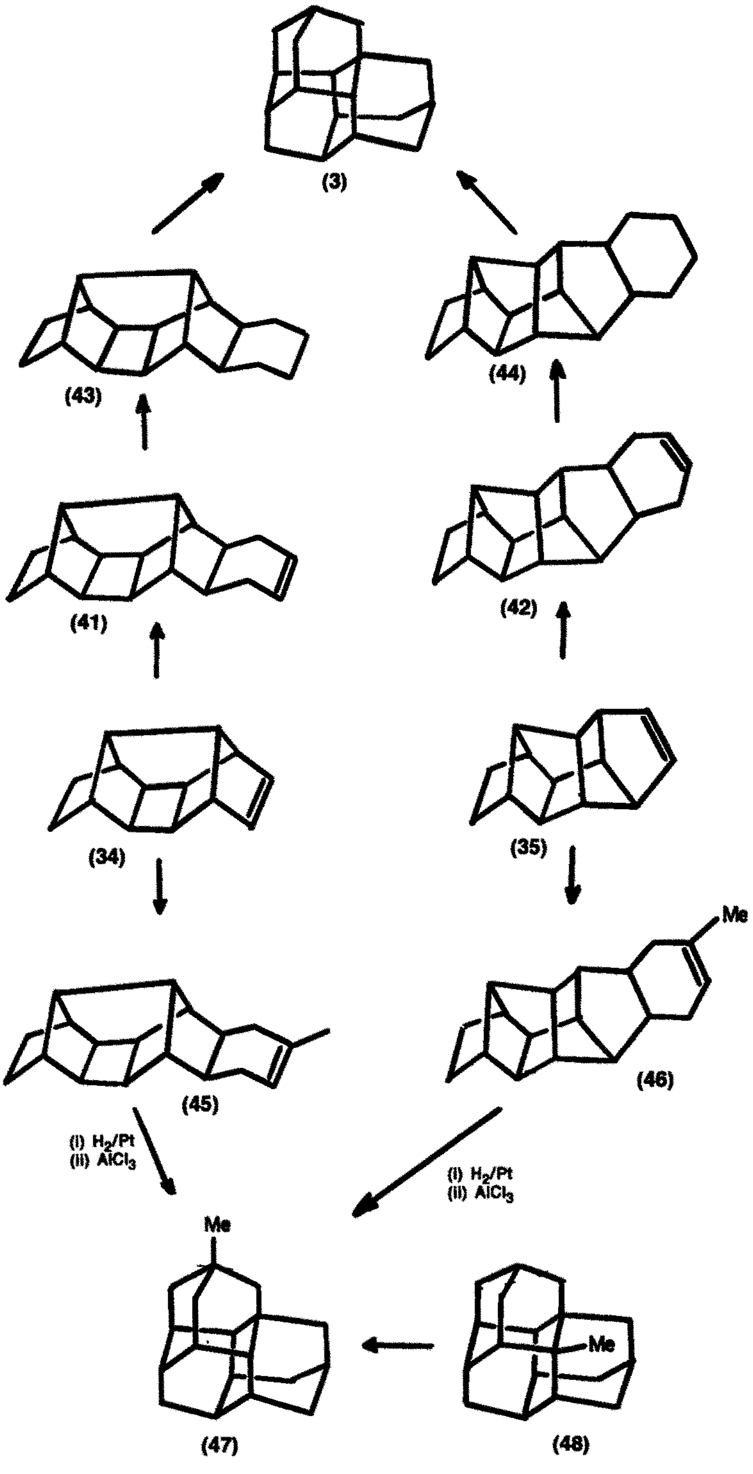
Although olefins **34** and **35** are separable by distillation, separation is quite unnecessary on route to triamantane: both are equally effective building blocks. Diels–Alder addition of butadiene (Scheme 7) at 180° produces adducts **41** and **42** which readily form dihydro derivatives (**43** and **44**) on catalytic hydrogenation. Exposure of **43** and **44** to aluminium chloride in hot cyclohexane for several days produces triamantane (**3**) in 60% yield. This remarkable transformation has not been subjected to the graphical analysis described earlier for the formation of adamantane, methyladamantane, and diamantane. To produce a graph of manageable size would require numerous approximations on the possible pathways and severe restrictions on the number of heptacyclooctadecanes involves. There are many thousands of heptacyclooctadecane isomers and there may be literally hundreds of energetically and mechanistically accessible pathways operating between **43** and **44** and triamantane, but examination of the structures does not reveal any obvious preferred pathway. Numerous intermediates have been observed in the reaction; none has been isolated or identified. An intriguing aspect of the mechanism is the fact that although precursors (**43** and **44**) are structurally quite different in character, they are transformed into triamantane with equal ease. This route to triamantane is easily modified to allow the introduction of Me substituents. If, instead of butadiene, the Diels–Alder reaction of **34** and **35** is



Scheme 6.

