

5-Methoxy Participation in Solvolysis and Secondary Deuterium Isotope Effects

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Specifically deuterated 4-methoxy-1-pentyl brosylates (1P-1,1- d_2 , 1P-2,2- d_2) and 5-methoxy-2-pentyl brosylates (1S-2- d , 1S-1,1,1- d_3 , 1S-OCD₃) were prepared, their solvolysis rates measured in 95% ethanol and the corresponding kinetic secondary deuterium isotope effects calculated. It was found that the α -effects are strongly reduced in magnitude, which is in contrast with results obtained with several compounds solvolyzing via π - or σ -participation. The effect found with 1P-1,1- d_2 ($k_H/k_D = 0.96$) is significantly different from the one measured with 1S-2- d ($k_H/k_D = 1.06$). This difference in the magnitude of the effects must reflect a relatively small difference in the structures of the two transition states, since both 1P and 1S solvolyze via the same intermediate 2. It is concluded that the magnitude of the α -effect is a sensitive measure of the amount of bridging only if the new bond is already quite strong in the transition state.

β -Deuterated brosylates give small effects which differ in magnitude ($k_H/k_D = 0.96$ with 1P-2,2- d_2 and 1.08 with 1S-1,1,1- d_3) corroborating the conclusion that the new C—O bond is strong in the transition state of both reactions but stronger with 1P than with 1S.

Results obtained in this work are in accord with the earlier conclusion that reduced β -effects in solvolysis of *exo*-2-norbornyl, 3-cholesteryl, cyclobutyl and 1-methylcyclobutyl derivatives are due to bridging.

The inverse isotope effect obtained with 1S-OCD₃ ($k_H/k_D = 0.95$) is »inductive« in origin and indicates that the methoxy oxygen bears a considerable amount of positive charge in the reaction transition state.

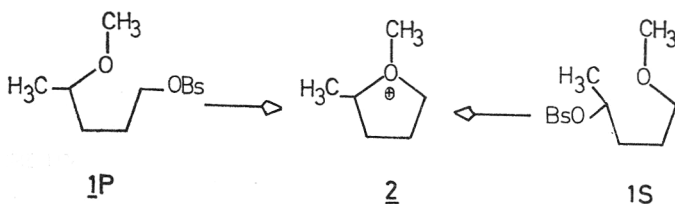
INTRODUCTION

Solvolysis of both 4-methoxy-1-pentyl brosylate (1P) and 5-methoxy-2-pentyl brosylate (1S) are anchimerically assisted and proceed via the formation of the same intermediate oxonium ion 2.¹

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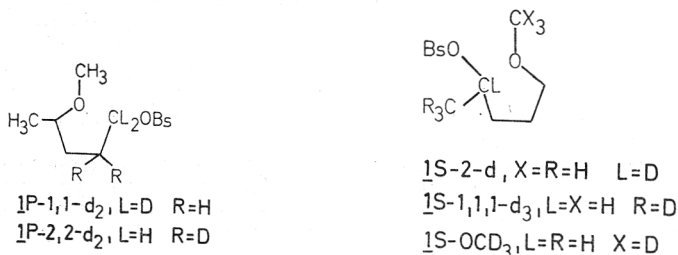
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This mechanistically unambiguous example of a neighboring group participation is eminently suitable as a model for studying how bridging affects the magnitude of secondary deuterium isotope effects. The results can then be compared to those obtained with compounds solvolyzing by way of σ - or π -participation. In the latter type of reaction, isotope effects have been used² as mechanistic probes and it seemed of interest to search for analogies and/or differences between n -participation and other types of participation. The results of such an investigation are here presented and the mechanistic implications discussed.

