Identification of Intermediates in the Trifluoromethanesulfonic Acid Catalyzed Adamantane Rearrangement of 2,3-*endo*- and -*exo*-Tetramethylenenorbornane

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Eleven intermediates of unknown structure, besides 6,7-*exo*-trimethylenebicyclo[3.2.1]octane (*exo*-**7**) and homoadamantane (**8**), have been detected in the trifluoromethanesulfonic acid catalyzed adamantane rearrangement of 2,3-*endo*- and -*exo*-tetramethylenenorbornane (*endo*-**1** and *exo*-**1**) via 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **9**). Eight of these unknowns were now identified as 1,2-*endo*- and -*exo*-tetramethylenenorbornane (*endo*-**2** and *exo*-**2**), 1,2-trimethylenebicyclo[2.2.2]octane (**3**), [3.3.3]propellane (**4**), 1,2-*exo*-trimethylene-*cis*-bicyclo[3.3.0]octane (**5**), 1,7-*exo*-trimethylenebicyclo[3.2.1]octane (**6**), 7-methylisotwistane (**10**), and 1-methylisotwistane (**11**). Although ^{13}C NMR spectroscopy offered enough basis of structure determination for compounds with more or less symmetricity, independent syntheses were necessary for asymmetrical compounds. Time-conversion study of *endo*-**1**, *exo*-**1**, and **9** suggested that four (unknown C_2, *endo*-**2**, *exo*-**2**, and **3**) of these 11 intermediates were formed directly from the precursors and, therefore, true intermediates to **9**. Addition of adamantane or 1-methyladamantane to the reaction of *exo*-**1** effected increase in proportions of these four intermediates, accompanied by a considerable acceleration of the isomerization rate. The stable intermediate **9** then rearranges to a mixture of unknown C_1 and D, *exo*-**2**, **3**, **4**, **5**, **6**, *exo*-**7**, **8**, **10**, and **11**, of which only **8**, **10** and **11** isomerize to methyladamantane, while the others are in equilibrium with **9**.

In the aluminum chloride catalyzed adamantane rearrangement of 2,3-*exo*-tetramethylenenorbornane (*exo*-**1**)[1,2] was isolated 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, **9**)[3,4] as an intermediate.[5,6] The compound was shown to be one of the most stable tricycloundecane isomers on the basis of molecular mechanics calculation.[5] Careful examination of the reaction mixture enabled us to isolate and identify two other intermediates, 6,7-*exo*-trimethylenebicyclo[3.2.1.]octane (*exo*-**7**) and homoadamantane (**8**).[7] Our recent findings on the trifluoromethanesulfonic acid catalysis of the rearrangement,[7] together with use of fast isomerizing precursors[8] such as 2,3-*endo*-tetramethylenenorbornane (*endo*-**1**),[9] 2,3-trimethylenebicyclo[2.2.2]octane,[6-8,10] and 6,7-*endo*-trimethylenebicyclo[3.2.1]octane (*endo*-**7**),[8] indicated more than 20 intermediates of unknown structure to show up during the rearrangements. In this study, partially completed isomerization reactions were quenched and the mixture of products were separated into fractions by VPC and chemical reactions. Eight among 11 unknowns thus isolated in the rearrangement of 2,3-*endo*- and -*exo*-tetramethylenenorbornane (*endo*-**1** and *exo*-**1**) were assigned structures by means of independent syntheses or ^{13}C NMR spectroscopy.

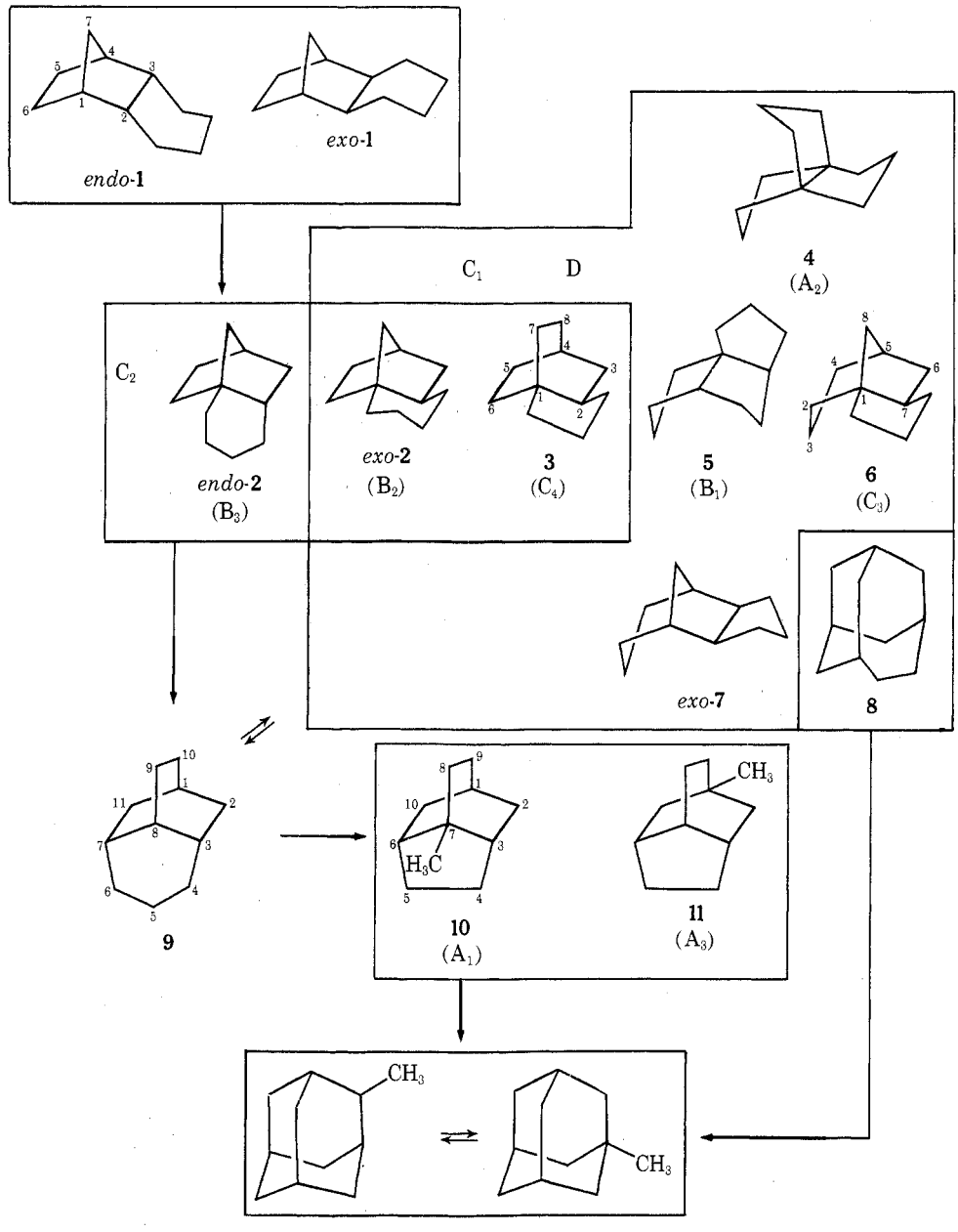
Identification of Unknown B_2, B_3, C_3, and C_4. Distribution of products in the isomerization of 2,3-*endo*- and -*exo*-tetramethylenenorbornane (*endo*-**1** and exo-**1**) as well as that of 4-homoisotwistane (**9**) was determined, as listed in Table I, on a Golay (capillary) column VPC–mass spectrometer with which was also taken the mass spectrum of each intermediate.[11] Fractions B and C were isolated with a preparative VPC[11] to measure total and off-resonance proton-decoupled ^{13}C NMR spectra. It was indicated that all the components of the fractions had quaternary carbon atoms. Little information will be obtainable by spectral methods about the structure of the unknowns, unless we have appropriate reference compounds. Therefore, syntheses of tricycloundecanes having quaternary carbon atoms were investigated.

