Pathways of the Trifluoromethanesulfonic Acid Catalyzed Rearrangement of *cis*-2,3-Trimethylenebicyclo[2.2.2]octane to 4-Homoisotwistane

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Structures of two major intermediates (unknowns D and E) in the trifluoromethanesulfonic acid catalyzed rearrangement of *cis*-2,3-trimethylenebicyclo[2.2.2]octane (**1**) to 4-homoisotwistane (**6**) were determined to be *endo*-2,8-trimethylenebicyclo[3.3.0]octane (**5**) and 2,4-bishomobrexane (**3**), respectively, by ^{13}C NMR spectrometry and independent syntheses. By-products and other intermediates identified among minor products of the reaction were 2,4-bishomobrendane (**4**), *cis-exo*-6,7-trimethylenebicyclo[3.2.1]octane (**8**), 1,2-trimethylenebicyclo[2.2.2]octane (**10**), and 1,*exo*-2-trimethylene-*cis*-bicyclo[3.3.0]octane (**11**). Time-conversion study on **1** as well as **3**, **4**, and **5** demonstrated that the overall rearrangement pathway was a dual process with the intermediacy of **3** in one route and cations of **10** on the other, both giving **5** and **6** competitively. Postulation of two different cations (**4b** and **4d**) as the key intermediates for each competitive reaction offered the best explanation for the experimental results.

cis-2,3-Trimethylenebicyclo[2.2.2]octane (tricyclo[5.2.2.-$0^{2,6}$]undecane, **1**, Scheme I) has been found to undergo acid-catalyzed multiple step skeletal rearrangement via 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **6**) as a stable intermediate.[1] The overall reaction is thermodynamically controlled, giving methyladamantanes as ultimate products. However, it is possible by the use of Brønsted acids, which are relatively mild catalysts, to bring the rearrangement to a halt at the stage of 4-homoisotwistane.[1b,c] The effect is undoubtedly the consequence of the kinetic control of the reaction associated with a relatively high rate of the rearrangement of the precursor **1**, as compared to sluggish isomerization of the intermediate **6**, under Brønsted acid catalysis.[1c]

Several intermediates have been recognized during the rearrangement of **1** to **6**.[1,2] Although minor intermediates were found coincidently identical with some of those encountered in the rearrangement of *cis-exo*- and *cis-endo*-2,3-tetramethylenenorbornane,[1d] structures of two key intermediates (unknowns D and E) have been left undetermined. We report here structure determination of these compounds by ^{13}C NMR and independent syntheses.[2] Isomerization reactions of these key intermediates were also studied. The most probable pathways of the rearrangements were constructed by reference to these experimental results.

Results

Rearrangement reaction of the precursor *cis*-2,3-trimethylenebicyclo[2.2.2]octane (**1**) as well as intermediates was

Scheme I

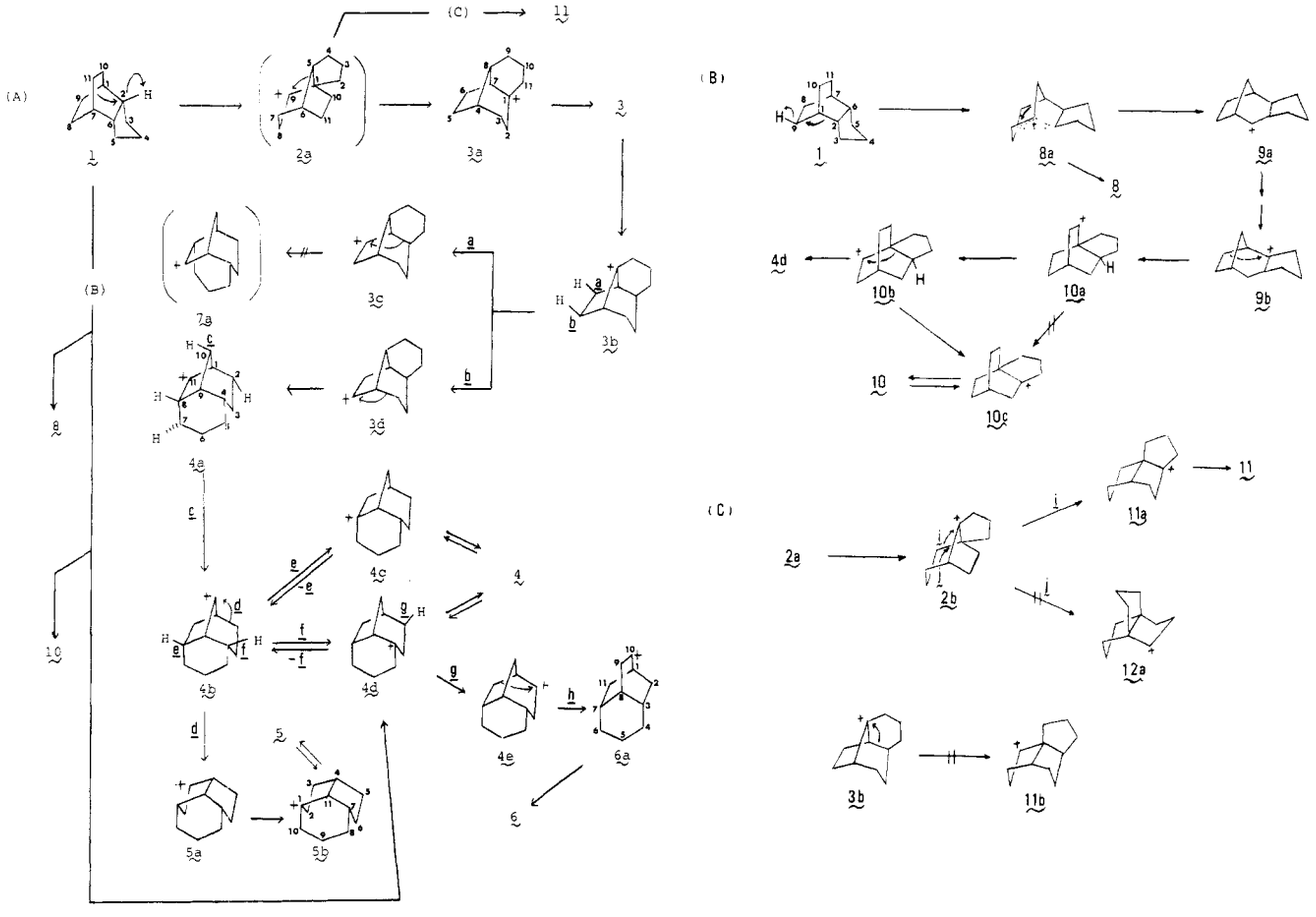


Table I. Rearrangement of Tricycloundecanes[a]