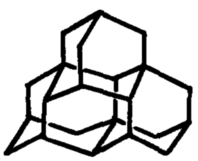
conducted with isoprene, adducts 45 and 46 are obtained. Hydrogenation of this mixture followed by aluminium chloride treatment gives a mixture of methyltriamantanes containing a preponderance of the 9-isomer (47). Steric considerations suggest that 9-methyltriamantane (47) should be the thermodynamically most stable of the four possible bridgehead isomers. In fact, aluminium chloride-catalysed isomerisation of 2-methyltriamantane (48), prepared by methylation of 2-bromotriamantane, produces the 9-isomer as the major product of equilibrium.[44]

Adamantane, diamantane, and triamantane are conveniently grouped together as the lower polyman-



Scheme 7.

tanes. All three are now readily available in quantity via cationic rearrangement; each exists in a single isomeric form; and their chemical behaviour, particularly in substitution reactions, has been developed in a general way so as to make them useful substrates for mechanistic studies. The higher polymantanes begin with tetramantane and, in contrast, consideration of their chemistry poses new problems because tetramantane is the first member of the series capable of existing in more than one isomeric form. Tetramantane, $C_{22}H_{28}$, has three possible isomers designated isotetramantane, C_{3v}(**4**), *anti*-tetramantane, C_{2h}(**5**), and *skew*-tetramantane, C_2(**6**), to emphasise their topological relationship with isobutane (**49**) and the *anti* and *skew* conformations of n-butane, (**50** and **51**), respectively.[45] The *anti* and *skew* tetramantanes each contain two quaternary C atoms the relationship being 1,4 and 1,2, respectively; the *iso* form has three quanternary C atoms in a 1,3,5 relationship. Molecular mechanics calculations indicate that the order of thermochemical stability of the tetramantane isomers is *iso* > *anti* > *skew*, with the *iso* and *anti* forms separated by less than 2 kcal/mol.[46]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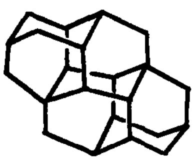
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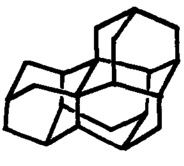
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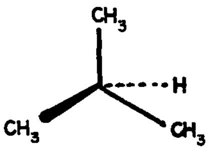

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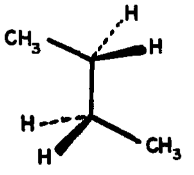

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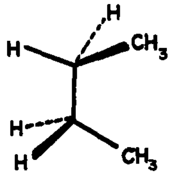
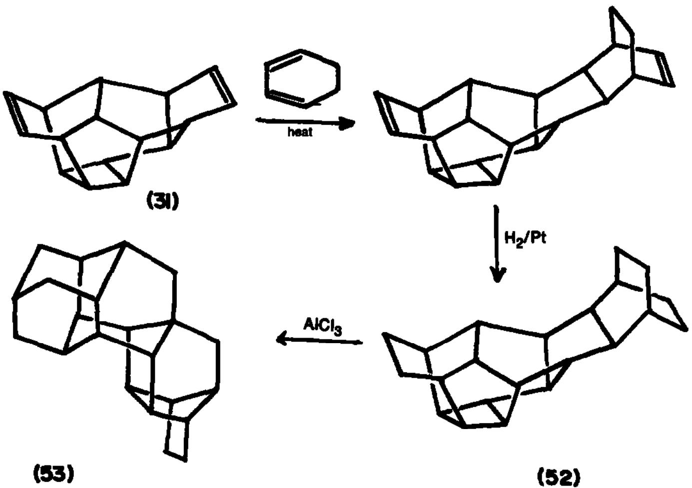


(51)

The question arises as to whether the carbo-cation rearrangement route can be extended to these large multicyclic, isomeric systems. The first problem is that of finding a suitable precursor since very few large polycyclic hydrocarbons of molecular formula $C_{4n+6}H_{4n+12}$ are known. A second uncertainty concerns the actual mechanism of rearrangement, i.e. will unfavourable kinetic factors associated with the intervention of crucial carbocation intermediates eventually outweigh the inherently favourable thermodynamics of polymantane production? And third, since it seems unlikely that thermodynamic control will persist to the extent that the tetramantane isomers will interconvert readily, will the possibility of producing one or other of the isomers unpredictably or complex mixtures of all three become a limiting factor in the carbocation rearrangement route.

