is more than fortuitous. The extended independence now demonstrated casts doubt upon the ion pair or ion–neutral pair mechanism for benzylic systems, even for *p*-methoxy. We therefore believe that the evidence points to SN2-like transition states for solvolysis and a "sandwich" (ion triplet) mechanism for the azide reaction with *p*-methoxybenzyl chloride. It should be emphasized that the suggestion of an SN2-like transition state does not imply a necessarily concerted mechanism, since it could, if loose, still lead to carbonium ion type intermediates. The magnitudes and constancy of the observed chlorine and sulfur KIE suggest that the mechanism may well be concerted, however, as might be expected for a primary system passing through a relatively tight transition state,[34] not sterically loosened by congestion at the central carbon atom.[14,15]

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References and Notes

(1) (a) Supported by the National Science Foundation through Grants GP-22,803 and GP-34,491X. (b) For further details, cf. M. P. Friedberger, Ph.D. Dissertation in Chemistry, University of Pennsylvania, 1975.
(2) A. Fry, "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, Chapter 6.
(3) S. E. Scheppele, *Chem. Rev.*, **72**, 511 (1972).
(4) J. W. Hill and A. Fry, *J. Am. Chem. Soc.*, **84**, 2763 (1962).
(5) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *Chem. Commun.* 1032 (1970).
(6) G. Kohnstam, A. Queen, and B. Shillaker, *Proc. Chem. Soc., London*, 157 (1959).
(7) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).
(8) C. G. Swain, W. D. Burrows, and B. J. Schowen, *J. Org. Chem.*, **33**, 2534 (1968).
(9) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).
(10) K. B. Schowen, Ph.D. Thesis in Chemistry, Massachusetts Institute of Technology, 1964 [R. L. Schowen, *Prog. Phys. Org. Chem.*, **9**, 275 (1972), ref 75].
(11) C. G. Swain, T. Rees, and L. J. Taylor, *J. Org. Chem.*, **28**, 2903 (1963).
(12) R. A. Sneen, G. R. Felt, and W. C. Dickason, *J. Am. Chem. Soc.*, **95**, 638 (1973).
(13) C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80**, 4089 (1958).
(14) E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967).
(15) G. J. Frisone and E. R. Thornton, *J. Am. Chem. Soc.*, **90**, 1211 (1968).
(16) D. G. Graczyk and J. W. Taylor, *J. Am. Chem. Soc.*, **96**, 3255 (1974).
(17) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 6031 (1969).
(18) This fortuity is not quite rigorously established, because the solvents are different,[4,16] although the fact that the chlorine KIE are the same strongly suggests that the solvent change has no influence in this case.
(19) W. G. Brown, "Organic Reactions", Vol. VI, Wiley, New York, N.Y., 1951, Chapter 10, pp 491–492.
(20) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).
(21) W. H. Saunders, Jr., and S. Asperger, *J. Am. Chem. Soc.*, **79**, 1612 (1957).
(22) L. Melander, "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y., 1960, pp 48–50.
(23) C. G. Swain, E. C. Stivers, Jr., J. F. Reuwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).
(24) C. A. McDowell, "Mass Spectrometry", McGraw-Hill, New York, N.Y., 1963, pp 404 and 405.
(25) R. Quelet and J. Allard, *Bull. Soc. Chim. Fr.*, **4**, 1468 (1937).
(26) W. H. Saunders, Jr., *Chem. Ind. (London)*, 1661 (1963).
(27) A. M. Katz and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **91**, 4469 (1969).
(28) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Am. Chem. Soc.*, **88**, 2594 (1966).
(29) R. A. Sneen and H. M. Robbins, *J. Am. Chem. Soc.*, **94**, 7868 (1972).
(30) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 4821 (1971).
(31) G. A. Gregoriou, *Tetrahedron Lett.*, 233 (1974).
(32) P. J. Daïs and G. A. Gregoriou, *Tetrahedron Lett.*, 3827 (1974).
(33) D. J. McLennan, *Tetrahedron Lett.*, 2317 (1971).
(34) V. F. Raaen, T. Juhlke, F. J. Brown, and C. J. Collins, *J. Am. Chem. Soc.*, **96**, 5928 (1974).
(35) A. V. Willi, C.-K. Ho, and A. Ghanbarpour, *J. Org. Chem.*, **37**, 1185 (1972).
(36) K. M. Khoshy, R. E. Robertson, and W. M. J. Strachan, *Can. J. Chem.*, **51**, 2958 (1973).
(37) V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, Jr., *J. Am. Chem. Soc.*, **92**, 232 (1970).
(38) V. J. Shiner, Jr., "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, Chapter 2.
(39) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(40) D. A. Winey and E. R. Thornton, *J. Am. Chem. Soc.*, **97**, 3102 (1975).
(41) J. M. W. Scott, *Can. J. Chem.*, **48**, 3807 (1970).
(42) J. M. W. Scott and R. E. Robertson, *Can. J. Chem.*, **50**, 167 (1972).
(43) M. H. Abraham, *J. Chem. Soc., Chem. Commun.*, 51 (1973).
(44) D. J. McLennan and P. L. Martin, *Tetrahedron Lett.*, 4215 (1973).
(45) R. C. Williams and J. W. Taylor, *J. Am. Chem. Soc.*, **96**, 3721 (1974).
(46) C. R. Turnquist, J. W. Taylor, E. P. Grimsrud, and R. C. Williams, *J. Am. Chem. Soc.*, **95**, 4133 (1973).
(47) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Am. Chem. Soc.*, **94**, 1364 (1972).
(48) J. Bron, *Can. J. Chem.*, **52**, 903 (1974).
(49) E. P. Grimsrud and J. W. Taylor, *J. Am. Chem. Soc.*, **92**, 739 (1970).
(50) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).
(51) D. G. Lesnini, P. D. Buckley, and R. M. Noyes, *J. Am. Chem. Soc.*, **90**, 668 (1968).
(52) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 132 (1975).

