Tetrahedron Vol. 37, No. 25, pp. 4465 to 4477, 1981
Printed in Great Britain.

0040-4020/81/254465-13$02.00/0

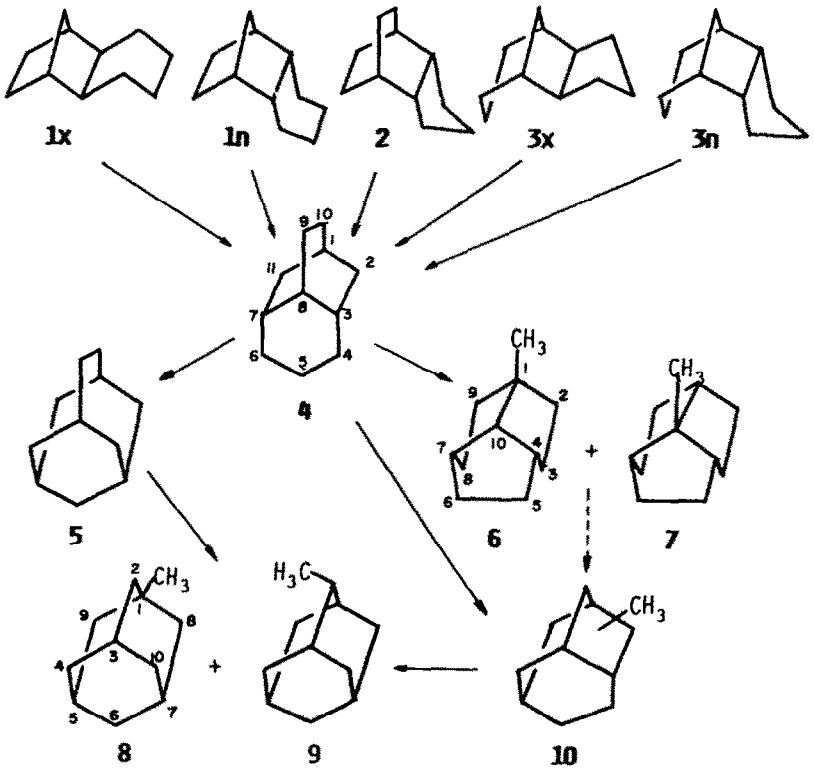
ACID CATALYZED RING CONTRACTIONS IN *ENDO*-2,8-TRIMETHYLENE-*CIS*-BICYCLO[3.3.0]OCTYL CATIONS TO METHYLPERHYDROTRIQUINACENES. ONE OF THE METHYL EXTRUSION PROCESSES IN THE TRICYCLOUNDECANE REARRANGEMENT

YOSHIAKI FUJIKURA, NAOTAKE TAKAISHI and YOSHIAKI INAMOTO*
Tochigi Research Laboratories, Kao Soap Company, Ltd. 2606 Akabane, Ichikaimachi, Tochigi 321-34, Japan

(*Received in U.S.A.* 16 *March* 1981)

Abstract—Sulfuric acid catalyzed ring contractions with extrusion of a methyl group were examined for alcohol and olefin derivatives (**28–31**) of *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane (**11**), which was one of the two possible progenitors, among altogether 69 isomers, for methylperhydrotriquinacenes (**6**, **7** and **12**), the only methyltricyclodecane intermediates found so far, in the tricycloundecane rearrangement. Only minor amounts (1.6–2.0%) of methylperhydrotriquinacenes were formed from these reactants **28–31**, and the results support the earlier theoretical conclusion that the methyl extrusions were in general energetically quite unfavorable processes owing to the formation of primary carbinyl cations at the expense of more stable secondary bridge or tertiary bridgehead ones. Reaction pathways for these precursors **28–31** were discussed with reference to those of perhydrotriquinacene 2-carbinyl cations (**33a**'s), which corresponded to some of the ring contraction product cations from **28–31**.

The ultimate products of acid catalyzed skeletal isomerizations of tricycloundecanes are 1- and 2-methyladamantane (**8** and **9**, Scheme 1). It has been demonstrated that the rearrangement process is conventionally divided into two stages: from the precursors to the stable intermediate, 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **4**), and from 4-homoisotwistane to the methyladamantanes. The earlier stage of the rearrangement, which leads to the stable intermediate **4**, has been studied rather extensively with the use of some representative precursors **1x–3n**.[1–3] In the later stage is involved one of the most intriguing problems from the mechanistic viewpoint: at which step does the ring contraction to extrude the methyl group take place? Theoretical considerations of the rearrangement pathways,[3] based on empirical force field-calculated ther-



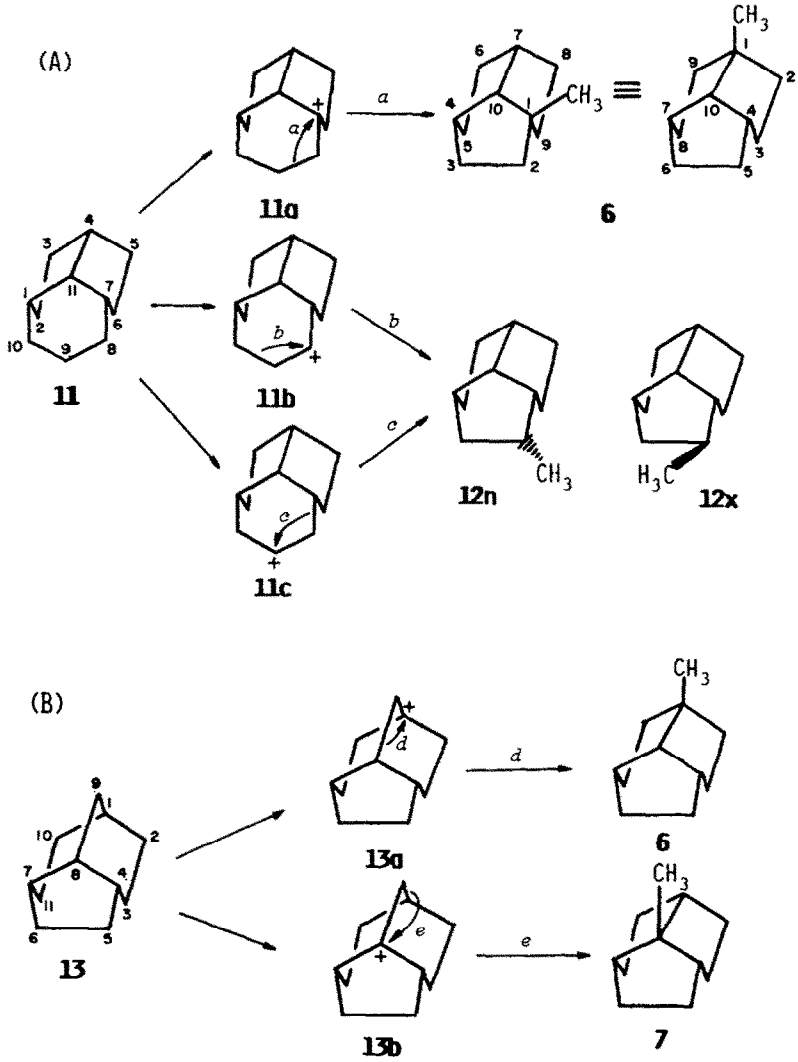
Scheme 1.

modynamic stabilities of the tricycloundecanes and methyltricyclodecanes before and after the ring contractions, did not help decisive choice among the many possibilities. Experimentally, no full account of these procesees has been presented hitherto.

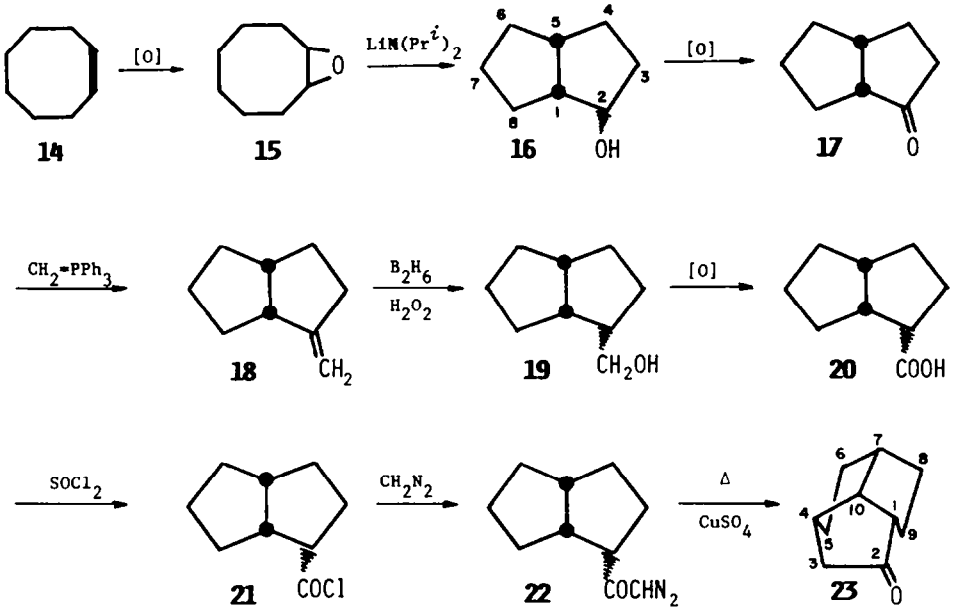
The only experimental evidence for the ring contraction in the rearrangement is given by Schleyer *et al.* for the formation of methyladamantanes (**8** and **9**) in a single step from homoadamantane (**5**).[4] Schleyer also proposed[1,3,4] that the immediate precursors to the methyladamantanes should theoretically be some methylprotoadamantanes (**10**).[5] Detection of methylprotoadamantanes, in spite of their reasonable stabilities, has not been realized in any of the isomerization experiments examined so far. However, intermediacy of methyl protoadamantanes offered the best explanation for the inter-conversion between 1- and 2-methyladamantane,[6] as well as for the formation of methyladamantanes in the rearrangements of 2- and 4-homoprotoadamantane.[7]

Our recent identification of 1- and 10-methylperhydrotriquinacene (1- and 10-methyltricyclo[5.2.1.0^{4,10}]decane, **6** and **7**, respectively) in the rearrangement mixture[8] demonstrated the presence of other methyl extrusion routes than that via homoadamantane (**5**). The results also suggested, in accordance with the theoretical prediction,[3] the possible existence of many ring contraction routes other than the above two. Further studies are thus required for a better understanding of the ring contraction stage in the tricycloundecane rearrangement.

