

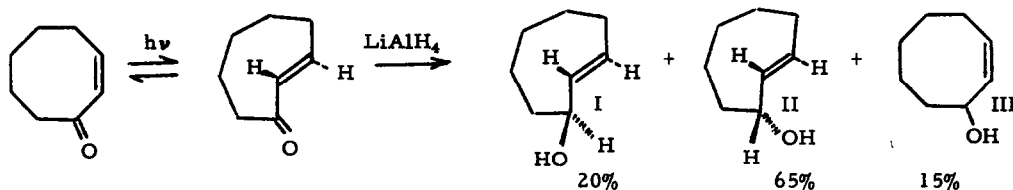
SOLVOLYSIS OF trans-CYCLOOCT-2-ENYL 3,5-DINITROBENZOATES<sup>1</sup>

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In order to determine the effect of a strained trans-double bond on the solvolysis of an allyl derivative, we have examined the epimeric trans-cyclooct-2-enyl 3,5-dinitrobenzoates. The alcohols were prepared by the photolysis of cyclooct-2-enone<sup>3</sup> followed by lithium aluminum hydride reduction.<sup>4</sup>

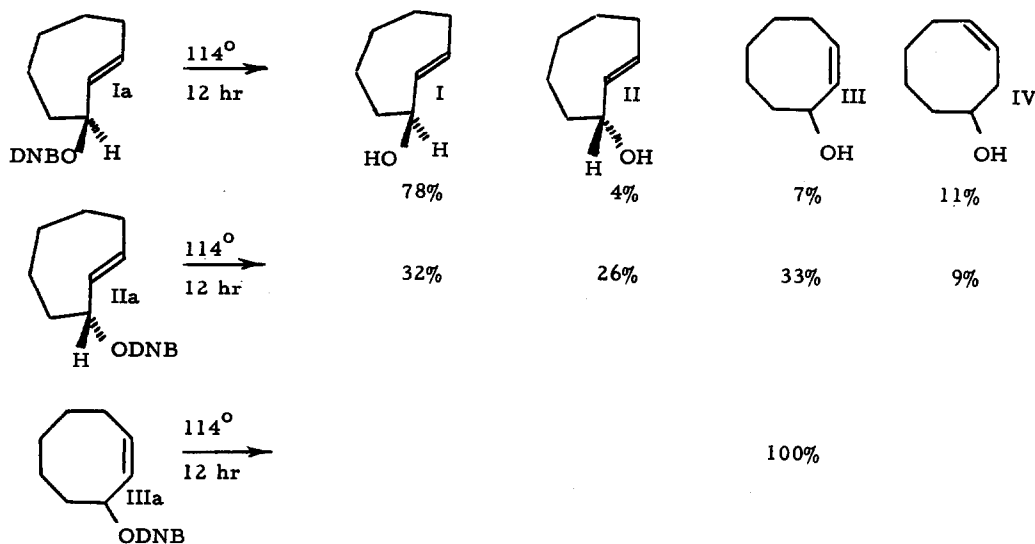


The identification of the trans-trans-isomer, I, was accomplished by comparing its nmr spectrum and vpc retention time with those of the product from the hydrolysis of 8-bromobicyclo[5.1.0]octane.<sup>5</sup> The trans-cis isomer, II, was identified by conversion to trans-bicyclo[6.1.0]nonan-cis-2-ol.<sup>4</sup>

The alcohols were converted to the 3,5-dinitrobenzoates, and the rates of solvolysis were determined in 80% aqueous acetone. The rates of solvolysis are summarized in Table I, and the products are shown below.<sup>6</sup>

Table I. Rates of Solvolysis in 80% Aqueous Acetone

3,5-Dinitrobenzoate	T, °C	k×10 <sup>6</sup> , sec <sup>-1</sup>	ΔH <sup>‡</sup> , kcal/mole	ΔS <sup>‡</sup> , eu
<u>trans-trans</u> , Ia	134.4	19.3 ± 0.8	21.1	-28.9
	113.8	4.57 ± 0.12		
<u>trans-cis</u> , IIa	134.4	23.4 ± 0.7	22.8	-24.4
	113.8	4.96 ± 0.15		
<u>cis</u> IIIa	134.4	17.3 ± 0.5	29.1	-9.6
	113.8	2.43 ± 0.08		



All three compounds react at similar rates, which are 60-100 times greater than that of cyclooctyl 3,5-dinitrobenzoate. This is a relatively small rate increase in comparison to other allylic systems.<sup>7</sup> Severe steric interactions seem to prevent effective allylic participation in the formation of the ion. When the 1-deuterio derivatives of Ia-IIIa were solvolyzed, only the product III from labeled IIa showed any appreciable deuterium scrambling (32%).<sup>8</sup> Thus the trans-allyl cations, trans, trans in nature from Ia and trans, cis from IIa, are not symmetrical, and react with solvent at the carbon which originally held the leaving group.

Control experiments were carried out to see if III and IV might be formed from acid-catalyzed isomerization of I and II. It was found that despite the four-fold excess of amine added to buffer the 3,5-dinitrobenzoic acid, significant isomerization did occur under the reaction conditions. The alcohol, I, was converted to III and IV and with IV predominating, whereas II gave mainly II and III in equal amounts along with a small amount of IV. The reactivity of II was considerably greater than that of I. The product ratio found in the solvolysis of IIa is almost the same as that found in the acid catalyzed isomerization of II.

Since no deuterium shift was found in IV derived from labeled Ia and IIa, it is clear that IV is not formed by a transannular hydrogen shift mechanism. Rather, it is probably

formed along with III by the protonation of the double bond of I or II followed by loss of a proton at either the 2- or 4-positions.

The remarkable difference in activation parameters between the cis- and trans-cyclo-octenyl derivatives suggests a significant difference in the nature of the activated complexes formed. The trans-double bond appears able to decrease the activation energy for ionization, but does so at the expense of an unfavorable entropy term. The decrease in activation energy does not, however, result from a "symmetrical" allyl cation, as indicated by lack of deuterium scrambling. Conformational problems appear to play a major role in these solvolyses. This question will be considered in detail in a subsequent publication.

#### References

1. This investigation was supported by a grant from the National Science Foundation.
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3. P. E. Eaton and K. Lin, J. Amer. Chem. Soc., 86, 2087 (1964).
4. K. B. Wiberg and T. Nakahira, J. Amer. Chem. Soc., 93, 5193 (1971). The alcohols have been prepared by different synthetic routes by G. A. Whitham and M. Wright, J. Chem. Soc. C, 886 (1971).
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6. The product studies were carried out in 60% acetone in order to decrease the reaction times. A four-fold excess of N,N-diisopropylethylamine was used to buffer the acid formed.
7. Cf. A. C. Cope and P. E. Peterson, J. Amer. Chem. Soc., 81, 1643 (1959); D. Cook, A. Diaz, J. P. Dirlam, D. Littams, M. Sakai and S. Winstein, Tetrahedron Lett., 1405 (1971).
8. The extent of deuterium scrambling was determined by nmr ( $\pm 3\%$ ).