Conjugate Addition of Hydrogen Cyanide to 5β-Hydroxy-10β-methyl-1(9)-octal-2-one. A Reinvestigation

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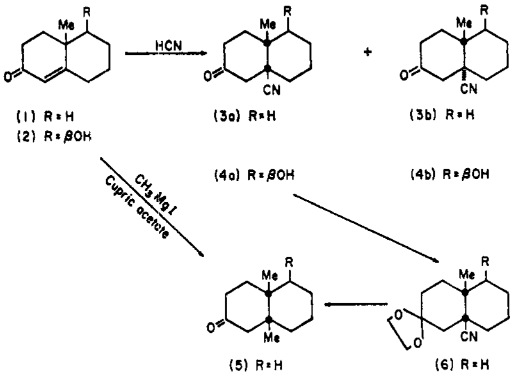
Conjugate addition of hydrogen cyanide to 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2**) gave a mixture of two ketonitriles (**4a**) and (**4b**). From unequivocal chemical studies and nmr spectral data the major product with mp 158–159° (**4b**) was assigned the *trans* configuration and the minor product with mp 189–190° (**4a**) was assigned the *cis* configuration. Earlier assignments of configuration of these compounds are revised.

Conjugate addition of hydrogen cyanide to bicyclic enones, to introduce angular cyano groups was previously studied by several investigators.[2] In all cases where angular cyanation occurred, the resulting product contained a higher proportion of *trans* isomer than the *cis* product. Recently Banerjee and Angadi[3] have studied the addition of hydrogen cyanide to 10β-methyl-1(9)-octal-2-one (**1**) and 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2**) and arrived at some conflicting results. They had observed that addition of hydrogen cyanide to **1** (Scheme I) in ethanol acetic acid solution at 0° gave a mixture of *trans*- and *cis*-cyano ketones (**3b,** mp 107–108°) and (**3a,** mp 136–137°) in the ratio of 15:1. However, under exactly similar conditions, addition of hydrogen cyanide to 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2**) gave the opposite results. The major product of the reaction mixture, according to these authors, was the *cis* isomer (**4a,** mp 158–159°) and the *trans* compound (**4b,** mp 189–190°) was obtained only in small quantity. The stereochemical configurations assigned to these compounds were mainly based on the infrared (ir) spectra of the hydrolyzed products and no unequivocal proof was provided. In the light of earlier work[2] and on other steric considerations, the stereochemistry assigned is difficult to reconcile with **4a** and **4b.** The β side of the octalone **2** is more hindered by the presence of the 10β-methyl group and the 5β-hydroxyl function, and one would have predicted on steric grounds the formation of a higher proportion of the α-cyano (*trans*) product. We have, therefore, decided to reinvestigate the stereochemistry assigned to these products by unambiguous chemical methods and through nmr spectral data.

SCHEME I



We have repeated the cyanation of **1** and obtained a mixture of cyano ketones **3b,** mp 107–108°, and **3a,** mp 136–137°, as described by Banerjee and Angadi.[3]

Marshall, *et al.*,[4] have synthesized *cis*-9,10-dimethyl-2-decalone (**5**) through conjugate addition of methylmagnesium iodide to **1** and established its stereochemistry with certainty. Since this reference compound was available for direct comparison, we decided to transform the angular cyano function of ketone **3a,** mp 136–137°, which was assigned the *cis* configuration, to a methyl group.[5] The cyano ketone **3a** was treated with ethylene glycol and *p*-toluenesulfonic acid to give the dioxolane derivative **6.** Lithium aluminium hydride reduction of **6** at 0° followed by base hydrolysis, Wolff–Kishner reduction,[6] and subsequent removal of the protective ketal group by reaction with 80% acetic acid gave *cis*-9,10-dimethyl-2-decalone (**5**) identical with the ketone synthesized by Marshall, *et al.*[4] This confirms the *cis* configuration assigned to **3a** by Banerjee and Angadi.[3] The compound **3b,** mp 107–108°, was therefore assigned the *trans* configuration.

