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Note

Secondary Deuterium Isotope Effects in Solvolysis of Cyclopentyl *p*-Bromobenzenesulfonate in Dioxane-Water Mixtures. Stereochemistry of E1 and S_N1 Reactions*

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In the continuation of our study[1] on the relationship between the magnitude of secondary deuterium isotope effects and the reaction pathways in solvolytic S_N1 and E1 reactions, we report the results obtained in different dioxane—water (D—W) mixtures with specifically deuterated cyclopentyl brosylates. For this purpose, required cyclopentanol, cyclopentanol-1-*d* (α-*d*), *cis*-cyclopentanol-2-*d* (*cis*-β-*d*), *trans*-cyclopentanol-2-*d* (*trans*-β-*d*) and cyclopentanol-2,3,5,4-d_4 (β-d_4) were prepared as described by Streitwieser *et al.*[2] The corresponding brosylates were prepared by the usual Tipson procedure[3]. The deuterium content was greater than 93% in all of deuterated compounds as was determined by mass spectral analysis. The position of deuterium in each case was established by means of the paramagnetic shift reagent induced ^{1}H n. m. r. spectra[4] with $Pr(DPM)_3$***. The titrimetric rates were obtained employing the automatic potentiometric method maintaining a constant pH setting at 6.8. The rate constants were calculated from the standard integrated first-order law using a nonlinear least-squares program. The rate constants and the isotope effects are presented in Table I. No trend was observed in the rate constants between 20 and 80% of reaction. Each number represents the mean of at least eight kinetic measurements. Neither common ion rate depression effect nor special salt effect was detected. Added salt, $LiClO_4$ or NaOBs in the range from 0.0025 M to 0.030 M, caused at most a slight increase of 6% in the solvolysis rate of cyclopentyl brosylate in 70 vol % D—W at 40 °C.

The product yields were determined by gc using 10% UCON on Chromosorb and a flame ionization detector. The experimental procedure was identical to the procedure described in the product study determination of cyclopentyl brosylate in ethanol-water (E-W) mixtures.[1] The products were shown to be stable under the reaction condition as well as on the gc column. The results are presented in Table II.

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*** Tris(dipivalomethanato)praseodimium (III).

TABLE I

First-Order Rate Constants and Secondary Deuterium Isotope Effects in Solvolysis of Cyclopentyl Brosylates in Dioxane-Water Mixtures at 40 °C

Vol % Dioxane	Isotope Effects[a,b]				$k/10^{-4}$ s^{-1} all H[c]
	α-*d*	*cis*-β-*d*	*trans*-β-*d*	β-d_4	
60	1.19	1.14	1.18	1.84	8.96 ± 0.06
70	1.17	1.15	1.17	1.80	3.03 ± 0.02
80	1.20 ± 0.05	1.15 ± 0.05	1.20 ± 0.06	1.76 ± 0.08	1.00 ± 0.03

[a] k_H/k_{D_n}, *n* is the number of deuterium atoms. [b] Standard errors are less than 1% of the value if not indicated. [c] Uncertainities are standard errors.

TABLE II

Product Compositions[a] *in Solvolysis of Cyclopentyl Brosylates in Dioxane-Water Mixtures at 40 °C*

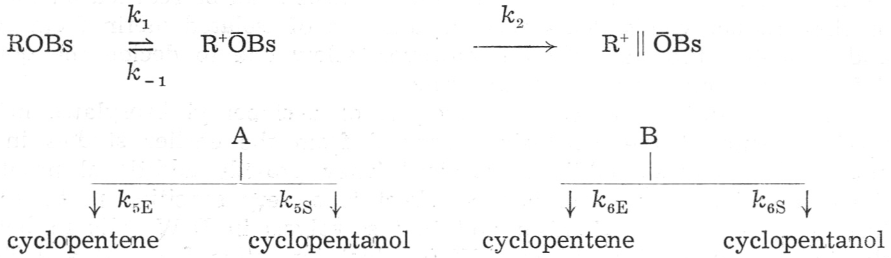
Vol % dioxane	Product	Mol %				
		All H	α-*d*	*cis*-β-*d*	*trans*-β-*d*	β-d_4
60	Alkene[b]	31.4	31.4	30.3	31.3	23.2
	Alcohol[c]	68.6	68.6	69.7	68.7	76.8
70	Alkene[b]	31.6	30.4	31.3	29.6	23.1
	Alcohol[c]	68.4	69.6	68.7	70.4	76.9
80	Alkene[b]	31.4	32.2	31.7	32.9	25.7
	Alcohol[c]	68.6	67.8	68.3	67.1	74.3

