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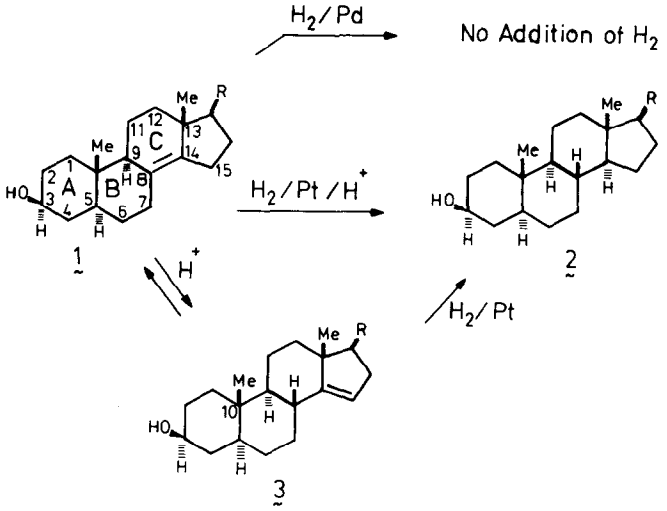
LETTER TO THE EDITORS

Apparent 1,3-Intramolecular Hydrogen Shifts

We have stated that the failure of cholest-8(14)-en-3β-ol, **1**, to be hydrogenated over a palladium catalyst in neutral media indicates that the suprafacial 1,3-sigmatropic shift of hydrogen, proposed by Smith and Swoap (*1*), does not occur in this steroid (*2*). In a recent paper, Smith *et al.* imply that our conclusion, though possibly valid in the compound examined, does not exclude the proposed 1,3-intramolecular shift in other systems such as (+)-apopinene (*3*).



As a general proposition, their assertion cannot be challenged but we suggest that the structural differences between this unsaturated steroid and, for example, cyclohexene or (+)-apopinene, is not great enough to prevent the operation of the Smith–Swoap mechanism in one but not the other system.

Recently, Anderson *et al.* calculated that the suprafacial 1,3-shift is "...forbidden when propylene is adsorbed on a Pt_{18} cluster and that the intramolecular shift observed in catalytic studies must involve coadsorbed allyl and a hydrogen atom" (*4*). The calculated barrier of the disallowed process is 3.4 eV compared to 0.7 eV for hydrogen abstraction to form adsorbed allyl and adsorbed hydrogen. The conclusions reversed earlier support for the Smith–Swoap mechanism, which was based upon an extended Hückel analysis of a cruder model for the transformation (*5*). We amplify our previous argument as follows.

Cholest-8(14)-en-3β-ol, **1**, can by hydrogenated catalytically over platinum only if the reaction medium is sufficiently acidic (*6*). The product is cholestanol, **2**, which has hydrogen attached at C-8 in the β-configuration (*7*). We suggest that this reduction succeeds because the acid catalyst is able to deliver a proton to either face of the double bond. Only if the proton becomes attached to C-8 in the β-configuration, however, is a carbocation formed which can be

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transformed to an isomer of **1** (choles-14(15)-en-3β-ol, **3**) which is hydrogenated. The isomer of cholestanol which has the epimeric configuration at C-8 is not produced because of the increase in internal strain which accompanies the formation of the *cis* configuration at the junction of the B and C rings. Too little of the required unsaturated isomer is formed to compete with the hydrogenation of **3** (see Ref. (*2*)).

If the proposed suprafacial 1,3-hydrogen shift did occur when **1** is adsorbed on palladium, the isomer **3** would be formed and, in the presence of hydrogen, be reduced to cholestanol. We had noted that the only allylic hydrogen atoms in **1** which exchange readily with D_2 over palladium black in ethanol are those with the α-configuration. The β-hydrogens attached at C-7 and C-15 are unaffected. The slower rate of exchange at C-15 relative to exchange at C-8 was interpreted by us to imply a difference in the stability of the allylic intermediates. The difference in energy, however, is less than 1.4 kcal/mol because the rates of exchange differ by less than a factor of 10.

The phenomena to which the Smith–Swoap mechanism have been attributed appear to be rapid processes which must have small activation energies. For example, Ledoux *et al.* attribute to this mechanism the isomerization of butenes without exchange with D_2 on a nickel catalyst (*8*). They note that the mechanism is increasingly favored over isomerization with exchange as the temperature is lowered. To make such a facile process unobservable by a change in structure requires that the change cause a very large increase in the activation energy. Such an effect would be unprecedented for an intramolecular isomerization in which the involved groups differ as little in geometry as those in the steroid molecule, **1**, and apopinene.

We suggest that alkene isomerization without exchange with D_2 or perdeuteropropane over metal catalysts (Ni, Fe, Pd) indicates a situation in which the hydrogen atom which is abstracted from the alkene exchanges with D_2 or C_3D_8 more slowly than the rate of reassociation and the desorption of the isomeric alkene (*9*). The experimental conditions which are reported to increase the proportion of unexchanged isomers are lowered temperatures, a low pressure of D_2 (D_2 is undetected when perdeuteropropane is the source of deuterium on Pd films at 150–200°C) (*10*), and a few Torr of alkene which is more than enough to saturate the surface. The surface is likely to hold very little weakly bound deuterium and be covered by carbonaceous material, conditions which could slow the surface migration of H or D. Apparently, some of the reaction centers at which isomerization can occur are isolated from one another as well as from centers at which exchange, isomerization, and the addition of D_2 can take place (or only exchange and isomerization if perdeuteropropane is the deuterium source) (*11*).

REFERENCES

1. Smith, G. V., and Swoap, J. R., *J. Org. Chem.* **31,** 3904 (1966).
2. Ku, V., Palmer, J., Siegel, S., and Clough, R., *J. Catal.* **44,** 449 (1976).
3. Smith, G. V., Molnar, A., Khan, M. M., Ostgard, D., and Yoshida, N., *J. Catal.* **98,** 502 (1986).
4. Anderson, A. B., Kang, D. B., and Kim, Y., *J. Amer. Chem. Soc.* **106,** 6597 (1984).
5. Anderson, A. B., *J. Chem. Phys.* **63,** 4430 (1975).
6. Fieser, L., and Fieser, M., "Steroids," pp. 271–274. Reinhold, New York, 1959.
7. The designation of the configuration of a group which is attached to the steroid nucleus is relative to the attachment of the methyl group at C-10, α- being trans or anti, β- being cis or syn.
8. Ledoux, M. J., Gault, F. G., Bouchy, A., and Roussy, G., *J. Chem. Soc. Faraday Trans. 1* **76,** 1547 (1980). (Reference (*3*) lists additional reports of this research group.)
9. This possibility was recognized in the early papers on this subject by the late Professor Gault and his associates. See, for example, Hilaire, L., and Gault, F. G., *J. Catal.* **20,** 267 (1971).
10. Tourade, R., Hilaire, L., and Gault, F. G., *J. Catal.* **32,** 279 (1974).
11. Siegel, S., Outlaw, J., Jr., and Garti, J., *J. Catal.* **52,** 102 (1978).

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