[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

An Investigation of Anchimeric Assistance in Certain Homoallylic Alcohols

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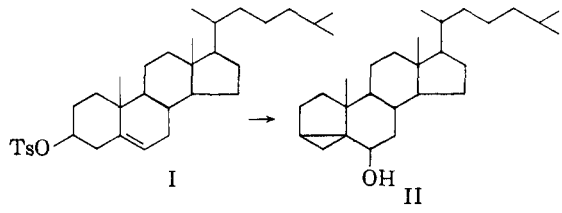
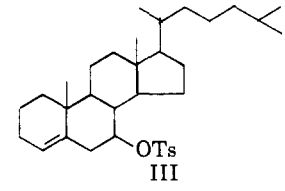
Several homoallylic alcohols have been prepared and their *p*-toluenesulfonate esters solvolyzed in aqueous dioxane. Rate studies indicate that double bond participation occurs during the solvolysis of the esters.

The phenomenon in organic chemistry known as anchimeric assistance (neighboring group participation) has been observed in many types of molecules.[1a,b] Participation of the neighboring vinyl group in solvolytic displacement reactions is well recognized, the *i*-steroid rearrangement being a classical example of this effect.[2a-d] Molecular geometry is of great importance in the participation of such double bonds, for whereas cholesteryl *p*-toluenesulfonate (I) clearly gives evidence for assistance in ionization (the formation of 3,5-cyclocholestan-6β-ol (II) and a faster rate than the saturated esters cyclohexyl *p*-toluenesulfonate and cholestanyl *p*-toluenesulfonate), epicholesteryl *p*-toluenesulfonate does not. In cholesteryl *p*-toluenesulfonate the ester group is equatorial and in a position relative to the double bond so that the π-electrons of the double bond may overlap with the developing empty *p*-orbital at C-3; in epicholesteryl *p*-toluenesulfonate the ester group is axial and the geometry of the system is not favorable for participation.[3a-c]



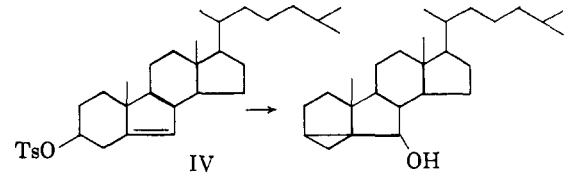
I II

ψ-Cholesteryl *p*-toluenesulfonate (III) fails to give indication of anchimeric assistance upon undergoing solvolysis, although the ester group is equatorial and seemingly properly situated for participation.[4a,b] This result has been explained in terms of the rigidity of the B-ring, due to the trans B/C-ring fusion.[4a] Epi-ψ-cholesteryl *p*-toluenesulfonate also fails to exhibit homoallylic participation.[5]



III

While these results indicate that definite geometric requirements must be met in order for such participation to occur, it is possible to have some deviation from the basic cholesterol structure and still observe a significant amount of homoallylic participation, for B-norcholesteryl *p*-toluenesulfonate (IV) does solvolyze with anchimeric assistance of the double bond at a rate one-half that of cholesteryl *p*-toluenesulfonate to yield 3,5-cyclo-B-norcholesterol (V).[6]



IV V

Consideration of the above-mentioned facts led to the decision that a study of the rates of solvolysis of the *p*-toluenesulfonates of certain bicyclic alcohols which contain the essential homoallylic structural features of cholesterol, but which lack the C and D rings (represented by figure VI) would be instructive. If the rates were significantly greater than those of saturated analogs, and of a magnitude comparable to cholesterol derivatives, this evidence would indicate the occurrence of anchimeric assistance of the double bond.

(1) (a) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956). (b) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Holt, New York, 1959.

