Table III. Thermochemical Values (kcal mol^{-1})

R	D(R–H)^a	$\Delta H_f{}^\circ{}_0$(R–H)^b	$\Delta H_f{}^\circ{}_0$(R)^b	$\Delta H_f{}^\circ{}_0$(R–R′)^b	$E_{\min}$(R–R′)^c	R′
CH_3	104 ± 1^d	−16.0^h	34.9	−16.5	87.3	CH_3
CH_2F	101^e	−53.9^i	−7.1	−59.4^j	88.2	CH_3
CH_2F	101^e	−53.9^i	−7.1	−102.8^j	89.6	CH_2F
CHF_2	101^e	−106.4^i	−59.3	−114.6^i	91.2	CH_3
CF_3	106 ± 1^f	−165.0^i	−112.1	−175.1^i	98.9	CH_3
CF_3	106 ± 1^f	−165.0^e	−112.1	−319.0^i	95.8	CF_3
CH_2Cl	100^g	28.7^g	28.7^g	−23.2^g	87.8^g	CH_3
CH_2Cl	100^g	28.7^g	28.7^g	−26.9^g	85.3^g	CH_2Cl

^{a} These are experimental values reported at 298°K unless specified otherwise. We have assumed that these values are bond dissociation enthalpies and made our corrections to 0°K accordingly. ^{b} Tabulated for 0°K. ^{c} $E_{\min} = D^\circ(R-R^1)$ at 0°K plus 1 kcal mol^{-1}. ^{d} See ref 43. ^{e} Measured at 200° by ref 44; see text for justification. Error limits are larger than for $D(CH_3-H)$ and $D(CF_3-H)$. ^{f} See ref 45. ^{g} See ref 10 and 11. The $E_{\min}$ values for C_2H_5Cl and $C_2H_4Cl_2$ differ by 0.6 kcal mol^{-1} from our earlier work because the conversion to 0° was done in a slightly different way. ^{h} JANAF Thermochemical Tables. ^{i} See ref 41; these values are based upon the revised ΔH_f(HF,aq). ^{j} See text of Appendix.

200°. Comparison of the activation energies[19] for H abstraction by CF_3 also indicates the bond dissociation energies of CH_3F and CH_2F_2 to be nearly equal and perhaps slightly higher than for CH_3Cl. Bromination studies of fluoroalkanes[45] seem reliable and indicate the $D(CH_2F-H)$ to be less than $D(CH_3-H)$ or $D(CF_3-H)$. An additional reservation arises because $\Delta H_f{}^\circ(CH_3F)$ has not been accurately measured, although Lacher and Skinner seem to be confident of −55.9 kcal mol^{-1} at 298°K.

The $\Delta H_f(CF_3)$ seems firmly established due to the measurements of Amphlett and Whittle[45] of $D^\circ(CF_3-H) = 106.7 \pm 0.5$ kcal mol^{-1}. Such a value leads to quite high energies for bonds attached to CF_3. However, recent measurements[8b] of chemical activation rate constants for $CH_3CH_2CF_3$ activated by $CH_3 + CH_2CF_3$ and $CF_3 + CH_2CH_3$ also support a difference of approximately 4.5 kcal mol^{-1} between two carbon–carbon bonds.[46]

The $E_{\min}$ for n-C_3H_7F formed by association of C_2H_5 and CH_2F was taken as 83.9 kcal mol^{-1}. This follows from $\Delta H_f{}^\circ{}_{298}(C_3H_7F)^{41} = -67$ kcal mol^{-1}, the value for $\Delta H_f{}^\circ(CH_2F)$ in Table III, and the usual $\Delta H_f{}^\circ(C_2H_5)$ based upon $D^\circ(C_2H_5-H)$ of 98 kcal mol^{-1}.

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(45) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 64, 2130 (1968).

(46) On the other hand recent mass spectrometer work (T. C. Ehlert, *J. Phys. Chem.*, 73, 949 (1969)) favors $\Delta H_f{}^\circ{}_{298}(CF_3) = 102.5 \pm 3$ kcal mol^{-1}.

