Supernumerary larval molts in *Galleria mellonella* could be produced by injection of 2000–4000 TU of each compound per animal. This dosage level is equivalent to that required to obtain a similar response with the natural juvenile hormone. Further biological experiments with these compounds in insects of different orders are currently in progress.

Acknowledgments. The authors are indebted to Dr. C. C. Sweeley, Department of Biochemistry, University of Pittsburgh, for providing the mass spectra. These studies were aided by grants from the National Science Foundation (GB-5475 and GB-6244) and the National Institutes of Health (GM-13598-02) to the University of Wisconsin.

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Received July 28, 1967

Steroids and Steroidases. V.[1] On the Mechanism of Action of the Δ^5-3-Ketoisomerase of *Pseudomonas testosteroni*

Sir:

During our investigations on the Δ^5-3-ketoisomerase of *P. testosteroni*, which effects the isomerization of Δ^5-3-keto steroids to the corresponding Δ^4-3-ketones, it became of interest to compare the acid-, base-, and enzyme-catalyzed reactions.

Previous studies on base-catalyzed isomerizations of Δ^5-3-keto steroids have been hindered by multiple product formation.[2] However, when solutions of buffers, such as Tris–HCl, pH range 8.5–9, or aqueous sodium hydroxide, pH >10, were used, clean isomerizations to Δ^4-3-ketones were observed. Using aqueous sodium hydroxide solutions in the pH range 10.6–11.7, androst-5-ene-3,17-dione isomerized with over-all second-order kinetics, the reaction being first order with respect to both steroid and hydroxide ion concentrations.

Loss of the C_4 hydrogen atom has been shown to be the rate-determining step for both acid- and enzyme-catalyzed isomerizations of androst-5-ene-3,17-dione.[3] A comparison of the pH 10 isomerization of androst-5-ene-3,17-dione with that of its 4,4-dideuterio analog showed a primary kinetic isotope effect of 3.2, thus indicating C_4 proton abstraction to be rate determining for the base-catalyzed reaction also.

The Δ^5-3-ketoisomerase of *P. testosteroni* is the most active enzyme known,[4] and the rates of the acid-, base-, and enzyme-catalyzed reactions of androst-5-ene-3,17-dione are in the ratio 1:700:(17 × 10⁶). In an attempt to ascertain where the enzymic isomerization gains its advantage over those catalyzed by acid and base, the activation parameters were determined.[5] As seen from the values recorded in Table I, the facility of the enzymic process is mainly due to an extremely low enthalpy of activation. The differences in the entropies of activation for the three processes are not very great, and the $\Delta S^{\ddagger}$ value of -16.8 cal deg^{-1} mole^{-1} for the enzymic catalysis is consistent with the development of charge separation in the transition state as required by the mechanism proposed by Ringold and Malhotra.[3]

Table I. Activation Parameters for the Isomerization of Androst-5-ene-3,17-dione[a]

	Catalyst		
	HCl, pH 0.88[b]	Tris-HCl, pH 8.82[b]	Enzyme[c]
Enthalpy of activation, $\Delta H^{\ddagger}$, kcal mole^{-1}	14.0 ± 0.1	11.4 ± 0.1	5.0 ± 0.1
Entropy of activation, $\Delta S^{\ddagger}$, cal deg^{-1} mole^{-1}	-19.6 ± 0.4	-15.5 ± 0.4	-16.8 ± 0.4

[a] Data obtained with 1.6% aqueous methanol solutions and a steroid concentration of 0.05 μmole/ml. [b] Temperature range 15–40°. [c] Temperature range 15–30°.

Acknowledgments. We are grateful to the National Research Council of Canada and to the Province of Ontario, Department of University Affairs, for financial support of this work, and to the Canadian Universities Foundation for the award (to D. C. W.) of a Commonwealth Scholarship. We also thank Dr. P. Talalay for providing us with a starter culture of *P. testosteroni* and Mr. D. G. Glass for its large-scale growth.

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(5) Direct comparison of the activation parameters for the acid-, base-, and enzyme-catalyzed reactions is considered to be reasonable since the same rate-determining step is involved in each case.

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Received July 24, 1967

Correlations between Carbon-13 and Boron-11 Chemical Shifts. I. The Alkanes and Analogous Boron–Nitrogen Compounds[1]

Sir:

Chemical shift data for carbon-13 and boron-11 nuclei are not very extensive because of a number of well-known features which are unfavorable toward magnetic resonance measurements.[2] A clear correlation of chemical shift between the two nuclei in related types of compounds would have considerable value from both a practical as well as a theoretical viewpoint.

The amine boranes and the closely related compounds, the diborazanes and cycloborazanes, may be viewed as the inorganic analogs of the alkanes in which one or more carbon–carbon linkages have been replaced by a corresponding number of isoelectronic boron–

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(1) The support of the University of North Carolina Materials Research Center under Contract SD-100 with the Advanced Research Projects Agency and of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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