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Studies on the Terpenoids and Related Alicyclic Compounds. XV.[1) Reduction of α-Ketol Acetates of 5α-Santanolide and the Stereochemistry of O,O-Acyl Rearrangement of *vic*-Diol Monoacetates in the Cyclohexane Ring System[2)

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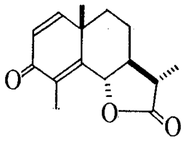
Reduction of α-ketol acetates (**5**, **6**, **7**, and **8**) of 5α-santanolide with $NaBH_4$ and $LiAlH(OBu^t)_3$ were investigated. The structure of diol monoacetates (**9**—**16**) was determined by means of spectroscopic methods and some chemical transformation reactions, oxidation and acetylation. Their conformations are discussed from their NMR data. O,O-Acyl rearrangement was observed in the $NaBH_4$ reduction of α-ketol acetates (**5**, **6**, and **8**). The acid- and base-catalyzed O,O-acyl rearrangements of diol monoacetates (**9**—**16**) were also investigated. The acyl migration mechanisms are proposed.

Keywords——sesquiterpenoid; santanolide; 1,2-ketol acetate; 1,2-diol monoacetate; reduction; O,O-acyl rearrangement; mechanism; stereochemistry; conformation; NMR

In the previous papers, the chemical transformations of α-santonin (**1**) into some sesquiterpene α-methylene-γ-lactones have been reported.[4) We have attempted to synthesize the tumor inhibitory sesquiterpenoid, vernolepin[5) (**2**), from **1**. The first important step of



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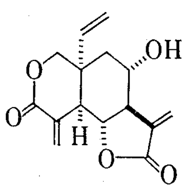

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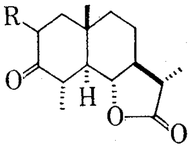
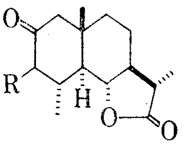
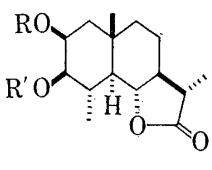


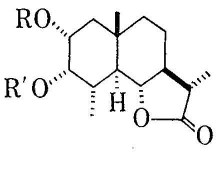
3 : R=H
5 : R=β-OAc
6 : R=α-OAc



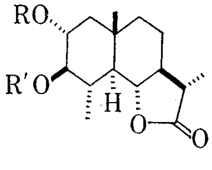
4 : R=H
7 : R=α-OAc
8 : R=β-OAc



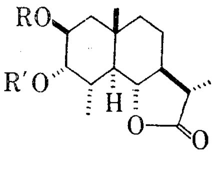
9 : R=Ac, R′=H
10 : R=H, R′=Ac



11 : R=Ac, R′=H
12 : R=H, R′=Ac



13 : R=Ac, R′=H
14 : R=H, R′=Ac



15 : R=Ac, R′=H
16 : R=H, R′=Ac

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1) Part XIV: K. Yamakawa, K. Nishitani, and K. Azusawa, *Heterocycles*, **9**, 499 (1978).
2) Preliminary results were reported at the 20th Symposium on the Chemistry, Terpenes, Essential Oils, and Aromatics, Akita, Oct., 4—6, 1976, Symposium Papers pp. 251—253.
3) Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*
4) K. Yamakawa, K. Nishitani, and T. Tominaga, *Tetrahedron Lett.*, **1975**, 2829; K. Yamakawa, T. Tominaga, and K. Nishitani, *ibid.*, **1975**, 4137; K. Yamakawa, K. Nishitani, and A. Yamamoto, *Chem. Lett. Jpn.*, **1976**, 177; K. Yamakawa, K. Nishitani, and K. Azusawa, *Heterocycles*, **8**, 103 (1977); K. Yamakawa, K. Nishitani, and K. Azusawa, *ibid.*, **9**, 499 (1978).
5) S.M. Kupchan, R.J. Hemingway, D. Werner, A.T. McPhail, and G.A. Sim, *J. Am. Chem. Soc.*, **90**, 3596 (1968).

this chemical transformation seems to be an activation of the C-10 methyl group of a santanolide.⁶⁾ Therefore we attempted to reduce 2-oxo-3-acetoxy-5α-santanolides (**7** and **8**) which were prepared from 2-oxo-5α-santanolide (**4**) in order to synthesize 3-acetoxy-2β-hydroxy-5α-santanolides (**10** and **16**) as key intermediates.

In the course of the reduction of the α-ketol acetates of 2- and 3-oxo-5α-santanolides (**3** and **4**), we found the formation of O,O-acyl rearrangement products. In this paper we wish to report the reduction of the four α-ketol aoetates (**5**, **6**, **7**, and **8**) with some metal hydride complexes and the investigation of the configuration and the conformation of the reduction products, *vic*-diol monoacetates (**9**—**16**), by means of some chemical evidences and nuclear magnetic resonance (NMR) spectra. The stereochemistry of these O,O-acyl rearrangement reactions of all pairs of *vic*-diol monoacetates (**9**–**10**, **11**–**12**, **13**–**14**, and **15**–**16**) in the cyclohexane system by acid or base catalysts was also studied.

Results and Discussion

Reduction of α-Ketol Acetates with Metal Hydride Complexes

Reduction of α-ketol acetates (2β-acetoxy-3-one⁷˒⁸⁾ (**5**), mp 174—175°; 2α-acetoxy-3-one⁹⁾ (**6**), mp 199—200°; 3α-acetoxy-2-one⁷⁾ (**7**), mp 185—187°; and 3β-acetoxy-2-one¹⁰⁾ (**8**), mp 210—211°) derived from **3** and **4** with metal hydride complexes, lithium tri-*t*-butoxyaluminum hydride ($LiAlH(OBu^t)_3$) and sodium borohydride ($NaBH_4$), was investigated. The structure of the reduction products, diol monoacetates (**9**—**16**), was determined from NMR spectrometry and some transformation reactions such as oxidation to the known ketol acetates (**5**—**8**), which are described below.

Reduction of **5** with $LiAlH(OBu^t)_3$ was stereoselective and the product consisted entirely of 2β-acetoxy-3β-ol (**9**), mp 165—167°, whereas that with $NaBH_4$ gave a mixture of diol monoacetates. The mixture was separated by preparative thin-layer chromatography (TLC) into (**9**; 46% yield), 2β-acetoxy-3α-ol (**15**; 9% yield), mp 191—193°, and an acyl rearrangement product, 3β-acetoxy-2β-ol (**10**; 18% yield), mp 172—175°.

Reduction of **6** under the same conditions as for the epimer (**5**) with $LiAlH(OBu^t)_3$ gave 2α-acetoxy-3α-ol (**11**; 39% yield), mp 166—167°, and 2α-acetoxy-3β-ol (**13**; 34% yield), mp

TABLE I. Yield of the Reduction Products of Ketol Acetates

Ketol acetate	Reagent[a]	Product yield (%)							
		9	**10**	**11**	**12**	**13**	**14**	**15**	**16**
5	A	100							
	B	46	18					9	
6	A			39		34			
	B[b]			22	32	4			
7	A			24	15				55
	B				Trace				99
8	A	10	80						
	B	52	22						

a) A; $LiAlH(OBu^t)_3$ in THF, B; $NaBH_4$ in ethanol.
b) A mixture of stereoisomeric diols was obtained in 23% yield.