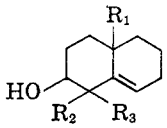
(2) (a) E. S. Wallis, E. Fernholz, aud F. T. Gephart, *J. Am. Chem. Soc.*, **59**, 137 (1937). (b) M. Hafez, G. Halsey, and E. S. Wallis, *Science*, **110**, 474 (1949). (c) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 3361 (1952). (d) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

(3) (a) L. C. King and M. J. Bigelow, *J. Am. Chem. Soc.*, **74**, 6238 (1952). (b) C. W. Shoppee and D. D. Evans, *J. Chem. Soc.*, 540 (1953). (c) E. J. Becker and E. S. Wallis, *J. Org. Chem.*, **20**, 353 (1953).

(4) (a) R. J. W. Cremlyn, R. W. Rees, and C. W. Shoppee, *J. Chem. Soc.*, 3790 (1954). (b) C. W. Shoppee, G. H. R. Summers, and R. J. W. Williams, *J. Chem. Soc.*, 1893 (1956).

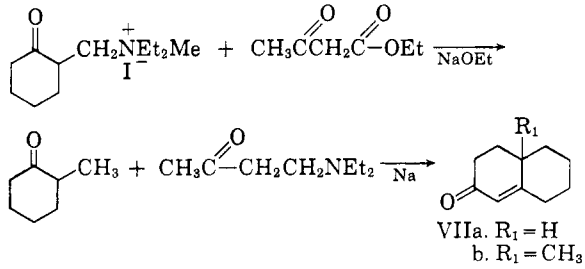
(5) G. J. Kent and E. S. Wallis, *J. Org. Chem.*, **24**, 1235 (1959).

(6) W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **78**, 4736 (1956).



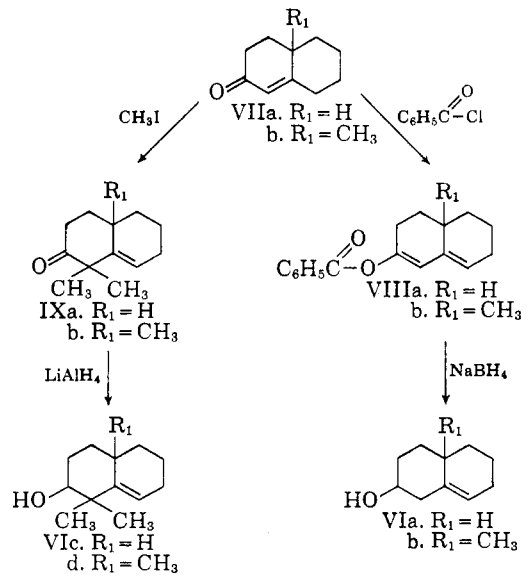
VIa. $R_1 = R_2 = R_3 = H$
b. $R_1 = CH_3$; $R_2 = R_3 = H$
c. $R_1 = H$; $R_2 = R_3 = CH_3$
d. $R_1 = R_2 = R_3 = CH_3$

One of the key intermediates, Δ^4-octalone-3 (VIIa) was prepared by the condensation of acetoacetic ester with the methiodide salt of diethylaminomethylcyclohexanone in ethanol with sodium ethoxide as the condensing agent.[7a,b] A second key intermediate, 9-methyl-Δ^4-octalone-3 (VIIb) was prepared by reaction of diethylaminobutanone-3 with 2-methylcyclohexanone in the presence of sodium metal, excess *o*-methylcyclohexanone serving as solvent.[8]



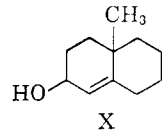
VIIa. $R_1 = H$
b. $R_1 = CH_3$

Δ^4-Octalone-3 and 9-methyl-Δ^4-octalone-3 were refluxed overnight with benzoyl chloride in petroleum ether to give the respective enol benzoates, VIIIa and b[7b]; reduction with sodium borohydride in aqueous ethanol[9a,b] gave $\Delta^{5(10)}$-octalol-3 and 9-methyl-$\Delta^{5(10)}$-octalol-3 (VIa and b), respectively.



