a yellow solution and a dark residue. Recrystallization of the residue from benzene–cyclohexane furnished 0.4 g (25%) of 1-fluoro-2-acetylaminonaphthalene (**2a**), mp 117–120° (lit.[2] mp 120–121°). Hydrolysis of 0.25 g (1.1 mmol) of **2a** with 30 ml of 6 *N* hydrochloric acid followed by neutralization with sodium hydroxide solution furnished 0.17 g (96%) of 1-fluoro-2-naphthylamine (**2b**), mp 34–35°.[8] *Anal.* Calcd for $C_{10}H_8FN$: C, 74.5; H, 4.97; F, 11.8; N, 8.70; mol wt, 161. Found: C, 74.2; H, 5.04; F, 11.6; N, 8.66; mol wt, 161.

Reaction of **2b** (50 mg, 0.3 mmol) with isoamyl nitrite (0.5 mmol) in tetrahydrofuran[9] (1 ml) furnished 1-fluoronaphthalene (23%) which was identical with authentic material.

The cooled petroleum ether solution furnished 0.55 g (43%) of 1,1-difluoro-2-naphthone (**3**) as pale yellow needles, mp 49–50.5°. Sublimation at 40° (0.5 mm) furnished pure **3** with little loss of material: mp 50.5–52°; ir (melt between salt plates) 1700 cm^{-1} (C=O); nmr (CCl_4) δ 6.12 (two sets of triplets, 1 H, C=CHC=O, J_{H-H} = 10, J_{H-F} = 2.8 Hz), 7.31–7.99 (m, 5 H, aromatic and CH=CC=O). Irradiation at δ 6.12 resulted in the collapse of a doublet centered at δ 7.36 among the aromatic protons. *Anal.* Calcd for $C_{10}H_6F_2O$: C, 66.7; H, 3.3; F, 21.1; N, 0.00; mol wt, 180. Found: C, 66.4; H, 3.4; F, 21.9; N, 0.05; mol wt, 180.

Reduction of 0.15 g of **3** in 30 ml of absolute alcohol using 0.1 g of 5% palladium on carbon at 15 psi for 2 hr furnished, after work-up, material which showed hydroxyl but no carbonyl absorption in its ir spectrum and no olefinic protons in its nmr spectrum. An analytically pure sample was not obtained.

2-Naphthylamine (1b). CF_3OF was bubbled into a solution of 3.0 g (0.02 mol) of **1b** in 60 ml of chloroform. 2-Naphthylamine was consumed completely within 15–60 min. Glpc showed the presence of **3**, **2b**, and a third unidentified component in a 3:1:5 ratio, respectively. Filtration of the mixture furnished 1.2 g of gray residue. The filtrate was concentrated on a rotary evaporator at room temperature. The ir spectrum of the mixture showed strong absorptions at 2200 and 1800 cm^{-1} characteristic of an amine salt.[6] Chromatography of the crude mixture on a 15 × 1 in. Florisil column (1:1 benzene–hexane) furnished 0.7 g (19%) of **3**. Benzene eluent furnished 1-fluoro-2-naphthylamine (**2b**, 9%). A pink solid (0.4 g) identical with the material filtered from the reaction mixture from **1a** was obtained on further elution with ether. The solid did not contain the 2200 and 1800 cm^{-1} ir absorbances.

2-Naphthol (1c). CF_3OF was slowly bubbled into a solution of 2.9 g (13.0 mmol) of **1c** in 30 ml of chloroform until glpc analysis no longer showed the presence of **1c**. Two major products were indicated by both glpc and tlc. Nitrogen was bubbled into the reaction mixture to facilitate the removal of residual CF_3OF. The reaction mixture was filtered (0.2 g residue) and concentrated on a rotary evaporator to give a dark, viscous oil. The crude material was chromatographed on a 8 × 0.5 in. column of neutral alumina [1:1 benzene–petroleum ether (60°)], furnishing 0.5 g (20%) of pure **3**. Chloroform–benzene (7:3) eluted 0.32 g of **2c**. Recrystallization from petroleum ether produced 0.3 g (14%) of **2c**: mp 74–75°; ir (KBr) 3250 cm^{-1} (OH); nmr ($CDCl_3$) δ 5.2 (broad, 1 H, OH) and 7.1–8.2 (m, 6 H, aromatic). On careful drying, the δ 5.2 absorption appeared as a doublet, J = 4 Hz. Since no change was observed in the aromatic portion of the spectrum, the coupling occurred between the hydroxyl proton and the fluorine atom. Intramolecular hydrogen bonding was negligable as deduced from the large hydroxyl proton chemical shift dependence on the concentration of the solution.

