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Trifluoromethanesulfonic Acid Catalyzed Rearrangement of 2- and 4-Homoprotoadamantane to Methyladamantanes and the Existence of Methylprotoadamantane Route. Empirical Force Field Calculations

Naotake Takaishi, Yoshiaki Inamoto,* Koji Aigami, and Yoshiaki Fujikura

Wakayama Research Laboratories, Kao Soap Company, Ltd., 1334 Minatoyakushubata, Wakayama 640-91, Japan

Eiji Ōsawa

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Mituyosi Kawanisi and Takeo Katsushima

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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Brief treatment of 2-homoprotoadamantane (**10**) with trifluoromethanesulfonic acid gave 4-homoisotwistane (**4**), homoadamantane (**7**), and 2-methyladamantane (**6**), while similar treatment of 4-homoprotoadamantane (**11**) afforded **4**, **6**, 1-methyladamantane (**5**), 2,4-bishomobrendane (**15**), and *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane (**14**), but no trace of **7**. The absence of **7** in the latter reaction mixture precludes the possibility of intermediacy of **7** as the source of **6**. Instead, methylprotoadamantanes (**9**) are suggested to form transiently and directly from **11** by ring contraction and give rise to **5** and **6**. Reaction mixture composition from **10** can be rationally explained by assuming the intermediacy of 2-homoadamantyl cation (**7a**), the product of one 1,2-alkyl shift in **10**, but the possibility of intermediacy of 3-methylprotoadamantane (3-Me-**9**) as the direct source of **6** cannot be excluded. Proposed mechanisms agree well with empirical force field calculations on the enthalpies of formation and geometry of cations.

In the course of the study on acid-catalyzed multistep rearrangement of tricycloundecanes, it has been established[1,2] that isomers such as *cis-exo-* and *cis-endo*-2,3-tetramethylenenorbornane (**1**), *cis*-2,3-trimethylenebicyclo[2.2.2]octane (**2**), and *cis-endo*-6,7-trimethylenebicyclo[3.2.1]octane (**3**) first isomerize to a stable intermediate, 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **4**), which then rearranges to the final equilibrium mixture of 1- and 2-methyladamantane (**5** and **6**) upon prolonged treatment with catalyst (Scheme I).

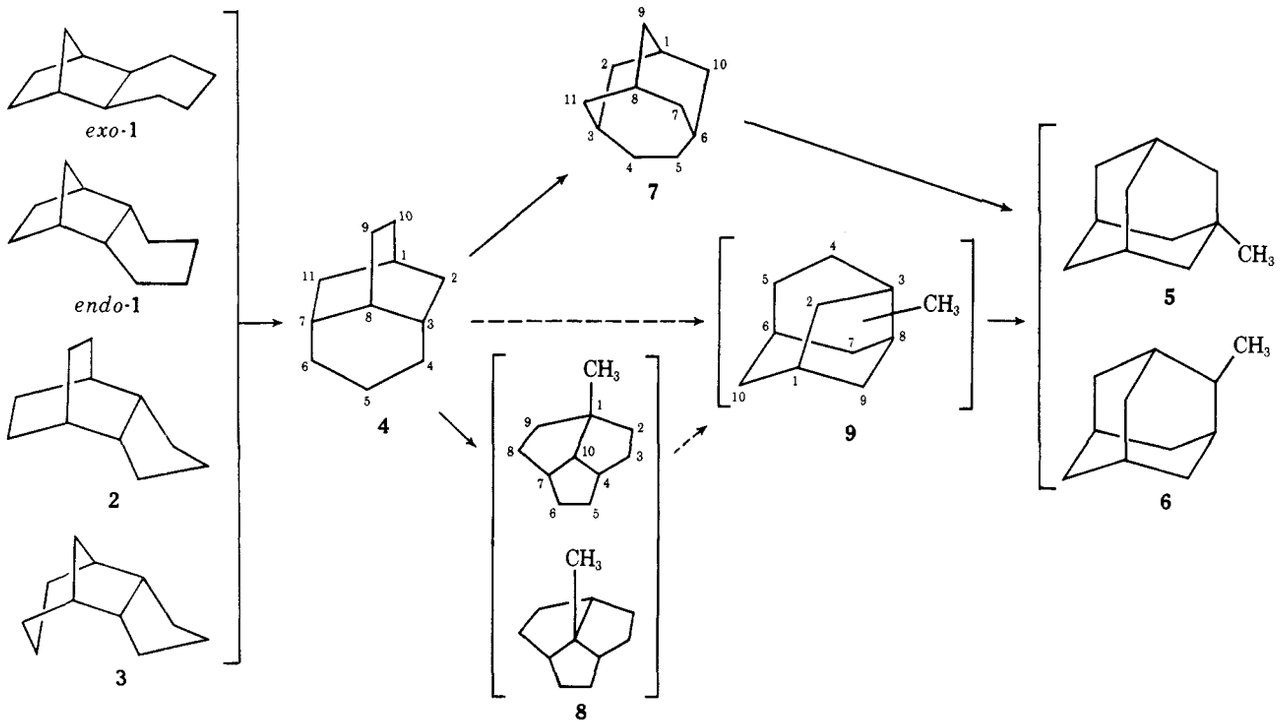
Complex pathways connecting **1**[2d,3] and **2**[2e] to **4** were recently elucidated experimentally[2d,e] as well as theoretically.[3] However, there remains much to be clarified on the reaction sequence from **4** to methyladamantanes. One of the most intriguing problems associated with the "later" rearrangement paths that start from **4** is at which stage of the rearrangement the methyl group is extruded out of the ring system. Thermodynamically, the extrusion of a methyl group should be slightly exothermic.[4] The activation energy of the methyl extrusion step is, however, supposed to be relatively high because of the primary carbonium ion character of the transition state,[3] and for this reason the step is kinetically unfavorable. As a consequence, the methyl extrusion process is postponed until very late stages of the multistep rearrangement sequence unless especially favorable conditions are provided.

