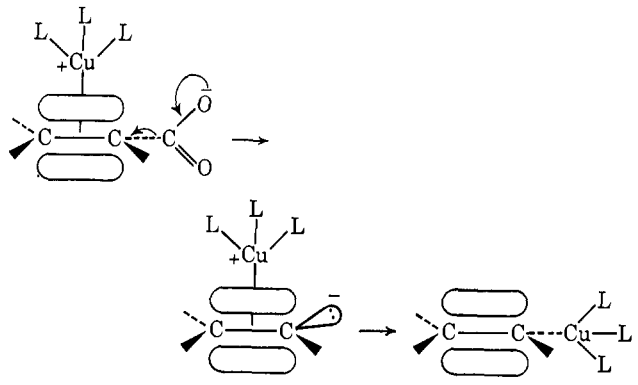

L = ligand

heterocyclic amine could promote the reaction by (1) stabilizing the π complex ("soft" ligands tend to flock together[9]) and/or (2) increasing the electron-withdrawing ability of the cuprous ion. The intermediacy of a σ-bonded organocopper intermediate[10] is suggested by the trapping experiments of Nilsson,[4] the coupling results reported above,[12] and the fact that in the case of cuprous *o*-nitrobenzoate, the presence of water (0.5 mol/mol of salt) greatly increases the extent of nitrobenzene formation at the expense of symmetrical biaryl.[13]

The novel concept that a metallic ion may be capable of stabilizing the transition state of a reaction in which a negative charge is being generated on an atom whose p orbital is involved in π-bond formation with the metal ion has a number of possible implications, some of which we hope to investigate.

Of immediate practical application are the findings: (1) that this reaction can be very conveniently executed by utilizing the free carboxylic acid in the presence of cuprous oxide which behaves as a catalyst, (2) that nitrogen heterocyclic chelating agents are capable of considerably increasing the rate constant or of allowing a lower reaction temperature when quinoline is used as the solvent, and (3) that the reaction can be conducted in noncomplexing solvents, provided that complexing agents are present. Finally, there are preliminary indications that it is important to maintain a nitrogen atmosphere during the reaction, since the presence of oxygen sharply decreases the cuprous ion concentration and increases that of cupric ion, which causes an oxidative decarboxylation[5] (phenyl benzoate is produced from cupric benzoate). The partiality shown in the literature for the use of copper rather than its salts[14] can very likely be traced to this last factor since inert atmospheres have not generally been used.

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Kinetic Isotope Effects in the Aqueous Ethanolysis of Deuterated Cyclopentyl Brosylates[1]

Sir:

Several papers have appeared in the literature which have dealt with the solvolysis of cycloalkyl brosylates and tosylates in various solvent systems, *e.g.*, acetolysis of deuterated cyclopentyl tosylates,[2] aqueous ethanolysis of deuterated *cis*-4-*t*-butylcyclohexyl brosylates,[3] aqueous ethanolysis of deuterated *trans*-4-*t*-butylcyclohexyl brosylates,[4] and acetolysis of deuterated cyclohexyl tosylates.[5] Comparison of these papers revealed differences between the two ring systems. The cyclopentyl system tended to show isotope effects that were cumulative in nature, whereas in the cyclohexyl system they were noncumulative in nature. Also for the cyclopentyl system it was observed that the *cis* isotope effect was greater than that of the *trans* isomer which was opposite to that observed for the cyclohexyl system. Because of these differences a reinvestigation of the cyclopentyl system was undertaken.

Cyclopentanol-1-d_1 was prepared by reducing cyclopentanone with lithium aluminum deuteride.[2] *cis*-Cyclopentanol-2-d_1 was prepared by deuteriboration of cyclopentene which was a modification of the Brown[6,7] method in which diborane-d_6 is generated *in situ* from boron trifluoride and lithium aluminum deuteride.[8] *trans*-Cyclopentanol-2-d_1 was prepared by the action of lithium aluminum deuteride on cyclopentene epoxide.[2] Cyclopentanol-2,2,5,5-d_4 was prepared by repeated exchanges of cyclopentanone with weakly basic D_2O followed by reduction of this ketone with lithium aluminum hydride.[2] The brosylates of the various alcohols were prepared by the usual Tipson procedure.[9] These were analyzed[10] by combustion, and the per cent deuterium was obtained by the falling drop technique. The brosylates were chosen rather than the tosylates used in Streitwieser's work because it was more convenient to handle the higher melting compound. Also, the solvolyzing media was changed from acetic acid to 70 vol % ethanol in order that the rates of solvolysis could be monitored by a conductance method. It is felt that despite these minor changes a comparison of the data can still be made.

Results of product analysis of the solvolysis mixture by gas chromatography are given in Table I.

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(10) J. Nemeth, Urbana, Ill. 61801.

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.

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(14) V. J. Shiner, Jr., and C. J. Verbanic, *ibid.*, **79**, 373 (1957).
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The solvolysis of the cyclopentyl brosylates in aqueous ethanol is thought to proceed through a limiting, SN1, 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 ≠ 1.8530 = $(1.1533)^2(1.1803)^2$ = (*cis*-2-d_1)^2·(*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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