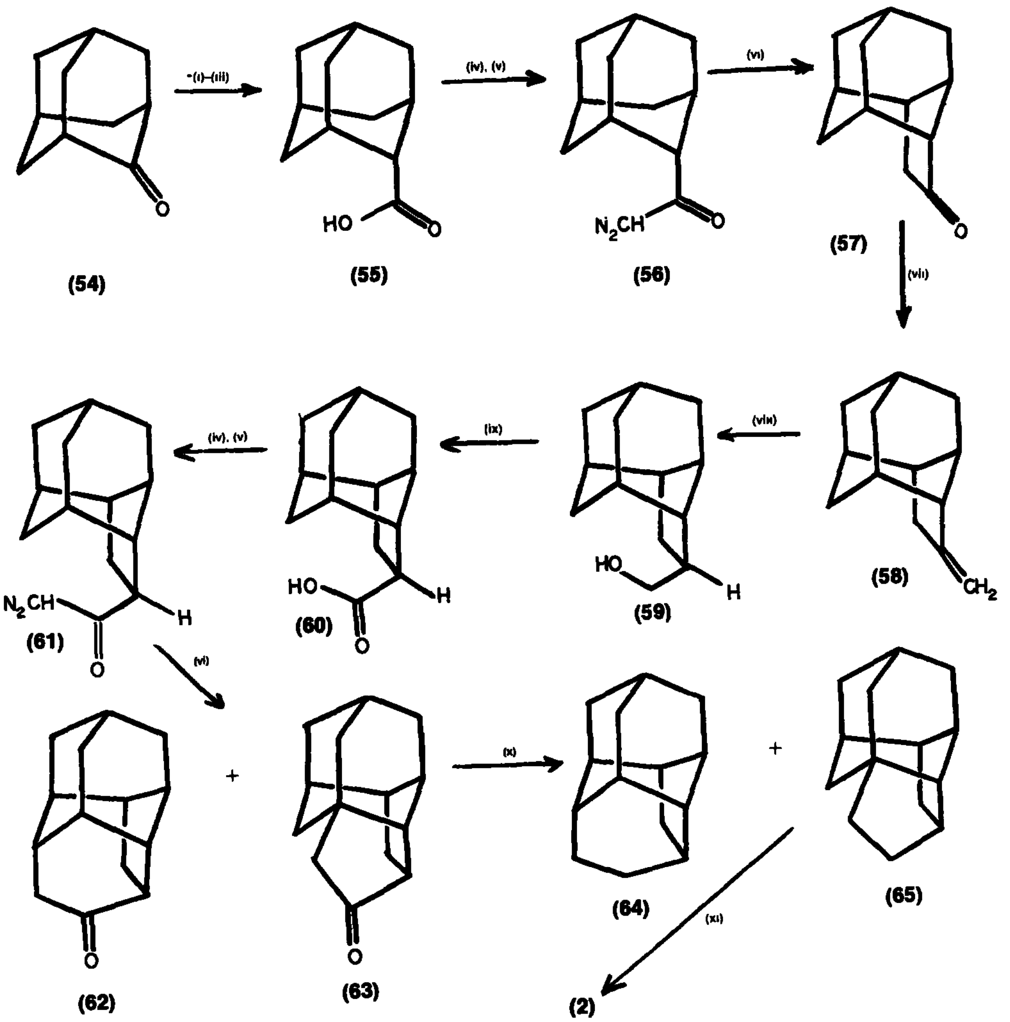
In fact, finding a precursor of the correct molecular formula does not guarantee success even though the rearrangement may appear very feasible thermodynamically. Schleyer *et al.*[45] prepared a strained $C_{22}H_{28}$ polycycle (**52**) from cyclooctatetraene dimer **31** by cycloaddition of cyclohexadiene with subsequent hydrogenation (Scheme 8) only to find that this precursor did not rearrange fully into tetramantane but stopped short at a less regular structure **53** in which only two of the admantane units are complete. Since all of the tetramantane isomers are almost certainly more thermodynamically stable than **53**, the structure of which incorporates a highly strained norbornane unit, the reason for the failure of this attempt must be kinetic (mechanistic) not thermodynamic. Even prolonged exposure of **53** to



Scheme 8.

aluminium bromide at 150° does not further the rearrangement, rather the molecule is destroyed by fragmentation. Clearly, the crucial cationic intermediate necessary for initiating the next step or a bond shift associated with that step is inaccessibly high in energy.

The failure to produce tetramantane by aluminium halide-catalysed rearrangement and the inherent difficulties of the whole approach led inevitably to a search for alternative methods for the construction of the polymantanes. Two groups working independently devised a new approach to the problem of some generality. It is free of some of the uncertainties of the thermodynamic rearrangement approach and is based on the idea that it should be possible to elaborate any member of the polymantane series into the next higher member by adding two new rings with four C atoms (single homologation) or into the second higher member by adding four new rings utilising eight C atoms (double homologation). Schleyer *et al.*[47] using conventional methodology illustrated this approach by synthesising diamantane from adamantane whereas our approach had as its objective the synthesis of one or other of the tetramantane isomers. The



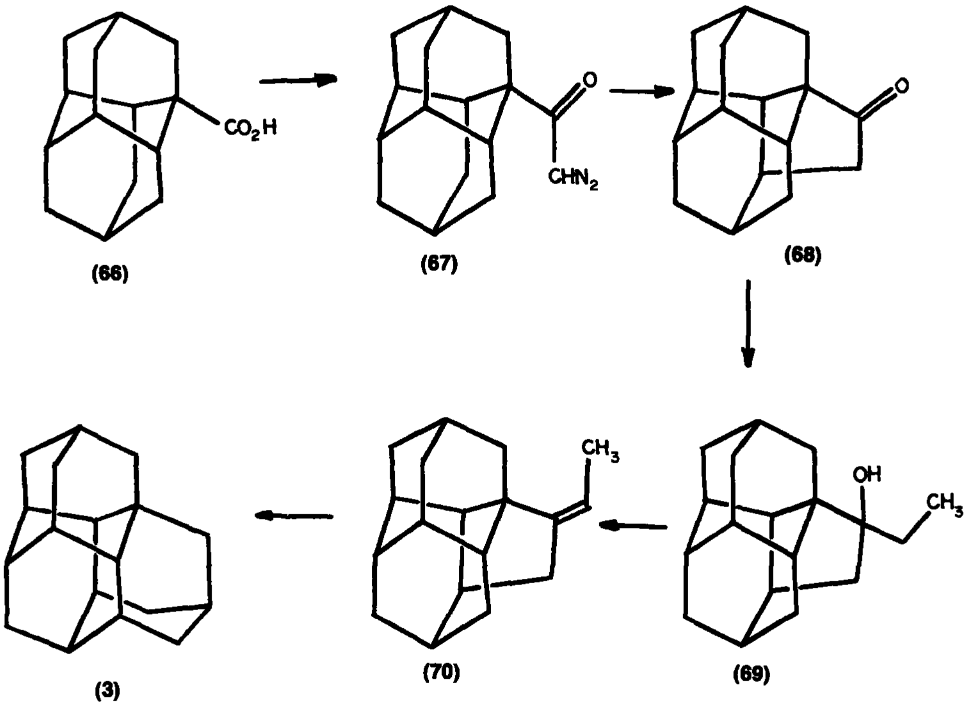
(i) $Me_2SO{=}CH_2$ (ii) $Et_2O \cdot BF_3$ (iii) CrO_3 (iv) $SOCl_2$ (v) CH_2N_2
(vi) $CuSO_4$/toluene (vii) $Ph_3P{=}CH_2$ (viii) $B_2H_6/H_2O/NaOH$ (ix) CrO_3
(x) N_2H_4/KOH (xi) $AlBr_3/CS_2$.