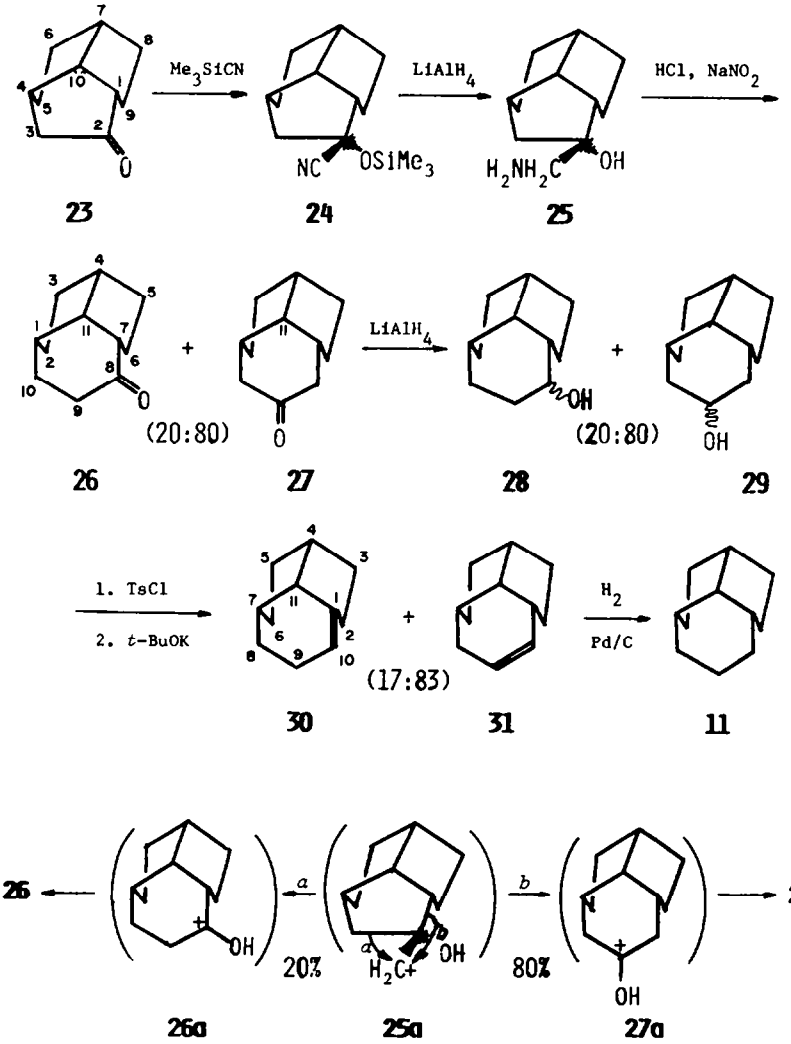
In this paper is described an experimental study on the acid catalyzed ring contraction in *endo* - 2,8-trimethylene - *cis* - bicyclo[3.3.0]octane (tricyclo[5.3.1.0^{4,11}]undecane, **11**, Scheme 2) system leading to methylperhydrotriquinacenes. According to the theoretical survey,[3] only two, among sixty-nine, reasonably stable tricycloundecane isomers, are cited as the progenitors of methylperhydrotriquinacenes, i.e. the immediate precursors giving rise to methylperhydrotriquinacenes in a single 1,2-alkyl shift resulting in ring contraction with methyl extrusion. These two tricycloundecanes are **11** and *endo* - 2,8 - ethanobicyclo[3.3.1]nonane (tricyclo[5.2.2.0^{4,8}]undecane, **13**).[9] The former tricycloundecane was shown[2c] to exist always in the rearrangement reaction mixtures in equilibrium with the stable intermediate 4-homoisotwistane (**4**). Therefore, **11** should be a very probable candidate for the progeni-



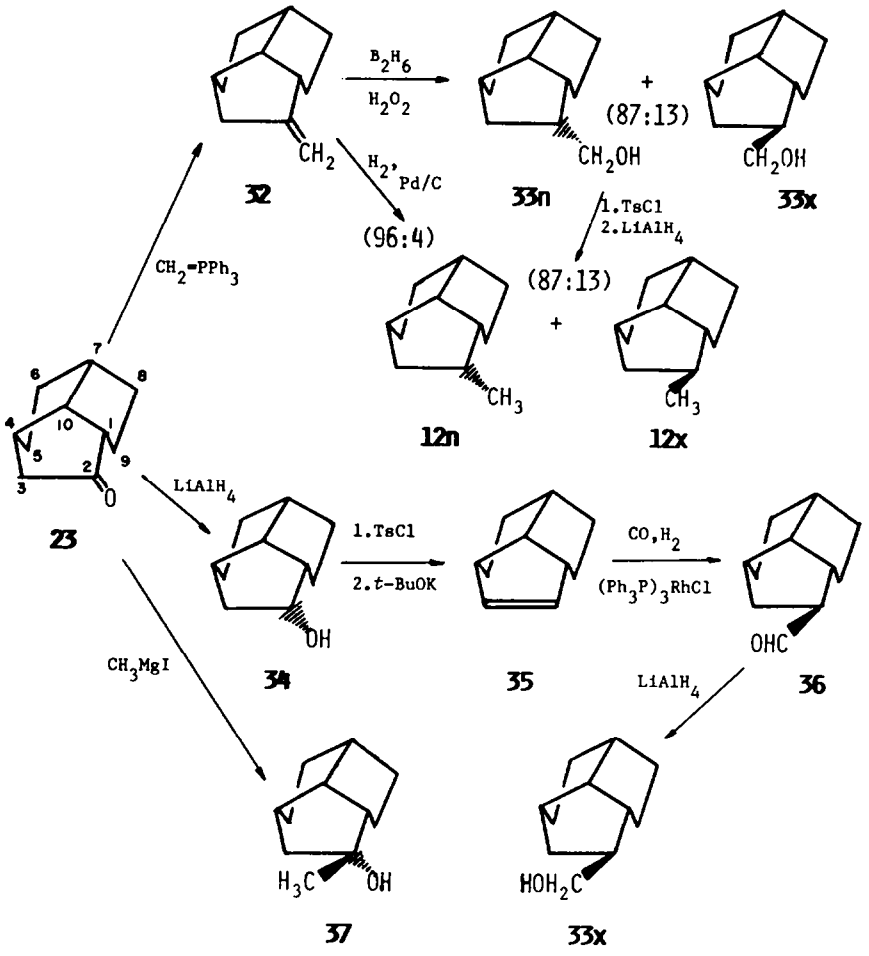
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

tors of methylperhydrotriquinacenes. On the other hand, the latter isomer **13** has never appeared in any of the rearrangement experiments and seems to be irrelevant as a direct progenitor to the present ring contraction problem in the overall tricycloundecane rearrangement pathways.

RESULTS

As shown in Scheme 2(A), the ring contractions to methylperhydrotriquinacenes should occur in the 7-, 8-, and the 9-cation (**11a**, **11b** and **11c**, respectively) of *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane (**11**). These cations were generated from the corresponding alcohols (**28** and **29**, Scheme 4) or olefins (**30** and **31**) under hydride transfer reduction rearrangement conditions (97% sulfuric acid-*n*-pentane at room temperature). As the 11-8- and -9-yl cations (**11b** and **11c**, Scheme 2) may afford 2-methylperhydrotriquinacenes (**12n** and **12x**) via the ring contraction products, tricyclo[5.2.1.$0^{4,10}$]dec-2-ylcarbinyl cations (**33na** and **33xa**, Scheme 6), the corresponding carbinols **33n** and **33x** as well as the methyl derivatives **12n** and **12x** were also prepared, and the reactions of the carbinols were examined. These new compounds, all derived from 2-ketoperhydrotriquinacene (**23**, Scheme 3),[10] were synthesized according to the routes shown in Scheme 4 and 5, as described below.

Synthesis

The key starting material 2-ketoperhydrotriquinacene (**23**) was prepared through a different route (Scheme 3) from that of Paquette.[10] *cis*-Bicyclo[3.3.0]octan-*endo*-2-ol (**16**), prepared from cyclooctene (**14**) via its epoxide **15** after the method of Cope *et al.*,[11] was oxidized with Jones reagent to the corresponding 2-one **17**.[12] The ketone **17** was treated with methylene-triphenylphosphine to afford the 2-methylene derivative **18**.[13] Hydroboration of **18** in the usual manner gave the *endo* primary alcohol **19**[14] in 89% selectivity. The carbinol **19** was oxidized with Jones reagent to the acid **20**.[14] The acid was converted to the diazoketone **22** via the acid chloride **21**,[14] and the diazoketone was pyrolyzed in the presence of cupric sulfate to give predominantly (92%) 2-ketoperhydrotriquinacene (**23**).[10] Thus, the intramolecular carbene insertion in the diazoketone **22** occurred preferably into the bond between the C-8 and the *endo*-8-H.

2-Ketoperhydrotriquinacene (**23**) prepared in this way was converted to the cyanohydrin silyl ether **24** by treatment with trimethylsilyl cyanide[15] (Scheme 4). The cyanohydrin ether **24** was found to consist of only one major constituent (98%) on examination with Golay column vpc, indicating that one of the configurational isomers was formed preferentially.[16] This isomer is considered to be of the *exo*-cyano-*endo*-trimethylsilyloxy configuration **24** on the basis of the steric approach

control of the reagent.[13b,c] The *exo*-cyano configuration for **24** is consistent with the preferable formation (80%) of *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 9 - one (**27**) over that (20%) of the 8-one isomer **26** in the following Demjanow–Tiffeneau ring enlargement of the aminoalcohol **25** derived from **24** by lithium aluminum hydride reduction, because the *exo*-aminomethyl compound **25** in the ring enlargement can assume a perpendicular transition state[17] which is of lower energy than the parallel one that is the transition state the hydroxycarbinyl cation should travel through if the cation from the aminoalcohol had the opposite, *exo*-hydroxy-*endo*-carbinyl configuration. The deamination-ring enlargement products **26** and **27** were separable only on Golay vpc. Preferable formation of the 9-one **27** is a consequence of preferable migration of the C-1 bridgehead (path *b*, Scheme 4) over that of the C-3 methylene (path *a*) in the carbinyl cation **25a**. This regioselectivity is opposite to that in the same, well-known reaction of 2-norbornylcarbinyl system, in which the C-3 methylene migrated preferably over the C-1 bridgehead,[18] and we do not have any rational explanation for the discrepancy at present.

