

# HOMOALLYL REARRANGEMENT IN THE ALKYLATION OF HOMOALLYL ESTERS BY TRIALKYLALANES

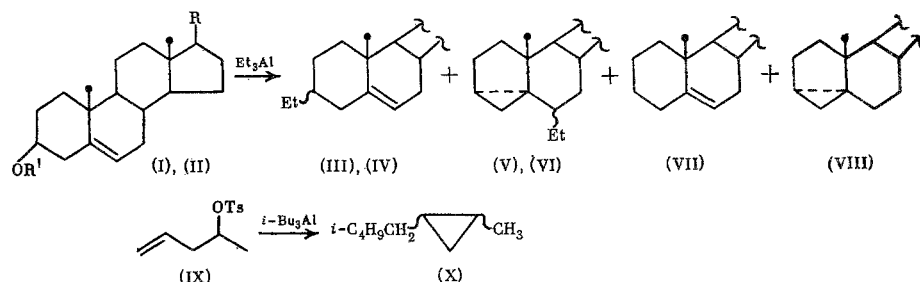
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We established the occurrence of a homoallyl rearrangement during the reaction of tosylates and acetates of homoallyl alcohols with trialkylalanes.

The reaction of 3 $\beta$ -tosyloxy- $\Delta^5$ -cholestene (I) and androstene (II) with triethylaluminum [(I) or (II):Et<sub>3</sub>Al = 1:3, CH<sub>2</sub>Cl<sub>2</sub>, 25°C] produces steroids III-VI with a quantitative yield. The V:III and VI:IV ratios are approximately equal to 6:1. Under these conditions cholesterol (about 40%) forms from cholesterol acetate, and reduction products of the acetate, viz., i-cholestane (VIII) and  $\Delta^5$ -cholestene (VII) are observed in the hydrocarbon fraction along with the alkylation products (65%).

The reaction of methylallylcarbonyl tosylate (IX) with triisobutylaluminum produces hydrocarbon X with a 74% yield.



R = Ts, Ac, R = C<sub>8</sub>H<sub>17</sub>(I); H(II). R = C<sub>8</sub>H<sub>17</sub> (III), (V), (VII), (VIII); H(IV), (VI).

The known steroids VII and VIII were obtained by a back synthesis by the reduction of tosylate (I) by LiAlH<sub>4</sub>. Steroids III, IV, and V were identified in the form of the epoxides according to their PMR spectra ( $\delta$ , ppm): 2.87 (d, H<sup>6</sup> in  $\alpha$ -hydroxy, J<sub>6,7</sub> = 4.0 Hz), 3.0 (d, H<sup>6</sup> in  $\beta$ -hydroxy, J<sub>6,7</sub> = 2.5 Hz). Data from IR and mass spectrometry were also used.

6-Ethyl-3,5-cyclocholestane (V), n<sub>D</sub><sup>20</sup> 1.5080, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +35.4° (7.07, CHCl<sub>3</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3060. PMR spectrum ( $\delta$ , ppm): 0.09 (d.d, 1H, C<sup>4</sup>, J<sub>gem</sub> = 5.0, J<sub>3,4</sub> = 8.0 Hz), 0.40 (d.d, 1H, C<sup>4</sup>, J<sub>gem</sub> = 5.0, J<sub>3,4</sub> = 3.8 Hz), 0.70 (s, 3H, C<sup>18</sup>), 0.83 (s, 3H, C<sup>19</sup>). m/z 398.

6-Ethyl-3,5-cycloandrostane (VI), n<sub>D</sub><sup>20</sup> 1.5179, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +13.5° (4.44, CHCl<sub>3</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3060. PMR spectrum ( $\delta$ , ppm): 0.09 (d.d, 1H, C<sup>4</sup>, J<sub>gem</sub> = 4.8, J<sub>3,4</sub> = 8.0 Hz), 0.40 (d.d, 1H, C<sup>4</sup>, J<sub>gem</sub> = 4.8, J<sub>3,4</sub> = 3.8 Hz), 0.74 (s, 3H, C<sup>18</sup>), 0.83 (s, 3H, C<sup>19</sup>). m/z 286.

1-Methyl-2-isopentylcyclopropane (X), bp 113-115°C, n<sub>D</sub><sup>20</sup> 1.4135. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3080. PMR spectrum ( $\delta$ , ppm): 0.08 m and 0.40 m (2H, C<sup>3</sup>), 0.70-1.75 (broadened multiplet, 16H, CH<sub>3</sub>, CH<sub>2</sub>, CH). m/z 126.