Transannular Dipolar and Neighboring Group Effects in Simple Oxygen Heterocycles on Rates of Solvolysis of Arenesulfonates[1]

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Abstract: The rate of acetolysis of the following arenesulfonates has been studied at 85°: 4-tetrahydropyranyl (**1b**, **1d**), 3-tetrahydropyranyl (**2b**), 4-tetrahydrothiopyranyl (**3b**), 1-methoxy-3-pentyl (**4b**), 1,5-dimethoxy-3-pentyl (**5b**), and 3-tetrahydrofuranyl (**6b**). All of the heterocyclic compounds showed substantial rate reductions, compared to the open-chain methoxy compounds **4b**, **5b**, and cyclohexyl and cyclopentyl arenesulfonates. The rate retardation is attributed to a transannular dipolar field effect exerted by the heterocyclic oxygen atom. This explanation is supported by measurement of the carbonyl stretching frequency of the related ketones, **1c**, **2c**, **6c**, 2- and 4-methoxycyclohexanones, cyclohexanone, and cyclopentanone. Within the series of arenesulfonates studied, 3-tetrahydropyranyl brosylate solvolyzed much faster than predicted, in spite of the rate-retarding dipolar effect. This relatively rapid rate is attributed to the promoting effect on the solvolysis of 1,3-transannular oxygen participation, which has not been noted before. Such participation is not important with the 4-tetrahydropyranyl or the 3-tetrahydrofuranyl compounds for reasons of strain.

It is well known that methoxyl groups can assist solvolysis and displacement reactions through intermediate formation of methoxonium ions.[2] This phenomenon, in which we became interested[3,4] during some structural studies on natural products, is examined in the present paper by studying rates of solvolysis of arenesulfonates in which the ether oxygen affecting sol-

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(1) In memory of Winston Danae Walters: "And gladly wolde he lerne, and gladly teche."

(2) (a) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958); (b) E. Allred and S. Winstein, *J. Am. Chem. Soc.*, **89**, 3991 (1967); **89**, 3998, 4008, 4012 (1967).

(3) D. S. Tarbell, *et al.*, *ibid.*, **83**, 3096 (1961).

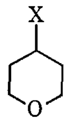
(4) (a) E. R. Novak and D. S. Tarbell, *ibid.*, **89**, 73 (1967); (b) A. W. Friederang and D. S. Tarbell, *J. Org. Chem.*, **33**, 3797 (1968); (c) J. R. Hazen, and D. S. Tarbell, *Tetrahedron Lett.*, 5927 (1968); (d) J. R. Hazen, *ibid.*, 1897 (1969); R. J. Gargiulo and D. S. Tarbell, *Proc. Nat. Acad. Sci. U. S.*, **62**, 52 (1969).

Table I. Summary of First-Order Solvolysis Constants in Acetic Acid at 84.80° [a]

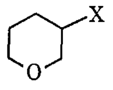
	Concn, M	[NaOAc], M	k, sec^{-1}
3-Tetrahydropyranyl brosylate (**2b**)	0.03695	0.0394	$2.47 \pm 0.02 \times 10^{-5}$
4-Tetrahydropyranyl brosylate (**1b**)	0.0350	0.0386	$1.40 \pm 0.02 \times 10^{-5}$
	0.03375	0.03825	$1.44 \pm 0.03 \times 10^{-5}$
4-Tetrahydropyranyl tosylate (**1d**)	0.0380	0.0385	$3.72 \pm 0.04 \times 10^{-6}$
	0.03755	0.0385	$3.69 \pm 0.03 \times 10^{-6}$
	0.0376	0.0386	3.62×10^{-6}
4-Tetrahydrothiopyranyl tosylate (**3b**)	0.0372	0.0394	$5.37 \pm 0.09 \times 10^{-6}$
	0.0388	0.0394	$5.25 \pm 0.06 \times 10^{-6}$
Cyclohexyl brosylate (**7**)			4.52×10^{-4} [b]
Cyclohexyl tosylate	0.0378	0.0385	$1.36 \pm 0.02 \times 10^{-4}$ [c]
3-Tetrahydrofuranyl brosylate (**6b**)	0.0367	0.0394	$5.50 \pm 0.03 \times 10^{-6}$
	0.0365	0.0394	$5.52 \pm 0.07 \times 10^{-6}$
1-Methoxy-3-pentyl brosylate (**4b**)	0.0290	0.0384	$3.51 \pm 0.02 \times 10^{-4}$
	0.0309	0.0381	$3.56 \pm 0.01 \times 10^{-4}$
1,5-Dimethoxy-3-pentyl brosylate (**5b**)	0.0296	0.0384	$8.14 \pm 0.07 \times 10^{-5}$
	0.0361	0.0381	$8.20 \pm 0.13 \times 10^{-5}$

