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TRIFLUOROMETHANESULFONIC ACID CATALYZED REARRANGEMENT OF HOMOADAMANTANE

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Homoadamantane (1) rearranges under CF_3SO_3H catalysis to 1- and 2-methyladamantane (2 and 3, respectively), tricyclo[5.3.1.0^{3,8}]undecane (4), *exo*-tricyclo[5.3.1.0^{1,5}]undecane (5), tricyclo[6.3.0.0^{1,5}]undecane (6), *exo*-tricyclo[5.3.1.0^{2,6}]undecane (7), and an unknown tricycloundecane (8). That the 2-homoadamantyl cation (11) is the key intermediate in going from 1 to 4 is indicated by the result of hydride transfer reduction of 2-homoadamantanol (17) in H_2SO_4.

The acid catalyzed rearrangement of the tricycloundecanes have proven to be more complex than those of the tricyclodecanes.[2-13] All tricyclodecanes rearrange to adamantane, but intermediates can be detected only in a few instances.[2,3] In contrast, while 1-methyladamantane (2) is the $C_{11}H_{18}$ stabilomer,[4-6] mixtures of products are commonly obtained by isomerization of other tricycloundecanes.[4-13]

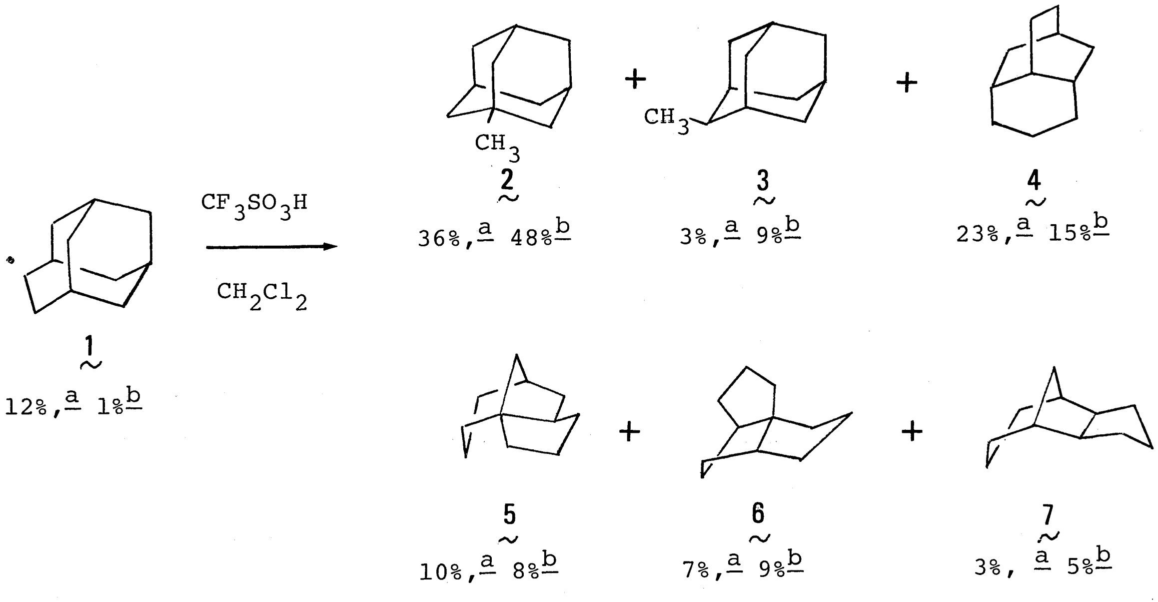
These transformations necessarily must involve many consecutive and competitive reactions. The role of homoadamantane (1) in these complex reaction scheme is still quite obscure. In the presence of a Lewis acid 1 rearranges to an initial 1:2 mixture of 1- and 2-methyladamantane (2 and 3) probably *via* the 3- and 4-homoadamantyl cations (11 and 10, respectively).[8,9] The reaction of 4-homoadamantene with $AlBr_3$ in CS_2 yielded 3 and tar,[9b,10] but the cation 10 generated by protonation of 4-homoadamantanol in 96% sulfuric acid / pentane gave a 1:1:2

mixture of 1, 3, and 4-homoisotwistane(tricyclo[5.3.1.0^{3,8}]undecane, 4).[11] 1- and 3-Homoadamantanol in 75% sulfuric acid produced almost equal mixtures of 1, 2, 3, and 1-adamantylcarbinol.[12] Homoadamantane (1) was found to be one of over thirty intermediates formed in the trifluoromethanesulfonic acid catalyzed rearrangement of *cis*-*exo*- and *cis*-*endo*-2,3-tetramethylenenorbornane[5] and *cis*-2,3-trimethylenebicyclo[2.2.2]octane.[6]