Scheme 9.

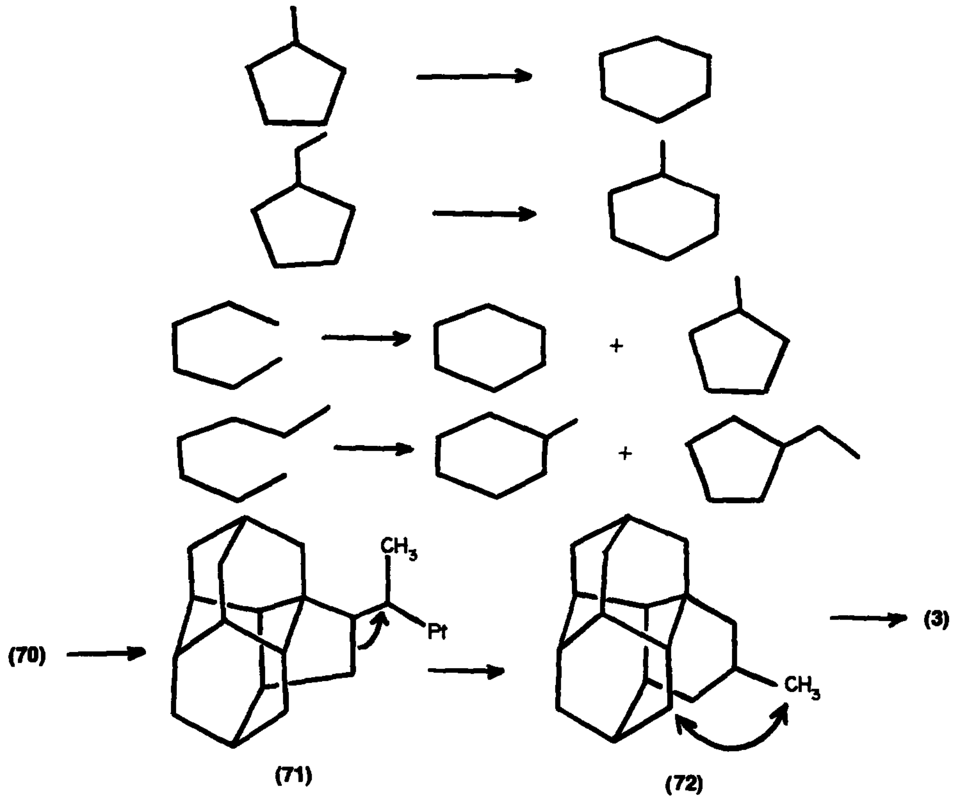
Schleyer synthesis is summarised in Scheme 9. It involves the stepwise addition of two rings to the adamantane nucleus utilising two ketocarbeniod insertion reactions and terminates in a reaction characteristic of all protoadamantyl derivatives, namely, a 1,2-bond shift. Adamantanone (54) was converted via standard procedures into the 2-carboxylic acid (55) and thence to the α-diazoketone (56). Copper-catalysed decomposition of the diazoketone produced the cyclopentanone derivative (57). Two more C atoms and another ring were added by repeating this process. Thus ketone 57 was successively converted into olefin 58, alcohol **59**, carboxylic acid **60** and α-diazoketone **61**. Copper-catalysed decomposition of this diazoketone produced two ketones (**62** and **63**) which on Wolff–Kishner reduction afforded the hydrocarbons (**64** and **65**). Hydrocarbon **64** is a protodiamantane, i.e. the structure is related to diamantane by a single 1,2-bond shift. It was known already from studies with protoadamantyl derivatives that this highly exothermic 1,2-bond shift can be brought about under very mild conditions.[24] In fact, brief treatment of both hydrocarbons (**64** and **65**) with aluminium bromide produced an essentially quantitative conversion to diamantane (**2**).

The early stages of the alternative homologation procedure developed in Belfast are similar to those described above, the first ring being assembled via a diazoketone insertion reaction.[48,49] The later stages are quite different, however, consisting in the key operation of a new, novel gas-phase catalytic procedure for the construction of relatively unstrained bridged-ring carbocycles. The details of this approach were explored for the elaboration of diamantane into triamantane[48] and then were applied to the first synthesis of a tetramantane isomer.[49]

Diamantane-1-carboxylic acid **66** (Scheme 10) was prepared by Koch–Haaf carboxylation of diamantan-1-ol and converted into the diazoketone **67**. Copper-catalysed decomposition of **67** furnished the cyclopentanone **68**. Ethylmagnesium bromide and **68** produced the tertiary alcohol **69** which could be dehydrated in benzene containing iodine to the olefin **70**. The final step was brought about on a 2% platinum on silica catalyst in the gas phase in hydrogen. When olefin **70** was vapourised in a stream of hydrogen and passed over the catalyst at 430° triamantane **3** was produced in 21% yield. This unusual transformation is in fact a composite example in a multicyclic system of two reactions well known in catalytic reforming,[50] one of the basic petroleum refining processes. In catalytic reforming, petroleum-range hydrocarbons, including those formed from larger hydrocarbons by cracking, are reconstituted or "reformed" without changing their C atom content. Reforming reactions, which include isomerisation of n-alkanes to their branched-chain isomers, ring-enlargement/contraction of cycloalkanes, hydrogenation, dehydrocyclisation of acyclic alkanes, and dehydrogenation, lead to a marked improvement in fuel quality as measured by the octane number. Catalysts for reforming are usually platinum or platinum alloys on a solid support. The reforming reactions pertinent to the synthesis of triamantane from olefin **70** are ring enlargement/contraction and dehydrocyclisation, the most important examples of which are, respectively, the reversible conversion of methyl and ethylcyclopentane into cyclohexane and methylcyclohexane and the cyclisation of n-hexane and n-heptane to cyclohexane, methylcyclopentane, methylcyclohexane, and ethylcyclopentane (Scheme 11). Conversion of **70** into triamantane contains the