Addition of hydrogen cyanide to 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2**)[3] gave a mixture of cyano ketones **4a,** mp 189–190°, and **4b,** mp 158–159°.[7] The formation of the cyano ketones **4a** and **4b** was approximately in the ratio of 1:2 as determined from a succession of experiments. As described in the earlier example, we decided to transform the angular cyano function to a methyl group and then identify the product with the Marshall ketone **5.** Ketone **4a,** mp 189–190°, was treated (Scheme II) with ethylene glycol and *p*-toluenesulfonic acid to give the ethylene ketal **7,** mp 115–116°. The melting point for the ketal derived from the same ketone was recorded by Banerjee and Angadi[3] as 168–170°. We then wanted to verify

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[1] This work represents in part a thesis submitted by J. E. Burdett, Jr., to the Graduate School of St. Mary's University, San Antonio, Texas, 1968, in partial fulfillment of the requirements for the degree of Master of Science.

[2] (a) W. L. Meyer and N. G. Schnautz, *J. Org. Chem.*, **27,** 2011 (1962); (b) N. G. Kundu and P. C. Dutta, *J. Chem. Soc.*, 533 (1962); (c) W. Nagata, I. Kikkawa, and M. Fujimoto, *Chem. Pharm. Bull.* (Tokyo), **11,** 226 (1963).

[3] D. K. Banerjee and V. B. Angadi, *Tetrahedron*, **21,** 281 (1965).

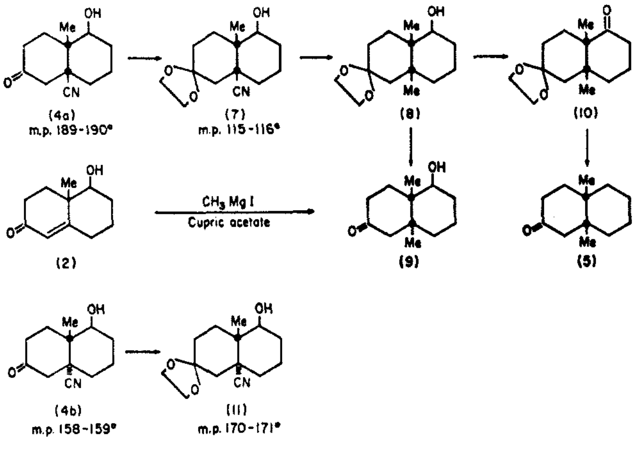
[4] J. A. Marshall, W. I. Fanta, and H. Roebke, *J Org. Chem.*, **31,** 1016 (1966).

[5] (a) W. Nagata, S. Hirai, H. Itazaki, and K. Takeda, *Ann Chem.*, **641,** 196 (1961); (b) W. Nagata, *Tetrahedron*, **13,** 287 (1961); (c) W. Nagata and I. Kikkawa, *Chem. Pharm. Bull.* (Tokyo), **11,** 289 (1963).

[6] Haung-Minlon, *J. Amer. Chem. Soc.*, **68,** 2487 (1946).

[7] The identity of these compounds was established by direct comparison (ir and mixture melting points) with samples kindly provided by Professor D. K. Banerjee.

SCHEME II



the ketal derived from the cyano ketone **4b,** mp 158–159°. We have prepared the ethylene ketal **11,** mp 170–171°, by treating **4b** with ethylene glycol and *p*-toluenesulfonic acid. This again was not in agreement with the recorded melting point which was given as 105–106° for **11.** This discrepancy first brought our attention to the possibility that the ketals prepared by Banerjee and Angadi[3] from the ketones **4a** and **4b** became switched in the delineation of the physical constants and hence led to incorrect stereochemical assignments.

Lithium aluminium hydride reduction of ketal **7** followed by base hydrolysis and Wolff–Kishner reduction[6] gave the 9,10-dimethyl ketal **8.** Compound **8** was deketalized with dilute acetic acid to give *cis*-5β-hydroxy-9β,10β-dimethyl-2-decalone (**9**). The *cis*-decalone **9** was prepared by us by an alternative unambiguous method. Conjugate addition of methylmagnesium iodide to 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2**)[4] gave **9** in about 40% yield. The ketal **8** was further oxidized with the Sarett reagent[8] to give the ketone **10.** Wolff–Kishner reduction of **10** and subsequent deketalization with dilute acetic acid gave the Marshall ketone **5.** Since the *cis*-9,10-dimethyl-2-decalone (**5**) was obtained from cyano ketone **4a** of mp 189–190°, this ketone likewise possesses the *cis* ring fusion.