1,2-Trimethylenebicyclo[2.2.2]octane (**3**)[3] is one of the two tricycloundecanes ever synthesized that are asymmetrical and contain quaternary carbon atoms.[12] The synthesis of **3**[3] was repeated to give an authentic specimen. The specimen was found to be identical with unknown C_4 on comparison of their VPC retention times and mass spectra.

1,6-Tetramethylene-2-norbornene was prepared[13] through an intramolecular Diels–Alder reaction of 1-(5-hexenyl)cyclopentadiene. Hydrogenation of the compound should give another asymmetrical tricycloundecane with a quaternary carbon atom. Although Brieger and Anderson[13] did not examine the homogeneity, nor determine the configuration, of their 1,6-tetramethylene-2-norbornene, we found a specimen synthesized according to their method to be a mixture. Separation of the olefin mixture, however, was impossible even in Golay columns, but hydrogenation over palladium on charcoal catalyst revealed the presence of two components in 2:1 ratio. We assigned the structure of 1,2-*exo*-tetramethylenenorbornane (*exo*-**2**) to the more abundant component for the following reasons. Exo compounds are usually more stable than endo isomers, as exemplified in 2,3-trimethylenenorbornane (**20**),[14] **1**,[8] and 6,7-trimethylenebicyclo[3.2.1]octane (**7**).[8] This would also be true for epimers of **2**. The reasoning may be supported by the exclusive formation of 1,6-*exo*-trimethylene-2-norbornene (**12**) in the intramolecular Diels–Alder addition of 1-(4-pentenyl)cyclopentadiene,[15] where the endo epimer would be too strained to be formed. An additional methylene group, however, should release a part of the strain in 1,6-*endo*-trimethylene-2-norbornene and make the energy difference between epimers of 1,6-tetramethylene-2-norbornene less than it would be without the additional methylene group. Thus 1,6-*endo*-tetramethylene-2-norbornene may have some degree of stability and could be formed in the reaction of 1-(5-hexenyl)cyclopentadiene. Secondly, the more abundant component of the mixture was eluted ahead of the other in several VPC columns. We have noticed exo isomers of 2,3-trimethylenenorbornane (**20**), **1**, and **7** to have shorter retention times than the corresponding endo isomers. The more abundant component of the mixture was in this way assigned the structure of *exo*-**2**. *exo*-**2** was then found to have the same VPC retention times as those of unknown B_2, and their mass spectra were also identical. Similarly, unknown B_3 was identified as *endo*-**2**.

1,7-*exo*-Trimethylenebicyclo[3.2.1]octane (**6**), another new, asymmetrical tricycloundecane containing a quaternary carbon atom, was obtained from 1,6-*exo*-trimethy-

Chart I



lene-2-norbornene (**12**)[15] through a series of reactions. Dichlorocarbene ring expansion[7,8,16] of **12** gave in 47% yield a mixture consisting of 84% 3,4-dichloro-5,6-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**13**) and 16% 3,4-dichloro-1,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**14**). The more abundant constituent of the mixture was assigned the structure **13** because of the ^{1}H NMR signal (δ 4.18) of the mixture assignable to the 4 proton showed a singlet. By sodium–liquid ammonia dechlorination[8,17] the mixture was transformed in 31% yield into a mixture of 86% 5,6-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**15**) and 14% 1,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (**16**). No structural alteration was assumed during dechlorination. Both olefins were hydrogenated over palladium on charcoal catalyst to the identical product, **6**, in 96% yield (Chart II).

Total and off-resonance proton-decoupled ^{13}C NMR spectra of thus synthesized authentic **6** (Table II) contained 11 resonances that comprised one singlet, two doublets, and eight triplets. All the signals had a similar intensity, except for the singlet at lowest field, which was less intense than the others and hence assigned to the quaternary carbon atom. The spectrum, therefore, was in good agreement with the structure. Compound **6** was found identical with unknown C_3 on comparison of VPC retention time and mass spectra.

^{13}C NMR Spectra as Supporting Evidence for the Identification of Unknowns. Identification of unknown B_2, B_3, C_3, and C_4 by VPC retention time and mass spectrum as described in the preceding section is further supported by ^{13}C NMR spectroscopic evidences. Fraction C isolated from the reaction mixture of run 21 (Table I) on a preparative VPC[11] consisted only of C_3 (**6**) and C_4 (**3**) in about 3:1 ratio, as shown in Table I. The fraction exhibited 21 ^{13}C NMR signals in a total decoupled spectrum. These absorptions could be divided into two sets according to the relative intensity: each ten signals with relative intensities of 3 and 1, respectively. The last one, with an intensity of 4, should belong to both sets. One resonance at lowest field in each set had somewhat smaller intensity than other members of the set it belonged to. Eleven signals with higher intensities including one with an intensity of 4 were divided into one singlet for the lowest field signal, two doublets, and eight triplets, on off-resonance proton decoupling. The chemical shifts, relative intensities, and splittings in the

Table I
Distribution of Intermediates in the Rearrangements of Tricycloundecanes[a]

Run	Reactant	Catalyst (mol equiv)[d]	Reaction time, hr (min)	Product,[b] %[c] A_1 (10)	A_2 (4)	A_3 (11)	1-Me-Ad	B_1 (5)	B_2 (*exo*-2)	B_3 (*endo*-2)	C_1 (unknown)	C_2 (unknown)	C_3 (6)	C_4 (3)	2-Me-Ad	*exo*-7	D (unknown)	9	Homo-adamantane
1	*endo*-1	T (1.0)	(1)						4.0	3.5		2.1		0.7			2.1	21.8	
2			(2)						8.8	6.2		3.5		1.3			2.2	42.1	
3			(4)						15.4	8.2		4.2		1.4			5.1	59.4	
4			(17)						15.5	7.7		4.4		1.5			5.0	58.1	
5			2						14.3	6.8		4.3		1.6			5.0	57.8	
11	*exo*-1	T (1.0)	24						1.5	0.3		0.7		0.3		0.4	1.5	10.4	0.3
12[e]			(10)						7.8	4.1		2.0		0.7			1.0	8.3	
21	*exo*-1	T (3.0)	5.5	0.5		1.0	2.3	8.9	11.6		0.2		14.8	5.0	2.6	3.3	2.8	43.0	2.5
31	*exo*-1	A (0.15)	(14)			0.7		2.9	17.2				7.9	3.6	2.9	0.6	2.8	45.8	
32			(40)	0.6		1.9	1.5	10.6	8.1				13.9	5.2	6.3	4.0	2.6	44.3	1.0
33			(80)	1.2		2.0	3.7	13.7	4.2		0.3		13.9	4.6	7.7	5.1	3.2	37.1	2.3
34			3	2.6	1.0	5.0	28.9	9.8	0.5		1.1		4.5	1.2	23.7	5.3	0.7	14.5	0.3
41	9	T (2.0)	(35)					1.0					2.1	5.2	0.2	0.2	3.9	83.5	
42			2					1.6					3.7	6.3	0.7	0.9	4.6	79.0	
43			6					2.7	0.3				6.6	7.6	1.2	1.4	4.8	70.9	0.8
51	9	T (4.0)	1	0.1		0.3	1.6	8.2	2.1				14.7	4.9	3.2	4.1	4.5	51.8	2.3
52			100	3.1	0.7	6.2	20.3	11.6[f]	0.9		1.5		5.1	1.4	25.2	5.5	1.3	15.0	1.2

[a] 100 mg of reactant in 5 ml of methylene chloride at reflux. [b] Combined yield of the intermediates and final products (methyladamantanes) were almost quantitative. Products were analyzed on a Golay GC–MS and aligned in the order of increasing retention time. [c] That of the VPC peak area. In case the sum of figures is less than 100, the balance consists of the unreacted starting material together with a few percent by-products. [d] T, trifluoromethanesulfonic acid; A, aluminum chloride ($AlCl_3$). Figures in parentheses are molar equivalents of the catalyst to reactant. [e] A reaction in the presence of 0.2 molar equiv of 1-methyladamantane. All the 1-methyladamantane detected in product analysis was considered to be that added at the beginning, and percentage composition of the products was calculated for the rest of the compounds. [f] Considered to contain a small amount of unknown compound(s) other than those which have been detected so far, as is indicated by mass spectrum.

