Photolysis of 4,5-Epoxycholest-2-enes

James M. Coxon and Gregory S. C. Hii
Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

Abstract
Photolysis of 4α,5-epoxy-5α- and 4β,5-epoxy-5β-cholest-2-enes in acetone (3000-Å lamps) effects molecular rearrangement to α-nor-α-homo-5β- and -5α-cholest-2-en-6-ones respectively.

The photolysis of α,β-epoxy olefins has received relatively little attention.\(^1\) We now report the photolysis of two steroid epoxy alkenes of this type. The epoxides, 4α,5-epoxy-5α- and 4β,5-epoxy-5β-cholest-2-enes (1) and (2), were prepared by solvolysis of 4α,5-epoxy-5α-cholestan-3α-yl tosylate in collidine and 4β,5-epoxy-5β-cholestan-3β-yl tosylate by heating with Li₂CO₃-dimethylformamide respectively.\(^2\)

\[\text{hv} \quad \text{acetone} \]

(1) \hspace{1cm} (5) \hspace{1cm} (3)

(2) \hspace{1cm} (6) \hspace{1cm} (4)

The α-epoxide (1) was irradiated at 3000 Å for 10 h and gave a good yield (60%) of α-nor-α-homo-5β-cholest-2-en-6-one (3). The identity of this compound follows from the infrared carbonyl absorption at \(\nu_{\text{max}}\) 1709 cm\(^{-1}\), from the absence of a conjugated chromophore as shown by the ultraviolet spectrum, and from the p.m.r. spectrum which shows two vinyl protons and C5–H deshielded by alkene and carbonyl moieties.

The structure was further established by hydrogenation to A-nor-B-homo-5β-cholestan-6-one, a known compound.³

Irradiation of the β-epoxide (2) was less efficient and gave A-nor-B-homo-5α-cholesta-2-en-6-one (4), which proved difficult to purify and was not obtained in a crystalline form. The identity of this product follows from the carbonyl absorption in the infrared spectrum at νmax 1709 cm⁻¹, the p.m.r. spectrum which showed two olefinic protons and C5-H deshielded by the alkene and ketone groups and by conversion into the known A-nor-B-homo-5α-cholestan-6-one by hydrogenation. The ketone produced was impure, and attempts to purify it resulted in epimerization to the equilibrium mixture of 5α- and 5β-isomers. The crystalline 5β-isomer was treated with aqueous sulphuric acid in dioxan to produce an equilibrium mixture (c. 4 : 1) of 5α- and 5β-ketones. These molecular rearrangements are not without precedent and 2,5-dimethyl-4,5-epoxyhex-2-ene has been reported⁴ to give 3,5-dimethylhex-4-en-2-one. The yield of A-nor-B-homo-5β-cholesta-2-en-6-one from irradiation of 4α,5-epoxy-5α-cholesta-2-en-2-ene makes this a viable route to C240 (20). 4α,5-Epoxy-5α-cholest-2-ene makes this a viable route to C240 (20).

C 5-H led to sharpening of the signals due to the other two protons. 3.58 and 3.90 (108 mg) crystallized as needles, m.p. 83-84°, νmax 1709 cm⁻¹, 7[^3]H[3] 230 nm (ε 20), 240 (20). P.m.r. δ 0.72 (C18-H₃), 0.82 and 0.90 (side chain methyls), 1.15 (C19-H₃), 3.58 (W H/2 6 Hz, C5-H), 5.55 and 5.90 (W H/2 8 Hz, C2-H and C3-H). Double irradiation at C2-H, C3-H or C5-H led to sharpening of the signals due to the other two protons. O.r.d. (in ethanol) [Φ]_338 +1954, [Φ]_325 -2490, [Φ]_320 -3352, [Φ]_315 -4501, [Φ]_300 -5364, [Φ]_290 -4884, [Φ]_290 -2298, [Φ]_281 0, [Φ]_278 +575, [Φ]_275 +1053, [Φ]_269 +1244, [Φ]_265 +1149, [Φ]_260 +575, [Φ]_256 0 (Found: C, 84.3; H, 11.5%; M+ 384.3403. C24H40O requires C, 84.4; H, 11.5%; M+ 384.3392).