Anal. Calcd for $C_{10}H_7FO$: C, 74.1; H, 4.4; F, 11.7; mol wt, 162. Found: C, 74.3; H, 4.4; F, 12.0; mol wt, 162.

Attempted preparation of **2c** from 1-amino-2-naphthol hydrochloride by a Balz–Schiemann reaction failed in two attempts.

9-Acetylaminoanthracene (4). CF_3OF was bubbled into a solution of 0.78 g (3.3 mmol) of **4** in 30 ml of chloroform. The reaction was monitored by tlc on silica gel (chloroform). Three products were detected but one major component accounted for more than 90% of the products. All **4** was consumed in 2 hr. Nitrogen was passed through the reaction mixture to remove residual CF_3OF. The solvent was removed on a rotary evaporator and the tan residue was chromatographed on a 10 × 0.5 in. column of alumina (benzene), furnishing a light yellow solid which after recrystallization from benzene yielded 0.65 g (95%) of **5**, mp 282–284°. The identity was proven by comparison with authentic anthraquinone.

Anthrone (6). A solution of 1.5 g (7.0 mmol) of **6** in 50 ml of chloroform was treated with CF_3OF for 3 hr. Tlc on silica gel (chloroform) showed the presence of two components. Removal of the chloroform on a rotary evaporator gave 1.6 g of yellow solid. Chromatography on a 10 × 1 in. column of silica gel (benzene) furnished 0.9 g (55%) of yellow **6**. Benzene–chloroform (1:1) elution furnished an orange solid after removal of the solvents. Recrystallization from benzene–petroleum ether gave 0.55 g (35%) of 10,10-bianthronyl (**7**): mp 262–268° dec (lit.[10] mp *ca.* 270–275° dec); ir identical with a published spectrum; nmr ($CDCl_3$) δ 4.75 (s, 1 H, benzylic proton) and 6.7–8.0 (complex, 8 H, aromatic); mol wt, 386 (calcd mol wt, 386).

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the office of Research and Projects, Southern Illinois University.

Registry No.—**1a**, 581-97-5; **1b**, 91-59-8; **1c**, 135-19-3; **2a**, 19580-15-5; **2b**, 14554-00-8; **2c**, 51417-63-1; **3**, 51417-64-2; **4**, 37170-96-0; **6**, 90-44-8; **7**, 4393-30-0; CF_3OF, 373-91-1.

References and Notes

(1) Petroleum Research Fund Postdoctoral Fellow, 1972–1973.
(2) D. H. R. Barton, A. K. Ganguly, R. H. Hesse, S. N. Loo, and M. M. Pechet, *Chem. Commun.*, 806 (1968).
(3) J. Kollonitsch, L. Barash, and G. A. Doldouras, *J. Amer. Chem. Soc.*, **92**, 7494 (1970).
(4) T. B. Patrick and J. A. Schield, *Tetrahedron Lett.*, 445 (1973); T. B. Patrick, J. A. Schield, and D. G. Kirchner, *J. Org. Chem.*, **39**, 1758 (1974).
(5) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Permagon Press, Oxford, 1966.
(6) N. B. Colthup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 281.
(7) D. E. Applequist and R. Searle, *J. Org. Chem.*, **29**, 987 (1964). We thank Dr. Applequist for providing a sample of **8**.
(8) H. F. Bassilios, M. Shawky, and A. Y. Salem, *Bull. Soc. Chim. Belg.*, **75**, 577 (1966), report mp 174° for **2b**. Their elemental analysis was determined only for nitrogen to be 8.7%. 2-Azo- and 2-azoxy-1-fluoronaphthalene, possible compounds from their synthesis, have nitrogen percentages of 8.80 and 8.38%, respectively.
(9) J. I. G. Cadogen and G. A. Molina, *J. Chem. Soc., Perkin Trans. 1*, 541 (1973).
(10) J. S. Meek, W. B. Evans, V. Godefroi, W. R. Benson, M. F. Wilcox, W. G. Clark, and T. Tiedeman, *J. Org. Chem.*, **26**, 4281 (1961).