[a] Composition based on capillary gc peak areas corrected by the factor obtained from the chromatogram of the standard mixture made from the pure compounds. [b] Cyclopentene. [c] Cyclopentanol.

The configuration of cyclopentanol product relative to that of the starting material was obtained by two independent spectroscopic measurements. (a) As starting material for the preparation of the brosylate, *cis*-β-*d* was used and a ^{1}H n.m.r. spectrum[1] of 0.2 M solution of alcohol and 0.05 M of Pr(DPM)$_3$ in CCl$_4$ was recorded at 100 MHz. Using tetramethylsilane (TMS) as external standard, a diminished proton signal was found at $\tau \approx 15$ corresponding to the deuterium at *cis*-β-proton.[1,4] The spectrum of alcohol isolated from the reaction mixture after 10 half-lives of the reaction in 80 vol % D-W, was identical to the spectrum of *trans*-β-*d* compound with diminished proton signal at $\tau \approx 12$.[1] This is the proof that the substitution reaction occurs with about 95% inversion of configuration on the reacting carbon in 80 vol % D-W.

(b) The ^{2}H n.m.r. spectrum of starting *cis*-β-*d* alcohol was recorded on the Varian HR-220 operating at 33.8 MHz with the white noise decoupler centered at 220 002 587 MHz giving a broad single peak at $\tau \approx 9.04$ and small singlet at $\tau \approx 8.86$ indicating the presence of 7% of *trans*-β-*d*. TMS-d_{12} was an external standard. The concentration was 1.8 M in CHCl$_3$. Authentic *trans*-β-*d* alcohol gives a signal at $\tau = 8.85$ under the same conditions. Alcohol, isolated after 10 half-lives of solvolysis of the brosylate prepared from *cis*-β-*d* (containing 7% *trans*) was recorded under the same conditions giving two signals at $\tau \approx 8.87$ and $\tau \approx 9.07$ with peak areas corresponding to 85% *trans*-β-*d* and 15% *cis*-β-*d*, respectively.These results indicate 96% inversion and 8% of retention of configuration on the reaction center during the solvolysis.

The results in Table I indicate that the following reaction scheme should apply:



The products are formed from both ion pairs depicted as tight ion pair (A) and solvent separated ion pair (B). The α-*d* effects (second entry) are larger than 1.15, expected if either k_1 *or* k_{5S} processes are rate-determining.[1,5,6] On the other hand, the effects are smaller than 1.24, expected if k_2 is rate determining.[1]

The β-effects on *cis*-β-*d* and *trans*-β-*d* are somewhat higher than in E-W[1] and smaller than in trifluoroethanol-water (TFE-W)[1] solutions, which is an additional indication of different processes being involved. The effect on solvolysis of the β-d_4 compound is also in between the two extremes and does not change significantly with the change of the solvent composition. This effect would not change even if the k_{5E} processes and k_{6E} were rate determining because the change in solvent does not cause a change of olefin composition (Table II).This is a strange phenomenon which is probably explained by the fact that the change in solvent induces a change in the olefin fraction in opposite directions in the two intermediates. The olefin fraction is probably lowered in A and raised in B by changing solvent from 60 vol D-W to 80 vol D-W. The facts supporting this can be seen from the results in E-W and TFE-W solutions where in the E-W solution the yield of olefin goes from 27% to 12% as the composition of ethanol in the solvent change from 80 vol % to 100%, respectively, and the percentage of olefin goes from 42% to 76% in TFE-W when the trifluoroethanol content of the solvent risen from 70 to 97.5.[1] In E-W mixtures it has been previously shown that solvolysis of cyclopentyl brosylate goes through A with k_5 rate determining whereas in TFE-W solution, the products are formed from B with k_2 rate determining.[1]

The stereochemistry of alcohol formation is in accord with the results obtained previously[1] in that nucleophilic attack either on A or on B results in near complete inversion of configuration of the reacting carbon.