Patterning the preparation of 4,4-dimethyl-$\Delta^{5(10)}$-octalol-3 (VIc) and 4,4,9-trimethyl-$\Delta^{5(10)}$-octalol-3 (VId) after that used in the synthesis of 4,4-dimethylcholesterol,[10] 4,4-dimethyl - Δ^5 - octalone - 3 (IXa) and 4,4,9-trimethyl-Δ^5-octalone-3 (IXb) were prepared by geminal dimethylation of Δ^4-octalone-3 and 9-methyl-Δ^4-octalone-3, respectively; reduction with lithium aluminum hydride gave the desired geminally dimethylated octalols.

The proof of structure of the octalols, especially that they are homoallylic with the hydroxyl group equatorial and cis with respect to the bridgehead, may now be discussed. First of all, the methods of preparation would be expected to give the desired system. To show that the unsaturated alcohols (all gave positive bromine addition tests) were not allylic, they were treated with manganese dioxide (in chloroform), a reagent known to oxidize allylic alcohols.[11] The allylic alcohol 9-methyl-Δ^4-octalol-3 (X) was readily oxidized (as evidenced by the de-



X

velopment of a conjugated ketone band and diminution of the hydroxyl band in the infrared), but none of the supposed homoallylic alcohols investigated gave evidence for any more than very slight oxidation.

Recently it has been shown that the presence or absence of the phenomenon of intramolecular hydrogen bonding in unsaturated alcohols (as observed in the OH stretching region of the infrared) may be used as a criterion for assignment of configuration.[12] If an octalol possessed an axial hydroxyl, a bonded OH stretching peak (due to bonding between the hydroxyl and the double bond) might be expected; if the hydroxyl were equatorial, this geometry would preclude any such interaction. In only one case (a small amount of side product in the preparation of VIb) was evidence for intramolecular hydrogen bonding found.

As further evidence for the nature of the hydroxyl group, two of the octalols were reduced on Adams catalyst[13] to the corresponding decalols.[14a-e] It

(7) (a) E. C. deFeu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, **53**, (1937). (b) S. Gates, Ph.D. thesis, Princeton University, 1954.

(8) M. Yanagita and K. Yamakawa, *J. Org. Chem.*, **22**, 291 (1957).

(9) (a) B. Belleau and T. F. Gallagher, *J. Am. Chem. Soc.*, **73**, 4458 (1951). (b) W. G. Dauben and J. F. Eastham, *J. Am. Chem. Soc.*, **73**, 4463 (1951).

(10) R. M. Moriarty and E. S. Wallis, *J. Org. Chem.*, **24**, 1274 (1959).

(11) O. Mancera, C. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953).

(12) P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

(13) *Org. Syntheses*, **II**, 191 (1943).

(14) (a) W. G. Dauben, E. Hoerger, and N. K. Freeman, *J. Am. Chem. Soc.*, **74**, 5206 (1952). (b) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **74**, 4420 (1954). (c) A. S. Dreiding and A. J. Tomasewski, *J. Am. Chem. Soc.*, **77**, 168 (1955). (d) A. S. Hussey, H. Liao, and R. H. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953). (e) Progress in Stereochemistry, Vol. I, p. 168, W. Klyne, Ed., Academic Press, New York.

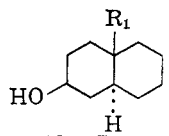
TABLE I

Compound	Rate, k_1 Sec.$^{-1}$		
$\Delta^{5(10)}$-Octalyl-3	50.06°	75.09°	99.96°
p-Toluenesulfonate (XII)	4.18×10^{-6}	5.91×10^{-5}	5.08×10^{-4}
9-Methyl-$\Delta^{5(10)}$-octalyl-3	50.04°	75.09°	100.00°
p-Toluenesulfonate (XIII)	1.69×10^{-5}	2.47×10^{-4}	2.19×10^{-3}[a]
4,4-Dimethyl-$\Delta^{5(10)}$-octalyl-3	50.00°		
p-Toluenesulfonate (XIV)	7.73×10^{-5}		
4,4,9-Trimethyl-$\Delta^{5(10)}$-octalyl-3	50.00°	75.09°	
p-Toluenesulfonate (XV)	7.25×10^{-5}	1.13×10^{-3}	
trans-2-Decalyl (XVI)			100.00°
p-Toluenesulfonate			2.57×10^{-5}
cis-10-Methyl-2-*trans*-decalyl			99.99°
p-Toluenesulfonate (XVII)			3.48×10^{-5}