RESULTS

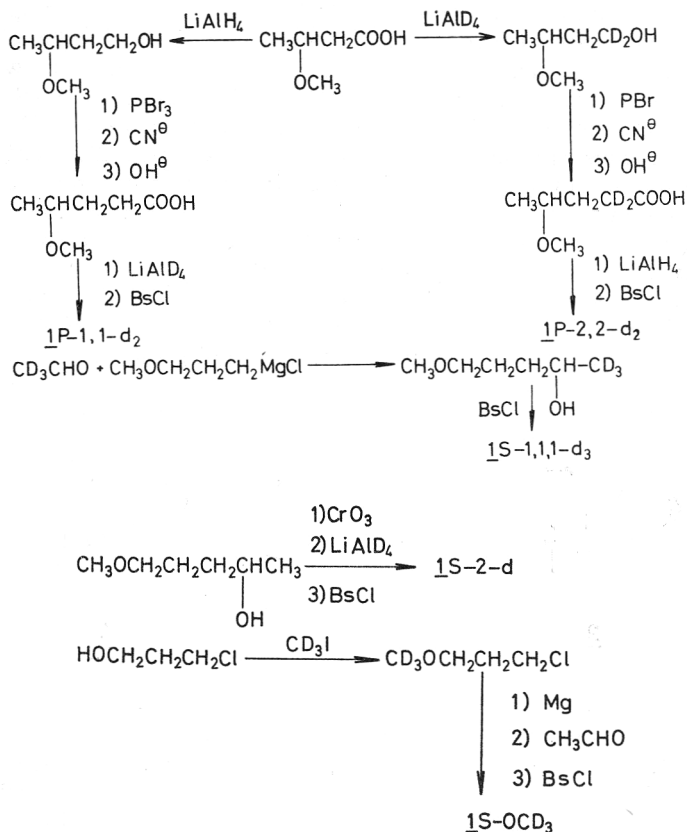
Five specifically deuterated brosylates **1P-1,1-*d*₂**, **1P-2,2-*d*₂**, **1S-2-*d***, **1S-1,1,1-*d*₃** and **1S-OCD₃**, were prepared by straightforward procedures outlined in Scheme and described in detail in the Experimental section. The solvolysis



rates of these brosylates and of their undeuterated analogues **1P** and **1S** were followed in 95% ethanol at 40.5 °C by continuous titration of the liberated acid using an automatic recording pH-stat. Typically, 0.02 mmol of the brosylate was dissolved in 20 ml of the solvent and the acid titrated with sodium ethoxide in 95% ethanol. In all cases, the first order rate law was obeyed to at least 80% completion. The first order rate constants were calculated by means of a least-squares program. The results are presented in the Table. The k_H/k_D values are slightly different from preliminary results discussed elsewhere², which does not affect any of the conclusions reached.

It has been shown that in acetic acid **1P** rearranges into **1S** and vice versa.¹⁰ Since this internal rearrangement could obscure the results, it was necessary to ascertain that it does not occur in 95% ethanol. Therefore, **1P** and **1S** were solvolyzed separately in this solvent for one half-life, the reaction quenched and the unreacted sulfonate ester isolated. Examination of the NMR spectra of the recovered ester indicated the absence of any significant amount of the isomeric brosylate. By this method probably 2% of material could escape detection. However, this extent of rearrangement is not kinetically significant and would not influence the interpretation of the results.

SCHEME



TABLE

Solvolysis Rates of 4-Methoxy-1-pentyl Brosylate (1P), 5-Methoxy-2-pentyl (1S) Brosylate and of their Deuterated Analogues in 95% Ethanol at 40.5 °C

| Compound | No. of runs | $k \times 10^{-4}/\text{s}^{-1}$ ^a | $k_{\text{H}}/k_{\text{D}}$ ^a | $\frac{k_{\text{H}}/k_{\text{D}}}{\text{per D at } 25.0\text{ }^\circ\text{C}}$ ^c |
|-------------------------|-------------|---|--|--|
| 1P | 4 | 3.19 ^b (7) | | |
| 1P-1,1-d ₂ | 4 | 3.34 ^b (1) | 0.955 (21) | 0.976 |
| 1P | 6 | 3.52 (4) | | |
| 1P-2,2-d ₂ | 7 | 3.66 (6) | 0.962 (19) | 0.980 |
| 1S | 11 | 4.02 (2) | | |
| 1S-2-d | 5 | 3.81 (4) | 1.055 (12) | 1.029 |
| 1S-1,1,1-d ₃ | 8 | 3.73 (2) | 1.078 (8) | 1.040 |
| 1S-OCD ₃ | 5 | 4.22 (3) | 0.953 (8) | 0.975 |

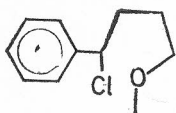
^a Numbers in parenthesis are standard deviations of the mean, i. e. 3.19 (7) = 3.19 ± 0.07;

^b At 40.0 °C;

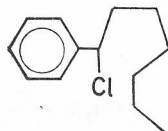
^c Assuming normal temperature dependence.

