Table I. Conversions of Thiols[a] and Disulfides[b] to Chlorides

product	substrate	% yield of RCl[c]	bp, °C		n^{25}_{D} obsd	n^{20}_{D} lit.
			obsd	lit.[d]		
3a	n-C_3H_7SH	62	e	47	1.3855	1.3879
3b	n-$C_6H_{13}SH$	66	134-137	135	1.4195	1.4199
3c	i-C_3H_7SH	42	33-34	36	1.3835	1.3777
3d	t-C_4H_9SH	37	e	52	1.3875	1.3857
3e	$C_6H_5CH_2SH$	67	176-184	179	1.5405	1.5391
3f	C_6H_5SH	29	131-133	132	1.5264	1.5241
3g	p-$CH_3C_6H_4SH$	12	150-155	162	1.5250	1.5150
3c	$(i\text{-}C_3H_7S)_2$	67	33-35	36		
3d	$(t\text{-}C_4H_9S)_2$	41	49-50	52		
3f	$(C_6H_5S)_2$	30	128-132	132		
4	$HOCH_2CH_2SH$	20[f]	e	83	1.4432	1.4448
5	CH_3COSH	71	45-48	51	1.3840	1.3898

[a] SO_2Cl_2 (1 mol) and $(C_6H_5)_3P$ (1 mol). [b] SO_2Cl_2 (1 mol) and $(C_6H_5)_3P$ (2 mol). [c] Isolated yields. ^{1}H NMR-indicated products were >98% pure. [d] "Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1980. [e] Accurate boiling points could not be obtained in all cases. [f] 1,2-Dichloroethane.

studied mechanistically.[10] The overall reactions involved in our procedure are as shown in Scheme I.

Other features to emerge from this study include the observations that oxygen-containing substituents such as OH, COOH, NO_2 interfere seriously with the reaction. Thus, no trace of the corresponding chloride was obtained from the reaction of 3,3′-dithiobis[propanoic acid] under our conditions, while we also observed that 2-mercaptoethanol gives 1,2-dichloroethane (**4**), in rather low yield, as the sole isolated product. Only a trace of ethylene sulfide was observed spectroscopically in this reaction, in contrast to the results of Baldwin and Hesson.[11] In the two cases which these workers describe, however, it is perhaps significant that the β-hydroxy group involved is tertiary. 4–Nitrobenzenethiol led rapidly to intractible products, although whether this was primarily due to the nitro group or to the use of an aromatic thiol (q.v.) we are unable to say. In contrast to these findings, we have found (Table I) that thioacetic acid is efficiently converted to acetyl chloride (**5**) under our conditions.

In marked contrast to the successful procedure reported above for the aliphatic thiol → chloride conversions, we have met with very limited success in the aromatic series. In addition to the two examples quoted in Table I, which proceed in rather poor yield, we found no trace of the corresponding chloride in analogous reactions with 4-bromobenzenethiol and 3-methoxybenzenethiol, in addition to the 4-nitrobenzenethiol mentioned earlier. In the light of these disappointing results it seem inappropriate to speculate on a possible mechanism for those cases in the aromatic series where reaction did occur.

Since our study was completed, we have very recently noted the results of Oae and Togo[12] on the conversion of primary aliphatic thiols to the corresponding *iodides* by using a triphenylphosphine–iodine reagent system in refluxing benzene. The mechanism suggested by these authors does *not* invoke the intermediacy of a sulfenyl iodide, but rather displacement of iodide by the thiol (or thiolate ion) from the intermediate iodotriphenylphosphonium ion, formed by prior reaction of iodine with triphenylphosphine.

The method here described constitutes a reliable general procedure for the synthetic conversion RSH (or RSSR) → RCl under mild conditions, with the exceptions already noted.

Experimental Section

Preparation of 1-Chlorohexane. 1-Hexanethiol (5.9 g, 50 mmol) was cautiously added, with stirring, to sulfuryl chloride (6.75 g, 50 mmol) at −23 °C. The mixture was stirred for 30 min at this temperature, forming the corresponding sulfenyl chloride. Powdered triphenylphosphine (13.15 g, 50 mmol) was then added slowly to this orange-red liquid. The semisolid reaction mixture slowly lost color on manual stirring before becoming colorless upon completion of the addition of the triphenylphosphine. 1-Chlorohexane (4.0 g, 66%) was distilled directly from the mixture as a colorless liquid: bp 134–137 °C; n^{25}_{D} 1.4195.