Chart II

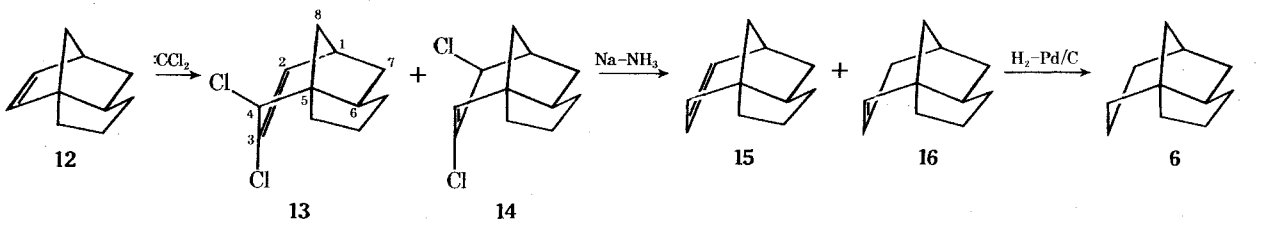


Table II
^{13}C NMR Spectra of Tricycloundecanes

Compd: Notation as unknown	Compd: Structure	^{13}C NMR signals, ppm (multiplicity, rel intensity)[a]
	endo-**1**	20.4 (t, 2), 20.7 (t, 2), 23.0 (t, 2), 39.3 (d, 2), 39.9 (t, 1), 41.2 (d, 2)
	exo-**1**	19.6 (t, 2), 23.6 (t, 2), 30.0 (t, 2), 33.1 (t, 1), 42.6 (d, 2), 43.3 (d, 2)
B_3	*endo*-**2**	23.2 (t, 1), 26.5 (t, 1), 26.9 (t, 1), 27.2 (t, 1), 32.2 (t, 1), 33.7 (t, 1), 35.1 (t, 1), 36.9 (d, 1), 45.0 (d, 1), 45.3 (t, 1), 46.5 (s, 0.7)
B_2	*exo*-**2**	24.6 (t, 1), 26.5 (t, 1), 30.6 (t, 1), 31.6 (t, 1), 34.2 (t, 1), 37.6 (d, 1), 37.7 (t, 1), 38.4 (t, 1), 39.3 (t, 1), 42.1 (d, 1), 46.3 (s, 0.6)
C_4	**3**[b]	21.8 (1), 24.4 (1), 26.0 (1), 29.3 (1), 29.4 (1), 31.3 (1), 32.6 (1), 36.1 (1), 44.4 (1), 48.0 (1), 50.4 (s, 0.5)
A_2	**4**	31.8 (t, 3), 39.4 (t, 6), 60.4 (s, 1.7),
B_1	**5**	26.8 (t, 2), 33.5 (t, 2), 33.6 (t, 2), 42.1 (t, 2), 52.4 (d, 2), 62.0 (s, 0.5)
C_3	**6**	21.3 (t, 1), 26.8 (t, 1), 31.9 (t, 1), 35.6 (t, 1), 37.2 (t, 1), 38.3 (t, 1), 38.6 (t, 1), 39.0 (d, 1), 44.4 (t, 1), 47.4 (d, 1), 52.9 (s, 0.7)
A_1	**10**	24.8 (t, 1), 28.4 (q, 1), 31.7 (t, 3), 40.5 (t, 2), 45.5 (d, 1), 52.8 (d, 2), 62.8 (s, 0.8)
A_3	**11**	24.8 (t, 1), 27.8 (q, 1), 31.7 (t, 1), 31.8 (t, 2), 40.5 (t, 2), 45.5 (d, 2), 51.4 (s, 0.7), 61.7 (d, 1)

[a] In parts per million downfield from the internal Me_4Si standard. [b] The signal was constructed from that of the mixture of 3 and 6. Fine structure of the signals of 3 was too complex to be analyzed because of a small concentration of 3 in the mixture. See text and also ref 18.

spectra of unknown C_3 thus constructed from those of the fraction C were in complete agreement with the corresponding values of authentic **6** listed in Table II. The remaining 11 resonances should be assigned to unknown C_4 (**3**), and reported in Table II.[18] These resonances became so complex, mainly because of low intensity, on off-resonance proton decoupling that no definite fine structure could be observed except for the singlet at lowest field.

Although authentic *endo*-**2** and *exo*-**2** were not isolated on a preparative VPC from their mixture prepared above (*exo*-**2**:*endo*-**2** 2:1), ^{13}C NMR spectra of each compound were obtainable from those of the mixture on consideration of the intensity. Eleven, stronger absorptions among 21 for the mixture were assigned to the more abundant constituent, *exo*-**2**, while the remaining ten were assigned to *endo*-**2**. The 11th resonance of *endo*-**2** coincided with one of *exo*-**2**'s resonance (26.5 ppm), as evidenced from its intensity (3). Fine structure of the off-resonance proton decoupled spectrum of the mixture was analyzable fairly easily to deduce splitting of each absorption. Spectra of *endo*-**2** and *exo*-**2** constructed in this way are listed in Table II. The fraction B isolated from the reaction mixture of run 4 (Table I) contained only unknown B_2 (*exo*-**2**) and B_3 (*endo*-**2**) in 2:1 ratio. Total proton-decoupled spectrum of the fraction B was exactly a reproduction of what was observed from the standard spectra of *exo*-**2** and *endo*-**2** taken in 2:1 intensity ratio.

Consideration of the intensity and splitting of the signals in relation to the symmetry property of the molecule is the only way of assigning ^{13}C NMR signals in polycyclic hydrocarbons,[19] unless appropriate reference compounds with definitely assigned spectra are available. Assignment of the signals of above four asymmetrical intermediate tricycloundecanes was impossible since no such reference spectrum was available at present.

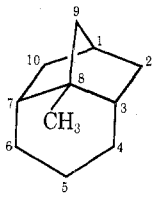
Structure of Unknown A_1, A_2, and A_3. Aluminum chloride catalyzed isomerization of *exo*-**1** (run 34) gave a mixture containing a reasonably large amount (8.6%) of fraction A. Treatment of the mixture with bromine at room temperature followed by fractional distillation of the product enabled the isolation of a mixture of unbrominated compounds. These were found on VPC analysis mainly consisted of unknown A's, B's, C's, and *exo*-**7**. 1- and 2-methyladamantane, **9**, and homoadamantane were thus almost completely removed from the isomerization product. The result is well understood in view of the high reactivity of bridgehead hydrogens of methyladamantanes,[20-22] homoadamantane,[21] and **9**[23] toward bromine. Fraction A concentrated in this procedure was then separated from the other unbrominated hydrocarbons on the preparative VPC. Isolated fraction A was again fractionated on VPC, when the former (early eluted) and the latter parts of the peak were collected spearately. The former part of the peak comprised A_1, A_2, and A_3 in 3.3:1.0:1.3 ratio, while the latter part contained them in 1.1:1.0:3.2 ratio.

