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Acid-Catalyzed Rearrangements of [4.3.2]- and [3.3.3]Propellanes, Tricyclo[4.3.2.$0^{1,5}$]undecanes, and Tricyclo[6.3.0.$0^{1,5}$]undecanes

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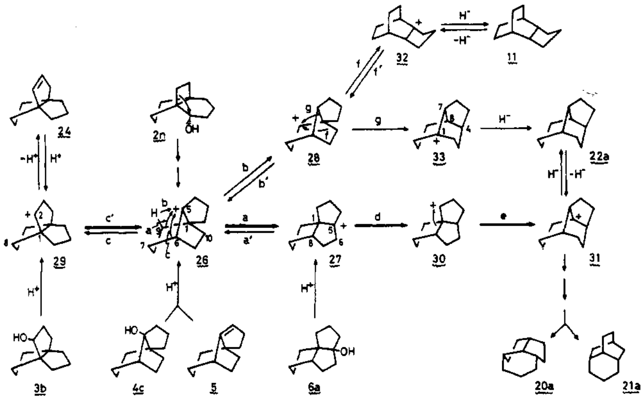
Acid-catalyzed rearrangements of [4.3.2]propellanols **2x** and **2n**, [3.3.3]propellanol (**3b**), tricyclo[4.3.2.$0^{1,5}$]-undecanes **4b–d** and **5**, and tricyclo[6.3.0.$0^{1,5}$]undecanes **6a,b** were studied. Tricycloundecanes **4d** and **6b** rearranged under CF_3SO_3H catalysis to 1- and 2-methyladamantanes together with 12 tricyclic hydrocarbons. The [4.3.2]- and [3.3.3]propellan-2-ols **2x**, **2n**, and **3b**, the tricyclo[4.3.2.$0^{1,5}$]undecan-6(5)-ols **4b,c**, and tricyclo[6.3.0.$0^{1,5}$]-undecan-5-ol (**6a**) were converted into mixtures of tricyclic hydrocarbons by reductive rearrangement with hydride transfer (97% H_2SO_4–pentane) and into tricyclic carboxylic acids by the Koch–Haaf reagent (97% H_2SO_4–HCO_2H). The alcohol **3b** also rearranged in 50% H_2SO_4–THF at reflux to the alcohols **4c** and **6a** plus tricyclo-[6.3.0.$0^{1,5}$]undec-6-ene (**34**). The structures of products were assigned by comparison of ^{13}C NMR spectra, chemical correlation with known compounds, and single-crystal X-ray analysis. Rearrangement pathways at the early stage of the reaction are discussed.

We have reported that the acid-catalyzed rearrangement of [4.3.2]propellan-2-one (1) gives [3.3.3]propellan-2-one (**3a**) or tricyclo[4.3.2.$0^{1,5}$]undecane derivatives such as **4a** in the absence or presence of a nucleophile.[2] We have also reported on a remarkable stereoelectronic effect in the rearrangements of *exo*- and *endo*-[4.3.2]propellan-2-ols **2x** and **2n**.[3] Thus, **2x** rearranged via a 1,2-alkyl shift of the central propellane bond to give tricyclo[4.3.2.$0^{1,5}$]undecan-6-ol (**4b**), while **2n** underwent migration of the external cyclobutane bond to give the 5-hydroxy derivative **4c**, which then afforded tricyclo[6.3.0.$0^{1,5}$]undecan-5-ol (**6a**) via a second alkyl shift (path a in Scheme I).[4] Since tricycloundecanes **3a**, **4a–c**, and **6a** possess the basic frameworks of polyquinane-type natural products such as modhephene (**7**),[5] quadrone (**8**),[6] and isocomene (**9**),[7] respectively, this skeletal rearrangement should provide an efficient method for the construction of polyquinane-type skeletons.[8] By utilizing this rearrangement, we have synthesized not only the hydrocarbons **3c**,[2] **4d**,[3] **5**,[9] and **6b**[3] but also descarboxyquadrone (**10**),[9] which has almost the same level of antitumor activity as **8**.[10]

Scheme I



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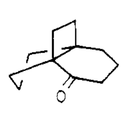

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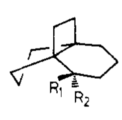
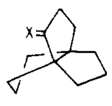
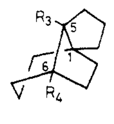


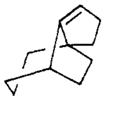
2x R$_1$=OH, R$_2$=H
2n R$_1$=H, R$_2$=OH



3a X=O
3b X=H,OH
3c X=H$_2$



4a R$_3$=OH, R$_4$=Cl
4b R$_3$=H, R$_4$=OH
4c R$_3$=OH, R$_4$=H
4d R$_3$=R$_4$=H
4e R$_3$=H, R$_4$=CO$_2$H
4f R$_3$=H, R$_4$=Cl



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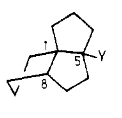
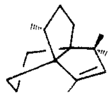


6a Y=OH
6b Y=H



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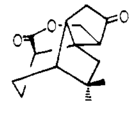

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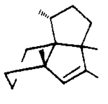

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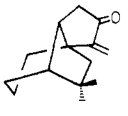