The cyano ketone **4b** of mp 158–159° and the ketal **11,** mp 170–171°, obtained from it must therefore be regarded as having the *trans* ring junction.

Additional evidence regarding the stereochemistry of the cyano ketones **4a** and **4b** and the ethylene ketals **7** and **11** derived from them was secured through the nmr spectral data. Williamson, *et al.*,[9] have recently shown that a quantitative additivity effect of substituents on the chemical shift of the angular methyl group applies in the decalin ring system, just as it does to steroids. We have applied the additivity principle to determine configurations. In Table I, chemical shifts of C-10 methyl protons of requisite decalins are given. In Table II, the contribution of each substituent to the methyl group chemical shift is given. In Table III, observed and calculated chemical shifts of C-10 methyl protons for both *cis* and *trans* isomers of 5β-hydroxy-9-cyano-10-methyldecalin-2-one and its 2-ethylene ketals are recorded. From the data presented in Table III we could conclude the cyano ketone of mp 189–190° (**4a**) possessed the *cis* ring junction and the cyano ketone of mp 158–159° (**4b**) has the *trans* ring junction. Similarly the ketal of mp 115–116° (**7**) must be assigned the *cis* configuration, whereas the ketal of mp 170–171° (**11**) has the *trans* configuration. The line widths at half-height of angular methyl groups for the *trans* fused isomers are found to be always larger than that for the *cis* fused isomers.[10,11] In Table IV, the values of $\Delta W_{h/2}$ were presented. This data also supports that compounds **4b, 3b,** and **11** have the *trans* ring junction, whereas **4a, 3a,** and **7** have the *cis* configuration.[12]

TABLE I

CHEMICAL SHIFTS OF C-10 METHYL PROTONS IN DECALINS AT 60 MHz[a]

Compound	*cis*, cps	*trans*, cps
10-Methyldecalin	57.7[b]	49.7[b]
10-Methyl-2-decalone	71.6[b]	62.9[b]
5β-Hydroxy-10-methyl-2-decalone	70.2	62.6
2,2-Ethylenedioxy-5β-hydroxy-10-methyldecalin	57.7	50.8
9-Cyano-10-methyl-2-decalone	85.6	70.7

[a] Except as noted, all the compounds were prepared in our laboratories and the chemical shifts were measured on a Varian A60-A nmr spectrometer employing 10% w/v solutions in deuteriochloroform using 2% tetramethylsilane (TMS) as an internal standard at a scanning speed of 0.1 cps. [b] Data from Robinson.[10]

TABLE II

SHIELDING EFFECT OF SUBSTITUENTS ON C-10 METHYL PROTONS IN DECALINS AT 60 MHz[a]

Decalin	*cis*, cps	*trans*, cps
2-Keto	+13.9	+13.2
5β-Hydroxy	−1.4	−0.3
2-Ethylene ketal	+1.4	+1.4
9-Cyano	+14.0	+7.8

[a] A positive value denotes a downfield shift caused by a substituent.

The nmr spectra of *cis*-9,10-dimethyl-2-decalones (**5**) and **9** showed some interesting features. The angular methyl groups of **5** appeared as sharp singlets, whereas compound **9** with a 5β-hydroxy substituent exhibited one of the methyl groups (presumably at C-9) as a doublet ($J = 0.9$ cps). In steroids the splitting of the angular methyl peaks, where observed, was attributed to stereospecific coupling of the tertiary methyl group with a proton four bonds away.[13–15] It was further indicated that the largest long-range couplings should be found when the system adopts the zigzag coplanar "M" or "W" configuration.[16–18] Splitting of the methyl peak into a doublet in *cis*-9-methyl-2-decalone and some

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(8) G. I. Poos, G. E. Arth, R. E. Beyler, and H. L. Sarett, *J. Amer. Chem. Soc.*, **75,** 423 (1953).