DISCUSSION

In anhydrous ethanol 1P and 1S solvolyze 99% and 95% respectively by the anchimerically assisted route (k_A)^{1b}. In this work 95% ethanol was used which has the same nucleophilicity as 100% ethanol³ but somewhat higher ionizing power.⁴ In anh. ethanol 1P solvolyzes 5% faster than 1S (at 25 °C)^{1b} while in 95% ethanol 1S is 16% more reactive than 1P (at 40 °C). These rate differences are most probably due only to the slightly different activation parameters or m values of the two substrates, but an increase in the contribution of the solvent unassisted reaction (k_C) with 1S in 95% ethanol could also be an explanation. If such were the case, then 1S would solvolyze in 95% ethanol 80% by way of k_A and 20% by way of k_C . It can be shown that this is an unrealistic overestimation of the importance of k_C . Thus relative solvolysis rates of 3 and 4 in 80% ethanol¹⁵ at 25 °C indicate that 3 reacts 95% by k_A . Since a phenyl group is much more powerful than a methyl group in promoting the k_C process by stabilizing the neighboring carbenium ion center, it can be concluded that the solvolysis of 1S in 95% ethanol is essentially completely controlled by k_A .



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 α -Deuterium Isotope Effects

The inverse α -deuterium isotope effect observed in solvolysis of 1P is analogous to those observed in S_N2 reactions^{6,7} indicating that bridging is very far advanced in the reaction transition state. Hence the solvolysis of 1P is essentially an internal direct displacement reaction, the participating methoxy group playing the role of the nucleophile. It is noteworthy that 1P-1,1- d_2 solvolyzes with the *largest inverse isotope effect yet reported* for a direct displacement reaction on a primary sulfonate ester. The effect measured (0.96 at 40 °C) can be compared to that reported for the hydrolysis of ethyl-1,1- d_2 tosylate (1.038 at 54.3 °C).⁸

It has been suggested⁹ that α -deuterium isotope effects may be lowered by participation of a neighboring group because the proximity of the internal nucleophile hinders the out-of-plane bending motions of the CH(D) bond so that there is less of a change in the relevant force constants in going from the ground state to the transition state. Reduced α -deuterium isotope effects have indeed been observed in solvolyses proceeding either by π ¹⁰ or σ ¹¹ participation but this attenuation is relatively small. In some cases no reduction in the α - d effect could be detected although the rate enhancements due to participation are large.¹² The conclusion can be reached that bridging is much stronger in the transition state for reactions proceeding by way of n -participation. The rationale is that n -electrons are free to form a new bond, while π or σ -electrons are not. Hence, π or σ -bridging can occur only at the expense of decreasing bonding energy elsewhere in the reactant and bridging is the result of a compromise.

The α -*d* effect measured in solvolysis of 1S ($k_H/k_D = 1.055$) can be compared to those observed in limiting solvolyses ($k_H/k_D = 1.22$)¹⁴ and in direct displacement reactions of secondary sulfonate esters (isopropyl brosylate in 90% ethanol at 25 °C, $k_H/k_D = 1.083$).¹⁵

Clearly, the S_N -2 like character or the k_A -process is again reflected in the α -*d* effect.

It is noteworthy that the difference in α -*d* effects between 1P and 1S is 10%.

Solvolysis rates of 1P and 1S are practically the same. Moreover, both reactions yield very nearly the same product mixtures consisting mainly of about equal amounts of compounds structurally related to 1P and 1S.^{1b}

These results indicate that the two transition states leading to the common intermediate 2 must have very similar energy contents. Since the reaction to form 2 out of either 1P or 1S is highly endothermic, it follows that the two transition states should also be structurally closely related.¹⁶ Yet a large difference in α -*d* effects is observed.

Since the reaction investigated is of the general type where two bonds to the reaction center are involved in the rate determining step, it is useful to discuss the results in terms of reaction coordinate diagrams proposed by More O'Ferrall¹⁷ and Jencks.¹⁸

The diagram, shown in Figure 1, is constructed by representing the two bond order changes on two perpendicular in plane axes. Potential energy changes associated with reacting bond order changes can be represented by contour diagrams in the third dimension, but are here not explicitly shown. Instead, the path of least energy is projected on the paper plane giving rise to a single line joining starting material to product and representing the reaction pathway.¹⁹ The potential energy is assumed to increase in both directions normal to the line and to decrease in both directions along the line at the point marked by an asterisk representing the reaction transition state. The displacement of the reaction pathway for 1P from the diagonal towards the lower left corner is based upon the reasonable assumption that the sum of the reacting bonds orders (Σ) will be less than unity along the whole reaction