When triphenyl phosphite (15.5 g, 50 mmol) was substituted for the triphenylphosphine above, a viscous liquid mixture resulted which avoided the need for manual stirring of the reaction mixture. The yield of 1-chlorohexane obtained on distillation in this case was 63%.

Preparation of Chlorobenzene. Benzenethiol (5.5 g, 50 mmol) was added dropwise, with stirring, to sulfuryl chloride (6.75 g, 50 mmol) at 0 °C, immediately forming the orange-red sulfenyl chloride. Powdered triphenylphosphine (13.15 g, 50 mmol) was added in portions over 1 h. In the final stages of the addition the reaction mixture became very stiff and had to be stirred manually with a spatula. The reaction flask was fitted with a stillhead and condenser, and chlorobenzene (1.6 g, 29%) was distilled from the mixture as a colorless liquid: bp 131–133 °C, n^{25}_{D} 1.5264.

Acknowledgment. We gratefully acknowledge financial support of this work by the Natural Sciences and Engineering Research Council of Canada and the Connaught Fund of the University of Toronto.

Registry No. 1a, 107-03-9; **1b**, 111-31-9; **1c**, 75-33-2; **1d**, 75-66-1; **1e**, 100-53-8; **1f**, 108-98-5; **1g**, 106-45-6; **2c**, 4253-89-8; **2d**, 110-06-5; **2f**, 882-33-7; **3a**, 540-54-5; **3b**, 544-10-5; **3c**, 75-29-6; **3d**, 507-20-0; **3e**, 100-44-7; **3f**, 108-90-7; **3g**, 106-43-4; **4**, 107-07-3; **5**, 75-36-5; $HOCH_2CH_2SH$, 60-24-2; CH_3COSH, 507-09-5.

Cyclobutylcarbinyl *p*-Bromobenzenesulfonate Solvolysis. A Study of Response to Solvent Ionizing Strength

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Received August 3, 1981

In our study of medium effects upon the rates of solvolysis of cyclopropylcarbinyl arenesulfonates, 3-OSO_2Ar, we found[1] that the log k_t values for the solvolysis of 3-

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[10] Overman, L. E.; O'Connor, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 771.

[11] Baldwin, J. E.; Hesson, D. P. *J. Chem. Soc., Chem. Commun.* **1976**, 667.

[12] Oae, S.; Togo, H. *Synthesis* **1981**, 371.

[1] Roberts, D. D.; Snyder, R. C., Jr. *J. Org Chem.* **1979**, *44* 2860.

Table I. Summary of Solvolysis Rate Constants for Cyclobutylcarbinyl and Cyclopentylcarbinyl Brosylates at 45 °C

substrate	solvent[a]	k_t,[b] s^{-1}
c-$C_4H_7CH_2OBs$	100	$(1.3 \pm 0.01) \times 10^{-6}$ [c]
	90	$(6.4 \pm 0.05) \times 10^{-6}$
	80	$(1.90 \pm 0.01) \times 10^{-5}$
	70	$(4.50 \pm 0.01) \times 10^{-5}$
	50	$(1.50 \pm 0.03) \times 10^{-4}$
c-$C_5H_9CH_2OBs$	100	$(2.15 \pm 0.03) \times 10^{-7}$ [d]
	90	$(5.6 \pm 0.03) \times 10^{-7}$
	80	$(1.13 \pm 0.01) \times 10^{-6}$
	70	$(2.10 \pm 0.01) \times 10^{-6}$
neophyl tosylate	50	$(8.9 \pm 0.01) \times 10^{-6}$ [e]

[a] Percent by volume of alcohol in aqueous ethanol mixtures. [b] Errors reported as one standard deviation unit from the mean. [c] Compares with a value of 1.3×10^{-6} s^{-1} reported earlier by Roberts and Wu.[6b] [d] Compares with a value of 2.1×10^{-7} s^{-1} reported earlier by Roberts and Wu.[6b] [e] Average of duplicate runs.