Both of these specimens of fraction A exhibited 13 resonances in total proton-decoupled ^{13}C NMR specta. Fine structure of the off-resonance proton decoupled spectra was clear enough to show splitting of each resonance signal. By comparison of intensities of the signals with reference to the concentration of the constituents, it was possible to construct each spectrum of the component compound.

Unknown A_2 had by far the simplest spectrum: three signals [s (rel intensity somewhat less than 2), t (6), and t(3)]. [3.3.3]Propellane (**4**) is definitely the only tricycloundecane[24] corresponding to the spectrum, and the assignment of the signals are quite unambiguous only on the basis of their intensities and fine structures. Although some [3.3.3]propellanones were known,[25] the hydrocarbon does not seem to have been prepared or detected before. The mass spectrum of **4** was also highly characteristic, comprising three strong peaks [150 (rel intensity 40, M^+), 107 (100), and 79 (27)], and is very well consistent with the structure.

A similarity in the mass spectra of A_1 and A_3 had suggested a similar skeletal structure for them. The view was strengthened by ^{13}C NMR spectra, which showed the presence of eight kinds of carbon atoms, including a quaternary and a methyl. Actually A_1 exhibited only seven resonances (Table II). However, the relative intensity of the signal at 31.7 ppm (3) indicates that two kinds of carbon atoms would have a coincidently identical chemical shift. Two sharp singlets in ^{1}H NMR spectra of the specimens of fraction A also confirmed the presence of a methyl in each

compound. The singlet methyl group in turn indicates that it would be one of the substituents on the quaternary carbon atom. Two alternative structures, **10** (and **11**) or **17** (and **18**), correspond to the ^{13}C and ^{1}H NMR spectra.



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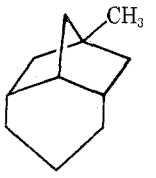

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However, the homobrendane structure (**17** and **18**) could be excluded for the following reasons. The C-5 atom of **9** has a ^{13}C NMR resonance at exceptionally high field (15.2 ppm). This was successfully explained[6,7] with a combined effect of two axial methylene groups (C-2 and C-11) at the C-3 and C-7 and one equatorial methylene (C-9) at the C-8. Homobrendane has similar structural features, and its 5-methylene carbon atom should exhibit a resonance at as high a field as 15 ppm. No such absorption was observed for specimens of fraction A.

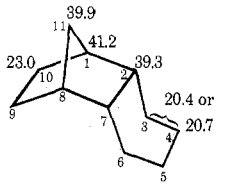
Secondly, mass spectra of A_1 and A_3 showed the base peak at *m/e* 94, indicating a loss of four carbon atoms to be the most favorable process. Fragmentation of ethano bridges (e.g., C-4 and C-5 followed by either C-2 and C-3, C-8 and C-9, or C-6 and C-10) in **10** and **11** may well account for the spectra, whereas **17** and **18** can not offer any convenient explanation.

Thirdly, result of the bromination of the isomerization mixture from *exo*-**1** may support the structure **10** and **11.** Bridgehead reactivity of bicyclononanes and -decanes was shown to be at least 10^3 times larger than that of bicyclooctanes and -heptanes.[21] Facile bromination of methyladamantanes (which may be regarded as 3,7-methanobicyclo[3.3.1]nonane), **9** (3,9-ethanobicyclo[3.3.1]nonane), and homoadamantane (3,7-methanobicyclo[3.3.2]decane), compared to that of B's, C's, and *exo*-**7** which are all bicyclooctanes and -heptanes, is in good agreement with the above reactivity. Low reactivity of A's therefore might be attributed to their bicyclic structure not larger than bicyclooctane. Structure **10** and **11** containing a bicyclo[3.2.1]octane skeleton can satisfy the requirement, but **17** and **18,** which are a bicyclo[3.3.1]nonane, cannot.

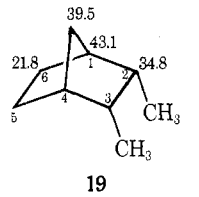
Comparison of the chemical shifts of the quaternary carbon atom and the tertiary carbon atoms giving the double intensity signals in A_1 and A_3 seems to help in determining the position (1 or 7) of the methyl group. The resonance of a carbon atom either in open chain or in ring system is always shifted to lower field by branching on that carbon atom and/or on the adjacent carbon atoms.[26] The chemical shift of the quaternary carbon atom of A_1 (62.3 ppm) is at lower field than that of A_3 (51.4 ppm). The result suggests assignment of the structure **10** to A_1, in which the quaternary (7) carbon atom should have a lower field signal under the influence of two vicinal (3 and 6) branchings. The assignment is supported by the comparison of the chemical shifts of the doublet carbon atoms at the 3 and 6 positions in both compounds (52.8 for A_1 and 45.5 ppm for A_3). Lower field absorption in A_1 would be ascribed to the effect of extra branching at the C-7 atom in **10.** Assignment of other signals of A_1 and A_3, except for the single intensity doublets, cannot be effected because of the lack of reference spectra.

Structure Determination of Unknown B_1. After fraction A had been isolated from the distilled unbrominated hydrocarbon mixture on the preparative VPC as described in the preceding section, fraction B was also collected in the same experiment. The fraction was found to contain 90% B_1 and 10% B_2 (*exo*-**2**). A total proton-decoupled ^{13}C NMR spectrum of fraction B comprised six peaks. Eleven signals of *exo*-**2,** which should appear in the spectrum, could hardly be discerned in noise signals. The lowest field signal (rel intensity less than 1) stayed singlet, while the other five (each with rel intensity 2) split into one doublet and four triplets, in off-resonance proton decoupling. The unique ^{13}C NMR spectra of unknown B_1 offered a sufficient basis for the determination of its molecular structure. 1,2-*exo*-Trimethylene-*cis*-bicyclo[3.3.0]octane (**5**), which has a molecular symmetry of C_2, is the only compound[27] corresponding to the observed spectra among all the possible tricycloundecane isomers.[24] No definite assignment of the signals, except the single-intensity singlet and the double-intensity doublet, was possible for this compound.

^{13}C NMR Spectra of 2,3-*endo*- and -*exo*-tetramethylenenorbornane (*endo*-1 and *exo*-1). ^{13}C NMR spectra of *endo*-**1** and *exo*-**1** do not seem to have been measured before. Their spectra (Table II) indicated an interesting correlation between the change in the chemical shifts and that in the configurations. Assignment of most of the signals of *endo*-**1** and *exo*-**1** was made with reference to those of 2,3-*endo*- and -*exo*-dimethylnorbornane (**19** and **20**)[28] as shown below, with the assumption that the carbon atoms in



endo-**1a**



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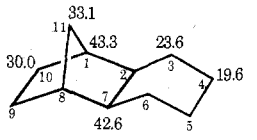
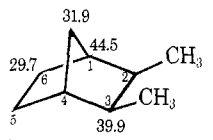


exo-**1a**



20

comparable molecular environments have similar chemical shifts.