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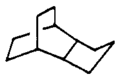
Tricyclo[4.3.2.0^{1,5}]undecane (**4d**) has been regarded as a key intermediate in the rearrangement of tricycloundecanes by Ōsawa,[11] Inamoto,[12,13] and co-workers. For instance, **4d** was postulated as the first-step intermediate in the CF_3SO_3H-catalyzed rearrangement of tricyclo[5.2.2.0^{2,6}]undecane (**11**) to 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane) (**21a**), although **4d** had not been isolated or characterized.[13] Tricyclo[6.3.0.0^{1,5}]undecane (**6b**), which was also obtained as a minor product in this reaction, was assumed to be derived from tricyclo[4.3.2.0^{1,5}]undecan-5-yl cation **26** (Scheme I).[13] Although [3.3.3]propellane (**3c**) is also related to cation **26**, it was not detected in the reaction.[13] Moreover, **3c** and **6b** were inferred to be mechanistic dead-ends in a thermodynamic sense.[11] In addition, an entry from a [4.3.2]propellane into "homoadamantane-land"[14] has not been found, although we have found an entry from [3.3.2]propellanes into "adamantane-land".[15]

We have now studied the acid-catalyzed rearrangements of tricycloundecane derivatives **2x**, **2n**, **3b**, **4b–d**, **5**, and **6a,b** in order to (i) determine the rearrangement pathways involving cation **26**, (ii) establish the skeletal rearrangement of the thermodynamic dead-ends **3c** and **6b**, and (iii) develop a new entry into "homoadamantane-land" from the [4.3.2]propellane system. We carried out the reactions with the following acidic reagents: CF_3SO_3H–CH_2Cl_2, 97% H_2SO_4–pentane (reductive rearrangement with hydride transfer), 97% H_2SO_4–HCO_2H (the Koch–Haaf reaction), and 50% aqueous H_2SO_4–THF. It was hoped that this study would provide information about the biogenesis of polyquinane terpenoids, especially of **7** and **9**[16] because they have been isolated from the same source.[5,7]

Results and Discussion

CF_3SO_3H-Catalyzed Rearrangement. The rearrangement of **4d** did not proceed smoothly with 1 equiv of CF_3SO_3H in refluxing CH_2Cl_2 but did so with 4 equiv of the acid. The product ratios were determined by GLC, and the time–conversion relationships are listed in Table I. We also made preparative runs under the same conditions to obtain sufficient quantities of products for structure determinations. The combined yields of hydrocarbons were 74–91% (Table I). The products were separated by preparative GLC and identified by comparison of ^{13}C NMR spectra with those reported in the literature.[13,17–21] The tricyclic hydrocarbons isolated were as follows: 1- and 10-methyltricyclo[5.2.1.0^{4,10}]decanes (**13** and **12**),[17] **3c**, 1- and 2-methyladamantanes (**14** and **18**),[18] **6b**, tricyclo[6.2.1.0^{1,6}]undecane (**15**),[19] tricyclo[5.3.1.0^{1,5}]undecane (**16**),[19] tricyclo[5.2.2.0^{1,5}]undecane (**17**),[19] tricyclo[5.3.1.0^{2,6}]undecane (**19**),[20] tricyclo[5.3.1.0^{4,11}]undecane (**20a**),[13] **21a**,[20] 2,4-bishomobrexane (tricyclo[5.4.0.0^{4,8}]undecane) (**22a**),[13] **11**,[13] and tricyclo[4.3.1.1^{3,8}]undecane (**23**).[21]



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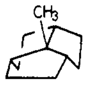

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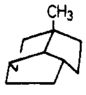

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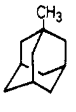

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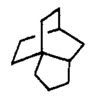

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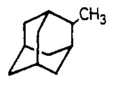

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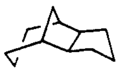

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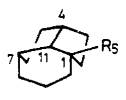
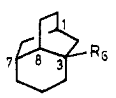
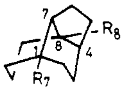


20a R$_5$=H
20b R$_5$=CO$_2$H

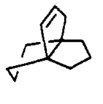


21a R$_6$=H
21b R$_6$=CO$_2$H



22a R$_7$=R$_8$=H
22b R$_7$=H, R$_8$=CO$_2$H
22c R$_7$=CO$_2$H, R$_8$=H

23



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As shown in Table I, **4d** rearranged to a number of tricyclic hydrocarbons including the $C_{11}H_{18}$ stabilomer 1-methyladamantane (**14**), which was obtained after a long reaction time. The results were similar to those in the rearrangement of **11**.[13] However, in the initial stage of the rearrangement of **4d**, more **6b** and less 2,4-bishomobrexane (**22a**) were detected in comparison with the rearrangement of **11**.[13]

Reaction of **6b** with 5 equiv of CF_3SO_3H in CH_2Cl_2 gave the same hydrocarbons as did **4d** (Table I), although the rearrangement of **6b** proceeded somewhat more slowly than that of **4d**. On the other hand, **3c** has been shown to be unreactive with 5 equiv of CF_3SO_3H.[17] From these results we are unable to elucidate the precise courses of the rearrangements, particularly at the early stage.

Reductive Rearrangements with Hydride Transfer. In order to investigate the early stage of the rearrangement

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[14] "Homoadamantane-land" refers to tricyclic $C_{11}H_{18}$ isomers that have reasonable thermodynamic stabilities, in analogy with "adamantane-land": Fort, R. C., Jr. "Adamantane. The Chemistry of Diamond Molecules"; Marcel Dekker: New York, 1976.

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Table I. CF_3SO_3H-Catalyzed Rearrangement of Tricycloundecanes 4d and 6d

		reactn time,	product,[a-c] %									
run	reactant	min (h)	12 + 3c + 13	14	6b + 15	16 + 17	4d	18	19	20a + 21a + 11	22a	23
1	**4d**	3[d]			4 (4:0)		70		1	20 (3:16:1)	5	
2		10			11	2	38		3	40	6	
3		30			18	5	18		4	50	4	1
4		180	1	1	21	16		4	3	51		3
5		(13)[e]	1 (3:1:6)	4	18 (17:1)	18 (16:2)		6	6	44 (7:37:0)		3
6	**6b**	10			87	1	1		1	10		
7		100[f]	trace	2	41 (39:2)	10 (8:2)	2	4	3	34 (4:29:1)	2	2
8		(48)[g]	3 (3:1:6)	36	8 (8:0)	5 (5:0)		34	3	10 (2:8:0)		1

[a] Arranged in order of increasing retention time. [b] Calculated from GLC peak areas. [c] Ratios in parentheses are calculated from ^{13}C NMR spectra. [d] Preparative run. Combined yield of products was 91%. [e] Preparative run. 74% combined yield. [f] Preparative run. 87% combined yield. [g] Preparative run. 86% combined yield.