Run	Reactant	Reaction time, min	Product,[b] %[c,d] 11	10	8	5[e]	6	1	4	3[f]
1	1[g]	5	1.7	0.3	1.1	12.1	11.9	37.8	1.4	32.0
2		10	2.0	0.5	1.0	13.4	14.9	33.2	1.3	29.1
3		15	2.2	0.6	1.0	15.9	17.5	31.5	1.3	27.1
4		30	2.4	0.7	1.0	19.4	21.0	24.6	1.2	25.6
5		60	2.8	1.0	1.0	21.5	29.2	17.5	1.2	20.2
6		120	3.2	1.4	0.9	19.8	39.4	11.9	1.1	15.5
7		240	3.8	1.2	0.8	15.1	59.3	6.0	1.1	6.8
11	3[g]	5	0.7	0.1		17.1	3.0	8.1		67.9
12		10	0.7	0.2		21.2	4.9	10.7	1.1	58.7
13		30	1.2	0.5		29.5	12.6	11.9	1.5	38.9
14		60	1.5	0.8		31.3	21.3	12.6	1.9	25.9
15		120	1.8	0.9		28.1	33.8	11.8	2.1	16.0
16		240	2.1	0.8		23.5	46.0	10.4	1.2	9.7
21	5[g]	5		0.6		65.8	23.7[h]		3.5	3.9
22		10		0.8		51.2	38.0[h]		2.6	4.4
23		30		1.3		30.8	57.5[h]		2.0	4.8
24		60		1.8		20.5	68.1[h]		1.7	3.9
25		120		2.1		11.9	79.2		1.3	2.7
26		240		2.5		6.3	84.6		1.0	2.1
31	4[g]	5		0.9		31.8	56.6		3.6	0.5
32		i0		1.8		30.0	58.3		2.3	0.9
33		30		1.9		24.4	65.9		1.7	1.6
34		60		2.4		18.2	72.9		1.4	1.9
35		120		2.8		12.8	78.7		1.2	1.7
36		180		3.2		9.1	82.4		1.2	1.5
37		240		3.5		9.1	82.2		1.1	1.4
41	4[i]	5		0.4		10.6	15.3		71.1	
42		10		0.4		14.8	21.3		60.5	
43		30		0.3		22.4	35.0		38.5	
44		60		0.4		27.3	44.5		22.5	0.7
45		120		1.0		29.4	52.2		10.4	1.0
46		180		1.1		30.0	55.6		6.2	1.2
47		240		1.1		28.7	58.4		4.4	1.3

[a] 100 mg (0.67 mmol) of reactant and 100 mg (0.67 mmol) or 50 mg (0.33 mmol) of CF_3SO_3H in 5 mL of CH_2Cl_2 at reflux. [b] Arranged in the increasing order of retention time. [c] Calculated from VPC peak areas. Combined yields of the products are almost quantitative. [d] Balance consists of the combined areas of four to five unidentified peaks. [e] Unknown D. [f] Unknown E. [g] With 100 mg (0.67 mmol) of the catalyst. [h] Mass spectrum of this peak was a little different from that of pure **6**, indicating contamination by some compound(s). [i] With 50 mg (0.33 mmol) of the catalyst.

studied under the catalysis of 1 or 0.5 molar equiv of trifluoromethanesulfonic acid in refluxing methylene chloride as solvent.[1b,c] Analysis and identification of the intermediates were made on Golay column GC–MS.[1b-d] No significant side reaction was evident in the rearrangement, and the combined yields of the intermediates and products were almost quantitative. Time–conversion relationships of these reactions are listed in Table I.

Structure determination of the two major intermediates (unknowns D and E) is described in the following paragraphs. Other intermediates detected and identified among minor products of the reaction were 2,4-bishomobrendane (tricyclo[6.2.1.$0^{4,9}$]undecane, **4**),[3] *cis-exo*-6,7-trimethylenebicyclo[3.2.1]octane (tricyclo[5.3.1.$0^{2,6}$]undecane, **8**),[1b-d] 1,2-trimethylenebicyclo[2.2.2]octane (tricyclo[5.2.2.$0^{1,5}$]undecane, **10**),[1d] and 1,*exo*-2-trimethylene-*cis*-bicyclo[3.3.0]octane (tricyclo[6.3.0.$0^{1,5}$]undecane, **11**)[1d] (Table I, Scheme I).

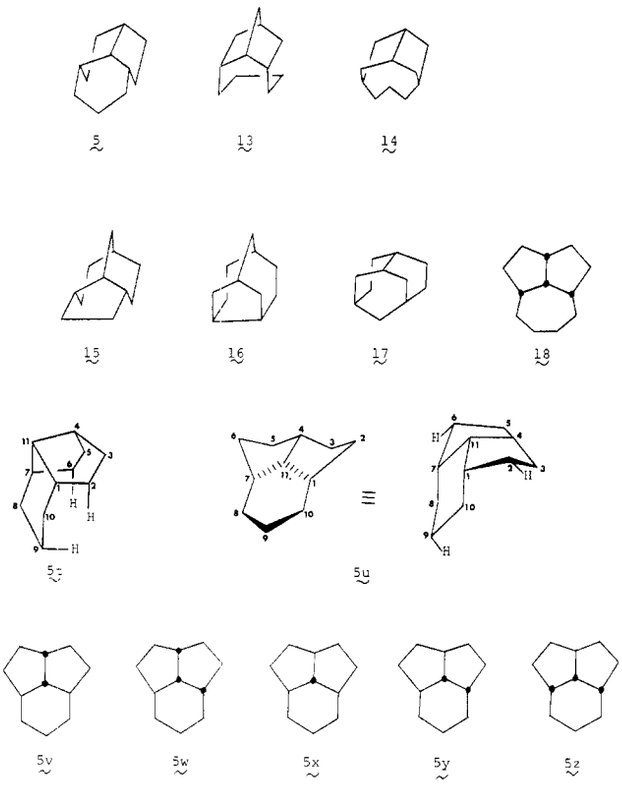
Structure of Unknown D (5). Unknown D, 4-homoisotwistane (**6**), and unreacted **1** are eluted together in one fraction in the preparative VPC.[1b] This fraction (unknown D/**6**/**1** = 33:43:24) was isolated from the reaction mixture of run 5. The total proton-decoupled ^{13}C NMR spectrum of the fraction showed 21 signals. Fourteen signals corresponding to those of **1** and **6** (six signals for **1**[4] and eight for **6**[1a,b]) were subtracted from these 21 to leave seven (one single-intensity triplet, three double-intensity triplets, two single-intensity doublets, and one double-intensity doublet), which were to be assigned to unknown D. This spectrum corresponds to a molecule of C_s symmetry with one methylene and two methine carbon atoms on the σ plane.