Homoadamantane (**7**) has long been known to participate in such methyl extrusion steps.[5] 4-Homoadamantyl cation (**7b**, Scheme V) rearranges directly into **6**[5a,6] and 3-homoadamantyl cation into **5**.[5b,c] However, homoadamantane does not seem to be the only entrance into methyladamantanes, because two methyl-bearing intermediates, 1- and 10-methylperhydrotriquinacene (**8**, Scheme I), have recently been isolated from the rearrangement mixture.[6]

In analogy with the tricyclodecane rearrangement sequence, where protoadamantane is the last intermediate before adamantane,[7,8] methylprotoadamantanes (**9**, Scheme I)[9] appear to be potential penultimate isomers in the tricycloundecane rearrangement. Schleyer[1a] has already indicated this possibility on intuitive grounds. Methylprotoadamantanes (**9**) are also claimed to be the most plausible intermediates in the conversion between 1- and 2-methyladamantane.[10] However, none of the ten isomers of **9** has ever been detected in the tricycloundecane rearrangement,[1-3] and this situation prompted us to design some experiments to clarify the expected role of **9**.

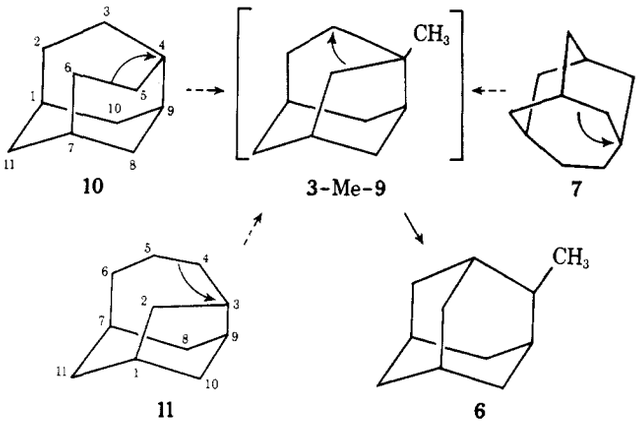
We chose 3-methylprotoadamantane (3-Me-**9**) as the target molecule because of two related reasons (Scheme II). Firstly, it is predicted to be the most stable of the six methylprotoadamantane isomers that lead to 2-methyladamantane (**6**) in single protoadamantane–adamantane rearrangement.[9] Secondly, 2-methyladamantane, rather than the 1-methyl

Scheme I



isomer (**5**), is considered a major entrance into the methyladamantane mixture, since **6** usually accumulates faster than **5** in the initial phases of many tricycloundecane rearrangements.[2,5] Three tricycloundecane isomers may give rise to 3-Me-**9** in one methyl extrusion process (Scheme II). They are **7**, 2-homoprotoadamantane (tricyclo[5.3.1.0^{4,9}]undecane, **10**),[11] and 4-homoprotoadamantane (tricyclo[5.3.1.0^{3,9}]undecane, **11**).

Scheme II



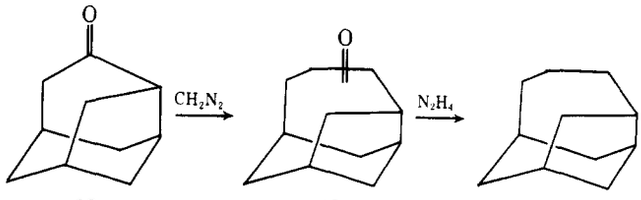
Rearrangement of **7** and related derivatives has already been studied extensively, but no trace of **9** was detected.[5] We describe here the rearrangement of **10** and **11**. However, any methyl extrusion in these compounds, if it occurs, may not necessarily represent the process actually occurring in the overall rearrangement, since **10** and **11** were not found among intermediates.[1,2] Nevertheless, the reaction is considered worth studying because it is a good probe for the process which has never been realized experimentally.

Results

Rearrangement of 2-Homoprotoadamantane (10). 10 was isomerized in methylene chloride solvent in the presence of trifluoromethanesulfonic acid to produce **4**, **6**, and **7** (Table I), as analyzed on Golay GC/MS.[2] No sign was seen of the formation of **9** in this rearrangement. Monotonous increase in the amount of the products suggests that they are formed almost directly from **10**. Other products and their distributions detected in minor amounts in later periods of the reaction were similar to those obtained in the rearrangement of **4**.[2d] These minor products, therefore, most probably originate in the once-formed **4**.

