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Skeletal rearrangements of cage compounds with medium rings

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ABSTRACT. Data on skeletal rearrangements in the chemistry of cage compounds are reviewed. The main principles of thermodynamically controlled isomerisation of cage hydrocarbons and syntheses of mono- and polycage structures are considered. Data on skeletal reconstruction accompanying functionally substituted carbo- and thia-containing cage-type polycyclanes are systematised. The rules for skeletal interconversions of isomeric tricyclic structures are considered.

The bibliography contains 99 references.

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I. Introduction

The chemistry of cage compounds, first arising with and receiving significant development from adamantane, now includes its structural isomers, homologues and heteroanalogues, polyadamantanes, and also carbo- and heterocage compounds of many other types. The method of synthesis by skeletal rearrangement occupies a conspicuous place in this region of chemistry, which is distinguished by structural diversity. The various skeletal reorganisations of non-cage polycyclanes into cage systems, skeletal transformations of cage compounds themselves into compounds with more stable isomeric structures and also the interconversions of cage structures, characteristic of individual groups, are widely represented.

Skeletal rearrangements form the basis of important routes for the synthesis of both cage hydrocarbons and of functional derivatives of cage polycyclanes. The synthesis of adamantane and its alkyl homologues from non-cage precursors (adamantisation) and the synthetic approaches to mono- and polycage hydrocarbons based on available precursors of other cage structures are based on isomerisation under the action of strong Lewis acids. The conversions of functionally substituted cage polycyclanes by addition, elimination and substitution reactions accompanied by skeletal rearrangements open a route to cage compounds of various classes. The skeletal transformations indicated are represented mainly by adamantisation in the monograph[1] and in the known reviews on the chemistry of adamantane and other cage compounds.[2–6] McKervey has also considered skeletal rearrangements of cage tricyclanes[7] and syntheses of polyadamantanes by isomerisation of penta- and hexacyclic hydrocarbons.[8] In recent years data have been obtained on the skeletal transformations of cage hydrocarbons, acting as intermediates in processes for the adamantisation of non-cage substrates, routes have been developed for the synthesis of a series of unique non-adamantane cage structures on the basis of skeletal conversions of actual cage compounds, and important general rules have become apparent for the skeletal reorganisations of cage compounds under the action of chemical reagents.

The present review is devoted to the correlation of data available at the present time on skeletal conversions of cage and thiacage compounds containing predominantly five- and six-membered rings. Systematisation of literature material has been carried out for a series of cage and polycyclic systems with the same number of rings and a single structural formula.

II. Skeletal transformations of cage tricyclanes

The discovery in 1975 of a single-stage method of synthesis of adamantane, and then of alkyladamantanes, by the isomerisation of available saturated tricycloalkanes with ten or more carbon atoms catalysed by strong Lewis acids, played an exceptionally important role in the development of the chemistry of adamantane itself and of cage compounds in general. Investigations on adamantisation of non-cage tricyclic precursors and especially of such hydrocarbons as *endo*-tetrahydrodicyclopentadiene (THDCP), perhydroacenaphthene and perhydrofluorene attracted much attention and culminated in the design of an industrial means of obtaining adamantane and preparative methods of synthesis of different alkyl homologues of it. Hydrocarbons of cage structure, represented mainly by isomers and homologues of adamantane, became the objects of further investigations on the thermodynamically controlled isomerisation of tricycloalkanes. Together with the isomerisation of the hydrocarbons indicated skeletal transformations of tricyclanes of cage structure also include skeletal rearrangements accompanying reactions of functional derivatives. Of the known types of similar rearrangements the present review includes mainly the transformations occurring without a change in the number of skeletal carbon atoms. Conversions of the 'adamantane–homoadamantane' and 'noradamantane–adamantane' types are not considered in the review.

1. Isomerisation of tricycloalkanes into adamantane hydrocarbons

The high thermodynamic stability of adamantane (1) in comparison with the stability of other structural isomers of $C_{10}H_{16}$-tricyclanes (Table 1) and the ability of certain Lewis acids to generate and support the concentration of cationic intermediates necessary to effect skeletal rearrangements form a basis for obtaining adamantane both from THDCP and from tricyclanes of cage structure. The isomerisation of the latter under the action of $AlBr_3$ proceeds under milder conditions and more rapidly than the isomerisation of THDCP which was shown for the example of twistane, tricyclo[4.4.0.0^{3,8}]decane, (2) [9] and protoadamantane, tricyclo[4.3.1.0^{3,8}]decane (3).[10] The latter together with 2,6-trimethylenenorbornane (5) are intermediates in the isomerisation of *exo*-1,2-trimethylenenorbornane (4).[11] The isomerisation of protoadamantane (3) into adamantane also occurs in the gas phase over Pd, Pt, and Rh at temperatures greater than 150 °C.[12]

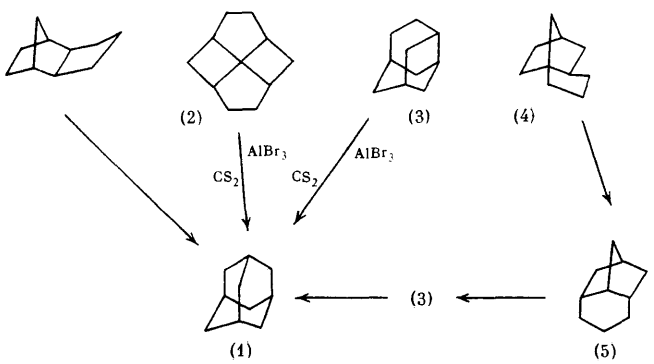
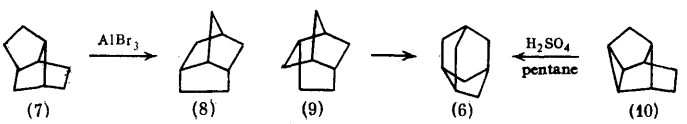


Table 1. Calculated data for the heats of formation of some $C_{10}H_{16}$-tricyclanes.[11]

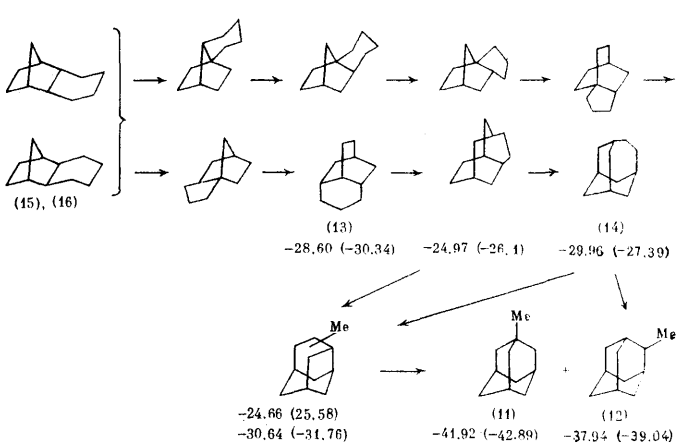
$C_{10}H_{16}$-isomers	H° (gas, 25 °C), kcal mol^{-1}
Adamantane (1)	−32.6
Protoadamantane (3)	−21.1
2,6-Trimethylenenorbornane (5)	−20.2
exo-1,2-Trimethylenenorbornane (4)	−16.7
Twistane (2)	−13.3
endo-Tetrahydrodicyclopentadiene	−16.8

The data presented are experimental confirmation of the theoretical mechanism proposed by Whitlock and Siefken for the conversion of THDCP into adamantane allowing for the heats of formation of the isomeric tricyclodecanes and based on a critical analysis of possible routes of conversion of intermediates (at least 2897 variants).[9] According to the indicated mechanism the process includes a series of sequential skeletal conversions of tricyclodecanes. The three final steps of this process are the conversions of (4) → (5) → (3) → (1).

An example of the isomersiation of C_9H_{14}-tricyclononanes to the lower homologue of adamantane is the conversion of brexane, tricyclo[4.3.0.0^{3,7}]nonane (7), under the action of $AlBr_3$ into noradamantane, tricyclo[3.3.1.0^{3,7}]nonane (6). The conversion indicated most probably proceeds through such intermediates as brendane, tricyclo[4.2.1.0^{3,7}]nonane (8), and twistbrendane, tricyclo[4.3.0.0^{3,8}]nonane (9).[13] The interaction of deltacyclane, tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (10) with sulphuric acid also leads to noradamantane and is the result of fission of the cyclopropane ring and subsequent isomerisation.[14]



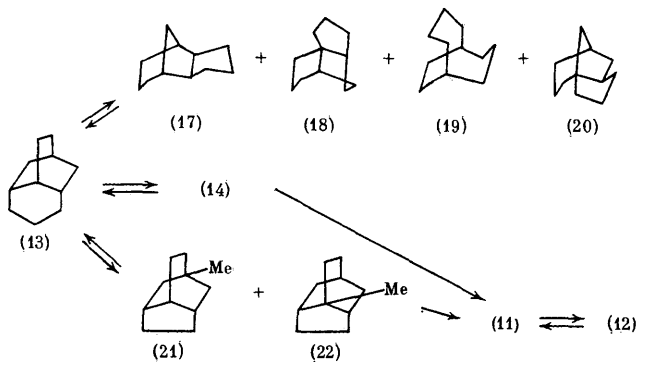
The isomerisation of C_{11}-tricyclic hydrocarbons into methyladamantanes (11) and (12) under the action of strong Lewis acids is similar to the isomerisation of $C_{10}H_{16}$-tricyclanes into adamantane and was described for the first time using non-cage precursors, viz. various tricycloundecanes and methyltricyclodecanes as examples. When studying these isomerisations 4-isohomotwistane, tricyclo[5.3.1.0^{3,8}]undecane (13), and homoadamantane, tricyclo-[4.3.1.1^{3,8}]undecane (14), were isolated and identified. Osawa and co-workers[15] have proposed the following mechanism for the isomerisation of tricycloundecanes (15) and (16) well-founded on calculated data for the thermodynamic stability of 69 isomeric C_{11}-tricyclanes. Values for the heats of formation of intermediates of carcase structure are given in the scheme.†