Among all the possible 69 reasonably stable tricycloundecanes,[5] six isomers (**5** and **13–17**, Chart I)[6] satisfy the above molecular symmetry. However, the abnormally high-field (16.7 ppm) single-intensity methylene carbon signal of unknown D is explained only with the *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane structure (**5**). The molecule **5** has the same structural feature (cf. **5t**) as **6**,[1a,b] 4-homobrendane (tricyclo[5.2.1.$0^{3,8}$]decane),[3] **4**,[3] and *endo*-3-hydroxy-9-methyl-9-azabicyclo[3.3.1]nonane[7] do, in which large upfield shifts of chair cyclohexane carbon signals are attributed to steric compression exerted by *endo*-hydrogens on two β-axial-methylene substituents.

The above structure assignment to unknown D is supported indirectly by mass spectrometry. Unknown D and *endo*-2,8-tetramethylene-*cis*-bicyclo[3.3.0]octane (**18**),[8] a higher homologue of **5**, exhibited a fairly similar spectral pattern in the region $m/e \leq 108$. This pattern is considered to originate in the *cis*-perhydropentalene ring commonly present in both compounds.

Compound **5** is known.[8,9] An authentic specimen of **5** was prepared according to the method of Rappoport.[9] Its GC–MS behavior and ^{13}C NMR spectrum were identical with those of unknown D. Access to a large size sample of **5** was made after the method of Jacobson[10] by intramolecular insertion

Chart I



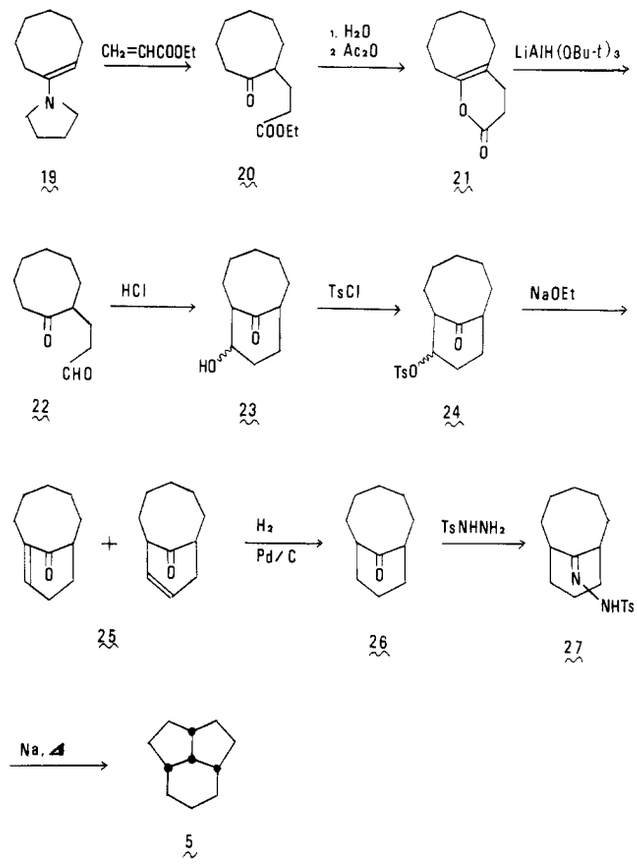
of carbene generated from bicyclo[5.3.1]undecan-11-one tosylhydrazone (**27**, Scheme II). The corresponding ketone (**26**) was synthesized from cyclooctanone enamine (**19**)[11] via the route shown in Scheme II. Synthesis of the keto ester **20** through the hydroxybicycloundecanone **23** followed those of the corresponding cyclohexanone derivatives.[12] The tosylate **24** was liquid, whereas the isomerically pure *endo*-tosylate was a solid.[13] This indicates **23** and **24** to be mixtures of configurational isomers, as was the case for 2-hydroxybicyclo[3.3.1]-nonan-9-one.[12b] Treatment[13b] of the tosylate with sodium ethoxide gave a mixture (97:3) of bicycloundecenone **25**, the IR and ^{1}H NMR spectra of which agreed with those of a 98:2 mixture of bicyclo[5.3.1]undec-1(10)- and -8-en-11-one.[13b] The mixture was hydrogenated over palladium on charcoal catalyst to the ketone **26**.[14] Sodium salt of the tosylhydrazone **27** was pyrolyzed[10] to afford **5**.

Conformation of *endo*-2,8-Trimethylenebicyclo[3.-3.0]octane (5). The 16.7-ppm signal of **5** unequivocally determines its conformation to be **5t**, where the *cis*-perhydropentalene ring (C-1 through C-7 and C-11) is flapped toward the endo side to accommodate the chair cyclohexane (C-11, C-7 through C-10, and C-1) with two β-axial-methylene substituents (C-2 and C-6). The alternative conformation (**5u**) with the chair cyclohexane, but with the perhydropentalene puckered toward the exo side, holds equatorial C-2 and C-6.

The same consideration helps exclude all the other possible configurational isomers (**5v–z**) of **5**. None of them bears the di-β-axially substituted cyclohexane partial structure. Exclusion of **5v–z** is also consistent with the kinetic results that unknown D persisted throughout the rearrangement reaction. Isomers **5v–z** are considerably strained compared to **5t**[15] and should disappear during long reaction.

Structure of Unknown E (3). Unknown E constitutes a single fraction in the preparative VPC.[1b] Crude unknown E was isolated from the reaction mixture of run 2. Subsequent purification on VPC afforded a pure (92%) sample, which solidified on standing at ambient temperature. Its ^{13}C NMR spectrum comprised seven triplets and four doublets. The

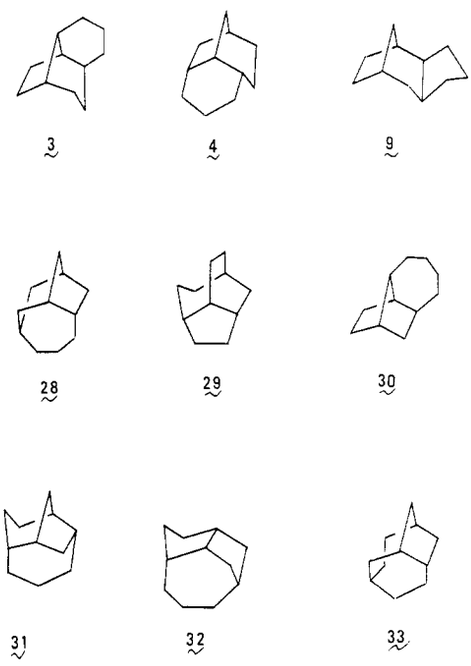
Scheme II



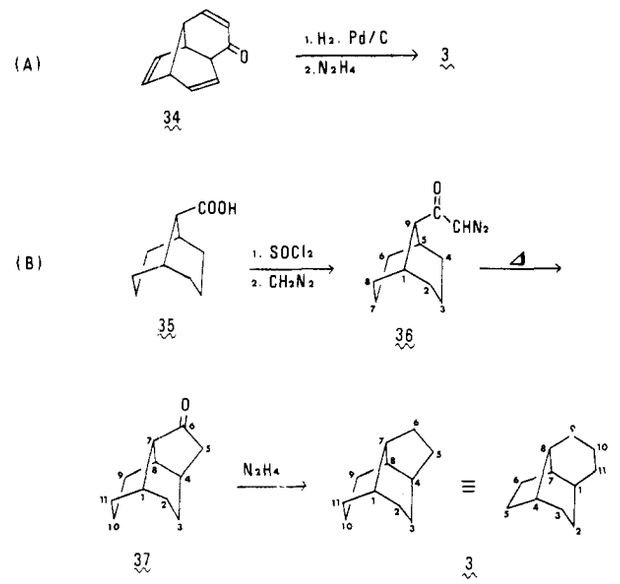
molecule was thus shown to be asymmetric, yet contain no quaternary carbon atom. Nine structures (**3, 4, 9,** and **28–33,** Chart II)[6] correspond to the ^{13}C NMR spectrum.

