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A NEW CYCLIC SILYL DIOXY DERIVATIVE OF A CIS DIOL

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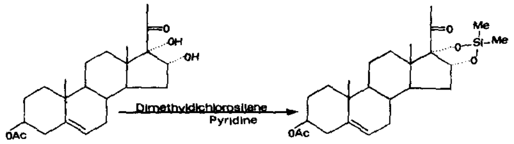
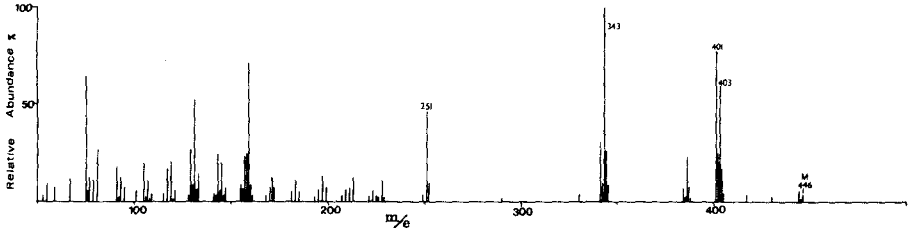
In this laboratory work has recently been undertaken to modify polar steroids with a view to giving them higher volatility for gas chromatography separation and measurement (1). In this connection new cyclic silyldioxy compounds have been formed by reaction of a cis diol with a difunctional silane such as dimethyldichlorosilane. These derivatives are the silicon analogues of acetonides and the term siliconides accurately describes them because they can be considered analogous derivatives of a (hypothetical) "silicone". The importance of these compounds merited the preparation and characterisation of a typical siliconide.



The derivative chosen was that of 3β-acetoxy-16α, 17α-dihydroxypregn-5-en-20-one because the corresponding acetonides of this type of diol are particularly stable (2). 3β-Acetoxy-16α, 17α-dihydroxypregn-5-en-20-one (1g.) was dissolved in dimethyldichlorosilane (1ml.), pyridine (1ml.) and benzene (8ml.); after one hour the solvent was evaporated under vacuum and the residue was leached with anhydrous ether. The ethereal solution was evaporated and the residue was recrystallised from ether-hexane, to give needles (400mg.) m.p. 166-168°. Found C, 67.6; H, 8.7. $C_{25}H_{38}O_5Si$ requires C, 67.2; H, 8.6%. Infrared absorption (CS_2); 1736, 1713, 1240, 1041 and 798 $cm.^{-1}$ The infrared spectrum shows the absence of -OH stretching frequency indicating the involvement of both the 16α and 17α hydroxyl groups in the formation of the derivative. A mass spectrum was run on an A.E.I. MS9 instrument using a solid insertion probe and an ionisation voltage of 70 e.v.



Mass spectrum of 3β-acetoxy-16α, 17α-dihydroxypregn-5-en-20-one dimethyl siliconide.

Metastable Peaks					
m/e Calcd.	m/e Found	Transition	m/e Calcd.	m/e Found	Transition
304.8	304.8	386 ⟶ 343	290.0	290.1	401 ⟶ 341
291.9	292.0	403 ⟶ 343	183.7	183.7	343 ⟶ 251

The mass spectra of siliconides are of interest because of recent research into the fragmentation patterns of both trimethylsilyl ethers (3) and acetonides (4). The striking aspect of the breakdown of this 16α, 17α-siliconide is the ready loss of the 17β-acetyl side chain giving peaks at m/e 403 (M-43) and at m/e 401 (M-2-43). The base peak m/e 343 (M-103) arises from the loss of the 17β-acetyl side chain and the acetate of ring A with associated proton expulsion. Two hydrogen atoms (the origin of which is uncertain) are lost during the fragmentation, giving rise to peaks at m/e 444 (M-2), 401 (M-43-2) and 341 (M-43-60-2). The loss of two hydrogen atoms is also associated with the removal of the silyldioxy group; this is shown by a peak at m/e 251 (M-43-60-92) with no peak at 253. The metastable peak at m/e 183.7 indicates that the transition 343 ⟶ 251 (corresponding to the loss of the silyldioxy group and the two hydrogen atoms is not a stepwise fragmentation.

ACKNOWLEDGEMENTS

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