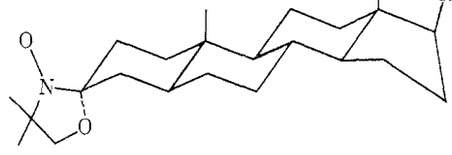
Nitroxides. LVIII. Structure of Steroidal Spin Labels

Pierre Michon and André Rassat*

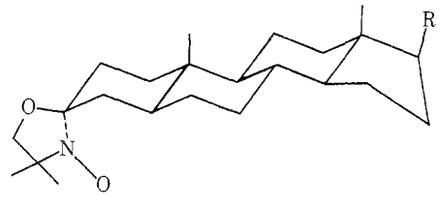
Laboratoire de Chimie Organique Physique (Equipe de Recherche Associée au Centre national de la Recherche scientifique), Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, B. P. 85, Centre de Tri, F.38041 Grenoble-Cedex, France

Received August 10, 1973

Spiro oxazolidine steroidal nitroxides[1] are widely used as spin labels in biological membranes.[2-4] In spite of its interest for orientation studies, the configuration of the spiro ring system has never been established. There are two possible isomers:[5] radical **1a**, in which the nitrogen is



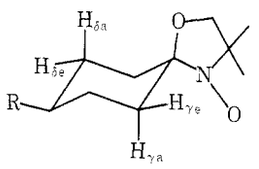
1a



1b

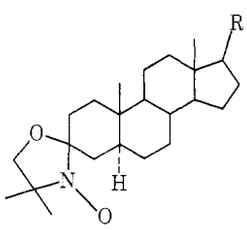
equatorial (e) relative to the steroid A ring, and radical **1b,** in which nitrogen is axial (a). Structure **1a** is generally postulated without experimental evidence.[6,7]

We have recently studied oxazolidinyloxy radicals prepared from substituted cyclohexanones.[8] We have shown by electron spin resonance (esr) and by nuclear magnetic resonance (nmr), through comparison with *tert*-butyl cyclohexyl nitroxide,[9] that only one isomer **2** is obtained, in which the cyclohexane is in the chair form, and nitrogen is equatorial. The following hyperfine coupling constants (hcc) have been measured: $a_{H\gamma a} = -0.7$ G; $a_{H\gamma e} = -0.65$ G; $a_{H\delta a} = +0.17$ G; $a_{H\delta e} = +1.06$ G.

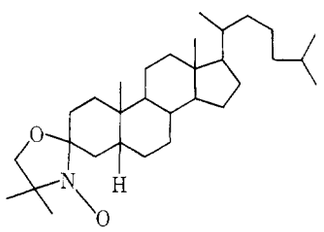


2a, R = H
b, R = *t*-Bu

We have studied radicals **3**[2] (mp 175°), **4**[1] (mp 176°), and **5** (mp 94–98°) prepared from 5α-androstan-17β-ol-3-one, 5α-cholestan-3-one, and 5β-coprostan-3-one. In each case, a single radical was obtained.



3, R = OH
4, R = C_8H_{17}

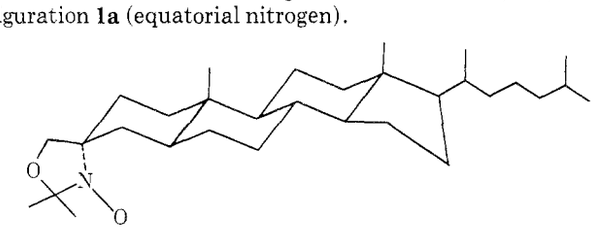


5

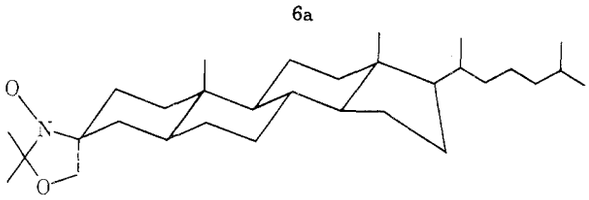
The esr spectrum of the three radicals is the normal nitroxide triplet, the hyperfine structure (Figure 1a) being identical for the three radicals. Although the 5α and 5β isomers may look different, radicals **3, 4,** and **5** have the same protons in the A ring (two axial γ, two equatorial γ, two axial δ, and one equatorial δ proton). Since the electron–proton hcc are very stereospecific,[10,11] all three radicals probably have the same geometry.

If we assume the same configuration for radicals **3, 4,** and **5,** and for radical **2b,** the esr spectrum of the former radicals should be reconstituted by using the γ and δ hcc determined for radical **2b:** the computer-simulated spectrum (Figure 1d) is identical with the experimental spectrum.

This is the first evidence that the steroidal radicals studied have the same configuration as radical **2,** *i.e.,* configuration **1a** (equatorial nitrogen).