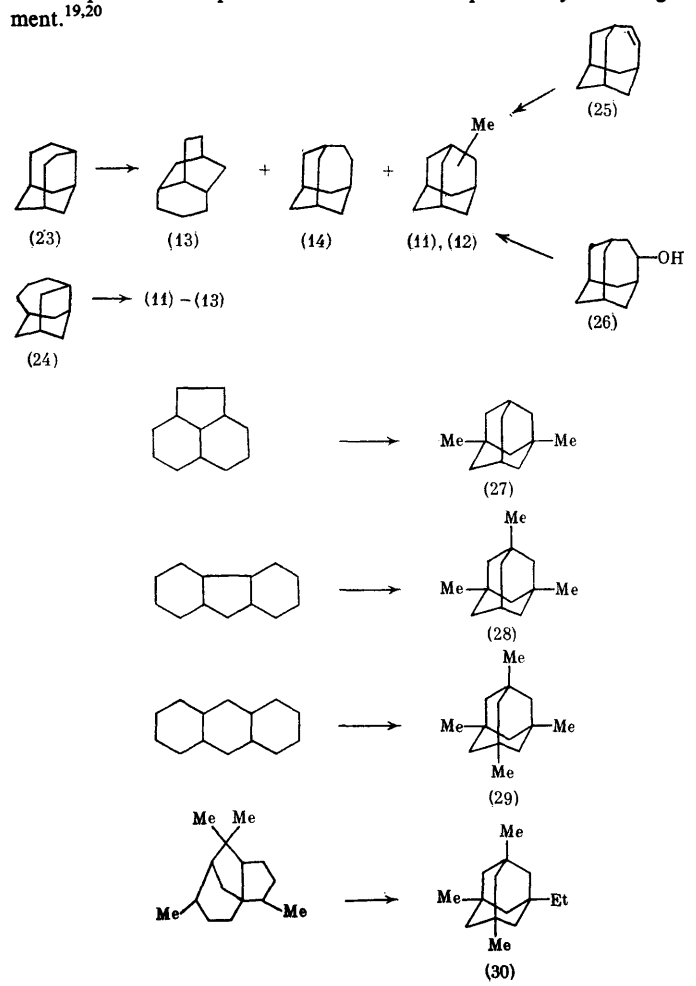
The isomerisation of 4-isohomotwistane (13) was the subject of a separate study carried out under kinetically controlled conditions using Brønsted acid (CF_3SO_3H, H_2SO_4). Under the action of these agents a complex mixture of isomeric tricyclanes was obtained from the compound indicated. The mixture contained tricycloundecanes (17)–(20), which are thermodynamically less stable than the initial compound, together with the more stable isomers,

† Here and subsequently data are given calculated according to Engler and in parentheses according to Allinger (in kcal mol^{-1}).

methylhomotwistanes (21) and (22) and homoadamantane (14), which is slowly converted into methyladamantanes (11) and (12).[16,17]

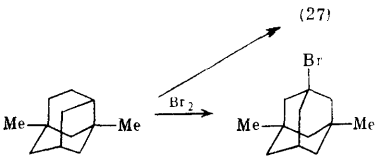


Definite differences were established between the conversions of the isomeric homoprotoadamantanes (23) and (24) under the action of CF_3SO_3H. Homoadamantane (14) predominates in the mixture of structural isomers obtained from hydrocarbon (23). The isomerisation of compound (24) under the same conditions leads predominantly to compound (13).[18] The latter also predominates in the mixture of isomers (11–14) formed on conversion of homoadamantene (25) and homoadamantanol (26) in conc. H_2SO_4 in the presence of pentane which is accompanied by rearrangement.[19,20]



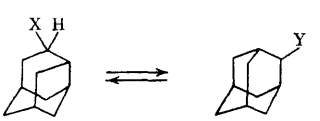
According to concepts[7] developed in recent years the isomeric polycycloalkanes with the same number of rings and same empirical formula are isomerised under the action of strong Lewis acids under thermodynamically controlled conditions to the most stable isomer of the given series, viz. the so-called stabilomer.

Thus adamantane is the stabilomer of the $C_{10}H_{16}$-tricyclanes, noradamantane is the stabilomer of the C_9H_{14}-tricyclane series and 1-methyladamantane of the $C_{11}H_{18}$-tricyclane series. The corresponding alkyl homologues of adamantane (27)–(30) play the role of stabilomers in the series of tricylanes from $C_{12}H_{20}$ to $C_{15}H_{26}$. Usually non-cage compounds serve as precursors of these compounds. Individual examples of the skeletal interconversions considered for compounds of cage structure are represented only in the $C_{12}H_{20}$ series.[7,21]



2. Skeletal interconversions of functionally substituted adamantanes and protoadamantanes

The thermodynamically controlled isomerisation of $C_{10}H_{16}$-tricyclanes comprises a cascade of rearrangements terminating in the rearrangement of protoadamantane into adamantane. The rearrangement indicated may be considered to be irreversible in the hydrocarbon series. In contrast to the hydrocarbons, the possibility of reciprocal skeletal conversions of the following type has been established for functionally substituted protoadamantanes and adamantanes.

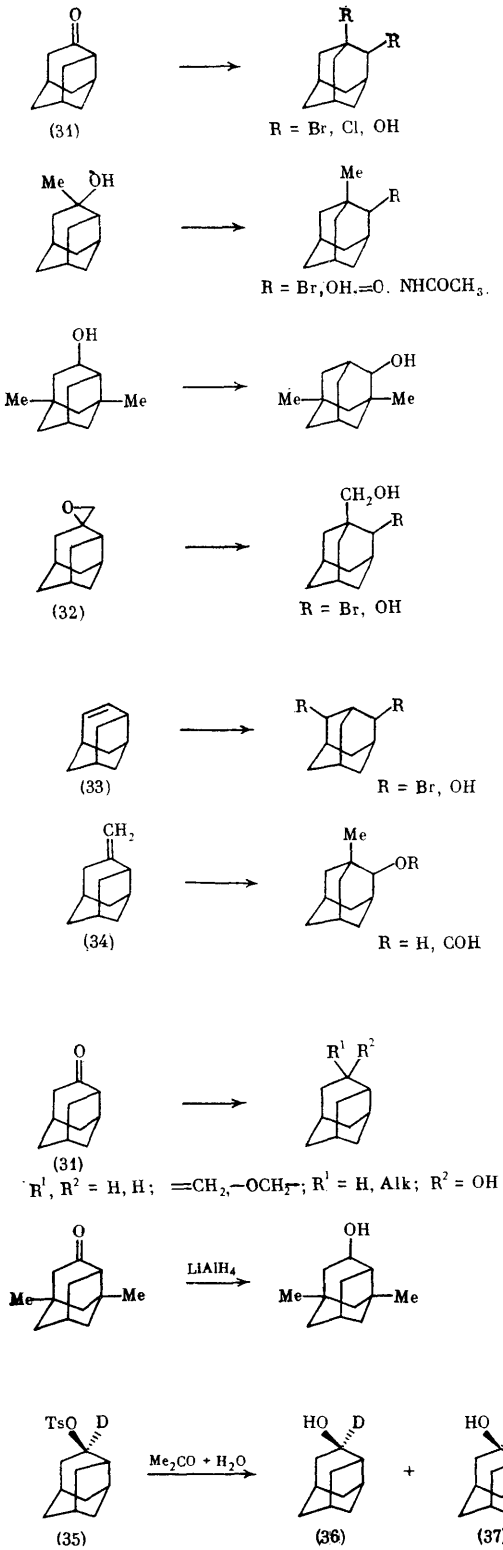


The 'protoadamantane → adamantane' rearrangement proceeds readily and completely in reactions of protoadamantan-4-one (31), its ethyleneketal,[10,22,23] alkyl substituted 4-hydroxyprotoadamantanes,[21,22,24–27,28] on interacting protoadamantane-4-spiro-oxirane (32) [28] with electrophilic reagents and also in reactions proceeding in the presence of acids. Some examples of reactions of the type indicated are shown below.