Table II. Reductive Rearrangement with Hydride Transfer of Tricycloundecane Derivatives

		reactn time,	yield,[a]	product,[b,c] %				
entry	reactant	min (h)	%	24	4d	20a + 21a + 11	22a	others[d]
1	**4b**	2	24		100			
		60			97			3
		(24)			96			4
2	**4c**	2	28	4		33 (12:16:5)	59	4
		10		1		42	53	4
		60				52	45	3
		360				81	11	8
		(24)	25			85 (16:59:10)		15
3	**5**	2	41	9		26 (7:11:9)	62	3
		10				39	55	6
		60				66	28	6
		360	35			82 (11:65:6)		18
4	**2x**	10	32		98			2
		60			96			4
		(24)			92			8
5	**2n**	2	22	6		25 (5:12:8)	49	20 (12)[e]
		10		2		39	41	18 (11)[e]
		60				62	20	18 (9)[e]
		360				79	5	16 (8)[e]
		(24)	31			70 (11:51:8)		30 (4)[e]
6	**6a**	3	27	3		29 (8:11:10)	64	4
		10		trace		58	37	5
		60				65	31	4
		360				80	13	7
		(24)	37			84 (10:69:5)		16
7	**3b**	2		1		58	38	3
		5	36	1		64 (10:49:5)	32	3
		60				71	25	4
		360				85	13	2
		(24)				89		11

[a] Isolated yield of total hydrocarbons. [b] Calculated from GLC peak areas. [c] Ratios in parentheses are calculated from ^{13}C NMR spectra. [d] Some unidentified products were obtained. [e] Percent ratios in refer to those of an unidentified product i. See the Experimental Section.

pathways of the di- and triquinane skeletons **4d**, **3c**, and **6b** into the stable intermediate **21a**, we carried out reductive rearrangements with hydride transfer of their derivatives **4b**, **4c**, **5**, **3b**, and **6a** using 97% H_2SO_4–pentane.[22] In such reactions, skeletal rearrangement of dead-end intermediates would be promoted because of the ease of carbocation formation, and determination of product structures would be simplified because the positions of the initial carbocation centers are known. The time–conversion relationships of the reactions are summarized in Table II.

Treatment of the 6-hydroxy derivative **4b** with the acid at room temperature (about 20 °C) for 2 min gave **4d** without skeletal rearrangement in 24% yield as a sole product. On the other hand, similar treatment of the

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[22] Takaishi, N.; Inamoto, Y.; Tsuchihashi, K.; Aigami, K.; Fujikura, Y. *J. Org. Chem.* **1976**, *41*, 771.

Table III. Koch–Haaf Reaction of Tricycloundecanols

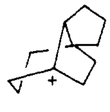
run	reactant	reactn temp, °C	$[HCO_2H]$/[reactant]	yield,[a] %	product,[b] %				
					20b + **21b**	**22b**	**22c**	**4e**	other
1	**4c**	rt	4	39	25	34	38		3
2		0	4	51	18	47	34		1
3		−15	40	63	8	60	30		2
4		−15	300	100	3	81	14		2
5		rt	300	66	33 (27:6)[c]	43	22		2
6	**2n**	0	300	91	17	64	17		2
7	**3b**	rt	300	61	13	68	16		3
8		−15	200	89	1	86	11		2
9	**6a**	rt	300	77	34	44	20		2
10		−15	300	89	4	78	16		2
11	**2x**	0	300	84				100	
12	**4b**	rt	200	81				95	5

[a] Isolated yield of total acids or their methyl esters. [b] Calculated from GLC peak areas of the methyl esters. [c] Calculated from ^{13}C NMR spectrum.

5-hydroxy derivative **4c** furnished tricycloundecanes **11**, **20a**, **21a**, and **22a** along with [3.3.3]propell-2-ene (**24**) in 25–28% yields. The structure of **24** was established by the identity of its ^{13}C and ^{1}H NMR spectra with those of an authentic sample prepared independently from **3a**. Interestingly, rearrangements of the olefin **5**, the triquinane alcohol **6a**, and [3.3.3]propellanol (**3b**) afforded the same hydrocarbons in ratios similar to those from **4c**. These results establish the rearrangement of the dead-end propellane skeleton.

Treatment of the exo alcohol **2x** with 97% H_2SO_4–pentane for 10 min gave mainly **4d** as in the case of **4b**, while similar treatment of the endo alcohol **2n** afforded the mixtures of **11**, **20a**, **21a**, **22a**, and **24** that were obtained from **4c**. These results demonstrate an entry from the [4.3.2]propellane system into "homoadamantane-land".