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6) An activation procedure was performed by Tatsuno; Y. Fujimoto and T. Tatsuno, The 98th Annual Meeting of Pharmaceutical Society of Japan, Okayama, Apr., 3—5, 1978. Abstract of Papers, p. 326.
7) K. Nishitani, Dissertation of Master's Degree, Science University of Tokyo, March, 1973.
8) P.L. Kamat, A.M. Shaligram, and A.S. Rao, *Indian J. Chem.*, **14B**, 157 (1976).
9) K. Yamakawa, *J. Org. Chem.*, 24, 897 (1959).
10) K. Yamakawa, S. Kidokoro, N. Umino, R. Sakaguchi, T. Takakuwa, and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), 21, 296 (1973).

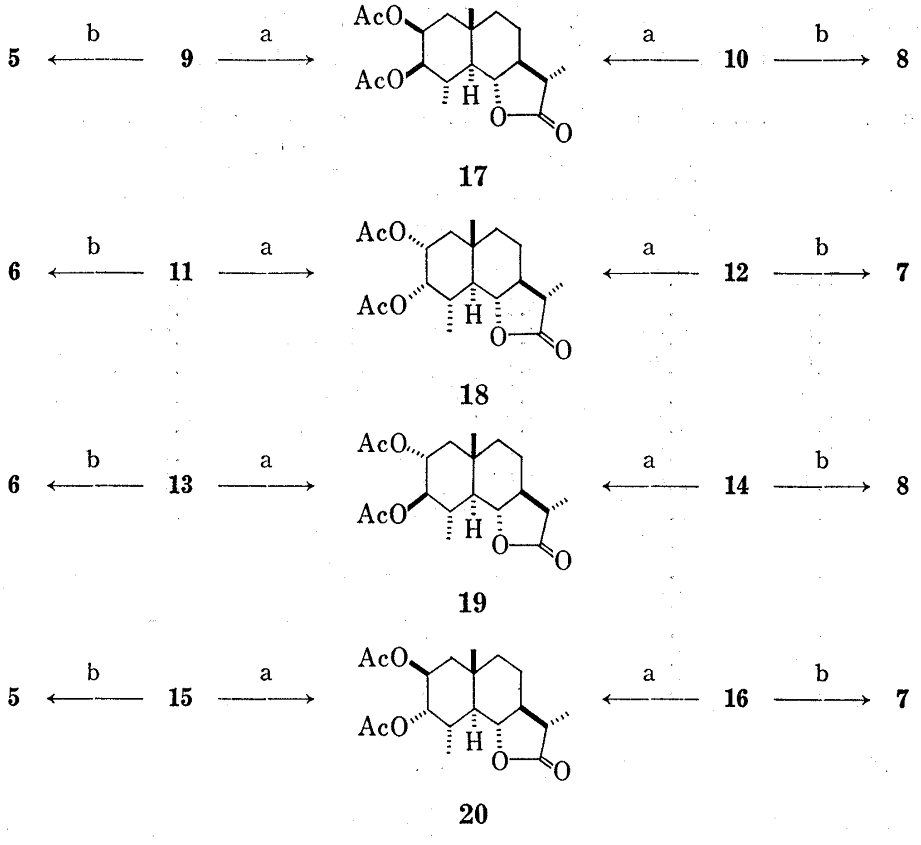
200—202°, while **6** was reduced with $NaBH_4$ to afford (**11**; 22% yield), (**13**; 4% yield), and an acyl rearrangement product 3α-acetoxy-2α-ol (**12**; 32% yield), mp 160—162°.

Reduction of **7** with $LiAlH(OBu^t)_3$ gave a mixture of 3α-acetoxy-2β-ol (**16**; 55% yield), mp 178—179°, 3α-acetoxy-2α-ol (**12**; 15% yield), and an acyl rearrangement product, 2α-acetoxy-3α-ol (**11**; 24% yield), while that of **7** with $NaBH_4$ gave **16** stereoselectively. Reduction of **8** with $LiAlH(OBu^t)_3$ furnished 3β-acetoxy-2β-ol (**10**; 80% yield) as a predominant product, together with an acyl rearrangement product, 2β-acetoxy-3β-ol (**9**; 10% yield), while **8** was reduced with $NaBH_4$ to give an acyl rearrangement product (**9**; 52% yield), together with (**10**; 22% yield).

These results are summarized in Table I. The conformation of the ring A of the ketol acetates (**6**, **7**, and **8**) was deduced to be a chair from but that of the ketol acetate (**5**) to be a twist form by their NMR analysis.[7,8] The formation of major reduction products of the ketol acetates (**5**—**8**) can be explained in terms of the predominant equatorial attack of the reducing reagents on the ketone carbonyl groups.

Stereoformulae of Diol Monoacetates (9—16)

Infrared (IR) spectra of all the stereoisomeric diol monoacetates (**9**—**13**, **15**, **16**, and the new rearrangement compound (**14**) as will be described below) showed absorption bands due to the hydroxyl group, γ-lactone, and acetyl-carbonyl groups. These stereoformulae of the diol monoacetates (**9**—**16**) were confirmed by some chemical transformation reactions as described below.



a; Ac_2O, pyridine b; CrO_3-pyridine complex

Chart 1

Oxidation of the stereoisomeric diol monoacetates (**9** and **15**, and **11** and **13**) with chromium trioxide-pyridine complex gave the known 2β-acetoxy-3-one[7,8] (**5**) and 2α-acetoxy-3-one[9] (**6**), respectively. Thus, the structures of **9** and **15**, and **11** and **13** were confirmed as 2β-acetoxy-3-ols and 2α-acetoxy-3-ols, respectively.

According to the procedure described above, oxidation of the stereoisomeric diol monoacetates (**12** and **16**, and **10** and **14**) afforded the known 3α-acetoxy-2-one[9] (**7**) and 3β-acetoxy-2-one[10] (**8**), respectively. Therefore, the stereoformulae of **12** and **16**, and **10** and **14** were respectively confirmed as 3α-acetoxy-2-ols and 3β-acetoxy-2-ols.

From these results, the configuration of the acetoxyl group in all diol monoacetates (**9**—**16**) was confirmed.

Configuration of the hydroxyl group in all the diol monoacetates (**9**—**16**) was then investigated. Acetylation of 2β-acetoxy-3-ol (**9**) and 3β-acetoxy-2-ol (**10**) with acetic anhydride in pyridine gave 2β,3β-diacetate (**17**), mp 213—213.5°. Consequently, the β configuration of the hydroxyl groups in 2β-acetoxy-3-ol (**9**) and 3β-acetoxy-2-ol (**10**) was confirmed.

