THE JOURNAL OF Organic Chemistry®

Volume 27, Number March 12, 1962

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN]

Experiments Directed toward the Total Synthesis of Terpenes. I. The Synthesis of 1β,9-Dimethyl-6,6-ethylenedioxy-*cis*-decalone-2

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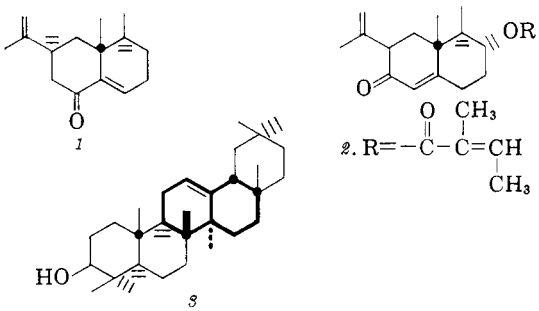
Received October 12, 1961

The title compound, a potentially useful intermediate in the total synthesis of sesquiterpenes and triterpenes, has been prepared in 23% over-all yield from 5-hydroxy-10-methyl-$\Delta^{1(9)}$-octalone-2 in seven steps. Two other routes to the title compound were investigated and found unsatisfactory. One of these was the conjugate addition of methylmagnesium bromide to two 6,6-ethylenedioxy-$\Delta^{1(9)}$-octalone-2 derivatives and the other was a seven step sequence starting with 1,4-diketo-2-methoxy-10-methyl-*cis*-$\Delta^{2,b}$-hexahydronaphthalene.

From a synthetic standpoint we were struck by the close similarity between the sesquiterpenes eremophilone (*1*)[2] and petasin (*2*),[3] and the C/D ring system of the triterpenes, such as β-amyrin (*3*).



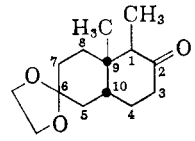
It appeared that if a careful choice of the kind and location of functional groups were made, the same decalin system could serve as an intermediate in the total synthesis of each of the above terpenes. The placement of two oxygen functions at positions 2 and 6 of the necessary carbon skeleton—*i.e.*, 1,9-dimethyldecalin—is obvious in the cases of petasin (*2*) and β-amyrin (*3*). For eremophilone (*1*) the C-2 oxygen will have to be removed, but the C-6 oxygen will be necessary for the introduction of the potential isopropenyl side chain. One reason for choosing a decalin system with which to work was so that we could avail ourselves of the directive influence of the *cis*-fusion. Thus, *if* the *cis*-fused decalin reacts through a conformation like that of the steroid *cis*-A/B ring system, we can expect that the appropriate choice of reaction conditions will allow substitution on either side of the C-2 and C-6 oxygen functions. Thus, another requirement we must impose on the C-2 and C-6 functions is that they help stabilize the desired steroidal conformation of the *cis*-decalin system. Such a compound might be 1β,9-dimethyl-6,6-ethylenedioxy-*cis*-decalone-2 (*4*), where the steroidal conformation (*4a*) should be sterically more favorable than the conformation (*4b*) by virtue of the C-6 ethylenedioxy group. The decalone (*4*) also offered the advantage that the two saturated carbonyl functions were differentiated in that one was protected as the ketal. We report here the initial efforts in this synthetic program that have been successful in making large quantities of the β-decalone (*4*) available for further study.

The first approach that was investigated was based on the cuprous bromide-catalyzed 1,4-addition of methylmagnesium bromide to $\Delta^{1(9)}$-

(1) (a) Dow Chemical Company Fellow, 1958–1959; Sun Oil Company Fellow, 1959–1960. (b) The senior author is very grateful to the Research Corporation for a grant that made this work possible.

(2) L. H. Zalkow, F. X. Markley, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 6354 (1960), and earlier references cited therein.

(3) D. Herbst and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 4337 (1960) and earlier references cited therein.



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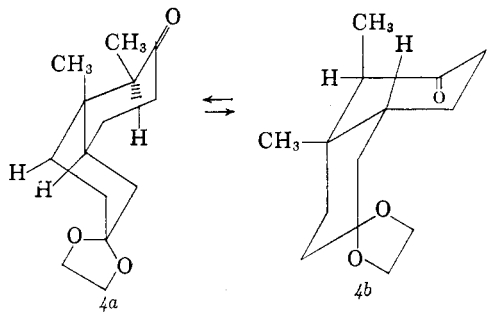
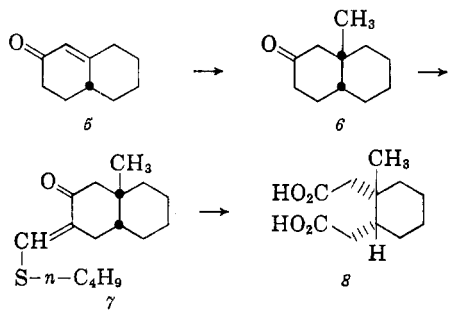


4a 4b

octalone-2 (*5*) reported by Birch and Robinson[4] to produce exclusively the 9-methyl-*cis*-decalone-2 (*6*) in 60% yield. Repetition of this work verified in every detail the results of the earlier workers. The original structure proof offered[5] for the *cis*-decalone (*6*) entailed nitric acid oxidation to the *cis*-diacid (*8*), a result that requires that the *cis*-



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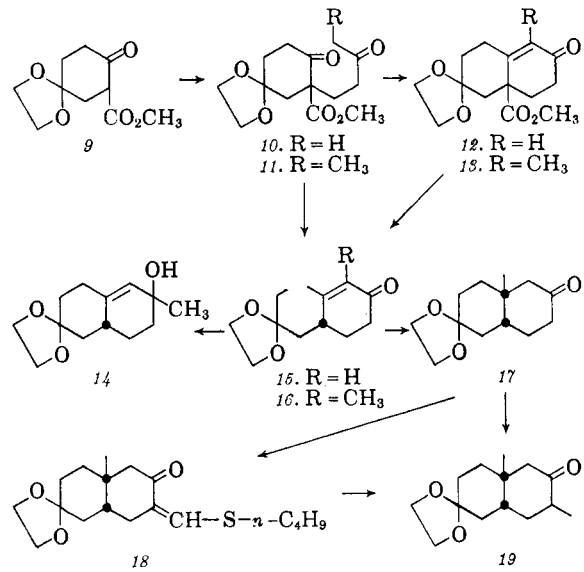
decalone (*6*) enolize to the C-3 methylene. It seemed reasonable, then, that acylation reactions could be expected to take place with the introduction of a C-3-acyl residue. Inasmuch as this orientation was to be a necessary later part of the synthetic scheme directed toward the sesquiterpenes *1* and *2*, advantage was taken of the availability of the *cis*-decalone (*6*) to test this hypothesis. Condensation of this ketone with ethyl formate in the presence of sodium methoxide[6] and then etherification[7] of the resulting hydroxymethylene derivative with *n*-butyl mercaptan afforded a 65% over-all yield of a pure *n*-butylthiomethylene ketone. That this was indeed the 3-*n*-butylthiomethylene derivative (*7*) was demonstrated by oxidation to the known *cis*-diacid (*8*) with hydrogen peroxide in methanolic sodium methoxide in 58% yield. This result again substantiates the *cis*-fusion of the decalone (*6*) and demonstrates that hydroxymethylation takes place preferential at the 3-position.