Rearrangement of 4-Homoprotoadamantane (11). 11 was prepared from protoadamantan-4-one (**12**)[12,13] through ring enlargement with diazomethane[14] followed by Wolff–Kishner reduction of the resulting ketone mixture (**13**, Scheme III). Structure **11** of the reduction product was confirmed by

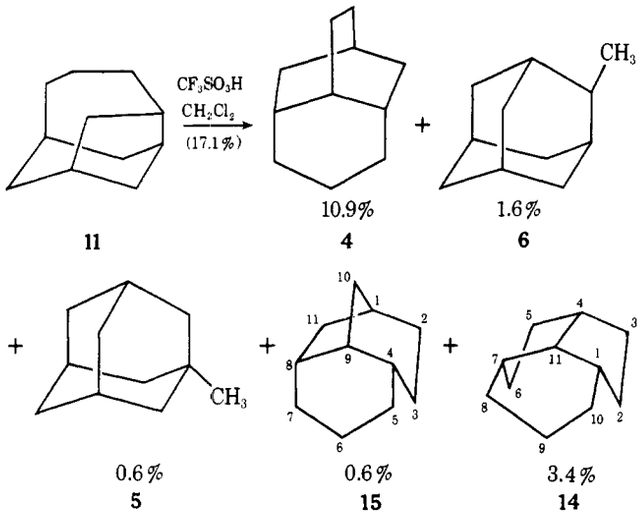
Scheme III



mass (*m/e* 150) and ^{13}C NMR spectra (no element of molecular symmetry).

11 was refluxed in methylene chloride with 1 molar equiv of trifluoromethanesulfonic acid for 3 min. Under these conditions, only 17.1% of the starting **11** isomerized to a mixture of **4**, **5**, **6**, *endo*-2,8-trimethylene-*cis*-bicyclo[3.3.0]octane (**14**),[2e] and 2,4-bishomobrendane (**15**)[15] (Scheme IV). Other isomers which should be produced from and equilibrated with the once formed **4** under prolonged treatment with the catalyst[2] were not detected in this reaction mixture. Therefore, the reaction conditions employed can be considered mild enough to render little possibility of the secondary conversion of the immediate isomerization products. In sharp contrast to the rearrangement of **10**, **7** was not detected at all. We believe that the *absence* of **7** in the reaction mixture is noteworthy in connection with the rearrangement mechanism discussed below.

Scheme IV



Discussion

No methylprotoadamantane (**9**) was actually detected in the present experiments. However, the formation of **6** in the rearrangement of **11** under essentially kinetically controlled conditions seems to indicate the intermediacy of 3-Me-**9** as shown in path b of Scheme V. The possibility of the formation of **6** by way of **4** can be excluded by the fact that no other product of the secondary conversion of **4**[2d] was detected except for **14** (see below). On the other hand, if **6** were formed from **7** (Scheme V), **7** should also have been detected in the reaction, as it *was* detected in the rearrangement of **10** under similar reaction conditions (Table I). Thus we speculate that the path a, which would have led to 2-homoadamantyl cation (**7a**),[5b] never took place in the present reaction of **11**. 3-Me-**9** is then the most plausible intermediate in the proposed two-step isomerization of **11** to **6**.

The small amount of **5** is likely to have formed along a similar pathway as that to **6**, namely, via either 6-Me-**9** along path c or *endo*-4-Me-**9** along path d, or both. An alternative possibility for the formation of **5**, that by a secondary conversion of once-formed **6**, should be negligible, since **5** was entirely absent in the reaction mixtures from **10** which contain **6** (Table I). Indeed slow interconversion between **5** and **6** under trifluoromethanesulfonic acid catalysis has been well established.[2]

Since path a is crossed out in the rearrangement of **11**, at least under the present reaction conditions, the observed formation of **4** cannot be explained by way of **7**,[5b] and an alternative path e from **11**-8-yl cation may be invoked. The same cation seems to explain also the formation of **15** (path f), as discussed below.

14, formally designated as unknown D,[2] has been frequently observed in many of the tricycloundecane rearrangements and considered to belong to one of those "dead end" intermediates which equilibrate with the stable intermediate **4**.[2,3] However, the ratio of **14** to **4** observed in the present study (1:3) is much larger than the equilibrium ratio (1:10),[2] and this is one of the reasons why the route to **14** via **4** is neglected in Scheme V. We suggest path g by way of **15a** to be the major route to **14** by taking advantage of the likelihood that the last of the observed products, **15**,[15] may well be the result of one-step isomerization of **11** along path f.

The product distribution in the rearrangement of **10** (Table I) indicates that this isomerization is rather simple and straightforward, giving 2-homoadamantyl cation (**7a**) as the major intermediate (according to path h). The observed products can be explained fully by this cation, since the behavior of **7** and its various cations in the rearrangement is well understood.[5] Thus **7a** leads to **4** via path i. **7a** readily gives 4-homoadamantyl cation (**7b**) by 1,3-intramolecular hydride shift,[5b,c] and the ring contraction path j from **7b** to **6** is well established by isotope experiments.[5a] Path k, an alternative route to **6**, may not be excluded in view of the intermediacy of 3-Me-**9** in the reaction of **11**, as inferred above.