Acetylation of the diol monoacetates (**11**—**16**) was carried out as described below; 2α-acetoxy-3-ol (**11**) and 3α-acetoxy-2-ol (**12**) were treated with acetic anhydride to afford the same diacetate, 2α,3α-diacetate (**18**), mp 161—163°. Acetylation of 2α-acetoxy-3-ol (**13**) and 3β-acetoxy-2-ol (**14**), and that of 2β-acetoxy-3-ol (**15**) and 3α-acetoxy-2-ol (**16**) gave 2α,3β-diacetate (**19**), mp 170—172°, and 2β,3α-diacetate (**20**), mp 166—168°, respectively. Consequently, the stereoformulae of these diol monoacetate (**9**—**16**) were confirmed from the chemical correlation between the diol monoacetates and the ketol acetates (**5**—**8**) or the diacetates (**17**—**20**).

Conformational Proof of Diol Monoacetates (9—16) and Diol Diacetates (17—20) from NMR Spectrometry

Conformational studies of the diol monoacetates (**9**—**16**) and the diol diacetates (**17**—**20**) were made by NMR spectroscopy. Chemical shifts and coupling constants of 2-H, 3-H, 10-methyl, and acetylmethyl group of **9** to **20** are shown in Table II.

Table II. NMR Data of the Diol Monoacetates (**9**—**16**) and the Diol Diacetates (**17**—**20**)

Compound	Chemical shift[a] (δ) and coupling constant (J=Hz)			
	10-CH_3	CH_3COO–	2-H	3-H
9	1.08	2.17	5.13 (q, J=3)	3.23 (dd, J=10, 3)
10	1.21	2.10	4.10 (q, J=3)	4.55 (dd, J=10, 3)
11	1.02	2.03	5.00 (ddd, J=12, 5, 3)	3.79 (t, J=3)
12	0.97	2.10	3.96 (td, J=10, 3)	5.12 (t, J=3)
13	1.03	2.01	4.92 (ddd, J=12, 10, 5)	3.10 (t, J=10)
14	1.01	2.12	3.82 (ddd, J=12, 10, 5)	4.43 (t, J=10)
15	1.08	2.05	4.92 (q, J=3)	3.62 (t, J=3)
16	1.15	2.02	3.85 (q, J=3)	4.75 (t, J=3)
17	1.14	2.00 2.08	5.30 (q, J=3.6)	4.52 (dd, J=11, 3.6)
18	1.02	1.92 2.05	5.04 (ddd, J=12, 5, 3)	5.20 (t, J=3)
19	1.09	1.96 2.03	5.09 (ddd, J=12, 10, 5)	4.65 (t, J=10)
20	1.07	2.04 2.05	4.85 (2H, m, $W1/2$=9)	

a) Chemical shifts are given in ppm relative to TMS.

In the NMR spectra of 2β-acetoxy-3β-ol (**9**) and 3β-acetoxy-2β-ol (**10**), the coupling constants of 1–2, 2–3, and 3–4 were 3, 3, and 10 Hz, respectively, and the signal of 10-methyl group of **9** appeared at a field 0.13 ppm higher than that of **10**, which was explained by the Kawazoe rule.[11] Therefore, the conformation of **9** and **10** in ring A should be a chair

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[11] Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.* (Tokyo), **10**, 338 (1962); Y. Kawazoe, Y. Sato, T. Okamoto, and K. Tsuda, *ibid.*, **11**, 328 (1963); T. Okamoto and Y. Kawazoe, *ibid.*, **11**, 643 (1963).

form in terms of the 1,3-diaxial relationship between 10-methyl group and 2-acetoxyl group. The 2β,3β-diacetate (**17**) derived from **9** and **10** should possess a chair form in the ring-A, because the coupling constants of 1–2, 2–3, and 3–4 are 3.6, 3.6, and 11.0 Hz, respectively.

NMR spectra of 2β-acetoxy-3α-ol (**15**) and 3α-acetoxy-2β-ol (**16**) had the same coupling constants, 1–2=2–3=3–4=3 Hz, and the signal due to the 10-methyl group of **15** appeared at a field 0.07 ppm higher than that of **16**.

From these NMR data, the conformation of the ring-A of **15** and **16** should be a chair form since the 10-methyl and acetoxyl groups of **15** should have 1,3-diaxial relationship. The conformation of 3α,3β-diacetate (**20**) is assumed to be a chair form in the ring-A because of the same coupling constants of 1–2, 2–3, and 3–4 as in **15** and **16**.

The conformation of 2α-acetoxy-3α-ol (**11**) should be a chair form in the ring-A because the coupling constants of 1–2, 1′–2, 2–3, and 3–4 are 12, 5, 3, and 3 Hz, respectively, while in 3α-acetoxy-2α-ol (**12**) the coupling constants of 1–2, 1′–2, 2–3, and 3–4 are 10, 10, 3, and 3 Hz, respectively, and its conformation is not determined as yet. However, the conformation of the ring-A of 2α,3α-diacetate (**18**) derived from **11** and **12** is assumed to be a chair form because the coupling constants of 1–2, 1′–2, 2–3, and 3–4 are 12, 5, 3, and 3 Hz, respectively. Conformation of both 2α-acetoxy-3β-ol (**13**) and 3β-acetoxy-2α-ol (**14**) should be a chair form in the ring-A since the coupling constants of 1–2, 1′–2, 2–3, and 3–4 are 12, 5, 10, and 10 Hz, respectively. Similarly, 2α,3β-diacetate (**19**) derived from **13** and **14** should have a chair form because of the same coupling constants as in **13** and **14**.

O,O-Acyl Rearrangement Reaction

There are many acyl migration reactions which proceed by the SN 2 reaction accompanied by the inversion of the configuration.[12,13] Stereochemistry of the intramolecular rearrangement reaction has been worthy of remark both in the fields of natural products and organic reaction mechanisms. Some O,O- and N,O-acyl migrations with retention of the configuration have been observed in the fields of carbohydrate,[14] steroid,[12] and alkaloid chemistry,[13] however very few O,O-acyl migrations have been reported in the cyclohexane ring system.

Taub *et al.*[15] reported the acyl migration in the $NaBH_4$ reduction of C-20 carbonyl group of corticosterone acetate. We also found that reduction of α-ketol acetates (**5**—**8**) with $NaBH_4$

Table III. Ratios of Acyl Rearrangement Products

Starting material	Product	Ratio (reaction time [hr])		
			Catalyst	
		NaH	Methanolic HCl	BF_3-etherate
9	**9/10**	1.1/1(5)[a]	1.2/1(5),[b] 1.2/1(10)[a]	3.8/1(5)[a]
10	**9/10**	1.1/1(5)[a]	1/1.1(5),[b] 1.3/1(10)[a]	3.4/1(5)[a]
11	**11/12**	2.0/1(4)[a]	1/tr[c] (48),[b] 2.3/1(240)[a]	1/2.5(5),[b] 0/1(120)[b]
12	**11/12**	1.9/1(4)[a]	1/1(48),[b] 1/1.2(240)[a]	0/1(5),[b] 0/1(120)[b]
13	**13/14**	1.6/1(2.5)[a]	6.9/1(240)[a]	1/1(120),[b] 1/1.2(240)[a]
14	**13/14**	1.7/1(2.5)[a]	1/1.9(240)[a]	1/2(120),[b] 1/1.2(240)[a]
15	**15/16**	1/1(48),[b] 1/1(96)[b]		1/tr[c] (192)[b]
16	**15/16**	0/1(48),[b] 1/1(96)[b]		

All reactions were performed in dry benzene at room temperature.

a) Ratio of isolated yield.

b) Evidenced by NMR analysis.

c) Trace.