Lithium aluminum hydride reduction of the ketone mixture (**26** and **27**) produced four tricycloundecanols corresponding to the configurational isomers of the 8-ol (**28**) and the 9-ol (**29**). These alcohols were separated only on Golay vpc. The alcohol mixture was tosylated in the usual manner, and the tosylate mixture was treated with potassium *t*-butoxide to give a 17:83 mixture of *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]oct - 1(10) - ene (**30**) and -8-ene (**31**). The mixture of the olefins was hydrogenated over palladium on charcoal catalyst to afford almost quantitatively a single compound *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octane (**11**), which, coupled with the ^1H and the ^{13}C NMR spectra of the mixture, determined unambiguously the structures of the olefins **30** and **31**.

The configurational isomers (**12n** and **12x**, Scheme 5) of 2-methylperhydrotriquinacene were obtained as an 87:13 mixture from a mixture of the corresponding carbinols **33n** and **33x** by lithium aluminum hydride reduction after tosylation. The carbinol mixture, in turn, was derived from 2-ketoperhydrotriquinacene **23** by a Wittig reaction to the 2-methylene derivative **32** followed by hydroboration–oxidation. The more abundant constituent of the carbinol mixture and, hence, that of the methyl derivative mixture were assigned the *endo* configuration on the basis of the established preferable *exo* attack of diborane on polycyclic olefins. 2-Methylperhydrotriquinacenes (**12n** and **12x**) were also obtained by palladium on charcoal catalyzed hydrogenation of the methylene compound **32**. The stereoselectivity for the *endo* isomer (96:4) was higher in this hydrogenation than in the above hydroboration to the carbinol mixture **33** (87:13).

A pure sample of the *exo* carbinol **33x** was obtainable through a *tris*(triphenylphosphine)rhodium chloride catalyzed hydroformylation of tricyclo[5.2.1.$0^{4,10}$]dec-2-ene **35**, prepared from the ketone **23** by lithium aluminum hydride reduction to the *endo*-2-ol **34**,[10] tosylation, and elimination with potassium *t*-butoxide. The product 2-aldehyde **36** in the hydroformylation consisted only of one major constituent (98%) on Golay vpc, and the carbinol derived from the aldehyde was identical with the minor component **33x** of the hydroboration–oxidation products of the 2-methylene derivative **32**. The carbinol isomer via this route should therefore have an *exo* configuration **33x**. It may be pointed out that an *exo* selectivity in this hydroformylation of **35** is consistent with the likewise *exo* specificity in the same rhodium complex catalyzed hydroformylation of *endo* - dicyclopentadiene (*endo* - tricyclo[5.2.1.$0^{2,6}$]deca - 3,8 - diene),[19] and the fact supports indirectly the above configuration assignment to the carbinol isomers **33n** and **33x**.

Reaction of 2-ketoperhydrotriquinacene **23** with methyl-magnesium iodide afforded only one major (98% on Golay vpc) product. The configuration of this isomeric tertiary alcohol **37** would most probably be *exo*-methyl-*endo*-hydroxy, for the reasons of preferred attack of the Grignard reagent from the less hindered *exo* side.[13b,17]

Hydride transfer reduction-rearrangement

The mixture (20:80) of *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 8 - and - 9 - ol (**28** and **29**) obtained above was stirred with excess 97% sulfuric acid and *n*-pentane at room temperature for 5 min. The pentane layer was separated and analyzed by Golay column GC-MS. The products were identified with reference to authentic specimens of *endo*- and *exo* - 2 - methylperhydrotriquinacene (**12n** and **12x**) prepared above, 1- and 10 - methylperhydrotriquinacene (**6** and **7**),[8] 1,2 - trimethylenebicyclo[2.2.2]octane (tricyclo[5.2.2.$0^{1,5}$]undecane, **39**, Scheme 6),[2a,20] 4-homoisotwistane (**4**),[1-3,20] *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octane (**11**),[2c] 2,4 - bishomobrendane (tricyclo[6.2.1.$0^{4,9}$]undecane, **38**),[16] and 2,4 - bishomobrexane (tricyclo[5.4.0.$0^{4,8}$]undecane, **40**).[2c] The result (Run 1) is listed in Table 1.

Other reactants, tricyclo[5.3.1.$0^{4,11}$]dec - 1(10) - and - 8 - ene (**30** and **31**) mixture (Run 2), tricyclo[5.2.1.$0^{4,10}$]dec - *endo* - and - *exo* - 2 - ylcarbinol (**33n** and **33x**; 87:13) mixture (Run 3), pure *exo* carbinol **33x** (Run 4), and 2 - methyl - 2 - hydroxy - perhydrotriquinacene (**37**) (Run 5), were treated similarly with sulfuric acid and *n*-pentane to give the product distributions listed in Table 1.

A small amount (1.3–1.6%) of *endo*-2-methylperhydrotriquinacene (**12n**) was produced from the alcohols **28** and **29** and olefins **30** and **31** of the trimethylenebicyclo[3.3.0]octane (**11**) (Run 1 and 2). A little (0.7%) 1-methylperhydrotriquinacene (**6**) was also detected in the reaction of the alcohol mixture (**28** and **29**) (Run 1).

It would be appropriate to mention here that *endo*-2-methylperhydrotriquinacene (**12n**) was already detected in tricycloundecane rearrangements studied before. In the isomerizations of *cis,exo*- and *cis,endo*-2,3-tetramethyleneorbornane (**1x** and **1n**, Scheme 1) as well as 4-homoisotwistane (**4**) under trifluoromethanesulfonic acid catalysis,[2a] the fourth fraction of preparative vpc of the rearrangement product mixtures contained a compound of unknown structure designated as "Unknown C_1" (Table 1, Ref. 2*a*). Now, unknown C_1 was assigned the structure of *endo*-2-methylperhydrotriquinacene (**12n**) on comparison of the Golay GC-MS result and the ^{13}C NMR spectrum of the vpc fraction with those of an authentic specimen of **12n**.

In the same rearrangement reactions, 1 - *exo* - 2 - trimethylene - *cis* - bicyclo[3.3.0]octane, designated as "Compound B_1" in the third fraction of preparative vpc, was found to be contaminated, as the reactions proceeded, with some compound with unknown structure (Footnote *f* in the same Table). When the rearrangements were allowed to run until the content of methyladamantanes greatly (above 70%) increased, the third

Table 1. Hydride transfer reduction-rearrangement[a]

Run	Reactant	Product (%)[b]										
		7	6	8	12x	12n	9	39	4	11	38 & 40	Others[c]
1	28 + 29 (20:80)	0	0.7	0	0	1.3	1.8	3.7	32.9	51.4	6.0	2.3
2	30 + 31 (17:83)	0	0	0	0	1.6	0.6	2.7	36.9	53.1	4.3	0.8
3	33n + 33x (87:13)	0.2	0	0.2	0.5	11.8	3.0	1.5	67.6	12.5	2.1	0.5
(3-c)[d]	(33n)	(0.2)	(0)	(0)	(0.5)	(12.6)	(1.5)	(1.5)	(69.5)	(12.4)	(1.9)	(0.4)
4	33x	0.2	0	2.5	0.6	10.0	12.8	1.8	54.5	13.0	3.2	1.3
5	37	0	0	0	0	94.6	1.5	0	0	0	0	3.9

[a] 100 mg of a reactant, 1 g of 97% sulfuric acid, and 5 ml of n-pentane stirred vigorously at room temperature (~25°C).

[b] Calculated from VPC peak areas.

[c] Combined VPC peak areas of several unidentified compounds.

[d] Figures in parentheses are those corrected for pure 33n, as calculated from the corresponding values in Run 3 and 4 under additivity assumption.

fraction comprised *ca* the same amounts of this unknown and 1,*exo* - 2 - trimethylene - *cis* - bicyclo[3.3.0]octane (B_1), while 1, *exo* - 2 - and 1, *endo* - 2 - tetra-methylenenorborane (B_2 and B_3, or *exo*-**2** and *endo*-**2**, in the same table) in the same vpc fraction almost disappeared. Golay GC-MS and ^{13}C NMR measurements of the fraction at this reaction stage demonstrated that the unknown was identical with *exo*-2-methylperhydrotriquinacene (**12x**).

In the hydride transfer reduction rearrangements of the perhydrotriquinacene carbinols **33**, ring enlargements were by far the prevalent reaction pathways, and direct hydride transfers to give methylperhydrotriquinacenes **12** were limited to *ca* 10% (Run 3 and 4, Table 1). In contrast to the primary carbinols **33**, tertiary 2-methyl-2-hydroxyperhydrotriquinacene (**37**) predominantly (94.6%) underwent the hydride abstraction from outside to form the corresponding hydrocarbon **12** (Run 5). It is to be noted here that hydride transfer reductions in the alcohols **33** and **37** almost exclusively gave rise to the *endo*-methyl product **12n**.

