positive Cotton effects at 442 and 293 mμ and a negative Cotton effect at 323 mμ.

Anal. Calcd for $C_{17}H_{14}O_4S_3$: C, 53.94; H, 3.72. Found: C, 54.0; H, 3.81.

Registry No.—**7**, 24099-29-4; **9**, 24099-3-7; **11**, 24099-31-8; **16**, 24099-32-9; **17**, 3173-02-2; **18**, 2643-85-5; **20**, 24099-34-1; **21**, 24099-35-2.

Acknowledgments.—The author is indebted to Dr. T. R. Govindachari for a comparison sample of pimpinellin, to Jim Steward for the ORD results, and to Austin Griffiths, Jr., for identification of the plant material. This work was supported, in part, by an NSF Institutional Grant to San Francisco State College.

Solvolyses of A-Norcholesteryl *p*-Toluenesulfonate Derivatives. III[1,2]

ROBERT M. MORIARTY[3] AND K. BHAMIDIPATY

Department of Chemistry, The Catholic University of America, Washington, D. C. 20017

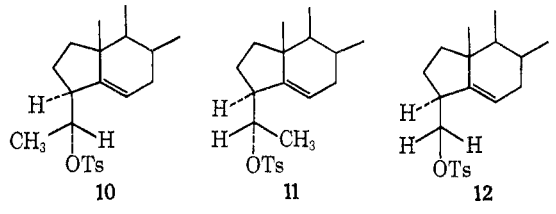
Received September 8, 1969

The syntheses and solvolyses of 3β-(1β-hydroxyethyl)-Δ⁵-A-norcholestenyl (**10**) and 3β-(1α-hydroxyethyl)-Δ⁵-A-norcholestenyl (**11**) *p*-toluenesulfonates are reported. The products of solvolysis in each case were similar to those formed in the solvolyses of the related ring-expanded cholesteryl derivatives, namely, 4β-methylcholesteryl (**7**) and 4α-methylcholesteryl (**4**) *p*-toluenesulfonates, respectively. The interrelationships among the various cationic intermediates in these solvolyses are discussed.

Experiments directed toward defining the structures of intermediary ions in the solvolyses of cholesteryl systems with methyl substituents in the A ring has led to a number of interesting results. The examples[4-8] shown in Scheme I summarize some of these findings.

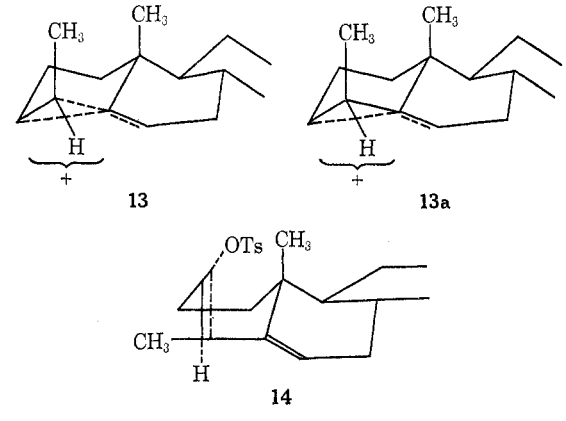
As can be seen, the configuration of the C_4 methyl group in **4** and **7** is extremely important with respect to the products of solvolysis. In the case of the 4α and equatorial orientation present in **4**, the outcome of the reaction is similar to tht observed in the unsubstituted cholesteryl system. The 4β and axial orientation of the methyl group in **7** caused the reaction to take a significantly different course, yielding the conjugated diene Δ³,⁵-4-methylcholestadiene (**8**) as the predominant product. A difference in the geometry of the A ring of **4** and **7** has been offered as an explanation for this divergent behavior.[5,6,8] Thus, the A ring of **4** is considered to exist in a chair form, while the A ring of **7**, in order to relieve the 1,3-diaxial methyl interaction, adopts either a flattened chair conformation[5,6] or a boat form.[8] These shapes should persist in the transition state. In the latter, the favorable geometry for elimination of *p*-TsOH is present, and this is obviously a very favored process. This process does not involve a homoallylic ion. The rate acceleration in solvolysis (*ca.* 200:1) for **7** compared with its saturated analog, 4β-methylcholestanyl *p*-toluenesulfonate,[6] could be due to both steric driving force and the stability of the transition state leading to the conjugated diene. On the other hand, some evidence was found to indicate that diene **8** was not a primary reaction product but rather resulted from a secondary reaction involving a highly reactive precursor.[6]

It was felt that a potential clarification of this point might be achieved from the solvolytic behavior of the A-ring-contracted compounds **10** and **11**. Whitham[9]



showed that **12** yielded the same products upon solvolysis as cholesteryl *p*-toluenesulfonate except that no hydrocarbon was formed, in contrast to the 1–2% obtained with cholesteryl toluenesulfonate. This result indicated the intermediacy of a common homoallylic ion resulting from each precursor *i.e.*, cholesteryl or A-nor-Δ⁵-cholestenyl.