(9) K. L. Williamson, L. R. Sloan, and T. Howell, *J. Org. Chem.*, **31,** 436 (1966).

(10) M. J. T. Robinson, *Tetrahedron Lett.*, 1685 (1965).

(11) K. L. Williamson, T. Howell, and T. Spencer, *J. Amer. Chem. Soc.*, **88,** 325 (1966).

(12) After we completed our studies we contacted Professor Banerjee and they have reinvestigated and confirmed our findings.

(13) D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, **85,** 2681 (1963).

(14) N. S. Bhacca, J. E. Gurst, and D. H. Williams, *ibid.*, **87,** 302 (1965).

(15) C. W. Shoppee, F. P. Johnson, R. Lock, and S. Sternhell, *Tetrahedron Lett.*, 2319 (1965).

(16) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83,** 2769 (1961).

(17) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84,** 1594 (1962).

(18) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964).

Table III

Observed and Calculated Chemical Shifts of C-10 Methyl Protons for Both *cis* and *trans* Isomers of 5β-Hydroxy-9-cyano-10-methyldecalin-2-one and its 2-Ethylene Ketal

Compound	Mp, °C	Obsd, cps	Calcd, cps		Differences between calculated and observed values, cps[a]	
			cis	*trans*	*cis*	*trans*
4b	158–159	69.5	84.2	70.4	14.7	0.9
4a	189–190	82.6	84.2	70.4	1.6	12.2
7	115–116	73.4	71.7	58.6	1.7	14.8
11	170–171	59.6	71.7	58.6	12.1	1.0

[a] Agreement within 2 cps of calculated and observed values in steroids is regarded as satisfactory: N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif. 1964, p 25.

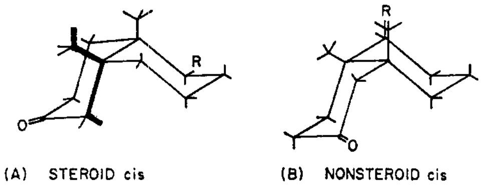
Table IV

Line Widths at Half-Height for Angular Methyl Groups[a]

Compound	Mp, °C	Angular methyl, $W_{h/2}$, cps	TMS, $W_{h/2}$, cps	$W_{h/2}$ − TMS $W_{h/2}$, $\Delta W_{h/2}$, cps
4b	158–159	1.25	0.75	0.50
4a	189–190	0.85	0.52	0.32
3b	107–108	1.5	0.65	0.85
3a	136–137	1.05	0.47	0.57
11	170–171	1.0	0.4	0.60
7	115–116	1.1	0.6	0.50

[a] Line widths measured on a Varian A60-A nmr spectrometer employing 10% w/v solutions in deuteriochloroform using 2% TMS as an internal standard at a scanning speed of 0.1 cps.

of its derivatives was observed by Robinson.[10] *cis*-9,10-Dimethyl-2-decalone and its derivatives could exist in either "steriod" or "nonsteroid" conformations A and B respectively, as shown in Figure 1. In the steroid conformation A, carbon–hydrogen bonds could satisfactorily assume the *trans* and coplanar M or W conformation so that there may be a long-range coupling of the C-9 methyl group with 1α hydrogen. In the nonsteroid conformation B such an arrangement is not readily possible and therefore may not have a large long-range coupling of the C-9 methyl group with 1α hydrogen. In view of the above it is reasonable to assume that **5** exists predominantly in the nonsteroid confromation B. The 5β-hydroxyl group in compound **9** exerts a strong 1,3 diaxial interaction with the C-9 methyl group in the nonsteroid conformation B; therefore, it could conveniently assume the steroid conformation A and hence the long-range coupling of the C-9 methyl group with 1α hydrogen. We have replaced all the enolizable hydrogens in **9** by deuterium[19] and obtained the nmr spectrum. As expected the splitting of the methyl peak disappeared.



(A) STEROID cis (B) NONSTEROID cis

(5) R = H
(9) R = β-OH

Figure 1.