Having been assured that the 1,4-addition of methylmagnesium bromide would generate a *cis*-fusion, we set out to make the desired decalone (*4*). To this end when the β-keto ester (*9*)[8] was condensed with methyl vinyl ketone in the presence of triethylamine[9] there resulted an 89% yield of the dione (*10*). Treatment of this dione (*10*) with sodium methoxide–methanol led to a 61% yield of the dicyclic ketone (*12*), which in turn could be decarbomethoxylated by a brief aqueous potassium hydroxide treatment whereby a 56% yield of the desired $\Delta^{1(9)}$-octalone-2 (*15*) was obtained. The same octalone (*15*) could be prepared in 67% yield directly by more prolonged treatment[10] of the dione (*10*) with aqueous potassium hydroxide.

When the octalone (*15*) was treated with methylmagnesium bromide in the absence of cuprous bromide, the allylic alcohol (*14*) was the sole product, isolated in 82% yield. In the presence of cuprous bromide, however, the conjugate addition proceeded well and afforded a 61% yield of the *cis*-decalone (*17*). Confirmation of the expected *cis*-ring fusion was obtained when this decalone



9 10. R = H 11. R = CH_3 12. R = H 13. R = CH_3 14 15. R = H 16. R = CH_3 17 18 19

(*17*) was reduced under Wolff-Kishner conditions[11] and the resulting ketal hydrolyzed. The ketone isolated in this manner was identical to the known 9-methyl-*cis*-decalone-3.

It remained but to introduce the C-1 methyl group to achieve our goal. However, this proved

(4) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943).

(5) R. P. Linstead, A. F. Millidge, and A. L. Walpole, *J. Chem. Soc.*, 1140 (1937).

(6) W. S. Johnson and H. Posvic, *J. Am. Chem. Soc.*, **69**, 1361 (1947).

(7) R. E. Ireland and J. A. Marshall, *J. Org. Chem., in press.*

(8) R. M. Lukes, G. I. Poss, and L. H. Sarett, *J. Am. Chem. Soc.*, **74**, 1401 (1952).

(9) N. L. Wendler, H. L. Slates, and M. Tishler, *J. Am. Chem. Soc.*, **73**, 3816 (1951).

(10) C. H. Shunk and A. L. Wilds, *J. Am. Chem. Soc.*, **71**, 3946 (1949).

(11) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1948).

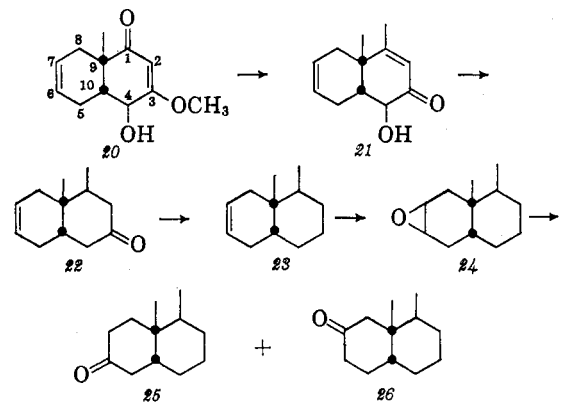
to be an insurmountable task, for an attempt to methylate the *n*-butylthiomethylene derivative (*18*) was unsuccessful. A low yield of monomethylated ketone was obtained by using one equivalent of sodium triphenylmethide[12] to enolize the decalone (*17*). The low yield of the reaction precluded its use in any multistage synthetic scheme, and, as a result of the unsuccessful bid to introduce a C-1 methyl into the *n*-butylthiomethylene, there seemed every reason to believe that this new monomethyl product was the 3-methyl derivative (*19*). Indeed, this was found to be the case, for when the *n*-butylthiomethylene derivative (*18*) was desulfurized[7] with Raney nickel, the same dimethyldecalone (*19*) was obtained. There seems little doubt that the *n*-butylthiomethylene group is in the 3-position; hence, the methylated decalone obtained directly from the ketone (*17*) must be the undesired 3-methyl derivative.

Having despaired of introducing the C-1 methyl group *after* the *cis*-fused decalone system was established, we investigated the possibility of affecting the conjugate addition of methylmagnesium bromide to the 1-methyl-$\Delta^{1(9)}$-octalone-2 (*16*). A minor modification of the previous synthetic scheme—namely, the use of ethyl vinyl ketone rather than the lower homolog—provided a 79% over-all yield of the desired octalone (*16*) from the β-keto ester (*9*). It is interesting to note that while the yields in the base catalyzed addition of the two vinyl ketones are approximately the same (dione *10*—89%; dione *11*—83%), the yield on cyclizing of dione *11* (95%) is much better than that obtained under identical conditions from dione *10* (67%).

Unfortunately, the preparation of the desired *cis*-decalone (*4*) was still not to be realized, for in spite of numerous attempts we were not able to realize any conjugate addition of methylmagnesium bromide to the octalone (*16*). It seems unlikely that the C-1 methyl group can have such a profound electrostatic effect on the mechanism of the conjugate addition; it is then exerting a steric effect. However, as the mechanism of this addition is obscure, it is not possible to say just how the reaction is affected by steric bulk in the α-position.

Concurrent with the above work another route to the 1,9-dimethyl-*cis*-decalin system was under study. This scheme, however, had as its final goal the decalone (*25*), which was related to eremophilone (*1*), but lacked the oxygen substituent in the second ring that was necessary for the synthesis of the other two natural products. Had this route proved successful, a modification at an earlier stage—namely, the octalone (*22*)—could have remedied this situation. While this work was in progress, Djerassi and co-workers[2,3] reported similar transformations in the *trans*-decalone series, and only that part of our work that bears on the *cis*-decalone series is discussed.