2,4-Bishomobrendane (**4**),[3] *cis-exo*-2,3-trimethylenebicyclo[3.2.1]octane (*exo*-tricyclo[6.2.1.0^{2,6}]undecane, **9**),[16] 4-homoprotoadamantane (tricyclo[5.3.1.0^{3,9}]undecane, **28**),[17] and *endo*-2,7-ethanobicyclo[3.2.2]nonane (tricyclo[5.3.-1.0^{4,8}]undecane, **29**)[18] are known. The isomers **4, 9,** and **28** had physical and spectral properties[16,17] different from those of unknown E, while **29** had a different melting point.[18] Selection

Chart II



Scheme III



among the remaining five structures (3 and 30–33) was made with reference to the kinetic result that unknown E was formed immediately and first from the precursor 1 (Table I, runs 1–7). This suggests 1 and unknown E to be connected through a relatively short reaction pathway. 2,4-Bishomobrexane (tricyclo[5.4.0.0^{4,8}]undecane, 3) can be derived from 1 only by two 1,2-alkyl shifts (cf. Scheme I, A), whereas more complicated transformations are required to reach the other four structures.

Tricyclo[5.4.0.0^{4,8}]undeca-2,5,9-trien-11-one (34) was prepared by the method of Groves.[19] Hydrogenation and subsequent Wolff–Kishner reduction of 34 (Scheme III, A) gave an authentic specimen of 3. GC–MS measurements and IR and NMR spectrometries established the identity of unknown E and 3. A large quantity of 3 was more conveniently prepared via the intramolecular carbene insertion reaction[20] of 9-diazoacetylbicyclo[3.3.1]nonane (36, Scheme III, B). The diazoketone 36 was prepared from bicyclo[3.3.1]nonane-9-carboxylic acid (35)[21] by the usual method.[20] The molecular symmetry of 36 guarantees that insertion into any one of C-2, C-4, C-6, and C-8 gives 37. Wolff–Kishner reduction of 37 led to the hydrocarbon 3.

Rearrangement Reaction of *cis*-2,3-Trimethylenebicyclo[2.2.2]octane (1). A plot of the conversion data for 1 (runs 1–7, Table I) vs. time revealed that two major intermediates 3 and 5 arose successively. This may suggest the reaction pathway to be consecutive: from 1 to 3 to 5 to 6. But this is not all. Extrapolation of the plot to zero time disclosed that both of the initial rates for the formation of 5 and 6 were not zero. The above simple consecutive scheme contradicts this evidence.

The discrepancy can be solved by assuming the two alternative schemes: (i) some additional direct route (bypass) is present from 1 to 5 and 6; or (ii) the above "bypass" is in fact the "main" route, and 3 arises in a dead end branching from this main route. Whichever possibility may be considered, at least one competitive step should be included that gives 5 and 6 simultaneously without intermediacy of any stable intermediate between the precursor 1 and the products 5 and 6.

All the minor intermediates (4, 8, 10, and 11) were formed in the rearrangement of 1. Particularly, 8 was detected only in this reaction.

Rearrangement Reactions of Intermediates. Rearrangements of the major intermediates 3 and 5, as well as a minor intermediate 4, were also studied. In view of the interconversion among bicyclo[3.3.0]-, -[3.2.1]-, and -[2.2.2]octane,[22] 4 could intervene in the transformation between 5 and 6. Results are shown in runs 11–47, Table I.

(i) 2,4-Bishomobrexane (3). This intermediate isomerized a little slower than the precursor 1 did. Major products were 5 and 6, similarly as those for 1. All the minor products except 8 were formed. Formation of some amount of 1 indicated a partial return to the precursor. Time–conversion plots showed that both of the initial rates for the formation of 5 and 6 were not zero also for this reactant, indicating the presence of a competitive pathway to 5 and 6.

It is to be noted here that the ratio of the product 5 to 6 in this competitive reaction of 3 is distinctively different from that in the reaction of 1. The ratio 5/6 before 10 min of reaction, where secondary conversion of the products 5 and 6 would have occured to a relatively small extent, is ca. 1:1 for 1 (runs 1–2) and ca. 5:1 for 3 (runs 11–12). An important conclusion from these results is that the "dead end" scheme for the overall rearrangement of 1 (case ii above) can be excluded unambiguously. Thus the "bypass" scheme is left as the only possibility.

(ii) *endo*-2,8-Trimethylenebicyclo[3.3.0]octane (5). This intermediate isomerized at about the same rate as that of 3. The major product was only 6. A little return to 3 was also observed. Minor products 4 and 10 were formed, but no 8 and 11 at all. Further return to 1 via 3 was not detected.

(iii) 2,4-Bishomobrendane (4). Only 5 and 6 were obtained as major products, in accordance with the expected intermediacy of 4 between 5 and 6. It is estimated from the ratio 5/6 in the initial reactions (runs 41–43) that the ratio of the rates for the formation of 5 and 6 from 4 is 2:3. It was also found that the isomerization rate of this intermediate was quite high, above 96% having vanished in 5 min (run 31). These results well account for the fact that 6 is the only major product from 5, and that 4 has been detected always only in small amounts in a variety of tricycloundecane rearrangements.[3,17]

Discussion

The qualitative kinetic behavior of the precursor and intermediates as described above indicates the presence of a fairly complicated pathway for the overall rearrangement of 1. The precursor 1 isomerizes to the first major intermediate 3. There exists competitively with this main route a bypass which affords the second major intermediate 5 and product 6. The first intermediate 3 in the main rearrangement route then isomerizes into 5 and 6 again in a competitive fashion. Possible intermediate cationic species involved in this kinetic scheme are discussed below with the aid of considerations on the stability of carbocations and products as well as the stereoelectronic factors in intramolecular alkyl shifts and hydride transfers.[5,17,23,24] Roles of minor products are also inferred from these mechanistic considerations.

