The Stereochemistry of Some Halogenated Steroids. Crystal Structures of 8β-Methyltestosterone 17β-Monobromoacetate and Testosterone 17β-*p*-Bromobenzoate

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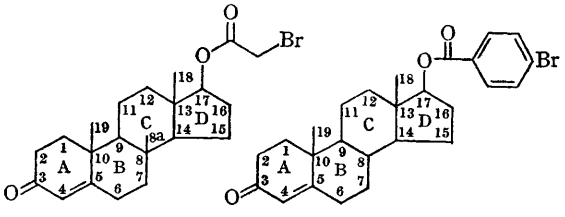
IN conjunction with Nagata's study of the 8β-substituted steroids, the Shionogi *X*-ray group has determined the molecular structures of 8β-methyltestosterone 17β-monobromoacetate (I) and testosterone 17β-*p*-bromobenzoate (II) by means of single-crystal *X*-ray analysis.

The following data were obtained using Cu-K_α radiation:

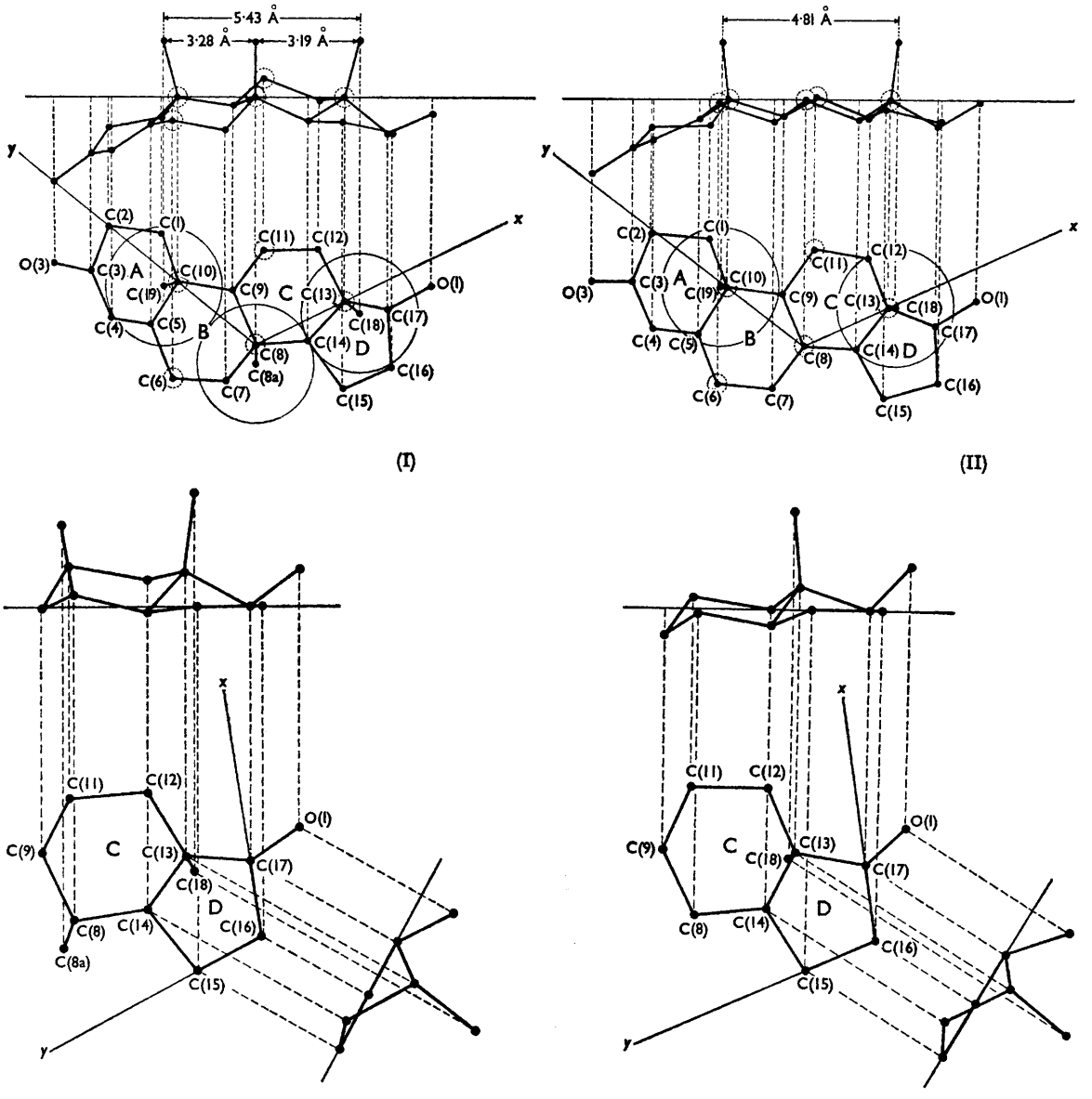
(I) 8β-Methyltestosterone 17β-monobromoacetate (M. Shiro and H. Koyama) $C_{22}H_{31}O_3Br$, M 423·4, orthorhombic, $a = 18{\cdot}51$, $b = 10{\cdot}36$, $c = 10{\cdot}63$ Å, $U = 2036$ Å^3, $D_m = 1{\cdot}378$ g.cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}380$ g.cm.$^{-3}$, space group $P2_12_12_1$.

(II) Testosterone 17β-*p*-bromobenzoate (T. Sato and H. Koyama) $C_{26}H_{31}O_3Br$, M 471·4, monoclinic, $a = 17{\cdot}78$, $b = 7{\cdot}08$, $c = 18{\cdot}05$ Å, $\beta = 95°$, $U = 2261$ Å^3, $D_m = 1{\cdot}385$ g.cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}385$ g.cm.$^{-3}$, space group $C2$.



(I) (II)

The crystal structures of (I) and (II) have been



FIGURE

determined by the three-demensional *X*-ray diffraction method. The intensities were measured with a Hilger and Watts linear diffractometer (with Mo-K_α radiation) equipped with SrO–ZrO_2 balanced filters. The structure was solved by the heavy-atom method and refined by the least-squares method based on 533 reflexions for (I) and 830 reflexions for (II) respectively (rejecting the intensities of lower indices with extremely strong extinction effect and those smaller than three times the standard deviation of the total counts).

At this time, anisotropic temperature factors have been used for the Br atoms only, and no hydrogen atoms have been included. At the present stage of refinement, the *R*-factor of (I) was 8·4% and of (II) 9·1%. In order to obtain

detailed information on the molecular shape and the conformational features of testosterone compounds, we have calculated the displacements from the plane through C(8), C(10), C(13) in the steroid nucleus and C(15), C(16), C(17) in the D-ring (see Figure).

The Figure shows that the molecular conformation (I), which contains the 8β-methyl, is clearly bent, in contrast with the planar overall shape of the ring system of "normal" testosterone (II). The Figure also shows that ring D of (I) has the half-chair and, ring D of (II) the β-envelope conformation. The standard deviations in the intramolecular bond distances and angles are $\sim$0·03 Å and $\sim$2·4° respectively.

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