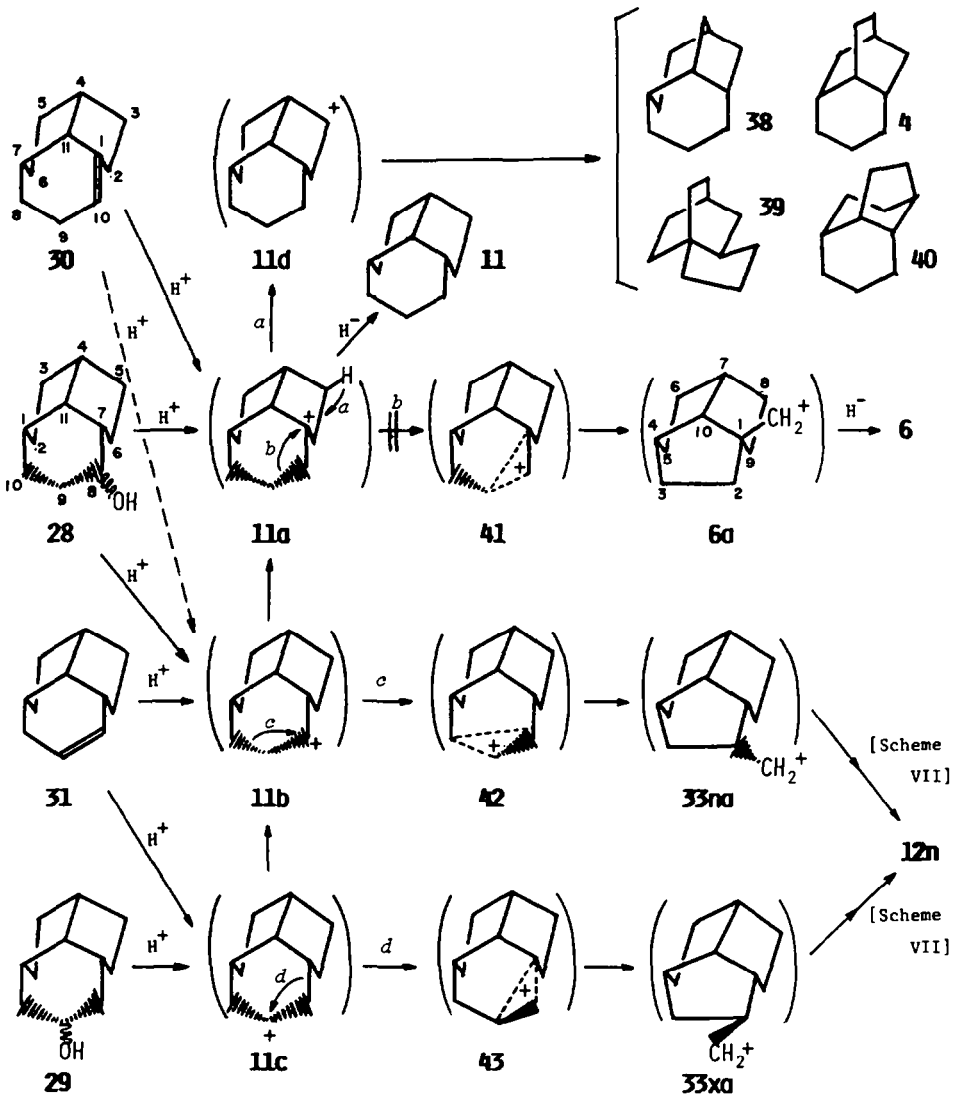
A major difference in the reactivities of the *endo* carbinol **33n** (on the basis of the calculated figures in Run 3-c, Table 1) and the *exo* one **33x** (Run 4) lies in that a fairly large amount (12.8%) of 2-methyladamantane (**9**) was formed from **33x**, as compared to that (1.5%) from **33n**. The extent of the ring enlargement to the tricycloundecanes **4**, **11**, **38–40** was reduced in **33x** by that much (combined tricycloundecanes 72.5%), as compared to that in **33n** (85.3%).

DISCUSSION

The methyl extrusion process, though to a very minor extent, did take place in the cations of the trimethylenebicyclo[3.3.0]octane **11** (Run 1 and 2), and this is the second experimental evidence for methyl extrusion, next to that in homoadamantane (**5**),[4] in the tricycloundecane rearrangement. Formation of only minor amounts of methylperhydrotriquinacenes is consistent with the theoretical conclusion[3] that the methyl extrusion process is only difficulty realizable mainly for energetic reasons. The result is also in accordance with the destinations of the perhydrotriquinacene carbinols **33**, which were predominantly toward the ring enlargement to give the trimethylenebicyclo[3.3.0]octane **11** and other tricycloundecanes (Run 3 and 4; path *b*, *c*, *f*, and *g*, Scheme 7).

The major product of ring contraction in the trimethylenebicyclo[3.3.0]octane derivatives **28–31** was *endo*-2-methylperhydrotriquinacene (**12n**). This ring contraction occurred most probably in the **11**-8-yl cation (**11b**, Scheme 6) by the shift of the C-10 methylene carbon atom via the transition state **42** (path *c*), as well as in the **11**-9-yl cation (**11c**) by the shift of the C-7 (or C-1) bridgehead via **43** (path *d*). The latter process, shift of a bridgehead, was of far minor contribution in the 2-norbornylcarbinyl ring enlargements.[18] In the trimethylenebicyclo[3.3.0]octyl system, however, shift of the C-1 (or C-7) bridgehead should be as likely to occur as that of the C-10 methylene, in considering the above-stated Demjanow–Tiffeneau ring enlargement of the aminoalcohol **25** (Scheme 4), which is the reverse of the ring contraction under discussion, to yield preferably the 9-one **27** over the 8-one **26**.

Although the ring contraction processes via **42** and **43** should give rise to both the perhydrotriquinacene *endo*- and *exo*-2-ylcarbinyl cations (**33na** and **33xa**, respectively; Scheme 6), the major product was a single configurational isomer, *endo*-2-methyl **12n**. This is explained well by presuming (i) a similar ease with which a common tertiary cation, the 2-methyl-2-yl **37a** (Scheme 7), is produced from **33na** and **33xa** by intramolecular 1,2-hydride transfers (path *d* and *e*, Scheme 7), and (ii) stereoselective intermolecular hydride transfer reduction of this tertiary cation **37a**. Since *endo*- and *exo*-2-methylperhydrotriquinacene (**12n** and **12x**) are calculated to have similar thermodynamic stabilities (ΔH_f° −30.59 and −30.88 kcal mol^{-1}, respectively),[3] no better explanation appears to be offered than that in terms of the stereoselective hydride transfer reduction in which the hydride source approaches from the less hindered *exo*



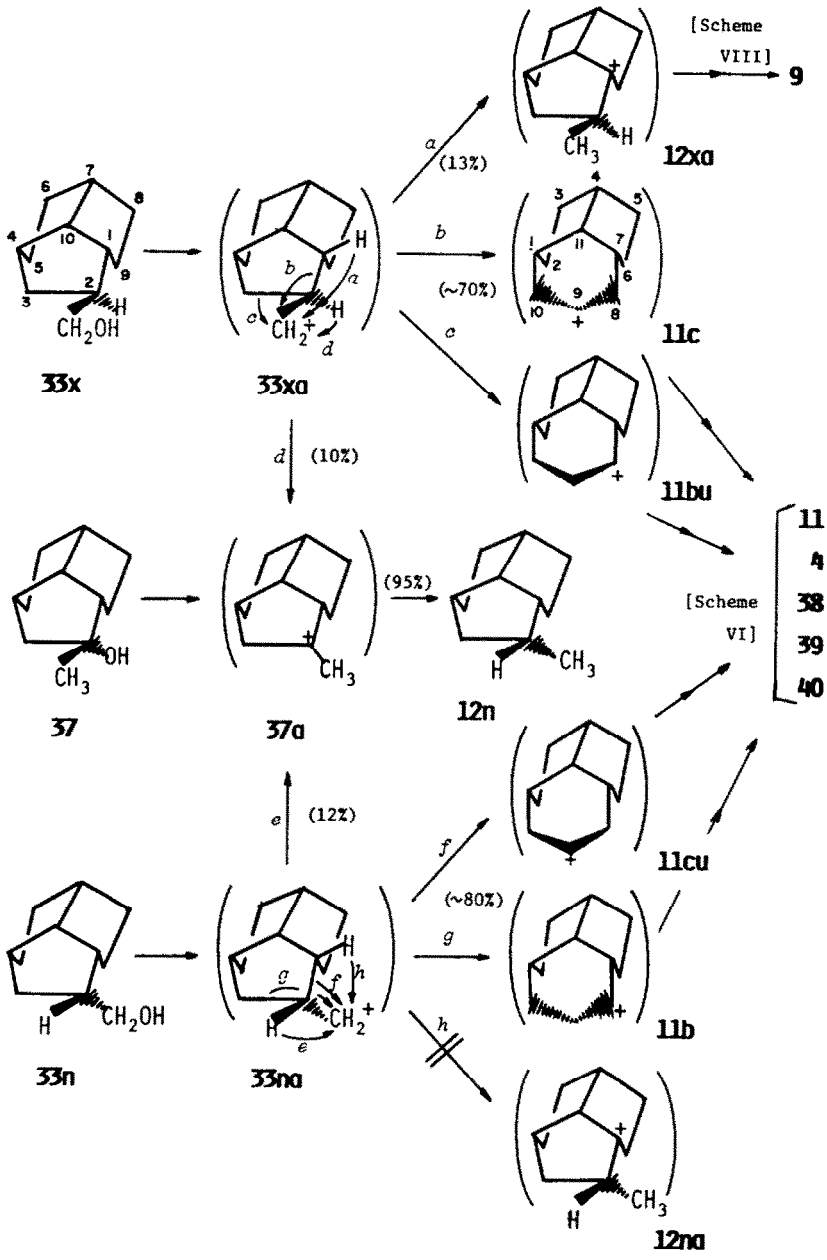
Scheme 6.

side[10] of **37a**. The steric approach control has been well established for complex metal hydride reagents, but any precedent example does not seem to exist for hydride donors.[21] The above presumptions (i) and (ii) also explain the formation of similar amounts of **12n** either from the *endo* carbinol **33n** (Run 3-c) or from the *exo* one **33x** (Run 4), as well as an almost exclusive formation of **12n** from the tertiary carbinol **37** (Run 5).

A little (0.7%) 1-methylperhydrotriquinacene (**6**) was detected in the reaction of the trimethylenebicyclo[3.3.0]octanols **28** and **29** (Run 1). The product does not seem to result from direct ring contraction in the 11-1-yl cation **11a** (path *b*, Scheme 6), because no 1-methyl product **6** was obtained from the corresponding olefins **30** and **31** (Run 2) which should also yield the 1-cation **11a**. The 1-methyl isomer **6** may be transformed from the once formed 2-methyl isomer **12**, and the most plausible route between them, and then to the 10-methyl isomer **7**, is shown in Scheme 9. This explanation, however, also meets with difficulty for the same reasons as above as well as because of the formation of no **6** from the 2-methyl-2-hydroxyperhydrotriquinacene (**37**) (Run 5; Scheme 7).