OPms in two hydroxylic solvent systems (namely, aqueous ethanol and acetic acid–formic acid) correlated with those for *exo*-2-norbornyl tosylate but yielded a dispersion[2] when plotted against the log k_t values for neophyl tosylate. This result led us to propose[1] that there is a characteristically different response to solvent effect by a substrate ionizing with neighboring-group assistance by bridging[3] from one ionizing with assistance by exhalted hyperconjugation[4] and that a graphical analysis of solvolysis rates in aqueous ethanol and acetic acid–formic acid may well serve as a useful test for differentiating between these two modes of delocalizing developing charge in the transition states of k_Δ processes.[5]

In this paper, we apply the proposed test for participation type to the solvolysis of cyclobutylcarbinyl brosylate (4-OBs), a substrate whose solvolytic behavior is known[6] to closely parallel that of 3-OPms. Also, as a corollary experiment, we apply the same test to the solvolysis of cyclopentylcarbinyl brosylate (5-OBs), a reaction known[6b] to proceed by competitive k_Δ and k_s processes and thus to be sensitive to varying solvent nucleophilicity.

The results of this study give further support to the proposal that neighboring-group participation by exhalted hyperconjugation is characterized by a different response to the solvent effect than that by bridging and, furthermore, that it is unlikely that the magnitude of nucleophilic solvent assistance in the solvolysis of 3-OPms or 4-OBs is significant.

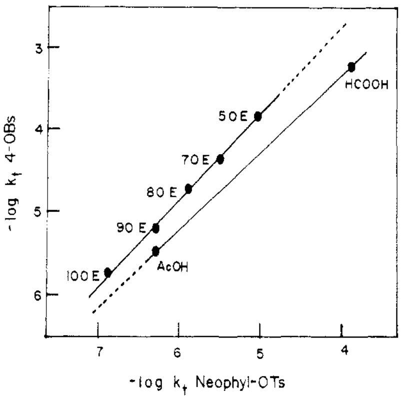

Figure 1. Plot of log k_t (4-OBs) against log k_t (neophyl tosylate) in various solvents at 45 °C. Data were taken from Table III.

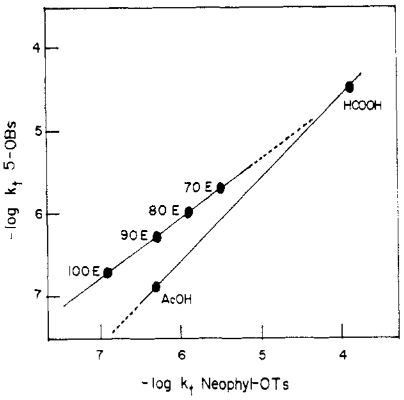

Figure 2. Plot of log k_t (5-OBs) against log k_t (neophyl tosylate) in various solvents at 45 °C. Data were taken from Table III.

The first-order rate constants for solvolysis of 4-OBs and 5-OBs in the two hydroxylic solvent systems are collected in Table I. The course of reaction was followed by titrating the liberated arenesulfonic acid, and in all cases the reaction followed strictly first-order kinetic law up to at least 75% conversion, furnishing, within experimental error, 100% of the theoretical amount of acid present.

Values[7] of m_{EW}, m_{AF}, $[k_{EW}/k_{AcOH}]_Y$, and $[k_{EW}/k_{HCO_2H}]_Y$ for solvolysis of 4-OBs and 5-OBs, as well as for selected other arenesulfonates, are collected in Table II. Neophyl tosylate is thought[8] to solvolyze with aryl participation uncomplicated by either internal return[9] or nucleophilic solvent assistance,[10] neopentyl tosylate with alkyl participation also uncomplicated by either internal return or nucleophilic solvent assistance,[11,12] and *exo*-2-norbornyl tosylate with anchimeric assistance accompanied by internal return but without nucleophilic solvent assistance.[13] Both 2-adamantyl tosylate[10a,14] and pinacolyl brosylate[13c,15]

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(2) For a discussion of "dispersion", see: (a) Kosower, E. M. "Physical Organic Chemistry"; Wiley: New York, 1968; pp 318–319. (b) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; p 171.

(3) (a) Winstein, S.; Morse, B. K.; Grunwald, E.; Schreiber, K. C.; Corse, J. *J. Am. Chem. Soc.* **1952** *74*, 1113. (b) Winstein, S.; Schreiber, K. C. *Ibid.* **1952**, *74*, 2165. (c) Brown, H. C.; Kim, C. J.; Lancelot, C. J.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 5244. (d) Brown, H. C.; Kim, C. J. *Ibid.* **1971**, *93*, 5765.

(4) (a) Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829. (b) Eaton, D. F.; Traylor, T. G. *Ibid.* **1974**, *96*, 1226. (c) Olah, G. A.; Liang, G. *Ibid.* **1975**, *97*, 6803. (d) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *Ibid.* **1979**, *101*, 5537.

