(s), 1460 (s), 1280 (s), 1220 (s), 1040 (s), mass spectrum, m/e 186 (M^+). Anal. Calcd for $C_9H_{11}ClO_2$: C, 57.95; H, 5.96; Cl, 18.93. Found: C, 57.95; H, 5.96; Cl, 18.93.

Tetraether 6. To a suspension of 1.06 g (0.046 mol) of sodium wire in 125 mL of anhydrous ether in a three-necked, 500-mL, round-bottomed flask equipped with a reflux condenser, mechancial stirrer, and a 125-mL pressure-equalizing addition funnel was added, under a nitrogen atmosphere, a solution of 5.0 g (0.027 mol) of 2,5-dimethoxybenzyl chloride in 100 mL of anhydrous ether. During the addition the solution was rapidly stirred and after the addition the reaction mixture was refluxed 48 h under a nitrogen atmosphere.

The suspension was then cooled to room temperature and methanol slowly added until further addition ceased to cause refluxing. This mixture was refluxed 2 h to assure decomposition and cooled, and water was added until the suspension became a colorless two-layered solution. The ether layer was separated and combined with additional ether extracts of the aqueous layer. the ethereal solution was washed twice with water, dried over sodium sulfate, and concentrated on a rotary evaporator. The solid residue was recrystallized from ether/hexane to afford 3.42 g (84%) of a white crystalline solid: mp 61–69 °C, NMR δ 2.85 (s, 4 H), 3.70 (s, 6 H), 3.75 (s, 6 H), 6.70 (s, 6 H); mass spectrum, m/e 302 (M^+). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.44; H, 7.35.

Bis Hydroquinone 7. A mixture of 100 mL of 48% hydrobromic acid, 100 mL of glacial acetic acid, and 2 g (0.0066 mol) of tetraether **6** was refluxed overnight under a nitrogen atmosphere. The solution was cooled, 250 mL water added, and the mixture extracted with several portions of ether. The combined ether layers were dried over sodium sulfate and concentrated on a rotary evaporator to provide 1.57 g (96.3%) of crude bis hydroquinone **7**. This crude material was used directly in the next reaction: NMR δ 2.80 (s, 4 H), 6.65 (m, 6 H).

[2-(1,4-Benzoquinonyl)ethyl]-1,4-benzoquinone (3). A mixture of 1.57 g of crude bis hydroquinone **7**, 150 mL of 2% H_2SO_4, 15 g (0.14 mol) of sodium chlorate, and 0.1 g of vanadium pentaoxide was warmed to 50 °C, with stirring, until the bluish black suspension of starting material changed to golden yellow. After cooling, the reaction mixture was extracted thoroughly with methylene chloride. The extract was dried over sodium sulfate, filtered through a silica gel column, and concentrated on a rotary evaporator. The golden solid thus obtained was recrystallized from methylene chloride/hexane to yield **3**: 1.07 g (67% from tetraether **6**); decomposition point 185 °C; NMR δ 2.70 (s, 4 H), 6.60 (s, 2 H), 6.80 (m, 4 H); mass spectrum, m/e 242 (M^+); IR 2980 (w), 1660 (s), 1600 (w), 1175 (s). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.41; H, 4.14. Found C, 69.30; H, 4.19.

Polarography of 3. the polarographic measurements were made with a Princeton Applied Research Model 170 electrochemistry system, using a dropping mercury electrode (DME) and a saturated calomel electrode (SCE) in a 10-mL H-type polarographic cell. The methylene chloride solution, 0.001 M in bis quinone **3** and 0.1 M in tetra-*n*-butylammonium tetrafluoroborate, was purged with nitrogen for 15 min before the run. A blank solution, consisting of 0.1 M *n*-Bu_4NBF_4 in CH_2Cl_2, was run to ensure that the waves observed were actually due to the bisquinone **3**. The half-wave potentials for this compound were found to be -0.450 and -0.830 V.

