

SIMMONS-SMITH METHYLENATION OF Δ^5 -STEROIDS

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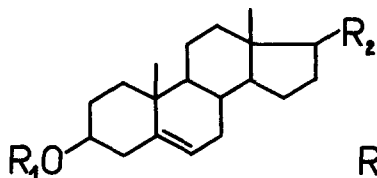
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Simmons-Smith methylenation of 5,6-unsaturated steroids represented by formulae 1-6 has been studied. The conditions used were similar to those described previously by Joska et al.^{1,2} for the analogous B-norsteroid derivatives. Products obtained are represented by formulae 9-12, 16-19, 23, 24, 28 and 29. Each reaction lead to a mixture of the both epimeric cyclo derivatives, and usually better yields were obtained with the acetates than with the alcohols. It has not been observed any influence of the configuration of the hydroxyl group at C₍₃₎ on the stereochemical course of the reaction. These results are different from those described recently by Templeton and Wie³. The configuration of the cyclopropane ring in the adducts has been assigned on the basis of the NMR evidence and also follows from the stereochemical course of the solvolytic reactions of the corresponding mesylates. The cationic species generated on acetolytic conditions from the mesylate 13 having favourable stereochemistry for further reaction with the cyclopropane ring gives rise to the endomethylene derivative 39. On the other hand, the ionic intermediates derived from the mesylates 20 and 30 undergo rearrangement followed by conjugative stabilisation the result being the B-homoderivative 40. By standard reactions the analogues of the physiological active steroids 32-34 and 35-38 have been synthesised.

REFERENCES

1. J. Joska, J. Fajkoš, and F. Šorm: Collection Czech. Chem. Commun. **33**, 2049 (1968).
2. J. Joska, J. Fajkoš, and F. Šorm: Collection Czech. Chem. Commun. **33**, 3342 (1968).
3. J.F. Templeton and C.W. Wie: Can. J. Chem. **49**, 3636 (1971).
4. J. Fajkoš, J. Joska, and F. Šorm: Collection Czech. Chem. Commun. **33**, 3324 (1968).

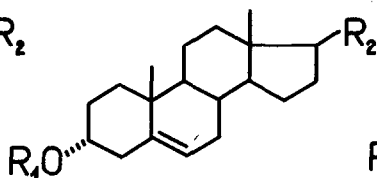


1 $R_1 = H, R_2 = C_8H_{17}$

2 $R_1 = Ac, R_2 = O$

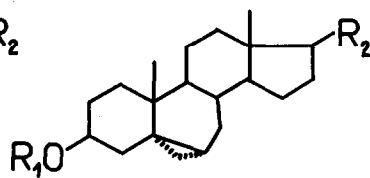
3 $R_1 = Ac, R_2 = C_8H_{17}$

4 $R_1 = Ac, R_2 = OBz$



5 $R_1 = H, R_2 = C_8H_{17}$

6 $R_1 = Ac, R_2 = C_8H_{17}$



7 $R_1 = H, R_2 = OH$

8 $R_1 = H, R_2 = O$

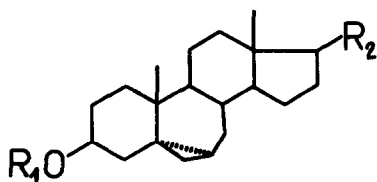
9 $R_1 = H, R_2 = C_8H_{17}$

10 $R_1 = Ac, R_2 = O$

11 $R_1 = Ac, R_2 = C_8H_{17}$

12 $R_1 = Ac, R_2 = OBz$

13 $R_1 = Mes, R_2 = C_8H_{17}$



14 $R_1 = H, R_2 = OH$

15 $R_1 = H, R_2 = O$

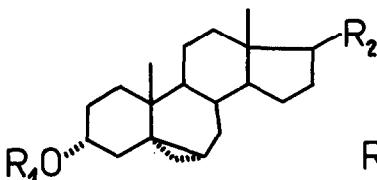
16 $R_1 = H, R_2 = C_8H_{17}$

17 $R_1 = Ac, R_2 = O$

18 $R_1 = Ac, R_2 = C_8H_{17}$

19 $R_1 = Ac, R_2 = OBz$

20 $R_1 = Mes, R_2 = C_8H_{17}$



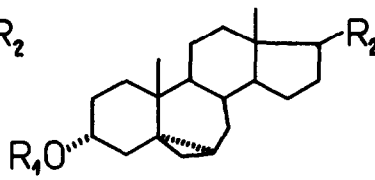
21 $R_1 = H, R_2 = OH$

22 $R_1 = H, R_2 = OBz$

23 $R_1 = H, R_2 = C_8H_{17}$

24 $R_1 = Ac, R_2 = C_8H_{17}$

25 $R_1 = Mes, R_2 = C_8H_{17}$



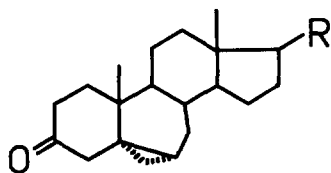
26 $R_1 = H, R_2 = OH$

27 $R_1 = H, R_2 = OBz$

28 $R_1 = H, R_2 = C_8H_{17}$

29 $R_1 = Ac, R_2 = C_8H_{17}$

30 $R_1 = Mes, R_2 = C_8H_{17}$

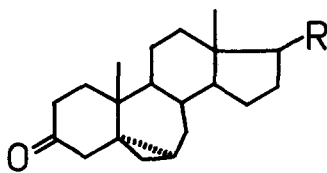


31 $R = C_8H_{17}$

32 $R = OH$

33 $R = O$

34 $R = \begin{matrix} OH \\ \diagdown \\ CH_3 \end{matrix}$

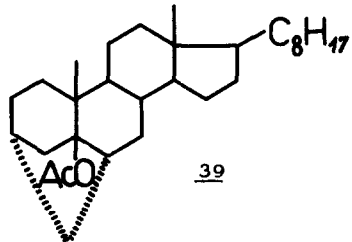


35 $R = C_8H_{17}$

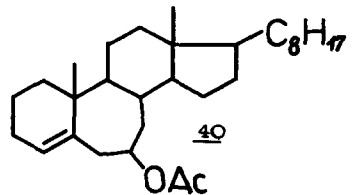
36 $R = OH$

37 $R = O$

38 $R = \begin{matrix} OH \\ \diagdown \\ CH_3 \end{matrix}$



39



40