Formation of a minor amount of 10-methylperhydrotriquinacene **7** from the carbinols **33n** and **33x** (Run 3 and 4) also can not be explained within the scope of the present interpretation. According to Scheme 9, no direct route is drawn between the 2- and 10-methyl isomers (**12** and **7**), but it is only via the 1-methyl isomer **6** which was not detected at all. Thus, the mechanism of the formation as well as interconversion of 1- and 10-methylperhydrotriquinacene (**6** and **7**) is left to further studies.

A considerably large proportion (12.8%) of 2-methyladamantane (**9**) was observed for the reaction of the *exo* carbinol **33x** (Run 4), as compared to that (1.5%) for the reaction of the *endo* isomer **33n** (Run 3-c). The difference seems to be explained with an inference that the cation **33xa** (Scheme 8) from the *exo* carbinol **33x** would undergo relatively easily the intramolecular 1,3-hydride transfer from the 1-bridgehead to form the stable 1-cation **12xa** (path *a*), whereas the *endo* cation **33na** could not perform the corresponding process (path *g* to give

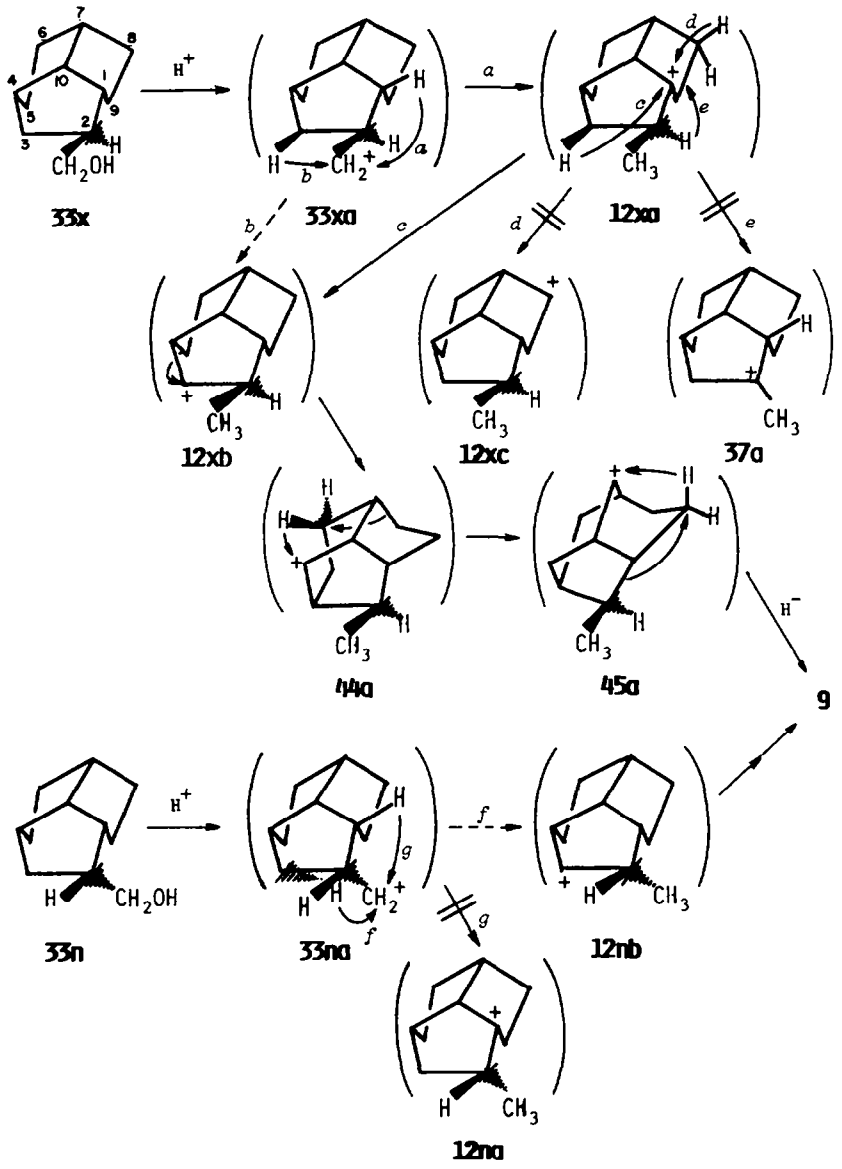


Scheme 7.

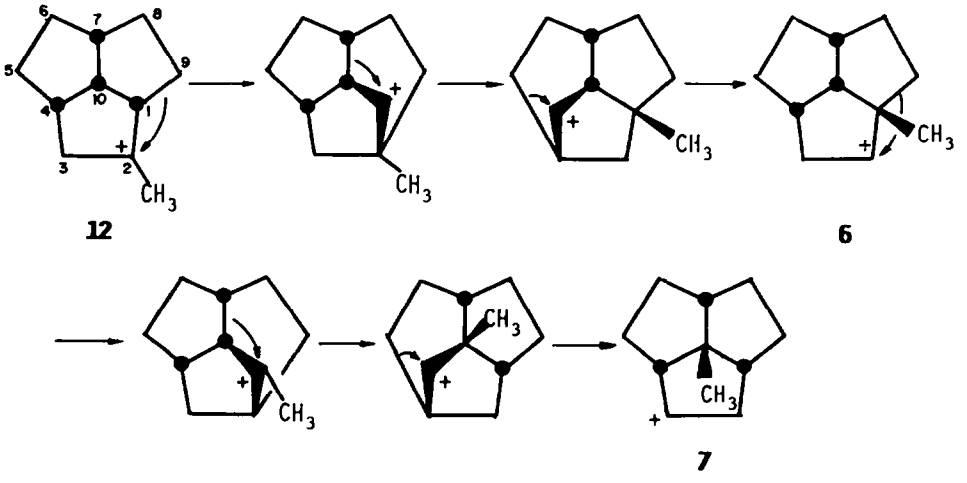
12na). This inference results from a consideration of orbital overlap between the vacant p on the carbinyl cation center and the 1-H σ. The overlap appears very favorable for **33xa**, but it is badly hindered sterically for **33na**.

The pathway from **12xa** to 2-methyladamantane (**9**) may be such as is depicted in Scheme 8, which involves an intramolecular 1,3-hydride transfer from *exo*-3-H (path *c*) to give the 3-yl cation **12xb**, the shift of C-5 to afford **44a**, and then the isomerizations to a methylprotoadamantyl cation **45a** and to 2-methyladamantane (**9**). The pathway is the same as that suggested by Paquette[16] for the parent perhydrotriquinacene. The cation **12xb** may be formed directly from **33xa** by a 1,3-transfer of *exo*-3-H (path *b*). The proportion of this process, however, should be far less than that of path *a* which gives a more stable bridgehead cation **12xa**. Notwithstanding, the corresponding process in **33na**, i.e. 1,3-transfer of *endo*-3-H to the *endo*-2-ylcarbinyl cation center to afford *endo*-2-methyl-3-yl cation **12nb** (path *f*), might explain a small (1.5%; Run 3-c) yield of 2-methyladamantane (**9**) in the reaction of the *endo* carbinol **33n**.

The path *c* in **12xa** (Scheme 8) would be the most favorable of all those intramolecular hydride transfers which possibly lead to skeletal rearrangements (path *c*–*e*). The path *e* is quite improbable because of little orbital overlap. The path *d*, transfer of *exo*-8-H which is geometrically equivalent to *exo*-3-H with respect to the C-1 cationic center, may be stereoelectronically as favorable as the path *c*, but the resulting 8-cation **12xc** should be less stable than is **12xb**, in which the β-carbon atom (C-2) of the C-3 cationic center is substituted by a methyl. Stabilization of carbocations by β-branching is a widely recognized phenomenon, stabilization by



Scheme 8.



Scheme 9.

3 kcal/mol being estimated for the secondary cations.[7,22]

No 1-methyladamantane (**8**) is considered to be formed from the *endo* carbinol **33n** (Run 3-c), although a little (2.5%) of it was obtained from the *exo* isomer **33x** (Run 4). A best explanation for this difference would be that 1-methyladamantane (**8**) is produced from once formed 2-methyl isomer **7**[6] only slowly under the present reaction conditions. If the ratio 1-/2-methyladamantane (**8**/**9**) is taken to be 2.5/12.8 as represented by the result of Run 4, 1.5% **9** (Run 3-c) should correspond to 0.3% **8**, which is close to the lower limit of detection in our Golay vpc system.

EXPERIMENTAL

All melting and boiling points were uncorrected. Conventional as well as Golay column vpc and GC–MS, IR and ^1H and ^{13}C NMR measurements were done on the same instruments as in the previous works.[2]

2-Ketoperhydrotriquinacene (*tricyclo*[5.2.1.0^{4,10}]*decan-2-one*, **23**). To a solution of 23.73 g (0.138 mol) of *cis* - bicyclo[3.3.0]oct - *endo* - 2 - ylcarbonyl chloride (**21**)[14] prepared according to the method of Scheme 3 in 100 ml of dry ether kept at 0° in an ice–water bath was added dropwise with stirring in a period of 1 hr a solution of diazomethane in 600 ml of ether obtained from 129 g (0.6 mol) of nitrosomethyl-*p*-toluenesulfonamide,[23] and the reaction was set aside overnight at ambient temperature. The ether solution was concentrated to give 20.4 g (83% yield) of crude 1 - (*cis* - bicyclo[3.3.0]oct - *endo* - 2 - yl) - 2 - diazoethan - 1 - one (**22**): IR (neat) 3050, 2100, 1720, 1630, 1150 cm^{-1}.

The decomposition of the diazoketone **22** was run in a high dilution apparatus[24] as follows. A solution of the crude diazoketone **22** obtained above in 600 ml of toluene was added dropwise with efficient stirring in a period of 24 hr into 2.5 l of toluene containing 43.9 g (0.275 mol) of finely powderized anhydrous cupric sulfate kept at reflux. The reaction was stirred vigorously under reflux for further 6 hr.