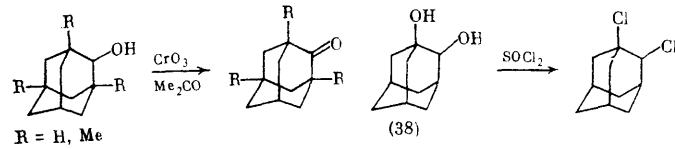
Rearrangement of the protoadamantane structure into adamantane also occurs in reactions of electrophilic addition to protoadamantene (33) [22,23,29] and to 4-methyleneprotoadamantane (34).[29]

The participation of compounds of the proto-structure in nucleophilic substitution reactions, in Grignard reactions and in the reduction of ketones with metal hydrides occurs with retention of the initial structure.[21–27,29–31]

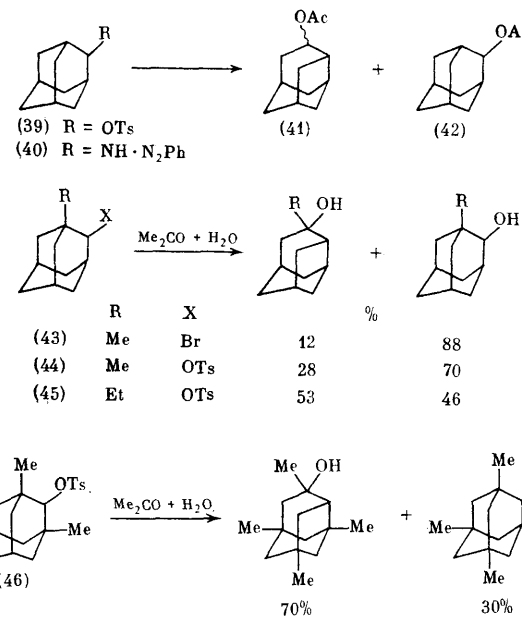
Hydrolysis of deuterated protoadamantyl tosylate (35) in 60% aqueous acetone leads to the isomeric alcohols (36) and (37). This result indicates the occurrence of a degenerate 'protoadamantane–protoadamantane' isomerisation.[10]



In the 2-substituted adamantane series the oxidation of alcohols[22,27] and the exchange of hydroxyl groups in diol (38) by Cl atoms under the action of $SOCl_2$ [22] proceed with retention of the adamantane structure.



The first example of an 'adamantane → protoadamantane' rearrangement was discovered by Whiting and co-workers[30,31] on acetolysis of 2-tosyloxyadamantane (39). The reaction product contained 0.4% acetate (41) of rearranged structure in addition to acetate (42) of the initial structure. On deamination of 2-aminoadamantane by the phenyltriazene method the yield of rearranged acetate from compound (40) was 7.5%. With the introduction of a substituent into the neighbouring junction position the tendency towards this rearrangement grows and was established for the examples of the hydrolysis of bromide (43) [32] and tosylates (44)–(46).[10,24,33–35]

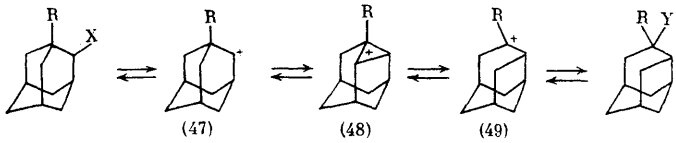


	R	X	%	
(43)	Me	Br	12	88
(44)	Me	OTs	28	70
(45)	Et	OTs	53	46

The mechanism proposed for the conversion of 2-substituted adamantanes into 4-substituted protoadamantanes in nucleophilic substitution reactions comprises the formation of 2-adamantyl cation (47) and its transformation through the bridging ion (48) into 1-protoadamantyl cation (49).

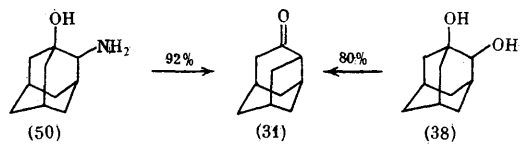
The presence of a substituent at the bridgehead position assists rearrangement since in this case the isomerised ion is tertiary which facilitates the course of a reaction by an S_N1 mechanism in difference to the initial secondary ion which reacts with difficulty in

a nucleophilic substitution reaction of S_N2 or S_N1 mechanism. Acids catalyse the reverse rearrangement.[33–37]

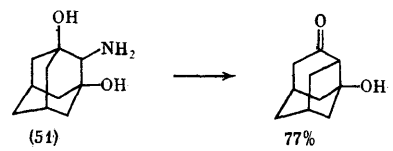


(47) (48) (49)

A high yield of rearrangement products is achieved on deaminating aminoalcohols (50) [10] and (51) [38] and on dehydration of alcohol (38) with dilute sulphuric acid.[22] In the case of compounds (38) and (50) the reaction indicated leads to the formation of protoadamantanone (31), a key compound in the protoadamantane series. However the conversion of the available 1-hydroxyadamantane under the action of $Pb(AcO)_2-I_2$ is chiefly used for obtaining preparatively the ketone indicated.[39,40]

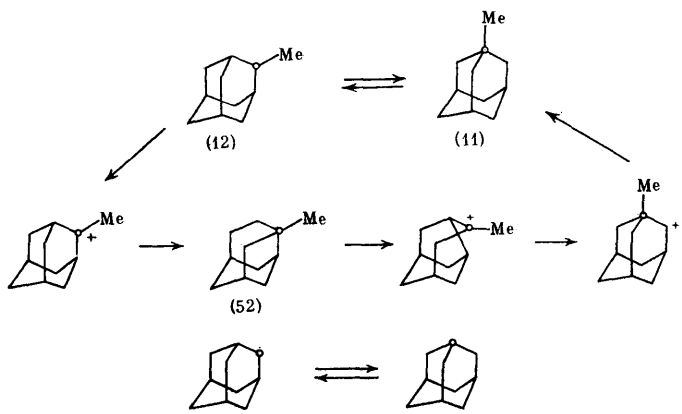


(50) (31) (38)



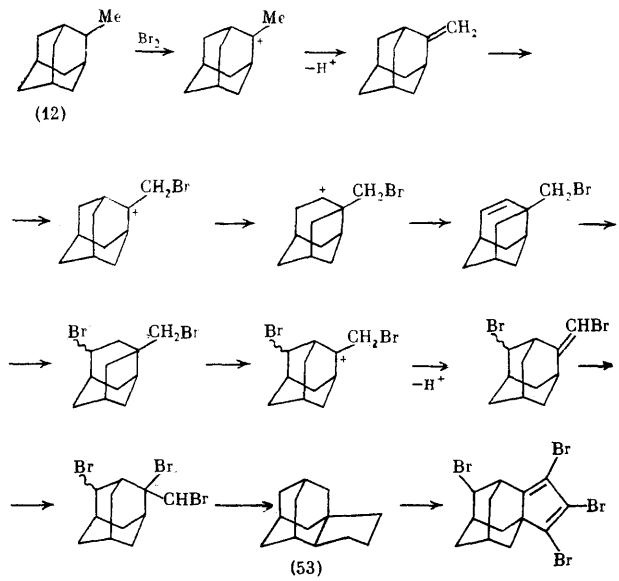
(51) 77%

It is assumed that skeletal reorganisations of the type being considered proceed like certain conversions of 2-alkyladamantanes and of adamantane itself under the action of strong Lewis acids or with the participation of electrophiles. The isomerisation of 2-methyladamantane (12) into 1-methyladamantane (11) under the action of $AlBr_3$ comprises a conversion of the 'adamantane–protoadamantane–adamantane' type according to the mechanism proposed by Majerski and Schleyer.[41] The degenerate isomerisation of adamantane itself under the action of $AlBr_3$ most probably proceeds by an analogous mechanism.[42] These conclusions were drawn on the basis of results obtained using isotopic labels.



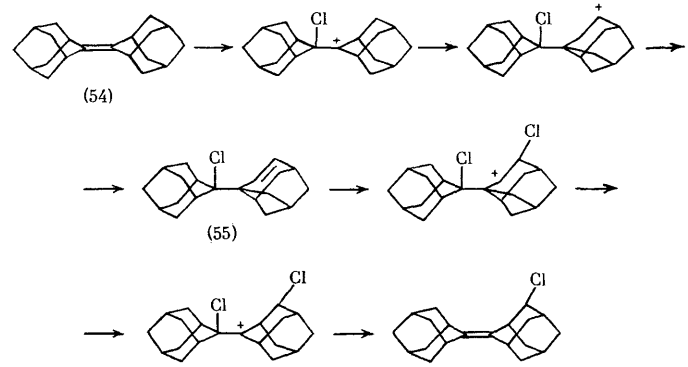
(12) (11) (52)

The course of the process through protoadamantyl intermediates is used to explain the formation of the unexpected bromination products from such adamantane hydrocarbons as 2-methyladamantane (12) [43] and 1,2-trimethyleneadamantane (53).[44]



(12) (53)

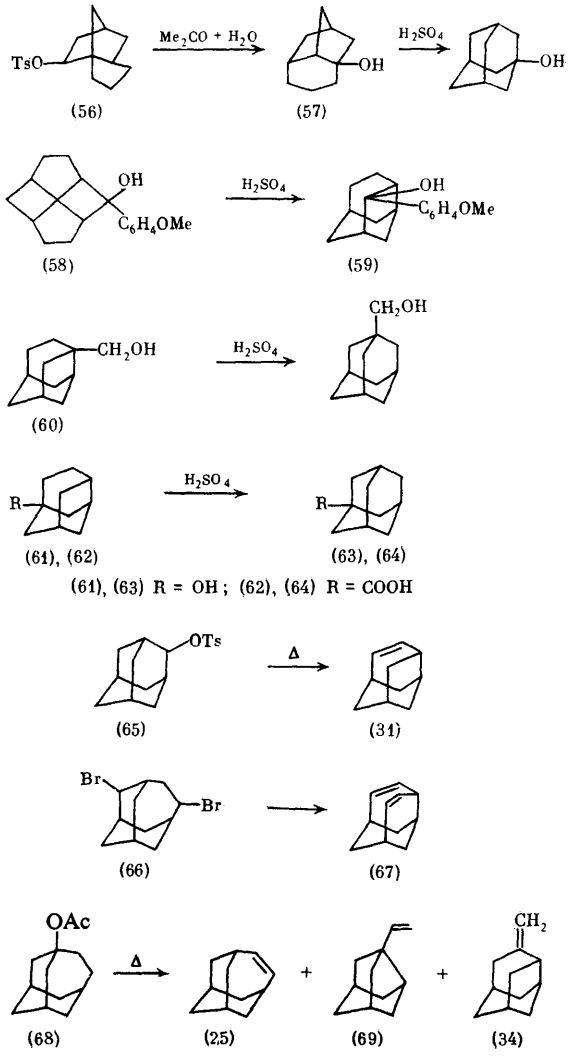
A mechanism has been proposed for the reaction of adamantylideneadamantane (54) with chlorine, the key stage of which is the formation of a protoadamantene-like intermediate (55).[45]