(5) (a) The validity of this proposal, of course, rests heavily upon the validity of the assumption that neophyl tosylate is an appropriate model for a primary arenesulfonate solvolyzing via the k_Δ pathway,[5b] at least as far as the transition state is concerned. On the basis of a growing body of data,[5b,8,10] this assumption is generally accepted as proven, so much so that rarely is any other model used as a reference system for the k_Δ pathway. (b) For a review, see: Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum: New York, 1976.

(6) Roberts, D. D. *J. Org. Chem.* **1974**, *39*, 1265. (b) Roberts, D. D.; Wu, C.-H. *Ibid.* **1974**, *39*, 1570. (c) Roberts, D. D. *Ibid.* **1976**, *41*, 486.

(7) For details of calculations, see ref 2b, pp 63–64.

(8) (a) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618. (b) Diaz, A.; Lazdins, I.; Winstein, S. *Ibid.* **1968**, *90*, 6546. (c) Shiner, V. J., Jr.; Serb, R. C. *Ibid.* **1976**, *98*, 862. (d) Ando, T.; Kim, S.-G.; Matsuda, K.; Yamataka, H.; Yukawa, Y.; Fry, A.; Lewis, D. E.; Sims, L. B.; Wilson, J. C. *Ibid.* **1981**, *103*, 3505.

(9) (a) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597. (b) Diaz, A.; Lazdins, I.; Winstein, S. *Ibid.* **1968**, *90*, 1904. (c) Goering, H. L.; Humski, K. *J. Org. Chem.* **1975**, *40*, 920. (d) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Vol 2.

(10) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658. (b) Schadt, F. L.; Bently, T. W.; Schleyer, P. v. R. *Ibid.* **1976** *98*, 7667.

(11) Liggero, S. H.; Sustmann, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4571.

(12) Roberts, D. D.; Snyder, R. C., Jr. *J. Org. Chem.* **1980**, *45*, 4052.

(13) (a) Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376. (b) Sargent, G. D. In "Carbonium Ions"; Olah, G. A., Schleyer, P. V. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 1099. (c) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137.

Table II. Summary of Solvent Paremeters Derived from the *m*Y Equation[7]

substrate[g]	m_{EW}	m_{AF}	$[k_{EW}/k_{AcOH}]_Y$	$[k_{EW}/k_{HCOOH}]_Y$
neophyl tosylate[a, b]	0.50	0.65	0.35	0.10
neopentyl tosylate[a, b]	0.52	0.56	0.48	0.18
exo-2-norbornyl tosylate[c, d]	0.90	0.90	0.42	0.62
2-adaOTs[c, e]	0.78	1.0	0.2	0.04
PinOBs[c, e]	0.73	0.84	0.59	0.23
c-PrCarOPms[c, d]	0.74	0.84	0.48	0.23
c-BuCarOBs[a, f]	0.55	0.61	0.59	0.38
c-PeCarOBs[a, f]	0.36	0.65	2.0	0.2

[a] 45 °C. [b] Calculated from data listed in Table III of ref 12. [c] 25 °C. [d] Taken from Table II of ref 1. [e] Taken from Table IV of ref 10a. [f] Calculated from data listed in Table III of this study. [g] Ada = adamantyl, Pin = pinacolyl, *c*-BuCor = cyclobutylcarbinyl, c-PeCar = cyclopentylcarbinyl, c-PrCar = cyclopropylcarbinyl.

Table III. Solvolysis Rates ($-\log k_t$)[a] for Selected Substrates in Various Solvents[b]

	solvent							
substrate	100E	90E	80E	70E	60E	50E	AcOH	HCOOH
neophyl tosylate[c]	6.90[d]	6.30[d]	5.90[d]	5.5[d]		5.05[e]	6.30[d]	3.89[d]
neophyl tosylate[f]	8.12[g]	7.47[g]	7.10[g]	6.77[h]	6.30[h]		7.60[g]	4.94[g]
4-OBs[c]	5.89[e]	5.19[e]	4.72[e]	4.35[e]		3.82[e]	5.47[i]	3.20[i]
5-OBs[c]	6.68[e]	6.25[e]	5.95[e]	5.68[e]			6.85[i]	4.46[i]
exo-2-norbornyl tosylate[f]	5.35[j]	4.15[j]	3.64[j]	3.22[j]			4.63[g]	1.29[g]
2-phenyl-1-propyl tosylate[f]		7.75[k]	7.54[k]	7.37[k]	7.05[k]		8.17[l,n]	5.95[l,n]

