

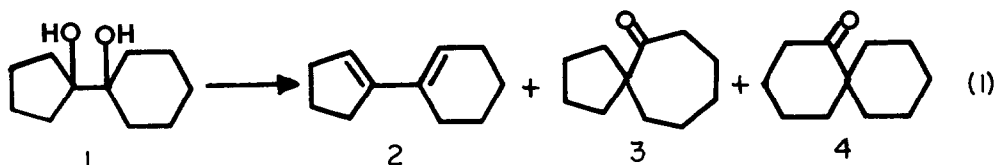
RING SIZE EFFECTS. II¹. AN EXAMINATION
OF CONDITIONS FOR THE PINACOL REARRANGEMENT

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ABSTRACT: The pinacol rearrangement, when performed at 0°C with concentrated sulfuric acid results in products reflecting rearrangement rather than dehydration. Also, under these conditions secondary skeletal reorganization does not occur.

Although there are a plethora of inspirational and elaborate studies to unmask the mechanistic mysteries associated with the pinacol rearrangement², it is becoming increasingly evident that the greatest obstacle to understanding the reaction is a well-defined reaction condition³. This was made abundantly clear by the work of Christol⁴, which demonstrated that product composition varied with the conditions utilized. As a necessary prelude to our attempt to assess ring-size effects in the pinacol rearrangement, we were forced to establish reaction conditions which would result in meaningful data. This paper reports these results.

Sands, in an early attempt to evaluate ring-size effects for the rearrangement, utilized 25% sulfuric acid at reflux as the reaction media⁵. The composition of products from this work consisted of the expected spiranones; but, diene made up a large portion of the product. Based on our earlier use of concentrated sulfuric acid at 0°C, we were encouraged to pursue the question of reaction conditions on the rearrangement (equation 1).



A first problem to be answered related to product stability. It is known that the products of pinacol rearrangement can suffer secondary skeletal reorganization⁶, and we have previously noted this in a highly strained spiranone¹. It appeared that at higher temperature and dilute sulfuric acid, the spiranone, (4), was the major product. Is this a result of higher temperature or the water content? We have examined sulfuric acid concentrations from 25% to 92% and find that at 0°C no secondary rearrangement of 3 to 4 occurs; however, at 97°C there is conversion at all acid concentrations.

We next examined the effects of acid concentration on products in the reaction (figure 1).

These combined experiments dramatically indicate that for the examination of subtle effects, such as ring-size, in the pinacol rearrangement, concentrated sulfuric acid at 0°C will be the reaction condition of choice. At this juncture we suggest that under these conditions, a large percentage of the product will reflect kinetic control and should give a more useful view of the mechanism for this rearrangement.

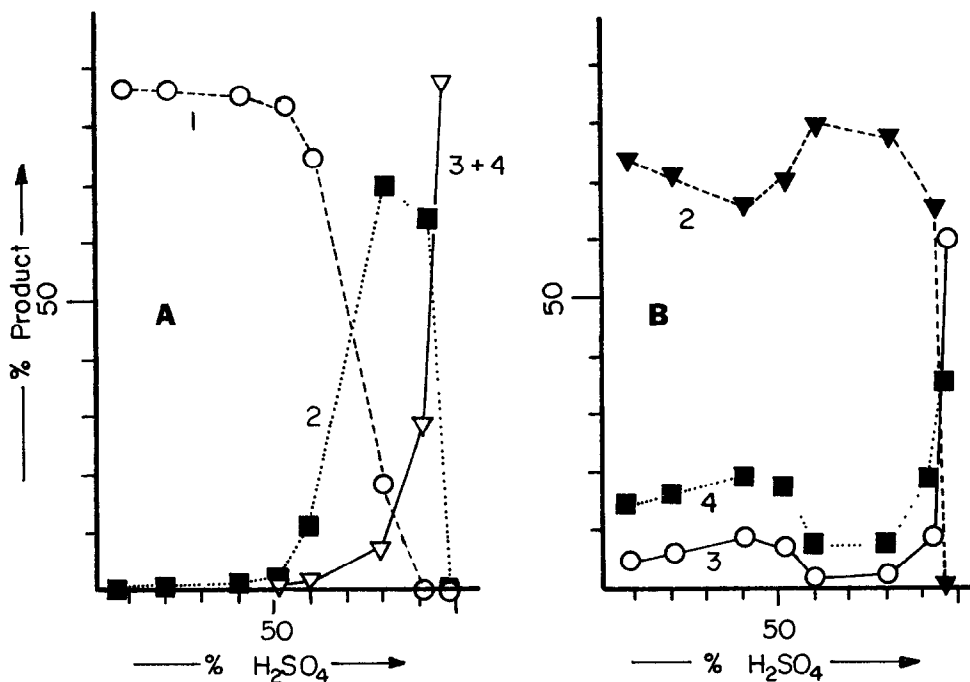


Figure 1. A) The Effects of Acid Concentration on the Reaction Profile*

B) The Effects of Acid Concentration on Product Composition*

*Data for the figure are from two independent analyses.

REFERENCES AND NOTES:

- For Part I of these studies, see:
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- For a well-written, but somewhat dated account of the pinacol rearrangement, see either:
 - C.J. Collins, *Quart. Rev.*, **14**, 357 (1960).
 - Y. Pocker, in *Molecular Rearrangements*, Vol. 1, edited by P. deMayo, Interscience, New York, 1963, pp. 15-25.
- H. Christol, A.P. Krapcho, and F. Pietrasanta, *Bull. Soc. Chim. Fr.*, 4059 (1969).
- A concise statement of the problems can be found in ref. 2a. See also ref. 1.
- R.D. Sands, *Tet.* **21**, 887 (1965).
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- D.G. Botteron and G. Wood, *J. Org. Chem.*, **30**, 3871 (1965). This work on ring-size effects, carried out with concentrated sulfuric acid at 0° , is partially rationalized on the results from a study with Sands^{5b}, utilizing 25% sulfuric acid at reflux. The results of our study demonstrating the possible problems associated with either using dilute acid or higher temperatures, require that the rationalizations be re-examined.

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