The key point in the solvolyses of **10** and **11** would be whether **10** yields diene **8** upon solvolysis in amounts similar to that obtained starting from **7**. This would indicate a common intermediate. Furthermore, it is very unlikely that diene can come directly from either the symmetrical homoallylic ion **13**, or the unsym-



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project under Grant 1347-A4.

(2) For part II see R. M. de Sousa and R. M. Moriarty, *J. Org. Chem.*, **30**, 1509 (1965).

(3) University of Illinois, Chicago Circle Campus, Chicago, Ill.

(4) (a) R. M. Moriarty and E. S. Wallis, *J. Org. Chem.*, **24**, 1274, 1987 (1959); (b) Y. M. Y. Haddad and G. H. R. Summers, *J. Chem. Soc.*, 769 (1959); (c) G. Just, S. Winstein, R. Sneen, F. Shortland, and D. N. Gupta, unpublished results; see D. N. Gupta, G. Schilling, and G. Just, *Can. J. Chem.*, **43**, 792 (1965).

(5) R. M. Moriarty and R. M. de Sousa, *J. Org. Chem.*, **28**, 3072 (1963).

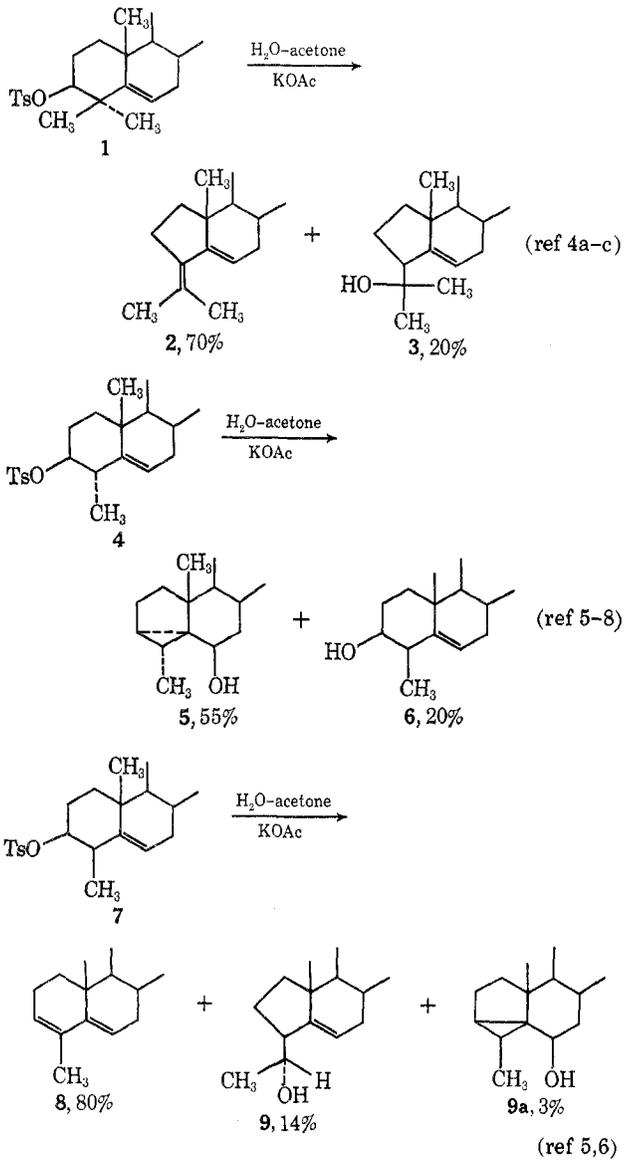
(6) R. M. de Sousa and R. M. Moriarty, *ibid.*, **30**, 1509 (1965).

(7) S. Julia, J.-P. Lavaux, S. R. Pathak, and G. H. Whitham, *C. R. Acad. Sci. Paris*, **256**, 1537 (1963).

(8) S. Julia, J.-P. Lavauax, S. R. Pathak, and G. H. Whitham, *J. Chem. Soc.*, 2633 (1964).

(9) G. H. Whitham and J. A. F. Wickramasinghe, *ibid.*, 1655 (1964)