Stereochemistry of Solvolytic Substitution of Cyclopentyl *p*-Bromobenzenesulfonate

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Abstract: The stereochemical result of solvolytic substitution of cyclopentyl-*2-d* *p*-bromobenzenesulfonate in several solvents has been determined by ^{2}H NMR. Cyclopentanol was found to be formed in the following solvents with the parenthetically indicated percent inversions: 70% ethanol–water (99%), 80% ethanol–water (100%), 80% dioxane–water (92%), and 80% 2,2,2-trifluoroethanol–water (100%). Cyclopentyl ethyl ether was formed in 70, 80, and 100% ethanol–water with 100, 96, and 99% inversion, respectively. Cyclopentyl 2,2,2-trifluoroethyl ether was formed in both 80 and 97.5% trifluoroethanol–water with 92% inversion-8% retention (errors are ~3%). The detailed mechanistic interpretation of these and earlier results on deuterium rate effects and elimination stereochemistry requires the existence of two product-forming ion pair intermediates.

Earlier studies[2,3] on the solvolysis of cyclopentyl *p*-bromobenzenesulfonate (I) have reported secondary deuterium rate effects[2] and the stereochemistry of the olefin-forming elimination reaction.[3] The steric course of cyclopentanol formation from *cis*-cyclopentyl-*2-d* *p*-bromobenzenesulfonate (*cis*-I-*2-d*) was originally determined through ^{1}H NMR analysis[2] using tris(dipivalomethanato)praseodymium(III)[4] as a shift reagent.[2] Subsequently an additional, more rapid, more precise method using ^{2}H NMR was developed.[2b] The ^{1}H NMR method did not prove satisfactory for determining the con-

Table I. ^{2}H NMR Analysis[a] of β-Deuterated Cyclopentanols

Sample	No. of expts	Rel integrals τ 9.04[b]	Rel integrals τ 8.86[b]	% inversion[c]
Starting cis alcohol[d]		0.93	0.07	
Trans alcohol[e]			1.00	
Pdt from 80E-W[f,g]	2	0.07	0.93	100
Pdt from 70E-W[f,g]	1	0.08	0.92	99
Pdt from 80D-W[f,h]	2	0.15	0.85	92
Pdt from 80TFE-W[f,i]	2	0.07	0.93	100

