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THERMAL BEHAVIOR OF EXO-5-SUBSTITUTED BICYCLO[2.1.0]PENTANES

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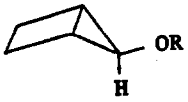
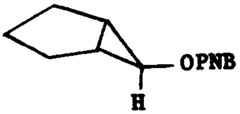
Recent investigations of the solvolytic behavior of exo-5-bicyclo[2.1.0]-pentyl derivatives (I) have uncovered a remarkable reactivity (1). Thus,

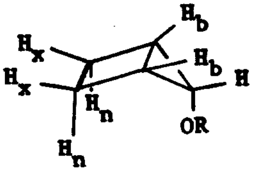


Ia, R = PNB

b, R = $CH_2C_6H_5$



II



III a, R = PNB

b, R = $CH_2C_6H_5$

Ia was estimated (1b) to solvolyze eighteen powers of ten more rapidly than exo-6-bicyclo[3.1.0]hexyl p-nitrobenzoate, II. In addition, the kinetic behavior of I toward solvolysis was remarkably insensitive to alteration of solvent polarity and changes in the nature of the leaving group. Yet, the products of the solvolysis (i.e. cyclopentadiene and 3-cyclopentenol) are typical of cationic intermediates. The explanation suggested for this surprising behavior entails a rate-limiting isomerization of Ia to its endo-epimer IIIa , which then undergoes ready solvolytic ring opening (allowed by orbital symmetry considerations(2)) to a cyclopentenyl cation to afford the observed products.

Our results suggest an activation energy for the exo-endo interconversion (i.e. I $\rightleftarrows$ III) of approximately 29 kcal/mole, about 10 kcal/mole lower than corresponding activation energies observed for bicyclopentyl derivatives unsubstituted at C-5 (3,4). This suggests a remarkable effect attributable to the C-5 substitutent, and raises questions regarding the nature of the *exo*-*endo* interconversion.

Cleavage of the internal cyclopropyl bond (cf. Scheme A, Fig. 1) to allow epimerization would *a priori* appear to be the most likely process involved in the isomerization since the energy of the transition state should reflect the release of some fraction of the large strain energy of the bicyclopentyl system (i.e. 54.1 kcal/mole (5)); however, we were compelled to consider an alternative process involving external bond cleavage (Scheme B, Fig. 1).

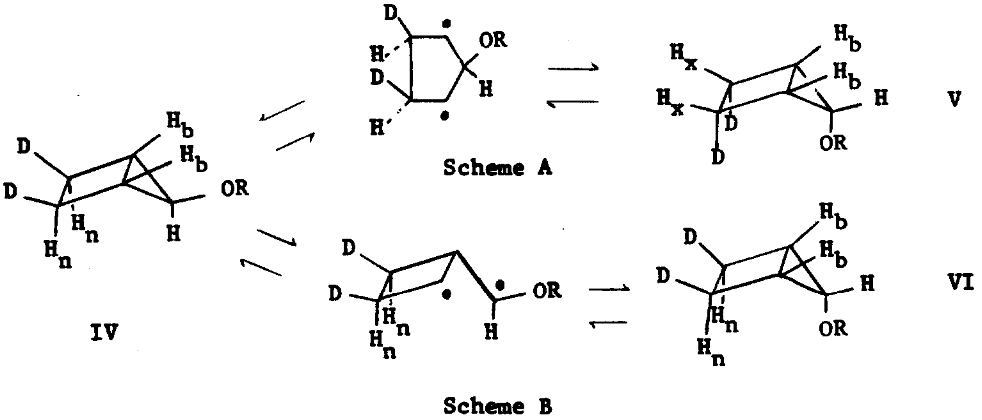


Figure 1. Thermal Isomerization of Bicyclo[2.1.0]pentanes by Central and External Bond Cleavage ($R = CH_2C_6H_5$).

Such a process might release less strain in the transition state (cf. 27.1 kcal/mole strain energy of cyclopropane (5)) but most significantly should be subject to a pronounced substituent effect, in accord with observation, since the substituent is borne on the developing radical center. Moreover, external bond cleavage had already been considered, although not tested, in closely related cases (4).

In an effort to delineate the process which occurs in the epimerization of Ib to IIIb, we synthesized *exo*, *exo*-2,3-dideuterio-*exo*-5-benzyloxybicyclo-[2.1.0]pentane, IV, by the appropriate modification of our previous synthetic route (1b,6).

It is clear from a consideration of Fig. 1 that central bond cleavage (Scheme A) leads to V which contains _exo_-protons on the two-carbon bridge, while external bond cleavage (Scheme B) leads to VI which contains _endo_-protons (H_n) in the same location. Moreover, the chemical shift of each of these protons is known from our knowledge of the nmr spectrum of III (cf. Table I). The predicted spectra of V and VI are included in Table I.

When the dideuterated _exo_-benzyl ether IV (7) was heated in a sealed tube at 95.0 ± 0.2°C in benzene-d_6 (0.9 M), the appearance of an _endo_-benzyl ether was signaled by the presence of a characteristic triplet (J = 5 Hz) at 3.29 ppm.

TABLE I

NMR Spectra of Deuterated Bicyclopentanes
(Benzene-d_6; ppm from TMS)

	H_x	H_n	H_b	
IIIb	2.00	1.70	1.56	exp. detd.
V	2.00	----	1.56	predicted
VI	----	1.70	1.56	predicted
Obs. Product From Therm. of IV	1.99	----	1.56	exp. detd.

In addition, signals grew in at 1.99 ppm and 1.56 ppm (cf. last entry in Table I) which can be assigned to the _exo_-protons (H_x) and bridgehead protons (H_b) of V, respectively. Moreover, the signal at 1.56 ppm is the complex pattern expected for the bridgehead protons of V, and not the doublet (J =.5 Hz) anticipated for the corresponding protons of VI (8). Indeed, decoupling of the _exo_-protons (H_x) of V caused the 1.56 ppm multiplet to collapse into a doublet (J = 5 Hz). These results demand that the principal, if not sole, mode of isomerization of these bicyclopentanes involves central bond cleavage (Scheme A, Fig. 1) (9).

The observed central bond cleavage rules out a direct, radical-stabilizing influence of the 5-substituent as being responsible for the facile _exo_-_endo_ interconversion. Although several factors may be involved, a destabilizing effect of the 5-benzyloxy substituent on the ground state bicyclopentane may predominate.

Following the recent work of Hoffmann and Stohrer, and Gunther (10), π-donating substituents at C-5 should weaken the central bond of the bicyclopentanes by interaction with the appropriate cyclopropane Walsh orbitals, thereby leading to a lowered activation barrier for isomerization.

We are exploring this point further.

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7. The nmr spectrum (benzene-d_6) of IV (R = benzyl) follows: 1.26 (s, 2H, H_n), 1.75 (s, 2H, H_b), 3.40 (s, 1H, C_5-H), 4.48 (s, 2H, benzyl CH_2), and 7.28ppm (m, 5H, aromatic H).
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9. We have not determined an equilibrium constant for the IV to V interconversion because of the appearance of 3-benzyloxycyclopentene in the nmr spectrum after 30% conversion to the endo-epimer. Analysis of this mixture is complicated by the facile conversion of V into 3-benzyloxycyclopentene under a variety of glpc conditions.
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