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12) R.U. Lemieux, "Molecular Rearrangements," Vol. 2, by P. deMayo ed., Wiley-Interscience, New York, 1964, pp. 763—769, 1121—1127.

13) D.J. Cram, "Steric Effects in Organic Chemistry," by M.S. Newman ed., Wiley and Sons Inc., New York, 1956, pp. 290—295.

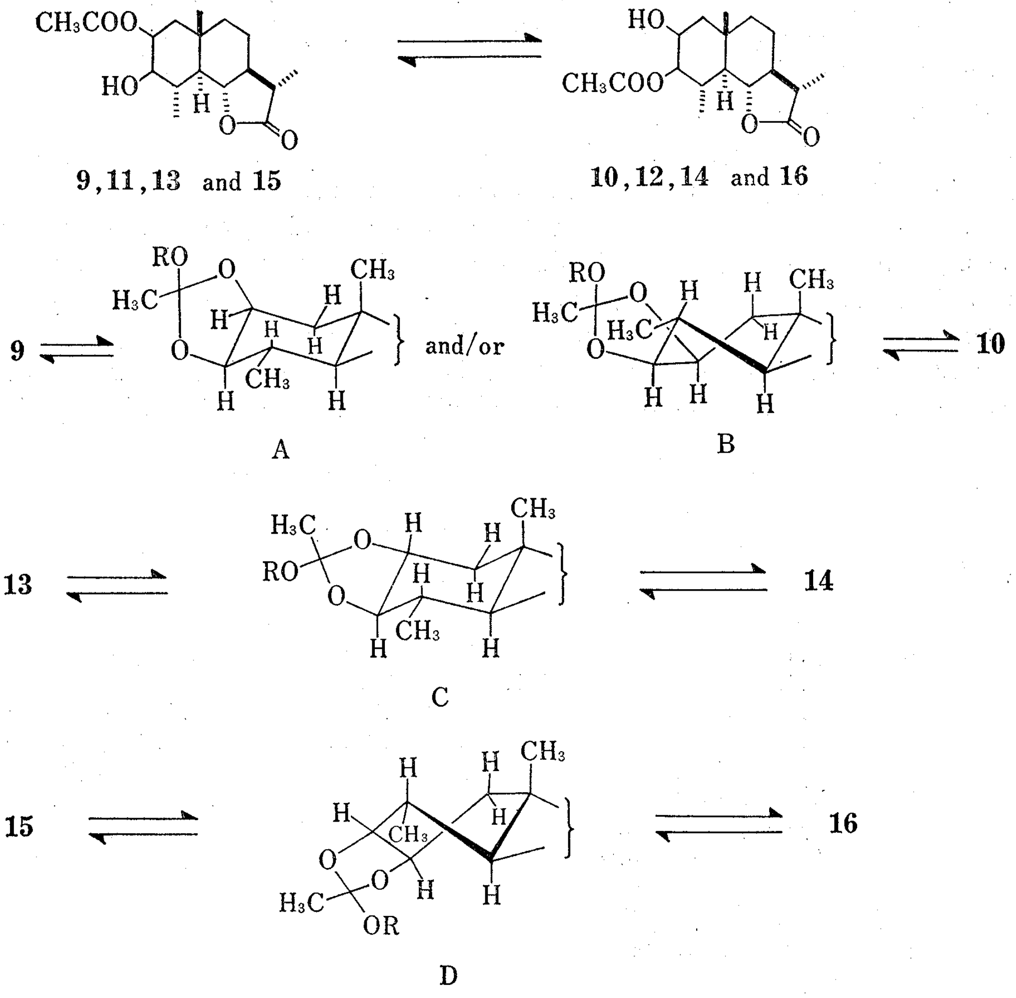
14) J.M. Sugihara, *Adv. Carbohyd. Chem.*, **8**, **1** (1953).

15) D. Taub, R.D. Hoffsommer, and N.L. Wendler, *J. Am. Chem. Soc.*, **81**, 3291 (1959).

furnished abnormal reduction products as described above. This suggests that the intramolecular O,O-acyl rearrangement may also occur in these reducing systems. Therefore, acid- and base-catalyzed acyl rearrangements of the diol monoacetates (**9**—**16**) were examined. In general, O,O-acyl migrations in carbohydrate and N,O-acyl migration in alkaloid fields were carried out in dilute hydrochloric acid–acetone or aqueous sodium hydroxide solution.[12,13] Treatment of the diol monoacetates (**9**—**16**) with aqueous acid or base gave acyl rearrangement products (**9**—**16**), however the ratios of the starting diol monoacetate to the rearranged product are not clear because of the formation of diols by hydrolysis. Consequently, these rearrangements were examined in detail at room temperature in benzene in the presence of three kinds of catalyst; sodium hydride, methanolic hydrochloric acid, boron trifluoride etherate. These experimental results are summarized in Table III.

The characters of these rearrangements can be summarized as follows: (a) The configuration at C-2 and C-3 is retained; (b) Acyl rearrangement of the 2,3-diaxial derivatives (**15** and **16**) is fairly slow; (c) 2,3-Axial-equatorial derivatives (**9**—**12**) are more easily rearranged than 2,3-diequatorial derivatives (**13** and **14**); (d) The yields of each rearrangement products are different according to the reagent used.

We will propose these rearrangement reaction mechanisms as shown in Chart 2.



R=H or BF_3 or Na

Chart 2

This intramolecular acyl rearrangement proceeds with retention of the configurations at C-2 and C-3 under acidic or basic conditions. The *cis*-diol monoacetates, 2β-acetoxy-3β-ol (**9**) and 3β-acetoxy-2β-ol (**10**), undergo rearrangement *via* the five-membered cyclic intermediate with chair form (A) and/or flexible form (B). In the diequatorial *trans*-diol monoacetates, 2α-acetoxy-3β-ol (**13**) and 3β-acetoxy-2α-ol (**14**), the intramolecular rearrangement also proceeds *via* the cyclic intermediate with chair form (C).

On the other hand, acyl migration of the diaxial *trans*-diol monoacetates, 2β-acetoxy-3α-ol (**15**) and 3α-acetoxy-2β-ol (**16**), was fairly slow, owing to the difficulty of the formation of the cyclic intermediate with flexible form (D). When the conformation of the ring-A of **15** and **16** is a chair form, the hydroxyl and acetoxyl groups are too far to form the cyclic intermediate (D).

The experimental result that 2,3-axial-equatorial derivatives (**9** and **10**) were more easily rearranged than 2,3-diequatorial counterparts (**13** and **14**) is explained in terms of steric acceleration. The repulsion between the 2-axial group and the 10-methyl group speeds up the formation of the cyclic intermediate (A and/or B). Difference in experimental results obtained by using different catalysts for the rearrangement will be considered to depend on the stability of their cyclic intermediates being influenced by the steric hindrance of R group in Chart 2.