We have now studied the trifluoromethanesulfonic acid catalyzed rearrangement of homoadamantane (1) itself. Mixtures of 1 (1.3 mmol), CF_3SO_3H (5.3 mmol), and CH_2Cl_2 (10 ml) were refluxed for 0.5 and for 23 hr, respectively. Each reaction was quenched with ice-water, the CH_2Cl_2 solution was separated, and the solvent was evaporated to yield 100% of a crude product mixture which was analyzed by Goaly GC-MS (SE-30 and Apiezon L columns, 60 - 70°). The products were identified by comparison of GLC retention times, mass spectra, and ^{13}C NMR spectra with those of authentic specimens.[5,6] The results are shown in Scheme 1.

Although the mechanism of reaction of trifluoromethanesulfonic acid with alkanes has not been established, the net effect in the present instances appears to be more or less indiscriminate generation of all possible homoadamantyl cations.

Scheme 1



[a] Product composition after 0.5 hr of the reaction;[14] an unidentified product (8, 4%) was also detected. [b] Product composition after 23 hr of the reaction;[14] 8, 3%.

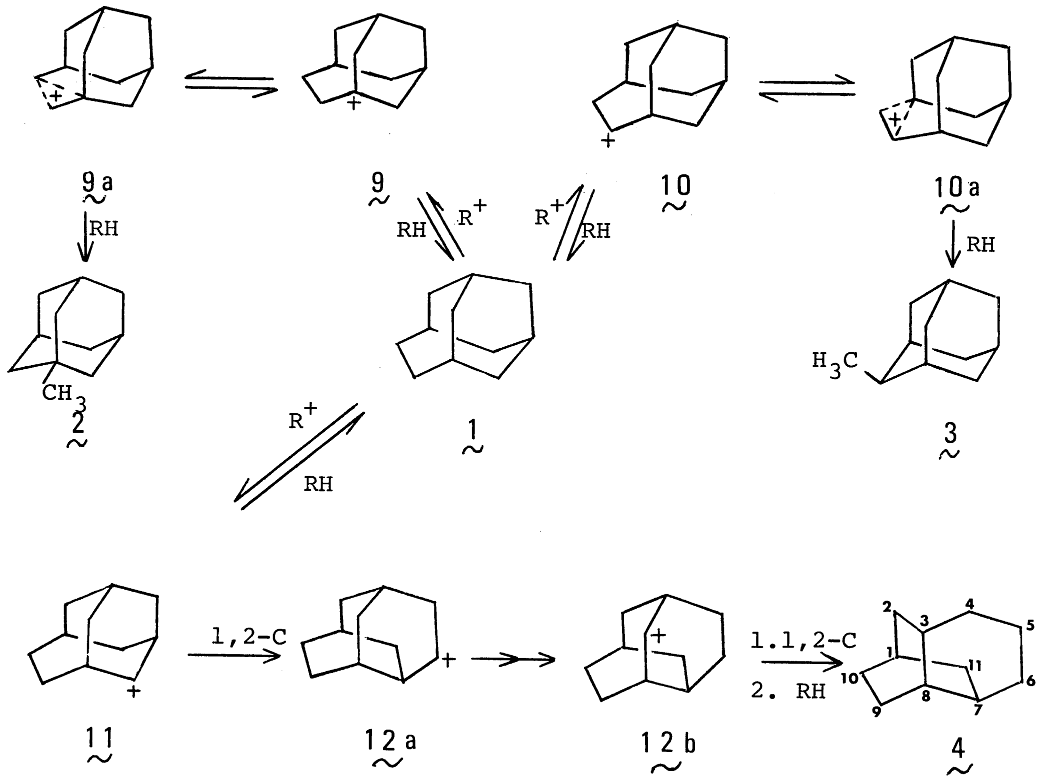
The 3- and 4-homoadamantyl cations (9 and 10) rearrange rapidly, probably *via* the unsymmetrically bridged ions 9a and 10a, to give 1- and 2-methyladamantane by hydride transfer reduction[9-13] (Scheme 2). 4-Homoisotwistane (4) can arise from the 2-homoadamantyl cation (11) which rearranges by a series of 1,2-carbon and hydride shifts *via* cations 12a and 12b as shown in Scheme 2.