When the ketal (*20*), obtained by zinc–acetic acid reduction[13] of the corresponding dione,[14] was treated with a large excess of methyllithium, it was possible to obtain a 97% yield of the unsaturated ketone (*21*). It was found that the next two necessary stages—namely, removal of the C-4 OH and saturation of the conjugated double bond—could both be conveniently carried out in one operation. Thus, when the acetate of the ketol



(*21*) was reduced with calcium in ammonia-methanol solution[15] and the resulting product oxidized with Jones reagent,[16] the ketone (*22*) was obtained in 44% yield. Wolff-Kishner reduction[11] of this ketone afforded 1,9-dimethyl-*cis*-octalin in 83% yield. A model of this olefin indicated that the β-oxide should be more readily formed, and if conformational integrity were maintained, the β-oxide could be reduced by lithium aluminum hydride and the resulting alcohol oxidized to the desired ketone (*25*). Unfortunately, this proved not to be the case. On reduction and oxidation of the oxide obtained from the olefin (*23*), there resulted a mixture of ketones—probably *25* and *26*. Gas-liquid chromatography of both the intermediate alcohol and the final ketone showed the presence of two major components in the ratio 70:30. The observation that both the 2,4-dinitrophenylhydrazone and semicarbazone of the ketonic product were mixtures bears out this conclusion. In each case a pure derivative was obtained by careful chromatography and repeated recrystallization. The fact that the melting points of these

(12) E. J. Corey and E. W. Cantrall, *J. Am. Chem. Soc.*, 81, 1745 (1959).

(13) A. J. Speziale, J. A. Stephens, and Q. E. Thompson, *J. Am. Chem. Soc.*, 76, 5011 (1954). The authors are grateful to Dr. Knowles of the Monsanto Chemical Company for a generous supply of 4-methoxy-2,5-toluquinone from which these materials were prepared.[14]

(14) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, 74, 4223 (1952).

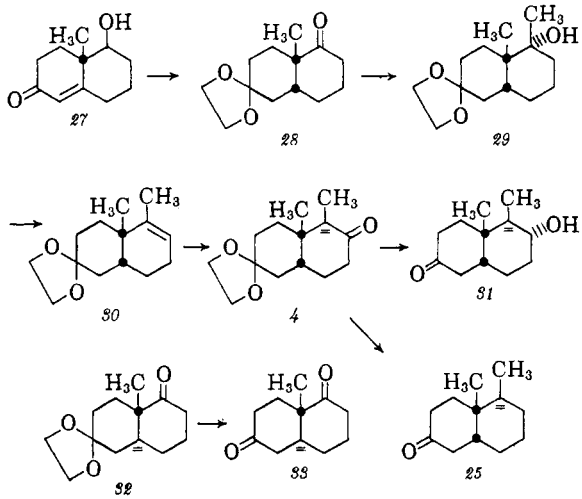
(15) J. H. Chapman, J. Elks, G. H. Phillips, and L. J. Wyman, *J. Chem. Soc.*, 4344 (1956).

(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); see also, C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, 21, 1547 (1956).

derivatives were not depressed when mixed with authentic material (see below) indicates that at least a portion of the ketonic mixture was the desired ketone (*25*).

Whether the ketonic mixture arose from a mixture of α- and β-oxides or from a mixture of conformations of the β-oxide was not investigated because of the success of the route outlined below. Whichever answer is correct, these results underscore the perfidious nature of the *cis*-decalin system, inasmuch as the same transformations carried out by Djerassi[2,3] with the corresponding 1,9-dimethyl-*trans*-Δ^6-octalin were quite successful.

We finally met success in our effort to find a workable synthesis of the *cis*-decalone (*4*) in an approach that began with the readily available unsaturated ketone (*27*).[17] The ketone ketal (*28*) was prepared in 62% over-all yield by the succession: catalytic reduction to the *cis*-decalin system, ketalization of the saturated ketone, and oxidation of the alcohol with Jones reagent.[16] Each of the intermediate products in this sequence was an oil and was not purified but carried on directly to the next stage. The major portion of the ketone ketal (*28*) could be isolated by direct crystallization—a fact that attests to the relatively high purity of the products from the intermediate reactions.



Careful chromatography of the mother liquors left after removal of most of the ketone ketal (*28*) afforded a small yield (7%) of the *trans*-isomer (*32*), hydrolyzable by mineral acid to the known *trans*-dione (*33*).[18]

Treatment of the *cis*-ketone ketal (*28*) with methyllithium afforded a 61% yield of the crystalline alcohol (*29*), which was readily dehydrated with iodine in 84% yield to the olefin (*30*). Completion of the synthesis of the desired decalone (*4*) was made possible by use of the elegant hydroboration reaction.[19] When the olefin was treated with boron hydride tetrahydrofuranate in tetrahydrofuran, and the resulting alcohol oxidized with Jones reagent,[16] there resulted a 71% yield [23% over-all from the unsaturated ketone (*27*)] of the pure, crystalline *cis*-decalone (*4*), m.p. 92–94°. With this decalone in hand we are in a position to continue the triterpenoid synthetic scheme. Similarly, reduction of the decalone (*4*) with lithium in ammonia-alcohol, and then ketal cleavage afforded a 70% yield of the hydroxy ketone (*31*), the key intermediate in the petasin[3] synthesis. Finally, Wolff-Kishner reduction[11] of the decalone (*4*) and then ketal cleavage afforded an 86% yield of the *cis*-decalone (*25*), the necessary intermediate for the eremophilone[2] scheme. The ketone (*25*) was shown to be entirely homogeneous by gas-liquid chromatography; the identity of the 2,4-dinitrophenylhydrazone and semicarbazone of this ketone substantiate the authenticity of the material prepared in the earlier scheme.

EXPERIMENTAL[20]

3-n-Butylthiomethylene-9-methyl-cis-decalone-2 (*7*). The crude hydroxymethylene derivative prepared from 75 g. (0.45 mole) of 9-methyl-*cis*-decalone-2 (*6*) with 114 gm. (1.97 moles) of commercial sodium methoxide and 150 gm. (2.03 moles) of purified ethyl formate in 700 ml. of dry benzene according to the procedure of Johnson and Posvic[6] was etherified[7] with 40.5 gms. (0.45 mole) of *n*-butyl mercaptan in *ca.* 700 ml. of benzene containing 200 mg. of *p*-toluenesulfonic acid. After the usual work-up, distillation of the product afforded 77.14 gms. (65%) of the *n*-butylthiomethylene derivative, b.p. 150–165° (0.12 mm.) with slight decomposition. On redistillation of a sample for analysis the derivative boiled at 162–163° (0.1 mm.).

Anal. Calcd. for $C_{16}H_{28}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 71.94; H, 9.70; S, 12.20.