Precipitates were filtered off, and the filtrate was concentrated. The residue was fractionally distilled to give 6.48 g (83% yield) of 2-ketoperhydrotriquinacene (**23**; 99.3% purity): b.p. 114° (12 mm); m.p. 70–71° (lit[10] m.p. 68.5–70.5°); IR (Nujol) 1740 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ_C 31.1 (t), 31.3 (t), 32.8 (t), 33.6 (t), 36.9 (d), 45.6 (t), 46.3 (d), 50.9 (d), 52.4 (d), 222.0 (s); mass spectrum (*m/e*), rel intensity) 150 (100, M$^+$), 107 (25), 106 (82), 93 (23), 81 (32), 80 (52), 79 (33), 68 (21), 67 (47). Found: C, 80.3; H, 9.1. $C_{10}H_{14}O$ requires: C, 80.0; H, 9.3%.

2-Cyano-2-trimethylsilyloxyperhydrotriquinacene (**24**).

A mixture of 3.11 g (20.7 mmol) of 2-ketoperhydrotriquinacene (**23**), 3.0 g (30 mmol) of trimethylsilyl cyanide, a small crystal of zinc iodide, and 20 ml of dry benzene was stirred at ambient temperature for 4 hr. Evaporation of the benzene gave 5.15 g (quantitative yield) of crude 2-cyano-2-trimethylsilyloxyperhydrotriquinacene (**24**): IR (neat) 2240, 1260, 1150, 1120, 990, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 9H; $Si(CH_3)_3$), 1.0–3.0 (complex m, 14H); mass spectrum (*m/e*, rel intensity) 249 (15, M$^+$), 234 (43), 208 (21), 207 (100), 108 (66), 80 (34), 79 (22), 75 (47), 73 (40), 67 (20).

2-Aminomethyl-2-hydroxyperhydrotriquinacene (**25**) *and its Hydrochloride.* The sample of crude 2-cyano-2-trimethylsilyloxyperhydrotriquinacene (**24**) obtained above was dissolved in 30 ml of dry ether, and the solution was added dropwise with efficient stirring to a suspension of 3.79 g (0.1 mol) of lithium aluminum hydride in 30 ml of ether in a period of 1 hr, and the mixture was heated under reflux with stirring for further 3 hr. The mixture was treated with water and a sodium hydroxide solution in the usual manner. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layer and ether extracts were washed with water and dried over anhydrous sodium sulfate. The ether was evaporated off to afford 3.45 g (92% yield) of crude 2-aminomethyl-2-hydroxyperhydrotriquinacene (**25**): m.p. 75–76°; IR (neat) 3600–3100, 1570 cm^{-1}; mass spectrum (*m/e*, rel intensity) 181 (1, M$^+$), 151 (100), 150 (27), 106 (20), 91 (56), 81 (23), 79 (29), 67 (33), 32 (61), 30 (39).

The crude amine **25** was dissolved in 50 ml of ether, and dry hydrogen chloride was bubbled through the ether solution for 2 hr at ambient temperature. The precipitates were filtered, washed with ether, and dried *in vacuo* to give 3.89 g (94% yield) of crude hydrochloride of **25**. Recrystallization from methanol–acetone gave a pure sample: m.p. 250–252° (dec in sealed tube); IR (KBr) 3650 – 3520, 2600, 1590, 1160, 1020 cm^{-1}. Found: C, 60.4; H, 9.6; N, 6.4; Cl, 16.7. $C_{11}H_{20}ONCl$ requires: C, 60.7; H, 9.3; N, 6.4; Cl, 16.3%.

endo - 2,8 - *Trimethylene* - cis - *bicyclo*[3.3.0]*octan* - 8 - *and* - 9 - *one* (*Tricyclo*[5.3.1.0^{4,11}]*undecan* - 8 - *and* - 9 - *one*, **26** *and* **27**). A sample (3.27 g, 15.0 mmol) of 2 - aminomethyl - 2 - hydroxyperhydrotriquinacene hydrochloride (**25** · HCl) and 2.04 g (10.5 mmol) of sodium acetate trihydrate were dissolved in a mixture of 2 ml of acetic acid and 15 ml of water. To the solution kept below 12° was added dropwise with stirring a solution of 1.14 g (16.5 mmol) of sodium nitrite in 5 ml of water, and the reaction was stirred at ambient temperature for 1 hr. The reaction mixture was extracted with three 50 ml portions of ether, and the combined ether extracts were washed successively with a saturated sodium bicarbonate and a sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the ether gave 1.55 g (63% yield) of a mixture of crude *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 8 - and - 9 - one (**26** and **27**): IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.8 (complex m). Found: C, 80.5; H, 9.6. $C_{11}H_{16}O$ requires: C, 80.4; H, 9.8%.

Golay GC–MS and ^{13}C NMR measurements revealed that the mixture comprised 20% 8-one **26** and 80% 9-one **27**. The 8-one **26**: mass spectrum (*m/e*, rel intensity) 164 (61, M$^+$), 136 (55), 122 (37), 109 (61), 107 (60), 93 (34), 80 (66), 79 (67), 67 (100), 41 (40). The 9-one **27**: ^{13}C NMR ($CDCl_3$) δ_C 32.4 (t, 2), 33.6 (t, 2), 38.2 (d, 2), 41.5 (t, 2), 44.5 (d, 1), 44.8 (d, 1), 211.5 (s, 1); mass spectrum (*m/e*, rel intensity) 164 (53, M$^+$), 135 (57), 107 (39), 94 (58), 81 (100), 80 (37), 79 (67), 68 (100), 67 (52), 41 (43).

endo - 2,8 - *Trimethylene* - cis - *bicyclo*[3.3.0]*octan* - 8 - *and* - 9 - *ol* (*Tricyclo*[5.3.1.0^{4,11}]*undecan* - 8 - *and* - 9 - *ol*, **28** *and* **29**). A solution of 1.32 g (8.1 mmol) of the mixture of *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 8 - and - 9 - one (**26** and **27**) obtained above in 10 ml of ether was added dropwise at ambient temperature with efficient stirring to a suspension of 0.61 g (16 mmol) of lithium aluminum hydride in 20 ml of ether, and the mixture was heated under reflux for further 1 hr. The cooled reaction mixture was treated in the usual manner to give 1.14 g (85% yield) of a mixture of crude *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 8 - and - 9 - ol (**28** and **29**): IR (neat) 3600–3100, 1070, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5–3.6 (complex m). Found: C, 79.8; H, 10.9. $C_{11}H_{18}O$ requires: C, 79.5; H, 10.9%.

Golay column vpc of the mixture showed four major peaks (63, 18, 7, and 6%) which comprised 94% of the total peak area. The mixture was used in the following reactions without any further purifications and structure determinations of the isomeric alcohols.

endo - 2,8 - *Trimethylene* - cis - *bicyclo*[3.3.0]*oct* - 1(10) - *and* - 8 - *ene* (*Tricyclo*[5.3.1.0^{4,11}]*undec* - 1(10) - *and* - 8 - *ene*, **30** *and* **31**). A sample (0.50 g, 6.3 mmol) of the mixture of *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octan - 8 - and - 9 - ols (**28** and **29**) obtained above was dissolved in 20 ml of pyridine. To the pyridine solution kept below 10° was added 1.2 g (6.3 mmol) of *p*-toluenesulfonyl chloride, and the mixture was stirred at the same temperature until the sulfonyl chloride dissolved. The reaction was set aside for 2 days in an ice box. The mixture was poured onto 100 g of cracked ice, and extracted with three 100 ml portions of ether. The combined ether extracts were washed with cold 2% hydrochloric acid and then with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent left a mixture of crude tosylates.

The tosylate mixture was dissolved in 30 ml of dimethyl sulfoxide containing 1.9 g (8.9 mmol) of potassium *t*-butoxide at ambient temperature, and the reaction was stirred overnight at the same temperature. The reaction mixture was poured onto 100 ml of water, and extracted with three 100 ml portions of *n*-pentane. The combined pentane extracts were washed with

three 100 ml portions of water, and dried over anhydrous magnesium sulfate. The solvent was evaporated off, and the residue was purified by silica gel column chromatography with *n*-pentane as eluent. Evaporation of the pentane from the eluate gave 0.18 g (41% yield) of a mixture of pure *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]oct - 1(10) - and - 8 - ene (**30** and **31**) in 17:83 ratio, as calculated from the Golay vpc peak areas: IR (neat) 3030, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.7 (complex m), 5.5–5.8 (m). Found: C, 89.3; H, 10.6. $C_{11}H_{16}$ requires: C, 89.1; H, 10.9.

Golay GC–MS and ^{13}C NMR measurements offered the following spectra of the isomers. The 1(10)-ene **30**: mass spectrum (*m/e*, rel intensity) 148 (56, M^+), 120 (100), 119 (78), 106 (52), 105 (34), 93 (60), 92 (47), 91 (83), 80 (30), 79 (59). The 8-ene **31**: ^{13}C NMR ($CDCl_3$) δ_C 26.6 (t), 33.1 (t and t), 34.0 (d), 34.7 (t), 37.8 (d), 38.0 (d), 43.9 (d), 44.9 (d), 124.0 (d), 130.7 (d); mass spectrum (*m/e*, rel intensity) 148 (65, M^+), 120 (100), 119 (78), 106 (50), 93 (56), 92 (49), 91 (75), 80 (55), 79 (91), 67 (33).

