Registry No.—**1a**, 822-93-5; **1b**, 18738-69-7; **1c**, 38868-43-8; **1d**, 10359-44-1; **1e**, 23510-65-8; **1f**, 27847-24-1; **1g**, 23603-63-6; **1h**, 693-86-7; **1i**, 4663-22-3; **1j**, 23772-96-5; **1k**, 27720-84-9; **2a**, 26047-84-7; **2b**, 38858-55-8; **2c**, 38858-56-9; **2c**, 27926-30-3; **2e**, 27829-87-4; **2f**, 27847-26-3; **2g**, 27847-25-2; **2h**, 38858-59-2; **2i**, 27847-27-4; **2j**, 38858-61-6; **2k**, 31776-08-6; TCNE, 670-54-2.

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Secondary Deuterium Isotope Effects in the Solvolysis of Cyclobutyl and Cyclopropylcarbinyl Methanesulfonates

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Deuterated cyclobutyl methanesulfonates **1a–d** and cyclopropylcarbinyl methanesulfonates **2a–d** were prepared and their solvolysis rates were measured in 60% aqueous diglyme. With cyclobutyl methanesulfonates, a reduced α effect, an inverse β effect, and a rather large normal γ effect were observed. These results indicate a strong 1–3 interaction in the transition state. The isotope effects found in solvolysis of cyclopropylcarbinyl methanesulfonates are inconclusive with respect to a possible bridging in the transition state. A degenerate internal rearrangement of cyclopropylcarbinyl methanesulfonate was demonstrated to occur during acetolysis.

Since the early work by Bergstrom and Siegel[1] and Roberts, *et al.*,[2] solvolytic rearrangements of cyclopropylcarbinyl and cyclobutyl derivatives remained on the scene of mechanistic chemistry.[3,4] However, even after two decades the exact structure of the solvolytic intermediate(s) is still ambiguous. Recent results[4,5] clearly showed that the cyclopropylcarbinyl → cycloproplycarbinyl, the cyclopropylcarbinyl → cyclobutyl, and the cyclopropylcarbinyl → allylcarbinyl rearrangements are highly stereospecific, the rotation of the methylene group being completely absent during rearrangements. This conclusion has been more recently confirmed by the nmr studies of stable cyclopropylcarbinyl and cyclobutyl cations generated from the corresponding alcohols in SbF_5–SO_2ClF solutions at low temperatures.[6] The nmr spectra showed three signals: two three-proton methylene doublets and a one-proton methine multiplet. Cyclobutyl and cyclopropylcarbinyl derivatives appear to solvolyze by forming in the rate-determining step one and two intimate ion pairs, respectively, which then further ionize to the corresponding equilibrating solvent-separated ion pairs.[7,8] A number of nonclassical structures for the intermediate cations could fit this scheme.

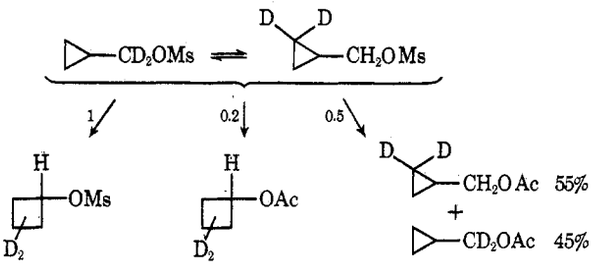
In this paper we wish to report about secondary isotope effect studies in the solvolysis reaction of cyclobutyl and cyclopropylcarbinyl methanesulfonates which lead, *inter alia*, to a reinterpretation of some earlier findings.[9]

(1) C. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, **74**, 145 (1952).
(2) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960), and references cited therein.
(3) Reviews: Chapters by H. G. Richey, Jr., and by K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1971.
(4) Z. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971), and references cited therein.
(5) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); **90**, 4195 (1968).
(6) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).
(7) Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **25**, 301 (1969).
(8) Z. Majerski, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 1636 (1970).
(9) S. Borčić, M. Nikoletić, and D. E. Sunko, *J. Amer. Chem. Soc.*, **84**, 1615 (1962).

Results

Specifically deuterated cyclobutyl methanesulfonates **1a–d** and cyclopropylcarbinyl methanesulfonates **2a–d** were prepared as described in the Experimental Section.