Controlled Potential Electrolysis of 3. The Princeton Applied Research Model 170 was also used for the controlled potential electrolysis. The electrolysis cell was a conventional three-electrode system: a mercury (instrument grade) pool working electrode (cathode), a saturated calomel reference electrode, and a Ag/AgCl auxiliary electrode (anode), which was separated from the solution by a fritted-glass disk. The reduction was done under a nitrogen atmosphere. The mercury pool was stirred rapidly throughout the electrolysis with a magnetic stirrer. Tetra-*n*-butylammonium tetrafluoroborate was used as the supporting electrolyte. Prior to the electrolysis the system was purged with nitrogen for approximately 20 min before the electrolysis was begun. The cell contained 1.0 g (4.132×10^{-3} mol) of bis quinone **3** dissolved in 250 mL of anhydrous methylene chloride which was 0.1 M in electrolyte. The electrolysis was started at -0.600 V vs. SCE and was complete in 4 h as indicated by a return to background levels of current. After electrolysis was complete, 2.7 g (2.648×10^{-2} mol) of acetic anhydride was added to the electrolysis cell with stirring and with no current passing through the cell. After being stirred overnight, the contents of the cell were poured into a separatory funnel. The mercury was taken off, and the methylene chloride solution was filtered and concentrated on a rotary evaporator. The residue was taken up in a minimum amount of methylene chloride, diluted with ether, and washed with water. The ether layer on being allowed to stand precipitated tetra-*n*-butylammonium tetrafluoroborate. The precipitated salt was filtered off, and the ethereal solution was dried over sodium sulfate and concentrated on a rotary evaporator. The crude material (0.6430 g) was chromatographed on Silicar CC-7 by using 25% ether/hexane. The first component (82.3 mg) was not characterized. The second component (62.6 mg) was not characterized. The third component (204.0 mg, 14%) was characterized. Spectral data are given below. The fourth component was a mixture and was identified as partially acetylated "third component" and constituted 208.3 mg.

Component three: NMR δ 2.16 (s, 3 H), 2.20 (s, 6 H), 3.30 (dd, 2 H), 5.68 (t, 1 H), 6.68, 6.92, 7.05 (m, 6 H), IR 1760 (s), 1480 (s), 1370 (s), 1170 (s), 1180 (s), 1230 (s), 1050 (m), mass spectrum, m/e 370 (M^+), 328, 281, 244, 100 (base peak). Anal. Calcd for $C_{20}H_{18}O_7$: C, 64.85; H, 4.91; O, 30.24. Found : C, 64.79; H, 4.97; O, 30.24.

Crystal Structure Determination. Single crystals of compound **8** ($C_{20}H_{18}O_7$) grown from an ether/hexane solution were used for the measurement of the X-ray diffraction data. Unit cell parameters were determined on a Syntex $P2_1$, four-circle diffractometer equipped with graphite monochromator (Bragg 2θ angle = 12.2°) by using MoKα radiation. Least-squares refinement of 15 reflections with Bragg angles ranging from 5.34° to 12.84° resulted in a = 11.094 (4) Å, b = 7.499 (4) Å, c = 23.141 (7) Å, and β = 98.70 (3°). The unit cell volume is 1903 (1) Å. The systematic absences were consistent with the space group $P2_1/a$. A total of 1911 integrated independent reflections with $4° < 2\theta < 50°$ were measured by using the 2θ–θ scan technique and found to have $I > 3\sigma(I)$. Lorentz and polarization corrections were made in the usual way, and the structure was solved by using the direct-methods procedure implemented in the SHELXTL program system (Nicolet XRD, Fremont, CA).

The positional and anisotropic thermal parameters were refined for all nonhydrogen atoms by using full-matrix least-squares analysis. The hydrogen atoms were placed in their calculated positions. The weights used were $1/\sigma^2(F) + 0.001\,F^2$, and the final reliability index R (defined as $\sum|F_o - F_c|/\sum F_o$) was 0.0741 and R_w (defined as $\sum w^{1/2}|F_o - F_c|\sum F_o w$) was 0.0735.