(54) (55)

Individual examples of skeletal rearrangements of other types are known in addition to the interconversions of 2-substituted adamantanes and 4-substituted protoadamanatanes for functionally substituted protoadamantanes and cage tricyclanes of other structure considered in this section. Thus the hydrolysis of tosylate (56) with a 1,2-trimethylenenorbornane structure in aqueous acetone leads exclusively to alcohol (57) with a 2,6-trimethylenenorbornane structure as the rearranged product. The latter is isomerised into 1-adamantanol on storage in sulphuric acid.[46] Under the same conditions 2-*p*-anisyltwistan-2-ol (58) is isomerised into alcohol (59) with a protoadamantane structure,[9] but the bridge-substituted protoadamantanes (60)–(62) are isomerised into the corresponding bridge-substituted adamantanes.[21,47] A mechanism may be proposed

for the isomerisation of compound (61) which includes stages analogous to the conversion of (52) → (11).

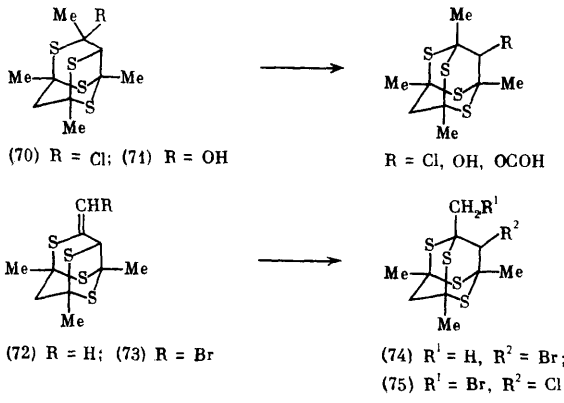


Rearrangements leading to olefins of related structure have been discovered in elimination reactions of derivatives of adamantane and homoadamantane. Thus pyrolysis of 2-adamantyl tosylate (65) leads to protoadamantene.[48] Dehydrobromination of dibromohomoadamantane (66) in hexamethylphosphoramide is accompanied by skeletal rearrangement and leads in 85% yield to diene (67) with the structure of a protohomoadamantane.[49] Olefins of rearranged structure, viz. 3-vinylnoradamantane (69) and 4-methyleneprotoadamantane (34), were also formed on pyrolysis of 1-acetoxyhomoadamantane (68) together with homoadamantene (25).[29]

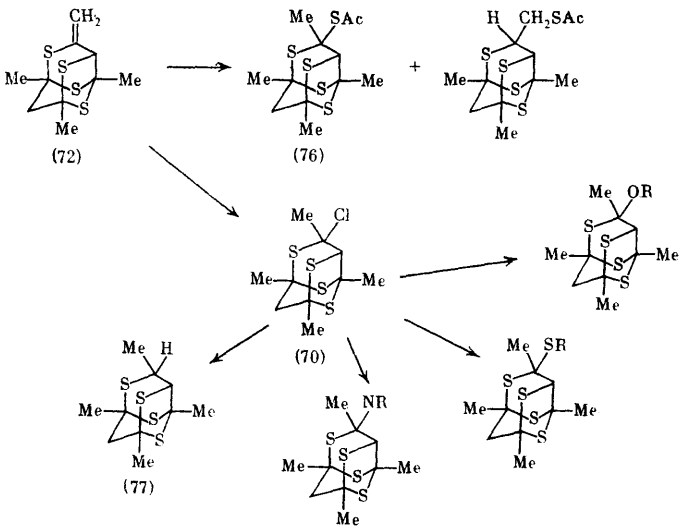
3. Skeletal conversions in the 1,3,5,7-tetramethyl-2,4,6,8-tetrathia(proto)adamantane series

Interconversions of isomeric cage structures occur in reactions of 2,4,6,8-tetrathia-analogues of adamantane and protoadamantane methylated at the bridge position.

Compounds of rearranged structure are formed from chloride (70) and alcohol (71) with a tetrathiaprotoadamantane structure under conditions of acid solvolysis.[50] Isomerisation of the chloride indicated occurs spontaneously on storage in the solid form for 10 days and also by the action of an excess of dry HCl in ether and in AcOH.[51] A similar rearrangement accompanies the hydrohalogenation of olefins (72) and (73) in AcOH,[52] which leads to bromide (74) and bromochloro-compound (75) respectively with a tetrathiaadamantane structure.

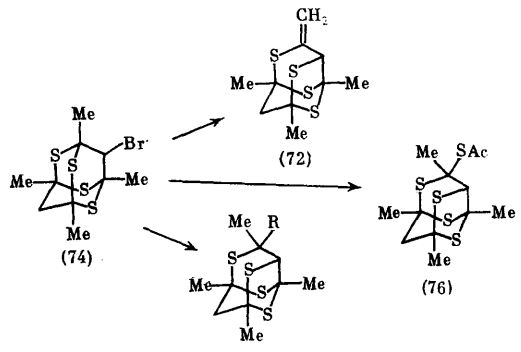


The reaction of olefin (72) with thioacetic acid[53] and its hydrochlorination under mild conditions[51] occur with retention of the proto-structure. Chloride (70) reacts readily with nucleophiles with the formation of compounds of the same structure.[54] Reductive dechlorination of the same chloride with $LiAlH_4$ leads to an *endo*-1-methyl-3,5,7-trimethyl derivative (77) with the proto structure.[55]



A 'tetrathiaadamantane → tetrathiaprotoadamantane' rearrangement accompanies the reaction of bromide (74) with nucleophiles. Thus with AcONa/NaOH or pyridine a dehydrobromination occurs leading to olefin (72) as the sole reaction product, on interaction

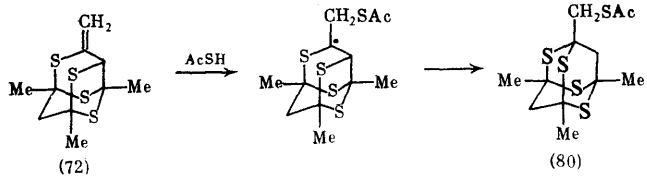
with AcSH in the presence of NaOH a rearranged thiolacetate (76) is formed.[54] Hydrolysis of compound (74) in 80% aqueous dioxan gives a mixture of alcohol (78) and olefin (72) in the ratio 2.8 : 1, and in 85% aqueous methanol a mixture of compounds (72), (78) and methoxy derivative (79) in the ratio 0.8 : 1 : 1.9.[51]



(78) R = OH; (79) R = OMe

The occurrence under ionic reaction conditions of a rearrangement of tetrathia(proto)adamantanes is analogous to the rearrangement of the 'adamantane ⇄ protoadamantane' type considered in the previous section. Since the synthetic availability of key compounds proved to be different in the carbo- and thia-containing tricyclane series different cycles of conversions were carried out, however on comparing a single reaction type in the series indicated their identical structural direction was well marked. It is important to record that in comparison with compounds of the adamantane series the 9-substituted tetrathiaadamantanes displayed a greater tendency towards rearrangement.

The occurrence of a rearrangement under radical reaction conditions was established in the interaction of olefin (72) with 1 equiv. thioacetic acid in ether, leading to thiolacetate (80). The rearrangement indicated had no analogy in the adamantane series.[53]



III. Isomeric conversions of tetracyclic hydrocarbons

Investigations on the thermodynamically controlled isomerisation of tetracyclanes have been carried out in the $C_{11}H_{16}-C_{16}H_{26}$ series. Hydrocarbons of cage structure were used in the first three series of tetracyclanes indicated in difference to tricyclanes as starting materials.

An *a priori* prediction of the stabilomer among $C_{11}H_{16}$ tetracyclanes was impossible. In accordance with the calculated heats of formation of 16 not too strained isomers selected from 2486 theoretically possible tetracyclanes of the composition indicated it was concluded[56] that 2,4-ethanonoradamantane (tetracyclo-(5.3.1.$0^{2,6}$.$0^{3,9}$]-undecane) (81) and 2,8-ethanonoradamantane-(tetracyclo-[6.2.1.$0^{2,6}$.$0^{3,10}$]undecane) (82) had approximately equal and the highest thermodynamic stability in the given series (Table 2).

Experimental data on the isomerisation of synthetically available isomers, viz. tetracyclo[6.3.0.$0^{2,6}$.$0^{2,9}$]undecane (83), noriceane(tetracyclo[5.3.1.$0^{1,6}$.$0^{4,9}$]undecane) (84) and methanotwistane (tetracyclo-[6.2.1.$0^{1,7}$.$0^{4,9}$] undecane) (85), enabled it to be established that 2,4-ethanonoradamantane (81) was the stabilomer in the series indicated. Thus isomerisation of tetracyclanes (83)–(85) under the action of $AlBr_3$ leads to a mixture of hydrocarbons (81) and (82) in the ratio 97 : 3 in addition to the disproportionation product (11).