The acetolysis of the cyclopropylcarbinyl derivatives is known to be accompanied by an internal return to cyclobutyl isomers.[2] Therefore, a degenerate cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement could also be expected. Such an internal return reaction could change the rate constant during the solvolysis of deuterated cyclopropylcarbinyl derivatives because of the label scrambling. In the present work we checked this possibility by following the acetolysis of cyclopropylcarbinyl-*1,1-d*$_2$ methanesulfonate (**2a**) in perdeuterated acetic acid at 37° using the nmr technique. The observed changes of the proton signals are shown in Figure 1. The spectra in Figure 1 clearly demonstrate the occurrence of a degenerate cyclopropylcarbinyl rearrangement reaction as well as the internal return into cyclobutyl methanesulfonate and the formation of two corresponding acetates. The relative rates obtained by integration of the final spectra are given in the scheme below.



These results are in good agreement with previous experimental evidence.[2,8]

Methanesulfonates **1a–d** and **2a–d** were solvolyzed in 60% aqueous diglyme at 40° and the reaction rates were followed by continuous titration of liberated acid by means of an automatic recording titrator. The rate constants and the corresponding kinetic isotope

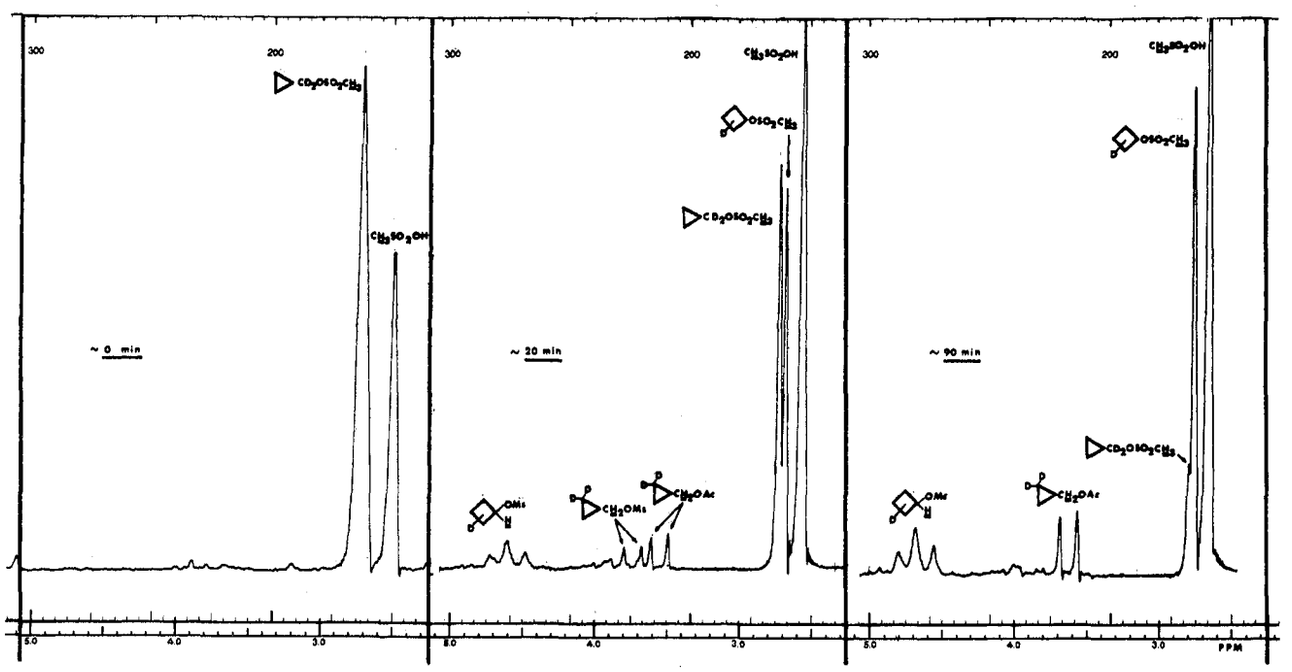


Figure 1.—The acetolysis of cyclopropylcarbinyl-*1,1-d*$_2$ methanesulfonate (**2a**) in CD_3COOD followed by nmr at 37°.

effects were calculated using a nonlinear least square program. The results are given in Table I.