SCHEME I



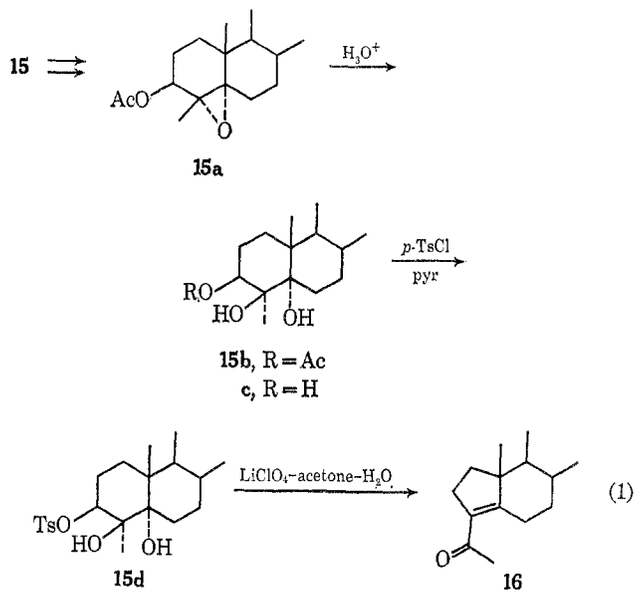
metrical ion **13a**, or that **10** would rearrange to a structure such as **14**, which has been proposed in order to explain the direct formation of diene **8** from **7**.[8] Structure **14** represents the transition state for E2 elimination of TsOH.

Solvolysis of **11** is of interest because it bears the same configurational relationship to **4** as **10** does to **7**. Comparison of the results of solvolysis of **10** and **11** offers a stringent test of the configurational integrity of intermediary ions in this series.

Results and Discussion

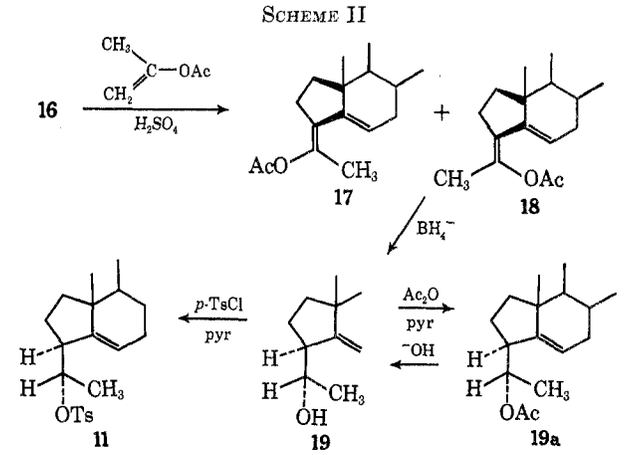
The alcohol precursor of tosylate **10**, namely ring-contracted alcohol **9**, was already available from the hydrolysis of **7**.[5,8] The synthesis of **11** proceeded from 4-methylcholestenone (**15**) using the method of Julia, Whitham, *et al.*,[8] to yield the A-ring-contracted conjugated ketone **16**. Alternatively **16** could be prepared as shown in eq 1.

Enolacetylation of **16** yielded a noncrystalline product which showed two vinyl methyl resonances possibly indicative of two stereoisomers **17** and **18** (Scheme II).