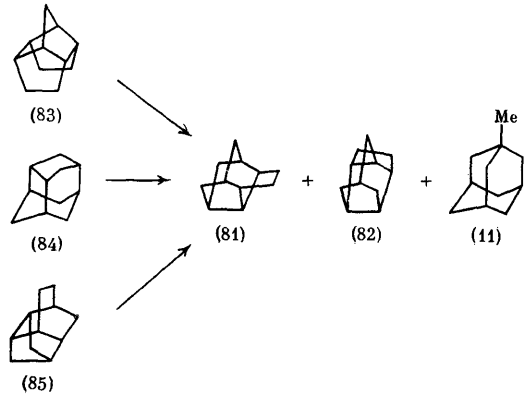
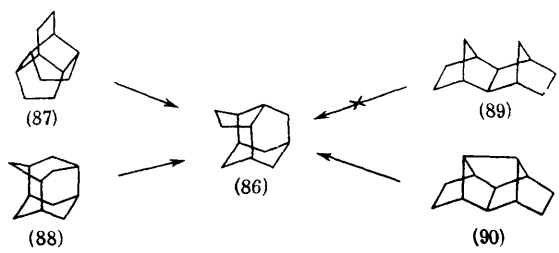


Table 2. Calculated data for the heats of formation of some $C_{11}H_{16}$-tetracyclanes.[56]

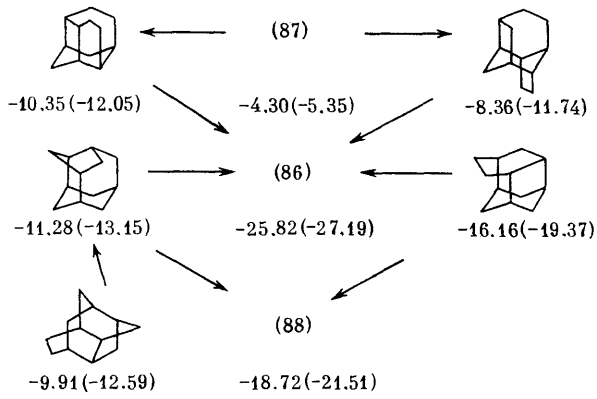
$C_{11}H_{16}$-isomers	$H°$ (gas, 25 °C), kcal mol^{-1}
2,4-Ethanonoradamantane (81)	−13.21 (−13.16)
2,8-Ethanonoradamantane (82)	−13.19 (−13.17)
Noriceane (84)	−7.21 (−10.42)
Tetracyclo[6.3.0.$0^{2,6}$.$0^{2,9}$]undecane (83)	−4.00 (−2.22)
Methanotwistane (85)	0.17 (−4.86)

The isomerisation of tetracyclanes (83) and (84) led directly to compound (81) while methanotwistane (85) was initially isomerised to hydrocarbon (82) which then isomerised slowly to (81). The formation of noriceane (84) was also recorded in the initial step of this process.

2,4-Ethanoadamantane, tetracyclo[6.3.1.$0^{2,6}$.$0^{5,9}$]dodecane (86), was detected for the first time by Landa and co-workers[57] in oil from Hodonin. Since compounds of the adamantane structure most probably arise in oil by isomerisation, Kent and Schleyer[58,59] put forward the hypothesis that 2,4-ethanoadamantane itself is the stabilomer in the $C_{12}H_{18}$-tetracyclane series. This was confirmed experimentally by carrying out the isomerisation of tetracyclo[6.4.0.$0^{4,12}$.$0^{5,9}$]dodecane (87) and iceane, tetracyclo-[5.3.1.1^{2,6}.$0^{4,9}$]dodecane,[88] to 2,4-ethanoadamantane (86) with $AlBr_3$.



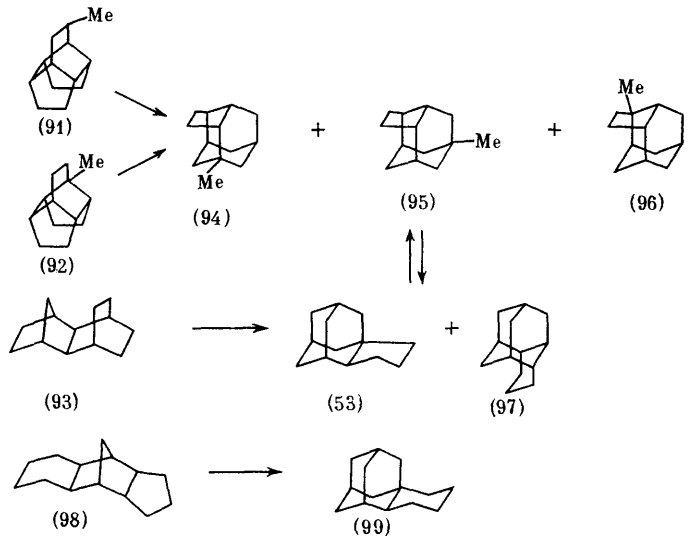
Possible routes for the rearrangement of $C_{12}H_{18}$ tetracyclanes are shown in the following scheme in which are given calculated values for the heats of formation of the hydrocarbons, i.e. for the initial, for possible intermediates and for the final isomerisation product.

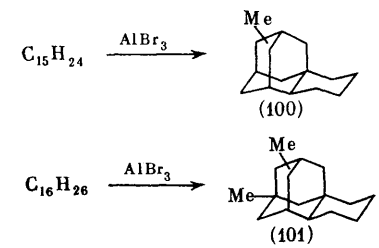


As is seen, 2,4-ethanoadamantane is 21–22 kcal mol^{-1} more stable than tetracyclane (87) and 6.7 kcal mol^{-1} more stable than tetracyclane (88). The ease of the (87) → (86) rearrangement is undoubtedly due to the fact that both possible routes of conversion include only two 1,2-alkyl shifts. In the case of iceane the rearrangement most probably occurs by transformation of the carbocation resulting from the action of the Lewis acid.

In difference to tetracyclanes (87) and (88) which have the same composition, tetracyclane (89) does not undergo isomerisation under the action of $AlBr_3$ but disproportionates leading to a $C_{12}H_{20}$-alkyladamantane.[58] It is interesting to note that 2,4-ethanoadamantane is formed together with other tetra- and pentacyclanes as the disproportionation product of the $C_{12}H_{16}$ pentacyclane (90),[59] and of a structural isomer of the latter (see section V).

The isomerisation of $C_{13}H_{20}$-tetracyclanes leads to various products depending on the structure of the substrate and the reaction conditions. A mixture of three isomeric methylethanoadamantanes (94)–(96) in the ratio 5:3:2 was formed under mild conditions from methyltetracyclododecanes (91) and (92). Similarly tetracyclotridecane (93) gave a 97:3 mixture of 1,2- and 2,4-trimethyleneadamantanes (53) and (97). Under forcing isomerisation conditions the reciprocal conversion of the indicated two groups of products was observed and a mixture was formed of compounds (53) and (94)–(97) in the ratio 42:27:19:8:3 together with products of side reactions. The calculated heats of formation of the compounds indicated did not correspond with the experimental results which does not permit a conclusion to be drawn as to the stabilomer in the series under consideration. On the other hand in the $C_{14}H_{22}$-tetracyclane series the experimental data on the isomerisation of hydrocarbon (98) and the calculated data indicated unequivocally that 1,2-tetramethyleneadamantane (99) is the stabilomer in this series.[60] The latter is also formed as a disproportionation product on rearranging certain $C_{14}H_{20}$-pentacyclanes (see section V).



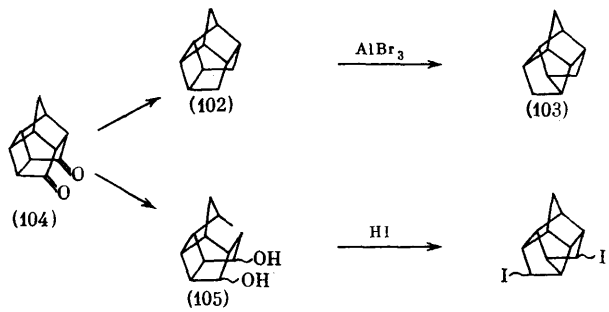


The isomerisation of tetracyclanes of composition $C_{15}H_{24}$ and $C_{16}H_{26}$ of non-cage structure with $AlBr_3$ leads to methyl- and dimethyl-substituted 1,2-tetramethyleneadamantanes (100) and (101) respectively.[61]

IV. Skeletal rearrangements of $C_{11}H_{14}$-pentacyclanes

Skeletal conversions in this series are mainly represented by the isomerisation of pentacyclo[6.2.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]undecane (102) into trishomocubane, pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (103), and by analogous skeletal rearrangements in reactions of numerous functionally substituted derivatives of pentacyclane (102). The latter are convenient subjects for investigation since they may readily be synthesised from the available diketone (104), itself the product of the photocyclisation of the Diels-Alder adduct of *p*-benzoquinone and cyclopentadiene. Proceeding from the diketone indicated, first Underwood and Ramamorthy,[62] and then Eaton and co-workers[63] by another route, effected the synthesis of trishomocubane. The formation of the trishomocubane structure in these syntheses occurred by intramolecular cyclisation in the corresponding tetracyclic intermediate. In several recent studies approaches have been developed to trishomocubane, and its mono- and disubstituted derivatives, based on the skeletal rearrangement of C_{11}-pentacyclic substrates. Thus trishomocubane has been obtained by the

isomerisation of pentacyclane (102) with $AlBr_3$.[64] The same authors have described a rearrangement leading to the trishomocubane structure in the reaction of diol (105) with HI.[65]



