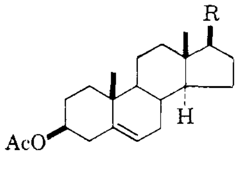
## A CONVENIENT SYNTHESIS OF 19-NORSTEROIDS

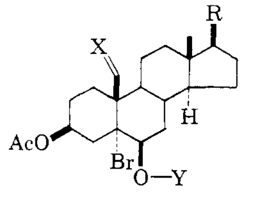
*Sir:*

The medical importance of 19-norsteroids is well known.[1] We wish to report a general conversion of readily available 3β-acetoxy-$\Delta^{5,6}$-steroids of the type (I) into the corresponding 19-nor compounds of the type (V) by the application of nitrite photolysis.[2]

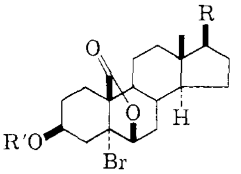
Treatment of (Ia, Ib and Ic) with hypobromous acid[3] gave the bromohydrins (IIa[3], Y = H, X = $H_2$), m.p. 172–174°; (IIb, Y = H, X = $H_2$) m.p. 171–172°, $[\alpha]^{26}\text{D}$ +1.9° (all rotations in 1% $CHCl_3$ solutions); (IIc, Y = H, X = $H_2$), m.p. 171–174°, $[\alpha]^{25.5}$ +7°. These bromohydrins were nitrosated using nitrosyl chloride and pyridine. Photolysis of the resulting nitrites (IIa, IIb and IIc, Y = NO, X = $H_2$) in toluene at 0° with a 500-watt Hanovia lamp gave the nitroso dimers which were rearranged to the oximes (IIa, X = NOH, Y = H), m.p. 176–180°, $[\alpha]^{21}\text{D}$ −35°; (IIb, X = NOH, Y = H) m.p. 178.5–180°, $[\alpha]^{26}\text{D}$ −11°; and (IIc, X = NOH, Y = H) m.p. 173–178°, $[\alpha]^{26}\text{D}$ −5.4°, respectively.

The 19-oximes with nitrous acid[2] gave the corresponding aldehydes (in hemiacetal form) which, without purification were oxidized with chromic acid in acetone to the lactones (IIIa, R′ = Ac), m.p. 170–172°, $[\alpha]^{22}\text{D}$ −16.2°; (IIIb, R′ = Ac), m.p. 221–229°, $[\alpha]^{27}\text{D}$ −13° and (IIIc, R′ = Ac) m.p. 153–157° and 161–164°, $[\alpha]^{22.5}\text{D}$ +13°. The lactone (IIIb, R′ = Ac) with peracetic acid enlarged the ring D to furnish the D-homodilactone (VI, R′ = Ac) m.p. 268–272°, $[\alpha]^{25.5}\text{D}$ −58.4°. The 3β-acetate in these lactones was removed with HCl in dioxane and water to yield the lactone alcohols (IIIa, R′ = H), m.p. 173.5–178.5°, $[\alpha]^{25.5}\text{D}$ −17.9°; (IIIb, R′ = H), m.p. 221–232°, $[\alpha]^{25.5}\text{D}$ +10°; (IIIc, R′ = H), m.p. 210–214°, $[\alpha]^{23}\text{D}$ +18° and (VI, R′ = H), m.p. 244–247°, $[\alpha]^{26}\text{D}$ −66.1°. Oxidation with chromic acid in acetone and treatment with hot pyridine or $HCl/CHCl_3$ yielded the conjugated ketones (IVa), m.p. 179–184°, $[\alpha]^{26}\text{D}$ −102°, $\lambda_{\max}^{\text{MeOH}}$ 238 mμ (ε = 12,500); (IVb) m.p. 291–293°, $[\alpha]^{23.5}\text{D}$ −86°, $\lambda_{\max.}^{\text{MeOH}}$ 235 mμ (ε = 12,000); (IVc) m.p. 236–239°, $[\alpha]^{23.5}\text{D}$ −246°; $\lambda_{\max}^{\text{MeOH}}$ 237 mμ (ε = 12,700); and (VII) m.p. 293.5–298.5°, $[\alpha]^{21.5}\text{D}$ −191°, $\lambda_{\max}^{\text{MeOH}}$ 233 mμ (ε = 16,200). The conjugated ketones (IVa, IVb, IVc, and VII) with zinc and acetic acid for fifteen minutes at reflux temperature, followed by mild acid treatment, gave 19-norcholestenone (Va) as a low-melting solid, $[\alpha]^{26}\text{D}$ +44.2°, $\lambda_{\text{mox}}^{\text{MeOH}}$ 240 mμ (ε = 14,000); 19-norandrostendione (Vb), m.p. 164–169°, $[\alpha]^{27}\text{D}$ +136°, $\lambda_{\max}^{\text{MeOH}}$ 241 mμ (ε = 17,000); 19-norprogesterone (Vc), m.p. 143–146°, $[\alpha]^{25}\text{D}$ +142°, $\lambda_{\max}^{\text{MeOH}}$ 240 mμ (ε = 17,000) 19-nortestolactone (VIII), m.p. 195–199°, $[\alpha]^{26}\text{D}$ −16.9°, $\lambda_{\max}^{\text{MeOH}}$ 238 mμ (ε = 17,000). The constants for (Vb, Vc and VIII) are in good agreement with the literature.[4,5,6]

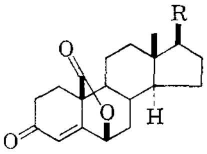




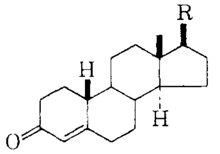
I, a, b, and c
II, a, b and c
a, R = cholesterol sidechain
b, R = 17-ketone
c, R = $CH_3$-CO



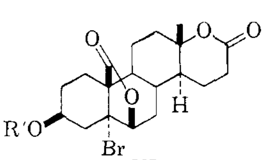
III, a, b and c



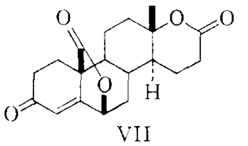
IV, a, b and c



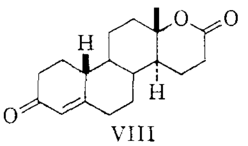
V, a, b and c



VI



VII



VIII

**Acknowledgment.**—We express our thanks to Dr. M. M. Pechet for his continued interest and encouragement and to Mrs. C. B. Pantuck, and the Misses A. Scott and L. T. Gendron for their able assistance throughout the course of this work. We thank Dr. L. E. Geller for preliminary experiments.

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## CONFIGURATIONAL STABILITY OF SULFONYL CARBANIONS GENERATED BY DECARBOXYLATION REACTION[1]

*Sir:*

Through a comparison of the rates of base-catalyzed racemization and isotopic exchange of I, it was concluded in a former study[2] that the sulfonyl carbanion was capable of maintaining configurational stability to a degree that varied widely with solvent. Thus $k_{\text{exchange}}/k_{\text{racemization}}$ ranged between 10 and about 2000. Another study revealed that sulfoxide and phosphine oxide groups in II and III

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