Experimental

All melting points were determined on a Yanagimoto Micro-Melting Points Apparatus and are uncorrected. IR spectra were measured in KBr pellets on a Hitachi Perkin-Elmer Model 225 grating spectrophotometer. Mass spectra were obtained with a Hitachi RMU-7M double focusing mass spectrometer with a direct insertion probe. The spectra were recorded at an ionizing voltage of 70 eV. Specific rotation were determined in $CHCl_3$ with a JASCO DIP-SL digital polarimeter. NMR spectra were obtained in $CDCl_3$ with a JEOL JNM-4H-100 spectrometer, the chemical shift data are given in ppm from TMS. Thin-layer chromatography (TLC) plates were prepared from Merck silica gel HF_{254}. Visualization of the thin-layer plates was affected by exposure to iodine vapor.

General Procedure for the Reduction of Ketol Acetates using $\mathrm{LiAlH(OBu^t)_3}$——To a stirred solution of ketol acetate in dry THF (1 mmol/20—30 ml) was added 1.2 equiv. of $\mathrm{LiAlH(OBu^t)_3}$ and stirring was continued at room temperature. The reaction was monitored by TLC and judged complete after 3—5 hr. After quenching the excess reagent by addition of 10% NH_4Cl solution, the THF was evaporated *in vacuo*. The residual complex was decomposed by addition of 10% HCl and extracted with EtOAc. The extracts were washed successively with $NaHCO_3$ solution and brine, and dried. After removal of the EtOAc *in vacuo*, the ratios of the diol monoacetates in the crude products were evidenced by NMR analysis. The crude products were separated into pure diol monoacetates by preparative TLC or fractional recrystallization.

Reduction of 3-Oxo-2β-acetoxy-5α-santanolide (5)——According to the general procedure, 308 mg (1 mmol) of **5** was treated with $\mathrm{LiAlH(OBu^t)_3}$ for 40 min to give quantitative yield of 2β-acetoxy-3β-hydroxy-5α-santanolide (**9**) as evidenced by NMR analysis. Recrystallization from EtOAc–hexane gave **9** as colorless plates, mp 165—167°. $[\alpha]_D^{23°}$ +94.1° (c, 0.35); IR spectrum cm^{-1}: 3547, 1758, 1741, 1725, 1242; Mass Spectrum *m/e* (rel. intensity %): 310 (6.9, M$^+$), 250 (100, [M−AcOH]$^+$), 235 (76.3); NMR spectrum δ: 1.08 (3H, s, 10-CH_3), 1.19 (3H, d, J=7 Hz, 4 or 11-CH_3), 1.23 (3H, d, J=7 Hz, 4 or 11-CH_3), 2.17 (3H, s, $OCOCH_3$), 2.30 (1H, OH), 3.23 (1H, dd, J=10, 3 Hz, 3-H), 3.90 (1H, t, J=10 Hz, 6-H), 5.13 (1H, q, J=3 Hz, 2-H). (Found: C, 66.04; H, 8.47. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

Reduction of 3-Oxo-2α-acetoxy-5α-santanolide (6)——According to the general procedure, 450 mg of **6** was treated with $\mathrm{LiAlH(OBu^t)_3}$ for 2 hr to give 367 mg (81.5% yield) of the crude diol monoacetate which was composed of about 50% **11** and 50% **13** as evidenced by NMR spectrometry. Recrystallization from EtOAc–hexane gave 95.6 mg (21% yield) of 2α-acetoxy-3β-hydroxy-5α-santanolide (**13**) as colorless columns, mp 200—202°. $[\alpha]_D^{23°}$ +14.3° (*c*, 0.77); IR spectrum cm^{-1}: 3593, 1765, 1725, 1243, 1227; Mass Spectrum *m/e* (rel. intensity %): 310 (0.7, M$^+$), 250 (97.4, [M−AcOH]$^+$), 235 (44.5). NMR spectrum δ: 1.03 (3H, s, 10-CH_3), 1.17 (3H, d, J=7 Hz, 4 or 11-CH_3), 1.22 (3H, d, J=6 Hz, 4 or 11-CH_3), 2.01 (3H, s, $OCOCH_3$), 2.07 (1H, OH), 3.10 (1H, t, J=10 Hz, 3-H), 3.78 (1H, t, J=10 Hz, 6-H), 4.92 (1H, ddd, J=12, 10, 5 Hz, 2-H). (Found: C, 65.74; H, 8.62. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

After removal of **13** from the mother liquor, the residue was purified by preparative TLC (EtOAc–benzene; 1: 2) to give two bands. The first band gave 177 mg (39% yield) of 2α-acetoxy-3α-hydroxy-5α-santanolide (**11**) which was recrystallized from EtOAc–hexane to afford a pure sample as colorless columns, mp 166—167°. $[\alpha]_D^{23°}$ +28.6° (*c*, 0.73); IR spectrum cm^{-1}: 3487, 1768, 1706, 1264; Mass Spectrum *m/e* (rel. intensity %): 310 (0.1, M$^+$), 250 (43.1, [M−AcOH]$^+$), 235 (6.5), 167 (27.6). NMR spectrum δ: 1.02 (3H, s, 10-CH_3), 1.18 (3H, d, J=6 Hz, 4- or 11-CH_3), 1.20 (3H, d, J=6 Hz, 4- or 11-CH_3), 2.03 (3H, s, $OCOCH_3$), 2.15 (1H, OH), 3.75 (1H, t, J=10 Hz, 6-H), 3.79 (1H, t, J=3 Hz, 3-H), 5.00 (1H, ddd, J=12, 5, 3 Hz, 2-H). (Found: C, 65.56; H, 8.51. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

The second band gave 57 mg (12.7% yield) of prisms which were identical with an authentic sample of 13.

Reduction of 2-Oxo-3α-acetoxy-5α-santanolide (7)——According to the general procedure, 150 mg of **7** was treated with LiAlH(OBu^t)$_3$ for 45 min to give quantitative yield of a crude product. It was separated into three bands by preparative TLC using EtOAc–benzene (1: 2). The first band gave 7.5 mg (5% yield) of the starting ketol acetate (**7**) which was identified by the comparison of NMR and IR spectra.

