Unusual Wagner–Meerwein Rearrangement in the Denitroamination of Steroidal 20*R*-Nitroamines: Crystal Structure of 17α-Methyl-12a-methylene-C(12a)-homo-18-nor-(13*S*)-androst-5-en-3β-yl Acetate

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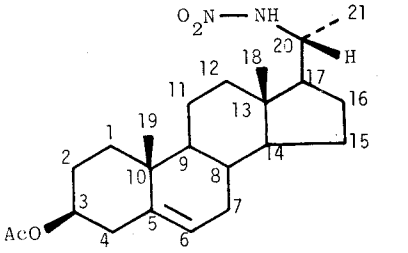
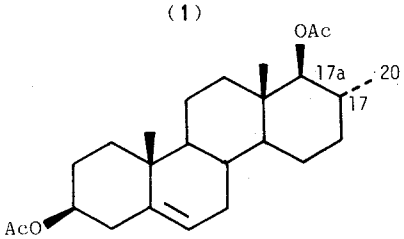
RAIMUNDO FREIRE,[a] JOSE A. SALAZAR,[a] ERNESTO SUÁREZ,[a,*] CARMEN BETANCOR,[b] DANIEL MELIAN,[b] THIERRY PRANGE,[c] and CLAUDINE PASCARD[c]

[a]*Instituto de Productos Naturales Orgánicos, C.S.I.C., La Laguna, Tenerife, Spain*
[b]*Departamento de Química Orgánica, Universidad de La Laguna, La Laguna, Tenerife, Spain*
[c]*Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France*

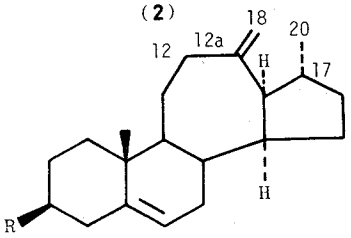
In previous papers[1,2] we have reported that treatment of several steroidal nitroamines with acetic anhydride and pyridine leads to nitrogen free-products. In the study of the denitroamination of the (20*R*)-nitroaminopregnane derivative (**1**) we found[2] that, in addition to substitution and β-hydrogen elimination products, the rearranged compounds (**2**) and (**4**) were formed. The structure of the C-homo compound (**4**) was tentatively assigned on the basis of ^{1}H n.m.r. and mass spectrometry data. Correlation of the ^{13}C n.m.r. chemical shifts of compounds (**3**) and (**4**) with those for compounds (**1**) and (**2**) seems to indicate that the cyclopentane and cycloheptane rings in (**4**) are *cis*-fused.



(**1**)



(**2**)



(**3**) R = OH
(**4**) R = OAc

As the stereochemistry at C-13 and C-17 is important in elucidating the mechanism of this Wagner–Meerwein-type rearrangement, we undertook a single-crystal *X*-ray analysis of (**4**) in order to establish its structure and stereochemistry unequivocally.

Crystal data: $C_{23}H_{34}O_2$, monoclinic, space group $P2_1$, a = 12.282(6), b = 9.466(5), c = 9.189(5) Å, β = 106.9(3)°, Z = 2. The crystal structure was solved by direct methods[6] and using a Patterson search program.[7] Atomic positional and thermal (anisotropic C, O; fixed isotropic H) parameters were refined by full-matrix least-squares calculations to R 0.095 over 1714 statistically significant $I \geq 2.0\sigma(I)$ reflections measured on a Philips PW-1100 four-cycle automatic diffractometer operating with graphite-monochromatized Cu-K_α radiation (λ = 1.5418 Å).

A view of the molecule is given in the Figure. The

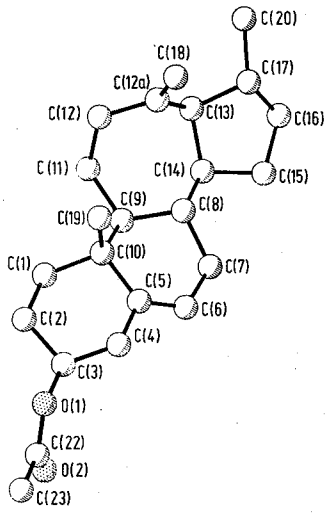


Figure *X*-Ray crystal structure of compound (**4**). Oxygen atoms are dotted

seven-membered ring is in a boat-shaped conformation with C-11 out of the mean plane of the molecule towards the α-face. The methylene C-18 atom adopts an axial position quite similar to that of the C-19 angular methyl group. The C–D ring junction is *cis* with 13- and 14-H both α and axial.

A reasonable mechanism to explain the formation of compounds (**2**) and (**4**) is presented in the full text.

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*To receive any correspondence.

Techniques used: Single-crystal *X*-ray analysis, ^{13}C n.m.r.

References: 9

Scheme: 1

Table 1: ^{13}C N.m.r. chemical shift data of compounds (**1**)–(**4**)

Table 2: Positional parameters and isotropic thermal parameters for the non-hydrogen atoms

Table 3: Anisotropic thermal parameters

Table 4: Positional parameters and fixed isotropic thermal parameters for the hydrogens

Table 5: Interatomic distances and angles

Appendix: Table of observed and calculated structure amplitudes

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