The above mixture of the 1(10)- and the 8-ene **30** and **31** (0.050 g, 0.34 mmol) in 30 ml of ethyl acetate was hydrogenated in an autoclave at 100° with 100 kg/cm^2 of hydrogen over 0.30 g of palladium (5%) on charcoal catalyst. The catalyst was filtered off, and the filtrate was concentrated to give 0.051 g (quantitative) of crude (92% Golay vpc purity) *endo* - 2,8 - trimethylene - *cis* - bicyclo[3.3.0]octane (**11**). Purification by preparative vpc yielded a pure sample which showed m.p., mixture m.p., and Golay GC–MS behavior in complete agreement with those of an authentic specimen.[2c]

2 - *Methyleneperhydrotriquinacene* (2 - *methylenetricyclo* - [5.2.1.$0^{4,10}$]*decane*, **32**). A solution of 9.1 g (26 mmol) of methyltriphenylphosphonium bromide and 2.9 g (26 mmol) of potassium *t*-butoxide in 45 ml of dimethyl sulfoxide was stirred at ambient temperature under nitrogen stream for 2 hr. To the solution was added dropwise with stirring at ambient temperature a solution of 2.5 g (17 mmol) of 2-ketoperhydrotriquinacene (**23**) in 10 ml of ether. The reaction was further stirred at the same temperature for 4 hr, and then heated under reflux for 2 hr. The cooled reaction mixture was diluted with 40 ml of water and extracted with three 20 ml portions of *n*-hexane. The combined hexane extracts were washed three times with a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The dried hexane solution was concentrated, and the residue was purified by alumina column chromatography with *n*-hexane as eluent to give 1.6 g (64% yield) of liquid 2-methyleneperhydrotriquinacene (**32**): IR (neat) 3060, 2980, 1760, 1660, 1460, 1430, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–3.0 (complex m, 14H), 4.8 (m, 2H; $=CH_2$); ^{13}C NMR ($CDCl_3$) δ_C 31.8 (t), 32.1 (t and t), 32.6 (t), 40.9 (t), 41.9 (d), 45.5 (d), 48.9 (d), 54.9 (d), 104.0 (t), 157.1 (s); mass spectrum (*m/e*, rel intensity) 148 (100, M^+), 133 (53), 120 (47), 119 (45), 106 (86), 105 (40), 93 (65), 92 (55), 91 (61), 79 (58). Found: C, 89.4; H, 10.6. $C_{11}H_{16}$ requires: C, 89.2; H, 10.8.

endo - *and* exo - 2 - *Hydroxymethylperhydrotriquinacene* (*tricyclo*[5.2.1.$0^{4,10}$]*dec* - endo - *and* - exo - 2 - *ylcarbinol*, **33n** *and* **33x**). To a mixture of 1.15 g (7.8 mmol) of 2-methyleneperhydrotriquinacene (**32**), 1.0 g (26.4 mmol) of sodium borohydride, and 30 ml of dry tetrahydrofuran was added dropwise with stirring at ambient temperature 5.09 g (26.4 mmol) of boron trifluoride etherate, and the mixture was stirred at the same temperature for further 3 hr. To the reaction mixture was added successively 5.5 ml of water, 5.5 ml of 3N sodium hydroxide solution, and 5.5 ml of 30% hydrogen peroxide solution, and the mixture was heated under reflux with efficient stirring for 4 hr. The reaction mixture was diluted with 20 ml of a saturated sodium chloride solution, and extracted with three 30 ml portions of ether. The combined ether extracts were washed with two 20 ml portions of a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The dried ether solution was concentrated, and the residue was purified by alumina column chromatography with ether as eluent. The eluate was concentrated to give 0.88 g (68% yield) of an 87:13 mixture of pure *endo*- and *exo*-2-hydroxymethylperhydrotriquinacene (**33n** and **33x**): IR (neat) 3330, 1090, 1060, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–3.0 (complex m, 15H), 3.41 (s, 1H: OH), 3.49 (d, $J = 6$ Hz, 2H; CH_2OH). Found: C, 79.4; H, 10.9. $C_{11}H_{18}O$ requires C, 79.5; H, 10.8.

Golay GC–MS and ^{13}C NMR measurements of the mixture gave the following spectra of the isomers. The *endo*-2-ylcarbinol **33n**: ^{13}C NMR ($CDCl_3$) δ_C 24.9 (t), 30.9 (t), 32.5 (t and t), 33.7 (t), 43.9 (d), 44.3 (d), 46.1 (d), 47.0 (d), 54.8 (d), 64.0 (t); mass spectrum (*m/e*, rel intensity) 148 (100), 135 (58), 120 (74), 119 (41), 106 (45), 93 (57), 81 (34), 80 (37), 79 (55), 67 (54). The *exo*-2-ylcarbinol **33x**: mass spectrum (*m/e*, rel intensity) 148 (46), 135 (100), 120 (94), 119 (60), 106 (51), 93 (77), 81 (46), 80 (39), 79 (78), 67 (95).

endo- *and* exo-2-*Methylperhydrotriquinacene* (endo- *and* exo-2-*methyltricyclo*[5.2.1.$0^{4,10}$]*decane*, **12n** *and* **12x**). (a) *Reduction of the carbinol tosylates.* To a solution of 0.48 g (2.9 mmol) of the mixture of *endo*- and *exo*-2-hydroxymethylperhydrotriquinacene (**33n** and **33x**) obtained above in 10 ml of pyridine kept below 10° was added with stirring 0.66 g (3.5 mmol) of *p*-toluenesulfonyl chloride, and the mixture was stirred at the same temperature for 1 hr. The reaction was set aside for 2 days in an ice box. The mixture was poured onto a mixture of 10 ml of concentrated hydrochloric acid and 50 g of cracked ice, and extracted with three 20 ml portions of ether. The combined ether extracts were washed with two 20 ml portions of a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The dried ether solution was concentrated to give 0.73 g (79% yield) of a mixture of crude tosylates: IR (neat) 3050, 1600, 1190, 1100, 960, 840, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.8 (complex m, 15H), 2.37 (s, 3H; $C_6H_4CH_3$), 4.02 (d, $J = 6$ Hz, 2H; CH_2O), 7.58 (q, 4H; $-C_6H_4-$).

The crude tosylate mixture (0.73 g, 2.28 mmol) was dissolved in 10 ml of ether, and the ether solution was added dropwise with efficient stirring into a suspension of 0.10 g (2.6 mmol) of lithium aluminum hydride in 10 ml of ether, and the mixture was heated under reflux for 4 hr. The reaction mixture was treated successively with water, 3N sodium hydroxide solution, and water in usual manner, and extracted with ether. The combined ether extracts were washed twice with a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Evaporation of the solvent and purification of the residue by preparative vpc gave 0.32 g (82% yield) of an 87:13 mixture of *endo*- and *exo*-2-methylperhydrotriquinacene (**12n** and **12x**): IR (neat) 2930, 2850, 1470, 1380 cm^{-1}. Found: C, 87.1; H, 12.0. $C_{11}H_{18}$ requires: C, 87.9; H, 12.1%.

Golay GC–MS and ^{13}C NMR measurements of the mixture gave the following spectra for the individual isomer. The *endo*-2-methyl **12n**: ^{13}C NMR ($CDCl_3$) δ_C 15.5 (q), 25.2 (t), 31.0 (t), 32.5 (t and t), 38.5 (d), 38.7 (t), 44.3 (d), 44.7 (d), 49.6 (d), 55.1 (d); mass spectrum (*m/e*), rel intensity) 150 (59, M^+), 121 (40), 108 (60), 107 (40), 94 (98), 93 (79), 80 (100), 79 (85), 67 (93). The *exo*-2-methyl **12x**: mass spectrum (*m/e*, rel intensity) 150 (61, M^+), 135 (43), 108 (82), 107 (38), 94 (63), 93 (72), 81 (43), 80 (100), 79 (78), 67 (86).

(b) *Hydrogenation of the methylene compound.* In a 100 ml autoclave were placed 0.56 g (3.8 mmol) of 2-methyleneperhydrotriquinacene (**32**), 50 ml of ether, and 0.1 g of palladium (5%) on charcoal catalyst, and the vessel was pressurized to 20 kg/cm^2 and heated at 40° for 1 hr. The catalyst was filtered off from the reaction mixture, and the filtrate was concentrated. The residue was purified by preparative vpc to give 0.53 g (93% yield) of a mixture of *endo*- and *exo*-2-methylperhydrotriquinacene (**12n** and **12x**). Golay GC–MS showed the mixture to be comprised 96% *endo* isomer **12n** and 4% *exo* one **12x**.

Tricyclo[5.2.1.$0^{4,10}$]*dec* - 2 - *ene* (**35**). *endo* - 2 - Hydroxyperhydrotriquinacene (*endo* - 2 - hydroxytricyclo[5.2.1.$0^{4,10}$]decane, **34**) was prepared from the 2 - ketoperhydrotriquinacene (**23**) by reduction within lithium aluminum hydride according to the method of Paquette.[10] The *endo*-2-ol **34** thus obtained was dissolved in 20 ml of pyridine, and tosylated with 2.5 g (13.1 mmol) of *p*-toluenesulfonyl chloride in the usual manner. The reaction mixture was extracted with ether, and the ether extracts were washed with cold 2% hydrochloric acid and water, and dried over anhydrous sodium sulfate. Concentration of the dried ether solution gave the crude tosylate.

A solution of the above tosylate and 1.11 g (10 mmol) of potassium *t*-butoxide in 50 ml of dimethyl sulfoxide was stirred at ambient temperature overnight. The reaction mixture was diluted with 100 ml of water and extracted with four 100 ml portions of *n*-pentane. The combined pentane extracts were

washed with three 200 ml portions of water, and dried over anhydrous magnesium sulfate. The pentane solution was concentrated, and the residue was purified by silica gel column chromatography with *n*-pentane as eluent to give 0.53 g (60% yield) of pure tricyclo[5.2.1.$0^{4,10}$]dec-2-ene (**35**): IR (neat) 3050, 910, 820, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–3.2 (complex m, 12H), 5.33 (s, 2H; C*H*=C*H*); ^{13}C NMR ($CDCl_3$) δ_C 31.1 (t, 2), 32.8 (t, 2), 46.0 (d, 1), 50.7 (d, 2), 52.6 (d, 1), 134.1 (d, 2); mass spectrum (*m/e*, rel intensity) 134 (11, M^+), 92 (54), 80 (86), 79 (99), 77 (41), 67 (54), 66 (46), 41 (57), 39 (100), 27 (78). Found: C, 89.4; H, 10.7. $C_{10}H_{14}$ requires: C, 89.5, H, 10.5%.

exo - 2 - *Formylperhydrotriquinacene* (exo - 2 - *formyltricyclo*-[5.2.1.$0^{4,10}$]*decane*, **36**). A solution of 0.50 g (3.7 mmol) of tricyclo[5.2.1.$0^{4,10}$]dec - 2 - ene (**35**), 0.020 g of *tris*(triphenylphosphine)rhodium chloride,[25] and 2 drops of triethylamine in 30 ml of benzene was placed in a 100 ml autoclave. The autoclave was pressurized with 80 kg/cm^2 of a 1:1 (v/v) mixture of carbon monooxide and hydrogen, and heated with stirring at 80° for 3 hr. The reaction mixture was concentrated, finally under reduced pressure, and the residue was purified with preparative vpc to give 0.43 g (70% yield) of pure *exo*-2-formylperhydrotriquinacene (**36**): IR (neat) 2810, 2710, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.9 (complex m, 15H), 9.62 (d, J = 2 Hz, 1H; C*H*O); mass spectrum (*m/e*, rel intensity) 164 (35, M^+), 146 (26), 136 (42), 135 (100), 107 (59), 94 (57), 93 (65), 81 (59), 79 (81), 67 (98). Found: C, 80.3; H, 9.9. $C_{11}H_{16}O$ requires: C, 80.4; H, 9.8%.

