

THE CHROMIUM VI OXIDATIVE CLEAVAGE OF BRIDGEHEAD ALCOHOLS

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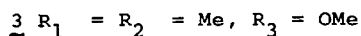
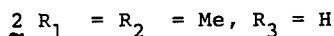
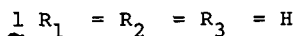
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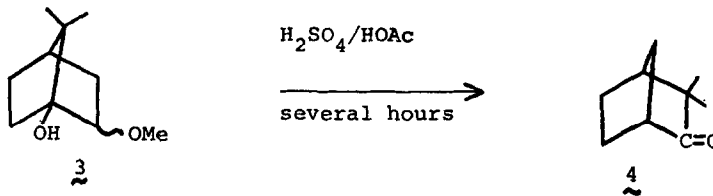
It has been previously demonstrated¹ that only the intermediate oxidation states of chromium may cause oxidative cleavage of certain secondary alcohols. Chromium VI may reasonably be expected to accomplish a like cleavage if the substrate alcohol is sufficiently reactive. Recently, Roček, and Radkowsky² have reported the chromic acid oxidation of 1-methyl cyclobutanol, which they claim to be the first example of direct oxidation of a tertiary alcohol by hexavalent chromium. We now report three cases of bridgehead alcohols in which the structural features are such that the alcohols neither dehydrate nor rearrange prior to undergoing direct oxidation by chromium VI.

Bicyclic systems have proved³ of great value in chromic acid studies. Bridgehead systems should prove similarly valuable in this field. The [2.2.1] bicyclic alcohols 1 and 2 were known and 3 proved⁴ readily accessible by the alkaline hydrogen peroxide oxidation of the bridgehead boronic acid.

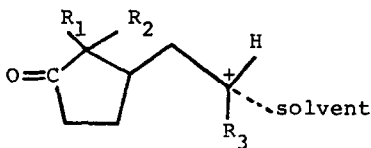


It seemed that such systems should provide the necessary reactivity and indeed, this expectation was realized.

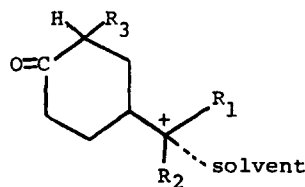
These alcohols are slow to react in acetate buffered chromic acid. In unbuffered 86% aqueous acetic acid they all react at a convenient rate to yield oxidized cleavage products without any acid catalyzed rearrangement products. For example, **3** does not yield any camphenilone **4** which is the product⁵ obtained when rearrangement is catalyzed by sulfuric acid.



The cleavage products may be considered to arise from breaking the $\text{C}_1 - \text{C}_7$ bond in competition with breaking the $\text{C}_1 - \text{C}_2$ bond. The relative yields then will be seen to depend on the substituents at C_2 and C_7 . Mechanistically these results are consistent with S_N type intermediates.



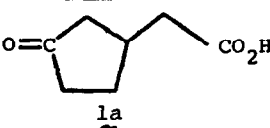
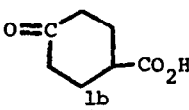
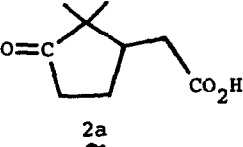
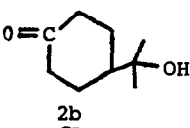
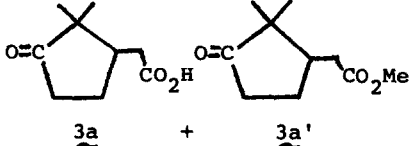
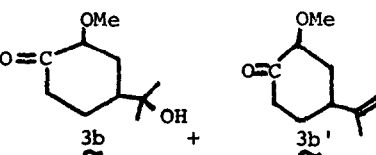
- 1a** ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$)
2a ($\text{R}_1 = \text{R}_2 = \text{Me}, \text{R}_3 = \text{H}$)
3a ($\text{R}_1 = \text{R}_2 = \text{Me}, \text{R}_3 = \text{OMe}$)



- 1b** ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$)
2b ($\text{R}_1 = \text{R}_2 = \text{Me}, \text{R}_3 = \text{H}$)
3b ($\text{R}_1 = \text{R}_2 = \text{Me}, \text{R}_3 = \text{OMe}$)

The percent conversions of oxidized material are summarized in Table 1. These results are consistent with the initial formation of a chromate ester which then fragments to product. Models suggest that a transition state with a trans-anti parallel arrangement of the O-Cr bond relative to the C₁-C_n bond is quite reasonable. Therefore, it is tentatively suggested that the two staggered mirror image conformers of the chromate ester of 1 lead uniquely to 1a. The one staggered meso conformer of the chromate ester of 2 leads uniquely to 2b.

TABLE 1
Percent Conversion 6,7,8

<u>Alcohol</u>				
	<u>C₁-C₂ (a type)</u>		<u>C₁-C₇ (b type)</u>	
<u>1</u>	 <u>1a</u>	16	 <u>1b</u>	0
<u>2</u>	 <u>2a</u>	0	 <u>2b</u>	9
<u>3</u>	 <u>3a</u> + <u>3a'</u>	35	 <u>3b</u> + <u>3b'</u>	25

The situation for 3 is more complex. One staggered conformer of the chromate ester of 3 leads to 3a plus 3a' while an energetically different staggered conformer of the chromate ester of 3 leads to 3b plus 3b'. Studies are currently in progress to further elucidate the mechanistic implications of these observations.

Acknowledgement

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P. T. Lansbury, et. alii, Chem. and Ind. (London), 653 (1961).
- (4) H. Minato, J. Ware and T. G. Traylor, J. Amer. Chem. Soc., 85, 3024 (1963)
- (5) J. J. Cawley and V. T. Spaziano, unpublished results.
- (6) Satisfactory elemental analyses were obtained for all new compounds.
- (7) Percent conversions were determined by vpc with a thermal conductivity detector and are estimated to be accurate to $\pm 5\%$.
- (8) Material balance in all cases was $96 \pm 4\%$. Only other compound found was starting material.