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SOLVOLYSIS OF TRANS-FUSED BICYCLO[6.1.0]NONYL-2 3,5-DINITROBENZOATES (1)

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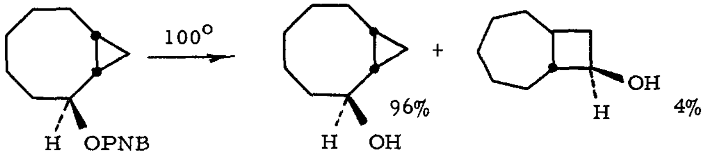
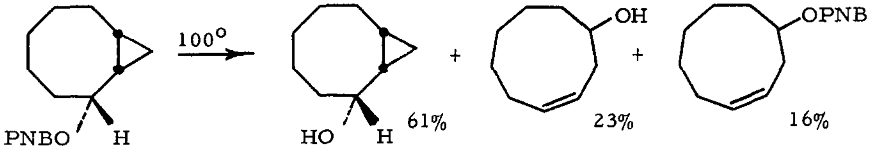
In the cases of the bicyclo[3.1.0]hexyl-2 and bicyclo[4.1.0]heptyl-2 derivatives, both epimers lead to the same product mixture which consist largely of the epimers corresponding to the reactant structure. (2,3) However, the epimeric cis-fused bicyclo[6.1.0]-nonyl-2 p-nitrobenzoates were reported to give different product mixtures (4):

Ia

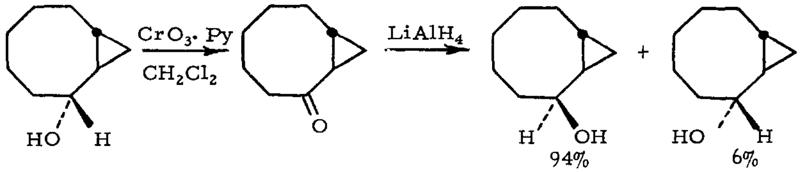


Ib

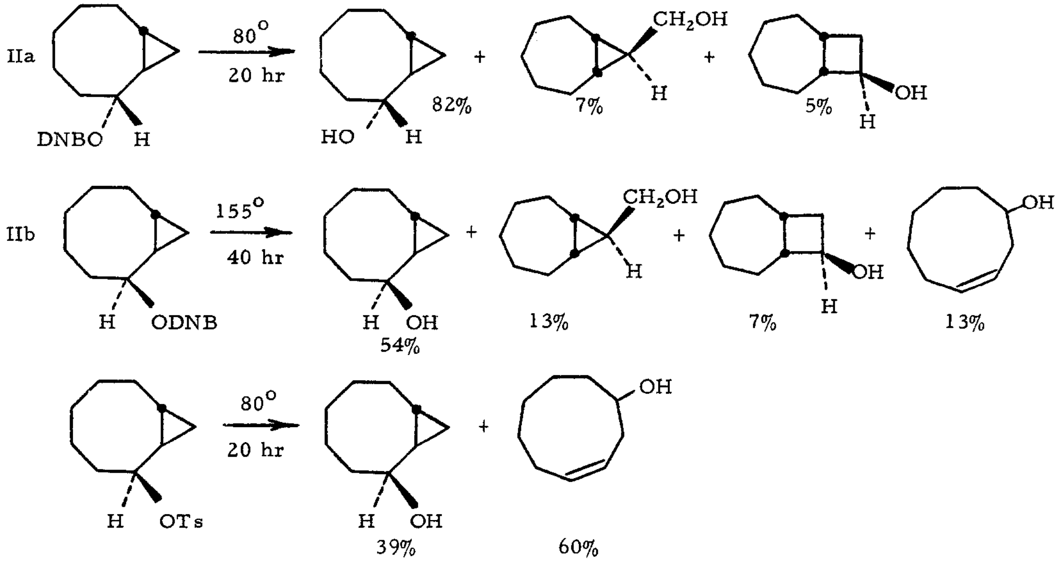


Since there was no cross-over in products, it was clear that the two compounds reacted via different cations. The same conclusion was reached with the bicyclo[5.1.0]octyl-2 derivatives by studies of racemization and deuterium scrambling (5).