Hydrogenation of A-nor-B-homo-5β-cholesta-2-en-6-one (30 mg) was effected by agitation in a nitrogen atmosphere of a solution of the compound in pentane containing palladium on carbon (20 mg; 5%) as catalyst. Isolation of the product in the usual manner and recrystallization from methanol gave A-nor-B-homo-5β-cholestan-6-one (22 mg) as needles, m.p. 93-94°, νmax 1709 cm⁻¹. P.m.r. δ 0.70 (C18-H₃), 0.82 and 0.90 (side chain methyls), 1.07 (C19-H₃), 3.02 (J₃,5 8 Hz, J₇,₅ 5 Hz, C5-H). O.r.d. (in ethanol) [Φ]_350 -1055, [Φ]_340 -1266, [Φ]_330 -1477, [Φ]_320 -2215, [Φ]_310 -3165, [Φ]_300 -3480, [Φ]_290 -3375, [Φ]_290 -1582, [Φ]_280 0, [Φ]_270 +1371, [Φ]_270 +3271, [Φ]_260 +3271, [Φ]_260 +3271.

4β,5-Epoxy-5β-cholest-2-ene.—A solution of 4β,5-epoxy-5β-cholest-2-ene (140 mg) in acetone was photolysed as above for 12 h and gave a crude reaction product which on rapid chromatography afforded starting material (19 mg) and α-norβ-homo-5α-cholest-2-en-6-one (c. 80% pure, 36 mg) as a relatively unstable oil. $v_{\text{max}}$ 1709 cm$^{-1}$. P.m.r. $\delta$ 0·71 (C18–H3), 0·82 (C19–H3), 0·82 and 0·90 (side chain methyls), 3·88 ($J_C6,12$ 6 Hz, C5–H), 5·80 (C2–H, C3–H) (Found: $M^+$ 384. C27H44O requires $M^+$ 384).

Hydrogenation of α-norβ-homo-5α-cholest-2-en-6-one (30 mg) catalysed by palladium on carbon (5%) for 9 h as above gave α-norβ-homo-5α-cholestan-6-one (c. 70% pure). $v_{\text{max}}$ 1704 cm$^{-1}$. P.m.r. $\delta$ 0·67 (C18–H3 and C19–H3), 0·82 and 0·90 (side chain methyls), 2·97 ($J_C6,12$ 15 Hz, C5–H). O.r.d. [α]$D_{20} +1930$, [α]$D_{320} +2122$, [α]$D_{330} +2894$, [α]$D_{320} +3860$, [α]$D_{311} +4631$, [α]$D_{305} +3860$, [α]$D_{295} +1736$, [α]$D_{288} 0$, [α]$D_{280} -1351$, [α]$D_{275} -1925$, [α]$D_{270} -1930$, [α]$D_{265} -1544$, [α]$D_{260} -1351$ (Found: $M^+$ 386·3551. Calc. for C27H46O: $M^+$ 386·3548). Lit.$^3$ m.p. 86–88°; $v_{\text{max}}$ 1702 cm$^{-1}$; p.m.r. $\delta$ 0·67 (methyls); o.r.d. $\alpha +136$.

Equilibration of α-norβ-homo-5β-cholestan-6-one

A mixture of α-norβ-homo-5β-cholestan-6-one (50 mg) in dioxan (5 ml) and aqueous sulphuric acid (0·1 ml; 20%) was heated under reflux in a nitrogen atmosphere for 2 h. Isolation of the product in the usual manner gave a mixture (c. 4 : 1) of α-norβ-homo-5α- and -5β-cholestan-6-ones. P.m.r. $\delta$ 0·67 (C18–H3 and C19–H3; 5α-ketone), 0·82 and 0·90 (side chain methyls), 1·07 (C19–H3; 5β-ketone). O.r.d. [α]$D_{295} +1425$, [α]$D_{330} +1730$, [α]$D_{320} +2341$, [α]$D_{320} +3461$, [α]$D_{310} +4174$, [α]$D_{300} +2850$, [α]$D_{290} 0$, [α]$D_{285} -1119$, [α]$D_{280} -2087$, [α]$D_{260} -2810$, [α]$D_{265} -2545$, [α]$D_{260} -1934$ (Found: $M^+$ 386·3544. Calc. for C27H46O: $M^+$ 386·3548). Lit.$^3$ o.r.d. $\alpha +88$.

Acknowledgment

The authors acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

Manuscript received 17 December 1975