The Main Route. Isomerization of the precursor *cis*-2,3-trimethylenebicyclo[2.2.2]octane (1) to 2,4-bishomobrexane (3) is best explained with the intermediacy of 1,*exo*-4-trimethylene-*cis*-bicyclo[3.3.0]octane (2, Scheme I, A). Similar transformations have also been suggested for trimethylenenorbornane[23] and tetramethylenenorborane[1d] as the first step of the rearrangement. Preferable ionization of C-2 in 1 as compared to that of the other bridgehead (C-1), as presumed above, seems to be rationalized by considering the stability difference in the corresponding carbocations of bicyclic structure.[24,25] In addition, ionization of C-1, although it may occur to a small extent, does not lead to any of the observed products in the present rearrangement.[26]

The cationic center in 2a is so situated that C-5 may be immediately shifted to this center to give the 3-1-yl cation 3a. However, no effective alkyl shift is possible in 3a which leads to further isomerization of 3.[27] The cation 3a, therefore, should

abstract hydride intermolecularly to afford the observed intermediate **3**.

Ionization of C-8 in **3** to give the cation **3b**, similarly as that of C-1 to afford **3a**, seems to be the process that is most likely to occur,[24,25] but here again none of the two possible alkyl shifts, except for a methyl extrusion, in **3b** is connected to the progress of the rearrangement pathway. The difficulty can be overcome by presuming the intramolecular 1,3 transfer of *exo*-5-H (path b) in **3b**, leading to the cation **3d**. The transfer of *exo*-6-H to give **3c** (path a) might be as much feasible as that of *exo*-5-H. However, this process would be a dead end, because the only possible alkyl shift in **3c** produces a considerably strained structure **7**.[5] Shift of C-3 in **3d** affords 2,4-bishomobrendan-11-yl cation (**4a**).

The only probable hydride transfer in **4a** would be that of *syn*-10-H (path c),[28] giving 4-10-yl cation **4b**. In **4b** three intramolecular processes seem to be favored: shift of C-2 leading to 5-3-yl cation (path d) and transfers of 4-H (path f) and 8-H (path e) giving 4-4-yl and 4-8-yl cations, respectively. Transfer of *exo*-2-H may be stereoelectronically equally favorable, but thermodynamically less favored because the process affords a less stable[23,24] secondary cation 4-2-yl (**4e**).

The cation **4e** would most probably be postulated to explain the formation of the 4-homoisotwistane structure (**6**). Since direct formation of **4e** from **4b** is improbable for the reasons stated above, the source of **4e** should be looked for in **4d**. This process (path g), however, would occur rather sluggishly, since it is generation of a secondary cation at the sacrifice of a tertiary one.[23,24]

Rearrangement of Intermediates. Postulation of **4b** can be fully consistent with the kinetics of the rearrangement of 2,4-bishomobrexane (**3**, runs 11–16). Firstly, competitive formation of **5** and **6** results from the species **4b** reacting along path d on one side and paths e and f on the other. Secondly, both the initial rates for the formation of **5** and **6** should not assume zero in this scheme, since only reactive cationic species (**4a–e**) are involved between the reactant **3** and the products **5** and **6**. Thirdly, predominant formation of **5** over **6** (5:1) is explained by postulating a slow process in the route leading to **6**, and this must be slower than any of the steps to **5**. The slow process would most probably be path g. The alkyl shift between the two secondary cations (path d), formation of the tertiary cation **4b**, and reduction of **5b** to **5** (reversal of a bridgehead ionization) would presumably be faster than path g.

Results of the rearrangement of 2,4-bishomobrendane (**4**, runs 31–47) also fit well to the scheme. The hydrocarbon ionizes[24] to 4-8-yl (**4c**) and 4-4-yl (**4d**) cations, which gives **5** and **6** competitively. As path g is a slow process, so should be the formation of **4b** either from **4c** (path −e) or from **4d** (path −f).[31] This inference would account for the formation of a similar amount of **5** and **6** (2:3) from **4**.

A larger amount of **3** was produced in the reaction of *endo*-2,8-trimethylenebicyclo[3.3.0]octane (**5**) than in that of **4**. If the scheme presented here is correct, this fact suggests that alkyl shifts would be faster than intramolecular hydride transfers, at least within the cations of **3**, **4**, **5**, and **6**.[32] Although "migratory aptitude" of various substituents in pinacol rearrangements was widely studied, similar comparison of the rates for 1,2-alkyl shifts and 1,3-hydride transfers does not seem to have been made so far. Estimation of such relative rates, by means of, e.g., solvolysis and related techniques, would certainly contribute to the clarification of the mechanism of acid-catalyzed multiple-step skeletal rearrangement of polycycloalkanes.

The Bypass. The kinetic results require any bypass scheme to satisfy the following three conditions: (i) the bypass should branch from the main route before **3** arises; (ii) no stable intermediate should be involved; (iii) the bypass should give **5** and **6** competitively, and the ratio **5**:**6** should be smaller in the bypass than in the main route. These conditions are fully met by the route shown in Scheme I, B.

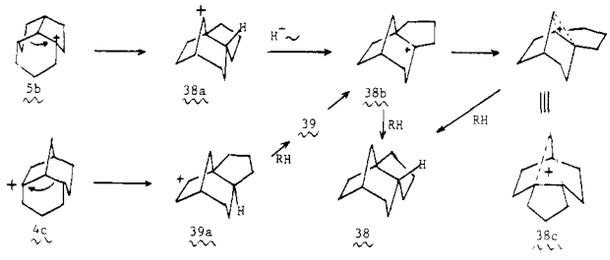
Ionization of a secondary carbon atom (C-9) in **1** might appear unfavorable[23,24] compared to that of the bridgehead C-2 (the main route), but this disadvantage could be overcome partly by the formation of the bridged[16,33] ion **8a**. In addition, thermodynamic stability[5] predicts the favorable formation of **8a** over that of **2a**. Moreover, the ionization of C-9 is strongly supported by the detection of by-product **8** only in the reaction of **1**.

The route from **8a** to 2,4-bishomobrendan-4-yl cation (**4d**) with the intermediacy of *cis-exo*-2,3-trimethylenebicyclo[3.2.1]octyl cations (**9a** and **9b**) and 1,2-trimethylenebicyclo[2.2.2]octyl cations (**10a** and **10b**) was demonstrated in the hydride transfer reduction–rearrangement of 1-*exo*-8-yl alcohol to **6**.[16] No hydrocarbon intermediate is involved in this bypass scheme (condition ii). The cation **4d** is estimated[34] to give **5** and **6** competitively in a 2:3 ratio (condition iii).

Conversion data for run 1, together with the assumption of no secondary isomerization of **3** formed, indicate that ~60% of **1** reacted is distributed between 30% of **3** in the main route and 30% (= 60 − 30) products in the bypass. Thus the main route and the bypass are of similar "width." Then combination of the two, that is, the overall rearrangement of **1**, should give **5** and **6** in a ratio 7:4 (= [5 + 2]:[1 + 3]). The figure is in fair agreement with the experimental value (1:1).