[a] Extrapolated from lower temperatures.

was felt that by reduction to decalols of known stereochemistry the relationship of the hydroxyl and bridgehead groups in the octalols could be indicated. $\Delta^{5(10)}$-Octalol-3 was reduced to an alcohol which by infrared, melting, and mixed-melting points was shown to be *trans*-2-decalol (*cis*-10-hydrogen-2-*trans*-decalol), XIa. As the hydroxyl group is equatorial and cis with respect to the upper bridgehead hydrogen in *trans*-2-decalol, the same relationship must have held for $\Delta^{5(10)}$-octalol-3.

9-Methyl-$\Delta^{5(10)}$-octalol-3 was subjected to reduction on Adams catalyst, and, while the product was not fully crystalline, the infrared indicated *cis*-10-methyl-2-*trans*-decalol, XIb. (The "cis" refers to the relationship between the bridgehead methyl and the hydroxyl; the "trans" refers to the ring fusion[14d].) The reduction product formed a 3,5-dinitrobenzoate which by infrared, melting, and mixed-melting points was shown to be that of *cis*-10-methyl-2-*trans*-decalol. The desired relationship therefore existed in the octalol.



XIa. $R_1 = H$
b. $R_1 = CH_3$

trans-2-Decalol and *cis*-10-methyl-2-*trans*-decalol were also desired in order to compare the rates of solvolysis of their *p*-toluenesulfonates with the rates of the *p*-toluenesulfonates of the corresponding octalols, $\Delta^{5(10)}$-octalol-3 and 9-methyl-$\Delta^{5(10)}$-octalol-3.

Lithium in liquid ammonia reduction[15,16] of Δ^4-octalone-3 and 9-methyl-Δ^4-octalone-3 gave the corresponding decalones, which upon lithium aluminum hydride reduction gave the decalols (some decalol was obtained directly from the lithium in liquid ammonia reduction).

The desired alcohols in hand, their *p*-toluenesulfonates were prepared and solvolyzed in 90% aqueous dioxane in the presence of lithium acetate. The kinetic results are given in Table I.

Strong evidence for neighboring group participation is the observation of a significant rate enhancement for a given compound relative to a model compound in which the potential participant is not present. In the case of 9-methyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate (XIII) and *cis*-10-methyl-2-*trans*-decalyl *p*-toluenesulfonate (XVII), the rate factor is sixty at 100° (corresponding roughly to a stabilization of 3 kcal.), this being highly indicative of participation of the double bond. $\Delta^{5(10)}$-Octalyl-3 *p*-toluenesulfonate (XII) also reacts faster than its corresponding decalyl *p*-toluenesulfonate (XVI) (by a factor of twenty), and thus with this unsaturated ester there is evidently also participation, although definitely less than in the case of 9-methyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate. It may be that the methyl group serves as an "anchor" conferring upon 9-methyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate a greater degree of skeletal rigidity, allowing the π-orbitals to overlap more effectively with the developing empty *p*-orbital at C-3.

Only a slight difference in rate (factor of 1.3) is observed between the two decalyl *p*-toluenesulfonates, indicating that the angular methyl group has much less of an effect upon the rates of the decalyl compounds than upon the rates of the corresponding octalyl *p*-toluenesulfonates, where the rate factor is four. Thus in the unsaturated esters the methyl group in conjunction with the double bond plays a key role in the solvolysis.

In contrast, in the cases of 4,4-dimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate (XIV) 4,4,9-trimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate (XV) the angular group seems to play only a minor role, for these geminally dimethylated *p*-toluenesulfonates undergo solvolysis at similar rates. While the rates may be similar, however, the relative rate increases brought about by geminal dimethylation of Δ^5-octalyl-3 *p*-toluenesulfonate and 9-methyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate are different; for whereas at 50° the relative rate factor for the bridgehead methyl series is 4.3 (XV: XIII), in the bridge-

(15) D. K. Bannerjee, S. Chatterjee, and S. P. Bhattacharya, *J. Am. Chem. Soc.*, 77, 408 (1955).

