Taylor and Mr. L. Dorfman for several helpful discussions and Mr. Dorfman's staff for microanalyses and spectra.

Registry No.—**1**, 25407-85-6; **2**, 42334-95-2; **3**, 42334-96-3; **4**, 23166-56-5; **5**, 23166-57-6; **6**, 23266-13-9; **7**, 23166-58-7; **8**, 23166-59-8; **9**, 42335-01-3; **10**, 42335-02-4; **12** 4-ene, 26047-64-3; **12** 5-ene, 26060-68-4; **13**, 23166-53-2; **14**, 23166-54-3; **15**, 23166-52-1; **16**, 42335-08-0; **17**, 42335-09-1; **18**, 42335-10-4; **19**, 42335-11-5; **20**, 25346-53-6; **21**, 42335-13-7; **22**, 42335-14-8; **23**, 42335-15-9; **24**, 42335-16-0; **25**, 42398-33-4; **26**, 26258-31-1; **26** epimer, 42447-95-0; **27**, 42335-17-1; **27** epimer, 42335-18-2; **28**, 25455-39-4; **28** epimer, 42335-20-6; **29**, 42335-21-7; **29** epimer, 42398-34-5; **30**, 42335-22-8; **31**, 42335-23-9; **32**, 25348-52-1; **33**, 25348-53-2; **34**, 25348-54-3; **35**, 42335-27-3; **36**, 35563-52-1; **37**, 25348-56-5; **38**, 42335-30-8; **39**, 42335-31-9; (*R*)-**40**, 42335-32-0; (*S*)-**40**, 42335-33-1; **42**, 25455-41-8; **43**, 41108-24-1; **46**, 42335-36-4; **47**, 42335-37-5; **48**, 42335-38-6; **49**, 42335-39-7; **50**, 42398-35-6; **51**, 42335-40-0; **52**, 42335-41-1; **53**, 42335-42-2; **54**, 42398-36-7; (*R*)-**55**, 42335-43-3; (*S*)-**55**, 42334-36-1; **56**, 42334-37-2; **57**, 42334-38-3; **58**, 42334-39-4; **59**, 42334-40-7; **60**, 42334-41-8; **61**, 20348-58-7; **62**, 42334-43-0; **63**, 20897-96-5; ethyl 2-bromoazelate, 760-95-2; thiophenol, 108-98-5; chloromethyl phenyl sulfide, 7205-91-6; *N*-hydroxyphthalimide, 524-38-9; *N*-phenylthiomethoxyphthalimide, 41108-32-1; phenylthiomethoxyamine, 41108-23-0.

A General Synthetic Approach to the Eudesmane Class of Sesquiterpenes

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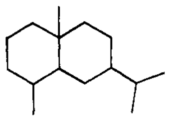
Received July 2, 1973

A versatile synthetic approach to the eudesmane class of sesquiterpenes is described. The key intermediate in the synthetic scheme is 6-methoxy-10-methyl-$\Delta^{6,7}$-octal-1-one (**4**). Elaboration of **4** into precursors which have been used in previous eudesmane sesquiterpene synthesis was accomplished in two manners. Wittig olefination of **4** with methylenetriphenylphosphorane followed by acid hydrolysis gave 1-methylene-10-methyl-6-decalone (**10**) which has previously been converted to atractylon and isoalantolactone. Incorporation of a carbomethoxy group at C-7 and removal of the carbonyl group at C-6 transformed **4** eventually into 7-carboxy-10-methyl-1-decalone (**11**) which has previously been converted to β-eudesmol.

The eudesmane class (see **1** for the general substitution pattern) of decalin sesquiterpanes has recently received considerable synthetic attention, especially β-eudesmol (**2**).[1] As part of our own synthetic studies, we have developed a general approach which allows elaboration from a common intermediate into diverse members of the eudesmane class. The synthesis of this intermediate and its conversion into compounds used in other eudesmane sesquiterpene syntheses is the subject of this paper.



