

THERMOLYSIS OF ELEMOL. SILVER (I) ION CATALYZED

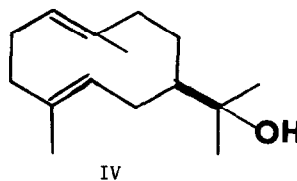
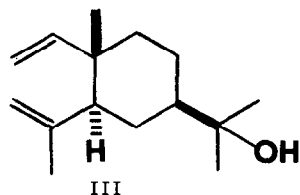
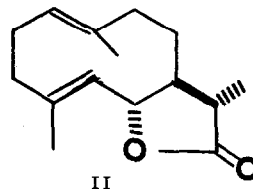
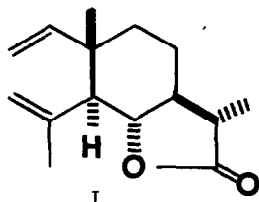
CONVERSION OF ELEMOL TO EUDESMOLS

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Recently the thermal reversibility of saussurea lactone (I) and dihydrocostunolide (II) was reported from this laboratory¹. This study has now been extended to elemol (III) with an objective of preparing hedycaryol² (IV) required in connection with another research project. Although we were not successful in isolating analytically pure hedycaryol, the results obtained during the thermolysis of elemol, especially silver (I) ion catalyzed carbocyclization of elemol (III) to eudesmols (V, VI) are worthy of preliminary communication. Despite several transformations³ of elemol known in the literature, the facile rearrangement reported herein constitutes the first example of a direct correlation of elemol (III) to eudesmols (V, VI).



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Heating of GLC* pure elemol (retention time: 50.4 min) in an atmosphere of nitrogen for 15 min at 210-220⁰ gave a solid, the GLC analysis of which at 110⁰,** besides elemol, revealed the presence of a second constituent (retention time: 76.5 min) comprising approximately 0.5% of the total area of gas chromatogram. Based on our thermolytic experiments on I, II and related compounds, the thermolysate was presumed to represent an equilibrium mixture of elemol and the second constituent, which *a priori* was the desired hedycaryol (IV). The crude thermolysate dissolved in ethyl acetate was exhaustively extracted with 20% aq. AgNO₃ to yield a mixture of 95% elemol and 5% hedycaryol in the organic phase. Further enrichment by chromatography over AgNO₃-silica gel column afforded a fraction containing elemol III (N.M.R. spectrum: 4.12, and 8.18 τ) and hedycaryol IV (N.M.R. spectrum: 8.40 τ) in approximately equal proportion.† Because of the small quantity of this fraction further purification was not possible.††

Elemol-silver nitrate adduct or elemol containing a trace of silver nitrate on heating at 210-220⁰ in an atmosphere of nitrogen for 15 min gave a mixture of products (GLC analysis). The crude thermolysate after extraction with 20% aq. AgNO₃ (*vide supra*) yielded a mixture of compounds in the organic phase, the N.M.R. spectrum of which revealed the presence of elemol III (4.15 and 8.28 τ), hedycaryol IV (8.41 τ), α-eudesmol V (4.67 and 9.22 τ) and β-eudesmol VI (5.53 and 9.30 τ). Chromatography of this mixture over AgNO₃-silica gel column led to the isolation of α-eudesmol V (0.8%

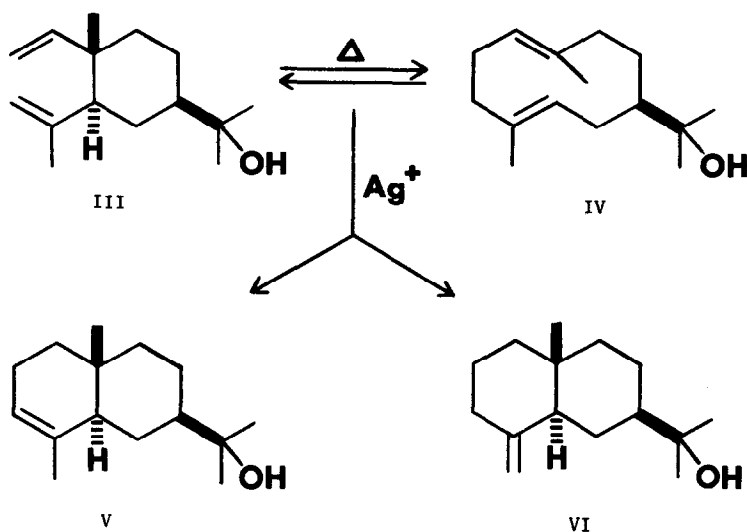
* All GLC analyses were carried out on a Mikrotek Gas Chromatograph Model MT-220 with flame ionization detector using a 5% SE-30 metal column (6 ft. x 0.25 in.) with 50 ml of helium/min as a carrier gas.

** Jones and Sutherland² have successfully conducted the gas chromatography of these compounds at 105⁰.

† N.M.R. spectra were obtained in CDCl₃ with a Varian Associates HA-60 spectrometer using TMS as internal standard. The N.M.R. spectrum of this fraction was completely devoid of any signal in the region characteristic for angular methyl of a bicyclic sesquiterpene, e.g., α-eudesmol V (9.22 τ) and β-eudesmol VI (9.30 τ), *vide infra*.

†† The reported short half life² of approximately 3 hrs at 100⁰ for hedycaryol (IV) could presumably be an additional contributory factor toward our experimental difficulties in its purification.

yield) and β -eudesmol VI (0.8% yield), rigorously identified by means of N.M.R. and G.L.C. comparisons with the authentic specimens. Thus, the silver (I) ion induced rearrangement of elemol to eudesmols could either proceed directly or *via* hedycaryol or both as depicted below:



In summary, to the best of our knowledge, silver (I) ion catalyzed transformation involving π -bonds reported herein is without any precedent.* The co-occurrence of elemol (III) and eudesmols (V, VI) in the citronella oil of the Ceylon variety** further suggests the catalytic role of heavy metal ions, besides enzymes, in the carbocyclization of olefinic substrates in nature. Investigations of this type of metal ion induced isomerizations will continue to be made.

* Recent reports⁴ have given evidence that molecules endowed with highly strained σ -bonds can experience skeletal rearrangements under the influence of silver (I) ion.

** Unpublished results secured by J. E. McCloskey. For full experimental details, see reference 5.

Acknowledgments

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