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UNSYMMETRICAL ALLYL CATIONS IN THE SOLVOLYSIS OF CYCLOALKENYL 3, 5-DINITROBENZOATES[1]

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The solvolysis of allyl derivatives normally is believed to lead to a symmetrical allyl cation.[3] Internal return also frequently proceeds via a symmetrical intermediate.[4] Unsymmetrical allyl cations might, because of conformational problems, be formed from cycloalkenyl derivatives. This possibility has now been examined.

The cycloalkenols labeled with deuterium were prepared by the lithium aluminum deuteride reduction of the corresponding cycloalkenone. This was not successful with cyclopentenone. The optically active alcohols were prepared by the t-butyl hydroperoxide oxidation of the cycloalkene catalyzed by the cupric salt of α-ethyl camphonate followed by lithium aluminum hydride reduction of the intermediate camphonate ester.[5]

The deuterium scrambling and racemization observed during the solvolysis of the corresponding 3, 5-dinitrobenzoates are summarized in Table I. The relative rates of solvolysis are given in Table II. Although we were not able to obtain the percent deuterium

Table I

Deuterium Scrambling and Racemization in Solvolysis of Cycloalkenyl-3 3, 5-Dinitrobenzoates[a]

3, 5-Dinitrobenzoate	%D-scrambling in product alcohol	$[\alpha]^{25}_{D}$[b] starting alcohol	$[\alpha]^{25}_{D}$[b] product alcohol	% Racemization
cyclooct-2-enyl	0±3	+ 5.98°	+5.52°	8±1
cyclohept-2-enyl	33±4	- 1.69°	-1.46°	14±3
cyclohex-2-enyl	56±3	-10.57°	-6.89°	36±1

a. 60% aqueous acetone, solvolyzed for 10 half-lives.

b. ±0.025°

Table II

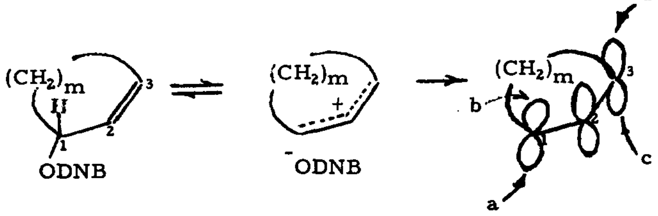
Rates of Solvolysis in 60% Aqueous Acetone

3, 5-Dinitrobenzoate	T, °C	$k \times 10^5$ sec^{-1}	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ eu	k_{rel} 100°
cyclooct-2-enyl	119.7 139.8	3.32±0.12 21.5 ±0.9	29.1	-5	1
cyclohept-2-enyl	85.5 105.4	9.69±0.35 66.0 ±2.3	25.3	-7	90
cyclohex-2-enyl[a]	50 75	0.32 5.31	24.4	-8	135
cyclopent-2-enyl[a]	50 75	57.8 621	20.6	-10	10900

[a] W. Sliwinski, unpublished results, Princeton University

scrambling for cyclopent-2-enyl 3, 5-dinitrobenzoate, the observation that a closely related compound gave 100% scrambling[6] strongly suggests that this will be the case here also.[7]

When the allylic cation is generated in the solvolytic reaction, the products are formed by attack of water at one of four positions:[8]



If the fraction of deuterium scrambling is given by S and the fraction of racemization is given by R, the extent of attack at the various positions may be described by:

$$a + b = 1 - S/2 \qquad a + d = 1 - R/2$$

$$c + d = S/2 \qquad b + c = R/2$$

$$a - c = 1 - S/2 - R/2$$

$$b - d = R/2 - S/2$$

It is not possible to separate the fraction of attack at each of the four positions. Thus, in Table III we give the values of (a+b), the fraction of attack at the site of the leaving group, (c+d), the fraction of attack at the terminus of the allyl system, (a-c) the difference in fraction of attack at the positions <u>cis</u> to the leaving group and (b-d), the difference in fraction of attack at the positions *trans*- to the leaving group. In addition, using the boundary condition that the fraction of attack at any position must be positive, ranges of possible values of attack at the several positions were obtained.

Table III

Solvent Attack on Cycloakenyl Cations

3, 5-Dinitrobenzoate	a+b	c+d	a-c	b-d	a	b	c	d
cyclooct-2-enyl	1.00	0.00	0.96	0.04	0.96	0.04	0.00	0.00
cyclohept-2-enyl	0.83	0.17	0.76	-0.10	0.80[b]	0.03	0.03	0.14
cyclohex-2-enyl	0.72	0.28	0.54	-0.10	0.63[c]	0.09	0.09	0.19
cyclopent-2-enyl	0.50[a]	0.50[a]	0.00	0.00	0.25	0.25	0.25	0.25

a. Estimated value

b. ±0.04 based on values given in preceding columns

c. ±0.09 based on values given in preceding columns

With cyclooct-2-enyl 3, 5-dinitrobenzoate, almost all of the product is obtained with retention of configuration. Considering the low rate of reaction, the small amount of racemization may well result from an S_N2 displacement. No significant attack occurred at the terminus of the allyl system. Clearly, allyl participation is minimal, and conformational problems restrict attack at the backside of the carbon bearing the leaving group.

Even with cyclohex-2-enyl 3, 5-dinitrobenzoate, the predominant reaction with solvent occurs at position *a*. This seems at first glance to be incompatible with the work by Goering and coworkers.[9] From polarimetric and titrimetric rate measurements, they concluded the intermediacy of a symmetrical allylic cation in the solvolysis and internal return process of cis- and trans-5-methylcyclohex-2-enyl p-nitrobenzoate in 80% aqueous acetone. But they also reported, along with their earlier finding of residual rotation in the products in ethanolysis and acetolysis of the corresponding chlorides, that the O^{18} scrambling experiment gave evidence for an unsymmetrical allylic cation intermediate in case of *trans*-5-methylcyclohex-2-enyl p-nitrobenzoate. Therefore, when a better leaving group, 3, 5-dinitrobenzoate, and more polar solvent, 60% aqueous acetone are used, it is not surprising to find the present *observation: a large extent of retention of configuration in the product.* Thus, we can conclude, even with cyclohex-2-enyl derivatives, that double bond participation in the formation of the cation is relatively weak. This is in good accord with the relative low solvolysis rate enhancement.

References

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