

X-Ray Structure of the Androsta-14,16-diene-Maleic Anhydride Adduct

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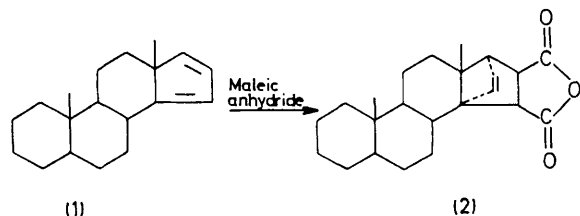
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Summary The Diels-Alder reaction of the reactive androsta-14,16-diene with maleic anhydride has been shown to be a β -attack of the D ring of the molecule.

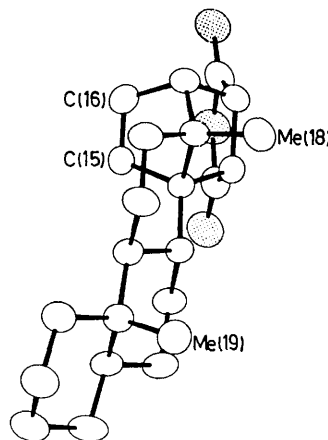
THE Diels-Alder reaction applied to the very reactive androsta-14,16-diene (**1**) using maleic anhydride as dienophile,¹ gives a single compound, m.p. 203 °C, $[\alpha]^{21} + 134^\circ$ (CHCl_3 , c 0.9). The stereochemistry of the adduct (**2**) cannot be established from spectrometric data. A β -side approach of the dienophile was expected to be the most probable, on the basis of initial work in the 17-stabilized pregnane series,² but the other possibility could not be ruled out.³ β -Attack was confirmed by the X-ray analysis of (**2**).



Suitable crystals of the adduct were obtained by slow evaporation of a CHCl_3 solution. The crystals are orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 6.617$; $b = 10.299$; $c = 27.830$ Å and $Z = 4$.

The intensities were collected with a Philips four circle diffractometer, using $\text{Cu-K}\alpha$ radiation with a graphite monochromator and 2033 reflections were recorded above

the background. The structure was solved by direct methods,⁴ by application of the phase function,⁵ and refined by a full-matrix, least-squares method to a final R index of 3.9%.



FIGURE

The general view of the molecule given (Figure) shows clearly the β -endo position of the maleic anhydride fragment and confirms that the upper face of the D ring is less hindered.

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¹ J. C. Beloeil and M. Fetizon, *Compt. rend.*, 1975, **279**, 347.

² P. Naylor and M. C. Whitting, *J. Chem. Soc. (C)*, 1955, 2970.

³ A. J. Solo, B. Singh, E. Shefter, and A. Cooper, *Steroids*, 1968, **11**, 637.

⁴ G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

⁵ C. Riche, *Acta Cryst.*, 1973, **A29**, 133.