1-Methyl-cis-cyclohexane-1,2-diacetic acid (*8*): *By alkaline peroxide oxidation of the thioenol ether* (*7*). A solution of 2 gm. (7.5 mmoles) of the thioenol ether (*7*) in 18 ml. of absolute methanol containing 0.3 gm. (0.013 mole) of sodium was cooled to 10° in an ice bath, and 10 ml. of 30% hydrogen peroxide was added dropwise over a 0.5-hr. period while maintaining the temperature between 10–20°. The solution was allowed to warm to room temperature, 10 ml. of 30% hydrogen peroxide added, and the reaction mixture refluxed for 1 hr. The solution was evaporated to *ca.* 15 ml., carefully acidified with concentrated hydrochloric acid, and cooled. Filtration afforded 1.26 gms. (78%) of the crude diacid, m.p. 188–191°, which on crystallization from alcohol–petroleum ether (b.p. 40–60°) gave 0.95 gm. (58%) of the pure material, m.p. 194–195° (reported,[5] m.p. 190°). A mixture of this material and that (m.p. 192–194°) obtained by nitric acid oxidation[5] of 9-methyl-*cis*-decalone-3[14] melted at 193–195°.

9-Methyl-cis-decalone-3. A solution of 2.0 gms. (0.009 mole) of the ketone ketal (*17*) in 50 ml. of diethylene glycol was reduced according to the Huang-Minlon modification of the Wolff-Kishner conditions with 1.5 gm. (0.03 mole) of 95% hydrazine hydrate and 2.0 gms. (0.03 mole) of potassium

(17) C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).

(18) A. J. Birch, E. Pridie, and H. Smith, *J. Chem. Soc.*, 4688 (1958); V. Prelog and D. Zäch, *Helv. Chim. Acta*, **42**, 1862 (1959).

(19) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

(20) Melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137.

hydroxide. The residue obtained after the usual work-up was dissolved in 10 ml. of acetone, treated with 5 ml. of 10% aqueous hydrochloric acid, and the solution warmed for 5 min. on the steam bath. The reaction mixture was diluted with 200 ml. of water and extracted four times with 50-ml. portions of ether. After drying, the ether was evaporated and the residue crystallized from petroleum ether (40–60°). In this manner there was obtained 0.92 gm. (61%) of 9-methyl-*cis*-decalone-3, m.p. 50–50.5°. The mixture of this material and that (m.p. 49.5–50.5°) prepared by catalytic hydrogenation[14] of 9-methyl-Δ^4-octalone-3 melted at 49.5–50.5°. The semicarbazone prepared from this material melted at 201–202° alone or on admixture with the semicarbazone (m.p. 201–202°) of the authentic *cis*-decalone (reported,[14] m.p. 201–202°).

4,4-Ethylenedioxy-2-carbomethoxy-2-(3-ketobutyl)-cyclohexanone (*10*). Following the procedure by Tishler and co-workers[9] 50 gm. (0.234 mole) of 4,4-ethylenedioxy-2-carbomethoxycyclohexanone[8] and 35 gm. (0.50 mole) of methyl vinyl ketone in 500 ml. of methanol containing 10 ml. of triethylamine were allowed to stand for 48 hr. at room temperature in a nitrogen atmosphere. At the end of this period an aliquot of the reaction mixture gave no coloration with 1% alcoholic ferric chloride. When the methanol was removed at reduced pressure and the residue crystallized from methanol-water, there was obtained 59.4 gm. (89%) of the dione (*10*), m.p. 68–71°. The analytic sample, obtained by three crystallizations from methanol-water and one from ethyl acetate–petroleum ether (40–60°), melted at 70–71.5°.

Anal. Calcd. for $C_{14}H_{20}O_6$: C, 59.12; H, 7.09. Found: C, 59.15; H, 7.07.

4,4-Ethylenedioxy-2-carbomethoxy-2-(3-ketopenyl)cyclohexanone (*11*). Using the same procedure used to prepare the dione (*10*), 39 gm. (0.182 mole) of the ketone (*9*) was condensed with ethyl vinyl ketone (24 gm.; 0.285 mole) in methanol solution. There resulted 44.3 gm. (82%) of the dione (*11*), m.p. 83–85°, after crystallization from methanol. The analytical sample, obtained after four recrystallizations from methanol, melted at 85–86°.

Anal. Calcd. for $C_{15}H_{22}O_6$: C, 60.40; H, 7.43. Found: C, 60.56; H, 7.57.

10-Carbomethoxy-6,6-ethylenedioxy-$\Delta^{1(9)}$-octalone-2 (*12*). A suspension of 9.5 gm. (0.0355 mole) of the dione (*10*) in 75 ml. of absolute methanol containing 1 gm. (0.0433 g.-atom) of sodium was warmed in a nitrogen atmosphere at 40° for 1 hr., during which time the reaction mixture became homogeneous. After a 2-hr. reflux period, 3.1 gm. (0.051 mole) of glacial acetic acid was added slowly at 15°. The crystals (4.27 gm.) that separated were filtered and most of the methanol removed from the filtrate at reduced pressure. The residue was extracted with benzene, and after the usual washings, evaporation of the benzene afforded 2.85 gm. of the same solid material. Recrystallization of these two crops from 20% aqueous methanol afforded 5.6 gm. (61%) of the octalone (*12*), m.p. 124–126°. The analytical sample, obtained after four further recrystallizations from 20% aqueous methanol, melted at 125–126°.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.17; H, 6.81. Found: C, 62.91; H, 6.89.

1-Methyl-10-carbomethoxy-6,6-ethylenedioxy-$\Delta^{1(9)}$-octalone-2 (*13*). Using the same procedure used to prepare the octalone (*12*), 5.0 gm. (0.0167 mole) of the dione (*11*) was cyclized in 77% yield (3.58 gm.; m.p. 100–102°) in 30 ml. of absolute methanol containing 0.46 gm. (0.02 g.-atom) of sodium. The analytical sample, obtained after three recrystallizations from aqueous methanol, melted at 101.5–103°.

Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.28; H, 7.19. Found: C, 64.37; H, 7.23.

6,6-Ethylenedioxy-$\Delta^{1(9)}$-octalone-2 (*15*). (*a*) *By decarbomethoxylation of the octalone* (*12*). A solution of 1.2 gm. (4.5 mmoles) of the octalone (*12*) in 40 ml. of a 4% aqueous methanolic potassium hydroxide solution was refluxed for 4 hr., neutralized to *p*H 6 with glacial acetic acid, and extracted with benzene. After the usual washing sequence, the residue obtained after removal of the benzene was crystallized from ethyl acetate–petroleum ether (b.p. 40–60°). In this manner there resulted 0.52 gm. (56%) of the octalone (*15*), m.p. 78–80°. After four further recrystallizations from the same solvent pair, the analytical sample had m.p. 80–81°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.75. Found: C, 69.18; H, 7.70.