The internal rearrangement of cyclopropylcarbinyl to cyclobutyl methanesulfonate under the experimental conditions used for kinetic measurements is known[7] to account for only 10% of the reaction products. Hence, it can easily be shown, on the basis of the relative rates in acetic acid as given in the scheme, that the maximum concentration of **2c** (**2a**) occurring during the solvolysis of **2a** (**2c**) is too low to produce experimentally detectable reaction rate changes.[10]

Discussion

Solvolysis of Cyclobutyl Methanesulfonates.—The α-deuterium isotope effect in the solvolysis of cyclobutyl methanesulfonate (1.10) is small compared to the maximum possible value for the solvolysis of a secondary sulfonate ester (1.22).[11] It is difficult to ascribe this reduction in magnitude of the isotope effect unequivocally to a single distinct cause. According to Shiner[11] a maximum α effect can be expected if in the reaction transition state there is no covalent bonding between the α carbon and either the leaving group or the nucleophile. In the particular case examined, nucleophilic participation by the solvent (k_s) is not probable, since the reaction products are extensively rearranged. Under the experimental conditions used in this work, it is possible that ionization (formation of the intimate ion pair) is the rate-determining step. In such a case, there would still be some covalent bonding between the reaction center and the leaving group in the transition state and the α effect should be reduced in magnitude. However, the effect is too low (by about 5%) to be ascribed to simple ionization as rate determining.[12a] On the other hand, maximum overlap calculations and ^{13}C–H coupling constants show that C–H bonding orbitals in cyclobutane have less p character ($sp^{2.65}$) than the corresponding orbitals in a tetrahedral carbon.[13] Since α-deuterium effects have been rationalized in terms of hybridization changes occurring at the reaction center, it is possible that the small α effect in the solvolysis of cyclobutyl methanesulfonate reflects this special hybridization in the ground state. Finally, neighboring group participation (k_Δ) is analogous, with respect to isotope effect, to nucleophilic partipation by the solvent (k_s). Streitwieser suggested[14] that participation could reduce the magnitude of the α effect. Available data demonstrate[15] that, indeed, the α effect is significantly reduced by participation, but only when the new bond is already rather strong in the reaction transition state. Thus, the reduced α effect measured in solvolysis of cyclobutyl methanesulfonate could also be ascribed to neighboring group participation.

Secondary β-deuterium isotope effects have been rationalized in terms of hyperconjugation and amount to $1.00 \leq k_H/k_D \leq 1.30$ per atom D, depending on the dihedral angle between the incipient empty p orbital and neighboring C–H(D) bonding orbitals.[16] The

(10) It appears from the nmr spectra that in acetolysis the maximum concentration of the rearranged cyclopropylcarbinyl methanesulfonate is reached by the time when one third of the final amount of the rearranged cyclopropylcarbinyl acetate is formed. At that time the concentration of both of these compounds is about equal. From these data and the relative rates in the scheme it can be calculated that the maximum concentration of **2a** (**2c**) in the acetolysis of **2c** (**2a**) is about 5% of the initial concentration of the starting methanesulfonate. During acetolysis, 60% of cyclopropylcarbinyl methanesulfonate internally rearranges to cyclobutyl methanesulfonate as compared with only 10% during solvolysis in 60% aqueous diglyme. It can be assumed that in the latter solvent the degenerate internal rearrangement would be also correspondingly less important.

(11) V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971), and references cited therein.

(12) Review: Chapter 2 by V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., ACS Monograph 167, Van Nostrand-Reinhold, Princeton, N. J., 1970, (a) pp 115–118; (b) p 98; (c) p 107; (d) p 121.

(13) M. Randić and Z. B. Maksić, *Chem. Rev.*, **72**, 43 (1972).

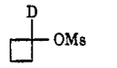
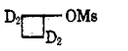
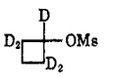
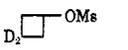
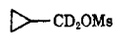
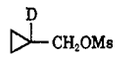
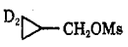
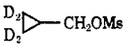
(14) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 173–175.

(15) Review: Chapter 3 by D. E. Sunko and S. Borčić in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., ACS Monograph 167, Van Nostrand-Reinhold, Princeton, N. J., 1970, and references cited therein.

(16) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **85**, 2416 (1963).