[a] In s^{-1}. [b] E = aqueous ethanol. [c] 45 °C. [d] Reference 12. [e] From the data in Table I. [f] 25 °C. [g] Reference 1. [h] Extrapolated from a plot of log k_t against $Y_{2\text{-AdOTs}}$. [i] Reference 6b. [j] Harris, J. M.; Mount, D. L.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 3139. [k] Reference 13c. [l] Winstein, S.; Schreiber, K. C. *Ibid.* **1952**, *74*, 2171. [m] Extrapolated from data at higher temperatures. [n] Calculated from rate constants for the brosylate assuming a OBs/OTs ratio of 3.0.

have been proposed as suitable models for limiting k_c solvolyses[16] uncomplicated by internal return.[17]

The data collected in Table II show the expected results. Thus the *m* values for 4-OBs are similar to those for other primary arenesulfonates solvolyzing by the k_Δ pathway, while the $[k_{EW}/k_{AcOH}]_Y$ and $[k_{EW}/k_{HCO_2H}]_Y$ ratios, although slightly higher than those for neophyl and neopentyl tosylate, are well below the values for primary and secondary arenesulfonates solvolyzing by either the k_s pathway or with appreciable nucleophilic solvent assistance.[2b,7,10] On the other hand, the increased sensitivity of the solvolysis of 5-OBs to nucleophilic solvent assistance is reflected by the decreased m_{EW} value and the increased $[k_{EW}/k_{AcOH}]_Y$ ratio.

Plots of the log k_t values for solvolysis of 4-OBs and 5-OBs against those of neophyl tosylate are given in Figures 1 and 2. In the both plots, a dispersion is observed, yielding correlation lines of different slopes for ethanol/water on the one hand and acetic acid–formic acid on the other. However, the patterns of the two dispersions are significantly different: divergent in the case of 4-OBs and convergent in the case of 5-OBs.

The divergent pattern for the 4-OBs data is consistent with the results obtained from the graphical analysis of the solvolysis data for 3-OPms and *exo*-2-norbornyl tosylate (see Figure 3), so we can conclude that its rates of solvolysis are characterized by a response to the medium effect similar to that of either 3-OPms or *exo*-2-norbornyl

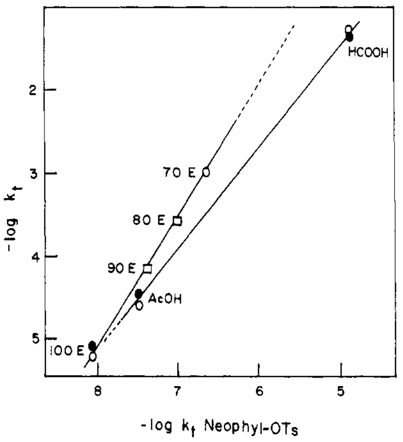

Figure 3. Plot of log k_t for 3-OPms (filled circles), *exo*-2-norbornyl tosylate (open circles), and points in common (open squares) against log k_t (neophyl tosylate) in variuos solvents at 25 °C. Data were taken from Table III and ref 1.

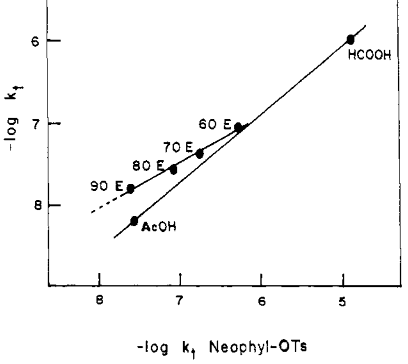

Figure 4. Plot of log k_t for 2-phenyl-1-propyl tosylate against log k_t (neophyl tosylate) in various solvents at 25 °C. Data were taken from Table III.

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[14] Bentley, T. W.; Schadt, F. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4821 and references listed therein.

[15] Shiner, V. J.; Jr. Fisher, R. D.; Dowd, W. *Ibid.* **1969**, *91*, 7748.

[16] For a review, see: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; Chapter 4.