Table I. Products of the Rearrangement of 2-Homoprotoadamantane (10)[a]

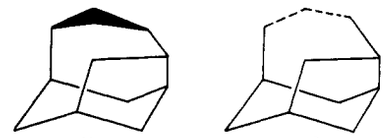
Reaction time, min	Product,[b] %[c] 4	6	7	10[d]	Others[e]
5	3.7	1.2	18.7	76.4	
20	7.5	2.3	35.8	53.3	1.1
270	11.6	4.4	68.1	13.6	2.3

[a] 7 mg (0.05 mmol) of **10**, 25.2 μL (0.3 mmol) of CF_3SO_3H, and 5 mL of CH_2Cl_2. [b] Identified on Golay GC/MS. [c] Calculated from Golay VPC peak area. [d] Unreacted starting material. [e] Secondary rearrangement products. See text.

3-Homoadamantyl cation is considered to be the major precursor of **5** in the rearrangement of **7**.[5b,c] The absence of **5** in the reaction mixture from **10**, therefore, may be taken to indicate that the formation of 3-homoadamantyl cation[5c] either by 1,2-intramolecular hydride shift[16] in **7a** or by hydride abstraction from neutral **7**[5b] is slow compared to other competing processes mentioned above.[17]

Molecular Mechanics Calculations. One of the key issues emerged from the present experiments is the fact that 2-homoadamantyl cation (**7a**) does *not* form from **11** (path a, Scheme V), a puzzling observation which can hardly be rationalized by merely examining conventional molecular models. No less intriguing is the detection of only a few products of rearrangement from both **10** and **11** despite many other, formally possible paths from these two starting materials (Chart I and II). We therefore performed extensive molecular mechanics calculations in order to gain insight into these puzzles.

Among two conformers of **11**, the endo form (**11a**) is calculated to be of about 2 kcal/mol lower enthalpy than the exo