Assignment of 39.9- and 33.1-ppm signals to the C-11 atoms in *endo*-**1a** and *exo*-**1a,** respectively, will be unequivocal on the basis of the intensities (1) and fine structures (triplet) of these signals. Since the tertiary C-2 and C-3 atoms are at higher field than the bridgeheads (C-1 and C-4) in both **19** and **20,** the double-intensity doublet signals at higher field in both *endo*-**1** and *exo*-**1** (39.3 and 42.6 ppm) were assigned to the angular atoms (C-2 and C-7 in *endo*-**1a** and *exo*-**1a**), while those at lower field (41.2 and 43.3 ppm) were assigned to the bridgeheads (C-1 and C-8). Supposing that 2,3-*exo*-dimethyl and 2,3-*exo*-tetramethylene groups may exert a similar influence on the chemical shifts of C-5 and C-6 in norbornane, the 30.0-ppm double-intensity triplet of *exo*-**1** was assigned to C-9 and C-10 in *exo*-**1a.** With the same reasoning, the 23.0-ppm signal in *endo*-**1** could be assigned to C-9 and C-10 in *endo*-**1a.**

The C-4 and C-5 atoms in *endo*-**1a** and *exo*-**1a** are in the same molecular environment except that the configuration of the C-1 and C-8 atoms are opposite to each other. Under the probably small influence of C-1 and C-8 on C-4 and C-5 in either isomer because of the separation by two carbon atoms, C-4 and C-5 in *endo*-**1a** should have a similar chemical shift as that of C-4 and C-5 in *exo*-**1a.** The 19.6- and either of the 20.4- and 20.7-ppm signals were thus assigned to these atoms in *exo*-**1a** and *endo*-**1a,** respectively. Distinction between the 20.4- and 20.7-ppm signals in *endo*-**1**

seems to be impossible only on the basis of reference spectra now available.

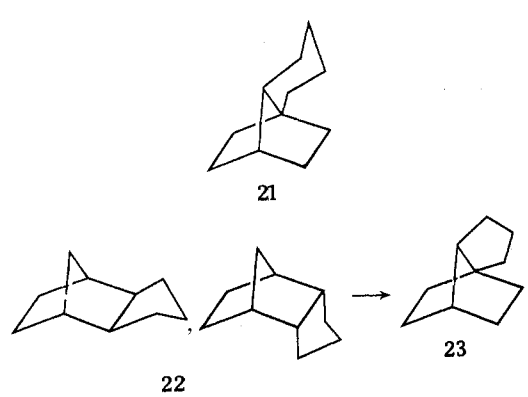
It may be interesting to note that the signal for the C-9 and C-10 atoms in *endo*-**1a** (23.0 ppm) is at fairly high field compared to that for the corresponding atoms in *exo*-**1a** (30.0 ppm). This would be ascribed to the effect of two β-axial substituents (C-2 and C-7) in *endo*-**1a**. Although the upfield shift of signals under the influence of this kind of nonbonded intereactions has been established in cyclohexanes[26] and norbornanes,[19,28] no example seems to have been recognized for tricycloundecanes. The signal for the C-11 atom in *endo*-**1a** (39.9 ppm) is at somewhat lower field than that of the corresponding atom in *exo*-**1a** (33.1 ppm). Comparison with the C-7 signal of norbornane (38.7 ppm)[26] indicates that the chemical shift of the C-11 in *endo*-**1a** is just normal, whereas that of the C-11 in *exo*-**1a** is brought upfield. Nonbonded interaction with C-3 and C-6 may also explain this upfield shift of C-11 in *exo*-**1a**.

Accelerated Isomerization of 2,3-*exo*-Tetramethylenenorbornane (*exo*-1) in the Presence of 1-Methyladamantane. It was found that the disappearance rate of *exo*-**1** under trifluoromethanesulfonic acid catalysis was greatly increased in the presence of 1-methyladamantane.[29] The reaction was accelerated progressively with increase in the amount of 1-methyladamantane added, until it amounted to about 0.2 molar equiv to *exo*-**1** (run 12), where disappearance of *exo*-**1** was about 10^2 times faster than that in its absence. Beyond that amount of 1-methyladamantane, no appreciable increase in the effect was observed. Presence of 1-methyladamantane in the reaction also affected the product distribution. Amounts of unknown C_2, *endo*-**2**, *exo*-**2**, and **3** relative to that of **9** were appreciably increased, compared to those in the reaction without 1-methyladamantane (run 11).

Adamantane also showed the same effect but to a lesser extent. In this case product analysis was nullified because of the coincidence of the VPC retention time of adamantane with that of fraction C or D depending on the column used. Addition of 1 molar equiv of methylcyclohexane brought about entire extinction of the rearrangement of *exo*-**1** in the presence of 1.5 molar equiv of the catalyst.

Discussion

A variety of tricycloundecane precursors have been shown[4-8,10] to isomerize first to the stable intermediate, 4-homoisotwistane (**9**), which then rearranges to final products, methyladamantanes. As would be evident from runs 1–5, 11, and 12 (Table I), four metastable intermediates, unknown C_2, *exo*-**2** (B_2), *endo*-**2** (B_3), and **3** (C_4), are involved in the rearrangement pathway from *endo*-**1** or *exo*-**1** to **9** (Chart I). It seems reasonable to assume that *exo*-**2**, *endo*-**2**, and **3** are derived from 1,7-tetramethylenenorbornane (**21**). The unstable intermediate **21** can be obtained from *endo*-**1** or *exo*-**1** by abstraction of 2-hydride and 1,2-alkyl shift of the 6-methylene group. Assumption of the intermediacy of **21** was made on the basis of the mechanism of the C_{10} adamantane rearrangement recently established by Schleyer,[30] in which 2,3-trimethylenenorbornane (**22**) gave unstable 1,7-trimethylenenorbornane (**23**) in the first, rate-determining step of the rearrangement. The intermediate **21** is indeed a C_{11} counterpart of **23**. An appropriate 1,2-alkyl shift in **21** would lead to either of *exo*-**2**, *endo*-**2**, and **3**.



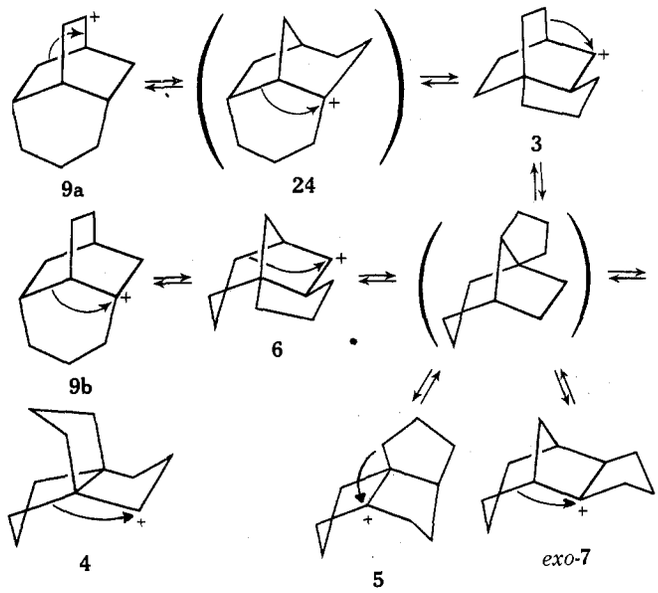
An increase in the proportion of C_2, *exo*-**2**, *endo*-**2** and **3** relative to **9** on the addition of 1-methyladamantane to the reaction of *exo*-**1** may be explained in terms of hydride transfer from 1-methyladamantane. Cations of C_2, *exo*-**2**, *endo*-**2**, and **3** formed from **21** should undergo two reactions competitively: one is hydride abstraction from any surrounding hydrocarbons to become neutral molecules, and the other is further rearrangement leading to **9**. 1-Methyladamantane should donate its tertiary hydrides very easily to cations. This decreases the concentration of the intermediate cations and hence of **9** derivable from them.