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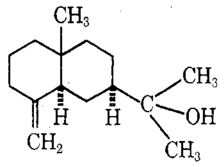

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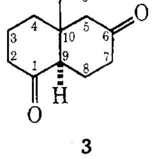
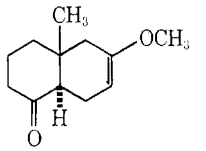
Our scheme was based on the use of a synthon of the diketone **3**. This type of intermediate, properly protected so that the carbonyl functions could be operated on selectively, would allow elaboration at both C-1 and C-7 as is required for the synthesis of the eudesmane sesquiterpenes. Also the presence of the carbonyl groups at C-1 and C-6 would allow stereochemical control of the ring fusion and the group at C-7 by equilibration at these centers. Finally the carbonyl function at C-6 would allow the synthesis of other eudesmane sesquiterpenes, such as the furanosesquiterpene atractylon,[2] not readily accessible by the earlier cited synthetic routes.



3

Our choice and initial synthetic goal for the protected diketone was the keto–enol ether **4**. This was conveniently prepared as outlined in Scheme I. Following a modified procedure of Birch,[3a] we prepared keto enol ether **8**[3] in good yield. Birch had suggested that prior reduction of the carbonyl group at C-1 to a hydroxyl group should increase the yield of enol ether–alcohol **7** in the subsequent Birch reduction step. This indeed proved correct as reduction of **5** with sodium borohydride to **6** followed by Birch reduction as previously described[3a] afforded crystalline **7** in 90% yield, whereas direct reduction of **5** gave yields on the order of 60%. Oppenauer oxidation of **7**[3a] gave crystalline enol ether–ketone **8** in yields in excess of 90%. Treatment of **8** with lithium dimethylcopper(I) gave the desired 1,4-addition product as an epimeric mixture at C-9. Under the aqueous work-up conditions the trans-fused product **4** predominated, constituting ~70%



4

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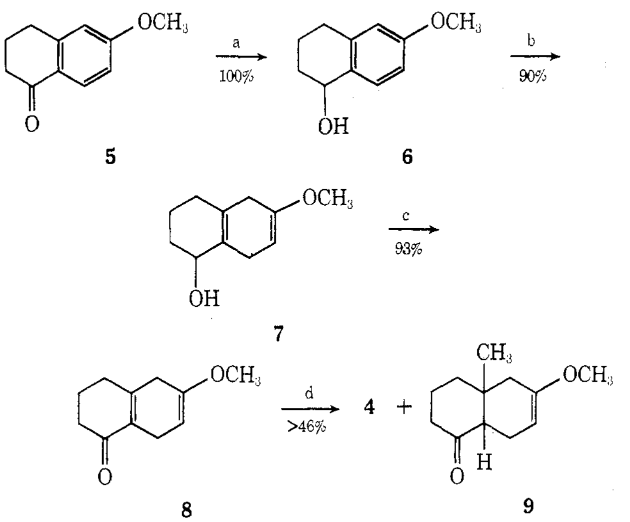
(1) For some previous syntheses of members of the eudesmane class, especially β-eudesmol, see (a) J. A. Marshall, M. T. Pike, and R. D. Carroll, *J. Org. Chem.*, **31**, 2933 (1966); (b) D. C. Humber, A. R. Pinder, and R. A. Williams, *ibid.*, **32**, 2335 (1967); (c) C. H. Heathcock and T. R. Kelly, *Tetrahedron*, **24**, 1801 (1968); (d) J. A. Marshall and M. T. Pike, *J. Org. Chem.*, **33**, 435 (1968); (e) J. W. Huffman and M. L. Mole, *Tetrahedron Lett.*, 501 (1971); *J. Org. Chem.* **37**, 13 (1972); (f) R. G. Carlson and E. G. Zev, *ibid.*, **37**, 2468 (1972).

(2) S. Taki and G. Hongo, *J. Pharm. Soc. Jap.*, **44**, 539 (1925). H. Hikino, Y. Hikino, and I. Yoshioka, *Chem. Pharm. Bull.*, **10**, 641 (1962); **12**, 755 (1964).

(3) (a) A. J. Birch, J. A. K. Quartey, and H. Smight, *J. Chem. Soc.*, 1769 (1952); (b) A. J. Birch, *Proc. Roy. Soc. N. S. W.*, **83**, 245 (1949); (c) N. N. Gaidamovich and I. V. Torgov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1682 (1961).