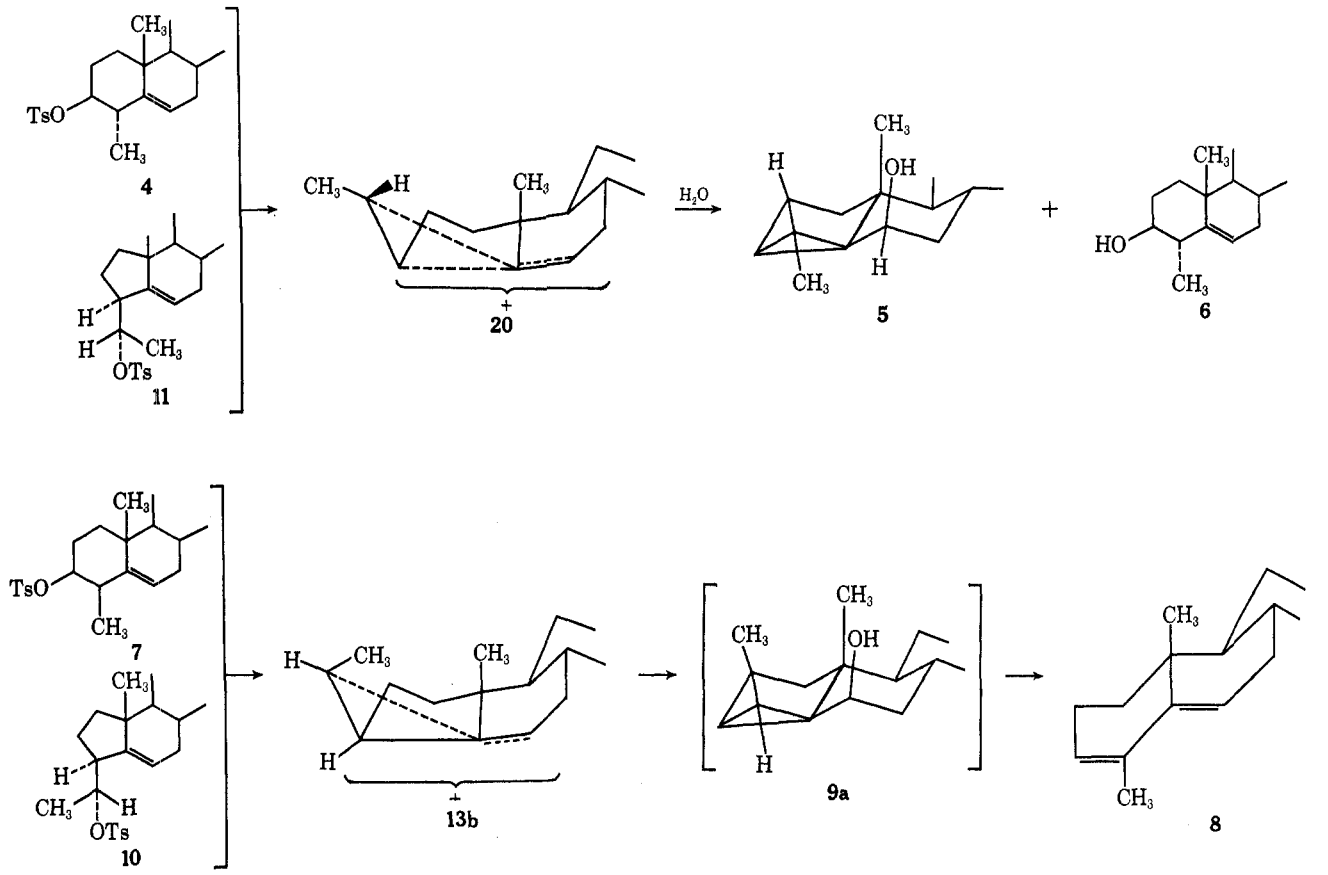
Borohydride reduction of a mixture of **17** and **18** to yield **19** requires comment since two new stereochemical centers are established, namely, at C_3 and at the carbon bearing the hydroxyl group. The initial step is probably hydrolysis of the enol acetate to yield 3-acetyl-A-nor-Δ^5-cholestene which is reduced more rapidly by borohydride than the prototropic shift to yield the conjugated ketone. The most favored mode of protonation of the enol at C_3 is from the α side.[9] Inspection of molecular models reveals that a significant steric difference exists for the carbonyl group once it is formed in the ketonization step. Thus reduction from the least hindered side, that is, away from the C_{19} angular methyl group, would lead expectedly to a predominance of 3β-(1α-hydroxyethyl)-Δ^5-A-norcholestene (**19**), and this is found to be the case. Tosylation under the usual conditions proceeds normally to yield a crystalline tosylate ester (**11**).

SCHEME II



As mentioned earlier, the epimeric ring-contracted alcohol **9** is obtained by hydrolysis of tosylate **7**. A potentially important observation was forthcoming in the attempted tosylation of **9**. Under the standard conditions, namely, *p*-toluenesulfonyl chloride in pyridine, the only product obtained was 4-methyl-$\Delta^{3,5}$-cholestadiene (**8**). In fact, attempted acetylation of **9** using acetic anhydride–pyridine at room temperature

SCHEME III



also yielded 4-methyl-$\Delta^{3,5}$-cholestadiene (**8**) as the predominant product. Furthermore, acid-catalyzed treatment yielded the diene.

In another experiment **9** and 1 equiv of *p*-toluenesulfonyl chloride were allowed to stand at room temperature for 5 hr in pyridine solution. Aqueous acetone (60%) and 3 equiv of sodium acetate were added, and the reaction system was kept at reflux overnight. An 85% yield of **8** was obtained.

Solvolysis of 3β-(1α-hydroxyethyl)-Δ^5-A-norcholestenyl tosylate (**11**) under buffered conditions yielded the same products as were obtained in the solvolysis of 4α-methylcholesteryl tosylate (**4**), namely, 4α-methyl-3α,5-cyclocholestan-6β-ol (**5**) (80%) and about 4% 4α-methylcholesterol (**4a**). Scheme III summarizes the reaction pathways for **10** and **11**.

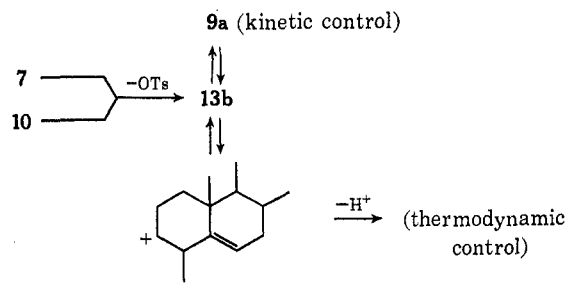
The fact that **11**, upon hydrolysis yields **5**, may be taken as indicating the incursion of the symmetrical ion **20**. Coordination with solvent occurs at C_6. This is a result completely analogous with the finding of Whitham[9] in the solvolysis of **12**.

We interpret the behavior of **10** to indicate that ion **13b** forms initially, and this ion may yield *i*-steroid **9a**, but this product is unstable. Under the reaction conditions it is converted to the product of thermodynamic control, namely **8**. The decreased stability of **13b** and the related *i*-steroid **9a** is due to the C_4–C_{10} dimethyl interaction as well as the C_6 axial hydroxyl group interaction in *i*-steroid **9a**. According to this hypothesis **9a** is the product of kinetic control.