Minor Products. Formation of **8** and **10** are most reasonably explained with the cations **8a** and **10c** involved in the bypass (Scheme I, B). Postulation of the cation **2a** as the precursor of **11** (Scheme I, C, path i) is consistent with the kinetic results (runs 1–7 and 11–16). Path j leading to a secondary cation **12a** of [3.3.3]propellane[1d] would be stereoelectronically as favorable as, but thermodynamically less favorable than, path i, and this seems to account for the absence of **12** in the present reaction products. A seeming possibility for the formation of **11** from **3b** (Scheme I, C) is similarly improbable because of the generation of a secondary cation **11b**.

Unidentified Intermediates. Examination of the stability of tricycloundecane skeletons[5] suggests some plausible structures for the unidentified intermediates in the present rearrangement (Table I, footnote d). One is the proposed intermediate **2**, which has never been prepared before, but is calculated to be as stable as **1** and **3**. Another is fairly stable 1,*endo*-2-trimethylenebicyclo[3.2.1]octane (tricyclo[6.2.-1.0^{1,5}]undecane, **38**), which may be formed from **5b** or **4c** as shown below and capable of existence as a symmetrical bicyclooctyl cation (**38c**).[33b,35] The stability of these hydrocarbons provides hope of trapping them in the rearrangement, so long as they are formed in high concentrations by appropriate choice in precursors and experimental conditions.



Experimental Section

All melting points are uncorrected. Measurements of IR, ^{1}H and ^{13}C NMR, and mass spectra as well as conventional VPC and Golay column GC–MS measurements were made on the same instruments as in the previous works.[1,3]

2,4-Bishomobrexane (3) by Reduction of Tricyclo[5.4.0.0^{4,8}]-undeca-2,5,9-trien-11-one (34). The tricycloundecatrienone **34** was

prepared according to the method of Groves.[19] A mixture of 0.16 g (0.001 mol) of **34**, 0.01 g of palladium (5%) on charcoal catalyst, and 20 mL of ether was shaken with hydrogen under atmospheric pressure at ambient temperature for 2 h. The catalyst was filtered off, and the filtrate was concentrated. The residue was mixed with 1.0 mL of 100% hydrazine hydrate, 0.5 g of potassium hydroxide, and 10 mL of diethylene glycol. The mixture was heated under reflux for 3 h. Water and excess hydrazine hydrate were distilled off and heating was continued under reflux (210 °C) for an additional 5 h. The mixture was poured onto 50 mL of cold water and extracted with five 10-mL portions of petroleum ether. Combined extracts were washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated. The residue was purified on preparative VPC to give 0.11 g (73% yield) of a pure sample of **3**: mp 75–76 °C (sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 20.9 (t), 23.9 (t), 25.1 (t), 28.9 (t), 30.1 (t), 31.0 (t), 33.1 (t), 34.6 (d), 39.5 (d), 40.2 (d), 41.0 (d); mass spectrum *m/e* (rel intensity) 150 (100, M^+), 122 (79), 121 (53), 94 (30), 93 (35), 81 (33), 80 (40), 79 (41), 67 (32), 41 (23).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.11; H, 11.98.

2,4-Bishomobrexane (3) by Intramolecular Carbene Insertion Reaction. (i) 9-Diazoacetylbicyclo[3.3.1]nonane (36). A mixture of 4.13 g (0.023 mol) of bicyclo[3.3.1]nonane-9-carboxylic acid (**35**)[21] and 10 mL of thionyl chloride was refluxed for 1 h. Excess thionyl chloride was distilled off azeotropically with benzene, and the residue was fractionally distilled in vacuo to give 4.1 g (95% yield) of 9-chlorocarbonylbicyclo[3.3.1]nonane: bp 108–110 °C (4 mm); IR (neat) 1800, 1450, 1050, 1010, 940, 900, 740 cm^{-1}.

The acyl chloride was dissolved in 40 mL of ether, and a solution of 0.1 mol of diazomethane in 40 mL of ether[36] was added dropwise below 10 °C for 1 h. The reaction was stirred at ambient temperature for an additional 1 h. Evaporation of ether gave 4.18 g (99% yield) of yellow crystalline crude diazoketone **36**: IR (Nujol) 3080, 2100, 1715, 1640, 1020, 970, 940, 900 cm^{-1}.

(ii) Tricyclo[5.4.0.0^{4,8}]undecan-6-one (37). In a high dilution apparatus,[20] a mixture of 7 g (0.044 mol) of anhydrous cupric sulfate and 500 mL of toluene was kept under reflux with vigorous stirring. A solution of the diazoketone **36** in 900 mL of toluene was added dropwise to the above mixture in a period of 6 h. The reaction was stirred for an additional 6 h. The reaction mixture was filtered, and the filtrate was evaporated. The residue was purified by chromatography on alumina eluted with benzene to give 2.81 g (74% yield based on the acyl chloride) of 2,4-bishomobrexan-6-one **37**: mp 91–92 °C (sealed tube); IR (Nujol) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3–2.6 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 19.7 (t), 23.8 (t), 24.2 (t), 28.0 (t), 31.9 (t and d), 36.6 (d), 37.8 (d), 46.8 (t), 51.7 (d), 221.8 (s); mass spectrum *m/e* (rel intensity) 164 (100, M^+), 121 (28), 120 (84), 95 (27), 94 (31), 93 (31), 81 (35), 80 (34), 79 (41), 67 (30).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.84; O, 9.74. Found: C, 80.23; H, 9.95.

(iii) 2,4-Bishomobrexane (3). The ketone **37** (2.2 g, 0.013 mol) was reduced in the usual manner by refluxing with 6.2 g (0.11 mol) of potassium hydroxide and 6.7 mL (0.14 mol) of 100% hydrazine hydrate in 70 mL of diethylene glycol. Extraction of the reaction mixture with *n*-hexane after dilution with water and evaporation of the solvent yielded 1.66 g (83% yield) of crude **3**. Purification by sublimation under slightly diminished pressure gave a pure sample: mp 75–76 °C (sealed tube). The melting point was not depressed on admixture with the authentic specimen prepared above. Spectral properties were also the same.

***endo*-2,8-Trimethylenebicyclo[3.3.0]octane (5).** Cyclooctanone pyrrolidine enamine (**19**)[11] was treated similarly as described for the cyclohexanone derivatives[12,13] to afford 2-ethoxycarbonylethylcyclooctanone (**20**), 9-oxabicyclo[6.4.0]dodec-1(8)-en-10-one (**21**), 2-formylethylcyclooctanone (**22**), 8-hydroxybicyclo[5.3.1]undecan-11-one (**23**), the tosylate (**24**) of **23**, and a mixture of bicyclo[5.3.1]-undec-1(10)- and -8-en-11-one (**25**).

The keto ester **20** (obtained in 60% yield): bp 124–125 °C (0.4 mm). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80; O, 21.21. Found: C, 69.23; H, 9.54.