Registry No. **3**, 20452-50-0; **4**, 33524-31-1; **5**, 3840-27-5; **6**, 20306-76-7; **7**, 10365-14-7; **8**, 86689-90-9; 8 trihydroxy derivative, 86689-91-0.

Supplementary Material Available: A structure (Figure 1) and tables of atomic coordinates for structure **8** (3 pages). Ordering information is given on any current masthead page.

1,3 Acyl Migration to an Epoxide. Reversible Rearrangement of 5,6β-Epoxyepicholesteryl Acetate

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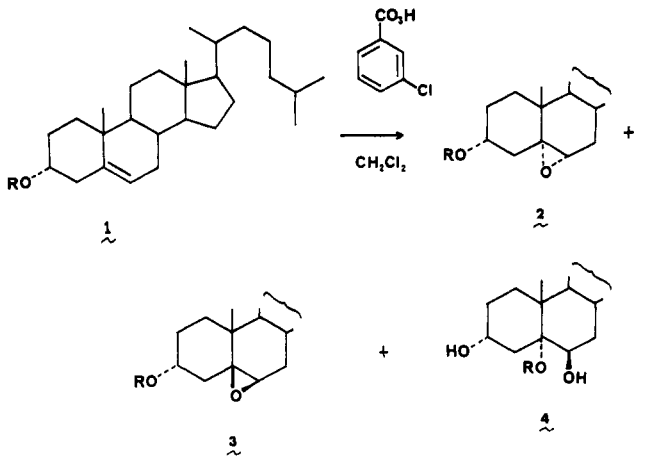
The work of Henbest in the 1950's established the directing influence of the hydroxyl function in epoxidation of allylic and homoallylic alcohols.[1] Thus epicholesterol (**1b**) reacts with peracids to give exclusively the α-epoxide

(1) Henbest, H. B.; Wilson, R. A. L. *J. Chem. Soc.* **1957**, 1958.

0022-3263/83/1948-3134$01.50/0

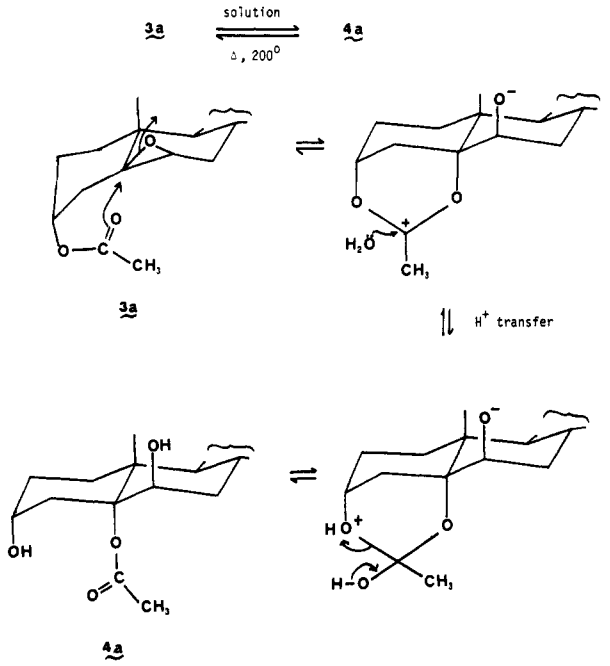
Scheme I. Reaction of Epicholesteryl Acetate (1a) with *m*-Chloroperoxybenzoic Acid[a]



1 2 3 4

[a] a, R = Ac; b, R = H.

Scheme II. Interconversions of 3a and 4a



2b (Scheme I), whereas the corresponding acetate **1a** is reported to give both α (**2a**) and β (**3a**) epoxides in the same reaction.[2]

The original report[2] of the epoxidation of **1a** noted the formation of a triol monoacetate of unspecified structure. We now report the structure of this compound as **4a**, the 5-monoacetate of cholestane-3α,5α,6β-triol. We also report its reversible formation from the β epoxide **3a** (Scheme II).