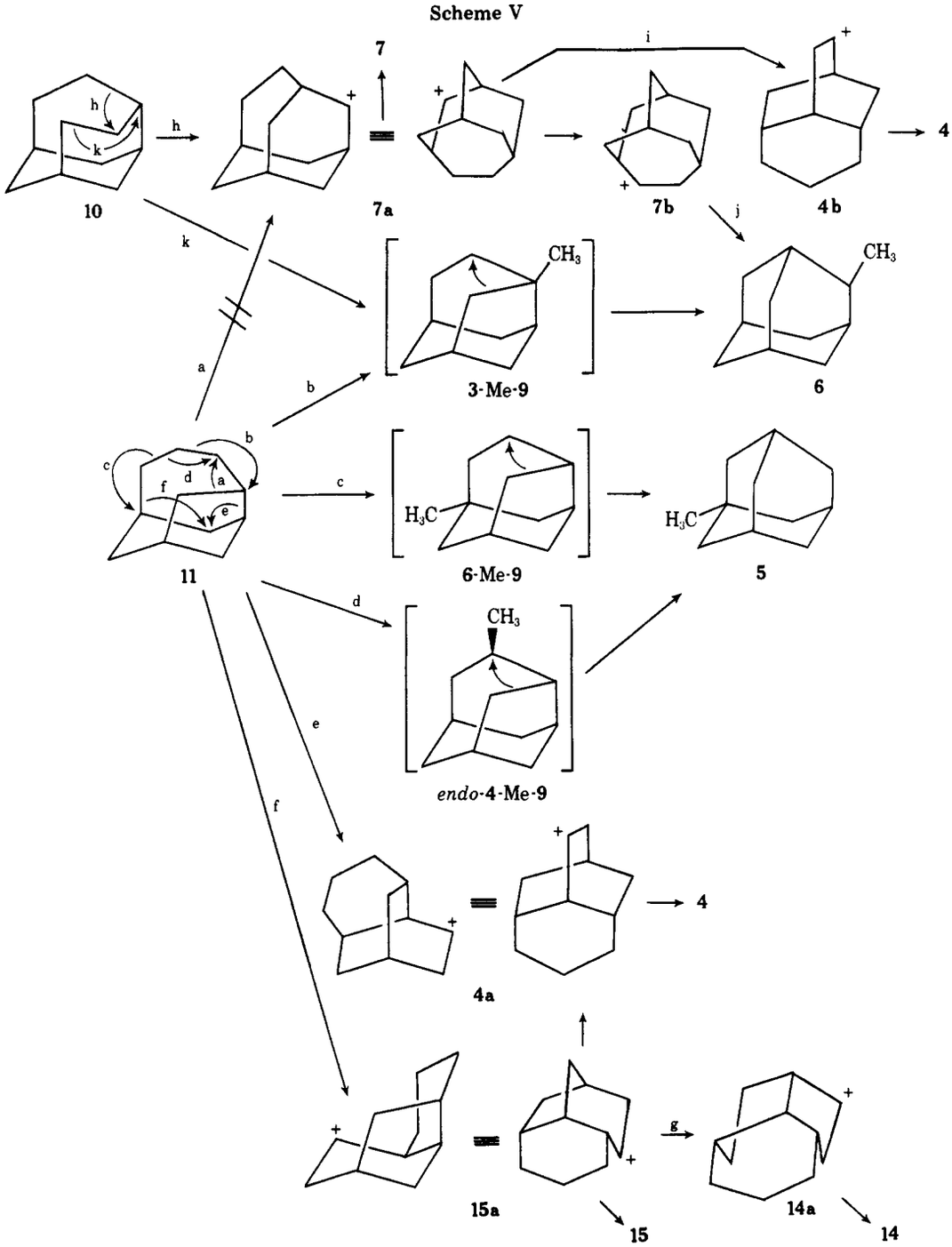


		11a	11b
ΔH_f° (calcd), kcal/mol	E[18a]	−21.61	−19.16
	A[18b]	−20.35	−18.65

form (**11b**). Although the calculated energy difference is barely outside the accuracy of the calculation,[18a] it is large enough to shift the conformational population largely to **11a** around room temperature and the subsequent analysis of **11** is based on the endo form **11a**. Chart I and II summarize energetic and geometric conditions for all the possible 1,2-alkyl shifts that start from various cations of **11a** and **10**. Energy terms considered are enthalpies of formation ($\Delta\Delta H_f^\circ$) of both starting and product cations relative to *tert*-butyl cation.[19,21] For "methyl extrusion" processes, $\Delta\Delta H_f^\circ$ could not be calculated, as force field parameters for the bridged ion intermediate or the transition state corresponding to concerted mechanism[3] are unknown. The available energetic criterion of the methyl extrusion process is the calculated heats of formation of methylprotoadamantanes.[3,9]

It has been recognized[3] that a geometric factor, the dihedral angle between the vacant orbital of carbonium ion center and the adjacent σ orbital about to migrate, is as important as