Rearrangement Pathways. Entries 1 and 4 in Table II indicate that rearrangement of the 6-yl cation **25** derived from **4b** or **2x** does not take place. This result follows from the absense of adjacent carbon or hydrogen atoms that would meet the steric requirements for an alkyl shift and hydride transfer to the carbocation center of **25**. On the other hand, it can be seen from entries 2, 3, and 5–7 in Table II that, at the initial stage of the reactions of **4c**, **5**, **2n**, **6a**, and **3b**, **22a** was formed as the major product, while at longer reaction times the amounts of **20a** and **21a** increased at the expense of **22a** and **24**. Consequently, it is reasonable to deduce that **22a** and **24** rearrange to **20a** and **21a**. Since the rearrangement pathway from **22a** to **20a** and **21a** has been well-documented by Inamoto et al. in the rearrangement of **11**,[13] we discuss the earlier stages—the rearrangement pathways leading to the formation of **11**, **22a**, and **24**.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Taking into account the mechanism of "homoadamantane rearrangements" elucidated by Ōsawa et al. using molecular mechanics,[11] we propose the rearrangement pathways shown in Scheme I. Apparently, three pathways are available from the 5-yl cation **26**. First, path a involves a 1,2-alkyl shift of the C(1)–C(9) bond to give the carbocation **27**. Second, hydride transfer in **26** from C(9) would afford the carbocation **28** (path b). Finally, path c involves a 1,2-alkyl shift of the C(6)–C(7) bond to furnish the secondary carbocation **29**. In view of the rearrangement behaviors of **2n**, **4c**, and **5** in 50% H_2SO_4–THF at 55 °C,[3,23] path a should be the kinetically most favored pathway of the three.

Consequently, it is reasonable to assume the pathway from **27** as follows: hydride transfer (path d) and the subsequent migration (path e) of the C(1)–C(8) bond of carbocation **30** give tricyclo[5.4.0.0^{4,8}]undecan-8-yl cation (**31**), which accepts a hydride ion to yield **22a**. Carbocation **31** was also postulated as a precursor of **20a** and **21a** by Inamoto et al.[13] However, another pathway from **26** to **22a** is possible: hydride transfer to give **28** (path b) followed by the migration of the C(1)–C(5) bond (path g), affording tricyclo[5.4.0.0^{4,8}]undecan-1-yl cation (**33**). This process was also proposed by Inamoto et al.[13] We were able to determine that the former route is the major path, as described in the next section. The formation of **11** is explained by the 1,2-alkyl shift of the C(1)–C(10) bond of carbocation **28** (path f) to give carbocation **32**, the "backward" pathway from **11**.[13]

As for the formation of the olefin **24** from **2n**, **4c**, **5**, and **6a** in the early stage of the rearrangement, path c followed by deprotonation of **29** is plausible, taking into account the formation of [3.3.3]propellan-2-one (**3a**) from [4.3.2]propellanone (**1**) in the absense of a nucleophile.[2] The formation of small amounts of **11** and **24** in the rearrangement of **6a** (entry 6) suggests the reverse route (path a′) from **27** to **26**. However, the rapid disappearance of **24** (entries 2, 3, 5–7) indicates that the "backward" rearrangement pathways, the protonation and the migration of C(8) (path c′) to **26**, take place smoothly.

Koch–Haaf Reactions. In order to determine which way **22a** is formed (path a → d → e or path b → g), we carried out Koch–Haaf reactions[24] of the alcohols **2n**, **3b**, **4c**, and **6a**. Since it is known that in this reaction the carbocations generated by H_2SO_4 are trapped by carbon monoxide to give carboxylic acids, the position of the carboxyl group should allow elucidation of the rearrangement course to **22a**.

We examined the reactions of **4c** under a variety of conditions, with the results summarized in Table III. In every reaction, the carboxylic acids **20b**, **21b**, **22b**, and **22c** were obtained in good yields. Distributions of the products were determined by treating the acids with diazomethane and analyzing the methyl esters by GLC. Since the esters of **20b** and **21b** could not be separated by GLC or column chromatography, they were characterized as a mixture. The ratio estimated in run 5 was approximately 4.2:1 by ^{13}C NMR. The methyl ester of **21b** was identified by

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[23] Under these conditions, **5** also rearranged to **6a** in 79% yield; see the Experimental Section.

[24] Haaf, W. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 739.

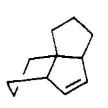
comparison of its ^{13}C NMR spectrum with that of an authentic sample.

Since we could not determine the tricyclic structures of **20b**, **22b**, and **22c** by spectroscopic data, they were converted to the corresponding hydrocarbons by using the modified Kochi reaction[25] followed by reduction of the chlorides with Bu_3SnH. Decarboxylation–chlorination of a mixture of **22b** and **22c** in a ratio of 92:8 with $Pb(OAc)_4$ and *N*-chlorosuccinimide in acetic acid and DMF (v/v, 1:5) afforded a mixture of two chlorides whose ratio was almost the same as that of **22b** and **22c**. Reduction of the chlorides with Bu_3SnH in cyclohexane at reflux using azobis(isobutyronitrile) as initiator gave only **22a** in 88% overall yield. It is therefore deduced that **22b** and **22c** possess the same 2,4-bishomobrexane skeleton. Moreover, the off-resonance decoupled ^{13}C NMR spectra of the methyl esters of **22b** and **22c** showed two singlets and three doublets, respectively. It therefore appears that their carboxyl groups are attached at either C(1) or C(8), considering the mechanism shown in Scheme I. Finally, **22b** was determined to be 8-carboxy derivative by X-ray crystallographic analysis of a sample (mp 127–129 °C) recrystallized from hexane. Accordingly, **22c** should be the 1-carboxy derivative. Similarly, a mixture of **20b** + **21b**, **22b**, and **22c** in a ratio of 11:59:30 was transformed as described above to the hydrocarbons **20a** + **21a** and **22a** in a ratio of 12:88 in 70% yield. Therefore, the skeleton of **20b** is deduced to be tricyclo[5.3.1.0^{4,11}]undecane (**20a**). Since the ^{13}C NMR spectrum of **20b** methyl ester showed 13 signals with two singlets and three doublets in spite of the symmetry of the parent skeleton, **20b** was shown to be the 1-carboxy derivative.