[a] Varian HR-220 instrument operating at 33.8 MHz. [b] In ppm with Me_4Si-d_{12} as an external standard and using a white noise decoupler centered at 220 002 587 Hz. Concentration was about 1 M in $CHCl_3$. [c] Balance to 100% is retention; error is ~3%. [d] Original sample of *cis*-cyclopentanol-*2-d* from which the *cis*-I-*2-d* used in the solvolyses was prepared; MS analysis showed 2% d_0 and 98% d_1 molecules. [e] Synthetic sample of *trans*-cyclopentanol-*2-d*; MS analysis showed 3.4% d_0, 91.8% d_1, and 4.8% d_2 molecules. The latter is apparently 1,*trans*-2-dideuteriocyclopentanol. [f] Isolated after ~10 half-lives of solvolysis of *cis*-I-*2-d*. [g] 80E-W is 80 vol % ethanol and 20 vol % water, etc. [h] 80D-W is 80 vol % dioxane and 20 vol % water. [i] 80TFE-W is 80 wt % 2,2,2-trifluoroethanol and 20 wt % water.

figuration of the β deuterium in the cyclopentyl ether products using $Pr(dpm)_3$, $Eu(dpm)_3$, $Pr(fod)_3$, or $Eu(fod)_3$. In this paper we report the stereochemical results of substitution for both alcohol and ether products of solvolysis of I in various solvents using the ^{2}H NMR method.

Results and Discussion

The required cyclopentanol-*1-d*, *cis*-cyclopentanol-*2-d*, *trans*-cyclopentanol-*2-d*, and cyclopentanol-*2,2,5,5-d*$_4$ were prepared as described previously.[2a,5] The deuterium content of each of these samples was determined by mass spectral analysis and the orientation of the label determined by means of the paramagnetic shift reagent induced ^{1}H NMR spectra with $Pr(dpm)_3$.[6] The *p*-bromobenzenesulfonate esters were prepared from these alcohols in the usual manner.[7] The ethyl ethers were prepared from the corresponding alcohols by the Williamson synthesis using the sodium cyclopentoxides and ethyl iodide.

The trifluoroethyl ethers were prepared from the cyclopentyl *p*-bromobenzenesulfonate esters by SN2 displacement with sodium trifluoroethoxide using the procedure described for SN2 type displacements on neopentyl toluenesulfonate.[8] This reaction of the cyclopentyl ester was found to proceed with 96% inversion (4% retention). These compounds were prepared in order to establish the exact ^{2}H NMR shifts for β deuterium in the corresponding cis and trans isomers. The cyclopentanols and cyclopentyl ethers were isolated by GC after approximately 10 half-lives in various solvents. The solvents were mixtures of ethanol–water (E–W), dioxane–water (D–W), and 2,2,2-trifluoroethanol–water (TFE–W). Cyclopentanol was isolated from each of the solvents; in addition, cyclopentyl ethyl ether was isolated from the E–W solvents and cyclopentyl trifluoroethyl ether from the TFE–W solvents. The product yields determined by GC analysis have been published previously.[2] The ^{2}H NMR spectra of the separated products were recorded on a Varian HR-220 spectrometer at 33.8 MHz with the white noise decoupler centered on 220 002 587 Hz. The solvent in which the NMR sample was dissolved was chosen from among several tested for the best separation of signals corresponding to cis and trans deuterium in the β position in the ^{2}H NMR spectrum. As a control experiment, cyclopentyl-*1-d p*-bromobenzenesulfonate was allowed to solvolyze in each of the solvents, and after isolation the ^{2}H NMR spectrum of each substitution product was recorded. Only one signal resulted in each case, indicating no migration of deuterium or other rearrangement. The total deuterium content of each of the isolated products was determined by mass spectral analysis and found to be identical, within experimental error, with that of the alcohol from which the reacting *p*-bromobenzenesulfonate ester was prepared, indicating that no deuterium exchange with the solvent occurred in any of the reactions.

Table II. ^{2}H NMR Analysis[a] of β-Deuterated Cyclopentyl Ethyl-Ethers

Sample	No. of expts	Rel integrals τ 8.94[b]	Rel integrals τ 8.84[b]	% inversion[c]
Cis ether[d]		0.93	0.07	
Trans ether[e]			1.00	
Pdt from 100E[f]	2	0.08	0.92	99
Pdt from 80E-W[f]	2	0.11	0.89	96
Pdt from 70E-W[f]	1	0.07	0.93	100

[a] See footnote *a* in Table I. [b] See footnote *b* in Table I. Concentrations were about 0.4 M in CCl_4. [c] See footnote *c* in Table I. [d] Prepared from cis alcohol; for MS analysis see footnote *d* in Table I. [e] Prepared from trans alcohol; for MS analysis see footnote *e* in Table I. [f] Isolated after ~10 half-lives of solvolysis of *cis*-I-*2-d*; number represents vol % of ethanol in aqueous alcohol.