Experimental Section[20]

trans- **and** *cis*-**9-Cyano-10-methyl-2-decalone (3b and 3a).**—These compounds were prepared exactly as described in the literature.[3] *trans* product **3b** melted at 107–108° and the *cis* compound **3a** melted at 136–137°. Their identity was established by comparison with authentic samples.[7]

trans- **and** *cis*-**9-Cyano-5β-hydroxy-10-methyl-2-decalone (4b and 4a).**—These compounds were prepared as described in the literature.[3] *cis* compound **4a** melted at 189–190°. *trans* compound **4b** melted at 158–159°. We have obtained the cyano ketones **4a** and **4b** in the ratio of 1:2. The identity of these compounds was established by comparison with authentic samples.[7]

2,2-Ethylenedioxy-9β-cyano-10β-methyldecalin (6).—To a solution of **3a** (2.0 g) in ethylene glycol (150 ml) *p*-toluenesulfonic acid (0.1 g) was added, the mixture was heated under vacuum, and the ethylene glycol was slowly distilled off. After about 120 ml of ethylene glycol was collected, the distillation was stopped and the reaction mixture was diluted with water (100 ml). The aqueous solution was neutralized with dilute sodium hydroxide and then saturated with sodium sulfate. The precipitated material was filtered off and crystallized from an ether–petroleum ether mixture. The analytical sample had mp 79–80°; ν_{max}^{KBr} 2240 and 1110 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.21 (s, CH_3), 3.93 (s, $OCH_2{\cdot}CH_2O$) ppm. *Anal.* Calcd for $C_{14}H_{21}O_2$: C, 71.48; H, 8.93. Found: C, 71.61; H, 8.99.

cis-**9,10-Dimethyl-2-decalone (5).**—To a solution of **6** (0.730 g) in dry tetrahydrofuran stirred at 0° was added lithium aluminum hydride (0.730 g) in dry tetrahydrofuran dropwise keeping temperature below 0°. After addition was complete, stirring was continued at this temperature for 6 hr. The excess hydride was decomposed with saturated sodium sulfate solution. Dry sodium sulfate (5 g) was added and the material was filtered. The precipitate was washed well with tetrahydrofuran and the solvent was removed. The residue was dissolved in methanol (60 ml), 2 *N* NaOH (7.5 ml) was added, and the mixture was

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(19) H. Budzikiewicz, D. Djerassi, and D. H. Williams, "Structural Elucidation of National Products by Mass Spectrometry," Alkaloids, Vol. I, Holden-Day, Inc., San Francisco, Calif., 1964, p 17.

(20) All melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Ir spectra were determined in a potassium bromide disk on a Perkin-Elmer (Model 21) spectrophotometer unless otherwise stated. Nmr spectra were run in deuteriochloroform using 2% TMS as an internal standard on a Varian A-60A nmr spectrometer. Woelm neutral aluminum oxide, activity III, was used for chromatography. Petroleum ether employed was that of Mallinckrodt reagent grade, bp 30–60°. All evaporations were carried out on a Büchi rotary evaporator at 60–80°. Microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

refluxed for 20 min. The solvent was evaporated, diluted with water, and extracted with chloroform. The chloroform extract was washed with water, brine, and dried (Na_2SO_4) and the solvent was removed. The residue (0.77 g) was dissolved in ethylene glycol (27 ml) containing potassium hydroxide (2.7 g) and the mixture was stirred at 100° for 10 min. Hydrazine hydrate (80% solution, 2.7 ml) was added, heating was continued for 1 hr, and then the temperature was raised to 190° and maintained there for 4 hr. The mixture was then diluted with water, saturated with sodium sulfate, and extracted with chloroform. The chloroform extract was washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The crude product was then deketalized by heating with 80% acetic acid (20 ml) for 15 min. Acetic acid was removed under vacuum and the residue was chromatographed on alumina. The fraction eluted with petroleum ether was crystallized from hexane to give *cis*-9,10-dimethyl-2-decalone (**5**, 0.115 g): mp 121–131°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1705 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.90 (s, CH_3), 1.04 (s, CH_3) ppm. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.91; H, 11.15. The ir and nmr spectra of our sample are identical with the spectra of an authentic sample kindly provided by Professor J. A. Marshall. Marshall, *et al.*,[4] reported a melting point of 108–118°. Our sample melted at slightly higher temperature (121–131°). In spite of repeated recrystallizations the melting range did not improve. A mixture melting point determination with Marshall's sample showed a melting range of 121–131°.