SCHEME I[a]

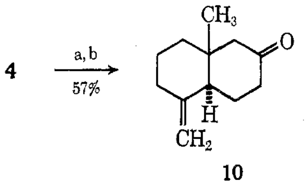


[a] a, $NaBH_4$, MeOH; b, $Na, NH_3(l)$, EtOH; c, $Al(i\text{-}PrO)_3$, CH_3COCH_3, $PhCH_3$; d, $Li(CH_3)_2Cu$, Et_2O.

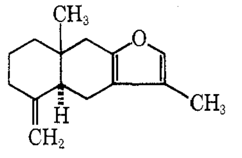
of the 1,4-addition product.[4,5] That the initially obtained product seemed to be the equilibrium mixture was indicated by treatment of the isolated 1,4-addition product with sodium methoxide in methanol to give the same ratio of **4** to **9** as previously observed. Florisil chromatography proved to be an easy method of separation and purification giving **4** in 35% isolated yield.

Despite the somewhat disappointing yield of the lithium dimethylcopper(I) reaction, the ease of preparation and purification of this masked diketone **4** caused us to explore its versatility in the synthesis of eudesmane sesquiterpenes. We investigated two approaches to the use of this compound. First we chose to directly functionalize the carbonyl group at C-1 while leaving the potential carbonyl group at C-6 for later elaboration. This approach, as outlined in Scheme II, led to a compound typified by the exocyclic methylene ketone **10**. This transformation was accomplished by treatment of **4**[6] with methylenetriphenylphosphorane in dimethyl sulfoxide[7] followed by acidic hydrolysis of the crude exocyclic methylene enol ether giving **10** in 57% yield. Compound **10** has been previously synthesized by a rather involved route by Minato[8] and used as a key intermediate in his syntheses of the eudesmane furanosesquiterpene atractylon[8] (**11**) and of the eudesmane sesquiterpene lactone isoalantolactone[9] (**12**).

SCHEME II[a]



[a] a, $Ph_3P{=}CH_2$, DMSO; b, H_3O^+.



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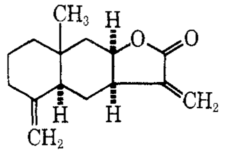

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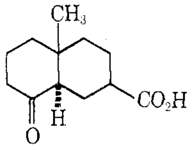
The second approach using **4** was directed toward the synthesis of the keto acid **13**, an intermediate in many



13

of the previous syntheses of β-eudesmol.[1c,e,f] In this sequence the carbonyl group at C-1 was reduced and protected while the carbonyl group at C-6 was utilized to introduce functionality at C-7. Then, after removal of the C-6 carbonyl group, the C-1 carbonyl group was regenerated. These transformations were carried out as indicated in Scheme III. Reduction of **4** with sodium borohydride followed by acidic hydrolysis of the resulting hydroxy enol ethers gave the epimeric mixture of hydroxy ketone **14** in 73% yield. Treatment of this mixture with sodium hydride in dimethyl carbonate followed by chromatography gave the crystalline keto carbonate ester **15** in 61% isolated yield and a fraction (21% yield) containing what seems to be mainly its C-1 epimer **16**. Although the asymmetry at C-1 would later be destroyed, it was convenient to continue the sequence with the crystalline epimer **15**. The stereochemical assignment of **15** will be discussed later in this paper.

The next transformation involved removal of the C-6 carbonyl group. After attempting several unsuccessful methods, this problem was solved by conversion of **15** to its crystalline thioketal **17** in 95% yield by treatment with ethanedithiol, glacial acetic acid, and a catalytic amount of *p*-toluenesulfonic acid. Desulfurization was accomplished using W-2 Raney nickel[10] in absolute ethanol to give crystalline carbonate ester **18** in 70% yield. Removal of the carbonate group was achieved by subjecting **18** to lithium aluminum hydride reduction to quantitatively afford the crystalline diol **19**. Finally the keto acid **13** was obtained in 53% yield by Jones oxidation[11] of the diol **17**. As **13** has

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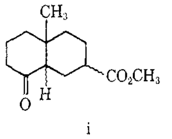
[4] The isomeric ratio between **4** and **9** was determined by nmr analysis. Carlson (see ref 1f) had shown that in a similar system the angular methyl signal in the cis-fused system occurs at lower field (δ 1.0 ppm in the case of **9**) than that in the trans-fused system (δ 0.75 ppm in the case of **4**).