Scheme V

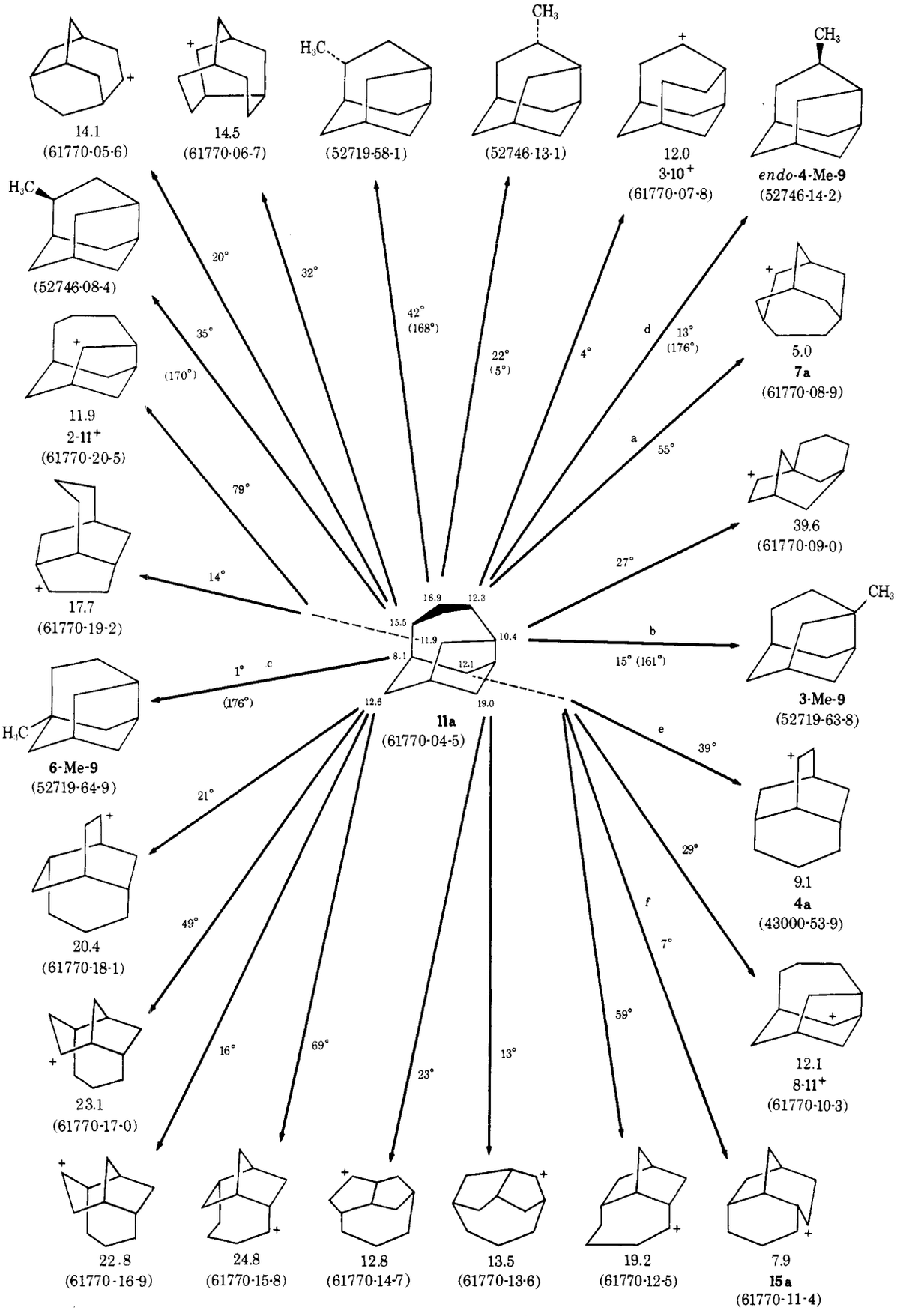


$\Delta\Delta H_f°$ in determining the course of the alkyl shift. The closer the angle to zero, the less will be the strain increase in the transition state of the 1,2-alkyl shift. These angles were estimated from the energy minimum structure of appropriate cations of **11a** and **10**. For the possible concerted mechanism of "methyl extrusion" process,[3] the dihedral angle between leaving and migrating bond should favorably be 180° as in the ideal trans-periplanar orbital disposition. The "trans" dihedral angles were estimated from calculated energy minimum structure of **11a** and **10** and given in Charts I and II in parentheses.

The analysis provides truly useful information related to the experimental observations presented above. Most of the 1,2-alkyl shift possibilities involve either too large an interorbital angle or too unstable a cation (or both). They are unlikely to occur,[3,7] and consequently only a few paths remain available to the first steps of rearrangement, in accordance with the observation of only six kinds of products in the initial phases of both reactions.

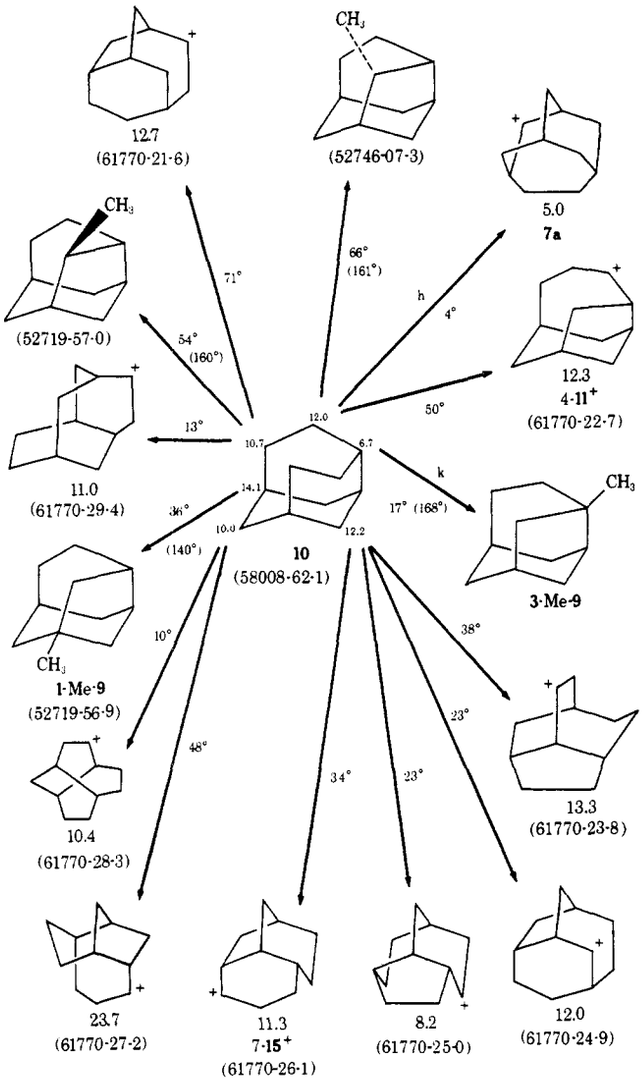
Concerning the rearrangement of **11a**, we first note that 2-homoadamantyl cation (**7a**) is energetically the most favorable ($\Delta\Delta H_f°$, 5 kcal/mol) among all the possible isomerization products, but this ion must be arrived at through an extremely unfavorable interorbital angle of 55° between the vacant orbital at C_4 and the C_2–C_3 bond of 4-**11a**$^+$. The barrier is high enough to exclude the possibility of reaching **7a** by path a in view of the fact that a 60° interorbital angle is regarded as an unsurmountable obstacle in the 1,2-alkyl shift on a rigid cage molecule.[10,16] The most favorable path as judged by the three criteria given in Chart I is e leading to **15a**, and thus this path is very likely the one which gave **15**. Other paths as theoretically feasible as e are b and c leading to 3-Me-**9** and 6-Me-**9**, respectively. Ready formation of bridgehead carbonium ions at C_3 and C_7 of **11a** ($\Delta\Delta H_f°$ = 10.4 and 8.1 kcal/mol, respectively) certainly assists the processes along these paths, in addition to favorable interorbital angles. We think that

Chart I



[a] Calculated heats of formation of cations $\Delta\Delta H_f^\circ$ (kcal/mol, 25 °C, relative to *tert*-butyl cation) and dihedral angle between vacant orbital of cationic center and adjacent, migrating σ bond in all possible 1,2-alkyl shifts on 4-homoprotoadamantane (11a) by Engler force field.[18a,19,21] Angles in parentheses correspond to concerted mechanism of methyl extrusion, for which trans-periplanar disposition (180° dihedral angle) between leaving and migrating orbitals in ideal. [b] Registry no. are in parentheses.