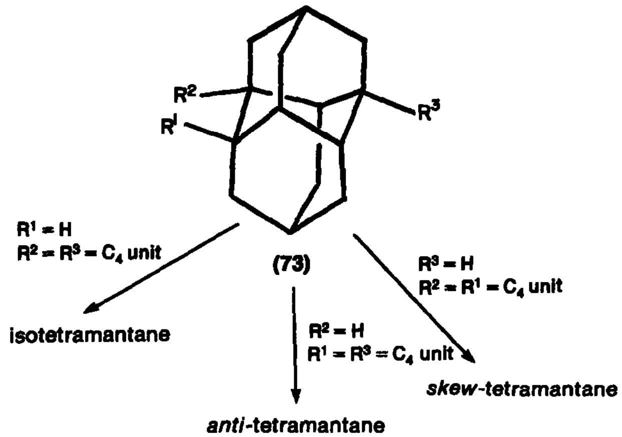
Scheme 10.



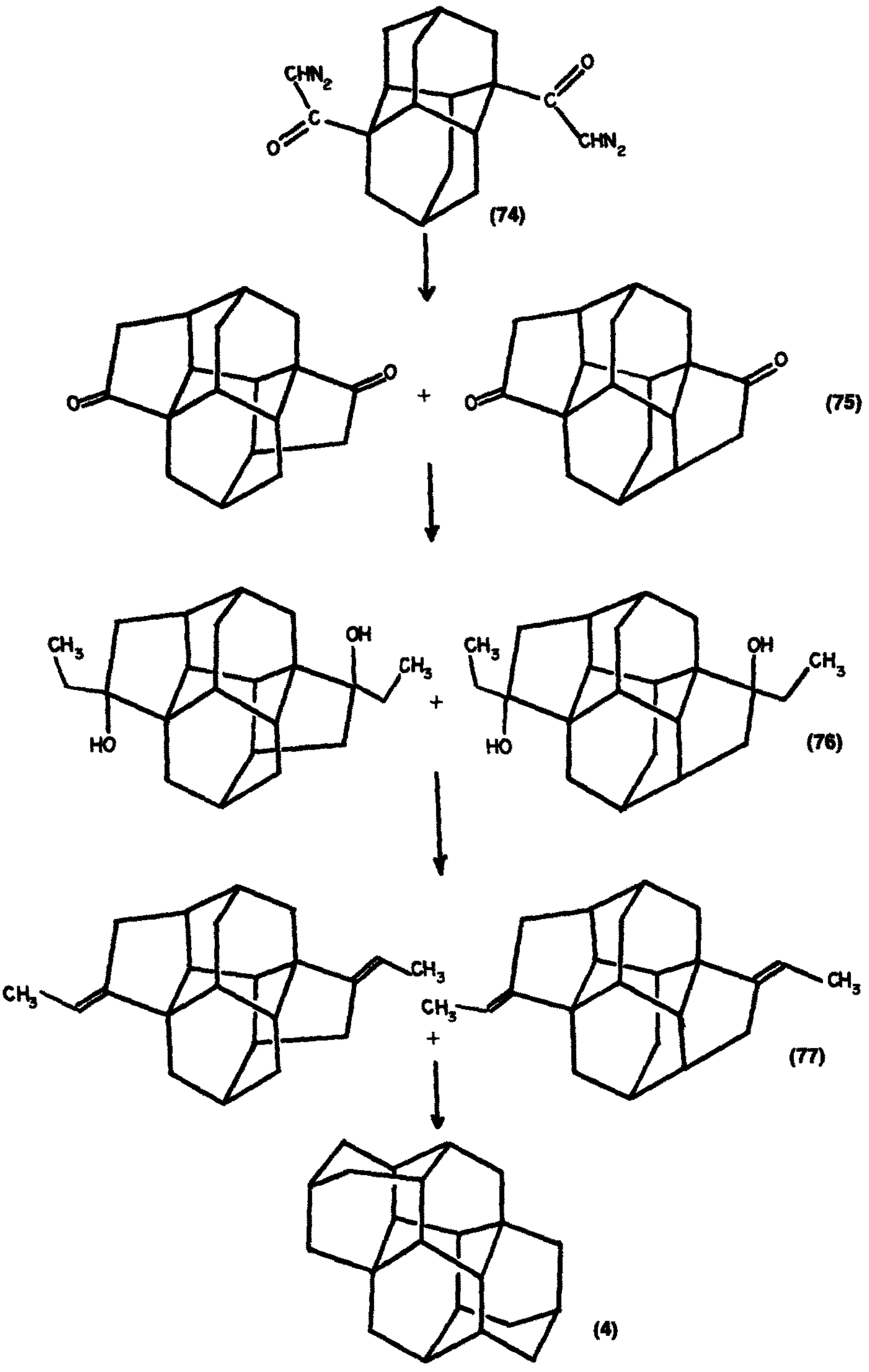
Scheme 11.

essential elements of these two processes, the overall change involving expansion of an ethylcyclopentyl system to a methylcyclohexyl system (which in this particular case has a strong thermodynamic driving force) followed by C–C bond formation with loss of hydrogen (dehydrocyclisation) between the methyl group and the methylene group indicated (Scheme 11) to form two new cyclohexane rings of the triamantane skeleton. Although the mechanisms of reforming reactions are still controversial,[51] the ring expansion reaction may proceed via a 1,2-bond shift to platinum in a surface alkyl such as 71.[52] A second platinum-mediated reaction removes two H atoms from 72 with concomitant formation of a new C–C single bond.

