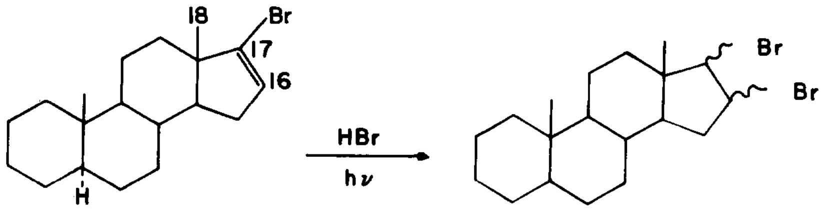
Tetrahedron Letters No. 21, pp. 1747-1748, 1971. Pergamon Press. Printed in Great Britain.

THE CRYSTAL AND MOLECULAR STRUCTURE OF 16β, 17β-DIBROMOANDROSTANE

J. Donohue, N. Mandel, E.B. Stockham, and F.V. Brutcher, Jr.

Department of Chemistry and Laboratory for Research on the Structure
of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received in USA 6 April 1971; received in UK for publication 14 April 1971)

As a part of a series of studies[1] of the conformational properties of ring D in the steroids photochemical addition of hydrogen bromide to 17-bromo-16-androstene[2], I, was carried out:



I II

The product II was obtained, once crystallized (methanol-ethyl acetate) in 59% yield, m.p. 140-142°. The large measured dipole moment of 3.46 ± 0.04 D (in benzene, 30° C) shows that the bromines are in the expected cis configuration, while nmr and ORD spectra suggest, but do not prove, that both H(16) and H(17) atoms are in the α-configuration, and thus that the Br(16) and Br(17) are beta and therefore topside. This tentative assignment is contrary to that simply predicted from an underneath, or α-attack of the bromine free radical, Br. An x-ray diffraction study of II was accordingly undertaken to settle this structural question.

Crystals of II from methanol-ethyl acetate were found to be monoclinic, with $a = 11.528$, $b = 11.128$, $c = 7.645$Å, $\beta = 110.6°$. The calculated density for two molecules per unit cell is 1.514 g cm^{-3}. Systematic absences observed on precession photographs, combined with the fact II is chiral, lead uniquely to space group $P2_1$-C_2^2. All reflections out to $\sin\theta/\lambda = 0.56$ were collected on a Picker four circle automatic diffractometer with CuKα. No absorption correction was applied to the 1,356 observed intensities, which were used to calculate a three-dimensional Patterson function. The positions of the bromine atoms obtained from this function were used to phase a three-dimensional electron density function in which all nineteen carbon atoms were easily recognized.

The positional and anisotropic thermal parameters were refined by full-matrix least squares to an R of 8.5%. An electron density difference map showed no residual density in excess of 1.1 e Å^{-3}, but also no peaks which could be identified with the expected positions of the hydrogen atoms, probably because of absorption errors.

The results show that the two bromine atoms are indeed cis, and in the β configuration. Some other structural details include: the conformation of ring D, which is intermediate between β-envelope and half-chair[1], two carbon-bromine bond distances of 1.94 and 1.96Å, a Br-C-C-Br torsion angle of 29.5°, and an intramolecular Br(17)···C(18) distance of 3.26Å. Intermolecular contacts are normal.

While the unexpected course of the reaction and the details of the structure determination and refinement will be discussed elsewhere, it is clear that any refinement of the possible mechanisms[3-5] of this reaction must take into account the fact that some factor other than an initial steric one by the C(18) angular methyl group on Br has exerted a strong control over the reaction.

This work was supported by the Advanced Research Projects Agency, Office of the Secretary of Defense.

References

1) F.V. Brutcher, Jr. and E. Leopold, J. Amer. Chem. Soc., 88, 3156 (1966).

2) A. Hassner and P. Catsoulacos, J. Org. Chem., 32, 549 (1967).

3) H.A. Goering, Angew. Chem., 70, 479 (1958).

4) P.F. Abell and C. Chiao, J. Amer. Chem. Soc., 82, 3610 (1960).

5) B.A. Bohm and P.I. Abell, Chem. Rev., 62, 599 (1962).