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Reductive Rearrangement with Hydride Transfer of Linearly and Angularly Fused Triquinanes

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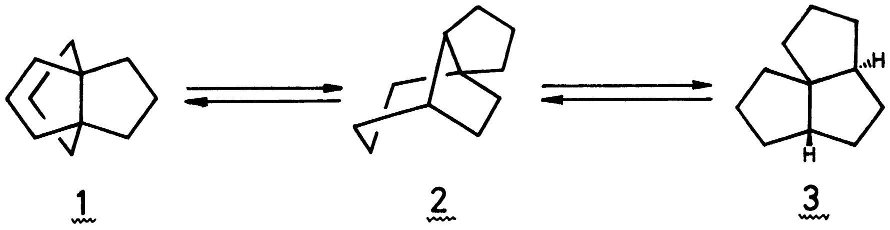
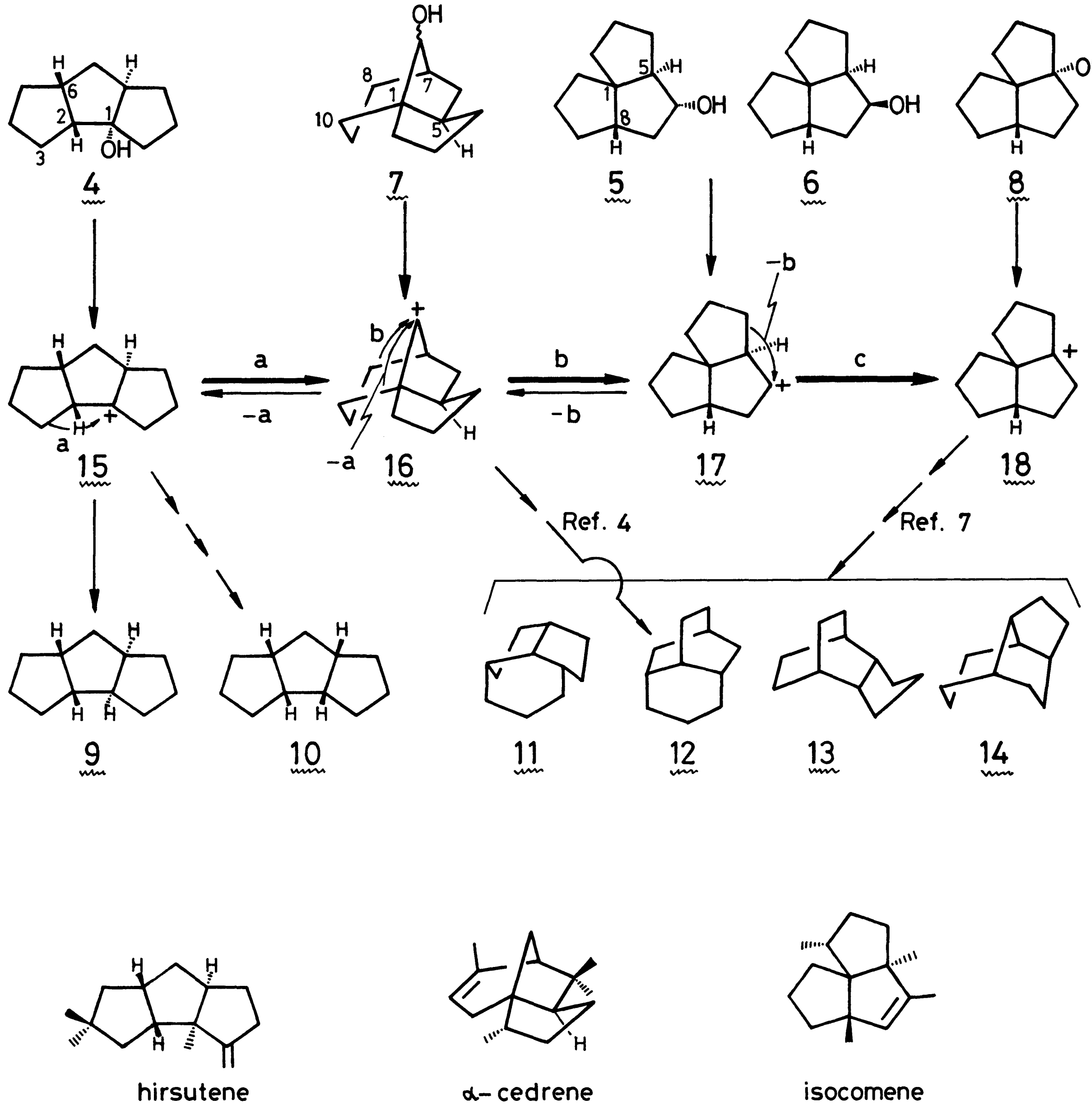
Relationship between linearly and angularly fused triquinanes is elucidated by reductive rearrangements with hydride transfer of tricyclo[6.3.0.0^{2,6}]undecan-1-ol, tricyclo[6.3.0.0^{1,5}]undecan-6-ols, and tricyclo[5.3.1.0^{1,5}]undecan-11-ol.