The success of this route to triamantane opened up the way to tetramantane via a double homologation of diamantane. Although double homologation is inherently more complex than single homologation, it was possible right at the outset to differentiate between the structural foundations necessary for each of the three tetramantane isomers. Considering the relationship between the three possibilities and the diamantane precursor 73 it is clear that isotetramantane requires four-carbon units



at positions R^2 and R^3, *anti*-tetramantane at positions R^1 and R^3, and *skew*-tetramantane at positions R^1 and R^2. Efforts were directed towards the *anti* isomer (**5**). The reaction sequence used was very similar to that employed in the single homologation of diamantane. Carboxylation of diamantane-1,6-diol produced the 1,6-diacid which was transformed into the bis-diazoketone (**74**) (Scheme 12).



Scheme 12.

Copper-catalysed decomposition of **74** produced a biscyclopentanone **75** which was probably a mixture of the two possible insertion products, although it appeared to be a single substance; either isomer was equally acceptable as an intermediate. Four more C atoms were added to **75** via a Grignard reaction with ethylmagnesium bromide, and the resulting diols **76** were dehydrated to the dienes **77**. Finally, when **77** was subjected to the gas-phase procedure on platinum at 360° a mixture of products was obtained from which *anti*-tetramantane (**5**) could be isolated in 10% yield by crystallisation from acetone. The diamondoid structure was confirmed by X-ray diffraction analysis.[53]

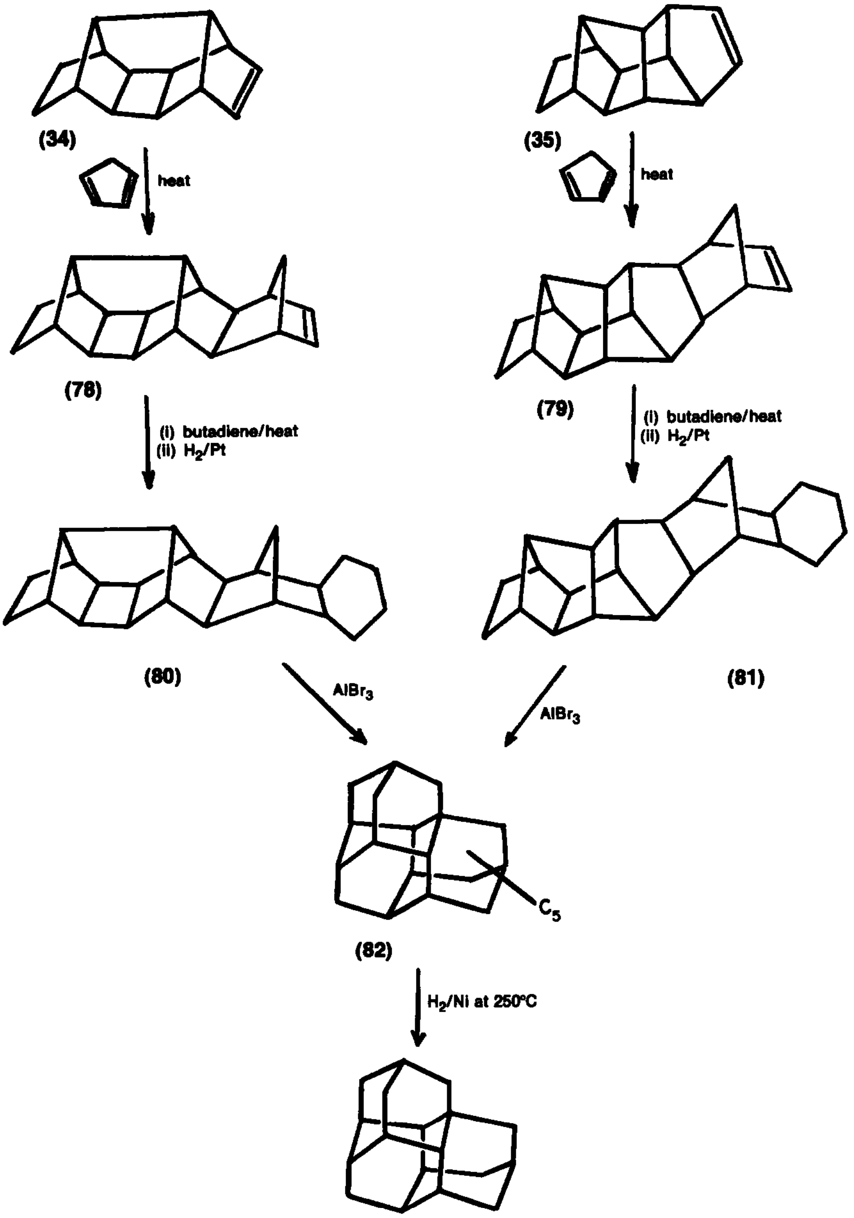
anti-Tetramantane possesses a range of interesting properties. The m.p. conforms to the trend towards lower m.p. exhibited by the earlier members of the polymantane series; furthermore, the m.p. in each case is preceded by an endothermic transition (two in the case of diamantane) to an orientationally disordered phase (m.p. and transition temperature in °C): adamantane (269, −65), diamantane (251, 174, 142), triamantane (224, 155), and *anti*-tetramantane (174, 159). The mass spectrum of *anti*-tetramantane is very similar to that of triamantane, both showing even less fragmentation than do adamantane and diamantane. This type of behaviour is consistent with a highly interlocked structure resistant to fragmentation and is typical of many multicyclic caged hydrocarbons. The IR spectrum of *anti*-tetramantane is remarkably featureless, consistent with a rigid structure of high symmetry. Apart from the CH and CH_2 bond stretching absorptions centred at 2900 cm^{-1}, there are only six sharp absorptions of moderately weak intensity. Classification of C–C bond lengths in *anti*-tetramantane according to the degree of substitution reveals a significant trend. The closer one comes to the situation in diamond itself, i.e. bonding between quaternary C atoms, the larger the measured bond length. Classification of the valence angles in a similar fashion shows that the largest (111.8°) and the smallest (107.4°) angles both occur at the unique quaternary C atom.