The second band gave 118 mg (78.7% yield) of solid which was composed of about 70: 30 of 3α-acetoxy-2β-hydroxy- and 2α-acetoxy-3α-hydroxy-5α-santanolides (**16** and **11**) as evidenced by NMR analysis. Recrystallization of the solid from EtOAc–hexane gave **16** as colorless prisms, mp 178—179° (reported$^{8)}$ mp 183—185°). $[\alpha]_D^{23^\circ}$ +23.4° (*c*, 0.73) (reported$^{8)}$ $[\alpha]_D$ +8.7°); IR spectrum cm^{-1}: 3440, 1780, 1717, 1254; Mass Spectrum *m/e* (rel. intensity %): 310 (0.14, M$^+$), 250 (37.5, [M−AcOH]$^+$), 235 (100), 165 (67). NMR spectrum δ: 1.06 (3H, d, *J*=7 Hz, 4- or 11-CH$_3$), 1.15 (3H, s, 10-CH$_3$), 1.18 (3H, d, *J*=8 Hz, 4- or 11-CH$_3$), 2.02 (3H, s, OCOCH$_3$), 2.55 (1H, OH), 3.85 (2H, m, *W*1/2=20 Hz, 2- and 6-H's), 4.75 (1H, t, *J*=3 Hz, 3-H). (Found: C, 65.97; H, 8.53. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

The third band furnished 22.3 mg (14.9% yield) of 3α-acetoxy-2α-hydroxy-5α-santanolide (**12**). Recrystallization from EtOAc–hexane gave pure sample as colorless plates, mp 160—162°. $[\alpha]_D^{23^\circ}$ +61.3° (*c*, 0.18); IR spectrum cm^{-1}: 3555, 3500, 1768, 1735, 1723, 1256, 1230; Mass Spectrum *m/e* (rel. intensity %): 310 (0.3, M$^+$), 250 (100, [M−AcOH]$^+$), 235 (47.2), 167 (40.0), 165 (18.9). NMR spectrum δ: 0.97 (3H, s, 10-CH$_3$), 1.08 (3H, d, *J*=7.5 Hz, 4- or 11-CH$_3$), 1.18 (3H, d, *J*=7 Hz, 4- or 11-CH$_3$), 2.10 (3H, s, OCOCH$_3$), 2.30 (1H, OH), 3.75 (1H, t, *J*=10 Hz, 6-H), 3.97 (1H, dt, *J*=10, 3 Hz, 2-H), 5.12 (1H, t, *J*=3 Hz, 3-H). (Found: C, 65.59; H, 8.51. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

Reduction of 2-Oxo-3β-acetoxy-5α-santanolide (8)——According to the general procedure, 308 mg of **8** was treated with LiAlH(OBu^t)$_3$ for 3 hr to give 297 mg of a solid which was found to be composed of 3β-acetoxy-2β-hydroxy-5α-santanolide (**10**; 80%), 2β-acetoxy-3β-hydroxy-5α-santanolide (**9**; 10%), and the starting ketol acetate (10%) by means of NMR spectrometry. Recrystallization from EtOAc–hexane gave 114 mg (36.8% yield) of **10** as colorless prisms, mp 172—175°. $[\alpha]_D^{23^\circ}$ +84.3° (*c*, 0.44); IR spectrum cm^{-1}: 3472, 1767, 1760, 1712, 1700, 1260; Mass Spectrum *m/e* (rel. intensity %): 310 (1.5, M$^+$), 250 (46.3, [M−AcOH]$^+$), 235 (100), 165 (62.6). NMR spectrum δ: 1.07 (3H, d, *J*=6 Hz, 4- or 11-CH$_3$), 1.19 (3H, d, *J*=6 Hz, 4- or 11-CH$_3$), 1.21 (3H, s, 10-CH$_3$), 2.10 (3H, s, OCOCH$_3$), 2.45 (1H, OH), 3.93 (1H, t, *J*=10 Hz, 6-H), 4.10 (1H, q, *J*=3 Hz, 2-H), 4.55 (1H, dd, *J*=10, 3 Hz, 3-H). (Found: C, 66.01; H, 8.47. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

General Procedure for the NaBH$_4$ Reduction of Ketol Acetates——To a stirred solution of ketol acetate in EtOH (1 mmol/30—40 ml) was added 1.1 equiv. of NaBH$_4$ at 0° and allowed to stand with stirring at room temperature. The reaction was monitored by TLC and judged complete after 30—90 min. The reaction mixture was slightly acidified by an addition of acetic acid, concentrated *in vacuo* and extracted with EtOAc. The extracts were washed successively with NaHCO$_3$ solution, water, and brine and then dried over Na$_2$SO$_4$. Evaporation of the EtOAc *in vacuo* gave a crude solid, in which the ratios of the resulting diol monoacetates were measured by NMR analysis. The mixture was separated into some diol monoacetates and purified by preparative TLC or fractional recrystallization.

Reduction of 3-Oxo-2β-acetoxy-5α-santanolide (5)——According to the general procedure, 308 mg of **5** was treated with NaBH$_4$ at room temperature for 30 min. After work-up as the usual manner a crude solid was separated into three bands by preparative TLC using EtOAc–benzene (1: 2). The first band gave 29 mg (9.4% yield) of 2β-acetoxy-3α-hydroxy-5α-santanolide (**15**). Recrystallization from benzene-hexane furnished a pure sample of **15** as colorless needles, mp 191—193°. $[\alpha]_D^{23^\circ}$ +45.8° (*c*, 0.39); IR spectrum cm^{-1}: 3505, 1755, 1713, 1258; Mass Spectrum *m/e* (rel. intensity %): 311 (1.2, M+1), 310 (0.8, M$^+$), 268 (2.9, [M−CH$_2$CO]$^+$), 250 (100, [M−CH$_3$CO$_2$H]$^+$), 235 (46, *m/e* 250−CH$_3$), 167 (76), 43 (63.3, [CH$_3$CO]$^+$). NMR spectrum δ: 1.08 (3H, s, 10-CH$_3$), 1.19 (6H, d, *J*=7 Hz, 4- and 11-CH$_3$'s), 2.05 (3H, s, OCOCH$_3$), 2.35 (1H, OH), 3.62 (1H, t, *J*=3 Hz, 3-H), 3.85 (1H, t, *J*=10 Hz, 6-H), 4.92 (1H, t, *J*=3 Hz, 2-H). (Found: C, 65.79; H, 8.52. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

The second band furnished 55 mg (17.7% yield) of 3β-acetoxy-2β-hydroxy-5α-santanolide (**10**) which was identical with an authentic sample of **10**. The third band gave 143 mg (46.2% yield) of colorless plates which were identified as **9** by comparing the IR and NMR spectra with those of an authentic sample.

Reduction of 3-Oxo-2α-acetoxy-5α-santanolide (6)——According to the general procedure, 500 mg of **6** was treated with NaBH$_4$ at room temperature for 1.5 hr. After work-up as the usual manner the resulting crude solid was separated into four bands by preparative TLC using EtOAc–benzene (1: 3).

The first band gave 5.8 mg (1.2% yield) of **6** which was identified by IR comparison with an authentic sample. The second band gave 110 mg (22% yield) of **11** which was identified by IR and NMR comparisons with an authentic sample. The third band gave 206 mg (41% yield) of a solid which was found to be composed of **12** (80%) and **13** (20%) by NMR analysis. The crude solid gave on fractional recrystallization 88 mg (17.5% yield) of **12** and 21 mg (4.1% yield) of **13** which were identified by comparing the IR spectra with those of authentic samples, respectively. The forth band furnished 116 mg (23% yield) of colorless needles which were considered to be a mixture of diols from the IR and NMR spectrum in which neither ester CO absorption (IR) nor CH$_3$ proton signal (NMR) due to acetoxyl group was observed.

Reduction of 2-Oxo-3α-acetoxy-5α-santanolide (7)——According to the general procedure, 200 mg of **7** was treated with $NaBH_4$ at 0° for 45 min. After the usual work-up 205 mg of crude solid was obtained, which was found to be composed of **16** and a trace of **12** by NMR analysis. Recrystallization from EtOAc–hexane gave 105.5 mg (52.8% yield) of **16** as colorless prisms which were identical with an authentic sample.