The Koch–Haaf reactions of **2n**, **3b**, and **6a** gave mixtures of **20b**, **21b**, **22b**, and **22c** in 69–91% yields. On the other hand, the reactions of **2x** and **4b** afforded only 6-carboxytricyclo[4.3.2.0^{1,5}]undecane (**4e**) in 81–84% yields, as in their reductive rearrangements. Since the Kochi reaction of **4e** afforded the known chloride **4f**[3] in 85% yield, the structure of **4e** was determined unambiguously. These results are also summarized in Table III.

From runs 1–10 in Table III, it can be seen that the amount of **22b** increases with increasing quantities of HCO_2H and with lower reaction temperatures. The above results clearly indicate that carbocation **31**, the precursor of **22b**, is formed primarily during the early stage of the rearrangements. We therefore conclude that cation **26** rearranges to **22a** mainly through path a → d → e. However, since the minor product **22c** should be derived from **33**, the route from **26** through path b → g to **22a** appears to be a minor competitive one.

Acid-Catalyzed Rearrangement of 3b in 50% H_2SO_4–THF. Finally, in order to ascertain that **3b** rearranges to cation **27** via **26**, we carried out the acid-catalyzed rearrangement of **3b** in 50% H_2SO_4–THF. No reaction occurred at 55 °C, but reaction at reflux (about 70 °C) for 120 h gave [3.3.3]propellene (**24**) (25%), tricyclo[6.3.0.0^{1,5}]undec-6-ene (**34**)[26] (2%), **6a** (18%), **4c** (trace), and recovered **3b** (19%). Formation of **34** may involve hydride transfer from C(6) in **27** and subsequent deprotonation because the symmetrical olefin **34** might be expected to be more stable than the bridgehead olefins that would be derived from **27** by direct deprotonation. Thus, it was confirmed that **3b** rearranges to tricyclo[6.3.0.0^{1,5}]undecane derivatives **6a** and **34** through path c′ → a as indicated in the section on reductive rearrangement. It should be noted that the rearrangement of the dead-end propellane skeleton into "homoadamantane-land" also occurs in 50% H_2SO_4–THF.



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In conclusion, the relationship between the three basic skeletons of the polyquinane natural products **7**–**9** has been elucidated as shown in Scheme I. These results suggest the possibility that the biogenesis of **7** and **9** produced from the same source involves an interconversion through a carbocation analogous to **26**.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise stated. Mass spectra were measured with a Hitachi RMU-6E spectrometer and are given in terms of m/e (relative intensity) compared with the base peak. ^{1}H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4 unless otherwise stated, and ^{13}C NMR spectra were taken on a JEOL JNM-FX-60S spectrometer in $CDCl_3$. Chemical shifts are reported as δ values in parts per million relative to Me_4Si (δ 0.0) as the internal standard. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC was conducted on a Varian Aerograph 920 gas chromatograph with a 10% FFAP column or 30% SE-30 column. Column chromatography was performed with Wako C-200 silica gel. Flash chromatography was carried out as described by Still et al.[27] with Merck silica gel 60 (particle size finer than 0.063 mm).

Materials. *exo*- and *endo*-[4.3.2]propellanols (**2x** and **2n**), tricyclo[4.3.2.0^{1,5}]undecane derivatives, i.e., the alcohols **4b** and **4c**, the hydrocarbon **4d**, and the olefin **5**, and tricyclo[6.3.0.0^{1,5}]undecane derivatives, i.e., the alcohol **6a** and the hydrocarbon **6b**, were prepared from [4.3.2]propellanone (**1**) as described previously.[3]

Tricyclo[3.3.3.0]undecan-2-ol (3b). A solution of 2.02 g (12.3 mmol) of [3.3.3]propellanone (**3a**)[2] in 20 mL of dry ether was added dropwise to a stirred suspension of $LiAlH_4$ in 10 mL of dry ether at 0 °C. The mixture was stirred at room temperature for 2 h. Water was added carefully, and 5% HCl was subsequently added to dissolve the white precipitate. The organic layer was separated, and the aqueous solution was extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was chromatographed to give the alcohol **3b**: 1.91 g (93%); mp 104–107 °C; IR (KBr) 3300, 1060 cm^{-1}; MS m/e 166 (M^+, 20), 109 (100), 108 (90), 107 (78); ^{1}H NMR 1.0–1.9 (m, 16 H), 2.34 (s, 1 H), 3.63 (t, 1 H); ^{13}C NMR 80.6 (d), 63.0 (s), 60.4 (s), 40.7 (t), 40.3 (t), 38.9 (t), 34.6 (t), 33.7 (t), 32.7 (t), 25.4 (t), 25.0 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.25; H, 10.99.

Rearrangement Reactions. CF_3SO_3H–CH_2Cl_2.[13] A sample of tricycloundecane **4d** or **6b** (100 mg, 0.67 mmol) and 400 mg (2.68 mmol) or 500 mg (3.35 mmol) of CF_3SO_3H in 5 mL of dry CH_2Cl_2 were heated under reflux. Aliquots were withdrawn from the reaction mixture and quenched by addition of cold water. The CH_2Cl_2 layer was separated, dried (Na_2SO_4), and subjected to GLC analysis. The results obtained from two or three experiments are summarized in Table I.

For a preparative run, a 1.02-g (6.80 mmol) sample of **4d** in 51 mL of CH_2Cl_2 was stirred at reflux for 3 min with 4.08 g (27.3 mmol) of CF_3SO_3H. The reaction mixture was cooled with ice water bath, and cold water was added. The organic layer was washed with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was removed carefully in vacuo, and the residue was distilled under reduced pressure (89–90 °C (48

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[25] Becker, K. B.; Geisel, M.; Grob, C. A.; Kuhnen, F. *Synthesis* **1973**, 493.

