Tetrahedron Letters No. 29, pp 2673 - 2676.
0040-4039/79/0715-2673$02.00/0

RING SIZE EFFECTS.III[1] CARBONIUM ION STABILITY AS A FACTOR IN THE COURSE OF THE PINACOL REARRANGEMENT

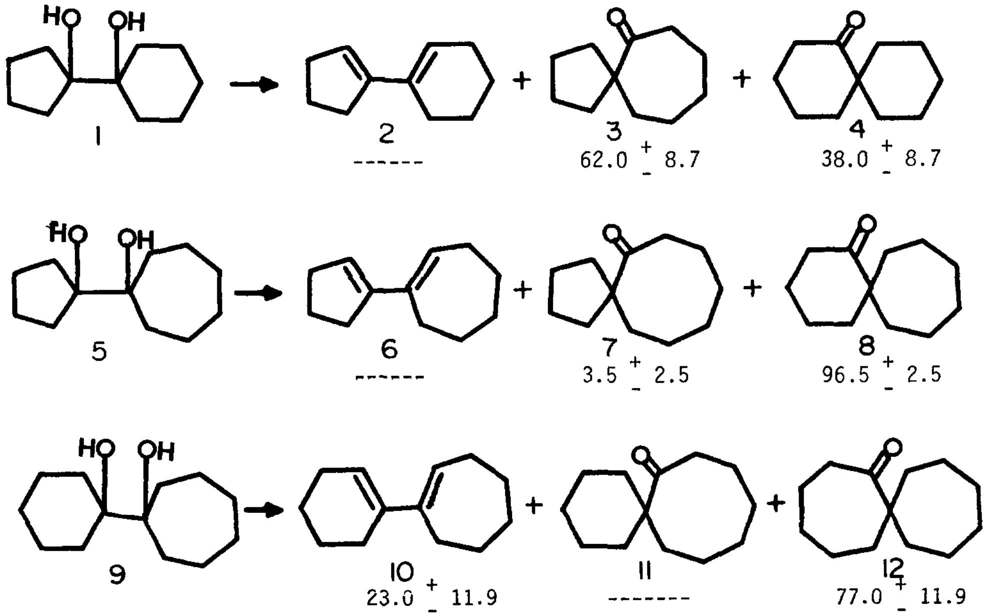
Bradford P. Mundy*, Ramanuajan Srinivasa, Rodney D. Otzenberger and A. Richard DeBernardis
Chemistry Department, Montana State University, Bozeman, MT 59717

ABSTRACT: The formation of the initial carbonium ion in the pinacol rearrangement will be the major factor in determining product composition when the reaction is carried out at 0°C with concentrated sulfuric acid.

With the observation that the reaction conditions of concentrated sulfuric acid at 0° gives excellent conversion to spiranones with minimal alkene formation[1], we embarked on an evaluation of the effect of ring size on the course of the pinacol rearrangement. The results of duplicate experiments are presented in table I.

Table I

PINACOL REARRANGEMENT



From these data, particularly with the assurance that these conditions are not causing secondary rearrangement, the following trends are noted.

$$C_6 \rightarrow C_7 > C_5 \rightarrow C_6;\ C_5 \rightarrow C_6 > C_7 \rightarrow C_8;\ C_6 \rightarrow C_7 > C_7 \rightarrow C_8$$

Whereas the data from the C_5-C_6 pinacol under the conditions utilized in these experiments are substantially different from those reported by Sands[2], the results with 5 and 9 are quite similar. Indeed, the greatest difference in the two investigations are:
(1) Our experiments were performed on pure pinacols, thus eliminating any chance for wrong interpretation of the results. (2) Our experiments were performed under conditions which precluded secondary rearrangement; thus, we are witnessing chemistry of the pinacols. (3) Our experiments were performed in duplicate, ensuring statistical validity to the results. With these facts in mind, how can we interpret these data?

From examination of ring strain data[3], $C_6 < C_7 < C_5 < C_8$. Thus, the preferential formation of 8 and 12 are consistent with strain arguments; however, the formation of 3 is not. The preferential formation of 4 under conditions of 25% sulfuric acid at reflux is consistent with secondary rearrangement to the more stable product[1].

An examination of relative reactivities of cycloalkyl tosylates[4] to acetolysis demonstrates the ease of carbonium ion formation to be $C_7 > C_5 > C_6$. Similarly, relative reactivities of cycloalkanones to sodium borohydride demonstrate the tendency to maintain sp^2 hybridization to be in the same order[5]. If we extend these ideas to the rearrangements listed in table I, we observe the following: (1) Carbonium ion formation of C_5 in 1 should be favored, resulting in 3 as the major product. (2) For 5, carbonium ion formation of C_7 should be favored, resulting in 8 as the major product. (3) Carbonium ion formation of C_7 in 9 should be favored, giving 12 as the major product. Thus, we find that under the conditions prescribed, carbonium ion formation can be utilized, *without exception*, to predict the major products of the pinacol rearrangement. We view this as an important reason to suggest that future studies of this rearrangement be carried out under the conditions described.