[17] Recently, however, on the basis of oxygen-18 scrambling data, Bunnett and Paradisi[18] confirmed this mechanistic proposal only for the pinacolyl system. On the other hand, they found that the solvolysis of 2-adamantyl benzenesulfonate, in both acetic acid and ethanol/water solvents, is complicated by a high fraction of internal return and, on the basis of this result, called for a reinterpretation of the proposal that the 2-adamantyl system is a suitable model for limiting k_c solvolyses.[19]

[18] Paradisi, C.; Bunnet, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 946.

[19] The choice of appropriate models for limiting k_c solvolyses is obviously critical to any estimate of nucleophilic solvent assistance. However, this has proven to be much more difficult than might seem to be the case. It appears that each chemical process has its own characteristics, and, as a result, solvolysis of even related arenesulfonates may be quite different mechanistically.

tosylate.[20] Equally important, the convergent pattern for the 5-OBs data is consistent with the results obtained from the graphical analysis of the solvolysis data for 2-phenyl-1-propyl tosylate (see Figure 4), another primary substrate that is known[13c,21] to react by competitive k_Δ and k_s processes whose ratio varies with solvent nucleophilicity as well as solvent ionizing power.[22]

The above results obviously support our contention that delocalization of charge in solvolytic transition states by exhalted hyperconjugation can be differentiated from that by bridging by a graphical analysis of solvolysis rates in aqueous ethanol and acetic acid–formic acid solvent systems. Furthermore, it is clear from the analysis of dispersion patterns that the different response to solvent effect by a substrate solvolyzing with assistance by strained C–C bonds (such as those in the cycloproyl and cyclobutyl groups) from one solvolyzing with phenyl or alkyl assitance cannot be explained by simply invoking nucleophilic solvent assistance.

Experimental Section

Cyclobutylcarbinyl p-bromobenzenesulfonate (4-OBs) was prepared by a published procedure[6b] in 40% yield: mp 25 °C [after recrystallization from a 10:1 mixture of petroleum ether (bp 30–60 °C)–ethyl acetate] (lit.[6b] mp 25 °C).

Cyclopentylcarbinyl p-bromobenzenesulfonate (5-OBs) was also prepared by a published procedure[6b] in 60% yield: mp 49.5–50.0 °C [after recrystallization from petroleum ether (bp 30–60 °C)] (lit.[24] mp 49.5–50.0 °C).

Solvents were prepared as previously described.[1]

Rate Measurements. The rates of solvolysis were followed titrimetrically. Reaction solutions were 0.03 M with the exception of the 50% aqueous ethanol runs for 4-OBs and neophyl tosylate which were respectively, 0.02 and 0.01 M. Rate measurements were accomplished by the ampoule technique, again with the exception of the 50% aqueous ethanol runs for 4-OBs and neophyl tosylate where the volumetric flask technique[1] was employed. In a typical run, 5-mL aliquots of the reaction solution were sealed under nitrogen in 10-mL ampules, thermostated in a constant-temperature bath held to ±0.05 °C of the reaction temperature, and then, at appropriate times, titrated as previously described.[1]

Registry No. 4-OBS, 51108-24-8; 5-OBS, 38806-24-5.

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[20] Plots of the log k_t values for solvolysis of 4-OBs against those of either 3-OPms or *exo*-2-norbornyl tosylate do indeed show good linearity.

[21] Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4829.

[22] Both water and ethanol are of comparable nucleophilicity,[23] consequently, for aqueous ethanol, increasing ethanol content produces little change in nucleophilicity. This is also true for acetic acid–formic acid.[23] On the other hand, water has a much greater ionizing power than ethanol as does formic acid compared to acetic acid.[23] As a result, increasing either the water content in aqueous ethanol or formic acid in acetic acid–formic acid solvents produces a sharp increase in ionizing power.

[23] See Table I in ref 10b.

[24] Felkin, H.; LeNy, G. *Bull. Soc. Chim. Fr.* **1957**, 1169.

Cyclopentenones from γ-Lactones. Synthesis of 2-(6-Carboxyhexyl)cyclopent-2-en-1-one, an Intermediate in Prostaglandin Synthesis

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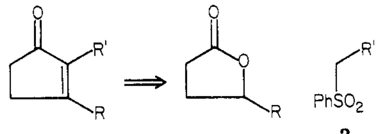
Scheme I



2 3

The most valuable methods for the construction of substituted cyclopentenones[1] are based on the transformation of compounds already possessing the carbocyclic framework,[2] or on the preliminary preparation of γ-dicarbonyl compounds, which successively undergo base-catalyzed cyclization.[3]

According to the latter approach we have recently developed a method to prepare cyclopentenones (**1**) from simple inexpensive γ-lactones (**2**) and alkyl phenyl sulfones (**3**), which contribute the C-2 ring carbon and the relative substituent R′ (Scheme I).