Table III. ^{2}H NMR Analysis[a] of β-Deuterated Cyclopentyl 2,2,2-Trifluoroethyl Ethers

Sample	No. of expts	Rel integrals τ 7.97[b]	Rel integrals τ 8.26[b]	% inversion[c]
Trans ether[d]		0.10	0.90	
Cis ether[e]		0.95	0.05	
Pdt from 97.5 TFE-W[f]	2	0.92	0.08	92[h]
Pdt from 97.5 TFE-W[g]	1	0.16	0.84	90[i]
Pdt from 80 TFE-W[f]	1	0.92	0.08	92[h]

[a] See footnote *a* in Table I. [b] See footnote *b* in Table I. Concentrations were about 1 M in benzene. [c] See footnote *c* in Table I. [d] Prepared from cis alcohol by an SN2 route. Integrals for cis alcohol are given in the first row and MS analysis in footnote *d* in Table I. [e] Prepared from trans alcohol by an SN2 route. Integrals for trans alcohol are given in the second row and MS analysis in footnote *d* in Table I. [f] Isolated after ~10 half-lives of solvolysis of *trans*-I-*2-d*. Numbers represent wt % of 2,2,2-trifluoroethanol in aqueous mixture. [g] Isolated after ~10 half-lives of solvolysis of *cis*-I-*2-d*; number represents wt % of 2,2,2-trifluoroethanol in aqueous mixture. [h] Calculated according to the composition of starting cis alcohol; see footnote *d*. [i] Calculated according to the composition of starting trans alcohol; see footnote *e*.

The stereochemical results are given in Tables I–III as follows: Table I, the cyclopentanol products from *cis*-I-*2-d* in the E–W, D–W, and TFE–W mixtures; Table II, the cyclopentyl ethyl ethers from *cis*-I-*2-d* in the E–W mixtures; Table III, the cyclopentyl trifluoroethyl ethers from *cis*-I-*2-d* and *trans*-I-*2-d* in the TFE–W mixtures.

The data of Tables I and II make it evident that substitution in E–W solvents occurs with complete inversion of configuration for both alcohol and ether products.

Earlier mechanistic investigations of secondary deuterium

rate effects[2a] and the stereochemistry of the elimination reaction[3] had led to the conclusion that in 70–90% E–W solvents the products were derived predominately by rate-determining attack on the reversibly formed intimate ion pair. The secondary α-deuterium rate effect (k_H/k_D) was 1.15 in all E–W solvents studied,[2a] and the formation of the cyclopentene elimination product was shown to be nonstereospecific[3] with anti elimination being preferred over syn by a factor of only 1.37. The complete inversion observed for the substitution products in 70E–W and 80E–W in the present work supports the same conclusion since nucleophilic attack of the intimate ion pair is expected to be highly stereospecific; the leaving group shields the front side of the reacting carbon and nucleophilic attack is only possible from the back side.

The results for the steric course of substitution in solvolysis in two TFE–W mixtures are given in Tables I and III. Although the alcohol product from 80TFE–W is formed with complete inversion, the trifluoroethyl ether from that solvent and from 97.5TFE–W shows about 90% inversion and 10% retention. From previous results on deuterium rate effects[2a] and elimination stereochemistry[3] it was concluded that the products were probably formed predominately from the solvent-separated ion pair intermediate with the formation of that intermediate from the intimate ion pair (k_2)[2a] being rate determining. The α-deuterium rate effect (1.24) was among the largest which has been measured for sulfonate ester solvolyses[9] and syn elimination was preferred over anti by a factor of almost 4.[3] The latter result indicates that internal elimination of the β hydrogen is accomplished in significant part by the leaving group;[3] trifluoroethanol is a relatively nonbasic solvent, and therefore the leaving group may play the role of base. There is the possibility that cis internal elimination by the leaving group occurs at the intimate ion pair stage in competition with rate-determining formation of the solvent separated ion pair, which could in turn yield additional elimination and substitution by solvent attack. The distinction between these two possibilities should be possible on the basis of the magnitude of the β-deuterium effects. Rate-determining syn elimination (in the reversibly formed intimate ion pair) should give a *primary* isotope effect contribution to the overall rate effect of a cis β-deuterium atom. Consequently, the cis β-*d* effect should be larger than the trans β-*d* effect and the β-d_4 effect should be larger than expected for a pure secondary effect[10] and larger than the square of the cis β-*d* effect times the trans β-*d* effect ("noncumulative" behavior).[11] Of course, the larger the elimination fraction, the more pronounced would be these effects.