Since we would expect 8 to be the major product from 5, whether invoking the ideas of carbonium ion stability or ring strain, how would changes in reaction conditions be reflected in product composition? Table II delineates the results of such a study.

TABLE II

REACTION CONDITIONS AND PRODUCT COMPOSITION

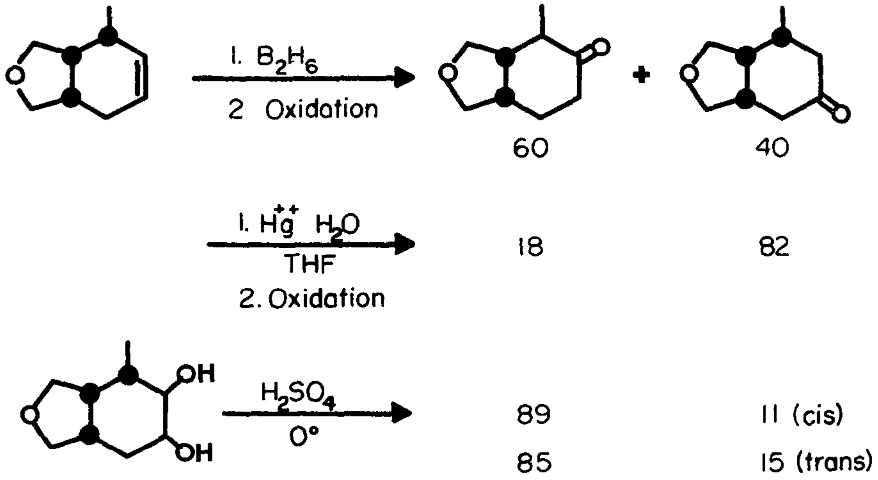
5 $\longrightarrow$	**6**	+	**7**	+	**8**
Conc. sulfuric acid, 0°	0.0		5.2		94.8
75% sulfuric acid, 0°	0.0		3.6		96.4
45% sulfuric acid, 0°	18.9		1.0		80.1
25% sulfuric acid, 0°	29.9		0.8		69.3

In this study, too, we observe that greatest spiranone formation occurs in the absence of water; and that the major spiranone is always 8. In our previous work we noted that the more stable spiranone is formed with 25% sulfuric acid; thus, supporting our rationalizations.

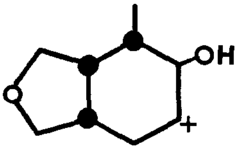
As a consequence of other work performed in our laboratory, we had the available substrates and products to compare hydroboration, oxymercuration and pinacol rearrangement in the same series. Although of admittedly different mechanisms, the first two reactions have received general recognition as being AntiMarkownikoff and Markownikoff hydration techniques, respectively. These terms carry a connotation of carbonium ion characteristic, and it seemed of interest to compare the pinacol rearrangement to these reactions (Table III).

TABLE III

COMPARISON OF PINACOL REARRANGEMENT, OXYMERCURATION, AND HYDROBORATION



These data for the pinacol rearrangement would require as the preferred carbonium ion



Greater stability of positive charge at this carbon atom is consistent with the data derived from both the hydroboration and oxymercuration studies, and reinforces the notion that carbonium ion formation from the pinacol, not alcohol basicity or product stability, will be the driving force directing the course of the reaction when it is carried out at 0^o with concentrated sulfuric acid. Future work from our laboratory will attempt to examine how subtle steric and stereochemical features can be expressed in the course of the reaction.

ACKNOWLEDGEMENT:

We take this opportunity to express our acknowledgement of the assistance of Prof. A. Paul Krapcho for his kind donation of authentic samples of the spiranones examined in this study.

REFERENCES AND NOTES:

(1) B.P. Mundy and R. Srinivasa, preceding paper.

(2) R.D. Sands, Tet., 21, 887 (1965).

(3) E.L. Eliel, N.L. Allinger, S.J. Angyal and G.A. Morrison, Conformational Analysis, Interscience, 1967, New York, page 193.

(4) A Streitwieser, Jr., Solvolytic Displacement Reactions, McGraw-Hill, New York, 1962 page 95.

(5) H.C. Brown and K. Ichikawa, Tet., 1, 221 (1957).

(Received in USA 20 February 1979)