6a

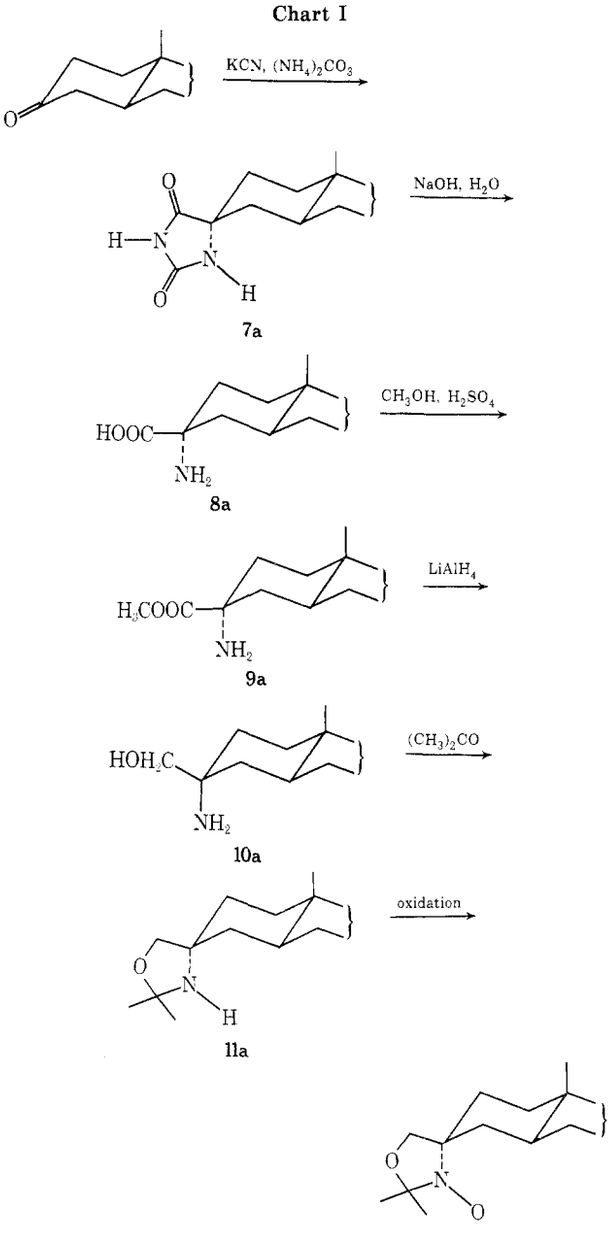


6b

In order to obtain some information on the other possible isomer, **1b** (axial nitrogen), we have prepared radicals **6a** and **6b** in which the only difference is a methylene–oxygen permutation, for which we expect a small influence on the proton hcc.

Chart I gives the different steps for the preparation of radical **6a.**

Chart I



It is known[12,13] that the hydantoin obtained from cholestanone is a mixture of isomers; the major product leads to the amino acid **8a** (mp 264°) in which the NH_2 group is axial (conclusion based on pK values and hydrolysis rate constants for both epimeric amino acids[13]).

When the reaction sequence described in Chart I was carried out on the pure amino acid **8a** (mp 264°), radical **6a** (mp 188°) was obtained. Since this reaction sequence does not change the configuration at the steroid 3 position, this radical **6a** has an axial nitroxide group.

In order to obtain the other isomer, the same reaction sequence was carried out on the mixture of both epimeric hydantoins **7a** and **7b.** Two different radicals were obtained (in 86.5:13.5 ratio) and separated by thin layer chromatography. The first eluted radical was identical