(*b*) *Directly*[10] *from the dione* (*10*). A mixture of 56.8 gm. (0.2 mole) of the dione (*10*) and 500 ml. of water containing 2 gm. of potassium hydroxide was stirred and brought to reflux in a nitrogen atmosphere. Then a solution of 28 gm. of potassium hydroxide in 250 ml. of water was added dropwise over a period of 3 hr. and the solution refluxed and stirred an additional 9 hr. After cooling, the aqueous mixture was extracted with ether, and the residue, obtained after the usual work-up, distilled. The octalone (*15*) (35.6 gm.; 85%) was collected in the range 138–150° (1.5 mm.). Crystallization from ethyl acetate–petroleum ether (40–60°) afforded 27.8-gms. (67%) of the octalone (*15*), m.p. 78–80° alone or on admixture with that obtained under part (*a*) above.

1-Methyl-6,6-ethylenedioxy-$\Delta^{1(9)}$-octalone-(2) (*16*). (*a*) *By decarbomethoxylation of the octalone* (*13*). Treatment of 5.0 gm. (0.018 mole) of the octalone (*13*) with 100 ml. of a 4% aqueous methanolic potassium hydroxide solution under the same conditions as described above afforded an 3.20 gm. (80%) of the octalone (*16*), m.p. 59–60° after recrystallization from petroleum ether (40–60°). The analytical sample, obtained after two further recrystallizations from the same solvent, melted at 62–63°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 8.28.

(*b*) *Directly*[10] *from the dione* (*11*). In the same fashion as outlined above for the dione (*10*), 14.9 gm. (0.05 mole) of the dione (*11*) was refluxed for 5 hr. with a total of 12.85 gm. of potassium hydroxide in 350 ml. of water. After the usual work-up, there was obtained 10.7 gm. (96%) of the octalone (*16*), m.p. 61–63°, after crystallization from petroleum ether (40–60°).

6,6-Ethylenedioxy-2-methyl-$\Delta^{1(9)}$-octalol-2 (*14*). To a solution of methylmagnesium bromide (from 0.4 gm. (0.016 g.-atom) of magnesium) in 350 ml. of ether in a nitrogen atmosphere at 0° was added a solution of 1.0 gm. (0.005 mole) of the octalone (*15*) in 50 ml. of ether. After the reaction mixture was stirred for 1 hr. at −10° to 0°, it was allowed to warm to room temperature over a 0.5-hr. minus period and then decomposed with cold, saturated aqueous ammonium chloride. After the usual work-up, the residue obtained on evaporation of the ether was crystallized from petroleum ether (60–75°) and afforded 0.92 gm. (82%) of the alcohol (*14*), m.p. 96–96.5° (introduced at 90°), as clusters of long needles. Further crystallization from the same solvent did not raise the melting point. The infrared spectrum showed no carbonyl absorption and a strong band at 2.90 μ (—O—H).

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.65; H, 8.98. Found: C, 69.69; H, 9.04.

9-Methyl-6,6-ethylenedioxy-cis-decalone-2 (*17*). Following the procedure of Birch and Robinson,[4] 7.2 gm. (0.035 mole) of the octalone (*15*) in 400 ml. of ether was added dropwise over a 3-hr. period to an ice salt-cooled (−10°) solution of methylmagnesium bromide (from 2.5 gm. (0.1 g.-atom) of magnesium) and freshly prepared cuprous bromide (0.2 gm.) 800 ml. of ether under a nitrogen atmosphere. After the addition was complete, the reaction mixture was warmed to room temperature (0.5 hr.), stirred, and refluxed for 3 hr., and then concentrated to approximately 300 ml. by distillation. The Grignard complexes were destroyed with cold, saturated, aqueous ammonium chloride, and the product isolated in the usual manner with ether. Distillation of the residue obtained after removal of the ether afforded 5.5 gms. (70%) of a colorless liquid, b.p. 123–129° (0.3 mm.), which solidified to an oily solid. Crystallization of this material from petroleum ether (40–60°) afforded 4.7 gms. (61%) of the *cis*-decalone (*17*), m.p. 76–79°. The analytical sample, obtained after

four further recrystallizations from the same solvent, melted at 79.5–80.5°. The infrared spectrum (Nujol mull) showed a strong band at 5.85 μ (saturated > C=O) and no absorption in the O–H stretching region.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.65; H, 8.98. Found: C, 69.49; H, 8.83.

9-Methyl-6,6-ethylenedioxy-3-n-butylthiomethylene-cis-decalone-2 (*18*). A solution of 1.12 gms. (5.0 mmoles) of the *cis*-decalone (*17*) and 4.7 ml. (3.8 gms.; 50 mmoles) of purified ethyl formate in 25 ml. of dry benzene was added over a 0.5-hr. period to an ice-cooled suspension of 2.70 gm. (50 mmoles) of commercial sodium methoxide in 50 ml. of dry benzene under a nitrogen atmosphere. After stirring overnight at room temperature, the reaction mixture was cooled and treated with excess saturated, cold, aqueous sodium dihydrogen phosphate. The benzene layer was separated, washed with water, dried (sodium sulfate), and the benzene evaporated.

The above hydroxymethylene derivative and 440 mg. (5.5 mmoles) of *n*-butyl mercaptan in 50 ml. of dry benzene containing a trace of *p*-toluenesulfonic acid were refluxed in a nitrogen atmosphere under a Dean-Stark water separator filled with Drierite for 5 hr. After the reaction mixture was cooled and worked up in the usual manner, there was obtained 1.50 gms. (96%) of oily solid. On chromatography of this material on 80 gms. of alumina (Merck) 1.0 gm. (64%) of the pure *n*-butylthiomethylene derivative (*18*), m.p. 84–86°, was eluted with 1500 ml. of 25% ether benzene. The analytical sample, obtained after two crystallizations from petroleum ether (40–60°), melted at 85–86°. The infrared spectrum showed absorption at 6.01 μ and 6.49 μ (—C(=O)—C=CH—S—R), and 9.2 μ (ketal).

Anal. Calcd. for $C_{18}H_{28}SO_3$: C, 66.62; H, 8.69; S, 9.88. Found: C, 66.78; H, 8.60; S, 9.87.

3,9-Dimethyl-6,6-ethylenedioxy-cis-decalone-2 (*19*). (*a*) *By methylation of 9-methyl-6,6-ethylenedioxy-cis-decalone-2* (*17*). Following the procedure of Corey,[12] 48.5 ml. of a 0.37 *N* ethereal solution of sodium triphenylmethide was added to a well stirred solution of 3.0 gms. (0.0135 mole) of the *cis*-decalone (*17*) in 75 ml. of dry ether. After stirring for 15 min. at room temperature, 34 gm. (0.25 mole) of methyl iodide was added, and the reaction mixture stirred for an additional 14 hr. at room temperature. The solution was filtered, the ether evaporated, and the residue adsorbed on 90 gm. of alumina (Merck) in petroleum ether (40–60°). Elution with the same solvent removed the triphenylmethane, while 2000 ml. of ether was required to remove the oily ketone ketal (1.4 gm.). On rechromatography of this material on 70 gm. of alumina (Merck) 1.1 gm. (34%) of solid methylated *cis*-decalone (19), m.p. 63–66°, was eluted with 3.5 l. of 50% benzene–petroleum ether (40–60°). The analytical sample, obtained after four crystallizations from petroleum ether (60–75°), melted at 68–69°.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.57; H, 9.42.