1,*exo*-7-Trimethylenebicyclo[3.2.1]octane (*exo*-tricyclo[5.3.1.0^{1,5}]undecane, 5), 1,*exo*-2-trimethylene-*cis*-bicyclo[3.3.0]octane (tricyclo[6.3.0.0^{1,6}]undecane, 6), and *cis*-*exo*-6,7-trimethylenebicyclo[3.2.1]octane (tricyclo[5.3.1.0^{2,6}]undecane, 7) are probably all formed from 4 *via* the 4-homoisotwisy-3-yl cation (13)[5] (Scheme 3). This species (13) appears to be the most stable of all 4-homoisotwistyl cations since carbonium ion substitution reactions yielded 3-substituted derivatives preferentially.[15] Formation of 5 can be explained by a 1,2-carbon shift as indicated (13, Scheme 3). Isomer 6 may be formed either directly from 5 (path *a*) or indirectly by path *b* to intermediate 14 and then by further rearrangement by path *e*. Isomer 7 could be formed *via* intermediate 14 (path *f*), or 15, or 16; the last two isomers could be produced from 5 by path *c* and *d*, respectively. The rearrangement of 15 to 7 is indeed a reversal of the key step[13] in the Brønsted acid catalyzed hydride transfer reduction-rearrangement of *cis*-*exo*-6,7-trimethylenebicyclo[3.2.1]-octan-2-ol (7-2-ol) to 4. The increase of the relative quantities of 6 and 7, and the decrease of 4 and 5 with reaction time (Scheme 1) are consistent with these suggestions. Russian workers[7] also have demonstrated the close relationships among tricycloundecanes 4 - 7, 15, and 16. Isomers 7, 15, and 16 rearranged in the presence of Lewis acid to give similar mixtures of 2 - 7.

The postulated intermediacy of the 2- and 3-homoadamantyl cations (11 and 9) was proved by generating these species by protonation of 2-homoadamantanol (17)[16] and 3-homoadamantanol (18),[18] respectively. A mixture of each alcohol (1 mmol), 96% H_2SO_4 (0.8 ml), and pentane (2 ml) was stirred at 25°. The reaction was quenched with ice-water, the pentane solution was separated, and the solvent was evaporated to yield 20% of a crude product mixture which was analyzed by Golay GC-MS as described above. The results are shown in Table 1.

The main product from 2-homoadamantanol (17) is 4-homoisotwistane (4) as expected. This is strong supporting evidence for the intermediacy of the 2-homoadamantyl cation (11) in the rearrangement of 1 to 4 (Scheme 2). Homoadamantane (1) and 2-methyladamantane (3) are probably formed by the hydride

Scheme 2



Scheme 3

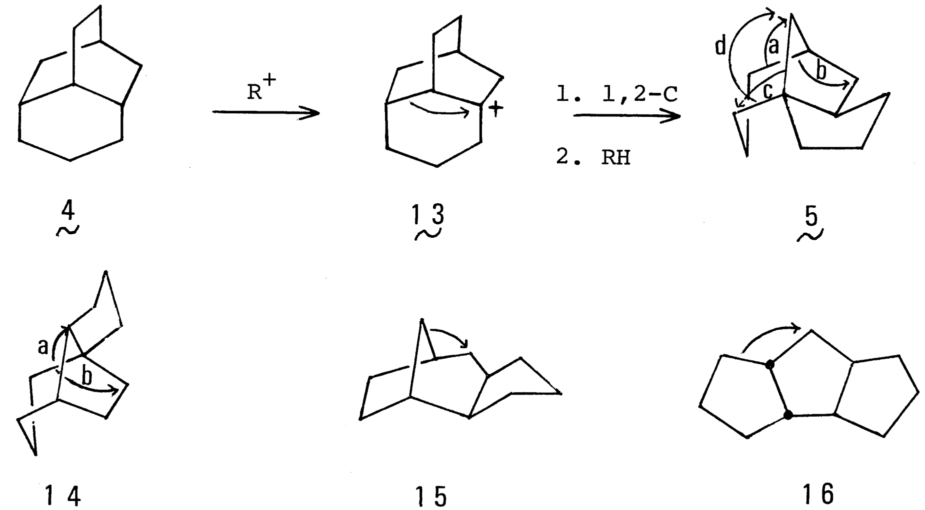


Table 1. Product Distribution in the Reaction of 2-Homoadamantanol (**17**) and 3-Homoadamantanol (**18**) with Sulfuric Acid / Pentane at 25°

Reactant	Time (min)	Product (%)			
		1	**2**	**3**	**4**
17	3	14	1	16	70
18	45	25	63	10	2

transfer reduction of **11** and **10a** which can be equilibrated rapidly *via* a 1,3-hydride shift.[8] 3-Homoadamantanol (**18**) gave mainly 1-methyladamantane (**2**) and **1**. This is consistent with the reaction mechanism shown in Scheme 2. 2-Methyladamantane (**3**) and **4** are probably formed from **1** *via* the cations **10** and **11**, respectively.

References and Notes

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1) Part of this work was carried out at Princeton University under general support by NSF Grant GP-29078X.

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