(16) M. Yanagita, K. Yamakawa, A. Tahara, and H. Ogura, *J. Org. Chem.*, 20, 1767 (1955).

head hydrogen series the factor (XIV: XII) is eighteen. The reason for this may be the same as that put forward to explain why 4,4-dimethylcholesteryl *p*-toluenesulfonate (XVIII) solvolyzes only four times faster than cholesteryl *p*-toluenesulfonate.[17] That is, whereas in 4,4,9-trimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate a C-4 methyl C-9 methyl metaaxial interaction is present, such is not the case with 4,4-dimethyloctalyl-3 *p*-toluenesulfonate, and in order to relieve some of the strain introduced by this meta axial interaction 4,4,9-trimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate may adopt a somewhat distorted molecular geometry reducing anchimeric assistance of the double bond to the ionization of the ester. Thus, while the geminal dimethyl group may be (1) electronic stabilization of the transition state and (2) shortening of the C-3:C-5 distance by a Thorp-Ingold effect bring about a rate enhancement, this enhancement is not as great as that observed in 4,4-dimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate, where the favorable effects (1) and (2) are not reduced by a deleterious change in the molecular geometry such as that proposed for 4,4,9-trimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate.

It is inevitable when considering the rates of solvolysis of *p*-toluenesulfonates such as those of the octalols VIa–d that they be compared to the rates of cholesteryl *p*-toluenesulfonate and 4,4-dimethylcholesteryl *p*-toluenesulfonate.[17] Δ^5-Octalyl-3 *p*-toluenesulfonate solvolyzes at a rate roughly one-fifth that of cholesteryl *p*-toluenesulfonate, whereas 9-methyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate which with the angular methyl group more closely resembles cholesteryl *p*-toluenesulfonate, has a rate three-fourths that of the classical exhibitor of anchimeric assistance. Furthermore the rates of 4,4-dimethyl-Δ^5-octalyl-3 *p*-toluenesulfonate, and 4,4,9-trimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate are 0.80 to 0.90 those of 4,4-dimethylcholesteryl *p*-toluenesulfonate, and the increase in rate observed when 9-methyl-Δ^5-octalyl-3 *p*-toluenesulfonate is geminally dimethylated is approximately the same as the increase observed when cholesteryl *p*-toluenesulfonate is similarly transformed. The comparisons lend further evidence to the conclusion that the octalols do exhibit anchimeric assistance.

EXPERIMENTAL[18]

Δ^4-Octalone-3 (VIIa).[7a,b]

9-Methyl-Δ^4-octalone-3 (VIIb).[5]

Δ^4-Octalone-3-enol benzoate (VIIIa).[7b] A mixture of 30 g. of VIIa and 60 ml. of benzoyl chloride in 200 ml. of petroleum ether (b.p. 67°) was refluxed overnight. At the end of this period the reaction mixture was subjected to vacuum distillation, and all material boiling at less than 101° (13 mm.) was removed. The residue was chilled in a Dry Ice–acetone bath to yield solid material which was taken up in ethanol; recrystallization gave 22.5 g. of crystalline enol benzoate, m.p. 48–51°.

Δ^5-Octalol-3 (VIa). Twenty-two grams of VIIIa was dissolved in 800 ml. of 95% ethanol and the solution cooled to −3°. To this stirred mixture was added dropwise a solution of 20 g. of sodium borohydride in 450 ml. of 70% ethanol over a six-hour period, the reaction temperature being kept at less than 5°. After addition was complete, the reaction mixture was allowed to warm up to room temperature, after which it was heated to boiling and 490 ml. of 5% sodium hydroxide solution added. Most of the ethanol was removed under reduced pressure, and after cooling the residual cloudy mixture was added to an excess of cold dilute hydrochloric acid. The mixture was promptly extracted with ether, and the ethereal solution washed successively with dilute aqueous sodium carbonate and water, dried (over magnesium sulfate), and filtered. Removal of the solvent gave a viscous yellow oil which when distilled yielded a small forerun of benzyl alcohol and 7.99 g. of Δ^5-octalol-3, (VIa), b.p. 101–107° (3 mm.).