Acceleration of the isomerization rate by 1-methyladamantane would be a result of an increase in the total concentraton of cationic species on addition of easily ionizable 1-methyladamantane. If abstraction of 2-hydride in *exo*-**1** is rate determining, as in the C_{10} adamantane rearrangement,[30] the process should be favored in the presence of more abundant cations which are capable of hydride abstraction and, therefore, Lewis acids. Methylcyclohexane may work more as a hydride donor than as an abstractor because its cation would be relatively unstable at the temperature of refluxing methylene chloride owing to the aliphatic nature.[31]

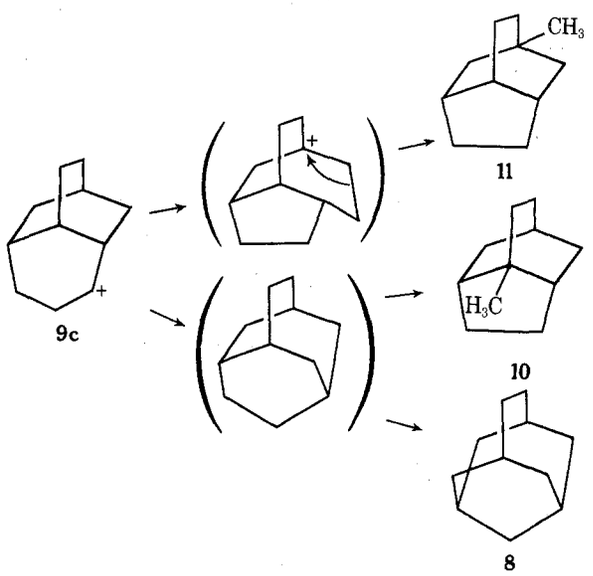
Of the four metastable intermediates derived from **21**, unknown C_2 and *endo*-**2** isomerized irreversibly to **9**, while *exo*-**2** and **3** seem to be in equilibrium with **9** since these two were formed also from **9** (runs 43–52). The fact that *endo*-**2** isomerized irreversibly to **9** whereas *exo*-**2** was in equilibrium with it may indicate a larger stability of *exo*-**2** than that of *endo*-**2**, and is in good agreement with the assignment of configuration for these isomers.

Rearrangement of **9** gives rise, in addition to *exo*-**2** and **3**, to a large number of products: unknown C_1 and D, [3.3.3]propellane (**4**, A_2), 1,2-*exo*-trimethylene-*cis*-bicyclo[3.3.0]octane (**5**, B_1), 1,7-*exo*-trimethylenebicyclo[3.2.1]octane (**6**, C_3), 6,7-*exo*-trimethylenebicyclo[3.2.1]octane (*exo*-**7**), homoadamantane (**8**), 7-methylisotwistane (**10**, A_1), and 1-methylisotwistane (**11**, A_3). All of these compounds except **10** and **11** seems to be in equilibrium with **9**, since rearrangement of them gave **9** as a product.[32] *exo*-**7** has been shown in a previous study[7] to be in equilibrium with **9**. The apparent equilibria between **9** and its isomerization products may be due to mutual interconversions among these compounds through 1,2-alkyl shift. An example of a mostly hypothetical isomerization sequence is cited below to show how interconversions might be realized. All the isomerizations in the scheme were so devised that they involved only assisted[33] or bridgehead ionization and 1,2-shift of those alkyl groups which were as much trans periplanar as possible to the developing(ed) vacant p orbital on the vicinal carbon atom.[34,35] This might make the scheme more than only imaginary. Intermediacy of 4-homoisotwist-3-yl cation (**9b**) would be highly probable because it should be the most stable of all the possible cations of **9** as is suggested from functionalization reactions of **9**.[23] The cation **9b** alone, however, could not explain a seemingly primary formation of **3** in the reaction of **9** (run 41). A

route from 4-homoisotwist-10-yl cation (**9a**) via 2,7-*endo*-trimethylenebicyclo[3.2.1]oct-2-yl cation (**24**) seems to be a possible alternative.



Methylisotwistanes (**10** and **11**) gave 1- and 2-methyladamantane as sole products of rearrangement.[32] A previous study[7] indicated the existence of a route via homoadamantane in the rearrangement of **9** to methyladamantanes. Accordingly, there should be at least three competitive pathways involving **8**, **10**, and **11**, respectively, from **9** to methyladamantanes. 4-Homoisotwist-4-yl cation



(**9c**) may be supposed as a common precursor to these intermediates, as shown in the scheme. Ionization of the 4-methylene group in **9** would be a process with relatively high activation energy that would account for the slow rearrangement of **9** to methyladamantanes, compared to that of **1** and other precursors to **9**.[6-8]

The result of the rearrangement of methylisotwistanes (**10** and **11**) seems to indicate that a methyl group once expelled out of a ring system can never be incorporated back again. The phenomenon was also observed in a mechanistic study of the conversion of 2-methyladamantane to the 1-methyl isomer using ^{13}C-labeled specimens[35] as well as in our study of the adamantane rearrangement of 2,4-*exo*-ethanobicyclo[3.3.1]nonane via 2-*endo*-methyl-2,3-*exo*-trimethylenenorbornane as an intermediate.[36] No return of the methyl group back into the ring would be an important clue in clarifying the rearrangement mechanism.[32]

Experimental Section

All melting and boiling points are uncorrected. Instruments for the measurement of spectra and for conventional and capillary column VPC were the same as were used in the previous work,[7,8,36] except that ^{13}C NMR spectra were measured at 25.14 MHz on a JEOL JNM PS-100 spectrometer equipped with JNM PFT-100 pulse Fourier transform. All the ir spectra were taken on neat samples. Deuteriochloroform was used as the solvent for NMR spectroscopy. Chemical shifts are reported in δ for protons and in parts per million downfield from internal Me_4Si standard for ^{13}C nuclei. Trifluoromethanesulfonic acid was a commercial product of 3M Co. Methylene chloride was dried over anhydrous calcium chloride and distilled immediately before use.

Authentic specimens of 6,7-*exo*-trimethylenebicyclo[3.2.1]octane (*exo*-**7**)[7] and 4-homoisotwistane (**9**)[10] were obtained before. 1,2-Trimethylenebicyclo[2.2.2]octane (**3**),[3] 1,6-tetramethylene-2-norbornene,[13] and 1,6-*exo*-trimethylene-2-norbornene[15] were prepared as described in the literature. Spectra of **3** synthesized:[18] ir 2930, 2860, 1460, 1450 cm^{-1} (lit.[3] ir 2942, 2868, 1461, 1454 cm^{-1}); MS *m/e* (rel intensity) 150 (40, M^+), 135 (12), 122 (17), 121 (100), 108 (10), 107 (15), 95 (12), 94 (30), 93 (24), 91 (11), 81 (25), 80 (32), 79 (36), 77 (11), 67 (28), 55 (13).

A Mixture of 1,2-*endo*- and -*exo*-Tetramethylenenorbornane (*endo*-2 and *exo*-2). A solution of 1.0 g (6.67 mmol) of 1,6-tetramethylene-2-norbornene in 30 ml of ether and 0.1 g of a palladium on charcoal catalyst (containing 5% metal) were placed in a 100-ml autoclave. After air in the vessel was replaced with hydrogen, the contents were hydrogenated with efficient stirring for 30 min at room temperature at a pressure of 5 kg/cm^2. The catalyst was filtered off from the reaction mixture, and the filtrate was fractionally distilled to give 0.9 g (89% yield) of a mixture containing 67% *exo*-**2** and 33% *endo*-**2**: bp 100–102° (36 mm); ir 2950, 2870, 1480, 1460, 1450, 1335, 1315, 1300, 1230, 1180, 1160, 1005, 910, 890, 880, 830 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.65; H, 12.30.