It seemed of interest to compare these results with those for the corresponding trans-fused compounds. The trans-cis isomer was obtained by the lithium aluminum hydride reduction of the corresponding ketone (6):



The alcohols were converted to 3,5-dinitrobenzoates in the usual fashion, and the solvolysis rates were determined in 80% aqueous acetone to give the data summarized in Table I. The relative rates of reaction are given in Table II. The products are summarized below:



Again, the trans-trans dinitrobenzoate gives none of the trans-cis product, and the trans-cis dinitrobenzoate gives none of the trans-trans product. The other saturated products are common to both reactants. However, this is at least in part due to the high temperature required for the solvolysis of IIb. When the corresponding tosylate was solvolyzed, none of the products from Ia were found.

Two interesting aspects of the reactions are the relative rates and the stereochemistry. From Table II it will be seen that whereas the two epimeric cis-fused isomers gave only a rate ratio of 22, the trans-fused isomers gave a rate ratio of 18, 200. This does not result from a rearrangement process since in both cases the major product was unrearranged. Clearly, each isomer gives a unique cation. The cations derived from IIa must have a particularly favorable geometry for interaction between the empty p-orbital and the cyclopropane ring since it is over 10 times as reactive as the more reactive cis-fused isomer. Correspondingly the developing cation derived from IIb must have a particularly poor geometry for such interaction since it is 1/65 as reactive as the less reactive cis-fused isomer.

Table I

Rates of Solvolysis in 80% Aqueous Acetone

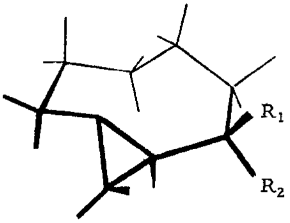
3, 5-Dinitrobenzoate	T, °C	$k \times 10^5$ sec^{-1}	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu
trans-*trans* (IIa)	80.0	45.0	23.6	- 7
	60.1	5.77		
trans-*cis* (IIb)	160.0	4.17	29.2	-12
	140.0	0.77		
cis-*trans* (Ia)	140.0	35.4	26.4	-11
	121.1	7.30		
cis-*cis* (Ib)	100.0	22.3	26.5	- 5
	80.0	2.81		

Table II

Relative Rates of Solvolysis at 100°

3, 5-Dinitrobenzoate	k_{rel}
trans-*trans* (IIa)	18200
trans-*cis* (IIb)	1
cis-*trans* (Ia)	65
cis-*cis* (Ib)	1410
cyclooctyl	~ 0.04

These conclusions seem reasonable when models are examined. In the case of IIa, the bridgehead-bridgehead bond is trans-antiparallel to the C-O bond being broken. With the *trans*-fused isomers, the central bond might well be expected to interact well with the developing *p*-orbital. The preferred conformation of IIb appears to be one in which the C-O bond lies over one of the external cyclopropane ring bonds. This unique conformation for a cyclopropylcarbinyl derivative might well be expected to be unfavorable for a stabilizing interaction in the activated complex.



IIa R_1 = H R_2 = ODNB

IIb R_1 = ODNB R_2 = H

All of the reactions in the cyclopropylcarbinyl-cyclobutyl-allylcarbinyl series have been found to be stereospecific (4, 7, 8) and the reactions involving cyclobutyl cations proceed in the fashion expected from orbital symmetry arguments (7). The present observations fall in this same pattern. Whereas the reaction of the cis-trans derivative, Ia, leads to the trans-fused bicyclo[5.2.0]nonyl ring system, the trans-trans derivative, IIa, gives the cis-fused bicyclo[5.2.0]nonyl ring system. The formation of the cis-fused bicyclo[5.1.0]octane-8-methanol from IIa also is the expected result. The production of bicyclo[5.1.0]octane-8-methanol and bicyclo[5.2.0]nonan-7-ol from IIb suggests that a crossover between the two bicyclo[6.1.0]nonyl-2 cations is possible at 155°. However, the crossover is not noted in the solvolysis of the more reactive tosylate corresponding to IIb.

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