[26] Cargill, R. L.; Foster, A. M. *J. Org. Chem.* **1970**, *35*, 1971. Also, see: Kakiuchi, K.; Kumanoya, S.; Ue, M.; Tobe, Y.; Odaira, Y. *Chem. Lett.* **1985**, 989.

[27] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

mmHg)) to give 0.93 g (91%) of hydrocarbons. The products were analyzed by GLC and separated by preparative GLC. The reaction of 1.95 g (13.0 mmol) of **4d** for 13 h afforded 1.44 g (74%) of the products.

The reactions of 1.02 g (6.80 mmol) of **6b** for 100 min and 1.63 g (10.9 mmol) of **6b** for 48 h with 5 equiv of CF_3SO_3H yielded 0.89 g (87%) and 1.40 g (86%) of hydrocarbons (92–94 °C (52 mmHg)), respectively. The results of the preparative runs are summarized in Table I.

Reductive Rearrangement with Hydride Transfer.[22] A reactant (100 mg) dissolved in 5 mL of pentane was mixed with 0.5 mL of 97% H_2SO_4, and the mixture was stirred vigorously at room temperature. The pentane layer was withdrawn at appropriate intervals and was added to a saturated $NaHCO_3$ solution. The organic layer was separated, dried (Na_2SO_4), and subjected to GLC analysis. Analytical runs for each substrate were undertaken three or four times, and representative results are listed in Table II with those of preparative runs.

A 500-mg (3.01 mmol) sample of **4b** in 25 mL of pentane was stirred for 2 min with 2.5 mL of 97% H_2SO_4. The solution was decanted quickly into cold water and separated. The organic layer was washed with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was removed carefully in vacuo and purified by preparative GLC to give 107 mg (24%) of **4d**.

The reactions of 485 mg (2.92 mmol) and 1000 mg (6.02 mmol) of **4c** for 2 min and 24 h as described above gave 123 mg (28%) and 230 mg (25%) of the hydrocarbons **11**, **20a**, **21a**, **22a**, and **24**, along with small amounts of unidentified hydrocarbons. The reaction of 700 mg (4.83 mmol) of **5** for 2 min or 6 h as described above afforded 286 mg (41%) or 248 mg (35%) of the same set of hydrocarbons. **24**: IR (CCl_4) 3030, 1605 cm^{-1}; MS *m/e* 148 (M^+, 73), 120 (38), 119 (100), 91 (49); ^1H NMR 1.61 (br s, 12 H), 2.24 (s, 2 H), 5.44 (s, 2 H); ^{13}C NMR 137.9 (d), 128.0 (d), 69.0 (s), 59.6 (s), 49.0 (t), 41.9 (t, 2 C), 39.6 (t, 2 C), 25.9 (t, 2 C). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.80; H, 10.91.

The reaction of 504 mg (3.04 mmol) of **2x** for 10 min as described above gave 146 mg (32%) of hydrocarbons containing mainly **4d**. The reaction of 700 mg (4.22 mmol) of **2n** for 2 min or 24 h as described above gave 141 mg (22%) or 195 mg (31%) of the hydrocarbons. In the reactions of **2n**, a considerable amount of an unidentified product **i** was obtained. **i**: MS *m/e* 150 (M^+, 42), 122 (100), 121 (48), 107 (50), 94 (30), 81 (30), 79 (50), 67 (28), 41 (22).

The reactions of 733 mg (4.42 mmol) and 1015 mg (6.17 mmol) of **6a** for 3 min and 24 h as described above gave 180 mg (27%) and 336 mg (37%) of the hydrocarbons, respectively.

The reaction of 700 mg (4.22 mmol) of **3b** for 5 min as described above gave 227 mg (36%) of the hydrocarbons.

Koch–Haaf Reaction.[24] To 16.3 mL (301 mmol) of 97% H_2SO_4 was added a small amount of 99% HCO_2H at the temperature indicated in Table III. To the slowly stirred mixture was added dropwise a solution of 100 mg (0.60 mmol) of a reactant in the amount of 99% HCO_2H shown in Table III during 2–3 h. After addition, the reaction mixture was stirred at that temperature for 1 h and poured onto crushed ice. The solution was extracted five times with hexane. The combined extracts were washed four times with 1.4 N potassium hydroxide solution. The combined alkaline solutions were washed with hexane and then acidified to pH 2 with ca. 35% HCl. The liberated carboxylic acids were taken up in ether, and the aqueous layer was extracted with ether. The combined ether extracts were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo to give crude carboxylic acids. The hexane extracts were combined, washed with brine, and dried ($MgSO_4$). The solvent was removed in vacuo to give a small to considerable (in runs at room temperature) amount of neutral oil, comprising **11** + **20a** + **21a** and **22a** (identified by GLC). The crude acidic products were chromatographed (eluent 20% ether–petroleum ether) to give a mixture of carboxylic acids that was analyzed by GLC after treatment with ethereal diazomethane. Alternatively, the crude acidic products were treated with ethereal diazomethane to afford crude methyl esters, which were purified by flash chromatography (eluent 3% ether–petroleum ether). The results are summarized in Table III with reaction conditions.