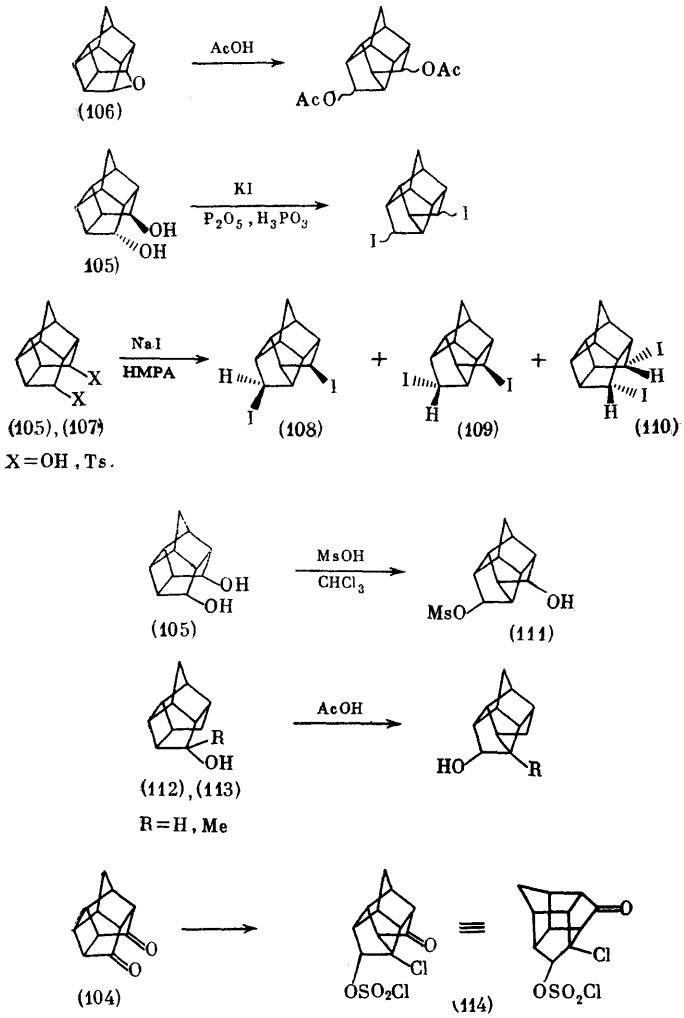
The interaction of diol (105) with a mixture of H_3PO_4, P_2O_5 and KI and fission of the oxygen bridge of the oxa-'bird-cage' (106) in AcOH is accompanied by rearrangement and leads exclusively to a trishomocubane derivative.[66] By reacting diol (105) and tosylate (107) with NaI in hexamethylphosphoramide, diiodides of rearranged structure (108) and (109) are formed together with diiodide (110) of initial structure.[67,68]

Table 3. Calculated data for the heats of formation of some $C_{11}H_{14}$-pentacyclanes.[65]

$C_{11}H_{14}$-isomers	H° (gas, 25 °C), kcal mol^{-1}
Trishomocubane (103)	9.38 (11.32)
Pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane (102)	19.62 (21.93)
Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (120)	23.88 (26.58)
Homobasketane (115)	40.99 (43.82)

A rearranged hydroxymesylate (111) is formed on reacting diol (105) with methanesulphonic acid.[69] Alcohols (112) and (113) are isomerised into the corresponding compounds of the trishomocubane structure by reaction with acetic acid.[70]

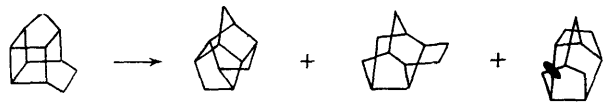
Compounds, which in their turn were obtained from diketone (104), are transformed in the above examples into the trishomocubane structure. The single example of a similar conversion of diketone (104) is its reaction with chlorosulphonic acid leading to a trisubstituted trishomocubane (114).[71–73]



Kent and co-workers[65] carried out an analysis of the stability of the isomeric cage $C_{11}H_{14}$-pentacyclanes which were selected from the 15358 possible cage isomers after excluding very strained structures. The results showed that trishomocubane itself is the thermodynamically most stable isomer in this series (Table 3). An insignificant difference in energy (10 kcal mol^{-1}) and the possibility of a (102) → (103) transition by a simple 1,2 shift in the secondary cation explains the ease of the considered rearrangement. It would be noted that examples of the reverse rearrangement, probable in reactions of functional derivatives of trishomocubane, have not as yet been described.

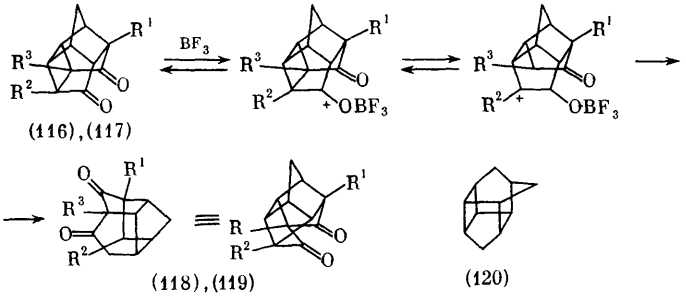


Results of studies[74] in which trishomocubane was obtained by isomerisation of homobasketane (115) with $AlBr_3$ are in agreement with the given theoretical analysis. The $C_{11}H_{16}$-isomers (81) and (82) were formed as well as compound (103) in the reaction indicated.



(115) (103), 82,0% (81), 6,4% (82), 11,1%

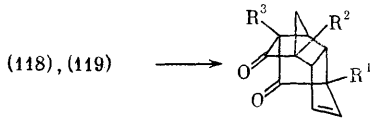
Introduction of alkyl groups at the α-position to the carbonyl group in diketone (104) may assist skeletal reorganisation which diketone (104) itself does not undergo. Thus dimethylketones (116) and (117) are isomerised by BF_3 etherate into compounds (118) and (119) respectively with the structure of a pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane.[75] The indicated isomerisation is even more interesting since the unsubstituted pentacycloundecane (120) is thermodynamically less stable than pentacycloundecane (102) (Table 3).



(116), (117) (118), (119) (120)

(116), (118) R^1=H ; R^2, R^3=Me ; (117), (119) R^1, R^2=Me, R^3=H.

The corresponding tetracyclic enediones (121) and (122) are obtained on pyrolysis of pentacyclic compounds (118) and (119).[75]

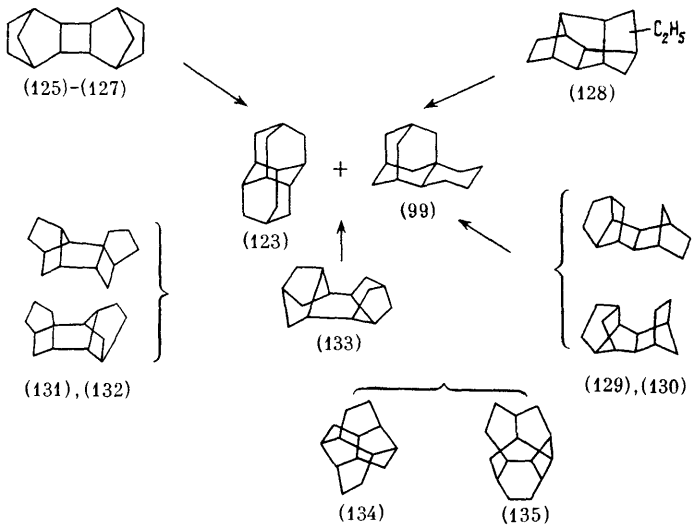


(118), (119) (121), (122)

V. Syntheses of polycage compounds of the condensed type based on skeletal transformations of monocage polycyclanes

The main principles of the thermodynamically controlled isomerisation of polycycloalkanes apparent in investigations on the synthesis of monocage structures have been further developed in approaches to polycage compounds of a condensed type of structure such as diamantane (123) and triamantane (124). In the same way that adamantane is the stabilomer of the $C_{10}H_{16}$-tricyclanes, diamantane is the stabilomer of the $C_{14}H_{20}$-pentacyclanes and triamantane the stabilomer of the $C_{18}H_{24}$-heptacyclanes. The problem of the selection of a suitable precursor proved to be a key issue in investigations on the synthesis of the polymantanes indicated.