The octalol formed a phenylurethane, m.p. 133–135°.

Anal. Calcd. for $C_{17}H_{21}NO_2$: C, 75.24; H, 7.80; N, 5.16. Found: C, 75.14; H, 8.02; N, 5.36.

9-Methyl-Δ^4-octalone-3-enol benzoate (VIIIb).[19] Reaction of 9-methyl-Δ^4-octalone-3 with benzoyl chloride in petroleum ether gave the ester (53%), m.p. 50–54°.

9-Methyl-$\Delta^{5(10)}$-octalol-3 (VIb). Reduction of VIIIb by sodium borohydride in aqueous ethanol gave the octalol (VIb) in 43% yield, b.p. 107–110° (5 mm.).

The octalol formed a *p*-nitrobenzoate, m.p. 69.5–70.5°.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.52; H, 6.71; N, 4.45.

4,4-Dimethyl-$\Delta^{5(10)}$-octalone-3 (IXa). Methylation of Δ^4-octalone-3 with methyl iodide in the presence of potassium *t*-butoxide as in the preparation of IXb gave IXa (40%), b.p. 116–121° (10 mm.), m.p. approximately 0–10°.

The octalone formed a 2,4-dinitrophenylhydrazone, m.p. 109–111°.

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.56; H, 6.29; N, 15.93.

4,4,9-Trimethyl-$\Delta^{5(10)}$-octalone-3 (IXb).[20]

4,4-Dimethyl-$\Delta^{5(10)}$-octalol-3 (VIc). Reduction of 4,4-dimethyl-$\Delta^{5(10)}$-octalone-3 with lithium aluminum hydride gave VIc (67%), b.p. 99–102 (2 mm.).

After 48 hr. the material solidified, and crystallization from petroleum ether gave a waxy alcohol, m.p. 80–85°.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.00; H, 11.31.

Chromatography of the alcohol on alumina gave crystalline alcohol (eluted with 35:15 benzene-petroleum ether), m.p. 86–88°. The infrared spectrum of VIc indicated the presence of a vinyl hydrogen, confirming the trisubstituted nature of the double bond.

The alcohol formed a phenylurethane, m.p. 149–151°.

Anal. Calcd. for $C_{19}H_{25}NO_2$: C, 76.22; 8.42; N, 4.68. Found: C, 76.10; H, 8.45; N, 4.92.

4,4,9-Trimethyl-$\Delta^{5(10)}$-octalol-3 (VId). Reduction of 4,4,9-timethyl-Δ^5-octalone-3 with lithium aluminum hydride gave a highly viscous alcohol (95%) which solidified within 24 hr., and was then crystallized from petroleum ether to yield fluffy white crystals of VId (56%); analytical sample m.p. 80–81.5°.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: 80.55; H, 11.66.

The alcohol formed a phenylurethane, m.p. 127–128.5°.

(17) W. J. A. VandenHeuvel, R. M. Moriarty, and E. S. Wallis (paper *in press*).

(18) Melting points (capillary) and boiling points are uncorrected. Analyses were performed by G. Robertson, Florham Park, N. J., and Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(19) This ester proved to be unstable, and decomposed within hours of preparation.

(20) M. Yanagita, M. Hirskura, and F. Seki, *J. Org. Chem.*, **23**, 841 (1958).

Anal. Calcd. for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 76.45; H, 8.77; N, 4.39.

9-Methyl-Δ^4-octalol-3 (X). 9-Methyl-Δ^4-octalone-3 was reduced with lithium aluminum hydride to give X (88%), b.p. 105–108° (2.5 mm.).