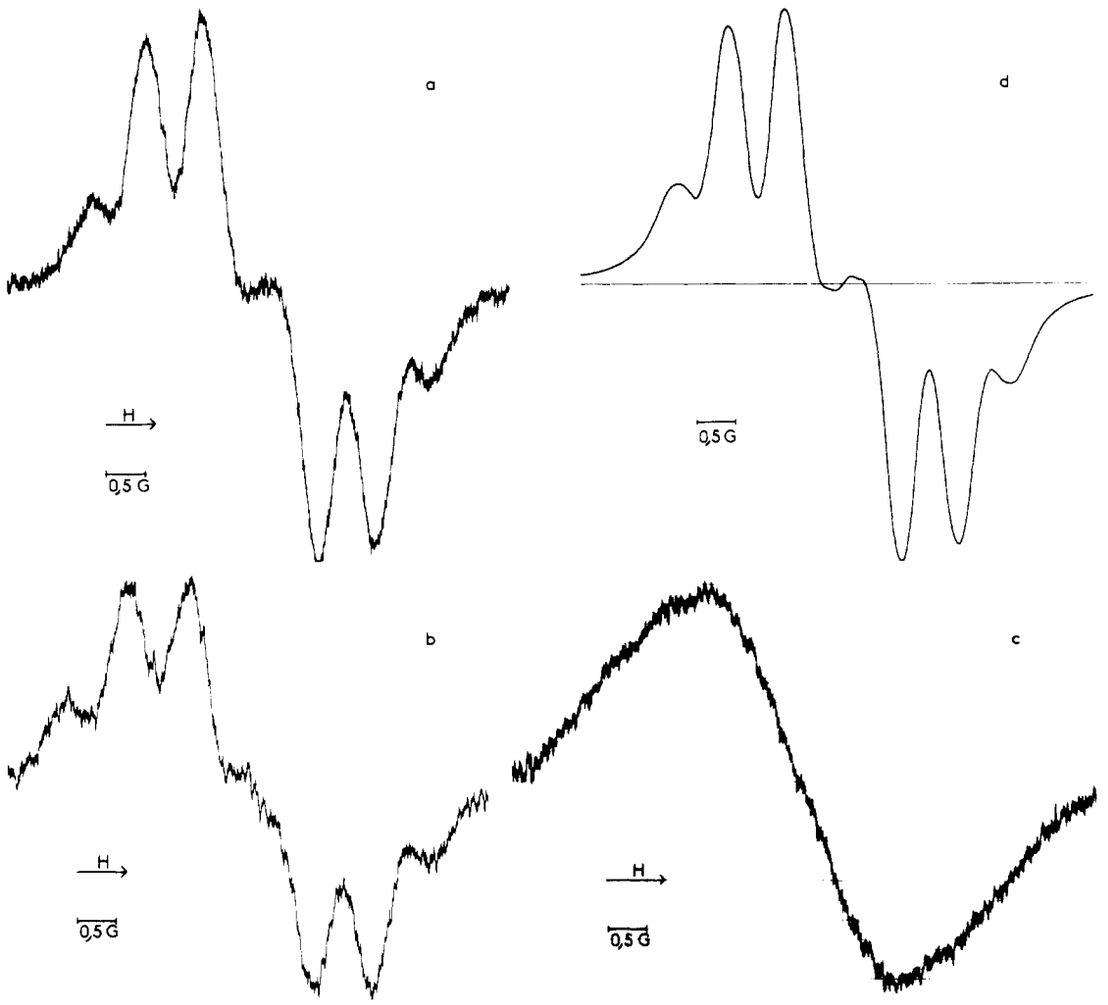


Figure 1. Low-field nitrogen line of the esr spectra, in degassed $CHCl_3$ at room temperature, of (a) radical **3**, (b) radical **6b**, (c) radical **6a**, (d) radical **3** (computer-simulated, $a_{H\gamma a} = a_{H\gamma e} = 0.7$ G; $a_{H\delta e} = 1.07$ G; $a_{H\delta e} = 0.2$ G; linewidth $\Delta H = 0.34$ G).

with **6a** (mp 188°) and the last eluted radical **6b** had mp 150–155°.

By comparing the yields of each step and the proportion of hydantoins **7a** and **7b**[13] and of radicals **6a** and **6b**, it can be safely concluded that the minor isomer comes from **7b**: the least abundant radical has an equatorial nitroxide group.

This minor isomer **6b** (mp 150–155°) displays a three-line esr spectrum, each line having a well-resolved hyperfine structure (Figure 1b) very similar to those of radicals **3**, **4**, and **5**. This confirms our hypothesis that methylene-oxygen permutation does not change hyperfine splittings. The major radical **6a** (mp 188°) displays the nitroxide three-line spectrum without resolution of the proton hyperfine structure (Figure 1c), the peak-to-peak linewidth being comparable to the one of radical **6b**. These results show that radical **1b**, if it exists, may have a three-line spectrum in which each line has no resolved proton hyperfine structure.

In conclusion, the synthesis of oxazolidine nitroxide from steroidal 3-ketones yields, in our hands, a single radical having an equatorial nitrogen relative to the steroid A ring.[14]

Experimental Section

4′,4′-Dimethylspiro(5α-cholestane-3,2′-oxazolidine). According to Keana,[1] 5α-cholestan-3-one (0.5 g) and an excess of 2-amino-2-methylpropan-1-ol (1.1 g) in xylene solution (40 ml) with a trace of *p*-toluenesulfonic acid were boiled for 5 days. Water was removed by azeotropic distillation. After extraction, 0.58 g of crystals was obtained (crude yield 98%): mp 123–124° (lit.[1] mp 124–125°); ir (Nujol) ν_{NH} 3300 cm^{-1}; nmr ($CDCl_3$) CH_3(4′,4′) 1.22, CH_2(5′) 3.56 ppm; nmr (C_6D_6) CH_3(4′,4′) 1.08, CH_2(5′) 3.45 ppm. No trace of another isomer was detected by nmr.