[5] This isomeric ratio is approximately the same as the total trans:cis ring fusion ratio found by Carlson (see ref 1f) after methoxide equilibration of i.



i

[6] It should be noted that the use of a mixture of **4** and **9** would probably be suitable here in that under the reaction conditions the cis-fused compound **9** would also give **10**. For examples see ref 1a and 1e.

[7] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 128 (1963).

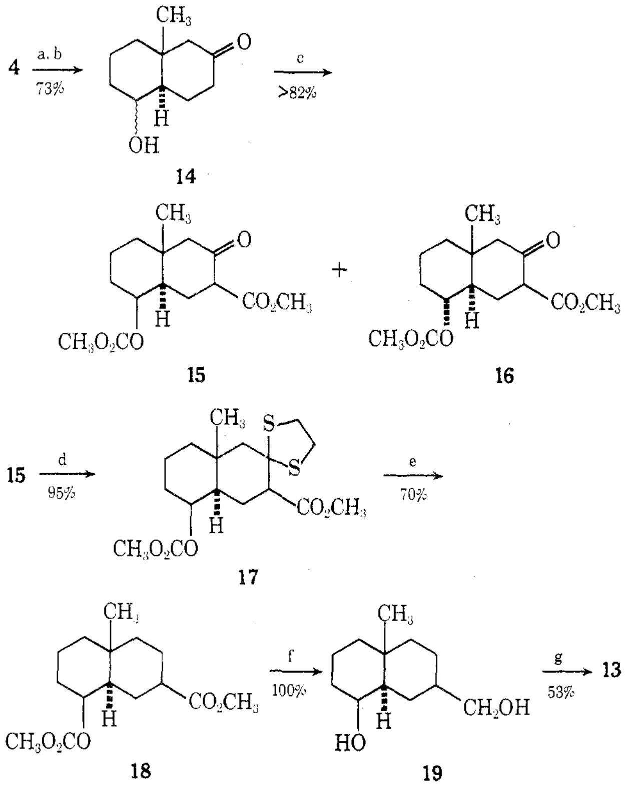
[8] H. Minato and T. Nagasaki, *Chem. Commun.*, 377 (1965).

[9] H. Minato and I. Horibe, *Chem. Commun.*, 531 (1965).

[10] R. Mozingo, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 181.

[11] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

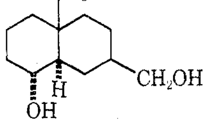
SCHEME III[a]



[a] a, $NaBH_4$, CH_3OH; b, H_3O^+; c, $(CH_3O)_2CO$, NaH; d, $HSCH_2CH_2SH$, HOAc, p-TsOH; e, W-2 Raney nickel, EtOH; f, $LiAlH_4$, Et_2O; g, CrO_3, H_2SO_4, CH_3COCH_3.

been previously converted into β-eudesmol,[1c] this constitutes a formal total synthesis of this eudesmane sesquiterpene.

Concerning the stereochemistry[12] of the keto carbonate ester **15**, the assignment was made from the following observations. The trans ring fusion follows from both the starting material **4** and the final product **13** which are known to possess this stereochemistry. The equatorial assignment to the carbomethoxy group at C-7 is consistent with the method of formation and again with transformation into **13**, possessing known equatorial carboxyl stereochemistry. Both of these assignments are predicated on the use of reactions not expected to cause epimerization at the centers of interest. Finally the axial stereochemistry of the carbonate group at C-1 was assigned by comparison of diol **19**, derived from **15** by reactions not involving that position, and diol **20**, obtained by Heathcock[1c] in his synthesis of β-eudesmol. Although the two diols are different (both by nmr and melting point), they are converted to the same keto acid **13** by Jones oxidation.[13] Since Heathcock has shown diol **20** to have the equatorial hydroxyl group at C-1, it follows that diol **19** and keto carbonate ester **15** have the axial orientation at that position. This is also consistent with the observation that the position of absorption of the angular methyl group in the nmr is sensitive to the nature of the function at C-1. This variation in angular methyl chemical shift can be seen in Table I. The shift to higher field in going from hydroxyl or carbonate to ketone at C-1 is consistent with a decrease in deshielding by virtue of the 1,3-diaxial interaction which is removed in the keto acid **13**. It can be seen that the angular methyl group in **20** has a high field chemical shift (δ 0.82 ppm) which is consistent with there being no interaction between the equatorial hydroxyl group at C-1 and the angular methyl group.