The octalol formed a *p*-nitrobenzoate, m.p. 78–79°; mixed m.p. with *p*-nitrobenzoate of 9-methyl-$\Delta^{5(10)}$-octalol-3, 54–60°.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.29; H, 6.82; N, 4.48.

Reduction of $\Delta^{5(10)}$-octalol-3. A solution of 2.5 g. of $\Delta^{5(10)}$-octalol-3 in glacial acetic acid was subjected to reduction on platinum oxide (24 hr. at room temperature) following the method for the reduction of cholesterol.[13] Workup gave unsaturated alcohol and 0.87 g. of white crystals which upon recrystallization from petroleum ether gave 0.64 g. of *trans*-2-decalol, m.p. 71–72°; mixed m.p. with authentic *trans*-2-decalol (of m.p. 74–75°)[21] 73.5–75°. The infrared spectra were identical.

trans-2-Decalol (XIa). *trans*-2-Decalone was reduced with lithium aluminum hydride to give (46%), m.p. 68–71°.

Lithium in liquid ammonia reduction of Δ^4-octalone-3.[15,16] VIIa was reduced as previously described. Workup gave 52% (based on starting ketone) of a mixture containing ketone (conjugated and unconjugated) and alcohol. The mixture was chromatographed on alumina; early elution with petroleum ether benzene gave 21% of saturated ketone. Elution with benzene ether yielded conjugated ketone. Finally, ether elution gave 43% of *trans*-2-decalol; recrystallization from petroleum ether yielded m.p. 68–70°.

Reduction of 9-methyl-Δ^5-octalol-3. A solution of 2.67 g. of VIb in glacial acetic acid was subjected to reduction on platinum oxide. Workup gave unsaturated alcohol and 0.89 g. of a semicrystalline alcohol which by infrared was shown to be *cis*-10-methyl-2-*trans*-decalol. The alcohol formed a 3,5-dinitrobenzoate, m.p. 102–105°; mixed m.p. with the 3,5-dinitrobenzoate of known alcohol (m.p. 108–109°) 106°–108°. The infrared spectra of the two esters were identical.

cis-10-Methyl-2-trans-decalol (XIb). 10-Methyl-2-*trans*-decalone was reduced with lithium aluminum hydride to give the alcohol (34%), m.p. 67–70° from petroleum ether. Further recrystallization gave m.p. 69–70° (reported 69–70°).[14c] Mixed m.p. with *trans*-2-decalol, 47–49°.

The alcohol formed a 3,5-dinitrobenzoate, m.p. 108–109° (reported 110–111°).[14c]

Lithium in liquid ammonia reduction of 9-methyl-Δ^4-octalone-3. VIIb was reduced and treated as previously described in the reduction of VIIa. Chromatography of the product gave 10-methyl-2-*trans*-decalone (37%), starting ketone, and *cis*-10-methyl-2-*trans*-decalol (23%).

$\Delta^{5(10)}$-Octalyl-3 p-toluenesulfonate (XII). A solution of 1.30 g. of $\Delta^{5(10)}$-octalol-3, 3.20 g. of *p*-toluenesulfonyl chloride and 20 ml. of pyridine was allowed to stand overnight at 5°. The solution was then poured into ice water, stirred for 15 minutes, and extracted with ether. The organic solution was washed successively with cold 6*N* hydrochloric acid and water, dried over sodium sulfate–potassium carbonate and filtered. Removal of ether yielded a viscous pale yellow oil which was dissolved in a minimum amount of petroleum ether and treated with decolorizing charcoal. Filtration gave a colorless solution which when chilled afforded an oil which could not be crystallized. The solution was therefore chilled to −75° at which point the *p*-toluenesulfonate separated as a glass; the mixture was centrifuged and the supernatent liquid poured away from the product (50%). This and other *p*-toluenesulfonates prepared had a characteristic doublet at 8.44 and 8.51 μ (infrared).