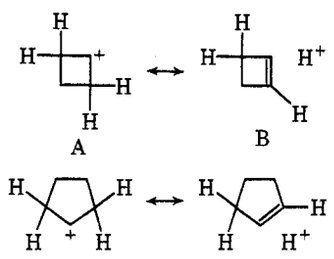
TABLE I

DEUTERIUM ISOTOPE EFFECTS IN THE SOLVOLYSIS OF THE CYCLOBUTYL (1)[a] AND CYCLOPROPYLCARBINYL (2)[b] METHANESULFONATES IN 60% AQUEOUS DIGLYME

Compd	Compd no.	Deuterium content %	Temp, °C	k_H/k_D[c]	k_H/k_D[d]
	1a	98	40	1.102 (1)	1.103 (1)
	1b	93	40	0.934 (6)	0.928 (6)
	1c	94	40	1.001 (4)	1.004 (4)
	1d	76	40	1.055 (3)	1.077 (2)
	2a	98	20	1.298 (1)	1.319 (1)
	2b	94	20	1.014 (1)	1.015 (1)
	2c	98	20	0.964 (3)	0.963 (2)
	2d	96	20	0.941 (4)	0.938 (3)

[a] Rate constant for undeuterated **1** was 2.725×10^{-4} sec^{-1}. [b] Rate constant for undeuterated **2** was 2.607×10^{-3} sec^{-1}. [c] The values of isotope effects were calculated from four to six individual rate constants for both deuterated and undeuterated compounds; the errors are given as standard errors, *e.g.*, 1.102 (1) = 1.102 ± 0.001. [d] The values corrected to 100% deuterium content.

inverse isotope effect observed in the solvolysis of **1b** is a quite unusual result[17] and requires a specific mechanistic interpretation. If the reaction transition state resembles a classical cyclobutyl cation, the unusual β effect cannot be due to conformational factors. On the basis of the increased angle strain it could be expected that the no-bond resonance structures such as B contribute less to the resonance hybrid describing the incipient cation than do the corresponding structures to the cyclopentyl cation. Thus different β-



isotope effects in these two cases could be explained by different amounts of hyperconjugative electron release from neighboring C–H(D) bonding orbitals to the electron-deficient carbon in the reaction transition state. However, this argument rests upon the assumption that the strain in cyclobutene relative to cyclobutane is higher than in cyclopentene relative to cyclopentane. In fact, there is no evidence for such an assumption. On the contrary, the difference in the heats of formation is larger for the cyclopentene–cyclopentane pair (27.0 kcal/mol) than it is for the cyclobutene–cyclobutane pair (21.1 kcal/mol).[19]

Therefore the effort to explain the inverse β effect observed with cyclobutyl-*2,2,4,4-d*$_4$ methanesulfonate in terms of a transition state resembling a classical cyclobutyl cation seems fruitless. A reasonable approach to this problem seems to be search for analogous behavior of other systems. A few years ago we suggested[20] that reduced β-deuterium isotope effect could be used as a criterion for neighboring group participation in solvolysis. It is an outstanding fact that, in solvolysis of compounds for which neighboring group participation has been demonstrated by other means, the corresponding β-deuterium effect is significantly reduced *in every single case*. This is illustrated in Table II by comparison[21-26] (when possible) with the appropriate model compound. Thus by analogy we ascribe the unusual β-deuterium isotope effect measured in the solvolysis of cyclobutyl methanesulfonate to neighboring group participation, *i.e.*, to a 1–3 bonding interaction in the rate-determining step.[27]

The observed rather large normal γ-deuterium effect is consistent with this conclusion. An analogous behavior has been observed in solvolysis of the γ-deuter-

(17) The observed rate increase can be compared with the β effect in solvolysis of cyclopentyl-*2,2,5,5-d*$_4$ brosylate (70% EtOH, 25°) where k_H/k_D equal to 1.88 was found.[18]

(18) J. O. Stoffer and J. D. Christen, *J. Amer. Chem. Soc.*, **92**, 3190 (1970).

(19) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(20) M. Nikoletić, S. Borčić, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967).

(21) R. Eliason, unpublished result.

(22) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 1489 (1968). The value reported in this communication for the exo compound, k_H/k_D = 1.014, was shown to be too low. See also B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, **92**, 3464 (1970).

(23) W. H. Saunders, Jr., S. Ašperger, and D. H. Edison, *J. Amer. Chem. Soc.*, **80**, 2421 (1958).