20

TABLE I

Compd	Angular methyl group chemical shift (δ, ppm) CCl_4	 CD_3COCO_3	 C_5H_5N
13	0.83	0.82	0.77
15	1.08	1.07	1.09
19	*a*	1.12	1.38
20			0.83[b]

[a] Solubility too low to obtain spectrum. [b] From ref 1c.

Experimental Section[14]

6-Methoxy-1-tetralol (6).—To a mixture of 53.6 g (304 mmol) of 6-methoxy-1-tetralone[15] in 920 ml of methanol at 0° was slowly added 24.0 g (631 mmol) of sodium borohydride. After stirring the mixture for 3 hr at room temperature, 300 ml of water was added dropwise. The resulting tan solution was concentrated and extracted with ether. The combined ether layers were washed with water and brine, dried, and concentrated to give 54.3 g, quantitative yield, of the crude alcohol **6**: ir (neat) 3400 cm^{-1} (OH); nmr (CCl_4) δ 3.6 (s, 3 H, OCH_3) and 4.4 ppm (m, 1 H, >CHOH). An α-napthylurethane derivative was prepared, mp 130–132° (lit.[16] mp 131–133°).

Formation and Separation of an Isomeric Mixture of 6-Methoxy-10-methyl-$\Delta^{6,7}$-octal-1-one (4 and 9).—To 14.6 g (7.68 mmol) of anhydrous copper(I) iodide in 150 ml of anhydrous ether was added 9.5 ml (15.4 mmol) of 1.63 *M* methyllithium at 0°. After 15 min, 0.914 g (5.1 mmol) of **8** in 60 ml of anhydrous ether was added dropwise. The mixture was stirred at 0° for 2 hr; then it was allowed to warm to room temperature as 100 ml of water was added. After filtration, the inorganic salts were crushed and thoroughly washed with ether. The filtrate was extracted with ether. The combined ether layers were washed with water and brine, dried, and concentrated to give 0.854 g of a crude mixture of **4** and **9**. Elution from Florisil with 75% petroleum ether–25% dichloromethane afforded 0.109 g, 11% yield, of **9**: ir (neat) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 1.1 (s, 3 H, angular CH_3), 3.4 (s, 3 H, OCH_3), and 4.5 ppm (m, 1 H, vinyl proton). Further elution from Florisil with 50% petroleum ether–50% dichloromethane afforded 0.348 g, 35% yield, of **4**: ir (neat) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 0.75 (s, 3 H, angular CH_3), 3.4 (s, 3 H, OCH_3), and 4.5 ppm (m, 1 H, vinyl proton); mass spectrum (*m/e*) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1285.

Equilibration of 4 and 9.—To a solution resulting from the addition of 0.39 g of sodium to 10 ml of anhydrous methanol was added 4.34 g (2.24 mmol) of a crude mixture of **4** and **9**. This

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(12) All compounds in this sequence are *dl* mixtures and only one enantiomeric form is given.

(13) For use of the Jones oxidation procedure for the oxidation of alcohols to enolizable ketones without epimerization of an asymmetry center α to the ketone function, see C. Djerassi, P. A. Hart, and E. J. Warawa, *J. Amer. Chem. Soc.*, **86**, 78 (1964).

(14) All melting points are uncorrected. Ir spectra were recorded on a Beckman IR-8 spectrophotometer and nmr spectra were recorded on a Varian A-60A instrument using tetramethylsilane as an internal standard. High-resolution mass spectra were obtained with a Varian M-66 spectrometer. Combustion analyses were done by Chemalytics, Inc., Tempe, Ariz. Petroleum ether used was reagent grade with boiling range 30–60°. All reactions were carried out under a nitrogen atmosphere. Anhydrous sodium sulfate was used as the drying agent. Florisil (60/100A) used for chromatography was purchased from Wilshire Chemical Co., Inc.

(15) Purchased from Aldrich Chemical Co.

(16) L. Long and A. Burger, *J. Org. Chem.*, **6**, 852 (1941).

solution was allowed to stir at room temperature for 48 hr after which water was added and the resulting mixture was extracted with ether. The combined ether layers were washed with water and brine, dried, and concentrated to afford 3.71 g, 85% yield, of a mixture of **4** and **9**. The spectral properties of this mixture were identical with those of the starting mixture, *i.e.*, the initial mixture from the lithium dimethylcopper reaction.