[a] The maximum temperature variation was ±0.05°. [b] Calculated from the data of H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956). [c] The calculated value, from the data of S. Winstein and E. Grunwald, *ibid.*, **70**, 821 (1948), of Brown and Ham, footnote *b*, and of S. Winstein, *et al.*, *ibid.*, **70**, 816 (1948), is $k = 1.35 \times 10^{-4}$ sec^{-1}.

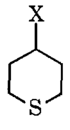
volysis is part of a heterocyclic system. Several open-chain methoxy arenesulfonates are included for comparison. The carbonyl stretching frequencies of most of the corresponding ketones have also been measured in a number of solvents to establish correlations with the solvolysis rates; 2-methoxy- and 4-methoxycyclohexanone were also studied. The compounds studied are indicated by structures **1**–**6**.



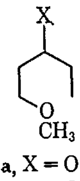
1a, X = OH
b, X = OBs
c, X = =O
d, X = OTos



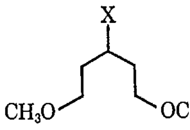
2a, X = OH
b, X = OBs
c, X = =O



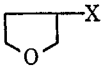
3a, X = OH
b, X = OTos



4a, X = OH
b, X = OBs

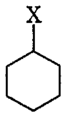


5a, X = OH
b, X = OBs

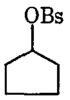


6a, X = OH
b, X = OBs
c, X = =O

The rate of solvolysis of cyclohexyl and cyclopentyl arenesulfonates **7** and **8** were also used for comparison.



7a, X = OTos
b, X = OBs



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All of the heterocycles (**1b**, **2b**, **3b**, **6b**) showed slower rates of solvolysis than the nonoxygenated model compounds **7** and **8**, or the open-chain methoxy analogs **4b** and **5b**. The slow acetolysis rates of the heterocyclic arenesulfonates correlate with the higher carbonyl stretching frequencies of the ketones (relative to the nonoxygenated cyclic ketones). These observations are explained by a transannular dipolar field effect exerted by the ether oxygen. 3-Tetrahydropyranyl brosylate (**2b**) solvolyzed faster than expected, in spite of the rate-retarding dipolar effect. This rate acceleration is attributed to 1,3-transannular oxygen participation.

Results and Discussion

The rates of solvolysis listed in Table I show some unexpected values. 4-Tetrahydropyranyl tosylate (**1d**) reacts more slowly by a factor of 2.7×10^2 than the corresponding cyclohexyl compound **7a**, making it obvious that there is no participation in the solvolysis by the ether oxygen *via* a boat conformation.[5] If the rate diminution in going from the cyclohexyl compound **7a** to the 4-tetrahydropyranyl derivative **1d** was to be explained solely by the inductive effect of the ether oxygen in **1d**, the magnitude of the inductive effect would have to be larger by a power of ten in **1d** than would be predicted, using *cis*- or *trans*-3-methoxycyclohexyl tosylate[6] or 3-methoxy-1-propyl brosylates[2a] as model compounds. In these compounds, the ether oxygen is about the same distance from the reaction center as the ring oxygen in the 4-tetrahydropyranyl sulfonate.