Reflux, for 5 days, without azeotropic distillation, of the same products gave the same result.

4′,4′-Dimethylspiro(5α-cholestane-3,2′-oxazolidine)-3′oxyl (4). The crude amine (0.57 g) in ether solution was oxidized by *m*-chloroperbenzoic acid (0.32 g)[15] in ether solution. The radical concentration was followed by esr (oxidation time 6 hr). When the esr signal was maximum, the solution was washed with 5% sodium bicarbonate solution and dried over sodium sulfate. By thin layer chromatography (silica gel, 90% pentane–10% ether), 0.43 g of yellow crystals was obtained (yield 72%): mp 176° (methanol–ether) (lit.[1] mp 175–176°); uv (cyclohexane) λ 450 mμ (ε ~12); esr ($CHCl_3$, $M/1000)a_N = 14.9$ G.

Changes in oxidation time (0.25–48 hr) did not lead to detection of another radical by thin layer chromatography.

4′,4′-Dimethylspiro(5β-cholestane-3,2′-oxazolidine) was prepared in the same manner as the oxazolidine above. Azeotropic distillation with 0.28 g of ketone and 0.6 g of 2-amino-2-methylpropan-1-ol in xylene solution (40 ml), after 5 days, followed by extraction, gave 0.32 g of viscous product (crude yield 97%): ir (Nujol) ν_{NH} ~3200 cm^{-1}; nmr ($CDCl_3$) CH_3(4′,4′) 1.2, CH_2(5′) 3.5 ppm.

4′,4′-Dimethylspiro(5β-cholestane-3,2-oxazolidine)-3′-oxyl (5) was prepared in the same manner as the radical above (4) using 0.32 g of crude amine and 0.6 g of *m*-chloroperbenzoic acid. After 4 hr oxidation time and thin layer chromatography, 0.24 g of product was obtained (yield 72%): mp 94–98° (methanol–ether); uv (cyclohexane) λ 450 mμ (ε ~9); esr ($CHCl_3$, $M/1000$) $a_N = 14.9$ G.

Anal. Calcd for $C_{31}H_{54}NO_2$: C, 78.75; H, 11.51; O, 6.77; N, 2.96. Found: C, 78.76; H, 11.58; O, 6.52; N, 2.85.

17β-Hydroxy-4′,4′-dimethylspiro(5α-androstane-3,2′-oxazolidine) was prepared as described above using 0.6 g of ketone and

1.8 g of 2-amino-2-methylpropan-1-ol in xylene solution (50 ml). After 7 days, the mixture was extracted to give 0.73 g of product: mp 79°; ir (Nujol) ν_{OH} 3500, ν_{NH} 3200 cm^{-1}; nmr ($CDCl_3$) $CH_3(4',4')$ 1.23, $CH_2(5')$ 3.55 ppm.

17β-Hydroxy-4',4'-dimethylspiro(5α-androstane-3,2'-oxazolidine)-3'-oxyl (3) was prepared as described above, using 0.73 g of crude amine and 0.53 g of *m*-chloroperbenzoic acid (oxidation time 5 hr). Thin layer chromatography gave 0.48 g of yellow product (yield 63%): mp 175–176° (methanol-water) (lit.[2] mp 172–174°); uv (cyclohexane) λ 450 mμ (ε ~13); esr ($CHCl_3$, $M/1000$) a_N = 14.9 G.

Spiro(5α-cholestane-3,5'-hydantoin) (7a). According to Maki,[13] a mixture of 5α-cholestan-3-one (3.86 g), ammonium carbonate (5.7 g), and potassium cyanide (2 g) in 80% ethanol (150 ml) was heated at 57–58° for 10 days. The precipitate was filtered, washed with water, and dried to give 4 g of white powder (yield 87%): mp 274°; ir (KBr) ν_{NH} 3200, ν_{CO} 1780 and 1730 cm^{-1}.

The crude product (0.200 g) was extracted repeatedly with ethyl acetate to give 0.125 g of white powder **7a**, mp 276° (lit.[13] mp 273–274°), ir (KBr) identical with that of crude product.

3α-Amino-5α-cholestane-3β-carboxylic Acid (8a). According to Maki,[13] **7a** (0.125 g, mp 276°), sodium hydroxyde (5 g), and water (5 ml) were heated for 1 hr with occasional addition of water. At the end of this time, a large amount of water was added and the mixture was filtered. The precipitate was dissolved by addition of 70% sulfuric acid. The sulfate obtained was treated with concentrated ammonia to give 0.100 g (yield 87%) of white product **8a**, mp 264° (lit.[13] mp 262–264°).