Apart from demonstrating the single and double homologation route to the larger polymantanes, these syntheses show how quite complex reactions with large organic molecules can be brought about in the gas phase. Gas-phase procedures of this type may be applicable to a wide variety of reactions for which liquid-phase methodology is limited, particularly for structures not having functional groups. Until now these reactions have been limited largely to petroleum refining processes.[54] Although triamantane is now readily available and could in principle be used to produce one or other of the pentamantane isomer, the chief weakness of the homologation approach is that it is multistep. Thus the quantities of *anti*-tetramantane produced in this way are insufficient to enable a full exploration of the chemistry of this interesting molecule. The great strength of the Lewis acid rearrangement approach is that if a suitable precursor can be found readily, the synthesis becomes effectively a single step operation.

One unsatisfactory aspect of the first attempt to produce tetramantane by rearrangement is the use of cyclooctatetraene dimer as the basic building block. As experience with diamantane and triamantane shows the choice of building unit is important and although triamantane was obtained from cyclooctatetraene dimer the yield compares very unfavourably with that obtained from precursors based on the binor-S rearrangement products **34** and **35**.

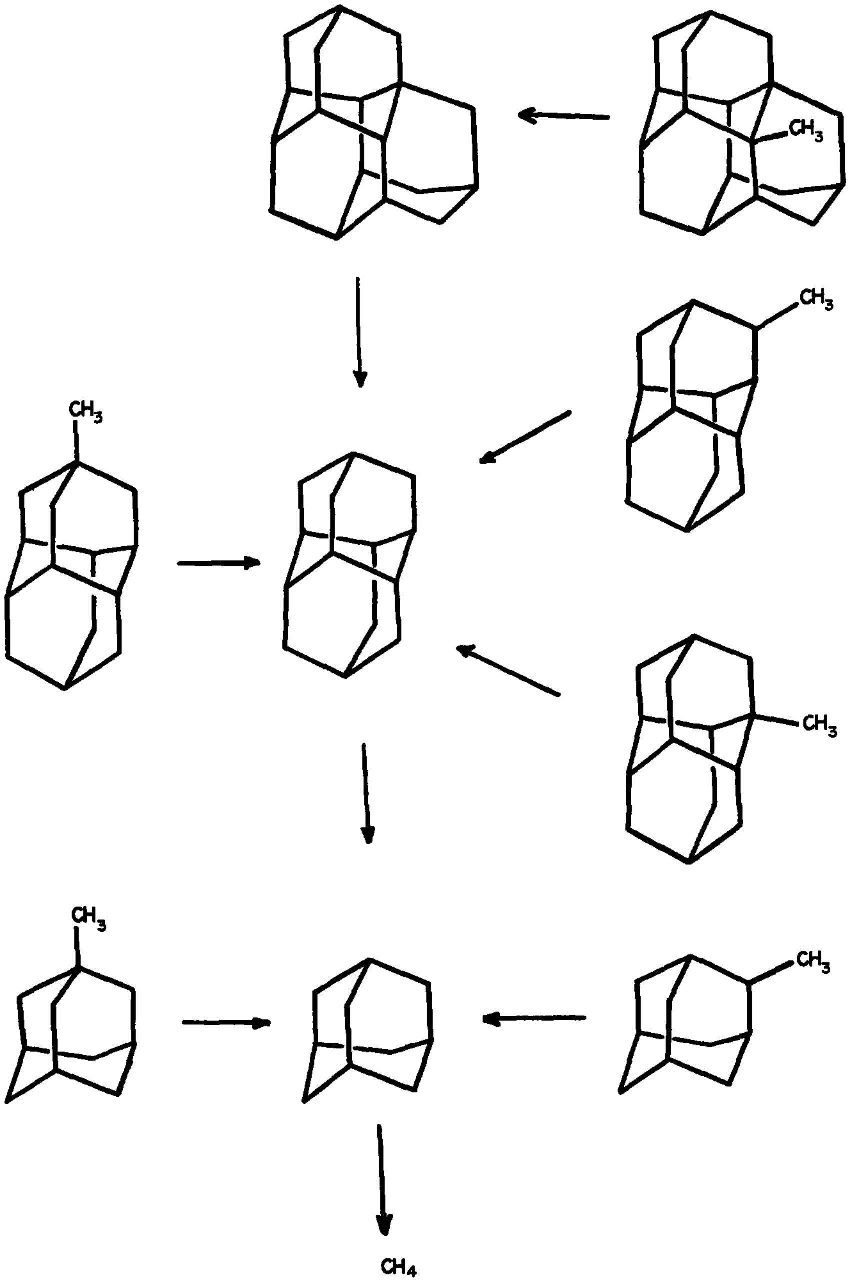
Following this line of thought attempts were made in Cork[55] to extend the rearrangement route by elaborating olefins **34** and **35** into tetramantane precursors, taking advantage, where possible, of the synthetic power of the Diels–Alder reaction. The process requires the addition of eight C atoms and three more rings since tetramantane is a nonacyclodocosane. Sequential addition of two molecules of butadiene to **34** and **35** is inadequate since the resulting adducts, while possessing the correct number of C atoms, contain one ring too few. However, a 3-ring addition can be realised easily via Diels–Alder reactions if one is prepared to accept precursors containing one C atom too many. It will be recalled that precursors containing "extra" C atoms invariably rearrange into alkylpolymantanes rather than less regular structures not possessing alkyl groups. Thus, tetramethylenenorbornane **13** and polycycles **45** and **46** are readily converted into methyladamantanes and methyltriamantanes, respectively. Accordingly, the expectation was that a C_{23} precursor might be induced to rearrange into one or more of the methyltetramantane isomers which could then be converted into a tetramantane by demethylation.

