New Steroidal Dihydrothiazoles

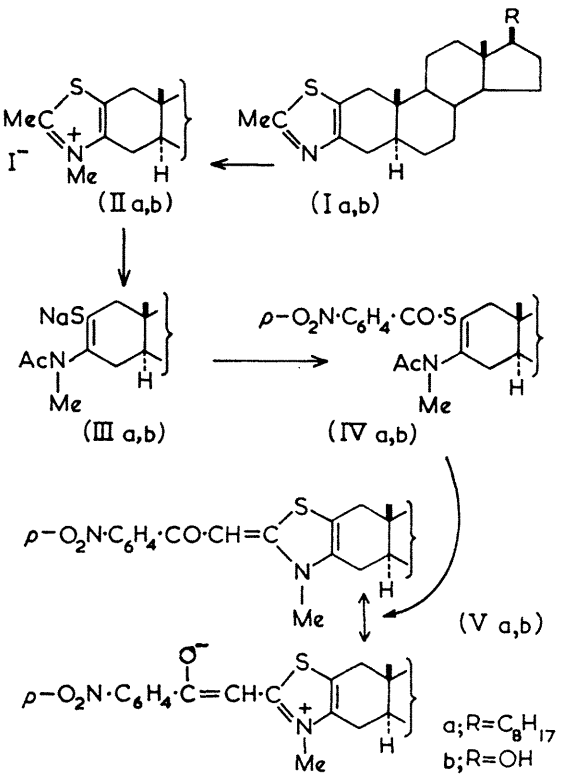
By VIORICA I. DENES* and GHEORGHE CIURDARU

(*Academy of the Socialist Republic of Rumania, Institute of Chemistry, Str. Donath* 65, *Cluj, Rumania*)

Summary New steroidal 2′,3′-dihydrothiazoles have been prepared by thermal rearrangement of thiolesters.

THE increasing interest in stereoidally fused heterocycles[1] prompted us to study the application in this field of our synthesis of the 2,3-dihydrothiazole ring[2,3] which involves thermal rearrangement of certain thiolesters possessing an adjacent acylated alkylamino-group. This electrocyclic[3] reaction led to a new type of dihydrothiazolo-steroid, *i.e.* 2′,3′-saturated, the previously described steroidal dihydrothiazoles being all 4′,5′-saturated.[4] The route proceeds through steroidal intermediaries which are interesting *per se*, and can be further extended in this area.

2′-Methylthiazolo[3,2-*d*]-5α-cholest-2-ene (Ia)[5] and 2′-methylthiazolo[3,2-*d*]-5α-androst-2-en-17β-ol (Ib),[6] respectively, were used as starting materials. Their quaternization with dimethyl sulphate and subsequent treatment with sodium iodide afforded the corresponding *N*-methylthiazolium iodides (IIa) (m.p. 253°) and (IIb) (m.p. 289—290°). Hydrolytic cleavage of these thiazolium salts with base yielded the thiolates (IIIa, b) which, without separation, were converted by means of *p*-nitrobenzoyl chloride into the thiolesters (IVa) (m.p. 95°) and (IVb) (m.p. 138°), respectively. On heating at 180° and 185°, respectively, these compounds underwent a rearrangement accompanied by elimination of water and gave the 2′,3′-dihydrothiazoles (Va) (m.p. 283°) and (Vb) (m.p. 254°), both crystallizing in dark red prisms. The spectroscopic data are in agreement with the mesomeric structures assigned for such compounds.[2,7]



We are grateful to Dr. F. Hodoșan for valuable suggestions.

(*Received, March 26th*, 1969; *Com.* 429.)

[1] G. I. Zhungietu and G. N. Dorofeenko, *Uspekhi Khim.*, 1967, **36**, 48.
[2] V. I. Dénes, Gh. Ciurdaru, and M. Fărcășan, *Chem. Ber.*, 1963, **96**, 2691; V. I. Dénes, Gh. Ciuradru, and M. Fărcășan, *Rev. roumaine Chim.*, 1964, **9**, 375.
[3] V. I. Dénes and Gh. Ciurdaru, (in the press).
[4] I. Kitagawa, I. Ueda, T. Kawassaki, and E. Mosettig, *J. Org. Chem.*, 1963, **28**, 2228; J. M. Krämer, K. Brückner, K. Irmuscher, and K.-H. Bork, *Chem. Ber.*, 1963, **96**, 2803; I. Kitagawa and Y. Sato, *J. Org. Chem.*, 1964, **29**, 339.
[5] J. Doorenbos and C. P. Dorn, jun., *J. Pharm. Sci.*, 1962, **51**, 414.
[6] J. A. Zderic, H. Carpio, A. Ruiz, D. Chávez, F. Kincl, and H. J. Ringold, *J. Medicin. Chem.*, 1963, **6**, 195.
[7] V. I. Dénes, Gh. Ciurdaru, and M. Fărcăsan, *Rev. roumaine Chim.*, 1965, **10**, 1045.