Mass spectra were taken on the Golay GC–MS instrument. *exo*-**2**: *m/e* (rel intensity) 150 (48, M^+), 135 (21), 122 (26), 121 (100), 108 (19), 93 (32), 81 (26), 79 (42), 67 (40), 41 (32). *endo*-**2**: *m/e* (rel intensity) 150 (69, M^+), 135 (75), 122 (30), 121 (100), 108 (40), 93 (50), 81 (40), 79 (66), 67 (54), 41 (57).

^{13}C NMR spectra were measured on the mixture, and the signals were allotted to each isomer according to their relative intensities (see text). Chemical shifts and multiplicities of the signals of *endo*-**2** and *exo*-**2** obtained in this way are listed in Table II.

A Mixture of 3,4-Dichloro-5,6-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (13) and 3,4-Dichloro-1,7-*exo*-trimethylenebicyclo[3.2.1]oct-2-ene (14). To a mixture of 4.3 g (0.032 mol) of 1,6-*exo*-trimethylenenorborn-2-ene (**12**), 7.2 g (0.128 mol) of sodium methoxide, and 40 ml of petroleum ether was dropped with efficient stirring 20 g (0.103 mol) of ethyl trichloroacetate in a period of 3 hr, while the reaction mixture was kept below 0° by external cooling in an ice–salt bath. The reaction mixture was stirred for another 4 hr at 0°, and then allowed to warm up to ambient temperature overnight. The mixture was poured onto 100 ml of an ice–water mixture. The separated aqueous layer was extracted first with four 50-ml portions of ether and then, after being acidified with 10% hydrochloric acid, with two 50-ml portions of ether. The combined organic layer and ether extracts were washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. Fractional distillation of the solution gave 4.1 g (47% yield) of a mixture consisting of 84% **13** and 16% **14**: bp 95–98° (0.25 mm); ir 2950, 2870, 1740, 1625, 1470, 1445, 1050, 970, 855, 740, 700 cm^{-1}; ^1H NMR δ 0.9–3.0 (complex m, 12), 4.18 (s, 1, CHCl), 6.07 (d, 1, J = 7 Hz, C=CH).

Anal. Calcd for $C_{11}H_{14}Cl_2$: C, 60.85; H, 6.50; Cl, 32.65. Found: C, 60.60; H, 6.50; Cl, 32.65.

13: MS *m/e* (rel intensity) 218 (9, M^+), 216 (13, M^+), 181 (37), 139 (29), 127 (36), 125 (100), 115 (15), 91 (25), 77 (22), 41 (30). **14**: MS *m/e* (rel intensity) 218 (18, M^+), 216 (27, M^+), 181 (25), 145 (35), 139 (29), 138 (69), 127 (39), 126 (36), 125 (100), 115 (28), 113 (68), 91 (30), 77 (47), 41 (25).

A Mixture of 5,6- and 1,7-*exo*-Trimethylenebicyclo[3.2.1]oct-2-ene (15 and 16). To 63 ml of liquid ammonia kept below −50° in a Dry Ice–acetone bath was added with stirring 7.8 g

(0.34 g-atom) of sodium metal in small portions in a period of 30 min, and the mixture was stirred for a further 30 min at the same temperature. A solution of 3.8 g (0.0175 mol) of the mixture of **13** and **14** prepared above in 30 ml of ether was added dropwise to the above mixture in a period of 45 min while the temperature was kept below −50°, and the reaction was stirred for another 2 hr at the same temperature. To the reaction mixture was added dropwise 30 ml of ether at room temperature while liquid ammonia was allowed to evaporate freely. Any unreacted sodium and sodium amide in the residue were decomposed by successive addition of methanol–ether mixture, methanol, and water. The aqueous layer separated was extracted with three 150-ml portions of ether. The combined organic layer and ether extracts were washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. Fractional distillation of the ether solution gave 0.8 g (31% yield) of a mixture consisting of 86% **15** and 14% **16**, bp 56–58° (5 mm).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.90; H, 11.05.

The mixture was separable on the conventional preparative VPC. **15**: ir 3010, 2920, 2850, 2800, 1625, 1435, 1370, 1255, 1000, 730, 710 cm^{-1}; ^1H NMR δ 0.9–2.61 (complex m, 14), 5.08–5.97 (complex m, 2); MS *m/e* (rel intensity) 148 (47, M^+), 120 (18), 119 (38), 106 (26), 105 (28), 94 (31), 92 (52), 91 (88), 79 (100), 77 (53), 67 (21), 66 (45), 41 (55). **16**: ir 3010, 2920, 2850, 2820, 1625, 1450, 1430, 900, 710, 690 cm^{-1}; MS *m/e* (rel intensity) 148 (48, M^+), 120 (13), 119 (33), 106 (26), 105 (30), 92 (54), 91 (70), 79 (64), 77 (29), 67 (27), 66 (100), 41 (24).

1,7-*exo*-Trimethylenebicyclo[3.2.1]octane (6). A solution of 0.3 g (2 mmol) of the mixture of **15** and **16** obtained above in 20 ml of ether was hydrogenated in a 100-ml autoclave over 0.05 g of the palladium on charcoal catalyst at room temperature at a pressure of 5 kg/cm^2. The reaction was completed in 30 min. The catalyst was filtered off, and the filtrate was evaporated to give 0.29 g (96% yield) of crude **6**, which was purified on a preparative VPC to yield a pure sample: ir 2940, 2930, 2860, 1465, 1450, 980, 870, 785, 660 cm^{-1}; ^1H NMR δ 0.7–2.5 (complex m); MS *m/e* (rel intensity) 161 (8, $M^+ + 1$), 150 (100), 135 (50), 122 (48), 121 (44), 108 (45), 107 (80), 95 (32), 94 (60), 93 (45), 81 (60), 80 (68), 79 (80), 67 (56), 55 (19), 41 (38). ^{13}C NMR signals are listed in Table II.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found:, C, 87.70; H, 12.20.

Bromination of an Isomerization Product of 2,3-*exo*-Tetramethylenenorbornane (*exo*-1) and Isolation of a Mixture of [3.3.3]Propellane (4), 7-Methylisotwistane (10), and 1-Methylisotwistane (11). A mixture of 30 g (0.2 mol) of the reaction mixture of run 34 (Table I) and 100 ml (1.94 mol) of bromine was stirred at room temperature for 2 hr. Most of excess bromine was evaporated under diminished pressure at ambient temperature. The residue was treated repeatedly with a cold, saturated solution of sodium hydrogen sulfite until all the remaining bromine had been removed, then washed successively with a saturated solution of sodium hydrogen carbonate and water and dried over anhydrous magnesium sulfate. The mixture was distilled, and the fraction (11.2 g) boiling at 65–75° (8 mm) was collected. The fraction was again distilled through a 1-ft Vigreux column to give 2.7 g of a fraction boiling at 71–72° (11 mm). The compositon of the fraction thus obtained was unknown A_1 (**10**), 8.7; A_2 (**4**), 5.7; A_3 (**11**), 16.2; B_1 (**5**), 30.2; B_2 (*exo*-**2**), 3.1; C_3 (**6**), 14.6; C_4 (**3**), 3.6; 2-methyladamantane, 0.5; *exo*-**7**, 16.2; **9**, 0.4%. Fraction A was then isolated from the above hydrocarbon mixture on the preparative VPC, and amounted to 0.75 g.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.72; H, 12.13.