Recently much attention has been focused on the biogenesis[1)] of polyquinane sesquiterpenes[2)] containing various tricycloundecane ring systems, each formally derivable by cationic cyclization of humulene. While the mutual transformations of tricycloundecanes ($C_{11}H_{18}$), i.e., "homoadamantane-land,"[3)] have been well-documented by Ōsawa,[4)] Inamoto,[5)] and their co-workers, little is known for the rearrangements of triquinane type $C_{11}H_{18}$.[6)] On that point, we have recently demonstrated[7)] the interesting relationship between the propellane and angular type triquinanes **1** and **3** through the diquinane **2** in "homoadamantane-land," which have the basic frameworks[2)] of natural polyquinanes, modhephene, isocomene, and quadrone, respectively. In this connection, we describe herein the reductive rearrangements with hydride transfer of cis-transoid-cis-tricyclo[6.3.0.0^{2,6}]-undecan-1-ol (**4**),[8)] having basic skeleton of linearly fused natural triquinanes such as hirsutene,[2)] and angularly fused triquinane alcohols, tricyclo[6.3.0.0^{1,5}]-undecan-6-ols (**5** and **6**),[9)] which could form the 6-yl cation **17** unlike the 5-yl cation **18**, to develop a new entry into the "land" from the linear triquinane.



The reductive rearrangement of the alcohols **4**-**6** were carried out using 97% H_2SO_4-pentane as described previously[7)] and the time-conversion relationships are listed in Table 1. Interestingly, treatments of them gave the same hydrocarbons, cis-transoid-cis- and cis-cisoid-cis-tricyclo[6.3.0.0^{2,6}]undecanes (**9** and



Scheme 1.

10),8) tricyclo[5.3.1.0^{4,11}]undecane (**11**),10) tricyclo[5.3.1.0^{3,8}]undecane (**12**),11) tricyclo[5.2.2.0^{2,6}]undecane (**13**),10) and tricyclo[5.4.0.0^{4,8}]undecane (**14**),10) in similar ratios.12)

Since reaction of tricyclo[6.3.0.0^{1,5}]undecan-5-ol (**8**) afforded the same products **11**-**14** via the cation **18** except the linear triquinanes **9** and **10** in ratios almost similar to those from **4**-**6** (Table 1),7) the former hydrocarbons may be produced through the same rearrangement route proposed previously.13) Therefore we consider the pathways from **4**-**6** to **9**-**14** as shown in Scheme 1, taking into account

Table 1. Reductive rearrangement with hydride transfer of tricycloundecanols

Reactant	Reactn time min(h)	Yield[a] %	Product/%[b] 9	10 + 11 + 12 + 13	14	Others[c]
4	2	19	6	40	46	8
				(4 : 5 : 28 : 3)		
	10		5	50	38	7
	60		6	57	32	5
	(24)	33	7	85	0	8
				(7 : 10 : 61 : 7)		
5	0.5	24	6	55	34	5
				(7 : 12 : 29 : 7)		
	5		6	59	30	5
	60		6	79	10	5
	360	37	7	85	4	4
				(6 : 12 : 60 : 7)		
6	2		5	61	29	5
	120	36	5	73	17	5
				(4 : 12 : 51 : 6)		
7	2		7	69	19	5
	60	30	5	84	7	4
				(4 : 11 : 65 : 4)		
8[d]	3	27		29	64	7
				(8 : 11 : 10)		
	10			58	37	5
	60			80	13	7
	(24)	37		84		16
				(10 : 69 : 5)		

a) Isolated yield of total hydrocarbons. b) The products are arranged in order of increasing retention time in GLC. The relative ratios of the products were calculated from GLC peak areas. Ratios in parentheses were calculated from ^{13}C NMR spectra because 10-13 were not separated in GLC. c) Some unidentified products were obtained. d) Data from Ref. 7.

the mechanism of "homoadamantane-land" elucidated by Ōsawa *et al*. using molecular mechanics.[4] The rearrangement of 4 proceeds via (i) the migration of C(2)-C(3) bond (path a) in the cation 15 derived from 4, (ii) 1,2-alkyl shift of C(7)-C(8) bond (path b) in the resulting cation 16 to give the cation 17, and (iii) 1,2-hydride shift (path c) to yield the cation 18. On the other hand, the cation 15 accepts a hydride to give 9 and the cisoid compound 10 although 10 can not be formed directly from 15.[14] From the results that reactions of 5 and 6 gave the linear triquinanes 9 and 10 even in the earlier stage, it can be seen that the "backward" pathways which involve the 1,2-alkyl shift of C(4)-C(5) bond in 17 (path -b) and the subsequent migration of C(10) in 16 to 15 (path -a) exists. In order to ascertain the route, similar reaction of tricyclo[5.3.1.0^{1,5}]undecan-11-ol (7)[9] from which the cation 16 could be derived was undertaken (Table 1). Since the same set of hydrocarbons was obtained in ratios similar to those from 4-6,[12] we propose an interesting mechanism; that is a formation in vitro of linearly and angularly fused triquinanes from the common intermediate diquinyl cation which is also the basic skeleton of natural cedrenoid sesquiterpenes such as α-cedrene.[2)] Not surprisingly, in the biogenesis like conversion of humulene well-studied by Matsumoto *et al.*, these rearrangement pathways such as path a → b have been also inferred.[15)]

References

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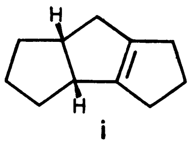
12) Neither reaction of **4** in 50% H_2SO_4-THF nor acetolyses of the tosylates derived from the corresponding alcohols **5**-**7** gave the rearrangement products.
13) In each earlier stage of the reactions of **4**-**7**, a larger quantity of **12** with a smaller amount of **14** were formed compared with the case of **8**. Therefore, an alternate route to **12**, for example via the cation **16**,[4)] may also operate as a by-path.
14) Probably, **10** may be formed via the corresponding *cis-cisoid-cis* cation derived by protonation of the olefin **i** which is produced by deprotonation of **15**.



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