Methyl 3α-Amino-5α-cholestane-3β-carboxylate (9a). According to Maki,[13] a solution of **8a** sulfate in methanol (20 ml) and concentrated sulfuric acid (4 ml) was refluxed for 8 hr. The methanol was evaporated and the residue was extracted with ether after neutralization with sodium carbonate solution. A 0.100-g yield (95%) of white product **9a** was obtained: mp 141° (methanol) (lit.[13] mp 141–141.5°); ir (Nujol) ν_{NH_2} 3300, ν_{CO} 1725 cm^{-1}; nmr (C_6D_6) CH_3 carboxylate 3.44 ppm.

3α-Amino-5α-cholestane-3β-hydroxymethyl (10a). **9a** (0.1 g, mp 141°) in ether solution was added to a suspension of lithium aluminum hydride (0.25 g) in ether solution (100 ml). The mixture was refluxed for 12 hr. The excess of hydride was decomposed,[16] the ether layer was filtered, and the solvent was removed. **10a** (0.084 g, yield 90%) was obtained: mp 155–158°; ir (Nujol) ν_{OH} ~3500 cm^{-1}; nmr (C_6D_6) CH_2 hydroxymethyl 3.12 ppm; nmr ($CDCl_3$) CH_2 3.25 ppm.

2',2'-Dimethylspiro(5α-cholestane-3,4'-oxazolidine) (11a). Azeotropic distillation of **10a** (0.08 g) with an excess of acetone and a trace of *p*-toluenesulfonic acid gave 0.082 g (yield 95%) of viscous oil **11a**: ir (Nujol) ν_{NH} 3200 cm^{-1}; nmr (C_6D_6) $CH_3(2',2')$ 1.4, $CH_2(5')$ 3.53 ppm; nmr ($CDCl_3$) $CH_3(2',2')$ 1.45, $CH_2(5')$ 3.58 ppm.

2',2'-Dimethylspiro(5α-cholestane-3,4'-oxazolidine)-3'-oxyl (6a). **11a** (0.08 g) was oxidized using 0.045 g of *m*-chloroperbenzoic acid. Thin layer chromatography (silica gel, 90% pentane–10% ether) gave 0.040 g (yield 47%) of yellow crystals of **6a**: mp 188° (ethanol); uv (cyclohexane) λ 450 mμ (ε ~9.5); esr ($CHCl_3$, $M/1000$) a_N = 15.2 G, no hyperfine structure (Figure 1c).

Anal. Calcd for $C_{31}H_{54}NO_2$: C, 78.75; H, 11.51; O, 6.77; N, 2.96. Found: C, 78.76; H, 11.56; O, 6.98; N, 2.85.

2',2'-Dimethylspiro(5α-cholestane-3,4'-oxazolidine)-3'-oxyl (6a and 6b). The same method as above was used on the crude hydantoin **7**, mp 274° (mixture of two epimeric hydantoins **7a** and **7b**), without purification of intermediate products. Hydrolysis of crude hydantoins (0.5 g, mp 274°) with sodium hydroxide gave 0.41 g of white product, mp 263° (mixture of two epimeric amino acids).

This crude mixture (0.41 g) in *ethanol* solution (100 ml) containing anhydrous hydrochloric acid was allowed to stand at room temperature overnight. The residue, obtained after evaporation of the ethanol, was extracted with ether to give 0.45 g of white product, mp 105° (mixture of epimeric amino esters): ir (KBr) ν_{CO} 1720 cm^{-1}; nmr ($CDCl_3$) CH_3 carboxylate 1.3 (triplet, J = 6 Hz), CH_2 carboxylate 4.2 ppm (quadruplet, J = 6 Hz).

This crude amino ester (0.12 g) was reduced with lithium aluminum hydride (0.25 g) to give 0.10 g of white solid, mp 155–157° (mixture of epimeric amino alcohols): ir (Nujol) ν_{OH} 3500 cm^{-1}; nmr ($CDCl_3$) CH_2 hydroxymethyl 3.25 ppm.

An azeotropic distillation of crude amino alcohols (0.1 g) with an excess of acetone gave 0.105 g of viscous product (mixture of two epimeric oxazolidines): ir (Nujol) ν_{NH} 3300 cm^{-1}; nmr ($CDCl_3$) $CH_3(2',2')$ 1.45, $CH_2(5')$ 3.57 ppm.

