Table I. Product Analysis[a] of Solvolysis of Cyclopentyl Brosylates in Ethanol–Water (70 vol %)

Brosylate	Cyclopentene	Cyclopentanol	Cyclopentyl ethyl ether
All H	22.1	45.9	32.0
cis-2-d_1	21.8	44.5	34.7
trans-2-d_1	19.5	44.5	35.0
2,2,5,5-d_4	14.0	44.1	41.9

[a] By flame ionization using 20% TCEP on Amakron SD, after 10 half-lives. Each product appears to be stable, by gas chromatographic analysis, in 70% ethanol–water with 10^{-2} *M* HOBs added for a period in excess of several days (20 half-lives).

Table II. Solvolysis of Cyclopentyl Brosylates[a]

Deuteration	$K \times 10^4$ sec^{-1}	K_H/K_D
All H	2.8014 ± 0.0023	
1-d_1	2.3603 ± 0.0009	1.1869
cis-2-d_1	2.4290 ± 0.0012	1.1533
trans-2-d_1	2.3735 ± 0.0009	1.1803
2,2,5,5-d_4	1.4837 ± 0.0011	1.8881

[a] In 70 vol % ethanol–water. *K* corrected to 100% deuterium. Four determinations were made for the all-H compound and duplicate measurements for the others.

The rate data, shown in Table II, were obtained by the precise conductometric determination[11] of the first-order solvolysis rate constants of the brosylates of the alcohols in 70 vol % ethanol at 25°. The precision of the conductometric method is ±0.05%.

Streitwieser observed a 1.22 isotope effect for the *cis* isomer and 1.16 isotope effect for the *trans* isomer, and because the *cis* isotope effect was larger than that of the *trans* isomer, he concluded that, if specific solvation of the β hydrogens is subject to the same stereochemical preferences as E2 eliminations, such solvation is not important in solvolytic displacement reactions.[2] Our kinetic data showed a larger isotope effect for the *trans* isomer than for the *cis* isomer. The lower amount of olefin produced from the *trans*-2-d_1 *vs.* the *cis*-2-d_1 supports the observation of a faster rate for the *cis* isomer. Thus the idea of specific solvation of the β hydrogens cannot be ruled out as a contributing factor to secondary isotope effects. This explanation is also in agreement with others[12–15] who also feel that specific solvation of the β hydrogens could lead to an elimination driving force in similar reactions. The possibility exists that the observed reversal in magnitude of the *cis* and *trans* isotope effects is due to a change in solvolyzing media from acetic acid used by Streitwieser to ethanol water used in this work. However, the results of Saunders and Finley,[5] who used acetolysis are in agreement with Shiner and Jewett,[3] who used ethanolysis in the cyclohexyl system. Changing from a tosylate to a brosylate group had little effect because checking several of these tosylates with the brosylates showed little difference in ethanolysis rates. Thus we feel that within the limits of error quoted by Streitwieser, one could not be certain whether his *cis* or *trans* effect was larger.

The solvolysis of the cyclopentyl brosylates in aqueous ethanol is thought to proceed through a limiting, S_N1, carbonium ion mechanism since the K_H/K_D for the 1-d_1 compound is 1.18.[16]

Successive β-deuterium substitution at conformationally equivalent sites leads to an apparent cumulative isotope effect, *i.e.*, the solvolytic rate retardation caused by tetradeuteration almost equals the square of that caused by mono-*cis*-deuteration times the square of that caused by mono-*trans*-deuteration: (2,2,5,5-d_4) = $1.8881 \neq 1.8530 = (1.1533)^2(1.1803)^2$ = (*cis*-2-d_1)$^2\cdot$(*trans*-2-d_1)^2. However, it is felt that this is a real difference, since the precision of these determinations was better than 0.1% This apparent cumulative behavior exhibited by the cyclopentyl system is best explained by hyperconjugation.[2,3,17]

This difference between the d_4 compound *vs.* the product of the squares of the *cis*-d_1 and *trans*-d_1 compounds (1.8881 *vs.* 1.8530) is comparable to the difference observed by Shiner and Jewett[4] for the solvolysis of *trans*-4-*t*-butylcyclohexyl brosylate (I). By a similar sequence, I-d_3(e,e,a)/I-d_1(a) = I-d_2(e,e) = 2.087/1.127 = 1.852 *vs.* 1.796 = $(1.340)^2$ = [I-d_1(e)]^2. This reflects the inability of the *trans* hydrogen or deuterium to obtain the desired *trans* coplanar relationship to the leaving group for both the cyclopentyl brosylate system, where the brosylate group is in the preferred equatorial type position (envelope structure for cyclopentanol), or for the cyclohexyl brosylate system, where the brosylate group is held in the equatorial position by the larger *t*-butyl group in the equatorial position.

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Hydrogen Participation in Open-Chain Arenesulfonate Solvolysis

Sir:

It was of interest to see if hydrogen participation, which is present in the solvolysis of *cis*-4-*t*-butylcyclohexyl brosylates,[1] also plays a role in the solvolysis of open-chain alkyl arenesulfonates. To do this, we have determined the effect of substitution of deuterium for the β hydrogens on the rate of solvolysis of 3-pentyl brosylate (I) and 2,4-dimethyl-3-pentyl brosylate (II).

3-Pentanol-2,2-d_2 was prepared by the reaction of propanal with the Grignard reagent of bromoethane-1,1-d_2.[2] 3-Pentanol-2,2,4,4-d_4 was prepared by exchange[3] of 3-pentanone in deuterium oxide containing

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potassium carbonate followed by reduction with lithium aluminum hydride to the alcohol.

