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POLARIMETRIC RATES IN SOLVOLYSIS OF exo- AND endo-2-BENZONORBORNENYL BROMOBENZENESULFONATES (1)

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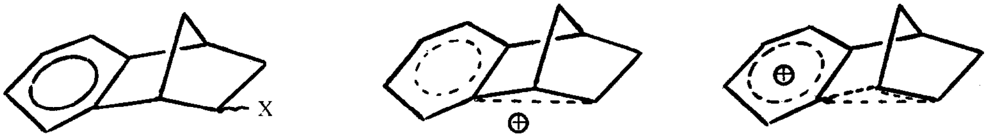
Interest in the nature of the 2-benzonorbornenyl cation has remained at a high level (3). Bartlett and Giddings (4) first proposed participation by the benzene ring and the nonclassical structure of the carbonium ion intermediate in solvolysis of 2-benzonorbornenyl brosylates (I-OBs). On the basis of the high exo/endo rate ratio and clean retention of exo configuration in solvolysis of the exo epimer, the delocalized, unsymmetrical, homobenzylic ion II was written for the intermediate cation in solvolysis of exo-I-OBs. More recently, we (5) reported that acetolysis of optically active exo-I-OBs gave racemic product, and we reasoned that the symmetrical intermediate, III, was more compatible with this result (6). As already pointed out by Cristol (8), it remained to be determined what contribution to loss of optical activity was made by internal return accompanying solvolysis. In this communication we report polarimetric rates in solvolysis of both exo- and endo-I-OBs and the optical activity of the resulting solvolysis products.



I II III

X = OH, OAc, OBs

Optically active exo-2-benzonorbornenyl acetate (exo-I-OAc) of $[\alpha]_D^{25}$ + 16.6° (c 3.8, $CHCl_3$) was prepared using the same method reported recently (9, 10). Lithium aluminum hydride reduction of the acetate gave exo-I-OH, mp 54-68°, $[\alpha]_D^{25}$ + 12.6° (c 2.4, $CHCl_3$). The exo brosylate, mp 67-84°, $[\alpha]_{3650}^{25}$ + 27.5° (c 1.7, AcOH), was prepared in the usual manner. Oppenauer oxidation of exo-I-OH to the ketone, followed by lithium aluminum hydride reduction, led to endo-I-OH, mp 69-90°, $[\alpha]_D^{25}$ + 35.3° (c 3.1, $CHCl_3$), brosylate mp 122-127°, $[\alpha]_D^{25}$ + 31.9° (c 2.0, $CHCl_3$). In order to interpret the experimental results, it is necessary that the above compounds have the same optical purity or that the relative optical purity is known. It is assumed that the above chemical conversions do not affect optical purity. The optical activity of some of the compounds was increased by recrystallization; however, this was done only after the optical activity was already known for the resulting product. The rates of acetolysis of the brosylates are summarized in Table I.

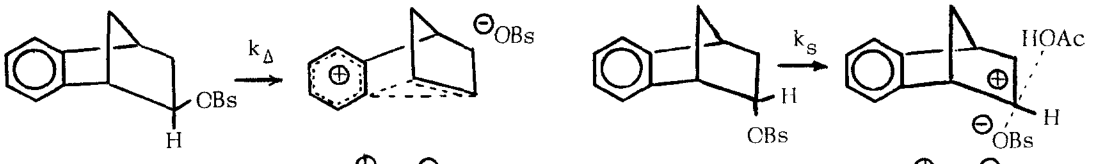
TABLE I

Titrimetric and Polarimetric Solvolysis Rates of exo- and endo-2-Benzonorbornenyl p-Bromobenzenesulfonates

Compd	Solvent	Concn., M	Other solute	Procedure	$10^6 k$ (sec^{-1})[a]	k_α / k_t
exo-I -OBs[b]	AcOH	0.052		Polarimetric	25.7 ± 0.6	4.16
exo-I -OBs[b]	AcOH	0.010		Titrimetric	6.18 ± 0.05	
exo-I -OBs[b]	AcOH	0.044	0.060 M NaOAc	Polarimetric	28.2 ± 0.3	
endo-I -OBs[c]	AcOH	0.017	0.020 M NaOAc	Polarimetric	10.5 ± 0.1	1.00
endo-I -OBs[c]	AcOH	0.017	0.020 M NaOAc	Titrimetric	10.5 ± 0.1	

[a]Mean value of two determinations; [b]25.0°; [c]100.0°.

As is clear from Table I, the k_α/k_t rate ratio for exo-I-OBs at 25° is 4.16 (11), and the k_α/k_t rate ratio for endo-I-OBs at 100° is 1.00. Ion-pair return is obviously substantial in acetolysis of the exo epimer. Using polarimetric rates, the exo/endo rate ratio becomes ca. 62,000 (4,12). The results are best interpreted by anchimerically assisted ionization (k_Δ) of exo-I-OBs, which gives the ion-pair III$^\oplus$OBs$^\ominus$. This ion-pair undergoes internal return and gives 99.9 ± 0.1% racemic exo-I-OAc. On the other hand, ionization of endo-I-OBs is anchimerically unassisted (k_s) and leads to classical ion-pair I$^\oplus$OBs$^\ominus$. The latter gives mainly leakage to the nonclassical ion III, 6% collapsing to optically active inverted exo-I-OAc (Table II).



exo-I -OBs III$^\oplus$OBs$^\ominus$ endo-I -OBs I$^\oplus$ OBs$^\ominus$

As regards ion-pair return in exo-I-OBs, the magnitude is similar to that previously found for exo norbornyl (13) and 3-phenyl-2-butyl brosylates (14). The amount of leakage found in acetolysis of endo-I-OBs is quite similar to endo norbornyl brosylate, where 7% inverted exo acetate was observed (13).

TABLE II

Solvolysis of Active 2-Benzonorbornenyl p-Bromobenzenesulfonates in Acetic Acid[a]

Compd	Obsd α for exo-I-OAc Degrees	Expected α without racemization Degrees	% Racemization
exo-I -OBs	+ 0.003 ± 0.002	+ 2.282	99.9 ± 0.1
endo-I -OBs	+ 0.137	+ 2.360	94

[a]ROBs 0.043 M; NaOAc 0.060 M. The brosylates were solvolyzed for 10 half-lives.

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References

1. Supported in part by the National Science Foundation.
2. (a) National Science Foundation Trainee, 1965-1969; (b) National Science Foundation Undergraduate Research Participant.
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6. As one of us pointed out very early (7) in connection with phenonium ions, it was initially not clear whether both unsymmetrically bridged and symmetrically bridged species needed explicit mention. However, no data are available, in our opinion, which demand the unsymmetrically bridged species as well as the symmetrical variety.
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10. Satisfactory carbon and hydrogen analyses were obtained for all optically active compounds. Rotations were taken in 1-dcm polarimeter tubes using a Perkin-Elmer Model 141 automatic polarimeter. The precision was ± 0.002°.
11. A similar k_{α}/k_t rate ratio has been observed for exo-I-OBs by H. Tanida and his coworkers (private communication).

12. The exo/endo rate ratio in acetolysis of exo- and endo-I-OBs is corrected from 7500 (4) to 15000. H. Tanida, K. Tori, and K. Kitahonoki, J. Am. Chem. Soc., **89**, 3212 (1967), reference 27.

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