

THE STRUCTURES OF TWO MAJOR INTERMEDIATES IN TRIFLUOROMETHANESULFONIC
ACID-CATALYZED REARRANGEMENT OF TRICYCLO[5.2.2.0^{2,6}]UNDECANE

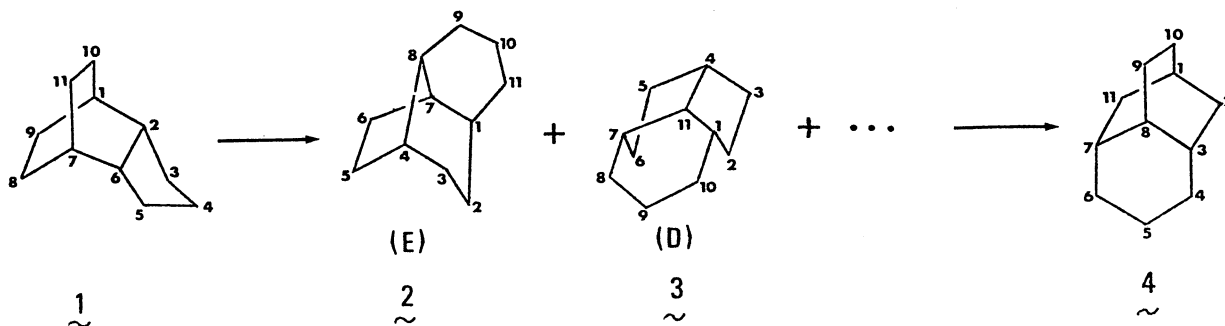
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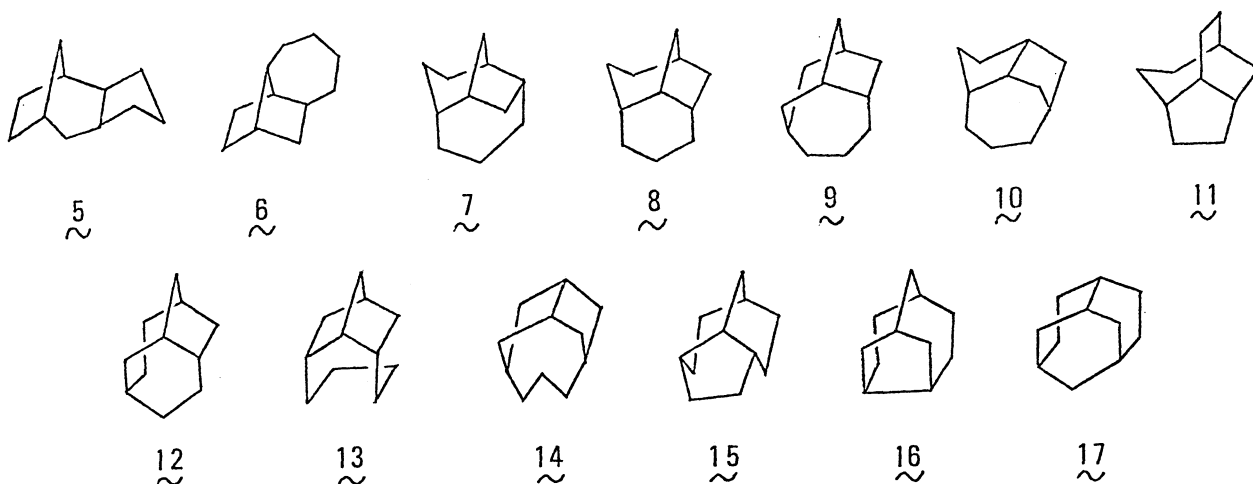
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Two major intermediates of unknown structure (unknown E and D) found in trifluoromethanesulfonic acid-catalyzed rearrangement of tricyclo[5.2.2.0^{2,6}]undecane (1) to 4-homoisotwistane (4) were identified as tricyclo[5.4.0.0^{4,8}]undecane (2) and tricyclo[5.3.1.0^{4,11}]undecane (3), respectively, by independent syntheses.

Brønsted acid catalysis in the rearrangement of cis-endo-2,3-trimethylenebicyclo[2.2.2]octane (tricyclo[5.2.2.0^{2,6}]undecane, 1) led to a predominant formation of 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane, 4) instead of methyladamantanes.¹⁻³ Methyladamantanes are thermodynamically the most stable isomers and, therefore, the ultimate rearrangement products.²⁻⁴ However, it was possible to make the rearrangement halt at the stage of 4-homoisotwistane (4) by appropriate choice in catalyst and reaction conditions.

In this rearrangement of 1 to 4, two major intermediates (unknown E and D)⁵ were detected among many others.³ It has been fully demonstrated²⁻⁴ that determination of the structure of intermediates is one of the most effective methods





of elucidating the reaction mechanism for this kind of complex, multiple step rearrangements. Structure determination of unknown E and D was thus undertaken.