Acetone was reduced with lithium aluminum deuteride to give 2-propanol-2-d_1 followed by treatment with phosphorus tribromide to give 2-bromopropane-2-d_1.[4] Part of the 2-bromopropane-2-d_1 was allowed to react, *via* the Grignard reagent, with 2-methylpropanal to give 2,4-dimethyl-3-pentanol-2-d_1 and part of the 2-bromopropane-2-d_1 was allowed to react, *via* the Grignard reagent, with ethyl formate to give 2,4-dimethyl-3-pentanol-2,4-d_2. The brosylates of the various alcohols were prepared by the usual Tipson procedure.[5]

The nmr analysis of the starting bromoethane-1,1-d_2 as well as the I-d_2 indicated that this alcohol was 98.7% β d_2. Nmr analysis of the I-d_4 indicated that this alcohol was 99.4% β d_4.

The nmr analysis of the II-d_1 and II-d_2 compounds showed them to be 100% β d_1 and d_2, respectively. This was to be expected since they were prepared from the same sample of 2-bromopropane-2-d_1 which showed no trace of α hydrogens according to nmr analysis. Nmr analysis of the brosylates likewise showed 100% d_1 and d_2, respectively, when prepared from these alcohols.

The rate data, shown in Table I, were obtained by the precise conductometric determination[6] of the first-order solvolysis rate constants of the brosylates in 70 vol % aqueous ethanol at 25°. The precision of the conductometric method is ±0.05%.

Table I. Solvolysis Data[a] for 3-Pentyl- and 2,4-Dimethyl-3-pentyl Brosylates

Compound	$K_1 \times 10^5$ sec^{-1}	K_H/K_D
$CH_3CH_2CHOBsCH_2CH_3$	5.9736	
$CH_3CD_2CHOBsCH_2CH_3$	4.5353	1.3171
$CH_3CD_2CHOBsCD_2CH_3$	3.4400	1.7365
$CH(CH_3)_2CHOBsCH(CH_3)_2$	9.3472	
$CD(CH_3)_2CHOBsCH(CH_3)_2$	6.8372	1.3671
$CD(CH_3)_2CHOBsCD(CH_3)_2$	4.4134	2.1179

[a] In 70 vol % ethanol–water at 25°. *K* corrected to 100% deuterium content.

For the case of the 3-pentyl brosylates, the data show that successive deuterium substitution leads to cumulative isotope effects, *i.e.*, the solvolytic rate retardation caused by the tetradeuteration equals the square of that caused by monodeuteration: $(\text{I-}d_4) = 1.7365 \cong 1.7348 = (1.3171)^2 = (\text{I-}d_2)^2$. This cumulative behavior observed for β-deuterium isotope effects is best explained by hyperconjugation.[7]

However, in the case of the 2,4-dimethyl-3-pentyl brosylates, the successive deuterium substitution does not lead to cumulative isotope effects; *i.e.*, the rate retardation caused by dideuteration does not equal the square of that caused by monodeuteration: $(\text{II-}d_2) = 2.1179 \neq 1.8690 = (1.3671)^2 = (\text{II-}d_1)^2$. The effect of each β-deuterium atom in the solvolytic transition state may be calculated using the expression of the form[7] $(K_H/K_D)_x = 2xx'/(x + x')$ where $(K_H/K_D)_x$ is the experimentally determined isotope effect for substitution of a single deuterium atom while x and x' are the effects of the first and second deuterium atoms in the transition state. This type of analysis leads to the isotope effects of 1.018 and 2.080 for the replacement of the first and second β hydrogens in 2,4-dimethyl-3-pentyl brosylates. As was suggested in the case of the *cis*-4-*t*-butylcyclohexyl brosylate,[1] this noncumulative isotope effect behavior is best explained in terms of neighboring participation in the solvolytic transition state. This is contrasted with the cumulative isotope effects for the 3-pentyl system which are attributed to hyperconjugation.

The K_H/K_D of 2.12 (Table I) for II-d_2 is very close to the K_H/K_D of 2.15 observed for 3-methyl-2-butyl-3-*d* tosylate reported by Winstein and Takahashi.[8]

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Thermal and Photo [3,3] Sigmatropic Rearrangements in the *cis*-2,2-Dimethyl-3-isobutenylcyclopropyl Isocyanate–3,6-Dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one System[1]

Sir:

In a previous paper[2] we have shown that *cis*-2,2-dimethyl-3-isobutenylcyclopropyl isocyanate (**2**) is stable in refluxing benzene, in contrast with the thermal instabilities of *cis*-2-vinylcyclopropyl isocyanate (**9**)[3a,b] and *exo*- and *endo*-benzonorcaradienyl isocyanate[3c] under similar conditions.

We wish to report in this communication the thermal [3,3] sigmatropic rearrangement (the Cope rearrangement) of **2** which afforded a novel aza analog of homocyclohexadienone (ii), **3** (3,6-dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one), having a very reactive imino ketone structure, and also the photo [3,3] sigmatropic rearrangement of **3** to **2**.

Pure **2**, bp 90° (20 mm), obtained by the Curtius rearrangement of the corresponding *cis*-azide **1**, was heated in dry *o*-xylene at the refluxing temperature (144°) for 60 hr, affording an equilibrium mixture of **2** and a product (**3**) in the ratio of 1:7 (glpc analysis). Distillation under reduced pressure (2 mm) gave a

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