Furthermore, it appears unlikely that diene **8** results directly from elimination of *p*-TsOH from **7** in the manner suggested by Whitham, *et al.*[9] Rather, we interpret diene **8** as coming from ion **13b** and *i*-steroid **9a**. This agrees with our earlier proposal that *i*-steroid **9a** → **8** under the buffered solvolytic conditions. The hypothesis that diene **8** derives from direct elimination of *p*-toluenesulfonic acid from the A-ring boat form **7** is rendered unlikely by the observation that only 1% diene is obtained in the solvolysis of 2,2-dimethylcholesteryl mesylate.[10] Thus if the boat form is favored in **7** owing to relief of the C_4–C_{10} dimethyl interaction, the same should apply to 2,2-dimethylcholesteryl mesylate.

The mechanism for conversion of **10** to **8** probably involves the intervention of the classical homoallylic ion. Both **7** and **10** yield the same nonclassical intermediary ion (**13b**). A small energy barrier separating the nonclassical and classical ion in this series suggests a reasonable route to diene **8** *via* deprotonation from the classical 4β-methylcholesteryl cation. Scheme IV summarizes this behavior.

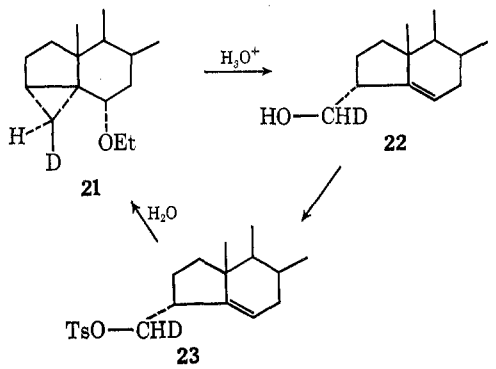
SCHEME IV



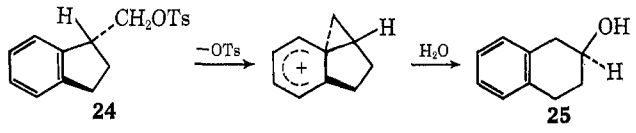
(10) S. R. Pathak and G. H. Whitham, *J. Chem. Soc.*, 193 (1968).

Finally a result found by Just, *et al.*,[11] in the 3α-A-norcholesteryl system is in complete agreement with the main ideas outlined above.

Acid-catalyzed treatment of the photolysis product **21** yields the ring-contracted alcohol **22** which upon tosylation and solvolysis regenerates **21** with retention of configuration of the deuterium.



The optical integrity of such a rearrangement has been demonstrated in the indanyl series for the conversion of (*R*)-1-indanylmethyl tosylate (**24**) to (*R*)-tetrahydro-α-naphthol (**25**) with 80% stereospecificity.[12]



Experimental Section[13]

4α-Methylcholestane-3β,4β,5α-triol 3-Acetate (15b).—To a solution of 1.65 g of **15a** in 500 ml of acetone was added a solution of 3.2 ml of 2 *N* sulfuric acid in 40 ml of water. The resulting solution was allowed to stand at room temperature for 5 days. At the end of this time the acetone was removed *in vacuo* and water was added. The reaction mixture was extracted thoroughly with ether, and the combined ether extracts were washed washed with a saturated solution of sodium bicarbonate. After drying with magnesium sulfate, the extracts were concentrated to dryness to yield a crystalline residue of 1.96 g which was recrystallized from acetone to yield 1.76 g, mp 213–216°. Recrystallization from acetone yielded 1.63 g, mp 218–220°. The analytical sample was prepared by recrystallization from acetone and had mp 218–220°.

Anal. Calcd for $C_{30}H_{52}O_4$: C, 75.60; H, 11.00. Found: C, 75.40; H, 10.91.

4α-Methylcholestane-3β,4β,5α-triol (15c).—**15b**, 1.051 g, was dissolved in 500 ml of methanol. In one portion 1.00 g of potassiumhydroxide was added and the reaction mixture was kept at reflux for 4 hr. The volume was then concentrated *in vacuo* to 50 ml and diluted with water. The solution was extracted seven times with 50-ml portions of ether. The combined extracts were washed with water and concentrated *in vacuo* to dryness. The crude product was crystallized from ether–methanol to yield 747 mg, mp 203–205° (lit.[14] 202°).

4α-Methylcholestane-3β,4β,5α-triol 3-*p*-Toluenesulfonate (15d).—The above triol (1.0 g) was dissolved in 5 ml of purified pyridine by gentle warming. The solution was cooled to 20° and 1.0 g of *p*-toluenesulfonyl chloride was added. The resulting solution solidified to a crystalline mass. After 12 hr at room temperature ice was added, and the crystalline mass was collected, washed thoroughly with water, and dried *in vacuo* to yield 1.2 g, mp 138–140°. Recrystallization from acetone yielded 900 mg of **18**, mp 141–142°. The analytical sample was prepared by recrystallization from acetone, mp 144–145°.