(24) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

(25) M. Tarle, unpublished results.

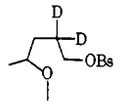
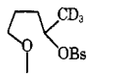
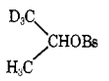
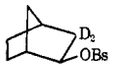
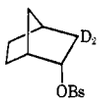
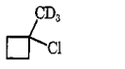
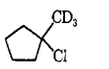
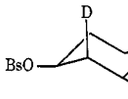
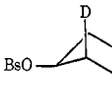
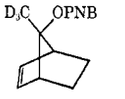
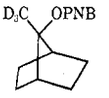
(26) M. Tomić and I. Szele, unpublished results.

(27) Recently we obtained the results[28] from theoretical calculations of the Wolfsberg–Stern[29] type. It appears that the inverse β effect is due to a low MMI factor of the Bigeleisen equation (k_H/k_D = MMI × EXC × ZPE). The ZPE factor is reduced in magnitude but is larger than unity.

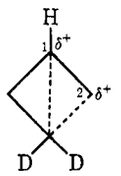
(28) B. Goričnik, Ph.D. Thesis, University of Zagreb, 1972.

(29) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 2618 (1966), and references cited therein.

TABLE II
SOLVOLYTIC β-DEUTERIUM ISOTOPE EFFECTS

Compd	k_H/k_D	Model compd	k_H/k_D	Ref
	0.98			15, 21
	1.09		1.19	15, 21
	1.10		1.26	15, 22
Ph_2CDCH_2OTs	1.01			23
$PhCD_2CH_2OTs$	1.00			23
	1.09		1.21	20, 24
	0.99		1.20	25, 15
	1.09		1.83	26

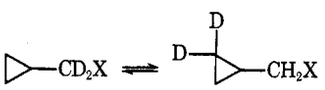
ated *exo*-2-norbornyl derivatives.[30] For compounds which do not solvolyze by anchimeric assistance, very small normal or slightly inverse γ-deuterium effects have been measured.[30] In our case, if bridging at γ carbon occurs in the rate-determining step, some changes of the γ-C–H(D) bond force constants can occur, resulting in a kinetic isotope effect. However, although an isotope effect can be expected, the direction of this effect is rather difficult to rationalize. If bridging is depicted as in the following figure[31] then it becomes apparent that the formation of the new



bond to the γ carbon is accompanied by a simultaneous breaking of another bond to the same carbon. It can be expected that the bond-breaking process will tend to increase k_H/k_D while the bond-forming process will tend to decrease this ratio. Considering the observed γ effect as analogous to α effects (with C_2 as the leaving group and C_1 as the nucleophile) it can be expected that the bond-breaking process will influence more the composite k_H/k_D value than the bond-forming process. Such a result is due to the exponential nature of the correlation between the magnitude of the α effect and the bond length attained by the bond forming/breaking process in the transition state.[15]

A similar analysis could be carried out for the situation pertaining to C_2 in the transition state. However, here the bond-breaking process is accompanied by the development of the positive charge, which (in the first approximation) is *not* the case at C_3. The electron-donating inductive effect of deuterium relative to protium will tend to make $k_H/k_D < 1.00$ and a composite, slightly inverse β-isotope effect is observed.

Solvolysis of Cyclopropylcarbinyl Methanesulfonates. —In a previous paper[9] we reported that the α-deuterium isotope effect in ethanolysis of cyclopropylcarbinyl benzenesulfonate was larger than that in acetolysis. In view of recent development in the understanding of α effects, such a result is rather surprising. Namely, the acetolysis is accompanied by a competitive internal rearrangement to cyclobutyl benzenesulfonate, while this is not the case in ethanolysis. This indicates that the formation of the intimate ion pair is probably rate determining in ethanolysis while the transformation of the intimate ion pair into external ion pair must be rate determining in acetolysis. Thus, in the transition state of acetolysis there should be no covalent bonding to the α carbon, a situation which is associated with the maximum possible α effect.[11] The transition state in ethanolysis involves probably some covalent bonding to the leaving group, and consequently the α effect should be *smaller* than in acetolysis. A possible explanation of this apparent discrepancy could be a cyclopropylcarbinyl → cyclopropylcarbinyl type of internal rearrangement competing with acetolysis which would scramble deuterium at positions 1, 3 and 4. Such a rearrangement would result in an



increasing trend in the rate constant with the per cent of completion of the reaction. This trend could have easily escaped detection by the experimental technique used in this early work.