Both the 3-methoxycyclohexyl and 3-methoxy-1-propyl arenesulfonates solvolyze "normally" at rates that agree fairly closely with those predicted by the Taft treatment of the inductive effect of the $-CH_2OCH_3$ substituent relative to the unsubstituted parent compounds,[6–8] as shown in the data of Table II.

On this basis, a rough estimate of the acetolysis rate of the 4-tetrahydropyranyl derivative relative to the same cyclohexyl derivative would be about 0.2–0.3. The observed rate ratio of 0.027 is thus, as mentioned, tenfold smaller than predicted. The abnormally slow solvolysis rate of the 4-tetrahydropyranyl derivative thus reflects the influence of something more than a simple inductive effect. This effect may reasonably be assumed to be due to a transannular dipole effect, in which the dipole associated with the ether oxygen atom destabilizes the incipient partial positive charge on the 4 carbon atom in the solvolysis transition state.

It might be argued that the compounds in Table II are not good models for the tetrahydropyranyl tosylate,

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(5) *Cf.* similar suggested participation in the Prins reaction by A. T. Blomquist and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 6025 (1957).

(6) D. S. Noyce, B. R. Thomas, and B. N. Bastian, *ibid.*, **82**, 885 (1960).

(7) A. Streitwieser, *ibid.*, **78**, 4935 (1956).

(8) S. Winstein and E. Grunwald, *ibid.*, **70**, 821 (1948).

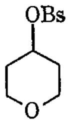
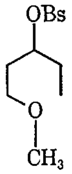
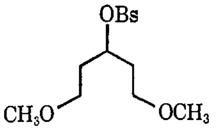
Table II. Taft Correlation for the Solvolysis of Some Methoxyl-Substituted Arenesulfonates

Compound	$(k_{OCH_3}/k_H)_{obsd}$[a]	$(k_{OCH_3}/k_H)_{calcd}$[a]	Conditions
$CH_3OCH_2CH_2CH_2OBs$	0.653[b]	0.444	Acetic acid, 75°
$CH_3OCH_2CH_2CH_2OBs$	0.666[b]	0.547	Ethanol, 75°
cis-3-Methoxycyclohexyl tosylate	0.18[c]	0.29	Ethanol, 75°
trans-3-Methoxycyclohexyl tosylate	0.285[c]	0.29	Ethanol, 75
trans-2-Methoxycyclohexyl brosylate	0.057[d]	0.015[e]	Acetic acid, 75°

[a] K_{OCH_3}/k_H, rate ratio of methoxyl-substituted to unsubstituted arenesulfonate; calculated value following ref 6. [b] Relative to *n*-butyl brosylate.[2a] [c] Relative to cyclohexyl tosylate.[6] [d] Relative to cyclohexyl brosylate.[8] [e] Does not take into account the small rate enhancement due to neighboring methoxyl group participation.

because the alkoxyl Taft substituent constant σ^* may have different values when the ether oxygen is part of a ring. However, it is clearly seen that the substituent constant is insensitive to the cyclic or acyclic character of the ether, from the solvolysis data for 2-tetrahydropyranylmethyl brosylate and 2-tetrahydrofuranylmethyl and (-ethyl) brosylate.[9] The data indicate that the β (or γ) ether oxygen exerts a normal rate-retarding inductive effect, even though it is a part of a ring system. The fact that in the 4-tetrahydropyranyl compounds there is more than one carbon chain through which the inductive effect must be transmitted does not appear to be a complicating factor.[10]

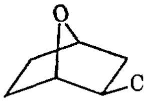
In order to show more conclusively that there is an abnormally large rate retardation in **1d** due to transannular dipole interactions, two compounds, **4b** and **5b**, which are structurally similar to 4-tetrahydropyranyl brosylate (**1b**), but which are acyclic, were prepared, and their solvolysis rates were measured. The observed relative rates for 4-tetrahydropyranyl (**1b**), 1-methoxy-3-pentyl (**4b**), and 1,5-dimethoxy-3-pentyl (**5b**) brosylates are as follows, using the data in Table II.