(*b*) *By desulfurization of 9-methyl-6,6-ethylenedioxy-3-n-butylthiomethylene-cis-decalone-2* (*18*). To a well stirred suspension of 1 tsp. of W-2 Raney nickel[21] in 50 ml. of absolute ethanol was added 420 mg. (1.3 mmoles) of the *n*-butylthiomethylene derivative (*18*), and the reaction mixture warmed to 60° and then allowed to cool for 1 hr. After filtration to remove the nickel and evaporation of the ethanol, the residue was adsorbed on 20 gm. of alumina (Merck) in petroleum ether (40–60°). Elution with 750 ml. of benzene afforded 250 mg. (81%) of the dimethyl-*cis*-decalone (*19*), m.p. 63–66°. On crystallization of this material from petroleum ether (60–75°) afforded 210 mg. (70%) of decalone, m.p. 67–69°. The mixture obtained from this material and that prepared under (*a*) above melted at 67–69°.

4-Hydroxy-1-keto-3-methoxy-9-methyl-cis-$\Delta^{2,6}$-hexahydronaphthalene (*20*). After the procedure of Speziale, Stephens, and Thompson,[13] 25 gm. (0.121 mole) of 1,4-diketo-2-methoxy-10-methyl-*cis*-$\Delta^{2,6}$-hexahydronaphthalene in 65 ml. of water and 200 ml. of glacial acetic acid was treated with 40 gm. of powdered zinc at such a rate as to maintain the temperature between 20–25°. After stirring for 5 hr., the zinc was removed by filtration, washed with 50 ml. of methanol, and the filtrate concentrated to one third the original volume. The concentrate was diluted with 100 ml. of water, extracted three times with 100-ml. portions of chloroform, and the combined chloroform extracted, washed with 5% aqueous sodium bicarbonate and water, and dried (sodium sulfate). When the residue obtained after evaporation of the chloroform was crystallized from benzene, there resulted 15 gm. (59%) of the ketal (20), m.p. 65–67°. The analytical sample, obtained after three further crystallizations from the same solvent, melted at 68°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.02; H, 7.62.

1,9-Dimethyl-4-hydroxy-3-keto-cis-$\Delta^{1,6}$-hexahydronaphthalene (*21*). To a solution of methyllithium [from 3.26 gm. (0.47 g.-atom) of lithium and 13 ml. of methyl iodide] in 50 ml. of dry ether was added a solution of 4.0 gms. (0.0192 mole) of the ketal (*20*) in 25 ml. of dry ether at such a rate so as to maintain gentle reflux. After the reaction mixture was refluxed for 10–14 hr., 100 ml. of cold water was added, and the product isolated by either extraction. After the usual washing sequence, removal of the ether afforded a white, crystalline solid. The infrared spectrum of this material showed no carbonyl absorption and only a band at 2.92 μ due to O—H stretching absorption. A portion of this material, crystallized twice from benzene, melted at 157° and corresponded to *1,9-dimethyl-1,4-dihydroxy-3-methoxy-cis-$\Delta^{2,6}$-hexahydronaphthalene.*

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.64; H, 8.92. Found: C, 69.82; H, 8.89.

Following the procedure of Woodward,[14] the remainder of the diol was dissolved in 40 ml. of methanol containing 4 ml. of 10% aqueous sulfuric acid, and the solution refluxed for 30 min. The solution was cooled, neutralized with solid potassium carbonate, and concentrated at reduced pressure. The product, isolated in the usual manner by ether extraction and crystallized from petroleum ether (60–75°), amounted to 3.6 gms. (97%) of the ketal (*21*), m.p. 65–66°. The analytical sample, obtained after two further crystallizations from the same solvent, melted at 66.5°. The infrared spectrum (liquid film) showed bands at 2.84 μ (O—H), 5.97 μ (unsaturated C=O) and 6.18 μ (> C=C<).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.25; H, 8.37.

1,9-Dimethyl-4-acetoxy-3-keto-cis-$\Delta^{1,6}$-hexahydronaphthalene. A solution of 0.7 gm. (0.00365 mole) of the ketal (*21*) in 5 ml. of anhydrous pyridine was treated with 1 ml. of acetic anhydride and allowed to stand at room temperature for 24 hr. The product, isolated in the usual manner and crystallized from petroleum ether (60–75°), amounted to 0.72 gm. (85%) of the acetate, m.p. 133–134°. The analytical sample, obtained after two further crystallizations from the same solvent, melted at 135–135.5°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 72.00; H, 7.80.

1,9-Dimethyl-cis-Δ^6-octalone-3 (*22*). In a modification of the procedure of Chapman and co-workers[15] a solution of 7.0 gms. (0.175 g.-atom) of calcium metal in 1500 ml. of dry liquid ammonia was treated with a solution of 3.0 gm. (0.0128 mole) of the ketol acetate in 50 ml. of dry tetrahydrofuran. After stirring for 5 min., 35 ml. of methanol was added at a dropwise rate over a period of 10 min.; at the end of the addition the blue had been discharged. The ammonia was removed in an air stream, the residue acidified with 3:1 aqueous hydrochloric acid and the product isolated in the

(21) R. Mozingo, *Org. Syntheses*, Coll. Vol. III, 181 (1955).

usual fashion by ether extraction. The material so obtained was shown to be a mixture of saturated ketone and alcohol and was oxidized in acetone solution at 10° with 2 ml. of Jones reagent (sufficient oxidant to impart a permanent orange-brown coloration to the reaction mixture). After the usual work-up, there resulted 1.20 gm. of crude product which on distillation afforded 1.0 gm. (44%) of the octalone (*22*), b.p. 128–130° (18 mm.). The analytical sample was obtained by evaporative redistillation of a sample at 120° (18 mm.) (bath temp.).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.60; H, 10.22.

The 2,4-dinitrophenylhydrazone of the octalone (*22*) melted at 183° after crystallization from ethanol.

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.33; H, 6.14; N, 15.64. Found: C, 60.35; H, 6.18; N, 15.74.

1,9-Dimethyl-cis-Δ⁶-octalin (*23*). When 4.6 gm. (0.026 mole) of the octalone (*22*) was reduced under the Huang-Minlon modification[11] of the Wolff-Kishner reduction using 7.2 ml. of 95% hydrazine hydrate and 5.50 gms. of 85% potassium hydroxide pellets, there was obtained 3.5 gms. (83%) of the *cis*-octalin (*23*), b.p. 100–104° (10 mm.). The analytical sample, obtained by redistillation, boiled at 115° (18 mm.). Gas-liquid chromatography of this material on a 10% glycol succinate–Chromsorb-W column at 130° showed only one peak, and the infrared spectrum showed no carbonyl absorption in the 5.85-μ region.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.71; H, 12.29.