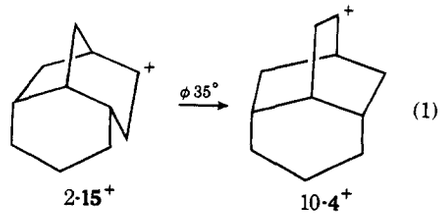
Chart II



[a] Calculated heats of formation $\Delta\Delta H_f°$ and interorbital angles of cations in all possible 1,2-alkyl shifts on 2-homoprotoadamantane (10) by Engler force field. See Chart I for explanation. [b] Registry no. are in parentheses.

these computational results lend further support to the methylprotoadamantane route.

Somewhat annoying in relation to the proposed reaction scheme (Scheme V) is the relatively large interorbital angle (39°) calculated for path e, which we expected to lead to the most abundant product 4 in one step, even though $\Delta\Delta H_f°$ values of both starting and product cations for path e are certainly favorable. An alternative way of obtaining 4 is suggested in eq 1. $\Delta\Delta H_f°$ values are satisfactorily low. The interorbital angle (35°) cannot be regarded as very favorable; nevertheless one may expect some lowering in activation energy from the neighboring methylene assistance similar to that observed in 2-bicyclo[3.2.1]octyl cation.[22]



(1)

	2-15+	10-4+
$\Delta\Delta H_f°$ (calcd), kcal/mol	11.2	9.1

The path g suggested in Scheme V to give the second most abundant product 14 is confirmed to involve a fairly favorable interorbital angle (13°) in 10-15+ ($\Delta\Delta H_f°$, 8.4 kcal/mol).

Among various possibilities of first steps in the rearrangement of 10, the formation of 7a by path h is clearly proved to be very favorable by our steric criteria. With the lowest interorbital angle (4°) and the lowest enthalpy of cation formation (5 kcal/mol), this path is most likely to represent the major source of observed 4 and 6. Force field calculations further support the suggested possibilities of the intermediacy of 3-Me-9 by path k as an alternative source of 6. Namely, 4-10+ is calculated to have the lowest enthalpy of formation (6.7 kcal/mol) among various 10 cations and the interorbital angle for methyl extrusion leading to 3-Me-9 to be in favorable range. 1-Me-9, the only potential intermediate from 10 leading to 1-methyladamantane (5), is less likely to form because of high $\Delta\Delta H_f°$ and a large interorbital angle in 11-10+. These results do not contradict the observed absence of 5 in the reaction of 10.

Conclusion

The failure to detect any methylprotoadamantanes in this study appears to have nullified the attempt to obtain direct evidence on their intermediacy in the rearrangement. However, absence of homoadamantane (7) in the reaction of 11 and presence of potentially favorable paths going through methylprotoadamantanes constitute indirect evidence that supports strongly the hypothetical intermediacy of methylprotoadamantanes. This evidence should be understood to suggest, but not to demonstrate, the role of methylprotoadamantanes as the last intermediate of the overall C_{11} rearrangement, since the inference was made on the basis of the isomerization of 11 which was not found among intermediates of the overall rearrangement. Further efforts will be concentrated on the study of the role of recently identified methylperhydrotriquinacenes (8) in the rearrangement, in order to clarify other aspects of the methyl extrusion process.

Experimental Section

Conventional VPC, Golay column GC/MS, ^1H and ^{13}C NMR, and mass spectrometry were made with the same instruments as in the previous works.[2] Rearrangement reactions of homoprotoadamantanes with 1 molar equiv of CF_3SO_3H and product analyses were conducted similarly as before.[2]

Computer calculations with program STRAIN[18a] were done on UNIVAC 1100 (Kao Soap Co.) and FACOM 230-75 (Hokkaido University).

4-Homoprotoadamantane (11). A solution of 6.0 g of potassium hydroxide in 30 mL of 50% aqueous methanol was added dropwise with efficient stirring to a mixture consisting of 15.0 g (0.1 mol) of protoadamantan-4-one, 51.4 g (0.24 mol) of *N*-nitroso-*p*-toluenesulfonamide, 150 mL of methanol, and 6 mL of water, while the reaction temperature was kept between 10 and 20 °C. The reaction mixture was stirred at the same temperature for an additional 3 h. The mixture was made acidic by the addition of 2 N hydrochloric acid. Methanol was distilled off from the mixture, and the residue was diluted with 100 mL of water. The mixture was extracted with three 200-mL portions of petroleum ether. Combined extracts were washed with 1% sodium hydrogen carbonate and then with water, and dried over anhydrous sodium sulfate. Solvent was evaporated off, and the residue was passed through an alumina column (eluted with benzene). The eluent was further purified on preparative VPC to give two fractions (ca. 3:2 area ratio) corresponding to homoprotoadamantanone (*m/e* 164).