The enol lactone **21** (80% yield): bp 110–111 °C (0.4 mm); IR (neat) 2920, 2860, 1760, 1695, 1140, 1110, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.4–2.8 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 24.0 (t), 26.2 (t), 26.5 (t), 28.6 (t), 28.9 (t, t, and t), 30.0 (t), 111.4 (s), 147.9 (s) 169.6 (s); mass spectrum *m/e* (rel intensity) 180 (84, M^+), 152 (100), 125 (46), 124 (36), 109 (65), 96 (39), 95 (48), 84 (38), 81 (41), 67 (52), 55 (46), 41 (39). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; O, 17.75. Found: C, 72.99; H, 9.18.

Golay GC–MS of this sample gave two peaks in 92:8 ratio. The minor peak may most probably be 9-oxabicyclo[6.4.0]dodec-7-en-10-one.

The keto aldehyde **22** (90% yield): bp 105–110 °C (0.5 mm); IR (neat) 2920, 2850, 2710, 1720, 1690, 1460, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.8 (complex m, 17 H), 9.70 (s, 1H, CHO); mass spectrum *m/e* (rel intensity) 182 (23, M^+), 126 (28), 121 (28), 98 (100), 84 (44), 83 (29), 69 (38), 67 (35), 55 (74), 41 (52). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96; O, 17.56. Found: C, 72.48; H, 9.66.

The hydroxybicycloundecanone **23** (32% yield): bp 140–148 °C (0.9 mm); IR (neat) 3400 (br), 2930, 2860, 1690, 1470, 1440, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–2.8 (complex m, 16 H), 3.03 (s, 1 H, OH), 4.20 (m, 1 H, CHOH); mass spectrum *m/e* (rel intensity) 182 (28, M^+), 98 (77), 95 (42), 83 (42), 81 (59), 79 (38), 68 (45) 67 (65), 55 (84), 41 (100), 39 (44). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96; O, 17.56. Found: C, 72.29; H, 10.13.

The tosylate **24** (79% yield): glassy solid; IR (neat) 2920, 2860, 1690, 1590, 1350, 1160, 1080, 890 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; O, 19.02; S, 9.53. Found: C, 64.10; H, 7.18; S, 9.3.

The bicycloundecenone **25** (74% yield): bp 82–84 °C (1 mm); IR (neat) 3020, 2920, 2840, 1690, 1450, 1370, 1130, 960, 950, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–3.1 (complex m, 15 H), 6.15 (s, i H, C=CH); mass spectrum *m/e* (rel intensity) 164 (88, M^+), 136 (61), 121 (58), 95 (56), 94 (61), 93 (93), 81 (56), 80 (100), 79 (93), 67 (84), 53 (93), 41 (82). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83; O, 9.74. Found: C, 80.76; H, 9.61.

The sample showed two peaks (97:3 area ratio) on Golay column GC–MS.

(i) Bicyclo[5.3.1]undecan-11-one (26). The bicycloundecenone **25** (4.0 g, 0.024 mol) was mixed with 0.1 g of palladium on charcoal catalyst and 40 mL of methanol, and hydrogenated under a pressure of 40 kg/cm^2 at ambient temperature for 5 h. The catalyst was filtered off, and the filtrate was concentrated. The residue was fractionally distilled to give 3.2 g (79% yield) of **26**: bp 75–78 °C (0.6 mm) [lit.[14a] bp 90–90.5 °C (1.5 mm)]; IR (neat) 2920, 2850, 1690, 1470, 1440, 1350, 1260, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–2.8 (complex m); mass spectrum *m/e* (rel intensity) 166 (34, M^+), 111 (73), 98 (100), 95 (35), 82 (28), 81 (49), 68 (30), 67 (69), 55 (62), 54 (45), 41 (78) [lit.[14b] *m/e* (rel intensity) 166 (40), 111 (87), 98 (100), 81 (30), 67 (37), 55 (46), 41 (41)].

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92; O, 9.63. Found: C, 79.51; H, 10.88.

(ii) Bicyclo[5.3.1]undecan-11-one Tosylhydrazone (27). A sample (2.8 g, 0.017 mol) of **26** obtained above was mixed with 4.48 g (0.024 mol) of *p*-toluenesulfonylhydrazine, 0.7 mL of 35% hydrochloric acid, and 100 mL of 95% ethanol. The reaction was heated under reflux for 3 h and then allowed to stand overnight at ambient temperature. The mixture was concentrated to one-third of the original volume, and set aside for crystallization. The precipitates were filtered and recrystallized from ethanol to give 4.5 g (89% yield) of the tosylhydrazone **27**: mp 189–190 °C.

Anal. Calcd for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.84; N, 8.38; O, 9.57; S, 9.57. Found: C, 64.78; H, 7.59; N, 8.2; S, 9.2.

(iii) *endo*-2,8-Trimethylenebicyclo[3.3.0]octane (5). Sodium metal (0.9 g, 0.039 g atom) was dissolved in 36 g of molten acetamide at 90–100 °C. The tosylhydrazone **27** (3 g, 0.009 mol) was added in small portions to the above mixture, and the reaction temperature was gradually raised to 175 °C over a period of 30 min. Evolution of nitrogen started at around 130 °C. The reaction was kept at 175 °C for 5 min, and then cooled to 90 °C in 20 min. Water (30 mL) was added dropwise to the reaction in 10 min. After being cooled to ambient temperature, the mixture was extracted with three 10-mL portions of *n*-pentane. Combined pentane extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated. The residue (1.15 g, 86% yield) gave on preparative VPC two fractions (the later eluted peak was accompanied by a shoulder on the shorter retention time side). The earlier eluted fraction (35%) was separated to give **5**: mp 49–50 °C (sealed tube); IR (neat) 2920, 2860, 1470, 1450, 1440, 1360, 1340, 890, 870, 850, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 16.7 (t, 1), 27.7 (t, 2), 33.2 (t, 2), 35.7 (t, 2), 39.0 (d, 2), 44.0 (d, 1), 44.2 (d, 1); mass spectrum *m/e* (rel intensity) 150 (34, M^+), 122 (100), 121 (49), 108 (10), 107 (12), 95 (9), 94 (24), 93 (41), 81 (29), 80 (56), 79 (44), 67 (34), 55 (13), 52 (4), 41 (33).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.01; H, 12.10.

The sample was analyzed on Golay GC–MS to be of 97% purity, and gave the same mass spectrum as that of an authentic specimen of **5** prepared according to the method of Rappoport.[9] The melting point was not depressed either on admixture with the authentic specimen.