1-Methylene-10-methyl-6-decalone (**10**).—To 3.55 g (260 mmol) of a 57% mineral oil dispersion of sodium hydride (twice washed with dry pentane) wad added 4.5 ml of anhydrous dimethyl sulfoxide. The mixture was heated to 70° for 30 min after which an additional 8.5 ml of anhydrous dimethyl sulfoxide and 22 g (61.6 mmol) of methyltriphenylphosphonium bromide were added. After 15 min, 6.0 g (30.9 mmol) of **4** was added in 2 ml of anhydrous dimethyl sulfoxide. The dark burgundy solution was stirred at 55° for 18 hr; then it was poured into ice and thoroughly extracted with pentane. The pentane layer was washed with an ice-cold 1:1 mixture of dimethyl sulfoxide–water, ice-cold water, and brine, dried, and concentrated to give 7.5 g of crude product. This material was dissolved in 10 ml of ether and placed in a flask containing 30 ml of 1% aqueous hydrochloric acid. After vigorous sitrring overnight, the mixture was extracted with ether. The combined ether extracts were washed with water and brine, dried, and concentrated to give 6.6 g of crude product. Elution with 25% petroleum ether–75% dichloromethane from Florisil afforded 3.1 g, 57% yield from **4**, of clear oily **10**: ir (neat) 1710 (C=O) and 890 cm^{-1} (C=CH$_2$); nmr (CCl$_4$) of δ 0.70 (s, 3 H, angular CH$_3$), 4.5 (m, 1 H, vinyl proton), and 4.8 ppm (m, 1 H, vinyl proton); mass spectrum (*m/e*) calcd for $C_{12}H_{18}O$ 178.1354, found 178.1357.

Epimeric Mixture of 1-Hydroxy-10-methyl-6-decalone (**14**).—To 1.61 g (8.3 mmol) of **4** in 20 ml of methanol at 0° was added 0.719 g (18.9 mmol) of sodium borohydride. The mixture was stirred 3 hr as it warmed to room temperature. After adding 15 ml of water, the mixture was concentrated and extracted with ether. The combined ether layers were washed with water and brine, dried, and concentrated to yield 1.56 g, 96% yield, of crude product. This material was dissolved in 5 ml of ether and placed in a flask containing 30 ml of 1% aqueous hydrochloric acid. After vigorous stirring overnight, the mixture was extracted with ether. The combined ether layers were washed with brine, dried, and concentrated to give 1.29 g of crude **14**. Florisil chromatography afforded 1.10 g, 73% overall yield from **4**, of the epimeric mixture **14**: ir (neat) 3460 (OH) and 1710 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.0 (s, 3 H, angular CH$_3$) and 3.9 ppm (broad m, 1 H, >CHOH); mass spectrum (*m/e*) calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1284.

Formation and Separation of an Epimeric Mixture of Methyl 7-Carbomethoxy-10-methyl-6-oxodecalin 1-Carbonate (**15** and **16**).—To 0.143 g (3.4 mmol) of a 57% mineral oil dispersion of sodium hydride (twice washed with dry pentane) in 2 ml of dry dimethyl carbonate was added 0.305 g (1.68 mmol) of **14** in 15 ml of dimethyl carbonate. The mixture was stirred at 50° for 3 hr after which it was poured into 100 ml of water, acidified, and extracted with ether. The combined ether layers were washed with water and brine, dried, and concentrated to give 0.480 g of a crude mixture of **15** and **16**. Elution with 50% petroleum ether–50% dichloromethane from Florisil afforded 0.107 g, 21% yield, of an oil which was presumed to be mainly **16**. Further elution gave 0.304 g, 61% yield, of crystalline **15**. Recrystallization from petroleum ether gave material with mp 88–89°: ir (CCl$_4$) 1650 and 1740 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.08 (s, 3 H, angular CH$_3$), 3.7 (s, 6 H, OCH$_3$), and 4.8 ppm (m, 1 H, –CHOCO$_2$CH$_3$).

Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 60.52; H, 7.26.