Anal. Calcd. for $C_{17}H_{22}O_3S$: C, 66.63 H, 7.24; S, 10.46. Found: C, 65.82; H, 7.24; S, 11.02.

9-Methyl-Δ^5-octalyl-3 p-toluenesulfonate (XIII). 9-Methyl-$\Delta^{5(10)}$-octalol-3 was allowed to react with *p*-toluenesulfonyl chloride in pyridine to give the non-crystalline *p*-toluenesulfonate XIII (48%).

Anal. Calcd. for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55; S, 10.01. Found: C, 66.96; H, 7.67; S, 9.58.

4,4-Dimethyl-$\Delta^{5(10)}$-octalyl-3-p-toluenesulfonate (XIV). 4,4-Dimethyl-$\Delta^{5(10)}$-octalol-3 was allowed to react with *p*-toluene sulfonyl chloride in pyridine to give the white crystalline *p*-toluenesulfonate XIV (56%), m.p. 70.5–71.5°.

Anal. Calcd. for $C_{19}H_{26}O_3S$: S, 9.57. Found: S, 9.24.

4,4,9-Trimethyl-$\Delta^{5(10)}$-octalyl-3 p-toluenesulfonate (XV). 4,4,-9-Trimethyl-Δ^5-octalol-3 was allowed to react with *p*-toluenesulfonyl chloride in pyridine to give the white crystalline *p*-toluenesulfonate XV (62%), m.p. 70.2–70.8°; mixed m.p. with 4,4-dimethyl-$\Delta^{5(10)}$-octalyl-3 *p*-toluenesulfonate, 62–64°.

Anal. Calcd. for $C_{20}H_{28}O_3S$: C, 68.94; H, 8.10; S, 9.18. Found: C, 68.80; H, 8.34; S, 8.98.

trans-2-Decalyl p-toluenesulfonate (XVI). *trans*-2-Decalol was allowed to react with *p*-toluenesulfonyl chloride in pyridine to give *trans*-2-decalyl *p*-toluenesulfonate (56%), m.p. 60–61°; reported 62.5–63°.[22]

cis-10-Methyl-2-trans-decalyl p-toluenesulfonate (XVII). *cis*-10-Methyl-2-*trans* decalol was allowed to react with *p*-toluenesulfonyl chloride in pyridine to give the white crystalline *p*-toluenesulfonate (45%), m.p. 55–56°.

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.06; H, 8.13; S, 9.93. Found: C, 67.20; H, 8.12; S, 10.20.

Treatment of the alcohols with manganese dioxide. A mixture of 1.0 g. of alcohol, 5.0 g. of manganese dioxide, and 25 ml. of chloroform was stirred at room temperature. The progress of any reaction was followed by removal of an aliquot portion from the mixture at a given time, filtration to remove the solid material, and evaporation of some of the solvent to yield a sample suitable for infrared analysis.

Infrared investigation for possible intramolecular hydrogen bonding.[23] Approximately 0.0001 mole of the alcohol was dissolved in 10 ml. of spectral grade carbon tetrachloride (dried over phosphorus pentoxide). A sample of the solution was placed in a 1-cm. quartz cuvette (solvent blank run in parallel) and the sample subjected to high resolution infrared spectroscopy with a Perkin-Elmer Model 21 double-beam spectrophotometer equipped with lithium fluoride optics. The curve was taken from 2.6 to 3.0 μ. A 5-ml. portion of the sample was then diluted with solvent to 10 ml., and the more dilute sample was subjected to the infrared analysis.

Determination of rates of hydrolysis. The rates of hydrolysis were determined by titration of aliquots (in sealed ampoules immersed in constant temperature oil baths) of the approximately $1 \times 10^{-2}M$ ester solutions with standard base after appropriate time intervals.

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(21) Known alcohol, compliments of Prof. R. K. Hill.

(22) I. Moritani, S. Nishida, and M. Murakami, *J. Am. Chem. Soc.*, **81**, 3420 (1959).

(23) The assistance of Prof. P. v. R. Schleyer is gratefully acknowledged.