Anal. Calcd for $C_{35}H_{56}O_5S$: C, 71.38; H, 9.58. Found: C, 71.07; H, 9.73.

3-Acetyl-Δ⁵-A-norcholestene (16) by Solvolysis of 15c.—Lithium perchlorate, 1.116 g, and dry calcium carbonate, 1.25 g, in 30 ml of tetrahydrofuran were stirred at room temperature. A solution of 720 mg of **15c** in 10 ml of tetrahydrofuran was added dropwise over a period of 1 hr. The reaction mixture was stirred under nitrogen for 1 hr, then kept at reflux for 72 hr. After cooling, ether was added and the solution was filtered from the insoluble part. The ether–tetrahydrofuran solution was washed with a saturated solution of sodium bicarbonate. The ether–tetrahydrofuran solution was dried with magnesium sulfate and concentrated to dryness to yield a clear viscous gum, 610 mg, which was crystallized by trituration with cold acetone. Recrystallization from acetone yielded 430 mg of **16**: mp 97–99°, $[\alpha]_D$ +83° (*c*, 1), λ_{max}^{EtOH} 257 mμ (ε 13,000); lit.[8] mp 97–99°, λ_{max}^{EtOH} 257 mμ (ε 13,000).

Enol Acetylation of 3-Acetyl-Δ⁵-A-norcholestene (16).—Ketone **16**, 1.148 g, was dissolved in 80 ml of freshly distilled isopropenyl acetate, and 2 drops of concentrated sulfuric acid were added. The solution was kept at reflux for 20 hr. The isopropenyl acetate was then removed *in vacuo*. Water was added, and extraction with ether (six 30-ml portions) was carried out. The combined extracts were then washed with a saturated solution of sodium bicarbonate followed by water. The ether extracts were dried and concentrated *in vacuo* to dryness. The resulting semicrystalline mass, 1.505 g, showed in the infrared (CCl_4) 1750 (C=O) and 1675 (C=C) cm^{-1}. The nmr (TMS, CCl_4) showed CH_3CO at 2.08 and 2.17 ppm possibly corresponding to *cis* and *trans* stereoisomers of the isopropenyl part (**17** and **18**).

Sodium Borohydride Reduction of Enol Acetates 17 and 18.—The crude enol acetate, 539 mg dissolved in 20 ml of 95% ethanol, was added dropwise to a stirred solution of 1.5 g of sodium borohydride in 30 ml of 95% ethanol at 0° over a period of 2 hr. The reaction was allowed to come to room temperature and was stirred for an additional 50 hr. At the end of this time excess borohydride was decomposed by addition of glacial acetic acid. Most of the ethanol was removed *in vacuo*, and 10 ml of 6 *N* hydrochloric acid was added. After thorough extraction with ether the combined ether extracts were washed with a saturated solution of sodium bicarbonate followed by water. The extracts were dried and concentrated to dryness *in vacuo* to yield 502 mg of crystalline product. This product was acetylated in the usual way, and the crude gummy acetate was chromatographed upon 30 g of silica gel. Elution with petroleum ether gave a hydrocarbon product, 60 mg, mp 57–59°. This was shown to be homogeneous by tlc on silica gel (10% benzene–petroleum ether). Further elution with 10% benzene–petroleum ether gave 340 mg, mp 85–86°. This acetate was recrystallized from acetone to yield 290 mg of **19a**: mp 104–106°; $\lambda_{max}^{CCl_4}$ 1730 (C=O) cm^{-1}; nmr (TMS, CCl_4) 2.00 (CH_3CO) and 5.40 (C=CH) ppm; $[\alpha]_D$ −28 (*c* 1). The analytical sample was prepared by recrystallization from acetone and had mp 105–106°.

Anal. Calcd for $C_{30}H_{50}O_2$: C, 81.49; H, 11.38. Found: C, 81.49; H, 11.11.

3β-(1α-Hydroxyethyl)-Δ⁵-A-norcholestene (19).—A solution of 255 mg of acetate **19a** in 270 ml of methanol containing 10 ml of water and 2.688 g of potassium carbonate was kept at reflux for 7 hr, then left at room temperature overnight. Most of the methanol was removed *in vacuo*, and the product was crystallized out upon addition of water. It was filtered and recrystallized from acetone to yield 176 mg, mp 88–90°. Recrystallization from acetone gave a sample, mp 99–100°, $[\alpha]_D$ −38° (*c* 1.2).

Anal. Calcd for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 83.88; H, 11.81.