Reduction of 2-Oxo-3β-acetoxy-5α-santanolide (8)——According to the general procedure, 308 mg of **8** was treated with $NaBH_4$ at 0° for 1.5 hr. Work-up as the usual manner gave a crude product which was found to be composed of **9** (60%) and **10** (40%) by NMR analysis. The crude product was separated to three bands by preparative TLC using EtOAc–benzene (1:2). The first band gave 39 mg (12.6% yield) of a solid which was found to be composed of **10** (90%) and **9** (10%) by NMR analysis. The crude solid was recrystallized from benzene–hexane to give 24 mg (7.7% yield) of **10** which was identified by IR comparison with an authentic sample. The second band gave 40.8 mg (13.2% yield) of a mixture of **9** and **10** in 5:4 ratio as evidenced by NMR spectrometry. The third band gave 132.8 mg (42.8% yield) of **9** as colorless crystals which were identified by IR and NMR comparison with an authentic sample.

Acetylation of the Diol Monoacetates

2β,3β-Diacetoxy-5α-santanolide (17)——Acetylations of **9** and **10** in the usual way (Ac_2O–pyridine) gave the corresponding diacetate (**17**), which gave on recrystallization from EtOAc–hexane a pure sample of **17** as colorless plates, mp 213—213.5° (reported8) mp 189—191°). $[\alpha]_D^{23°}$ +71.3° (*c*, 0.56) (reported8) $[\alpha]_D$ +102° (EtOH). IR spectrum cm^{-1}: 1766, 1734, 1247 and 1231. Mass Spectrum *m/e* (rel. intensity %): 352 (0.3, M^+), 292 (4.7, $[M-AcOH]^+$), 250 (100, $[M-Ac_2O]^+$), 235 (68, $[M-Ac_2O-Me]^+$). NMR spectrum δ: 1.14 (3H, s, 10-CH_3), 1.19 and 1.20 (each 3H, d, $J=7$ Hz, 4- and 11-CH_3's), 2.00 and 2.08 (each 3H, s, $OCOCH_3$), 3.91 (1H, t, $J=10$ Hz, 6-H), 4.52 (1H, dd, $J=11$, 3.6 Hz, 3-H), 5.30 (1H, q, $J=3.6$ Hz, 2-H). (Found: C, 64.88; H, 8.14. $C_{19}H_{28}O_6$ requires: C, 64.75; H, 8.01%).

2α,3α-Diacetoxy-5α-santanolide (18)——Acetylations of **11** and **12** in the usual way (Ac_2O–pyridine) gave the corresponding diacetate (**18**) which was recrystallized from EtOAc–hexane to give a pure sample of **18** as colorless plates, mp 161—163° (reported8) mp 151—153°). $[\alpha]_D^{23°}$ +33.6° (*c*, 0.69) [reported8) $[\alpha]_D$ +24.3° (EtOH)]. IR spectrum cm^{-1}: 1771, 1735, 1246, 1225. Mass Spectrum *m/e* (rel. intensity %): 352 (0.1, M^+), 292 (1.6, $[M-AcOH]^+$), 250 (100, $[M-Ac_2O]^+$), 235 (4.0, $[M-Ac_2O-Me]^+$). NMR spectrum δ: 1.02 (3H, s, 10-CH_3), 1.06 (3H, d, $J=7.5$ Hz, 4-CH_3), 1.18 (3H, d, $J=7.5$ Hz, 11-CH_3), 1.92 and 2.05 (each 3H, s, $OCOCH_3$), 3.75 (1H, t, $J=10$ Hz, 6-H), 5.04 (1H, ddd, $J=12$, 5, 3 Hz, 2-H), 5.20 (1H, t, $J=3$ Hz, 3-H). (Found: C, 64.90; H, 8.14. $C_{19}H_{28}O_6$ requires: C, 64.75; H, 8.01%).

2α,3β-Diacetoxy-5α-santanolide (19)——Acetylation of **13** and **14** in the usual way (Ac_2O–pyridine) furnished the corresponding diacetate (**19**) which gave on recrystallization from EtOAc–hexane a pure sample as colorless needles, mp 170—172° (reported8) mp 159—161°). $[\alpha]_D^{23°}$ +28.3° (*c*, 0.39) [reported8) $[\alpha]_D$ +15.7° (EtOH). IR spectrum cm^{-1}: 1772, 1741, 1246, 1221. Mass Spectrum *m/e* (rel. intensity %): 352 (0.1, M^+), 292 (3.9, $[M-AcOH]^+$), 250 (72.8, $[M-Ac_2O]^+$), 235 (11.4, $[M-Ac_2O-Me]^+$), 43 (100). NMR spectrum δ: 1.07 (3H, d, $J=6$ Hz, 4-CH_3), 1.09 (3H, s, 10-CH_3), 1.18 (3H, d, $J=7.5$ Hz, 11-CH_3), 1.96 and 2.03 (each 3H, s, $OCOCH_3$), 3.80 (1H, t, $J=10$ Hz, 6-H), 4.65 (1H, t, $J=10$ Hz, 3-H), 5.09 (1H, ddd, $J=12$, 10, 5 Hz, 2-H). (Found: C, 64.72; H, 8.18. $C_{17}H_{26}O_3$ requires: C, 64.75; H, 8.01%).

2β,3α-Diacetoxy-5α-santanolide (20)——Acetylations of **15** and **16** in the usual way gave the corresponding diacetate (**20**) which was recrystallized from EtOAc–hexane to give a pure sample of **20** as colorless needles, mp 166—168° (reported8) mp 155—157°). $[\alpha]_D^{23°}$ +50.0° (*c*, 0.34) [reported8) $[\alpha]_D$ +53.6° (EtOH)]. IR spectrum cm^{-1}: 1770, 1742, 1730, 1227. Mass Spectrum *m/e* (rel. intensity %): 352 (0.1, M^+), 292 (3.9, $[M-AcOH]^+$), 250 (100, $[M-Ac_2O]^+$), 235 (35.5, $[M-Ac_2O-Me]^+$), 43 (66.7). NMR spectrum δ: 1.07 (3H, s, 10-CH_3), 1.08 (3H, d, $J=7.5$ Hz, 4-CH_3), 1.19 (3H, d, $J=7$ Hz, 11-CH_3), 2.04 and 2.05 (each 3H, s, $OCOCH_3$), 3.82 (1H, t, $J=10$ Hz, 6-H), 4.85 (2H, m, $W1/2=9$ Hz, 2,3-H's). (Found: C, 64.71; H, 8.06. $C_{19}H_{28}O_6$ requires: C, 64.75; H, 8.01%).

General Procedure for the Oxidation of Diol Monoacetates with CrO_3-Pyridine Complex——Diol monoacetate was added to a stirred pyridine solution of an excess CrO_3-pyridine complex at 0°. After 14—45 hr stirring at room temperature, the reaction mixture was diluted with water and extracted with benzene. The extracts were washed successively with 10% HCl, $NaHCO_3$ solution and brine and dried over Na_2SO_4. Evaporation of the benzene *in vacuo* gave a ketol acetate. The identification of ketol acetate was made by IR and NMR comparison with those of an authentic sample.