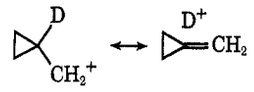
The occurrence of competitive deuterium scrambling during acetolysis of α-deuterated cyclopropylcarbinyl methanesulfonate has now indeed been demonstrated by the nmr technique as described in the Results section of this paper. Thus it appears that the k_H/k_D value for acetolysis reported previously[9] represents a composite α and γ effect and that the α effect is in fact larger.

It is difficult to estimate if the α-deuterium isotope effect of 1.32 reported in the present work is reduced in magnitude relative to the maximum possible effect. Primary alkyl derivatives normally do not solvolyze by the limiting dissociative mechanism, so that there is no good analogy for comparison. An isotope effect of 1.19 has been calculated for the change from CH_3-$CHDCl$ to CH_2=CHD.[12b] On the other hand, it has been shown that the tightness of binding of deuterium may be nearly the same in a carbonium ion pair as in an alkene.[12d] Thus it can be estimated that a maximum k_H/k_D value for the transformation $RCD_2Cl \rightarrow RCD_2^+$ of about 1.41 could be expected. As sulfonate esters solvolyze with larger α effects than the corresponding chlorides,[12a] it could be indeed concluded that the α effect in the solvolysis of the cyclopropylcarbinyl methanesulfonate is less than the possible maximum value. This is of course, consistent with a 1–3 interaction in the transition state, but is certainly not conclusive.

(30) J. M. Jerkunica, S. Borčič, and D. E. Sunko, *J. Amer. Chem. Soc.*, **89**, 1732 (1967).

(31) We do not pretend to represent accurately the structure of the transition state by this figure.

A very small β-isotope effect is not very informative with respect to neighboring group participation. A small β effect could here be expected for a variety of possible mechanisms. Even in the (most improbable) case that the transition state resembles a classical ion the no-bond resonance of the type



could be expected to be negligible and hence the isotope effect small.

Slightly inverse γ effects[32] can be explained without invoking bridging. Charge delocalization to C_3 and C_4 undoubtedly occurs in the rate-determining step. Thus, the inductive effect of deuterium could be responsible for the slightly increased rate of γ-deuterated compounds. Neither can the bridging be excluded because the measured k_H/k_D could be a composite effect in the way discussed previously for the solvolyses of γ- and β-deuterated cyclobutyl methanesulfonates.

In conclusion, secondary deuterium isotope effects indicate that the solvolysis of cyclobutyl methanesulfonate proceeds by way of anchimeric assistance with a strong 1–3 interaction in the transition state. In this respect, the evidence for the solvolysis of cyclopropylcarbinyl derivatives is not conclusive. In the latter case, it is quite possible that the enhanced rate is due predominantly or exclusively to vertical stabilization as discussed by Traylor.[34]

Experimental Section

Kinetic measurements were made on an automatic recording titrator (Radiometer, Copenhagen, TTT 11). Deuterium content in all compounds was determined by multiple integrations of the proton signals in the nmr spectra of appropriate intermediates in the synthetic sequence. Purity of the compounds was checked by vpc, ir, and nmr. Cyclopropylcarbinol-*1,1-d*$_2$, cyclopropylcarbinol-*2-d*$_1$, cyclopropylcarbinol-*3,3-d*$_2$, and cyclopropylcarbinol-*3,3,4,4-d*$_2$ were prepared as previously described.[9] Cyclobutanol-*2,2,4,4-d*$_4$ was obtained by repeated alkaline exchange of cyclobutanone in D_2O[2] followed by $LiAlH_4$ reduction.

1,3-Propandiol-*2,2-d*$_2$ (3).—The reduction of the deuterated dimethyl malonate with $LiAlH_4$ was done by Lambert's procedure.[35] A solution of 210 g (1.545 mol) of dimethyl malonate-d_2 (98% of deuterium) in 1000 ml of ether was added dropwise into a suspension of 86 g (2.26 mol) of $LiAlH_4$ in 1800 ml of ether under stirring. The reaction mixture was refluxed overnight, and then the solution of 7.7 g of NaOH in 160 ml of water was slowly added and the clear etheral layer was removed. The residue was washed with three 700-ml portions of boiling THF. Combined extracts were dried over anhydrous $CaSO_4$ and solvents were removed by distillation. The crude diol **3** was fractionated under vacuum, yielding 48.8 g (40.5%) of pure product, bp 120–125° (10 mm).