Diamantane was isolated for the first time from Hodonin oil[57] and was synthesied at almost the same time by a [2 + 2] rearrangement of norbornene photodimers (125)–(127).[76] In this synthesis the yield of diamantane was 1 to 10% depending on which stereoisomer was used. 1,2-Tetramethyleneadamantane (99) formed by disproportionation of the starting materials predominated in the reaction product.[77,78]



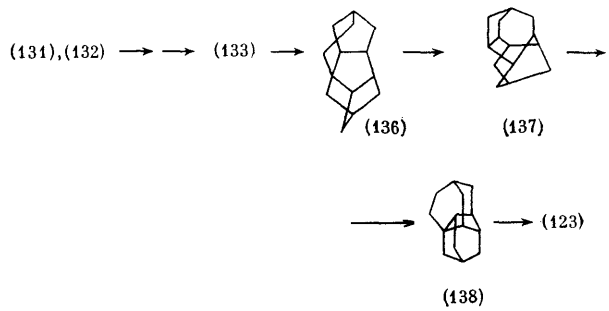
(125)-(127) (128) (123) (99) (133) (131), (132) (129), (130) (134) (135)

The search for other precursors then led to cage pentacyclane (128) isomerisation of which gave diamantane in 30% yield.[77,78] Diamantane was obtained in 25% yield on using hydrogenated Katz dimers (129) and (130).[78] The most suitable precursor for diamantane proved to be tetrahydro-Binor-S (131) and (132). On isomerisation of the latter with $AlBr_3$ in CS_2 the yield of diamantane was 65% and with $AlBr_3$ in CH_2Cl_2 82%.[77–80] One of the intermediates, viz. *trans*-pentacyclo[8.2.1.$1^{2,5}$.$0^{3,7}$.$0^{8,12}$]tetradecane (133), was isolated and identified during the conversion.[78] Recently the synthesis of diamantane in high yield by isomerisation of hydrogenated dimers of cycloheptatriene (134) and (135) has been described.[81]

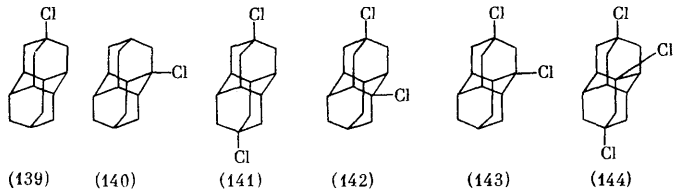
Table 4. Calculated data for the heats of formation of some $C_{14}H_{20}$-pentacyclanes.[82]

$C_{14}H_{20}$-isomers	$H°$ (gas, 25 °C), kcal mol^{-1}
Diamantane (123)	10.7
Protodiamantane (138)	31.1
Intermediate (137)	28.0
Intermediate (136)	40.8
Intermediate (133)	34.9
Tetrahydro-Binor-S (131)	62.16
(132)	54.15
(2+4)-dimers of norbornene (129)	49.77
(130)	57.15
(2+2)-dimers of norbornene *exo, trans, exo*-(125)	57.62
exo, trans, endo-(126)	62.57
endo, trans, endo-(127)	68.03

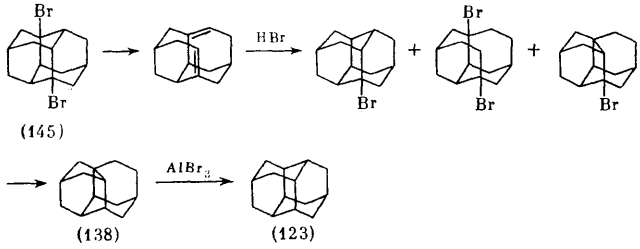
A theoretical analysis of the rearrangement of pentacyclotetradecanes into diamantane has been carried out.[82] According to the calculated data obtained for various precursors, for a vast number of possible intermediates and for diamantane itself, the latter was the thermodynamically most stable isomer among the $C_{14}H_{20}$-pentacyclanes (Table 4). A possible mechanism for the isomerisation of hydrocarbons (131) and (132) comprises the following sequence of skeletal conversions which is completed by the rearrangement of protodiamantane, pentacyclo[7.3.1.1^{4,2}.1^{1,7}.0^{6,11}]-tetradecane (138), into diamantane.



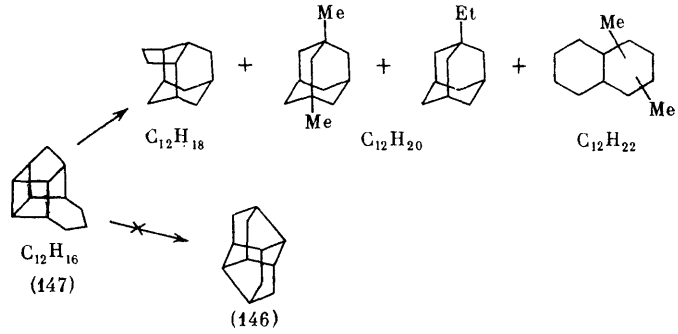
The possibility was shown in several examples of combining two steps, viz. the isomerisation of tetrahydro-Binor-S into diamantane and functionalisation of the latter. Thus chloroadamantanes (139) and (140) were obtained from tetrahydro-Binor-S with $AlCl_3$ and acetyl chloride, and dichloroadamantanes (141)–(143) were obtained on using $AlCl_3$ and paraformaldehyde.[80,83] Chlorosulphonic acid converts tetrahydro-Binor-S into 4,9-dichlorodiamantane (141) or into 1,4,9-trichlorodiamantane (144) depending on the duration of reaction.[84]



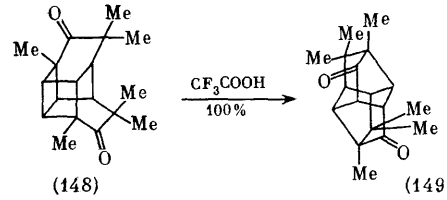
Gund and Schleyer[85] carried out the synthesis of protodiamantane (138) using dibromodiamantane (145) as starting material. Isomerisation of (138) into diamantane (123) proceeded readily with $AlBr_3$ or H_2SO_4 in methylcyclohexane.



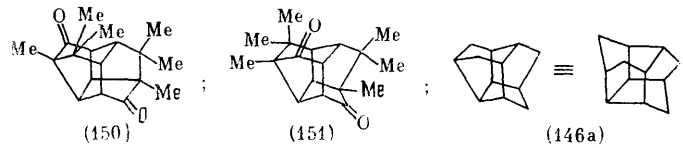
Attempts to obtain the lower homologue of diamantane, viz. bisnordiamantane (146) by the isomerisation of pentacyclo[5.5.0.0^{2,5}.0^{3,12}.0^{4,8}]dodecane (147) have been unsuccessful. The $C_{12}H_{16}$ hydrocarbon mentioned did not isomerise with $AlBr_3$ under mild conditions and under forcing conditions its conversion led only to a disproportionation product.[74]



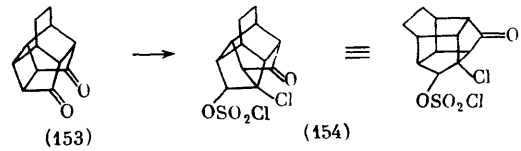
In contrast to hydrocarbon (147) the hexamethyldiketone (148) with the dihomobasketane structure, pentacyclo[6.4.0.0^{2,7}.0^{3,12}.0^{4,9}]-dodecane, readily isomerised in boiling trifluoroacetic acid or in benzene in the presence of toluene-*p*-sulphonic acid into compound (149) with the bisnordiamantane structure.[86] Theoretical analysis of the isomerisation showed that compound (149) is 3–6 kcal mol^{-1} less stable than isomers (150) and (151). In the C_{12} pentacyclane hydrocarbon series the stabilomer is pentacyclo[6.4.0.0^{2,6}.0^{3,11}.0^{4,9}]-dodecane (152), which is 8 kcal mol^{-1} more stable than bisnordiamantane (146).



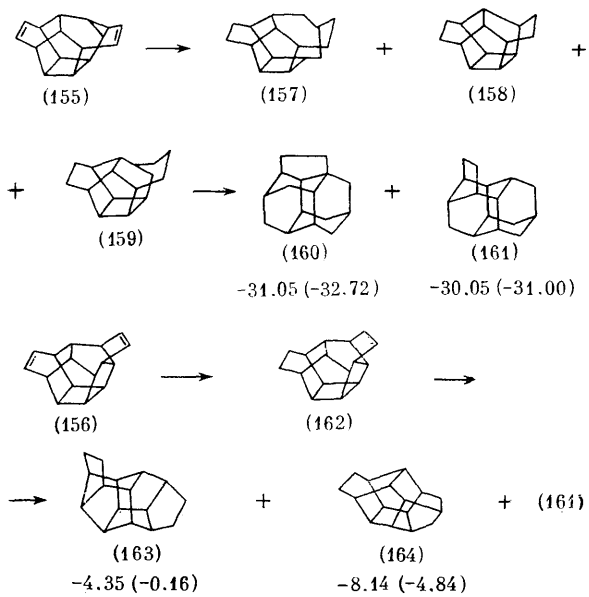
The fact that the isomerisation of compound (148) does not lead to the formation of the stabilomer is most probably explained by the absence of a suitable route for further skeletal isomerisation in this case.[87]



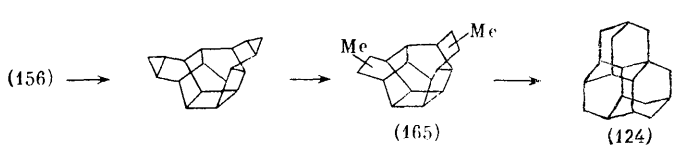
The reaction of diketone (153) with chlorosulphonic acid is accompanied by a skeletal rearrangement and leads to the chloro-keto-sulphonyl chloride (154) with a pentacyclo[7.3.0.0^{2,7}.0^{3,11}.0^{6,10}]-dodecane structure. The formation of the stabilomer structure was not observed in this case either.[72]