Thioketalization of 15.—To 0.308 g (1.03 mmol) of **15** was added 0.2 ml of ethanedithiol, 0.08 g of *p*-toluenesulfonic acid, and 2.5 ml of glacial acetic acid. This mixture was stirred at room temperature for 3 days after which it was poured into ether. The ether layer was washed with 3 *N* sodium hydroxide, water, and brine, dried, and concentrated to give 0.370 g of oily crystals. Recrystallization from ether gave 0.368 g, 95% yield, of crystalline **17**: mp 175–176.5°; ir (CCl$_4$) 1730 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.25 (s, 3 H, angular CH$_3$), 3.20 (m, 4 H, –SCH$_2$CH$_2$S–), 3.68 (s, 3 H, OCH$_3$), 3.75 (s, 3 H, OCH$_3$), and 4.8 ppm (m, 1 H, >CHOCO$_2$CH$_3$).

Anal. Calcd for $C_{17}H_{26}O_5S_2$: C, 54.52; H, 7.00; S, 17.12. Found: 54.79; H, 6.91; S, 16.50.

Methyl 7-Carbomethoxy-10-methyldecalin 1-Carbonate (**18**).—To 0.600 g (1.60 mmol) of **17** was added 8.1 g of W-2 Raney nickel[10] in 40 ml of absolute ethanol. The mixture was stirred with the aid of an overhead stirrer for 12 hr at 65° after which the catalyst was removed by filtration and the mixture was concentrated and taken up in ether. The ether layer was washed with brine, dried, and concentrated to give 0.408 g of crude product. Elution with 50% petroleum ether–50% dichloromethane from Florisil afforded 0.316 g, 70% yield, of crystalline **18**. A small sample was recrystallized from petroleum ether: mp 60.5–61.5°; ir (CCl$_4$) 1730 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.0 (s, 3 H, angular CH$_3$), 3.6 (s, 3H, OCH$_3$), 3.7 (s, 3 H, OCH$_3$), and 4.7 ppm (m, 1 H, >CHOCO$_2$CH$_3$).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63 36; H, 8.51. Found: C, 63.56; H, 8.39.

1-Hydroxy-7-hydroxymethyl-10-methyldecalin (**19**).—To 0.183 g (0.65 mmol) of **18** was added 0.343 g of lithium aluminum hydride and 10 ml of anhydrous ether. The resulting mixture was stirred at room temperature overnight after which 0.34 ml of water was cautiously added, followed by 0.26 ml of 20% sodium hydroxide then 1 ml of water. After filtration, the resulting salts were rinsed and triturated with ether. The combined ether fractions were concentrated to give 0.128 g, quantitative yield, of crystalline **19**. A small portion was recrystallized from ether: mp 139.5–141°; ir (CH$_2$Cl$_2$) 3620 cm^{-1} (OH); nmr (CD$_3$COCD$_3$) δ 0.1.12 (s, 3 H, angular CH$_3$) and 3.1–3.8 ppm (m, 3 H, >CHOH and >CH$_2$OH).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.39; H, 10.88

7-Carboxy-10-methyl-1-decalone (**13**).—To 0.100 g (0.51 mmol) of **19** in 5 ml of reagent grade acetone was added 1.1 ml of Jones reagent.[11] This mixture was stirred for 30 min at room temperature after which it was poured into water and extracted with ether. The ether layer was extracted with saturated aqueous sodium bicarbonate solution. The basic aqueous layer was acidified to pH 2 and extracted with ether. The combined ether extracts were dried and concentrated to give 0.060 g, 57% yield, of **13** as a clear oil which solidified on standing. Recrystallization from ether gave crystalline **13**: mp 123–125° (lit.[1c] mp 124–126°); ir (CCl$_4$) 2700–3200 (OH) and 1700 cm^{-1} (C=O); nmr (CCl$_4$) δ 0.83 (s, 3 H, angular CH$_3$) and 9.70 ppm (s, 1 H, COOH). There was no depression in melting point on admixing with an authentic sample.[17]

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Registry No.—**4**, 42246-03-7; **5**, 1078-19-9; **6**, 42246-05-9; **8**, 42249-32-1; **9**, 42246-06-0; **10**, 42246-07-1; **13**, 42246-08-2; α-OH-**14**, 42246-09-3; β-OH-**14**, 42246-10-6; **15**, 42246-11-7; **16**, 42246-12-8; **17**, 42246-13-9; **18**, 42246-14-0; **19**, 42249-33-2.

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