Treatment of **1a** with *m*-chloroperoxybenzoic acid gave, as the major product, the compound whose structure we now report as **4a**. Also obtained, following a hydrolytic workup, were the β-epoxy alcohol **3b** and the α-epoxy acetate **2a**. The ester function of **2a** is not hydrolyzed under conditions which cause hydrolysis of the acetate group of **3a**, presumably due to the trans A/B ring junction and the steric hindrance from the pseudoaxial epoxy oxygen at C-5α in **2a**. The structural assignment for **4a** follows principally from its ^{13}C NMR spectra and that of its reduction product **4b** (Table I). The shifts were assigned by comparison with values for similar triols and their derivatives.[3,4]

Table I. ^{13}C NMR Data of 4

carbon[a]	4a	4b
1	28.2	28.0
2	29.6	29.0
3	66.5	68.5
4	29.9	35.9
5	86.2	76.5
6	68.5	75.4
7	34.2	34.1
8	29.9	30.0
9	45.6	45.5
10	40.1	39.3
11	20.9	20.9
19	16.9	16.5

[a] Carbons 12–18 and 20–27 had chemical shifts similar shifts to those of the corresponding carbons of ring A and/or B substituted cholestanes.[3]

The chemical shifts of C-4, -5, and -6 in **4a** and **4b** are particularly diagnostic of the presence of the acetate function of **4a** at C-5. The ^1H NMR spectra of **4a** and **4b** (Experimental Section) are also consistent with the assigned structures. The upfield shift of the C-6α hydrogen on removal of the ester function from C-5 (δ 4.65–3.60 ppm) is attributed to the removal of a deshielding effect of the ester carbonyl group. This same phenomenon causes the C-4α hydrogen of **4a** to resonate at lower field (2.85 ppm) than the corresponding β-hydrogen (2.15 ppm): this difference is absent in the triol **4b**.

The rearrangement of the β-epoxide **3a** to **4a** has been carried out by using BF_3 as a catalyst;[5] the mechanism proposed for this rearrangement involves a cyclic 3α,5α-acetonium ion and thus provides a precedent for the mechanism outlined in Scheme II for the noncatalyzed rearrangement described herein. The mechanism of Scheme II requires the participation of a molecule of water.

When the epoxidation was carried out under strictly anhydrous conditions, **4a** was not detected (TLC) in the reaction mixture before the workup but was present to the extent of ca. 25% in the isolated product. When nondried solvents were used, TLC analysis indicated that **4a** was formed directly in the reaction mixture.

That **4a** can be produced from **3a** in the absence of a Lewis acid has been demonstrated by the observation that **3a** prepared by an alternative route (acetylation of the alcohol epoxide **3b**) readily converts to **4a** in solution. The reverse reaction can be brought about by heating a sample of **4a** under low-pressure above its melting point. This latter conversion presumably proceeds by intramolecular attack of the 3α-hydroxyl oxygen at the acetate carbonyl to give a 3α,5α-acetonium ion, followed by displacement from C-5 by the C-6β alcohol oxygen. The removal of water, dictated by the reaction conditions, renders the transformation irreversible in the direction **4a** to **3a**.

We therefore conclude that the triol monoacetate of Mousseron-Canet and Guilleux[2] is **4a**. The thermal conversion of **4a** to the 5,6β-epoxide **3a** provides an efficient route to the latter which avoids the complication of the intramolecular rearrangement discussed herein.

Experimental Section

Apparatus, Materials, and Methods. Melting points were determined with a Gallenkamp melting point apparatus and are

(2) Mousseron-Canet, M.; Guilleux, J.-C. *Bull. Soc. Chim. Fr.* **1966**, 3853.

(3) Blunt, J. W.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 439.

(4) Holland, H. L.; Diakow, P. R. P.; Taylor, G. J. *Can. J. Chem.* **1978**, *56*, 3121.