In 70TFE–W the cyclopentene yield is 42%, the cis-β-*d* effect is 1.21, and the trans β-*d* effect is also 1.21.[12] The β-d_4 effect is 2.15, essentially equal to the square of the product of the cis and trans β-*d* effects; $(1.21)^4 = 2.14$. This evidence strongly suggests that the elimination takes place *after* the rate-determining step, most probably from the solvent-separated ion pair. Unfortunately, because of the low solubility of the reacting ester in 70TFE–W, the stereochemical results were not done in this solvent. In 80TFE–W and in 90TFE–W the cyclopentanol is formed with 100% inversion and the cyclopentyl trifluoroethyl ether with about 92% inversion and 8% retention. It seems likely that similar results would obtain in 70TFE–W. It is unlikely that much substitution could occur at the intimate ion pair stage because this would lower the α-*d* rate effect from ~1.24 for k_2 rate determining toward 1.15 for rate-determining nucleophilic attack on the ion pair, and the observed value for the α-*d* rate effect in 70TFE–W is 1.23. Thus, substitution by water in the solvent-separated ion pair seems to occur with complete inversion. This is reasonable if the leaving group is solvated, as expected, mainly by the more potent hydrogen bonding donor, trifluoroethanol ("solvent sorting").[13] On the other hand, substitution at the solvent-separated ion pair stage by trifluoroethanol, as expected from the above line of reasoning, takes place both at the front side (8%) and at the back side (92%). The very strong preference for back side attack is somewhat surprising and may indicate that the TFE molecules on the front side are oriented with their OH ends near the sulfonate group and the negative CF_3 end near the positive carbonium ion center.

In 97TFE–W the β-*d* isotope effects indicate the incursion of rate-determining syn elimination. The cis β-*d* rate effect (1.25) is larger than the trans β-*d* rate effect (1.19), and the square of the product of these two numbers (2.21) is less than the observed β-d_4 rate effect (2.40). It is also found that syn elimination dominates anti elimination by a factor of about 4.[3] All of this points to rate-determining elimination by the leaving group in the reversibly formed intimate ion pair. The α-*d* effect is not reduced by rate-determining elimination because this does not involve the attachment of a new nucleophilic group at the α-carbon atom.[14]

Substitution must take place on the solvent separated ion pair *after* its irreversible formation from the intimate ion pair. The arguments made above concerning the α-*d* effect and the stereochemistry of substitution in 70TFE–W also apply in 97TFE–W.

In the D–W solvent mixtures, all of the mechanistic indicators discussed here fall in between those for the E–W solvents and those for TFE–W solvents and may be explained as follows: rate-determining product formation at the intimate ion pair stage competes with rate-determining formation of the solvent separated ion pair, and, of course, products are derived by attack on both ion pairs. The α-*d* effect (1.18) is between that expected for k_s rate determining (1.15) and k_2 rate determining (1.24); similarly the β-*d* effect (1.80) is between those for k_1 and k_2 rate determining, 1.52 and 2.14, respectively.[2a] Syn elimination seems to have only a slight preference (1.2:1) over anti. That some substitution product is derived from the solvent separated ion pair is indicated by the formation of substitution product with 92% inversion and 8% retention, although the possibility of a dioxonium ion intermediate clouds this picture somewhat.[15]

Thus isotope effects, product yields, and stereochemistry combine to give a systematic, detailed, and consistent picture of the change in solvolysis mechanism with the changing nucleophilicity of the solvent. The most important results are that the nonnucleophilic solvent (TFE) tends to promote (1) internal elimination at the intimate ion pair stage and (2) dissociation of the intimate ion pair to the solvent-separated ion pair because of the reduced rate of solvent attack on the tight ion pair. Further, substitution at the solvent-separated ion pair stage by the nonnucleophilic solvent involves predominate inversion with a small amount of retention, while water cosolvent attacks with complete inversion.