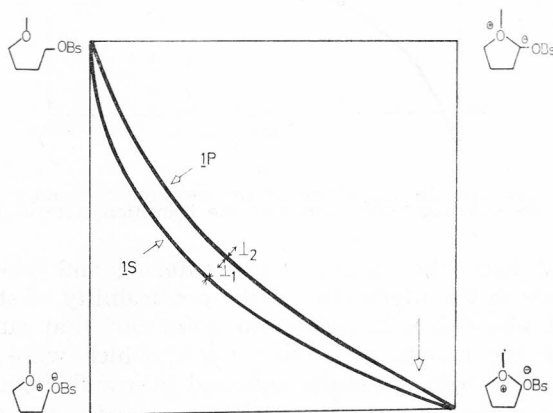


Figure 1.

pathway and attain unity at the two extreme points. In this manner, the old idea that bridging lags behind ionization²⁰ can easily be visualized.

What changes can be expected in the diagram if 1S is substituted for 1P? Since both compounds solvolyze at the same rate, the position of the transition state is not expected to be displaced along the reaction pathway (Hammond postulate).¹⁶ However, the movement normal to the reaction pathway \perp_1 and \perp_2 , representing a bound vibration should be affected. It can be expected that \perp_1 will be favored with 1S relative to 1P, since the reaction center in the former case is less electrophilic. The effect will be a displacement of the transition state and of the whole reaction pathway further towards the lower left corner, as shown in Figure 1. The result is a decrease in Σ at the transition state (Σ_{ts}) causing a decrease in the force constant for the CH(D) out-of-plane bending vibration and an increase in k_H/k_D , as observed. However, since the reactions are highly endothermic and since isotope effects indicate that Σ_{ts} is larger than in S_N2 reactions, the two transition states are to be placed not in the middle of the diagram but near the reaction product 2, as indicated by the arrow in Figure 1. In this region both pathways are about to converge in a single point and any differences in Σ_{ts} between the two transition states must necessarily be quite small. Thus it appears that when Σ_{ts} approaches unity, small variations in Σ_{ts} will cause large variations in the magnitude of the α -d effect. It is therefore indicated that we reformulate an earlier proposal²¹ and suggest an non-linear correlation between Σ_{ts} and the magnitude of α -d effect which is depicted in Figure 2. The maximum and the minimum values for

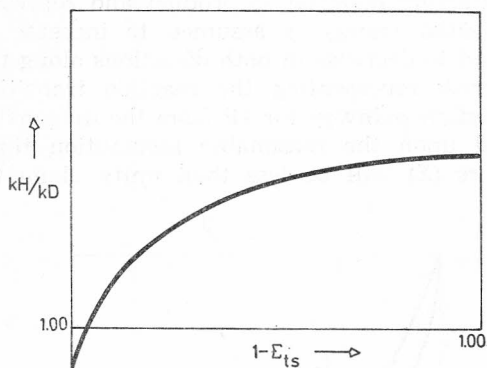


Figure 2. Correlation between the magnitude of the α -deuterium isotope effect and the sum of the reacting bonds orders at the transition state (Σ_{ts}).

k_H/k_D will depend upon the nature of the entering and leaving groups. Accumulated evidence in the literature for the applicability of such a correlation will be reviewed elsewhere. It suffice to point out that such a correlation explains not only the results of present work, which were obtained in the region of high Σ_{ts} , but also of results obtained in σ and π -participation where Σ_{ts} is much lower. α -Deuterium isotope effects seem to be a sensitive tool for probing for bridging only if bridging is very pronounced.

β -Deuterium Isotope Effects

β -Deuteration of the methylene group of 1P as in 1P-2,2- d_2 slightly accelerates the solvolysis rate. Here, oxygen participation requires a geometry of the transition state in which the dihedral angles between the developing empty p-orbital and the neighboring CD-bonding orbitals are about 60° . In solvolysis of tertiary halides²² such dihedral angles are associated with a β -effect of $k_H/k_D = 1.08$ per CD_2 -group. It seems therefore that the small inverse isotope effect observed with 1P-2,2- d_2 cannot be due to conformational factors alone but also to charge delocalization to oxygen which lowers drastically the hyperconjugative electron demand from CD-bonding orbitals. When hyperconjugative interactions are inhibited small inverse β -deuterium isotope effects are observed.²³

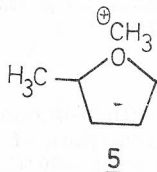
It is not quite correct to compare β -deuterium isotope effects obtained with 1P-2,2- d_2 (methylene- d_2) and with 1S-1,1,1- d_3 (methyl- d_3) because conformational restrictions to hyperconjugation with CD-bonds exist in the former case but not in the latter.