Compound			
	1b	**4b**	**5b**
Rel rate	1.0	24	5.6

Clearly, something more than a simple inductive effect is operative in **1b** because it solvolyzes still more slowly than the 1,5-dimethoxy compound **5b**, which possesses *two* rate-retarding alkoxyl groups, each the same number of carbon atoms away from the reaction center as the single oxygen atom in **1b**.[11] Furthermore, the relative rates suggest that the rate retardation in the heterocyclic sulfonate **1b** amounts to a factor between 5.6 and 24, or, approximately, a power of ten.

Similar rate retardations apparently occur in the solvolysis of the corresponding heterocyclic sulfide, because 4-tetrahydrothiopyranyl tosylate (**3b**) is much less reactive than cyclohexyl tosylate (by a factor of 28) and is only slightly more reactive than **1b**.

An even more striking rate retardation due to the incorporation of the oxygen atom into the ring system is obvious from the acetolysis rate of 3-tetrahydrofuranyl brosylate (**6b**), which reacts by a factor of 1.03 × 10^3 more slowly than cyclopentyl brosylate (**8**) at 85°. Again, even allowing for the normal rate-retarding inductive effect of the β oxygen atom, **6b** still solvolyzes more slowly by a factor of 10–15 than predicted. This factor is similar to that estimated for the six-membered ring heterocycle. Further, the retardation relative to cyclopentyl brosylate is in accord with that observed for *exo*-7-oxanorbornyl chloride (**9**) relative to norbornyl chloride.[12] Thus for **1b**, **6b**, and **3b**, there seems little doubt that there is a fairly substantial reduction in rate due to a transannular dipolar destabilization of the solvolysis transition state.



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Comparison of the acetolysis rate constant of 3-tetrahydropyranyl brosylate (**2b**) with those of the other heterocyclic derivatives reveals the unexpected result that **2b** is *more* reactive than 4-tetrahydropyranyl brosylate (**1b**) by a factor of nearly 2. Considering merely the simple inductive effect of the oxygen atom, it would have been expected that moving the leaving group closer to the electronegative oxygen atom would have resulted in *reduced* reactivity of the 3 derivative relative to the 4-brosylate.[13] A second anomaly is that 3-tetrahydrofuranyl brosylate (**6b**) is only 0.22 times as reactive as 3-tetrahydropyranyl brosylate (**2b**). Since the leaving group is β to the oxygen atom in both compounds, it might have been predicted that as a first approximation the inductive or electronic effects would also be quite similar and that the major differences in the reactivities of **2b** and **6b** would be due to the differences in ring size. It is well known that cyclopentyl derivatives are considerably more reactive than the corresponding cyclohexyl derivatives in solvolytic reactions;[14] the ionization process is energetically more favorable for the five- than the six-membered ring sulfonates. Similar considerations should apply to the relative reactivities of **2b** and **6b**, since it is known that the five- and six-membered ring oxygen heterocycles are conformationally very similar to cyclopentyl and cyclohexyl systems, respectively.[15]

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[9] G. T. Kwiatowski, S. J. Kavarnos, and W. D. Closson, *J. Heterocycl. Chem.*, 2, 11 (1965).

[10] C. F. Wilcox and C. Leung, *J. Am. Chem. Soc.*, 90, 336 (1968); F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, 89, 5677 (1967).

[11] The relative rates have not been corrected for the slightly greater (by a factor of 1.33) reactivity of acyclic secondary arenesulfonates than six-membered ring (cyclohexyl) arenesulfonates.[6] The adjusted relative rates using this factor of 1.33 are 1.0:18.3:4.2, but the conclusions drawn from the data are unchanged.

[12] J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, 79, 2533 (1957). Very recently, J. C. Greever and D. E. Gwynn, *Tetrahedron Lett.*, 813 (1969), have shown a striking rate retardation of solvolyses (and marked changes in products) in the acetolysis of the 5-keto-2-norbornyl brosylates, compared to the parent brosylates without the keto group. This rate retardation is attributed by these authors to dipolar interacton of the carbonyl group with the solvolysis center.