We believe that this is the first demonstration of what should be a generally useful technique for determining the stereochemistry of substitution using deuterium as a label and determining its orientation by ^2H NMR.

Experimental Section

Spectra. ^2H NMR spectra were recorded on a Varian-220 spectrometer at 33.8 MHz with a Hewlett-Packard white noise decoupler centered at 220 002 587 Hz. Chemical shifts were determined relative to tetramethylsilane-d_{12}. Concentrations in all cases were 0.4–1.0 M of the measured compound in the solvent indicated. Mass spectra were taken with slow scan on an AEI MS-9 double-focusing mass spectrometer.

Deuterated Cyclopentanols. Specifically deuterated *cis*-cyclopentanol-*2-d* (**1**), *trans*-cyclopentanol-*2-d* (**2**) and cyclopentanol-*1-d* (**3**) were prepared as described previously.[2a,5] Compounds **1**, **2**, and **3** gave signals at τ 9.04, 8.86, and 6.32, respectively. The results of ^2H NMR and mass spectral analysis are given in Table I.

Deuterated Cyclopentyl Ethyl Ethers. Specifically deuterated *cis*-

cyclopentyl-*2-d* ethyl ether (**4**), *trans*-cyclopentyl-*2-d* ethyl ether (**5**), and cyclopentyl-*1-d* ethyl ether (**6**) were prepared by the Williamson synthesis from **1, 2,** and **3,** respectively. In a typical preparation, 1.55 g of sodium was dispersed by stirring in refluxing xylene under a blanket of nitrogen. The xylene was replaced with 40 ml of ether, and a solution of 5.7 g of **3** in 20 ml of ether was added dropwise in 2 h with vigorous stirring. The reaction mixture was allowed to stand overnight, and 10.3 g of freshly distilled ethyl iodide was added dropwise into the resulting sodium alkoxide solution while a slight reflux of ether was maintained. After standing overnight, 5 g of crude product **6** was collected from the reaction mixture by distillation through a short Vigreux column at 120–130 °C. A small quantity was purified by GC on an 8 ft × ¼ in. column containing 20% Carbowax 20M on firebrick 60–80. ^{2}H NMR spectrum of **6** (1.0 M in $CHCl_3$) showed a single peak at τ 6.69 (α-*d*).

Compounds **4** and **5** under the same conditions showed the main signals at τ 8.94 and 8.84, respectively. Detailed ^{2}H NMR spectral analysis of **4** and **5** are given in Table II.

Deuterated Cyclopentyl Trifluoroethyl Ethers. Specifically deuterated *cis*-cyclopentyl-*2-d* trifluoroethyl ether (**7**), *trans*-cyclopentyl-*2-d* trifluoroethyl ether (**8**), and cyclopentyl-*1-d* trifluoroethyl ether (**9**) were prepared from the corresponding alcohols **2, 1,** and **3,** respectively, using the procedure described by Mosher et al. In a typical synthesis, 10 g of cyclopentyl-*1-d* brosylate, prepared from **3,** was added to a solution of hexamethylphosphoramide. The reaction apparatus consisted of a three-neck, round-bottom flask with a dropping funnel, a nitrogen inlet, and a trap cooled externally with dry ice. The mixture was slowly heated up to 130 °C while nitrogen bubbled through, and the distillate was collected in a dry ice trap. A small sample of the fraction distilling from 74 to 116 °C was purified by GC using the column described above for the purification of **6.** A 300-mg sample of **9** was collected. ^{2}H NMR showed only one peak at τ 4.78. Compound **7** showed a signal at τ 7.97 with a small peak (5%) at τ 8.26, whereas compound **8** showed the main signal at τ 8.26 with a small peak (10%) at τ 7.97. Evidently the displacement reaction was accomplished with ~96% of inversion at the reaction center.