Rearrangement Reactions. Rearrangement experiments were run in the same equipment as described in the previous report.[1b] Tricycloundecane (100 mg, 0.67 mmol) and 100 mg (0.67 mmol) or 50 mg (0.33 mmol) of trifluoromethanesulfonic acid in 5 mL of dry methylene chloride were heated under reflux. Aliquots were withdrawn from the reaction mixture, and the reaction was terminated by addition of cold water. The methylene chloride layer was separated, washed with a saturated sodium bicarbonate solution and water, and dried over anhydrous calcium chloride. The methylene chloride solution was analyzed for tricycloundecanes on Golay column (Apiezon L and Carbowax 20M) GC–MS. Identification of intermediates with known structure was made by comparison of GC–MS behaviors with those of authentic specimens.[1]

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Registry No.—**1,** 53432-45-4; **3,** 60887-91-4; **4,** 51027-87-3; **5,** 55820-81-0; **6,** 43000-53-9; **19,** 942-81-4; **20,** 63665-44-1; **21,** 63665-45-2; **22,** 63665-46-3; *endo*-**23,** 63665-47-4; *exo*-**23,** 63665-48-5; *endo*-**24,** 35717-03-4; *exo*-**24,** 63665-49-6; **25**-1(10)-ene, 35716-93-9; **25**-8-ene, 33283-28-2; **26,** 13348-11-3; **27,** 63665-50-9; **34,** 36825-06-6; **35,** 2018-80-6; **36,** 63665-51-0; **37,** 63665-52-1; thionyl chloride, 7719-09-7; 9-chlorocarbonylbicyclo[3.3.1]nonane, 63665-53-2; diazomethane, 334-88-3; *p*-toluenesulfonylhydrazine, 1576-35-8; trifluoromethanesulfonic acid, 1493-13-6.

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(26) For **1**-1-yl cation there appear to be three possible alkyl shifts, C-6, C-8, or C-11, that are stereoelectronically probable and give skeletal structures different from **1**. A shift of C-6 forms 1,7-tetramethylenenorbornane, which is the first intermediate in the rearrangement of *cis*-2,3-tetramethylenenorbornane,[1d] and seems to be irrelevant to the present reaction. A shift of C-8 or C-11 is an extrusion of a methyl group via primary carbocation. Formation of a primary cation is a process with high activation energy that should be least likely to occur.[5,17] This is the reason why the methyl extrusion process is postulated to be postponed to the very later stages of the tricycloundecane rearrangement.[5,17] Moreover, a methyl group, once extruded out of the ring system, never goes back into ring for the same reasons.[1d,5,17] The methyl extrusion process thus can not comprise any route to the observed products in the present experiments.
(27) Three alkyl shifts are possible to **3a.** One is shift of C-8 that is a return to **2a.** The two other shifts are extrusion of a methyl group. In addition, no probable intramolecular hydride transfer is possible either, that gives rise to other cation of **3** with the possibility of skeletal rearrangement.
(28) *endo*-2-, *endo*-7-, and 8-hydrogens might appear to be transferable, but this is less favorable. According to ^{13}C NMR measurement[3] and molecular mechanics calculations,[5] the most stable conformation of **4** is such that C-3 is flapped toward the endo side to give a chair cyclohexane (C-1 through C-4, C-9, and C-10, as in **4**). Orbitals of *endo*-2- and *endo*-7-H are so apart from the cationic p orbital on C-11 that transfer of these hydrides can not be realized. On the other hand, **4a** would require to assume a highly strained ethyleneprotonium-type transition state for the 1,2-transfer of 8-H. The strain is brought about by proton bridging to the bridgehead (C-8). The situation here is similar to that for electrophilic additions to bridgehead (anti-Bredt) olefins, and it is for this reason that bridged intermediates were excluded in the bromination of bicyclo[3.3.1]non-1-ene[29] as well as the hydration and oxymercuration of 4-homoisotwist-2-ene.[30]
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(31) This is indirectly supported by our previous experiment[3] that 4-homoisotwistan-*exo*-2-ol (**6**-*exo*-2-ol) gave **4** and **6,** but no **5,** on hydride-transfer reduction rearrangement. **6**-*exo*-2-ol forms the corresponding cation, which partly reduced to **6** and partly converted to **6a** by 1,3-hydride transfer. Path from **6a** to **4e** (path −h) to **4d** (path −g) proceeds smoothly, but path −f is slow to afford **4b.** Consequently, practically no **5** was obtained in this reaction.
(32) The cation **4b** produced from **4** via **4c** and **4d** is distributed between paths −c and d. It is assumed here that alkyl shift (path d) is faster than hydride transfer (path −c) in **4b,** and at the same time, alkyl shift in **4a** back to **3d** is also assumed to be faster than path −c. The rate-determining step from **4b** to **3** is then path −c, since the step from **4a** to **3d** and path −b (conversion of a secondary to a tertiary cation) are fast. Similarly, path d is assumed to be faster than the hydride transfer in **5a** to **5b,** and the latter process is rate determining in the route from **4b** to **5.** The ratio of the products **3** and **5** from **4** is then determined by the ratio of two hydride transfers, path −c and the step from **5a** to **5b.** The latter step is a transformation of a secondary into a tertiary cation, and should be much faster than the former, which is an interconversion between two secondary cations. As a result, **4b** is partitioned into **3** and **5** in a ratio 0.5:31.8 ∼ 1:60 (run 31). On the other hand, the cation **4b** produced from **5** is distributed among paths −c, e, and f. Paths e and f are much faster than −c, most of **4b** being converted to **4c** and **4d.** However, path g, which is rate determining in the route from **4b** to **6,** should be much slower than path −c. Therefore, although the concentration of **4b** is much smaller than that of **4d,** a reasonable amount of **3** is formed as compared to **6** (**3**/**6** = 3.9:23.7 ∼ 1:6; run 21). It is to be noted here, however, that the assumption of fast alkyl shift may not always hold. It seems that the assumption was valid for **3, 4, 5,** and **6** because differences among their stabilities (total energy of the skeletal structure) were quite small compared to the activation energies of hydride transfers. In other words, if an alkyl shift gives rise to a highly strained structure, thermodynamic control would prevail to make the alkyl shift unrealized, while hydride transfers are allowed (cf. discussion on the step from **3c** to **7a** following path a).
(33) (a) H. A. Walborski, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, **83,** 988 (1961); (b) H. L. Goering and M. F. Sloan, *ibid.*, **83,** 1397, 1992 (1961).
(34) Starting with **4d,** an equilibrium is set up quickly among **4d, 4,** and **4c** because paths −e, −f, and g are slow, whereas interconversion among **4d, 4,** and **4c** is fast. This is the same result as would be obtained if the reaction is started with the hydrocarbon **4.** Since ratio of **5** to **6** is 2:3 in the reaction of **4, 4d** would give **5** and **6** in the same ratio.
(35) J. A. Berson and R. Raynolds-Warnhoff, *J. Am. Chem. Soc.*, **84,** 682 (1962); R. W. Thies and L. E. Shick, *ibid.*, **96,** 456 (1974).
(36) F. Arndt, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p. 165.