Nevertheless, it is interesting that k_H/k_D in solvolysis of 1S-1,1,1- d_3 is larger than unity. On grounds of α -effects it was argued that bridging is slightly less pronounced in the transition state of the reaction with 1S than with 1P. With 1S there is somewhat less charge delocalization to oxygen which makes the transition state more carbenium ion like and increases the hyperconjugative electron demand from neighboring CD-bonds. The observed β -effects are consistent with this argument.

The results of this work demonstrate that n-participation reduces drastically β -deuterium isotope effects in solvolysis. This finding strengthens our conclusion that reduced β -effects in solvolyses of 3-cholesteryl,¹³ 1-methylcyclobutyl,²⁴ cyclobutyl²⁵ and *exo*-2-norbornyl²⁶ derivatives are also due to participation and bridging.

Remote Isotope Effect

Allred and Winstein^{1b} have observed some methyl-oxygen fission in solvolyses of 1P and 1S showing that the contribution of the structure **5** to the resonance hybrid describing the cationic intermediate **2** is not negligible. Therefore, the inverse isotope effect observed with 1S- OCD_3 can be explained in terms of the »inductive« electron releasing effect of deuterium relative to protium.



EXPERIMENTAL

All melting and boiling points are uncorrected. Literature references for boiling and melting points are for undeuterated analogues. The extent of deuteration was checked by NMR spectroscopy and was found to be $> 97\%$ in all cases.

4-Methoxy-1-pentanol-1,1-d₂

4-Methoxypentanoic acid²⁸ (3.0 g, 23 mmol) was reduced with lithium aluminum deuteride by the procedure of Doering and Young²⁹ yielding 1.9 g (16 mmol, 71% yield) of the carbinol, bp 81—82 °C at 10 mm* (lit. 84.2—85.0 °C at 14.5 mm).^{1b}

3-Methoxy-1-butanol-1,1-d₂

Methyl 3-methoxybutanoate (71.4 g, 0.54 mol) was reduced²⁹ with lithium aluminum deuteride yielding, after fractional distillation, 40.5 g (0.382 mol, 70% yield) of the carbinol, bp 159—160 °C (lit. 159—160 °C).²⁹

1-Bromo-3-methoxybutane-1,1-d₂

3-Methoxy-1-butanol-1,1-d₂ (40.5 g, 0.382 mol) was converted to the bromide with PBr₃³⁰ (23.4 g, 0.138 mol, 36.3% yield), bp 148—149 °C.

4-Methoxypentanoic-2,2-d₂ Acid

The Grignard reagent from 1-bromo-3-methoxybutane-1,1-d₂ (10.0 g, 59 mmol) was treated with CO₂ according to the procedure of Gilman and Kirby³¹ to give the carboxylic acid (1.9 g, 14 mmol, 24% yield), bp 135—137 °C at 28 mm (lit 72 °C at 0.2 mm).²⁸

4-Methoxy-1-pentanol-2,2-d₂

4-Methoxypentanoic-2,2-d₂ acid (1.9 g, 14 mmol) was reduced with lithium aluminum hydride²⁹ to yield 0.8 g of the carbinol (7 mmol, 48% yield, bp 83—84 °C at 12 mm (lit. 84.2—85.0 °C at 14.5 mm).^{1b}

5-Methoxy-d₃-2-pentanol

The Grignard reagent prepared from 5.5 g (51 mmol) of 1-chloro-3-methoxy-d₃-propane³² was reacted with acetaldehyde^{1b} (2.3 g, 54 mmol) to give the carbinol (2.4 g, 20 mmol, 39% yield), bp 77—78 °C at 13 mm (lit. 77.0—77.2 at 15 mm).^{1b}

5-Methoxy-2-pentanol-1,1,1-d₃

Grignard reagent prepared from 5.0 g (46 mmol) of 1-chloro-3-methoxy-propane³² was reacted with acetaldehyde-2,2,2-d₃³³ (2 g, 46 mmol) to give 3.0 g of the carbinol (21 mmol, 52% yield), bp 76—78 °C at 12 mm (lit. 77.0—77.2 at 15 mm).^{1b}