The reaction with 100 mg (0.60 mmol) (run 3), 500 mg (3.01 mmol) (run 1 or 5), or 1000 mg (6.02 mmol) (run 2 or 4) of **4c** as described above gave 226 mg (39%, run 1), 601 mg (51%, run 2), 73 mg (63%, run 3), 1168 mg (100%, run 4), or 415 mg (66%, run 5, as methyl esters) of the carboxylic acids **20b**, **21b**, **22b**, and **22c** with a small amount of an unidentified product. Methyl esters of **20b** and **21b** were not separated successfully and were therefore analyzed as a mixture in an approximate ratio of 4.2:1 (calculated from ^{13}C NMR spectrum): IR 1725, 1245, 1230, 1175, 1080 cm^{-1}; MS *m/e* 208 (M^+, 35), 149 (100), 148 (33), 67 (27); ^1H NMR 1.1–2.9 (m, 17 H), 3.58 and 3.60 (2s, 3 H); ^{13}C NMR 179.5 (s), 53.0 (s), 51.8 (q), 46.6 (d), 44.4 (d), 37.8 (d), 37.3 (t), 34.5 (t), 33.8 (t), 33.5 (t), 31.6 (t), 27.2 (t), 17.6 (t), for the methyl ester of **20b**, and 179.0 (s), 51.5 (q), 44.2 (s), 35.4 (t), 34.3 (d), 32.8 (d), 31.4 (t), 30.8 (t), 30.6 (t), 24.8 (t), 24.6 (d), 23.7 (t), 16.2 (t), for the methyl ester of **21b**, which was identical with an authentic sample provided by Dr. Y. Inamoto. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.85; H, 9.87.

22b: mp 127–129 °C; IR (KBr) 3500–2500, 1690, 1400, 1280, 1070, 940 cm^{-1}; MS *m/e* 194 (M^+, 10), 149 (100); ^1H NMR ($CDCl_3$) 1.0–2.7 (m, 17 H), 11.74 (br s, 1 H, exchanged with D_2O); ^{13}C NMR 185.4 (s), 52.9 (s), 41.5 (d), 41.4 (d), 34.9 (d), 31.8 (t), 30.3 (t), 29.1 (t), 28.4 (t), 27.3 (t), 22.7 (t), 20.8 (t). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.97; H, 9.42.

Methyl ester of **22b**: IR 1725, 1255, 1230, 1070 cm^{-1}; MS *m/e* 208 (M^+, 14), 149 (100); ^1H NMR 1.1–2.3 (m, 16 H), 2.34–2.56 (m, 1 H), 3.56 (s, 3 H); ^{13}C NMR 178.6 (s), 53.0 (s), 51.5 (q), 41.7 (d), 41.6 (d), 34.9 (d), 31.8 (t), 30.3 (t), 29.0 (t), 28.3 (t), 27.4 (t), 22.7 (t), 20.9 (t). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.77; H, 9.97.

Methyl ester of **22c**: IR 1725, 1265, 1240, 1220, 1070 cm^{-1}; MS *m/e* 208 (M^+, 18), 149 (100); ^1H NMR 1.1–2.3 (m, 17 H), 3.56 (s, 3 H); ^{13}C NMR 178.8 (s), 51.5 (q), 46.1 (s), 42.0 (d), 39.4 (d), 39.2 (d), 35.9 (t), 30.5 (t), 29.1 (t), 26.8 (t), 25.3 (t), 24.2 (t), 20.5 (t). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.74; H, 9.88.

The reaction of 50 mg (0.30 mmol) of **2n** as described above under conditions shown in Table III gave 57 mg (91%) of methyl esters of the carboxylic acids.

The reaction of 50 mg (0.30 mmol) of **3b** as described above under conditions shown in Table III gave 38 mg (61%, run 7) or 56 mg (89%, run 8) of methyl esters of the carboxylic acids.

The reaction of 500 mg (3.01 mmol, run 9) or 200 mg (1.20 mmol, run 10) of **6a** as described above under conditions shown in Table III gave 485 mg (77%) or 224 mg (89%) of methyl esters of the carboxylic acids, respectively.

The reaction of 500 mg (3.01 mmol) of **2x** or 450 mg (2.71 mmol) of **4b** as described above under conditions shown in Table III gave 491 mg (84%) or 428 mg (81%) of the carboxylic acid **4e**: mp 93–94 °C; IR (KBr) 3500–2500, 1690, 1400, 1280, 930 cm^{-1}; MS *m/e* 194 (M^+, 16), 166 (100), 149 (81), 121 (41); ^1H NMR 1.1–2.4 (m, 17 H), 12.08 (br s, 1 H, exchanged with D_2O). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.09; H, 9.36.

50% H_2SO_4–THF Reaction.[3] To a stirred solution of 500 mg (3.01 mmol) of **3b** in 5 mL of THF was added 1 mL of 50% H_2SO_4 at 0 °C. The resulting solution was stirred at 55 °C for 100 h, and then water was added. The mixture was extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ solution and brine and dried ($MgSO_4$). The solvent was removed in vacuo to give 435 mg of recovered **3b**. The reaction of 500 mg (3.01 mmol) of **3b** at reflux for 120 h as described above gave 110 mg (25%) of **24**, 9 mg (2%) of **34**,[26] 91 mg (22%) of **6a**, a trace amount of **4c**, and 95 mg (19%) of recovered **3b**, after chromatography.

The reaction of 500 mg (3.38 mmol) of **5** at 55 °C for 2.5 h as described above gave 441 mg (79%) of **6a**, 4 mg (1%) of **4c**, and 13 mg of recovered **5**.

Chemical Transformations of Carboxylic Acids 20b, 21b, 22b, and 22c into Tricycloundecanes 20a, 21a, and 22a. Modified Kochi Reaction.[25] A 330-mg (1.70 mmol) sample of **22b** and **22c** (in 92:8 ratio) and 1.39 g (10.2 mmol) of 98% *N*-chlorosuccinimide were dissolved in 12 mL of acetic acid and DMF (v/v, 1:5). The solution was freed of oxygen by bubbling with nitrogen for 15 min. To the stirred solution was added 754 mg (1.70 mmol) of $Pb(OAc)_4$, and nitrogen was bubbled again for 15 min. The reaction mixture was heated at 40–50 °C for 1 h. The solution was cooled and extracted with pentane. The combined extracts were washed successively with 20% perchloric acid, 10%

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potassium carbonate, and water. After being dried ($MgSO_4$), the solvent was removed in vacuo to give 293 mg of two chlorides in an approximate ratio of 91:9.