(5) Coxon, J. M.; Hartshorn, M. P.; Muir, C. N. *Tetrahedron* **1969**, *25*, 3925.

uncorrected. Infrared spectra were recorded with a Perkin-Elmer 237B spectrometer. Proton NMR spectra were obtained with Bruker WP-60 at 60 MHz and ^{13}C NMR spectra with a Bruker WP-60 at 15.18 MHz or a Bruker WH-400 at 100 MHz at the Southwestern Ontario NMR Centre, University of Guelph, with using $CDCl_3$ as the solvent and Me_4Si as an internal standard. Mass spectra were obtained with an AEI MS-30 spectrometer. Column chromatography was performed on silica gel (60–200 mesh) and thin-layer chromatography on Merck silica gel 60 F-254 (0.25 mm).

Epoxidation of 3α-Acetoxycholest-5-ene (1a). To a solution of **1a** [obtained by acetylation of epicholesterol (**1b**,[6] 5.0 g) in methylene chloride (200 mL)] was added *m*-chloroperoxybenzoic acid (3.0 g) in methylene chloride (50 mL) dropwise over 15 min at room temperature with constant stirring. The stirring was continued for an additional 5 h. Excess peracid was then destroyed with 5% sodium sulfite, and the reaction mixture was successively washed with water (3 × 150 mL), 5% sodium bicarbonate solution (3 × 100 mL), water (2 × 100 mL), and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated in vacuo. Crystallization from acetone–hexane afforded cholestane-3α,5α,6β-triol 5-acetate (**4a**): 1.35 g; mp 170–172 °C. Repeated crystallization from ethyl acetate–hexane afforded a sample: mp 196–197 °C (lit.[2] mp 65 °C, lit.[5] mp 181–182 °C) IR ν_{max}) 3500, 1740 cm^{-1}; ^1H NMR included signals at δ 0.66 (3 H, s, c-18 H), 1.13 (3 H, s, C-19 H), 2.0 (3 H, s, CH_3CO), 2.15 (dd, J = 4, 16 Hz), and 2.85 (d, J = 16 Hz) (AB q, C-4 H's), 4.20 (1 H, br s, C-3 H), 4.65 (1 H, br s, C-6 H); ^{13}C NMR, see Table I; MS m/z (relative intensity) 402 (M – CH_2CO, 4.5), 384 (97), 376 (22), 369 (72), 368 (12), 367 (18), 366 (40), 356 (21), 355 (16), 351 (12), 247 (26), 229 (29), 211 (34), 161 (34), 135 (69), 122 (57), 121 (63), 95 (100). Anal. Calcd for $C_{29}H_{50}O_4$: C, 75.28; H, 10.89. Found: C, 75.35; H, 10.82.

The remaining mother liquor would not be crystallized and was therefore concentrated to an oil, dissolved in methanol, and stirred with saturated methanolic sodium carbonate solution at 40 °C for 10 h. The solution was then concentrated, thoroughly extracted with methylene chloride, dried, and evaporated. The crude mixture was chromatographed, when elution with hexane–benzene gave 3α-acetoxy-5α,6α-epoxycholestane (**2a**): 0.265 g; mp 105–109 °C (from ethyl acetate–hexane) (lit.[2] mp 111–112 °C); ^1H NMR included signals at δ 0.65 (3 H, s, C-18 H), 1.10 (3 H, s, C-19 H), 2.07 (3 H, s, CH_3CO), 2.78 (1 H, d, J = 4 Hz, C-6 H), 5.12 (1 H, m, C-3 H). Anal. Calcd for $C_{29}H_{48}O_3$: C, 78.33; H, 10.88. Found: C, 78.07; H, 11.03. Also separated was 3α-hydroxy-5β,6β-epoxycholestane (**3b**): 0.79 g; mp 156–159 °C (lit.[2] mp 160–162 °C); IR (Nujol) ν_{max} 3420, 1350, 1240 cm^{-1}; ^1H NMR included signals at δ 0.64 (3 H, s, C-18 H), 1.0 (3 H, s, C-19 H), 3.10 (1 H, d, J = 4 Hz, C-6 H), 4.21 (1 H, m, C-3 H).