Chromium Trioxide–Pyridine Oxidation of 19.—The required complex was prepared by addition of 200 mg of chromium trioxide to 1.50 ml of pyridine. To this was added a solution of 50 mg of **19** in 0.50 ml of pyridine. The reaction mixture was allowed to stand at room temperature overnight. At the end of this time ice was added followed by water. Then the solution was extracted seven times with chloroform. The chloroform extracts were washed twice with water, dried, and concentrated to dryness *in vacuo*. The resulting gum was dried under high vacuum (0.001 mm) for 6 hr. Crystallization from acetone yielded 20 mg of 3β-acetyl-Δ⁵-A-norcholestene, mp 73–73° (lit.[8]

(11) G. Bauslaugh, G. Just, and E. Lee Ruff, *Can. J. Chem.*, **44**, 2837 (1966).

(12) D. Battail Robert and D. Gagnaire, *Bull. Soc. Chim. Fr.*, 208 (1966).

(13) Melting points were determined using a Kofler hot stage. Rotations were measured using chloroform solutions. Microanalyses were performed by G. I. Robertson, Florham Park, N. J. Nuclear magnetic resonance spectra were determined using a Varian A-60A.

(14) S. Julia and J-P Lavaux, *Bull. Soc. Chim. Fr.*, 1231 (1963).

73.5–75°). Warming of an ethanolic solution of 3β-acetyl-Δ⁵-A-norcholestene containing potassium hydroxide led to the development of the conjugated ketone chromophore present in 3β-acetyl-Δ⁵-A-norcholestene (**16**).

3β-(1α-Hydroxyethyl)-Δ⁵-A-norcholestene *p*-Toluenesulfonate (11).—To a solution of 600 mg of **19** in 5 ml of dry pyridine was added 600 mg of *p*-toluenesulfonyl chloride. The reaction solution was kept at room temperature for 18 hr. At the end of this time crushed ice was added, and the resulting mixture was extracted with ether. The combined ether extracts were washed in turn with a saturated solution of sodium bicarbonate, then water, and finally dilute hydrochloric acid. The dried extracts were concentrated to dryness *in vacuo* to yield 560 mg of crude tosylate. Repeated recrystallization from acetone yielded 320 mg, mp 86–89°. The infrared spectrum of this compound showed absorption characteristic of the *p*-toluenesulfonate ester at 8.43 and 8.50 μ. The nmr spectrum (TMS, CCl_4) showed an aromatic quartet at 7.23, 7.38, 7.70, and 7.85 ppm, aromatic CH_3 at 2.43 ppm, and vinyl proton at 5.30 ppm.

Anal. Calcd for $C_{35}H_{54}SO_3$: C, 75.73; H, 9.79. Found: C, 75.76; H, 9.69.

Solvolysis of 3β-(1α-Hydroxyethyl)-Δ⁵-A-norcholestenyl *p*-Toluenesulfonate (11).—A solution of 176 mg of **11** in 25 ml of acetone was kept at reflux for 10 hr. At the end of this period the acetone was removed *in vacuo*, and the resulting aqueous solution was extracted thoroughly with ether. The ether extracts were washed with water, dried, and concentrated to dryness *in vacuo* to yield 184 mg of an oil. The crude solvolysis product was chromatographed upon 10 g of Merck neutral alumina. Elution with pentane yielded 19.5 mg of an oil which showed four spots upon tlc. No pure compound could be isolated. Further elution with benzene yielded 59.5 mg, mp 85–91°. Recrystallization from acetone gave 46 mg, mp 95–97°, of 4α-methyl-3α,5-cyclocholestan-6β-ol (**5**). Repeated recrystallization from acetone raised the melting point to 102–103°. This was undepressed upon mixture melting point determination with an authentic sample[5] of melting point 101–103°. Further elution with chloroform yielded 6 mg of 4α-methylcholesterol (**6**), mp 164–165°. The melting point was undepressed upon admixture with an authentic sample.

Attempted Formation of 3β-(1β-Hydroxyethyl)-Δ⁵-A-norcholestenyl *p*-Toluenesulfonate (10).—The alcohol (100 mg, mp 114–117°) was dissolved in pyridine (1 ml), and 100 mg of *p*-toluenesulfonyl chloride was added at room temperature. After standing at room temperature for 12 hr, ice was added and the solution was extracted with ether. The ether extracts were washed with water, saturated bicarbonate solution, dilute hydrochloric acid solution, and finally with water. The dried extracts were concentrated to dryness to yield an oil which was crystallized from acetone to yield 46 mg, mp 73–74°. The properties of this material were identical with those of 4-methyl-Δ^{3,5}-cholestadiene (**8**).

Registry No.—**11**, 24343-84-8; **15b**, 1258-92-0; **15c**, 24298-81-5; **16**, 24298-82-6; **17**, 24298-83-7; **18**, 24298-84-8; **19**, 24298-85-9; **19a**, 24298-86-0.