5-Methoxy-2-pentanone

Oxidation of 5-methoxy-2-pentanol (5 g, 42 mmol) with CrO₃—H₂SO₄ reagent in acetone gave, after fractional distillation 3.3 g (28 mmol, 67% yield) of the ketone, bp 162—163 °C (lit. 154 °C).³⁵

5-Methoxy-2-pentanol-2-d

Lithium aluminum deuteride reduction²⁹ of 3-methoxy-2-pentanone (3.3 g, 28 mmol) gave, after fractional distillation, 2.7 g (23 mmol, 82% yield) of the carbinol, bp 73—74 °C at 12 mm (lit. 77.0—77.2 °C).^{1b}

p-Bromobenzenesulfonates

The reactions of the carbinols with p-bromobenzenesulfonyl chloride were performed using the low temperature procedure of Winstein and Heck.³⁶ The products were recrystallized from pentane-ether at —70 °C, giving the following mp: 1P, 17.3—17.9 °C; 1P-1,1-d₂, 17.1—17.8 °C; 1P-2,2-d₂, 17.2—17.7 °C (lit. 20.5—21.0 °C);^{2b} 1S, 24.2—24.6 °C; 1S-2-d, 24.2—24.7 °C; 1S-1,1,1-d₃, 24.2—24.8 °C; 1S-OCD₃, 24.8 °C (lit. 31.5—32.0 °C).^{1b}

Rearrangement Test

1S (0.2 g) was dissolved in 95% ethanol (20 ml) at 40 °C and allowed to solvolyze for one half-life (28 min). The reaction mixture was then poured on ice and the unreacted brosylate extracted four times with 50 ml portions of pentane—ether (1:1 by volume) solvent. After washing with 50 ml of water and 30 ml of a 10% solution of Na₂CO₃, the combined extracts were dried over MgSO₄ and the solvent evaporated in vacuo. The residue was recrystallized from ether-pentane at -70 °C yielding 52% of the starting material, mp 24.3—24.9 °C. Examination of the NMR spectrum indicated that recovered 1S was uncontaminated with isomeric 1P.

When 0.156 g of 1P was solvolyzed for one half-life (33 min), 43% of the starting material was recovered. Again, NMR spectrum indicated that pure 1P was recovered, uncontaminated with 1S.

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SAŽETAK

5-Metoksil-participacija u solvolizi i sekundarni deuterijski izotopni efekti

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Priređeni su specifično deuterirani 4-metoksi-1-pentil-brosilati (1P-1,1- d_2 , 1P-2,2- d_2) i 5-metoksi-2-pentil-brosilati (1S-2- d , 1S-1,1,1- d_3 , 1S-OCD₃). Izmjerene su brzine solvolize u 95% -tnom etanolu, te su izračunani odgovarajući sekundarni deuterijski izotopni efekti. Nađeno je da su α -efekti značajno umanjeni što je u suprotnosti s rezultatima dobivenim sa više spojeva koji solvoliziraju putem σ - ili π - participacije. Efekt pronađen za 1P-1,1- d_2 ($k_H/k_D = 0,96$) signifikantno se razlikuje od vrijednosti izmjerene za 1S-2- d ($k_H/k_D = 1,06$). Ta razlika u veličini efekta mora odražavati relativno male razlike u strukturama dvaju prijelaznih stanja jer kako 1P tako i 1S solvoliziraju putem istog međuprodukta 2. Zaključuje se da je veličina α -efekta osjetljiva mjera jakosti premoštavanja samo tada kada je nova veza već vrlo jaka u prijelaznom stanju reakcije.

β -Deuterirani brosilati daju male efekte koji se razlikuju po veličini ($k_H/k_D = 0,96$ sa 1P-2,2- d_2 i 1,08 sa 1S-1,1,1- d_3) što potvrđuje zaključak da je nova veza C—O jaka u prijelaznim stanjima obiju reakcija, ali da je jača kod 1P nego kod 1S.

Rezultati dobiveni u ovom radu u skladu su s ranijim zaključkom da su smanjeni β -efekti kod solvolize egzo-2-norbornil, 3-kolesteril-, ciklobutil- i 1-metilciklobutil-derivata uzrokovani premoštavanjem.

Kod solvolize 1S-OCD₃ zapažen je obrnuti izotopni efekt ($k_H/k_D = 0,95$) koji mora biti »induktivnog« podrijetla. Ovakav rezultat ukazuje da kisik metoksilne skupine nosi znatnu količinu pozitivnog naboja u prijelaznom stanju reakcije.

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