(6) Ishige, M.; Shiota, M. *Can. J. Chem.* **1980**, *58*, 1061.
(7) Tsui, P.; Just, G. *Can. J. Chem.* **1973**, *51*, 3502.

3α-Acetoxy-5β,6β-epoxycholestane (3a). This was prepared by acetylation of **3b**[7] using pyridine and acetic anhydride. The product was obtained as an oil; efforts to crystallize this made it less pure, a new TLC spot developing which corresponded to **4a**. Preparative TLC afforded **4a** identical with the sample obtained from the epoxidation of **1a**.

The following spectral data for **3a** were obtained on the oil: ^1H NMR included signals at δ 0.67 (3 H, s, C-18 H), 1.02 (3 H, s, C-19 H), 2.08 (3 H, s, CH_3CO), 3.03 (1 H, d, J = 3 Hz, C-6 H), 5.0–5.25 (1 H, m, C-3 H).

Conversion of 4a to 3α-Acetoxy-5β,6β-epoxycholestane (3a). The acetate **4a** (0.1 g) in a 25-mL round-bottomed flask under reduced pressure (0.1 mmHg) was melted on an oil bath maintained at 200 °C. After melting of **4a** was complete (5 min), the oil bath was removed and the flask allowed to cool. The resulting oil, following trituration with cold dry pentane, crystallized slowly at room temperature. Recrystallization from the same solvent gave a sample (0.68 g) which exhibited spectral and analytical data identical with those of **3a** obtained by acetylation of **3b**; mp 57–60 °C (lit.[5] mp 61.5–62 °C).

Conversion of 3a to 4a. The epoxide acetate **3a** (0.1 g) was dissolved in chloroform (15 mL) and left at room temperature. Evaporation of the solvent after 2 days and crystallization of the residue from ethyl acetate–hexane afforded the acetate **4a** (0.06 g), identical with a sample obtained from the epoxidation of **1a** (vide supra).

Cholestane-3α,5α,6β-triol (4b). The acetate **4a** (0.075 g) was dissolved in dry ethyl ether (30 mL), to which lithium aluminum hydride (0.050 g) in ether (25 mL) was then added dropwise under anhydrous conditions, with constant stirring, at 0 °C. The stirring was continued for an additional 4 h. Excess reagent was then distroyed by adding ethyl acetate, the precipitate dissolved in sulfuric acid solution (3 N, 20 mL), and the solution extracted with ether. The ethereal extracts were combined, washed with water, and dried over anhydrous sodium sulfate. On evaporation in vacuo, **4b** (0.05 g) was obtained: mp 198–201 °C (from acetone/hexane) (lit.[2] mp 205–206 °C); IR ($CHCl_3$ film) ν_{max} 3540 cm^{-1}; ^1H NMR included signals at δ 0.68 (3 H, s, C-18 H), 1.12 (3 H, s, C-19 H), 3.60 (1 H, m, C-6 H), 4.1–4.4 (1 H, m, C-3 H); ^{13}C NMR, see Table I; MS, m/z (relative intensity) 402 (M^+ – H_2O, 5.8), 384 (18.1), 369 (13.6), 247 (13.3), 229 (14.9), 211 (10.7), 161 (13.1), 159 (12.0), 149 (18.6), 147 (12.5), 137 (14.5), 95 (50.1), 57 (100); exact mass calcd for $C_{27}H_{46}O_2$ (M – H_2O) 402.350, obsd 402.350.

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Registry No. **1a**, 1059-85-4; **1b**, 474-77-1; **2a**, 4092-57-3; **3a**, 14456-17-8; **3b**, 24116-45-8; **4a**, 24116-59-4; **4b**, 2701-11-3.