A mixture of 0.2 g (1.33 mmol) of 1, 0.2 g (1.33 mmol) of trifluoromethanesulfonic acid, and methylene chloride (10 ml) was refluxed for 10 min, and the reaction was quenched by ice-water. A mixture of tricycloundecanes obtained in almost quantitative yield was fractionated on preparative VPC (SE-30, 150°), the last eluted fraction (31%) being collected to afford crude unknown E. A pure solid sample, giving only one peak on Golay VPC (SE-30 and Apiezon L, 60 - 70°), was obtained by double purifications on preparative VPC: mp 75 - 76° (sealed tube); IR (neat) 2930, 2870, 2730, 2680, 1480, 1450, 1340, 960, 900, 860 cm^{-1} ; ^1H NMR (CDCl_3) δ_{H} 1.0 = 2.2 (complex m); ^{13}C NMR (CDCl_3) δ_{C} (multiplicity) 20.9 (t), 23.9 (t), 25.0 (t), 28.8 (t), 30.1 (t), 31.0 (t), 33.1 (t), 34.6 (d), 39.5 (d), 40.2 (d), 41.0 (d); ms m/e (rel intensity) 150 (100, M^+), 122 (79), 121 (53), 108 (20), 107 (21), 94 (30), 93 (35), 81 (33), 80 (40), 79 (41), 67 (32), 41 (23). The ^{13}C NMR spectrum indicated that the molecule was asymmetric and moreover contained no quarternary carbon atom. Nine reasonably-stable tricycloundecanes (2, 5 - 12)^{6,7} among over 70 possible isomers⁸ are consistent with the ^{13}C NMR spectrum.

Tricyclo[6.2.1.0^{2,6}]undecane (cis-exo-2,3-trimethylenebicyclo[3.2.1]octane, 5) was prepared in a study of the acid-catalyzed rearrangement of tricycloundecanols.⁹ The spectral properties and the VPC behaviors of 5 were different from those of unknown E. A clue to further choice among the 8 other conceivable structures seems to be found in the kinetic behavior of unknown E in the rearrangement reaction: unknown E was formed first from 1. This suggests that unknown E is

formed from 1 via a relatively small number of isomerization steps. Tricyclo[5.4.0.0^{4,8}]undecane (exo-2,syn-8-trimethylenebicyclo[3.2.1]octane, 2) is mechanistically the closest to 1, since 2 can be derived by two 1,2-alkyl shifts from 1 after ionization of its angular (c-2) carbon atom, whereas more complicated, multiple transformations are required to reach the other structures, 6 - 12. Tricyclo[5.4.0.0^{4,8}]undeca-2,5,9-trien-11-one, which has the same molecular framework as that of 2, has been prepared by Groves.¹⁰ Synthesis¹¹ and subsequent hydrogenation over palladium on charcoal catalyst followed by Wolff-Kishner reduction of this tricycloundecatrienone gave an authentic specimen of 2. Golay GC-MS measurements and comparison of IR spectra definitely established the identity of unknown E and 2.

The concentration of unknown D was found to become maximum when the rearrangement reaction of 1 was run for 2 hr. The fraction (71%) eluted second from the last on the preparative VPC was separated, which was analyzed on Golay VPC to consist of 54% 4, 31% unknown D, and 15% unreacted 1. The ¹³C NMR spectrum of this mixture comprised 21 signals. Subtraction from these signals of 14 corresponding to those of 1 and 4 (6 signals for 1¹² and 8 for 4^{1-3a}) left 7 to be allotted to unknown D: δ_C (multiplicity, rel intensity) 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). The molecule of unknown D should thus have a C_s symmetry with one methylene and two methine groups on the σ plane.

Although 6 isomers (3,¹³ 13 - 17¹⁴) can satisfy this structural requirement, unknown D should most plausibly have the structure of tricyclo[5.3.1.0^{4,11}]undecane (cis-endo-2,8-trimethylenebicyclo[3.3.0]octane, 3) for the following reasons. The ¹³C NMR spectrum shows one methylene signal at an abnormally high field (δ_C 16.7). This signal reminds us of that (δ_C 15.2) assigned to C-5 of 4.^{2,3a} A large upfield shift of the cyclohexane carbon resonance was ascribed^{2,3a} to steric compression due to endo-hydrogens on the two β -axial-methylene substituents (C-2 and C-11 in 4). Of the above 6 isomers, only 3 has this structural feature.

This structure assignment of unknown D is indirectly supported by comparison of its mass spectrum (as determined on Golay GC-MS) with that of cis-endo-2,8-tetramethylenebicyclo[3.3.0]octane,^{13b,15} a higher homolog of 3. Both compounds exhibited a fairly similar spectral pattern in the region of $m/e \leq 108$; this is considered to arise from the bicyclo[3.3.0]octane system commonly

present in them. The structure of unknown D was determined unambiguously by comparison with an authentic specimen of 3 prepared according to the method of Rappoport: ¹³a mp 49 - 50° (lit., ¹³a 50°); IR (neat) 2920, 2860, 1460, 1450, 1440, 1360, 1340, 890, 870, 850, 790 cm⁻¹; ¹H NMR (CDCl₃) δ_H 1.1 - 2.2 (complex m); ms m/e (rel intensity) 150 (34, M⁺), 122 (100), 121 (49), 94 (24), 93 (41), 81 (29), 80 (56), 79 (44), 67 (34), 41 (33). The VPC retention time and the mass and ¹³C NMR spectra of both samples were in complete agreement with each other.

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- 5) For the notation of unknowns see Ref. 3b, Footnote 16.
- 6) Where configurational isomers are conceivable, only that structure which is considered the most stable is shown.
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- 11) An improved method was kindly informed us by Professor Groves.
- 12) δ_C (multiplicity, rel intensity) 20.4 (t, 2), 26.8 (t, 1), 27.4 (d, 2), 28.3 (d, 2), 30.2 (t, 2), 41.3 (t, 2).
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- 15) An authentic specimen was kindly supplied by Professor Paquette.

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