Syntheses of Methyl Malvalate and Methyl 5,6-Methano-5-undecenoate

WALTER J. GENSLER, KENNETH W. POBER, DANIEL M. SOLOMON, AND M. BRAWNER FLOYD

Department of Chemistry, Boston University, Boston, Massachusetts 02215

Received December 19, 1969

Malvalic acid, the major cyclopropene component in cottonseed oil, has been synthesized. When 1-chloro-7-hexadecyne reacts with diazoacetic ester in the presence of copper–bronze, the ester of 1-chloro-7,8-carboxymethano-7-hexadecene is formed. Treating the corresponding acid chloride with zinc chloride causes loss of carbon monoxide. Either sodium borohydride or lithium aluminum hydride reduces the resulting cyclopropenium compound to 1-chloro-7,8-methano-7-hexadecene. Replacing the chloro group with cyano yields malvalonitrile, which can be converted to methyl malvalate. An analogous sequence of steps has been applied to 1-chloro-4-decyne to produce methyl 5,6-methano-5-undecenoate. An alternate synthesis of methyl malvalate starts by using 1-chloro-7-hexadecyne as the precursor for methyl 8-heptadecynoate. This acetylenic ester is converted to 8,9-carboxymethano-8-heptadecenoic acid, the diacid chloride of which decarbonylates selectively in the presence of metallic chlorides to form the cyclopropenium acid chloride. After esterification, the resulting cyclopropenium ester is reduced with borohydride to methyl malvalate.

Malvalic acid and its homolog, sterculic acid, together with two other closely related fatty acids[1] are the only well-characterized naturally occurring cyclopropenes.[2] Methyl sterculate has been synthesized.[3,4] The present paper reports on syntheses of methyl malvalate (**8**)[5] as well as on the synthesis of a related cyclopropene, methyl 5,6-methano-5-undecenoate.

The malvalate synthesis starts with 1-decyne (**1**), which as its lithium derivative[6] couples with 1,6-dichlorohexane to form 1-chloro-7-hexadecyne (**2**). Dropping diazoacetic ester into a hot mixture of 1-chloro-7-hexadecyne and powdered copper–bronze produced the expected cyclopropene ester, which on saponification gave 1-chloro-7,8-(carboxymethano)-7-hexadecene (**3**). Our prior concern about the involvement of the carbon-to-chlorine bond was allayed when dodecyl chloride under the same conditions could be recovered largely unchanged. The acid chloride **4** from **3**, when mixed with anhydrous zinc chloride, smoothly lost carbon monoxide to give cyclopropenium ion **5**. Sodium borohydride in alkaline methanol or, better, lithium aluminum hydride in ether[7] reduced the cyclopropenium ion to the corresponding cyclopropene, 1-chloro-7,8-methano-7-hexadecene (**6**). The methanethiol adduct[8] of this cyclopropene, formed in 98% yield, was homogeneous according to gas–liqiud chromatographic assay. Replacing the chloro group with cyano by heating with sodium cyanide in dimethyl

(1) Sterculynic acid, as reported by A. W. Jevans and C. Y. Hopkins, *Tetrahedron Lett.*, 2167 (1968), and 2-hydroxysterculic acid, as reported by L. J. Morris and S. W. Hall, *Chem. Ind.* (London), 32 (1967), and by J. A. Recourt, G. Jurriens, and M. Schmitz, *J. Chromatogr.*, **30**, 35 (1967).

(2) F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

(3) W. J. Gensler, M. B. Floyd, R. Yanase, and K. W. Pober, *J. Amer. Chem. Soc.*, **91**, 2397 (1969); **92**, 2472 (1970).

(4) M. M. Schlosser, A. J. Longo, J. W. Berry, and A. J. Deutschman, Jr., *J. Amer. Oil Chem. Soc.*, **46**, 171 (1969).

(5) The structure of methyl malvalate has been defined by J. J. Macfarlane, F. S. Shenstone, and J. R. Vickery, *Nature*, **179**, 830 (1957); B. Craven and G. A. Jeffrey, *ibid.*, **183**, 676 (1959); A. C. Fogerty, A. R. Johnson, J. A. Pearson, and F. S. Shenstone, *J. Amer. Oil Chem. Soc.*, **42**, 885 (1965).

(6) *Cf.*, H. H. Schlubach and K. Repenning, *Justus Liebigs Ann. Chem.*, **614**, 37 (1958); G. Grimmer and J. Kracht, *Chem. Ber.*, **96**, 3370 (1963).

(7) *Cf.* R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963); H. E. Nordby, Doctoral Dissertation, University of Arizona, 1963; R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965); S. D. McGregor and W. M. Jones, *ibid.*, **90**, 123 (1968).

(8) *Cf.*, H. W. Kircher, *J. Amer. Oil Chem. Soc.*, **41**, 4 (1964); P. K. Raju and R. Reiser, *Lipids*, **1**, 10 (1964); N. K. Hooper and J. H. Law, *J. Lipid Res.*, **9**, 270 (1968). A longer reaction period than that originally called for was found to be beneficial.