1,9-Dimethyl-6,7-oxido-cis-decalin (*24*). A solution of 1.0 gm. (0.0061 mole) of octalin (*23*) in 4 ml. of benzene was treated with 11.1 ml. of a benzene solution of perbenzoic acid containing 0.076 gm. of peracid/ml., and the reaction mixture allowed to stand at 5° for 24 hr. When the product, obtained after the usual work-up, was distilled, there resulted 1.05 gm. (96%) of oxide, b.p. 85–90° (0.1 mm.), as a colorless, mobile liquid. The analytical sample was obtained by evaporative distillation of a small sample at 80° (0.1 mm.) (bath temp.).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.88; H, 10.97.

Lithium aluminum hydride reduction of the oxide (*24*). A solution of 1.32 gm. (0.0073 mole) of the oxide (*24*) in 10 ml. of ether was added to a suspension of 1.2 gm. (0.0315 mole) of lithium aluminum hydride in 25 ml. of ether, and the mixture refluxed for 3 hr. After the usual work-up, distillation afforded 1.28 gms. (96%) of a colorless, viscous liquid, b.p. 90–95° (0.1 mm.). The analytical sample of this material boiled between 160–180° (19 mm.). Gas-liquid chromatography of this alcohol on 10% glycol succinate–Chromsorb-W at 145° showed two major components in the ratio of 70:30, eluted at 6.8 and 7.6 min., respectively, and the infrared spectrum showed only O—H absorption at 2.85 μ.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.96; H, 12.03.

8,9-Dimethyl-cis-decalone-3 (*25*). (*a*) *By oxidation of the alcohol obtained from the oxide* (*24*). A solution of 517 mg. (2.84 mmoles) of the alcohol above afforded 480 mg. (94%) of ketonic mixture, b.p. 75° (0.2 mm.) (bath temp.), by oxidation with 0.75 ml. of Jones reagent[16] in 10 ml. of acetone at −10°. Gas-liquid chromatography of this material on a 10% glycol succinate–Chromsorb-W column at 130° showed that it consisted of two major components in the ratio 65:35. The infrared spectrum showed a strong band at 5.85 μ, but was not identical to that of the ketone prepared under (*b*) below.

The *2,4-dinitrophenylhydrazone* formed from 250 mg. of this ketonic mixture was eluted from a column of 10 gms. of Bentonite-Kiesulguhr (2:8) with 300 ml. of alcohol-free chloroform, and after crystallization from ethanol melted at 115° alone or on admixture with that prepared from the ketone under (*b*) below.

The *semicarbazone* formed from the remainder of the ketone sample by the procedure of Fieser[22] was also a mixture, which after repeated recrystallization from aqueous methanol afforded a small amount of material of melting point 190–191°, alone or on admixture with the same derivative prepared from the ketone (*25*) available under (*b*) below.

An attempt to prepare the oxime from material obtained in a similar oxidation reaction led only to an oily derivative.

(*b*) *By Wolff-Kishner reduction and hydrolysis of 1,9-dimethyl-6,6-ethylenedioxy-cis-decalone-2* (*4*). When the Huang-Minlon modification[11] of the Wolff-Kishner reduction was applied to 5.95 gm. (0.025 mole) of the ketone ketal (*4*) employing 5.00 gm. (0.10 mole) of 98–100% hydrazine hydrate and 6.60 gm. (0.10 mole) of 85% potassium hydroxide pellets in 100 ml. of diethylene glycol, the product, isolated from the cooled reaction mixture by ether extraction, was not purified but used directly in the ketal cleavage reaction.

The crude ketal in 20 ml. acetone and 20 ml. of 10% aqueous hydrochloric acid was warmed on the steam bath for 10 min. Then 100 ml. of water was added, and the product isolated by ether extraction. In this manner there was obtained 3.93 gms. (86%) of the *cis*-decalone (*25*), b.p. 60–62° (0.1 mm.). The analytical sample, obtained by redistillation, boiled at 75° (0.15 mm.). Gas-liquid chromatography of this material on a 10% glycol succinate–Chromsorb-W column at 180° showed only one sharp peak at 3.9 min.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.17; H, 11.23.

The *2,4-dinitrophenylhydrazone* prepared from this ketone melted at 115° after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.86; H, 6.70; N, 15.45.

The *semicarbazone* prepared by the procedure of Fieser[22] melted at 190–191° after two crystallizations from aqueous methanol.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.79; H, 9.77; N, 17.71. Found: C, 65.65; H, 9.74; N, 17.82.

The *oxime* prepared from 100 mg. (0.56 mmole) of the ketone (*25*) amounted to 94 mg. (87%) and melted at 147–148° after two crystallizations from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.79; H, 10.83; N, 7.17. Found: C, 73.83; H, 10.77; N, 7.12.

9-Methyl-6,6-ethylenedioxy-cis-decalone-1 (*28*). A solution of 22.3 gm. (0.11 mole) of 5-hydroxy-10-methyl-$\Delta^{1(9)}$-octalone-2 hydrate[17] in 150 ml. of ethanol was hydrogenated at room temperature and 40 p.s.i. over 3.2 gm. of 10% palladium-on-carbon. Hydrogenation was complete in 8 min. with absorption of 1 molar-equivalent of hydrogen, and after filtration, the ethanol was removed at reduced pressure. The residue could not be induced to crystallize and was used directly in the ketalization reaction. On one occasion when 500 mg. (2.74 mmoles) of the oily keto alcohol was oxidized with 0.7 ml. of Jones reagent[16] in 3 ml. of acetone, 350 mg. (71%) of the known[23] *9-methyl-cis-decal-1,6-dione*, m.p. 63–64.5°, was obtained.

The keto alcohol obtained above was dissolved in a mixture of 200 ml. of benzene containing 200 mg. of *p*-toluenesulfonic acid and 12 gms. (0.2 mole) of ethylene glycol, and the mixture was refluxed under a Dean-Stark water separator filled with Drierite for 16 hr. After the usual work-up and removal of the benzene at reduced pressure, the residue, which could not be induced to crystallize, was oxidized at 2–9° with 27.5 ml. (0.11 mole-equiv.) of Jones reagent[16] in 100 ml. of acetone. The reaction mixture was stirred for 10 min. at 10° after addition of the oxidant was complete and then diluted with 350 ml. of water, and the ketal ketone isolated by ether extraction. After the usual work-up and removal of the ether, the residue was triturated at −70° in petroleum ether (40–60°) where upon 20 gm. (80%) of the

(22) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd Ed., D. C. Heath and Co., Boston, p. 85.

