Effect of Raney Nickel on A/B Ring Fusion of Steroids

Kleiderer and Kornfeld¹ converted cholesterol, a 3-hydroxy- Δ^5 -steroid, into Δ^4 -cholestenone by heating cholesterol in toluene solution with Raney nickel in presence of cyclohexanone as hydrogen acceptor. Later, Romo² described the formation of 3-keto- Δ^4 -steroids from the 3-hydroxy- Δ^4 -steroids by the action of the same catalyst in presence of acetone or methyl ethyl ketone as hydrogen acceptor.

Chakravarti and Robinson³ reported the conversion of strychnine into neostrychnine in presence of Raney nickel in boiling xylene solution. This isomerization may be regarded as a dehydrogenation *cum* hydrogenation reaction. Proceeding similarly, in the present case, diosgenin was heated under reflux in xylene solution in presence of Raney nickel, but no appreciable change could be noticed. On repeating the experiment at a higher temperature, using a high-boiling solvent like *p*-cymene in place of xylene, diosgenin was found to be converted mostly into Δ^4 -dehydrotigogenone, $C_{27}H_{46}O_3$, m.p. 185–186°, $[\alpha]_D^{23}$ nil ($CHCl_3$), $\lambda_{max}^{alc.}$ 243 m μ (log ϵ 4.28), oxime m.p. 224° (decomp.), semicarbazone m.p. 247° (decomp.). When excess of Raney nickel was used in the above reaction, the major product was, however, found to be tigogenone, $C_{27}H_{44}O_3$, m.p. 205–206°, $[\alpha]_D^{22}$ –54° ($CHCl_3$), oxime m.p. 254–256° (decomp.), semicarbazone m.p. 263° (decomp.). Similarly, cholesterol was converted into Δ^4 -cholestenone in presence of the catalyst in boiling *p*-cymene solution. In presence of excess of the catalyst, the product obtained was cholestanone. Extending this reaction to other steroids, it was found that hecogenin gave hecogenone, stigmasterol gave Δ^{22} -dehydrositostanone and β -sitosterol gave sitostanone. It is significant that in these transformations of the 3-hydroxy steroids into the 3-keto steroids, unlike those carried out by Kleiderer and Kornfeld¹, and Romo², no hydrogen acceptor like cyclohexanone or methyl ethyl ketone was used.

All the compounds mentioned above have *trans* configuration with regard to the A/B ring fusion. An interesting fact was observed when the reaction was applied to steroids having A/B-*cis* configuration. In all such cases the corresponding *trans* compounds were obtained, indicating the stereo-specificity of the effect of Raney nickel on the A/B ring fusion. Thus both smilagenone and *epi*-smilagenin⁴ under the above conditions gave tigogenone, sarsasapogenin gave *neo*-tigogenone and coprostanone gave cholestanone.

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Elution Sequence as a Function of Temperature in Gas Chromatography

THE main hydrocarbons present in the essential oil of hop (*Humulus lupulus* L. var. Fuggles) are myrcene, farnesene, caryophyllene and humulene¹ (Fig. 1). In an attempt to find the best conditions for quantitative assay of these substances, hop oil hydrocarbon fraction was examined by gas chromatography over a range of column temperatures. It was noticed that when the temperature of analysis was decreased from 150° C. to 125° C., the separation of caryophyllene and farnesene, incomplete at 150° C., became non-existent at 125° C. However, when the analysis was carried out at 175° C. complete separation was achieved. This is the converse of the expected

Fig. 1. Gas chromatogram of hydrocarbon fraction of essential oil of hops. 150° C. 'Apiezon L' 10 per cent on 'Cellite'. 50 ml./min. argon flow-rate

Fig. 2. Changes in relative retention times for farnesene, (□), and caryophyllene, (○), on 'Apiezon L'. Humulene = 1.00