2,2-Ethylenedioxy-9β-cyano-5β-hydroxy-10β-methyldecalin (7).—A solution of **4a** (mp 189–190°, 2.6 g) in ethylene glycol (4 ml), *p*-toluenesulfonic acid (0.250 g), and benzene (250 ml) was refluxed using a Dean–Stark water separator for 15 hr. The mixture was washed with 10% sodium bicarbonate and water and dried (Na_2SO_4), and the solvent was evaporated. The residue was crystallized from ether–petroleum ether to give 2,2-ethylenedioxy-9β-cyano-5β-hydroxy-10β-methyldecalin (**7** 2.4 g). The analytical sample was crystallized from ether–petroleum ether: mp 115–116°; $\nu_{\max}^{\mathrm{KBr}}$ 3470, 2240, 1115, and 1085 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.22 (s, CH_3), 3.98 (m, $OCH_2 \cdot CH_2O$) ppm. *Anal.* Calcd for $C_{14}H_{21}NO_3$: C, 66.90; H, 8.42. Found: C, 67.10; H, 8.52.

2,2-Ethylenedioxy-5β-hydroxy-*cis*-9,10-dimethyldecaline (8).—To a solution of **7** (1.8 g) in dry tetrahydrofuran (50 ml) stirred at 0°, a solution of lithium aluminum hydride (1.8 g) in tetrahydrofuran (100 ml) was added dropwise keeping the temperature below 0°. After addition was complete, stirring was continued for an additional 8 hr. The excess $LiAlH_4$ was decomposed with saturated sodium sulfate solution, solid sodium sulfate (5 g) was added, and the solution was filtered. The solvent was removed and the total crude material was refluxed for 15 min in methanol (120 ml) containing 15 ml of 2 *N* NaOH. The solvent was evaporated, diluted with water, and extracted with chloroform. The chloroform extract was dried (Na_2SO_4) and evaporated. The residue (2.1 g) was dissolved in ethylene glycol (60 ml) containing potassium hydroxide (6.0 g). The mixture was heated at 100° for 15 min. Then hydrazine hydrate (80% solution, 6.0 ml) was added and heating was continued for 1 hr. The temperature was raised to 190° and maintained there for 4 hr. Water was added to the cooled reaction mixture, and the mixture was saturated with sodium sulfate and extracted with chloroform. The chloroform extract was washed with water and brine, dried (Na_2SO_4), and evaporated. The residue (1.8 g) was chromatographed on alumina to give 2,2-ethylenedioxy-5β-hydroxy-*cis*-9,10-dimethyldecalin (**8** 0.6 g). The analytical sample was crystallized from hexane: mp 81.5–83°; $\nu_{\max}^{\mathrm{KBr}}$ 3470 and 1097 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.85 (s, CH_3), 1.0 (s, CH_3), and 3.92 (m, $OCH_2 \cdot CH_2O$) ppm. *Anal.* Calcd for $C_{14}H_{24}O_3$: C, 70.0; H, 10.0. Found: C, 70.26; H, 10.19.

2,2-Ethylenedioxy-*cis*-9,10-dimethyldecalin-5-one (10).—Compound **8** (0.250 g) was dissolved in pyridine (5 ml), a solution of chromium trioxide (0.473 g) in pyridine (5 ml) was slowly added, and the mixture was left overnight. The pyridine was evaporated under high vacuum at room temperature. Water was added and the mixture was extracted with ether. The ether was washed with brine, dried (Na_2SO_4), and evaporated to give 2,2-ethylenedioxy-*cis*-9,10-dimethyldecalin-5-one (**10**, 0.230 g). The residue could not be crystallized. The analytical sample was sublimed under high vacuum [bath temperature 70° (0.001 mm)] and obtained as a colorless oil: $\nu_{\max}^{\mathrm{CHCl_3}}$ 1690 and 1090 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.98 (s, CH_3), 1.05 (s, CH_3), and 3.90 (m, $OCH_2 \cdot CH_2O$) ppm. *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.58; H, 9.24. Found: C, 70.23; H, 9.13.