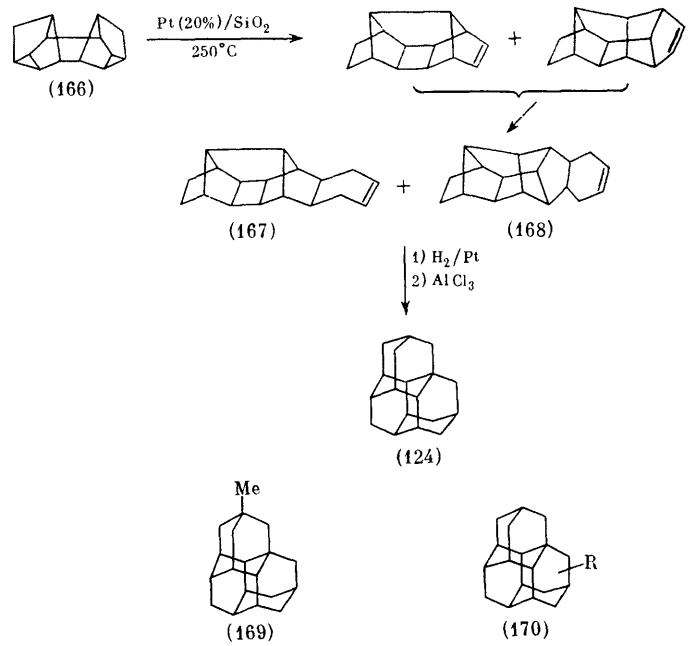
The synthesis of polymantanes of composition $C_{16}H_{20}$, isomers of ethanodiamantanes and diethanobisnordiamantane, was effected on the basis of the cage dimers of cyclooctatetraene (155) and (156). Hydrogenation of the first of these led to a mixture of hexacyclohexadecanes (157)–(159), the isomerisation of which with $AlBr_3$ gave a mixture of (C_1)-ethanodiamantane (160) (85%) and (C_s)-ethanodiamantane (161) (15%).[88] The first isomer is more stable than the second according to molecular mechanical calculations. From the product of hydrogenation of the second dimer, compound (162), a mixture was obtained of (C_2)-bisethano-bisnordiamantane (163) (73%) and compound (164) (13%) with a structure related to 'bird-cage'. Compound (161) (~20%) was also formed on using a complex containing $AlBr_3$ and t-butyl bromide and is the disproportionation product in the given reaction.



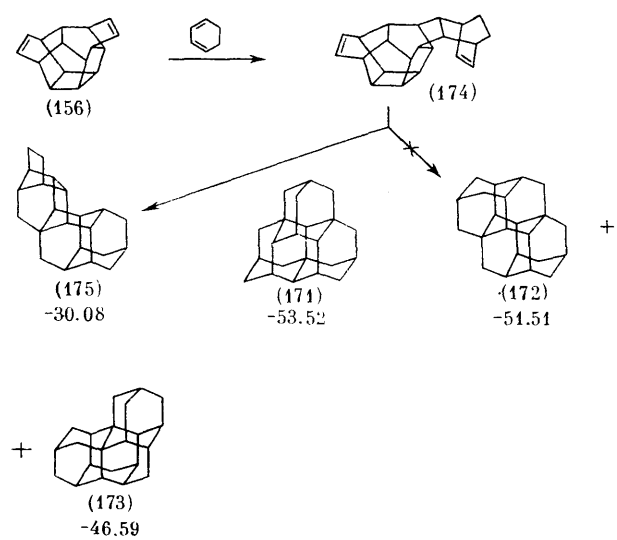
In the first synthesis of triamantane (124) by the isomerisation of $C_{18}H_{24}$ heptacyclanes Schleyer and co-workers[89] started from cyclooctatetraene dimer (156) which had served for the synthesis of polycyclane (165). Isomerisation of the latter with $AlBr_3$ led to triamantane in 1% yield.



Polycyclanes (167) and (168) obtained from Binor-S (166) proved to be the most suitable precursors of triamantane. Isomerisation of the dihydro derivatives of the latter led to triamantane (124) in 60% yield.[90] Methyltriamantane (169) and pentanotriamantane (170) were prepared by a modified diene synthesis using isoprene or cyclopentadiene as diene component.[8]



Attempts to obtain tetramantanes (171)–(173) by isomerisation of polcyclane (174), synthesised from cyclooctatetraene dimer (156), led only to a structural isomer of tetramantane, viz. bastardane (nonacyclo[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]-docosane) (175).[88] According to the calculated data shown in the scheme bastardane is less stable than tetramantanes (171)–(173). Thus the isomerisation process in the present example is not completed by the formation of the stabilomer but finishes at the stage of obtaining the kinetically stable structural isomer.



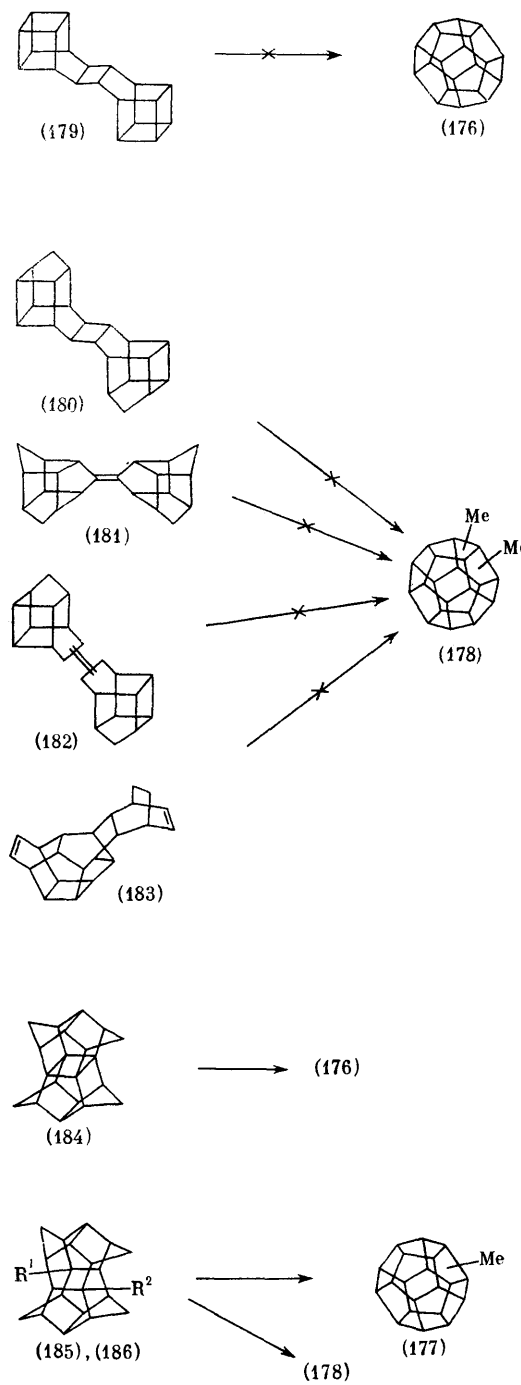
VI. Skeletal rearrangements of $C_{20}H_{20}-C_{22}H_{24}$ polycyclanes in approaches to the synthesis of dodecahedrane

The problem of the synthesis of dodecahedrane (176), a spherical system of composition $C_{20}H_{20}$, containing twelve repeatedly linked cyclopentane rings has attracted significant attention in the last decade.[91,92] Paquette and co-workers[93,94] reported the first preparation of dodecahedrane in 1982 by a 23 stage synthesis. Among the various approaches developed to achieve this goal were repeated attempts to obtain dodecahedrane and its alkyl homologues by the thermodynamically controlled isomerisation of polycage precursors. This synthetic route was exceptionally tempting since it might have enabled dodecahedrane to be obtained in one stage. Such an approach was based on the *a priori* hypothesis that dodecahedrane is the stabilomer of the $C_{20}H_{20}$ dodecacyclane series. The obtaining of the appropriate calculated data required to select the stabilomer in this series did not indeed seem possible in view of the astronomical number of isomeric cage structures.

Bicage compounds of various types were used as precursors in experimental attempts to isomerise dodecacyclanes into dodecahedrane or its alkyl homologues (177) and (178). The photodimer of basketane (179) [95] and the photodimer of homobasketane (180) [74] were subjected to isomerisation with Lewis acids. Attempts have also been described to isomerise bicage olefins (181) and (182) and also cage diene (183), obtained in the diene synthesis reaction of cyclooctatetraene dimer and cyclohexadiene.[74] They were all unsuccessful.

The bicage $C_{20}H_{20}$ dodecacyclane, 1,1,1,1-pagodane (184), recently attracted attention as a precursor of dodecahedrane. The former failed to isomerise to dodecahedrane with strong acids, however, the isomerisation was effected in the gas phase over a catalyst ($Pt/Re/Al_2O_3$, Pd/C, Rh/C, Pd/Al_2O_3).[96,97] The alkyl homologues of dodecahedrane (177) and (178) were obtained similarly. The corresponding compounds (185) and (186), with structures related to pagodane, were used as precursors.[97] This approach to the synthesis of dodecahedrane derivatives has been further developed.[98,99]

The data presented in the review demonstrate the wide synthetic possibilities of applying to cage compounds methods based on skeletal rearrangements and, most of all, on the thermodynamically controlled isomerisation of hydrocarbons. Investigations carried out up to the present time on the isomerisation indicated enable ideas to be formulated on stabilomer structure and applied in practice to the creation of new synthetic principles, previously unknown in organic chemistry. Doubtless further investigations in this area will serve as a basis for finding effective approaches to the many unique cage structures, including the hypothetical. It is also possible to suggest that further development of methods of synthesis of functional derivatives, including interconversions of isomeric structures may be found in the chemistry of cage and heterocage compounds.



(185) R^1=Me, R^2=H; (186) R^1, R^2=Me

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