Diels–Alder addition of cyclopentadiene to olefins **34** and **35** (Scheme 13) gave the crystalline adducts **78** and **79**. A second Diels–Alder reaction with butadiene at 190° gave nonacyclic olefins which were hydrogenated to the C_{23} hydrocarbons (**80** and **81**). Exposure of **80** and **81** to aluminium bromide in cyclohexane or chlorinated platinum alumina in the gas phase gave a complex mixture of new hydrocarbons. There are many methyltetramantane isomers and the complexity of the rearrangement mixture rendered the isolation of individual components impractical. It was decided, therefore, to subject the product mixture to controlled catalytic hydrogenolysis in the gas phase. The intention was two-fold. First, any methyltetramantanes present should demethylate to tetramantane and methane. And second, any rearrangement products containing strained rings should fragment readily leaving the mixture enriched in diamondoid structures. Recent work has shown that Me and other alkyl groups can be cleaved from the diamondoid nucleus with efficiency and high selectivity using catalytic hydro-



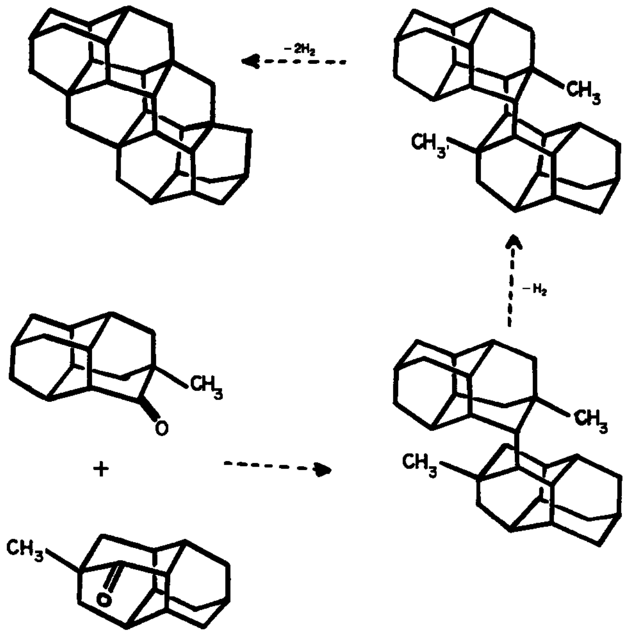
Scheme 13.

genolysis.[56] Thus, the methyladamantanes, the methyldiamantanes and 2-methyltriamantane can all be demethylated in the gas phase in hydrogen on nickel at temperatures in the range 150–250° (Scheme 14). The parent polymantanes are much more resistant to catalytic cleavage in hydrogen although complete degradation to methane does occur at higher temperatures. At 280° 2-methyltriamantane is successively degraded to triamantane, diamantane, adamantane and ultimately methane. When the product mixture obtained by rearrangement of **80** and **81** was subjected to gas-phase catalytic hydrogenolysis the major product isolated was *triamantane* (Scheme 13); no traces of a tetramantane isomer could be found. A reasonable interpretation of this observation, which requires, however, the assumption that nickel promotes only hydrogenolytic cleavage and not further rearrangement, is that the Lewis acid-catalysed rearrangement of precursors **80** and **81** proceeds along the polymantane route as far as triamantane and then encounters a mechanistic block which prevents it from reaching the tetramantane stage. The product or products are, therefore, structures of type **82** consisting of a regular triamantane portion to which is attached an irregular 5-carbon unit. Catalytic hydrogenolysis preferentially splits off the 5-carbon unit as methane leaving triamantane intact.



Scheme 14.

This failure to produce one or more of the tetramantanes from what appeared to be very promising precursors although not exhausting all the possibilities, does suggest that the efficacy of the Lewis acid-catalysed rearrangement approach is limited to the lower polymantanes. Nevertheless, the larger polymantanes remain challenging targets for synthesis. Preliminary indications from the chemistry of triamantane suggested that the larger polymantanes will prove to be valuable substrates in mechanistic and solid state studies. Thus triamantane is exceedingly reactive in ionic and free radical C–H substitution reactions[57] and in the crystalline state it displays a degree of molecular motion which makes it a useful probe for order-disorder studies in molecular crystals.[58,59] It is quite possible that new methods for carbon–carbon bond formation in multicyclic systems involving catalytic procedures in the gas phase will emerge. As we have demonstrated already, some catalytic reforming reactions can be used to effect in this area. The extension of these processes to even larger systems may be possible along the lines shown in Scheme 15. Thus a hexamantane might be constructed from two preformed diamantane units by an



Scheme 15.

initial union of 2-methyldiamantanone with itself by conventional coupling procedures followed by successive gas-phase catalytic dehydrogenation with formation of three carbon–carbon single bonds. However, it is a long way from methane to diamond.

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