This mixture of oxazolidine (0.105 g) was oxidized with *m*-chloroperbenzoic acid (0.06 g). Thin layer chromatography (silica gel, 90% pentane–10% ether) gave two products in 86.5:13.5 ratio: 0.044 g of yellow crystals, mp 188° (ethanol), identical with **6a**, and 0.007 g of yellow crystals **6b**, mp 150–155°, esr ($CHCl_3$, $M/1000$) a_N = 15.1 G, hyperfine structure (Figure 1b).

Registry No.—**3**, 39665-50-4; **4**, 51820-19-0; **5**, 51820-20-3; **6a**, 51231-13-1; **6b**, 51231-14-2; **7a**, 5119-47-1; **7b**, 5167-92-0; **8a**, 5071-18-1; **8b**, 5119-44-8; **9a**, 5071-19-2; **9b**, 5071-15-8; **10a**, 51231-15-3; **10b**, 51231-16-4; **11a**, 51231-17-5; **11b**, 51540-03-5; 4',4'-dimethylspiro(5α-cholestane-3,2'-oxazolidine), 51231-18-6; 5α-cholestan-3-one, 566-88-1; 2-amino-2-methylpropan-1-ol, 124-68-5; 4',4'-dimethylspiro-5β-chlolestane-3,2'-oxazolidine), 51231-19-7; 17β-hydroxy-4',4'-dimethylspiro(5α-androstane-3,2'-oxazolidine), 51231-20-0.

References and Notes

(1) J. F. W. Keana, S. B. Keana, and D. Beetham, *J. Amer. Chem. Soc.*, **89**, 3055 (1967).
(2) W. L. Hubbel and H. M. McConnell, *Proc. Nat. Acad. Sci. U. S.*, **63**, 16 (1969).
(3) L. J. Libertini, A. S. Waggoner, P. C. Jost, and O. H. Griffith, *Proc. Nat. Acad. Sci. U. S.*, **64**, 13, (1969).
(4) W. L. Hubbel and H. M. McConnell, *J. Amer. Chem. Soc.*, **93**, 314 (1971).
(5) J. C. Hsia, H. Schneider, and I. C. P. Smith, *Can. J. Biochem.*, **49**, 614 (1971).
(6) E. Sackmann and H. Träuble, *J. Amer. Chem. Soc.*, **94**, 4482 (1972).
(7) G. R. Luckhurst and A. Sanson, *Mol. Phys.*, **24**, 1297 (1972).
(8) P. Michon and A. Rassat, *Bull. Soc. Chim. Fr.*, 3561 (1971).
(9) T. A. J. W. Wajer, A. Mackor, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **90**, 568 (1971).
(10) R. Briere, H. Lemaire, A. Rassat, P. Rey, and A. Rousseau, *Bull. Soc. Chim. Fr.*, 4479 (1967).
(11) A. Rassat and J. Ronzaud, *J. Amer. Chem. Soc.*, **93**, 5041 (1971).
(12) L. Munday, *J. Chem. Soc.*, 4372 (1961).
(13) Y. Maki, M. Sato, and K. Obata, *Chem. Pharm. Bull.*, **13**, 1377 (1965); *Chem. Abstr.*, **64**, 9795 (1966).
(14) J. C. Williams, R. Mehlorn, and A. D. Keith, *Chem. Phys. Lipids*, **7**, 207 (1971), claim on the basis of esr spectra to have obtained both isomers.
(15) G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3283 (1965).
(16) V. M. Mićović and M. L. J. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

Trans Dehydration of Alcohols with Methyl(carboxysulfamoyl) Triethylammonium Hydroxide Inner Salt[1]

J. S. O'Grodnick,[2a] R. C. Ebersole,[2b] T. Wittstruck, and E. Caspi*

Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts 01545

Received August 10, 1973

During the course of our investigations into the mode of incorporation of hydrogen atoms of biosynthetic precursors into polyprenoids, we required a procedure applicable to microscale operations allowing the introduction of a double bond *via* a cis elimination of an hydroxyl function. A novel and convenient procedure for the dehydration of secondary and tertiary alcohols utilizing methyl(carboxysulfamoyl) triethylammonium hydroxide inner salt (**6**) claimed to proceed *via* cis elimination has been reported by Burgess, *et al.*[3] Indeed, these authors have shown that the dehydration of *threo*- and *erythro*-2-deuterio-1,2-diphenylethanol is a cis-elimination process. Based on this observation, the generality of the cis elimination was suggested.[3,4]

Dehydration of steroidal alcohols with the reagent **6** has been accomplished without affecting other functional groups of the molecule, such as ketones, unsaturated ketones, acetylenes, and acetates.[4] Because of the potential utility of this reagent, we undertook an exploration of the stereochemistry of the process.