Isolation of Substitution Products. The product separations and purifications were all done in the same general manner for all solvents and products, except for variations in reaction time and GC temperature. In a typical experiment *cis*-cyclopentyl-*2-d* brosylate (6 g) was dissolved in 50 ml of 80 vol % E–W. The solution was heated for 2.5 h at 40 °C (10 half-lives of reaction). Most of the mixture was distilled from the dissolved solids and dried on molecular sieves, Type 3A, Linde, 1/16 in. MCB 1167. The products were separated from each other and from the solvent by GC on an 8-ft 20% Carbowax 20M on firebrick 60–80 column at 150 °C. The samples collected in this way were purified again by GC at 90 °C for cyclopentyl-*2-d* ethyl ether and at 150 °C for cyclopentanol-*2-d*. Only small samples amounting to 200–300 mg of better than 99% pure products were isolated.

The ^{2}H NMR spectra for cyclopentanols, cyclopentyl ethyl ethers and trifluoroethyl ethers were taken in $CHCl_3$, CCl_4, and benzene, respectively. GC retention times of the products isolated in solvolysis were identical with those of the compounds prepared independently as described above; ^{1}H NMR spectra were consistent in all cases with the assigned structures.

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References and Notes

(1) (a) University of Zagreb; (b) Institute "Rugjer Bosković; (c) Indiana University.
(2) (a) K. Humski, V. Sendijarević, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **95,** 7722 (1973); (b) K. Humski, V. Sendijarević, and V. J. Shiner, Jr., *Croat. Chem. Acta,* **46,** 93 (1974).
(3) K. Humski, V. Sendijarević, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **96,** 6187 (1974).
(4) $Pr(dpm)_3$.
(5) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80,** 2326 (1958).
(6) K. Humski, L. Klasinc, D. Kovacević, and V. Kramer, *Croat. Chem. Acta,* **45,** 363 (1973).
(7) R. S. Tipson, *J. Org. Chem.*, **9,** 235 (1944).
(8) B. Stephenson, G. Solladie, and H. S. Mosher, *J. Am. Chem. Soc.*, **94,** 4184 (1972).
(9) V. J. Shiner, Jr., and W. Dowd, *J. Am. Chem. Soc.*, **93,** 1029 (1971); V. J. Shiner, Jr., M. W. Rapp, E. A. Halevi, and M. Wolfsberg, *ibid.*, **90,** 7171 (1968).
(10) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. H. Kessick, L. Mllakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91,** 4838 (1969); R. D. Fisher, R. C. Seib, V. J. Shiner, Jr., I. Szele, M. Tomić, and D. E Sunko, *ibid.*, **97,** 2408 (1975).
(11) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85,** 2413 (1963).
(12) The trans β-*d* effect originally measured using the titrimetric procedure was 1.23.[2a] This has recently been redetermined by R. Seib in these laboratories using the more precise conductometric method and found to be 1.21.
(13) J. B. Hyne, *J. Am. Chem. Soc.*, **82,** 5129 (1960).
(14) Partial double bond formation does not significantly reduce the α-*d* effect; fractionation factors for H vs. D at ethylenic carbon seem to be very similar to those at equivalently substituted carbonium ion centers (V. J. Shiner, Jr., "Isotope Effects In Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, p 107).
(15) H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.*, **87,** 287 (1965).

The Ester Enolate Claisen Rearrangement. Stereochemical Control through Stereoselective Enolate Formation[1a]

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Abstract: The [3,3] sigmatropic rearrangement of a number of allylic esters (**1**), as the enolate anions or the corresponding silylketene acetals, produces the γ,δ-unsaturated acids **2** in 66–88% yield. The mild conditions allow rearrangement of acid-sensitive and thermally labile esters. Rearrangement of ester **1g** affords (*E*)-4-decenoic acid (**2g**) with greater than 99% stereoselectivity. (*E*)-Crotyl propanoate (**12**) leads to erythro acid **14** when enolization is carried out in THF, but to the threo acid **15** when the solvent is 23% HMPA–THF. Results with a variety of esters demonstrate that kinetic enolization with lithium diisopropylamide gives selective formation of the geometrical enolate H in THF and the isomeric enolate I in HMPA–THF. Similar results are obtained with 3-pentanone.

Consideration of possible synthetic approaches to prostanoids suggested a convergent scheme which would incroporate the connection of a "top-half" and a "bottom-half" as a key step in the synthesis. Further analysis indicated that the required carbon–carbon bond could be generated by Claisen rearrangement of a properly designated substrate. This rear-