exo - 2 - *Hydroxymethylperhydrotriquinacene* (*tricyclo*[5.2.1.$0^{4,10}$]*dec* - exo - 2 - *ylcarbinol*, **33x**). A sample (0.13 g, 0.8 mmol) of *exo* - 2 - formylperhydrotriquinacene (**35**) was reduced with 0.50 g (13.2 mmol) of lithium aluminum hydride in 50 ml of ether, and the reaction mixture was treated in the usual manner. Vpc purification of the crude product gave 0.13 g (95% yield) of pure *exo*-2-hydroxymethylperhydrotriquinacene (**33x**): IR (neat) 3500–3100, 1090, 1050, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.8 (complex m, 15H), 2.8 (s, 1H; O*H*), 3.41 and 3.50 (AB q, J = 2 Hz, 2H; CH_2OH); ^{13}C NMR ($CDCl_3$) δ_C 31.7 (t), 31.8 (t), 32.0 (t), 32.1 (t), 35.6 (t), 43.6 (d), 44.9 (d), 47.4 (d), 47.6 (d), 54.6 (d), 66.6 (t). The sample showed the same Golay GC–MS behaviors as those of the sample of **33x** obtained above. Found: C, 79.2; H, 11.1. $C_{11}H_{18}O$ requires: C, 79.5; H, 10.7%.

exo - 2 - *Methyl* - endo - 2 - *hydroxyperhydrotriquinacene* (exo - 2 - *methyl* - endo - 2 - *hydroxytricyclo*[5.2.1.$0^{4,10}$]*decane*, **37**). An ether solution of methylmagnesium iodide was prepared from 0.486 g (20 mmol) of magnesium and 2.84 g (20 mmol) of methyl iodide in 5 ml of ether. To the ether solution was added dropwise with efficient stirring at ambient temperature 2.2 g (14.7 mmol) of 2-ketoperhydrotriquinacene (**23**) in a period of 14 min. The reaction was heated under reflux for 1 hr. The reaction mixture was cooled to 0°, and poured onto 20 ml of a 5% ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with three 15 ml portions of ether. The combined organic layer and ether extracts were washed twice with a saturated sodium chloride solution, and dried over anhydrous magnesium chloride. Evaporation of the solvent gave 2.2 g (90% yield) of crude *exo* - 2 - methyl - *endo* - 2 - hydroxyperhydrotriquinacene (**37**), which was purified with preparative vpc to afford a pure sample: m.p. 88–89°; IR (Nujol) 3500, 3100, 1160, 1120, 950 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.29 (s, 3H; CH_3), 1.4–3.0 (complex m, 15H); ^{13}C NMR ($CDCl_3$) δ_C 27.1 (t), 29.0 (q), 31.0 (t), 32.3 (t and t), 40.6 (d), 43.6 (t), 44.9 (d), 52.8 (d), 54.8 (d), 80.9 (s); mass spectrum (*m/e*, rel intensity) 166 (61, M^+), 151 (39), 148 (35), 108 (100), 97 (47), 91 (27), 84 (65), 80 (27), 79 (35), 67 (38). Found: C, 79.8; H, 10.7. $C_{11}H_{18}O$ requires: H, 10.9%.

Hydride transfer reduction-rearrangement. A mixture of 0.10 g of a reactant, 1.0 g of 97% sulfuric acid, and 5 ml of *n*-pentane was stirred vigorously at room temperature for 5 min. The reaction mixture was poured onto 20 g of cracked ice. The organic layer was separated, and the aqueous layer was extracted with three 10 ml portions of *n*-pentane. The combined organic layer and pentane extracts were washed with a saturated sodium bicarbonate solution and water, and dried over anhydrous magnesium sulfate. The solvent was evaporated off, and the residue (33–58% yield) was analyzed on Golay column GC–MS. The results are listed in Table 1.

Acknowledgements—The authors thank Prof. Eiji Ōsawa, Hokkaido University, for helpful discussions. A partial financial support by Grant-in-Aid No. 434025 from Ministry of Education is also gratefully acknowledged.

REFERENCES

[1]M. Farcasiu, K. R. Blanchard, E. M. Engler and P. v. R. Schleyer, *Chem. Lett.* 1189 (1973).

[2a]N. Takaishi, Y. Inamoto and K. Aigami, *Ibid.* 1185 (1973); N. Takaishi, Y. Inamoto, K. Tsuchihashi, K. Yashima and K. Aigami, *J. Org. Chem.* **40**, 2929 (1975); [b]N. Takaishi, Y. Inamoto, K. Aigami and E. Ōsawa, *Ibid.* 1483 (1975); [c]Y. Inamoto, N. Takaishi, Y. Fujikura and K. Aigami, *Chem. Lett.* 631 (1976); Y. Inamoto, K. Aigami, N. Takaishi, Y. Fujikura, K. Tsuchihashi and H. Ikeda, *J. Org. Chem.* **42**, 3833 (1977).

[3]E. Ōsawa, K. Aigami, N. Takaishi, Y. Inamoto, Y. Fujikura, Z. Majerski, P. v. R. Schleyer, E. M. Engler and M. Farcasiu, *J. Am. Chem. Soc.* **99**, 5361 (1977).

[4a]J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper and R. D. Nicholas, *Ibid.* **88**, 4475 (1966); S. H. Liggero, R. Sustman and P. v. R. Schleyer, *Ibid.* **91**, 4571 (1969); [b]K. Mlinaric-Majerski, Z. Majerski and E. Pretsch, *J. Org. Chem.* **41**, 686 (1976).

[5]D. Lenoir, R. E. Hall and P. v. R. Schleyer, *J. Am. Chem. Soc.* **96**, 2138 (1974).

[6]P. v. R. Schleyer and A. P. Wolf, *Ibid.* **92**, 5731 (1970).

[7]N. Takaishi, Y. Inamoto, K. Aigami, Y. Fujikura, E. Ōsawa, M. Kawanisi and T. Katsushima, *J. Org. Chem.* **42**, 2041 (1977).

[8]Y. Inamoto, K. Aigami, Y. Fujikura, N. Takaishi and K. Tsuchihashi, *Ibid.* **44**, 854 (1979).

[9]Synthesis of and preliminary survey on the ring contraction in this compound were reported by K. Aigami, N. Takaishi, Y. Inamoto and Y. Fujikura, *Abstr. 37th Spring Meeting Chem. Soc. Japan*, 1978, Tokyo, p. 747; and by Y. Fujikura, Y. Inamoto, K. Aigami and N. Takaishi, *Ibid.* p. 748.

[10]L. A. Paquette, G. V. Meehan and S. J. Marshall, *J. Am. Chem. Soc.* **91**, 6779 (1969).

[11]A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharman, *Ibid.* **82**, 6370 (1960); J. K. Whitesell and P. D. White, *Synthesis* 602 (1975).

[12]J. K. Crandall and L.-H. Chang, *J. Org. Chem.* **32**, 532 (1967).

[13a]G. W. Wittig and J. J. Hutchison, *Justus Liebigs Ann. Chem.* **741**, 79 (1970); [b]H. C. Brown and W. J. Hammer, *J. Am. Chem. Soc.* **89**, 1524 (1967).

[14]I. Tabushi, K. Fujita and R. Oda, *J. Org. Chem.* **35**, 2376 (1970).

[15a]D. A. Evans, G. L. Carroll and L. K. Truesdale, *Ibid.* **39**, 914 (1974); J. N. Zubric, B. I. Dunber, and H. D. Durst, *Tetrahedron Letters* 71 (1975); [b]R. O. Klaus, H. Tobler and C. Ganter, *Helv. Chim. Acta* **57**, 2517 (1974); [c]I. Ojima and S. Inaba, *Kagaku no Ryoiki* **31**, 38 (1977).

[16]This was also the case with 4 - homobrendan - 2 - one (tricyclo[5.2.1.$0^{3,8}$]decan - 2 - one). See N. Takaishi, Y. Fujikura, Y. Inamoto and K. Aigami, *J. Org. Chem.* **42**, 1737 (1977).

[17]Y. Fujikura, M. Ohsugi, Y. Inamoto, N. Takaishi and K. Aigami, *Ibid.* **43**, 2608 (1978).

[18]J. A. Berson, *Angew. Chem. Int. Ed. Engl.* **7**, 779 (1968).

[19]Y. Fujikura, Y. Inamoto, N. Takaishi and H. Ikeda, *Synth. Commun.* **6**, 199 (1976).

[20]A. Krantz and C. Y. Lin, *Chem. Commun.* 1287 (1971); *J. Am. Chem. Soc.* **95**, 5662 (1973).

[21]However, diethylsilane showed a selectivity originated from steric approach control in the case of the hydride transfer reduction of 3-methyl-3-cholestanyl cation: F. A. Carey and H. S. Tremper, *J. Org. Chem.* **36**, 758 (1971). The phenomenon was also observed for the sulfuric acid - *n* - pentane treatment of *cis*, *exo* - 2,3 - trimethylene - *exo* - 5 - methyl - *endo* - 5 - hydroxynorborane (*exo* - 8 - methyl - *endo* - 8 - hydroxy - *exo* - tricyclo[5.2.1.$0^{2,6}$]decane), which gave predominantly the cor-

responding *endo*-methyltricyclodecane: N. Takaishi, Y. Fujikura and Y. Inamoto, unpublished results.
[22]E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense and P. v. R. Schleyer, *J. Am. Chem. Soc.* **95**, 5769 (1973).
[23]T. J. de Boer and H. J. Backer, *Organic Syntheses*, Collect. Vol. IV, p. 250. Wiley, New York (1963).
[24]S. D. Burke and P. A. Grieco, *Org. Reactions* **26**, 361 (1979).
[25]D. Evans, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.* (*A*) 3113 (1968).