(23) S. Swaminathan and M. S. Newman, *Tetrahedron*, 2, 88 (1958).

ketone ketal (*28*), m.p. 68–72°, separated. Recrystallization of this material from petroleum ether (60–75°) afforded 16.4 gms. (62%) of the pure ketone ketal (*28*), m.p. 75–76.5°. The analytical sample, obtained after two further crystallizations from the same solvent, melted at 75.5–76.5°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.61; H, 8.95.

Hydrolysis of 400 mg. (1.8 mmoles) of the ketone ketal (*28*) in 5 ml. of acetone and 5 ml. of 10% aqueous hydrochloric acid afforded 300 mg. (92%) of *9-methyl-cis-decal-1,6-dione*, m.p. 64.5–66°. A mixture of this material and that prepared from the keto alcohol above melted at 63–64.5°.

When the noncrystalline residue (27 gm.) obtained after a similar run on 36.2 gm. (0.18 mole) of the hydroxy ketone (*27*) was chromatographed on 600 gms. of Alumina (Merck), 7.6 gm. of the *cis*-ketone ketal (*28*), m.p. 74–76°, was eluted with 13 l. of 50% benzene–petroleum ether (40–60°) [1st crop: [14.8 gms. (37%); total *cis*-ketone ketal (*28*) obtained: 22.8 gm. (57%)] and 2.8 gm. (7%) of *9-methyl-6,6-ethylenedioxy-trans-decalone-1* (*32*), m.p. 41–45°, was eluted with 4 l. of 50% benzene–petroleum ether (40–60°). The analytical sample of the *trans*-decalone (*32*), obtained after four further crystallizations from petroleum ether (40–60°), melted at 47–48°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.48; H, 8.92.

Hydrolysis of this material in aqueous acetone with 10% aqueous hydrochloric acid afforded the *trans*-dione (*33*), m.p. 56–57°, alone or on admixture with an authentic sample prepared by known methods.[18]

1,9-Dimethyl-6,6-ethylenedioxy-cis-decalol-1 (*29*). To a solution of methyllithium (prepared from 1.4 g. (0.2 g.-atom) of lithium and excess methyl bromide) in 100 ml. of dry ether was added 4.48 gm. (0.02 mole) of the ketone ketal (*28*) in 100 ml. of dry ether. The reaction mixture was refluxed overnight, cooled, and then worked-up in the usual manner, using 200 ml. of ice-cooled, saturated aqueous ammonium chloride to decompose the complexes. When the residue obtained after removal of the ether was crystallized from petroleum ether, there was obtained 3.1 gm. (65%) of the alcohol (*29*), m.p. 92–96°. Recrystallization from the same solvent afforded 2.6 gm. (61%) of purer material, melting at 96–98°. The analytical sample, obtained after two further crystallizations, melted at 98–98.5°.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.84; H, 9.91.

1,9-Dimethyl-6,6-ethylenedioxy-cis-Δ^1*-octalin* (*30*). A melt of 12.95 g. (0.054 mole) of the alcohol (*29*) was heated to 130°, and 200 mg. of iodine was added at 20-min. intervals over a period of 1 hr. The reaction mixture was cooled, worked up in the usual fashion by ether extraction, and the product, which was shown to have suffered some ketal cleavage by the presence of a medium band in the infrared spectrum at 5.85 μ, was reketalized with 10 ml. of ethylene glycol in 100 ml. of benzene containing 100 mg. of *p*-toluenesulfonic acid. On work-up and distillation of the product there was obtained 10.05 gm. (84%) of the octalin (*30*), b.p. 88–90° (0.2 mm.), as a colorless, mobile liquid. The analytical sample was obtained by redistillation and boiled at 74–75° (0.1 mm.).

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.39; H, 9.76. Found: C, 75.64; H, 9.97.

1β,9-Dimethyl-6,6-ethylenedioxy-cis-decalone-2 (*4*). The procedure used was essentially that outlined by Brown and co-workers.[19] To a well stirred suspension of 1.22 gm. (0.032 mole) of sodium borohydride in 150 ml. of dry tetrahydrofuran in a nitrogen atmosphere was added 10.05 gm. (0.045 mole) of the *cis*-octalin (*30*). Then 6.02 gm. of freshly distilled boron trifluoride etherate was added dropwise, the reaction mixture stirred at room temperature for 3 hr., and treated with 36 ml. of 10% aqueous sodium hydroxide. After removal of *ca.* 100 ml. of solvent on the steam bath, 36 ml. of 30% hydrogen peroxide was added dropwise while maintaining a gentle reflux on the steam bath. After an additional 0.5-hr. reflux, the reaction mixture was cooled, 250 ml. of water added, and the product isolated by ether extraction. The colorless oil (10.45 gms.) obtained after evaporation of the ether was oxidized without purification with 10.4 ml. of Jones reagent[16] in 50 ml. of acetone at 5–10°. The ketone isolated after dilution with 150 ml. of water and ether extraction amounted to 10.05 gms. and was chromatographed on 340 gm. of alumina (Merck). Elution with 6 liters of 2% ether-benzene afforded 7.9 gm. (76%) of crystalline ketone (*4*), m.p. 88–90°. On recrystallization from petroleum ether (30–60°) this material afforded 7.5 gm. (71%) of the pure ketone (*4*), m.p. 92–94°. The melting point could not be raised by further crystallization.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.53; H, 9.33

1β,9-Dimethyl-2α-hydroxy-cis-decalone-6 (*31*). A solution of 940 mg. (4 mmoles) of the ketone (*4*) in 40 ml. of dry ether was added to 500 mg. (71 g.-atom) of lithium in 50 ml. of liquid ammonia, and the reaction mixture stirred for 1 hr. Then 10 ml. of ethanol was added to discharge the blue color, and the reaction mixture worked up by ether extraction. Removal of the ether afforded 910 mg. (95%) of the corresponding hydroxy ketal, m.p. 74–77°; a small sample, purified for analysis by two crystallizations from petroleum ether (60–75°), melted at 78.5–79.5°.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.99; H, 10.09.

The bulk of the hydroxy ketal was hydrolyzed by warming 10 min. on the steam bath in 10 ml. of acetone and 5 ml. of 10% aqueous hydrochloric acid. The acetone was evaporated in an air jet, and the hydroxy ketone (*31*) isolated by ether extraction after 10 ml. of saturated salt solution was added. After evaporation of the ether and two crystallizations of the residue from petroleum ether (60–75°), there resulted 550 mg. (70%) of the *cis*-decalone (31), m.p. 87–90°. The analytical sample, obtained after two further crystallizations from petroleum ether (90–100°), melted at 92–93°.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.44; H, 10.27. Found: C, 73.33; H, 10.18.

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