By this method we have synthesized target molecules such as *cis*-jasmone and dihydrojasmone from γ-valerolactone and the proper sulfones.[3a] We now report a new synthesis of 2-(6-carboxyhexyl)cyclopent-2-en-1-one (**9**),[4] a useful prostanoid synthon, using γ-butyrolactone and sulfone **4** as building blocks, on the basis of the retrosynthetic analysis in Scheme I. The protected hydroxyl group in **4** is liable to be converted to the carboxylic function in the last step of the synthetic sequence (Scheme II).

The sulfone **4** was prepared in 44.5% yield from 1,8-octanediol by routine transformations, which involve monoiodination with iodidric acid in continuous extraction conditions,[5] tetrahydropyranylization[6] of the residue hydroxyl group, and iodide ion displacement by polymer-supported sulfinate anion.[7] The sulfone **4** was treated with 2 equiv of *n*-butyllithium in anhydrous tetrahydrofuran, and then a small amount of hexamethylphosphoric triamide and 1 equiv of γ-butyrolactone were added at −78 °C to give, after quenching with ammonium chloride, extraction, and column chromatography, the expected product **5** in 55% yield (68.7% based on reacted starting sulfone).

Cleavage of the carbon–sulfur bond with aluminum amalgam[8] afforded **6** in 85% yield, on which we accomplished the oxidation of the free hydroxyl group to aldehyde.[9] The best reagent, for the product yield (67% of **7**) and the easy workup, was found to be pyridinium

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[1] Ellison, R. A. *Synthesis* **1973**, 397. Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.

[2] For recent examples, see (a) Novak, L.; Baan, G.; Marosfalvi, J.; Szantay, C. *Chem. Ber.* **1980**, *198*, 2839. (b) Bernady, K. F.; Poletto, J. F.; Nocera, J.; Mirando, P.; Schaub, R. F.; Weiss, M. J. *J. Org. Chem.* **1980**, *45*, 4702. (c) Zima, G.; Barnum, C.; Liotta, D. *Ibid.* **1980**, *45*, 2736. (d) Becker, D.; Birnbaum, D. *Ibid.* **1980**, *45*, 570. (e) Funk, R. L.; Vollhardt, K. P. C. *Synthesis* **1980**, 118. (f) Barco, A.; Benetti, S.; Baraldi, P. G.; Simoni, D. *Ibid* **1981**, 199. (g) Birch, A. J.; Dahler, P.; Narula, A. S.; Stephenson, G. R. *Tetrahedron Lett.* **1980**, 3817. Birch, A. J.; Narula, A. S.; Dahler, P.; Stephenson, G. R.; Kelly, L. F. *Ibid.* **1980**, 979.

[3] For recent examples, see (a) Mussatto, M. C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1980**, *45*, 4002. (b) Matsuda, I.; Murata, S.; Izumi, Y. *Ibid.* **1980**, *45*, 237.

[4] (a) Sih, C. J.; Solomon, R. G.; Price, P.; Sood, R.; Peruzzotti, G. *J. Am. Chem. Soc.* **1975**, *97*, 857. (b) Bagli, J. F.; Bogri, T.; Deghenghi, R.; Wiesner, K. *Tetrahedron Lett.* **1966**, 465. For a recent synthesis of the methyl, ethyl, and butyl esters of the acid **9**, see ref 2a, 2b, and 2f, respectively.

[5] We followed the experimental procedure described for the analogue monobromination of diols with HBr: Butenandt, A.; Hecker, E.; Hopp, M.; Koch, W. *Justus Liebigs Ann. Chem.* **1962**, *658*, 39.

[6] Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S. *Synthesis* **1979**, 729.

[7] Manescalchi, F.; Orena, M.; Savoia, D. *Ibid.* **1979**, 445.

[8] Corey, E. J.; Chaykowsky, M. *J. Am. Chem. Soc.* **1971**, *87*, 1345.

[9] We have found more convenient to carry out the desulfonation on **5** prior to the oxidation step, since the aldehydic function is labile in the reducing conditions. The crude compound **6** obtained by desulfonation could be directly used in the oxidation step, but we obtained a slightly better yield by oxidizing the purified compound.

0022-3263/82/1947-0564$01.25/0