Reduction with Bu_3SnH. To a stirred solution of the above chlorides and 50 mg of AIBN in 7 mL of cyclohexane was added a solution of 594 mg (2.04 mmol) of Bu_3SnH in 5 mL of cyclohexane at room temperature under nitrogen. The solution was heated at reflux for 1 h. The solvent was removed in vacuo, and the residue was chromatographed (eluent petroleum ether) to give 220 mg (86% from **22b** and **22c**) of a hydrocarbon that was identical (^{13}C NMR) with **22a**.

Similar transformation of 381 mg (1.98 mmol) of the carboxylic acids **20b** + **21b**, **22b**, and **22c** (in ratio of 11:59:30) as described above gave 205 mg (70% overall yield) of **20a** + **21a** and **22a** with a ratio of 12:88. The tricycloundecanes **20a** and **21a** were identified by their ^{13}C NMR spectra, and their ratio was approximately 4:1.

Modified Kochi reaction of 221 mg (1.14 mmol) of **4e** as described above gave a chloride that was identical (^{13}C NMR) with the known compound **4f**.[3]

Preparation of an Authentic Sample of 24. A solution of 1.20 g (7.32 mmol) of **3a** and 1.36 g (7.32 mmol) of tosylhydrazide in 25 mL of methanol was heated at reflux for 5 h. The solvent was removed in vacuo to give the crude tosylhydrazone: IR (KBr) 3210, 1590, 1330, 1165 cm^{-1}.

To a stirred solution of the hydrazone in 30 mL of dry ether was added dropwise 14.6 mL (17.6 mmol) of 1.2 M MeLi in ether at 20–25 °C under nitrogen. The resulting reaction mixture was stirred at the temperature for 16 h. A small amount of water was added carefully, and then additional water was added. The organic layer was separated and washed three times with water. The combined aqueous layers were extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated carefully in vacuo. The residue was chromatographed (eluent petroleum ether) to give 587 mg (55% overall yield) of an olefin that was identical (MS, ^1H NMR, ^{13}C NMR) with **24**.

X-ray Analysis of 22b: formula $C_{12}H_{18}O_2$; $M_r = 194.27$; crystal selected from a sample recrystallized from hexane; triclinic, space group $P\bar{1}$; $a = 6.354$ (17) Å, $b = 6.712$ (2) Å, $c = 13.441$ (3) Å; $d_{calcd} = 1.230$ g cm^{-3}, $d_{obsd} = 1.245$ g cm^{-3}; $Z = 2$. The intensity data were measured on a CAD4 Enraf-Nonius diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) by θ–2θ scan technique. A total of 3043 independent reflections were measured for $\theta \leq 30°$, of which 2386 were considered to be observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using MULTAN 82 and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were refined with isotropic thermal parameters. The final discrepancy indices were $R = 8.33\%$ and $R_\omega = 6.71\%$ for the 2386 observed reflections. The final difference Fourier map was essentially featureless, with no peaks greater than ± 0.2 e $Å^{-3}$.

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Supplementary Material Available: Tables IV–IX listing final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for **22b** and ORTEP drawing of **22b** (6 pages). Ordering information is given on any current masthead page.

The pK_a of Areneselenenic Acids[1]

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The pK_a's of *o*-nitrobenzeneselenenic acid (**1a**) and three 4-substituted-2-nitrobenzeneselenenic acids (**1b–d**) have been determined at 25 °C in water. A Hammett plot of the pK_a's gives a ρ value for the ionization of ArSeOH (eq 3) of +1.4. The pK_a of **1a** is 10.45, which makes it 2.8 times weaker as an acid than phenol. Areneselenenic acids are therefore surprisingly weak acids. If the only influence of the *o*-nitro group on the acidity of **1a** is its inductive effect, the pK_a of benzeneselenenic acid (which cannot be measured directly because of the instability of PhSeOH) is predicted to be 11.5.

Areneselenenic acids (ArSeOH) play an important role as reactive intermediates in organoselenium reactions. For example, an areneselenenic acid is the "other product" in the synthetically important olefin-forming elimination of alkyl aryl selenoxides ($-CH-C-Se(O)Ar \rightarrow {>}C{=}C{<} + ArSeOH$),[2] and areneselenenic acids are thought to be generated as intermediates in the reduction of areneseleninic acids ($ArSeO_2H$) by a spectrum of reagents.[3]

In view of the relative ubiquity of areneselenenic acids as intermediates in selenium chemistry, information about their strength as acids would clearly be of considerable value. Such information has, regretably, not heretofore been available. This has undoubtedly been due to the fact that the vast majority of areneselenenic acids are of too limited stability and lifetime to permit straightforward measurement of their pK_a.

Previous research[4] in this laboratory has shown, however, that dilute solutions of *o*-nitrobenzeneselenenic acid, **1a** (ArSeOH, Ar = $o\text{-}O_2NC_6H_4$) are quite stable. These can be prepared either by hydrolysis of a solution of the corresponding selenenic anhydride ($ArSeOSeAr + H_2O \rightarrow 2\,ArSeOH$),[4] or by room-temperature decomposition of a concentrated solution of ethyl *o*-nitrophenyl selenoxide[5] ($ArSe(O)CH_2CH_3 \rightarrow ArSeOH + CH_2{=}CH_2$) followed by appropriate dilution.[6]

In the present work we have measured the pK_a of **1a** and of several 4-substituted-2-nitrobenzeneselenenic acids in water at 25 °C. We find that areneselenenic acids are surprisingly weak acids, much weaker than most organic

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