The fraction A was again fractionated on the preparative VPC, when the former and the latter shoulders of the VPC peak were collected separately. The middle part of the peak was repeatedly chromatographed until enough (each 0.2 g) of the former and the latter eluted fractions were obtained. Both fractions solidified on standing at room temperature. The former eluted specimen thus obtained comprised A_1, A_2, and A_3 in 3.3:1.0:1.3 ratio, while the latter eluted fraction was in 1.1:1.0:3.2 ratio. The former eluted specimen showed two sharp singlets in a ^1H NMR spectrum. They absorbed at δ 1.08 and 1.05 whose relative intensities were 3 and 1, respectively. On the other hand, the later eluted specimen gave the same singlets with relative intensities of 1 and 3. Therefore, the δ 1.08 signal was assigned to the protons of the 7-methyl group in **10**, the δ 1.05 signal to those of 1-methyl in **11**. ^{13}C NMR spectra of **4**, **10**, and **11** were constructed from those of the two mixture specimens, as stated in the text, and are listed in Table II.

The mass spectrum of each compound was measured on the Golay GC–MS instrument. **4**: *m/e* (rel intensity) 150 (40, M^+), 135 (20), 122 (9), 121 (6), 109 (18), 108 (16), 107 (100), 94 (14), 93 (10), 91 (7), 81 (8), 80 (14), 79 (27), 67 (17), 55 (8), 53 (6), 44 (17), 41 (12), 40 (16). **10**: *m/e* (rel intensity) 150 (45, M^+), 135 (20), 122 (11), 121 (14), 108 (11), 107 (32), 95 (30), 94 (100), 93 (30), 81 (39), 80 (20), 79 (36), 78 (5), 77 (14), 68 (9), 67 (29), 55 (21), 53 (16). **11**: *m/e* (rel intensity) 150 (11, M^+), 135 (11), 122 (5), 121 (11), 108 (10), 107 (32), 95 (13), 94 (100), 93 (19), 81 (36), 80 (20), 79 (25), 77 (8), 67 (15), 55 (8), 53 (6).

Isolation of a Mixture of 1,2-*exo*-Trimethylene-*cis*-bicyclo[3.3.0]octane (5) and 1,2-*exo*-Tetramethylenenorbornane (*exo*-2). After fraction A was collected on the preparative VPC as described in the preceding section, fraction B was also collected in a fractionation of the unbrominated hydrocarbon mixture boiling at 71–72° (11 mm). The fraction B contained 90% B_1 (**5**) and 10% B_2 (*exo*-**2**): ir 2960, 2940, 2860, 1590, 1470, 1450, 1370, 1310, 930, 910 cm^{-1}. The absorption at 1370 cm^{-1} was considered characteristic of **5**, because the absorption was entirely absent in the ir spectrum of an authentic mixture of *exo*-**2** and *endo*-**2**.

Mass spectrum of **5** taken in the Golay GC–MS: *m/e* (rel intensity) 150 (13, M^+), 135 (13), 122 (100), 121 (37), 108 (20), 107 (82), 95 (13), 94 (22), 93 (26), 82 (9), 81 (32), 80 (38), 79 (50), 77 (14), 68 (10), 67 (29), 65 (8), 55 (12), 41 (22).

Isomerization Reactions of Tricycloundecanes. The reaction was run in the same equipment as used in the previous work.[7] A mixture of 0.1 g (0.667 mmol) of a tricycloundecane in 5 ml of methylene chloride was refluxed in the presence of an appropriate amount of the catalyst. The reactant to solvent ratio was the same in preparative runs as in analytical runs. Isolation of products for preparation purposes was made by quenching the reaction mixture with cold water followed by washing the methylene chloride layer with a saturated sodium hydrogen carbonate solution and water. The methylene chloride solution was dried over anhydrous calcium chloride.

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Registry No.—*endo*-**1**, 54676-30-1; *exo*-**1**, 54676-30-1; *endo*-**2**, 55954-91-1; *exo*-**2**, 36150-95-5; **3**, 51095-23-9; **4**, 51027-89-5; **5**, 55925-58-1; **6**, 55954-92-2; *exo*-**7**, 53495-28-6; **9**, 43000-53-9; **10**, 55925-59-2; **11**, 55925-60-5; **12**, 16489-22-8; **13**, 55925-61-6; **14**, 55925-62-7; **15**, 55925-63-8; **16**, 55925-64-9; 1,6-tetramethylene-2-norbornene, 27017-54-5; ethyl trichloroacetate, 515-84-4.

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trans-**5**

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Addition of Sulfur Trioxide to Acid Halides and Esters

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Sulfur trioxide inserts into the carbon–halogen bond of acid fluorides and acid chlorides under mild conditions. The acyl fluorosulfates so formed are more stable thermally than the acyl chlorosulfates, but both types of product can revert to starting materials at elevated temperatures. As a class, these mixed anhydrides are strongly electrophilic, and examples of cationic polymerization and ether cleavage are presented. One example of formation of a methyl acyl sulfate from sulfur trioxide and a methyl ester is also described.

Although polyfluoroacyl fluorides were prepared earlier from sulfur trioxide and alkyl polyfluoroalkyl ethers,[1,2] the reaction of sulfur trioxide with the product acid fluorides was not reported in the literature.[3] As is shown in this paper, such reactions provide a convenient route to polyfluoroacyl fluorosulfates in quantity. Previous syntheses of fluoroacyl fluorosulfates involved mainly reactions of peroxydisulfuryl difluoride with substrates such as fluorinated anhydrides,[4] trifluoroacetyl bromide,[5] and bis(trifluoromethyl)ketene.[6]

Acyl Fluorosulfates. Preparation. Sulfur trioxide adds readily to fluoroacyl fluorides at 25–100°, with the required time and temperature dependent on the specific acid fluoride. For example, trifluoroacetyl fluoride reacted under pressure over a period of weeks with sulfur trioxide at 25° to form trifluoroacetyl fluorosulfate (**1**), whereas both α-*H*-hexafluoroisobutyroyl fluoride and perfluoromethacryloyl fluoride give **2** and **3**, respectively, in mildly exothermic reactions. Yields were good in all cases, and the fluoroacyl fluorosulfates have been purifiable by distillation provided the temperature is kept well below 100°. The reaction is reversible, and at elevated temperatures significant amounts of acid fluoride and sulfur trioxide are present.[7] Thus fluorosulfate **3** distilled as such at 46–48° (20 mm), but when heated at 1 atm to 125–140°, **3** distilled as a mixture of its precursors at ca 49°.

$$R_FCF + SO_3 \longrightarrow R_FCOSO_2F$$

$R_F = CF_3$ (**1**)
$R_F = CH(CF_3)_2$ (**2**)
$R_F = C(CF_3)=CF_2$ (**3**)
$R_F = CHFCF_3$ (**4**)
$R_F = CF(CF_3)SO_2F$ (**5**)

Side reactions are possible in some cases where α-H is present. Thermolysis of **2** at 120–155° (1 atm) gave 37% of bis(trifluoromethyl)ketene along with α-*H*-hexafluoroisobutyroyl fluoride. No such elimination of HF was observed when fluorosulfate **4** was pyrolyzed.

Carbonyl fluoride proved to be a special case. Reaction with sulfur trioxide occurred slowly in a glass vessel at 100° under pressure to give products apparently derived from fluorocarbonyl fluorosulfate. Major products were carbon dioxide, pyrosulfuryl fluoride, and bis(fluorosulfonyl) sulfate along with a trace of sulfuryl fluoride and small amounts of higher fluorosulfonyl compounds. The low yield of sulfuryl fluoride is an indication that fluorocarbonyl fluorosulfate is formed, but reacts readily with sulfur trioxide to form higher anhydrides which are degraded with loss of carbon dioxide to give fluorosulfonic anhydrides. The reaction should provide an attractive route to pyrosulfuryl fluoride, although one attempt to reproduce it on a molar scale at 125° in a metal bomb failed. Perhaps the equilibrium at