***cis*-9,10-Dimethyl-2-decalone (5) from 10.**—Compound **10** (0.16 g) was dissolved in ethylene glycol (6.7 ml) containing potassium hydroxide (0.50 g) and 80% hydrazine hydride (0.55 ml) was added. The mixture was heated at 100° for 1 hr and then the temperature raised to 190° and maintained there for 4 hr. Water was added to the cooled reaction mixture, and the mixture was saturated with sodium sulfate and extracted with ether. The ether extract was washed with brine and water, dried (Na_2SO_4), and then evaporated. The residue (0.14 g) was chromatographed on alumina and the product (0.04 g), eluted with petroleum ether, was heated with 80% acetic acid (1 ml) for 1 hr at 80°. The acetic acid was evaporated and *cis*-9,10-dimethyl-2-decalone (**5**) crystallized from hexane (the product was found to be identical with the one reported earlier): mp 121–131°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1705 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.90 (s, CH_3) and 1.04 (s, CH_3) ppm.

5β-Hydroxy-*cis*-9,10-dimethyl-2-decalone (9) from 8.—Compound **8** (0.050 g) was heated with 80% acetic acid (1 ml) for 15 min. Water was added to the cooled mixture and the mixture was extracted with ether. The residue was crystallized from ether–hexane to give 5β-hydroxy-*cis*-9,10-dimethyl-2-decaline (**9** 0.046 g). The analytical sample was crystallized from ether–hexane: mp 180–182°; $\nu_{\max}^{\mathrm{KBr}}$ 3460 and 1705 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.95 (s, CH_3) and 0.91 (d, $J = 0.9$ cps, CH_3) ppm. *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.46; H, 10.20. Found: C, 73.57; H, 10.40.

5β-Hydroxy-*cis*-9,10-dimethyl-2-decalone (9) from 2 by Conjugate Addition of Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from magnesium (2.4 g) and methyl iodide (8 ml) in ether (30 ml) a solution of 5β-hydroxy-10β-methyl-1(9)-octal-2-one (**2** 2.8 g) and cupric acetate (0.48 g) in tetrahydrofuran (100 ml) was added with stirring at −18°. After the addition, the reaction mixture was allowed to warm to room temperature (25°) and then stirred an additional 2 hr. It was then left overnight and decomposed with excess ammonium chloride (10%) and the organic material was extracted with ether. The ether extract was washed with brine, sodium thiosulfate (5% solution), and again with brine and dried (Na_2SO_4), and the solvent was evaporated. The crude material (2.46 g) was then chromatographed on alumina (75 g). The fractions eluted with benzene–ether (1:1) and ether were combined and crystallized from ether–hexane to give 5β-hydroxy-*cis*-9,10-dimethyl-2-decalone (**9**): mp 173–177° (1.1 g). Additional crystallization from ether gave the analytical sample: mp 180–182°; $\nu_{\max}^{\mathrm{KBr}}$ 3465 and 1703 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 0.95 (s, CH_3) and 0.91 ($J = 0.9$ cps, CH_3) ppm. *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.46; H, 10.2. Found: C, 73.21; H, 10.41.

The acetate was prepared by the usual pyridine and acetic anhydride method and was crystallized from acetone–hexane: mp 143–144°; $\nu_{\max}^{\mathrm{KBr}}$ 1730, 1710, and 1265 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.08 (s, $OCO \cdot CH_3$), 1.0 (s, CH_3), and 0.92 (d, $J = 0.9$ cps, CH_3). *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.59; H, 9.24. Found: C, 70.47; H, 9.27.

Registry No.—Hydrogen cyanide, 74-90-8; **2**, 878-47-7; **3a**, 880-38-6; **3b**, 943-95-3; **4a**, 18926-67-5; **4b**, 18944-81-5; **5**, 5523-99-9; **6**, 18926-69-7; **7**, 18926-70-0; **8**, 18944-82-6; **9**, 18926-71-1; **9** acetate, 18926-74-2; **10**, 18926-73-3; **11**, 18926-74-4.

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