The earlier eluted fraction: IR (Nujol) 1695, 1250, 1140, 1040, 980, 920 cm^{-1}; mass spectrum *m/e* (rel intensity) 164 (60, M^+), 108 (75), 107 (47), 95 (100), 93 (68), 81 (59), 80 (47), 79 (100), 68 (74), 67 (57), 41 (86).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.6; H, 9.7.

The later eluted fraction: IR (Nujol) 1695, 1320, 1310, 1260, 1200,

1130, 1050, 1020, 810 cm^{-1}; mass spectrum *m/e* (rel intensity) 164 (46, M^+), 109 (42), 96 (100), 83 (58), 80 (50), 79 (98), 67 (96), 66 (75), 41 (50).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.6; H, 9.8.

A mixture of 3.3 g (0.02 mol) of the combined VPC fractions of homoprotoadamantanone obtained above, 93 g (0.165 mol) of potassium hydroxide, 10 mL (0.207 mol) of 100% hydrazine hydrate, and 100 mL of diethylene glycol was heated under gentle reflux (ca. 160 °C) for 3 h. The reaction temperature was elevated gradually to 220 °C while water formed was distilled off, and the mixture was refluxed for an additional 2 h at that temperature. Combined reaction mixture and distillate were diluted with 100 mL of a saturated sodium chloride solution and extracted with three 50-mL portions of *n*-hexane. Combined hexane extracts were washed with two 50-mL portions of water and dried over anhydrous magnesium sulfate. Evaporation of the solvent and purification of the residue by sublimation under slightly diminished pressure gave 1.3 g (42% yield) of a pure sample of 4-homoprotoadamantane (11): mp 129–130 °C; IR (neat) 2910, 2850, 1460, 1230, 1100, 1020, 920, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.4 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 21.0 (t), 27.3 (t), 29.3 (d), 32.8 (t), 34.1 (d), 34.7 (t), 35.9 (d), 37.2 (t), 37.5 (t), 37.7 (d), 40.8 (t); mass spectrum *m/e* (rel intensity) 150 (86, M^+), 135 (44), 107 (44), 94 (54), 93 (65), 81 (62), 80 (68), 79 (100), 67 (86), 55 (46), 41 (78).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.1; H, 12.0.

Acknowledgment. We thank Professor P. v. R. Schleyer for a copy of program STRAIN, and Dr. E. M. Engler for instruction on the carbonium ion calculations.

Registry No.—**4,** 43000-53-9; **6,** 700-56-1; **7,** 281-46-9; **12,** 27567-85-7; **13** isomer 1, 61770-30-7; **13** isomer 2, 61770-31-8; trifluoromethanesulfonic acid, 1493-13-6.

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Selective Formation of Biaryls via Interaction of Polynuclear Arylcopper Compounds with Copper(I) Trifluoromethanesulfonate [Copper(I) Triflate][1]

Gerard van Koten,* Johann T. B. H. Jastrzebski, and Jan G. Noltes

Institute for Organic Chemistry, TNO, Utrecht, The Netherlands

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Selective formation of biaryls is observed upon interacting well-defined arylcopper cluster compounds (2-$Me_2NCH_2C_6H_4)_4Cu_4$, (4-$MeC_6H_4)_4Cu_4$, (2-$Me_2NC_6H_4)_4Cu_6Br_2$, and (2-$Me_2NC_6H_4)_4Cu_6OTf_2$ with equimolar amounts of CuOTf in benzene. It is shown that complex formation of the arylcopper cluster with CuOTf precedes the C–C-coupling process. In some cases these complexes are sufficiently stable to be isolated, e.g., (2-$Me_2NC_6H_4)_4$-Cu_6OTf_2 (from the 2/1 reaction of 2-$Me_2NC_6H_4Cu$ with CuOTf). Decomposition of the 2-MeC_6H_4Cu/CuOTf complex with NH_3/H_2O in the presence of oxygen affords, in addition to toluene and 2,2′-bitolyl, 2-$H_2NC_6H_4Me$ and 2-HOC_6H_4Me. The formation of the arylcopper–CuOTf complexes and hence biaryl formation can be inhibited by suitable ligands such as PPh_3. In the absence of built-in ligands in the arylcopper compound, e.g., (4-$MeC_6H_4)_4Cu_4$, the reaction with CuOTf can be made catalytic in CuOTf. The selective C–C-coupling reaction has been explained in terms of intraaggregate electron-transfer processes occurring in the intermediate arylcopper–copper triflate complexes. A mechanism is proposed based on valence disproportionation inside the copper core induced by charge transfer from the core to the electron-accepting OTf anions.

The 1/1 reaction of polymeric 2-(dimethylamino)phenylcopper[3] (I) with cuprous halides affords stable hexanuclear copper complexes which have $R_4Cu_6Hal_2$ stoichiometry.[4] The interaction of 2-[(dimethylamino)methyl]phenylcopper[5] (II) with cuprous halides gives rise to the formation of polymeric complexes with $(R'Cu{\cdot}CuHal)_n$ stoichiometry.[6] Both types