1,3-Dibromopropane-*2,2-d*$_2$ (4).—A 48-g (0.616 mol) portion of **3** was carefully added to stirred and cold (0°) PBr_3. Upon addition, the mixture was refluxed for 10 hr. The reaction mixture was then cooled to room temperature, 60 ml of water was added, and the product was extracted with methylene chloride. After work-up and distillation 70.1 g (55.2%) of dibromide **4**, bp 64–65° (13 mm), was obtained.

Cyclobutane-*3,3-d*$_2$-carboxylic acid (5) was prepared from 62 g (0.387 mol) of diethyl malonate and 66 g (0.32 mol) of **4** by standard procedure[36] in 62% yield. The boiling point of pure acid was 96–101° (10 mm).

Cyclobutyl-*3,3-d*$_2$-carboxamide (6).—To an equimolar mixture of **5** and triethylamine [13 g (0.1275 mol) and 12.9 g, respectively] in cold (−5°) chloroform the same (13.9 g) molar quantity of ethyl chloroformate was added, the mixture was swirled for 15 min, and then dry ammonia was passed through the mixture for an additional 15 min. After standing overnight at room temperature the reaction mixture was filtered, solvent was evaporated, and the residue was dissolved in hot benzene, filtered again, and diluted with hot *n*-hexane. Filtration after cooling to 20° gave 10.3 g (0.102 mol, 80.2%) of the amide **6**.

Cyclobutyl-*3,3-d*$_2$ Methyl Ketone (7).—Deuterated cyclobutyl carboxamide (**6**) (10.2 g) was added in small portions during 30 min into the solution of 0.436 mol of methylmagnesium iodide in dry ether. Upon refluxing overnight crushed ice was carefully added and the etheral layer was separated. The aqueous layer was acidified, saturated with NaCl, and exhaustively extracted with ether. After work-up and fractionation 3.8 g (0.038 mol) of the product **7**, bp 132–138° (759 mm), was obtained.

Cyclobutyl-*3,3-d*$_2$ Acetate (8).—A solution of 13.2 g (0.14 mol) of trifluoroperacetic acid in 40 ml of methylene chloride was added dropwise into a stirred suspension of 3.7 g (0.037 mol) of **7** and 24 g of Na_2HPO_4 in the same solvent. The reaction mixture was refluxed for 30 min, then cooled, filtered, washed with 10% aqueous Na_2CO_3 solution, and dried over $CaSO_4$. The crude product was distilled to give 2.3 g (0.0198 mol, 53.5%) of pure acetate **8**, bp 120–125° (758 mm).

Cyclobutanol-*3,3-d*$_2$ was obtained in 85.6% yield by alkaline hydrolysis of **8**. The deuterium content was 76%, determined by the nmr.

Methanesulfonates (**1a–d** and **2a–d**) of the corresponding alcohols were prepared in 65–80% yields according to the procedure published elsewhere.[7]

Registry No.—**1a**, 31053-86-8; **1b**, 31053-88-0; **1c**, 38645-08-8; **1d**, 38645-09-0; **2a**, 31053-87-9; **2b**, 38645-11-3; **2c**, 38645-12-4; **2d**, 38645-13-5; **3**, 38645-14-6; **4**, 38645-15-7; **5**, 38645-16-8; **6**, 38645-17-9; **7**, 38645-18-0; **8**, 38645-19-1; cyclobutanol-*3,3-d*$_2$, 24468-96-0; dimethyl malonate-*d*$_2$, 36647-07-1.

Acknowledgment.—This work has been supported in part by a grant from the Research Council of the Republic of Croatia.

(32) It should be mentioned that the γ effect per atom D is not significantly different for the dideuterated methanesulfonate and for the tetradeuterated analog, which is contrary to our earlier report.[9] At the time we were not fully aware of the difficulties encountered in the measurements of small isotope effects as discussed by Collins.[33]

(33) C. J. Collins, *Advan. Phys. Org. Chem.*, **2**, 63 (1964).

(34) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

(35) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1840 (1967).

(36) G. B. Heisig and F. H. Stodola, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 213.