Oxidation of 9 and 15——Oxidations of **9** and **15**, according to the general procedure, gave the same ketol acetate (**5**), mp 174—175°. (reported8) mp 171—173°). $[\alpha]_D^{22°}$ +171.9° (*c*, 0.57). UV spectrum: λ_{max}^{EtOH} 288 nm (ε 35); IR spectrum cm^{-1}: 1772, 1743, 1720, 1243. Mass Spectrum *m/e* (rel. intensity %): 308 (3.4, M^+), 266 (100, $[M-CH_2CO]^+$), 248 (2.6, $[M-AcOH]^+$). NMR spectrum δ: 1.00 (3H, s, 10-CH_3), 1.26 (3H, d, $J=7$ Hz, 11-CH_3), 1.38 (3H, d, $J=7$ Hz, 4-CH_3), 2.18 (3H, s, $OCOCH_3$), 3.85 (1H, t, $J=10$ Hz, 6-H), 5.54 (1H, dd, $J=12$, 7.5 Hz, 2-H). (Found: C, 66.40; H, 8.01. $C_{17}H_{24}O_5$ requires: C, 66.21; H, 7.85%).

Oxidation of 10 and 14——Oxidations of **10** and **14**, according to the general procedure, gave the same ketol acetate (**8**), mp 210—211°. (reported10) mp 210—211°). IR and NMR spectra of **8** were identical with those of an authentic sample of 2-oxo-3β-acetoxy-5α-santanolide.10)

Oxidation of 11 and 13——Oxidations of **11** and **13**, according to the general procedure, gave the same ketol acetate (**6**), mp 199—200°. (reported9) mp 198—200°), $[\alpha]_D^{23°}$ +73.7° (*c*, 2.29). UV spectrum: λ_{max}^{EtOH}

281 nm (ε 28). IR spectrum cm^{-1}: 1775, 1750, 1730, 1242. Mass Spectrum *m/e* (rel. intensity %): 308 (3.7, M$^+$), 266 (100, [M$-$CH$_2$CO]$^+$), 248 (3.6, [M$-$AcOH]$^+$). NMR spectrum δ: 1.21 (3H, d, J=7 Hz, 4- or 11-CH$_3$), 1.26 (3H, d, J=7 Hz, 4- or 11-CH$_3$), 1.33 (3H, s, OCOCH$_3$), 2.73 (1H, dt, J=18, 7 Hz, 4-H), 3.95 (1H, t, J=10 Hz, 6-H), 5.37 (1H, dd, J=13, 7 Hz, 2-H).

Oxidation of 12 and 16——Oxidations of **12** and **16**, according to the general procedure, gave the same ketol acetate (**7**), mp 185—187°. (reported[8] mp 172—174°). $[\alpha]_D^{22°}$ +43.0° (c, 0.65). UV spectrum: λ_{max}^{EtOH} 297 nm (ε 35). IR spectrum cm^{-1}: 1776, 1763, 1748, 1722, 1216. Mass Spectrum *m/e* (rel. intensity %): 308 (16, M$^+$), 266 (100, [M$-$CH$_2$CO]$^+$), 248 (19.5, [M$-$AcOH]$^+$). NMR spectrum δ: 0.93 (3H, s, 10-CH$_3$), 1.19 and 1.22 (each 3H, d, J=7 Hz, 4- or 11-CH$_3$), 2.12 (3H, s, OCOCH$_3$), 3.85 (1H, t, J=10 Hz, 6-H), 4.88 (1H, dd, J=3.0, 1.6 Hz, 3-H). (Found: C, 66.14; H, 8.03. $C_{17}H_{24}O_5$ requires: C, 66.21; H, 7.85%).

General Procedure for the Acyl Migration of Diol Monoacetates Using NaH in Benzene——To a stirred solution of diol monoacetate (30 mg) in dry benzene (6 ml) was added 2.0 mg of NaH and the resulting mixture was stirred at room temperature. The stirring was continued till the reaction was complete. The reaction mixture was diluted with benzene and washed with water and dried. The benzene was removed *in vacuo* to give a crude product which was analyzed by means of NMR spectrometry. The crude product was separated into pure diol monoacetates by preparative TLC. The identification of diol monoacetates was made by IR and NMR comparison with those of an authentic sample. The results were listed in Table III.

General Procedure for the Acyl Migration of Diol Monoacetates Using BF$_3$-Etherate Complex in Benzene——A solution of diol monoacetate (30 mg) in dry benzene (3 ml) containing three drops of BF$_3$-etherate was stirred at room temperature, till the reaction was complete. A few drops of NaHCO$_3$ solution was added to the reaction mixture and was extracted with EtOAc. The organic layer was washed with water and dried over Na$_2$SO$_4$. After usual work-up, analysis, purification, and identification of the products were made in the usual manner described above. The results were summarized in Table III.

General Procedure for the Acyl Migration of Diol Monoacetates Using HCl in Benzene——A benzene solution of diol monoacetate (50 mg in 10 ml) containing a drop of 1 N HCl–MeOH solution was stirred at room temperature. The HCl in this reaction mixture was quenched by an addition of NaHCO$_3$ and diluted with EtOAc. The resulting solution was washed with water and dried over Na$_2$SO$_4$. After usual work-up, analysis, purification, and identification of the products were made in the usual manner as described above. The results were summarized in Table III.

Separation of the Diol Monoacetates——a) The mixture of **7** and **8** was subjected to preparative TLC using hexane–EtOAc (1: 1) to give two bands. The first and the second bands gave **9** and **10**, respectively.

b) The mixture of **13** and **14** was chromatographed three times on preparative thin-layer plates using hexane–EtOAc (3: 1) to give two bands. The first band gave **13** and the second band gave 3β-acetoxy-2α-hydroxy-5α-santanolide (**14**) as colorless plates, mp 180—181° (recrystallized from EtOAc–hexane). $[\alpha]_D^{23°}$ +52.6° (c, 0.23). IR spectrum cm^{-1}: 3510, 1783, 1760, 1720, 1253. Mass Spectrum *m/e* (rel. intensity %): 310 (1.3, M$^+$), 250 (91.8, [M$-$AcOH]$^+$), 235 (100, [M$-$AcOH–Me]$^+$), 167 (35.7), 165 (43.9), 43 (84.7). NMR spectrum δ: 1.01 (3H, s, 10-CH$_3$), 1.08 (3H, d, J=7 Hz, 4-CH$_3$), 1.19 (3H, d, J=7 Hz, 11-CH$_3$), 2.21 (3H, s, OCOCH$_3$), 3.80 (1H, t, J=10 Hz, 6-H), 3.82 (1H, ddd, J=12, 11, 5 Hz, 2-H), 4.43 (1H, t, J=10 Hz, 3-H), 2.62 (1H, OH). (Found: C, 65.62; H, 8.56. $C_{17}H_{26}O_5$ requires: C, 65.78; H, 8.44%).

c) The mixture of **9** and **10** was chromatographed twice on preparative thin-layer plates using hexane–EtOAc (1: 1) to give two bands. The first and the second bands gave **9** and **10**, respectively.

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