The stereochemistry of olefin formation could not be followed precisely by the product study because of the low »isotope effect on the product ratio«,[1] which was 1.46 for the β-d_4 compound. It is very probable that the stereoselectivity between *cis*-β-proton and *trans*-β-proton is diminishing and gc method is not precise enough to detect the difference between the cyclopentene composition in solvolysis of *cis*-β-*d* and *trans*-β-*d*. In both cases, base has a chance to remove either the deuterium or one of the three protons available at positions C-2 and C-5. We have calculated the isotope effect on the product formation for the all H and β-d_4 compounds (1.456) and used this to estimate the olefin fraction for the *cis*-β-*d* and *trans*-β-*d* compounds. The calculated olefin fraction is 29.8 mol % which is within the experimental error of the observed value 31.1% for *cis*-β-*d* and 31.3% for *trans*-β-*d*. If elimination were stereospecifically *trans,* the olefin fraction is calculated to be 31.5 for the *cis*-β-*d* and 28.0 for *trans*-β-*d* brosylate. The latter value is still fairly close to the measured one so that no definite conclusion can be reached on the basis of the product yields. Mass spectral analysis of isolated olefin from *cis*-β-*d* and *trans*-β-*d* brosylate should, however, allow one to decide the question definitively. This work is in progress.

These results obtained on solvolysis of cyclopentyl brosylates in D-W mixtures support the conclusions derived from the earlier studies in E-W and TFE-W solvent published earlier.[1] They provide additional proof that the α-secondary deuterium isotope effect is a very sensitive probe for determining reaction mechanism and that solvolysis in D-W falls in between the two extremes obtained in E-W (product formation from A) and TFE-W (product formation from B).

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REFERENCES

1. K. Humski, V. Sendijarević, and V. J. Shiner, *J. Amer. Chem. Soc.* **95** (1973) 7722.
2. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.* **80** (1958) 2326.
3. R. S. Tipson, *J. Org. Chem.* **9** (1944) 235.
4. K. Humski, L. Klasinc, D. Kovačević, and V. Kramer, *Croat. Chem. Acta* **45** (1973) 363.
5. V. J. Shiner, Jr. and W. Dowd, *J. Amer. Chem. Soc.* **93** (1971) 1029.
6. V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi. and M. Wolfsberg, *ibid.* **90** (1968) 7171.

SAŽETAK

Sekundarni deuterijski izotopni efekti u solvolizama ciklopentil-*p*-brombenzensulfonata u smjesama dioksan-voda. Stereokemija E1 i S_N1 reakcija

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Mjereni su sekundarni deuterijski izotopni efekti slijedećih deuteriranih ciklopentil *p*-brombenzensulfonata: 1-*d, cis*-2-*d, trans*-2-*d* i 2,2,5,5-d_4. Kao otapala upotrijebljene su različite smjese dioksana i vode (V—D). Dobiveni se rezultati slažu s rezultatima dobivenim u voda—etanol (V—E) i voda—trifluoretanol (V—TFE) smjesama koji su već objavljeni. Svi rezultati pokazuju da se solvoliza u V—D odvija preko miješanog mehanizma i da se nalazi u sredini između dva ekstremna slučaja dobivenih u V—E (produkti nastaju iz unutrašnjega ionskog para) i V—TFE (produkti nastaju iz vanjskoga ionskog para). Određena je stereokemija nastajanja ciklopentanola kao supstitucijskog produkta i dokazana je gotovo potpuna inverzija konfiguracije (92% inverzije i 8% retencije). Stereokemija nastajanja ciklopentena kao eliminacijskog produkta nije određena jer metoda praćenja raspodjele produkata s pomoću plinske kromatografije nije bila dosta točna da bi se mogli izvesti konačni zaključci.

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