[13] R. W. Taft, Jr., *J. Am. Chem. Soc.*, 75, 423 (1953).

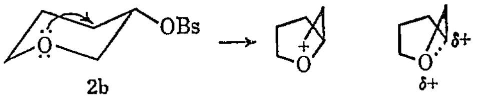
[14] H. C. Brown and G. Ham, *ibid.*, 78, 2735 (1956).

[15] S. C. Burket and R. M. Badger, *ibid.*, 72, 4397 (1950); F. E. Malherbe and H. J. Bernstein, *ibid.*, 74, 4408 (1952).

Therefore, since cyclopentyl brosylate is more reactive than cyclohexyl brosylate by a factor of 11 in acetic acid at 85° (Table I), a similar factor would be expected for the acetolysis rate of 3-tetrahydrofuranyl brosylate (**6b**) relative to 3-tetrahydropyranyl brosylate (**2b**). As mentioned above, the actual rate ratio is only 0.22.

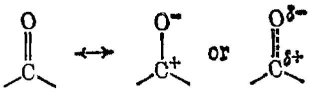
One might rationalize the greater reactivity of 3-tetrahydropyranyl brosylate (**2b**) as compared to the five ring 3-tetrahydrofuranyl compound (**6b**) by the *ad hoc* assumption that in the former case the transannular dipolar effect is absent, but that it is present in the latter. There is no apparent basis for this assumption, and none is provided by an examination of relevant molecular models.

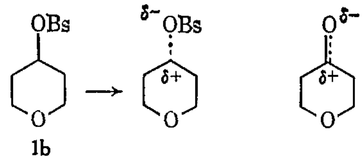
An alternate explanation for the enhanced reactivity of 3-tetrahydropyranyl brosylate (**2b**) is that, as expected, the solvolyses of all three heterocyclic derivatives **1b**, **2b**, and **6b** are subject (to a greater or lesser degree) to the rate-retarding dipole effect and that the rate of **2b** is accelerated relative to the other two (**1b** and **6b**) by transannular neighboring group participation by the ether oxygen. Such participation would yield either the bicyclic oxonium ion **10a** or a partially bonded (intramolecularly solvated) intermediate (or transition state) **10b**. That such participation should be more important for **2b** than for the other heterocycles finds reasonable explanation in the fact that analogous participation for the 4-tetrahydropyranyl or 3-tetrahydrofuranyl derivatives would involve much more ring strain. An oxabicyclo[2.1.0]pentyl oxonium ion (from **6b**) would be expected to be less stable than **10** since bicyclopentanes are less stable than bicyclo[3.1.0]hexanes.[16] The intervention of an oxabicyclo[2.2.0]hexyl oxonium ion (from **1b**) seems unlikely since it requires a torsionally strained boat-like transition state, in addition to ring-strain factors.



2b 10a 10b

Moriarty[17] has demonstrated a correlation between the rate-retarding effect of a transannular dipolar group on rate of solvolysis and the increase in carbonyl frequency of the ketone corresponding to the alcohol whose sulfonate is being solvolyzed. Therefore, the carbonyl frequencies of the ketones related to each of the compounds solvolyzed in the present work were measured. The electrical effects of substituents on the carbonyl frequency are well documented, and the carbonyl group, because of its polar nature, is a good model for the solvolysis transition state.[17] Thus the charge distribution, illustrated by the ground-state resonance hybrids, is quite similar to the charge distribution in the solvolysis transition state, as illustrated below.



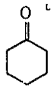
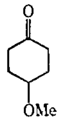
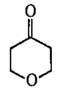
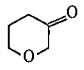
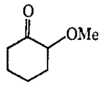
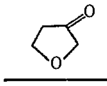


1b

It has been amply demonstrated that alkoxyl groups, like the halogens, can interact with the carbonyl group by a dipolar mechanism and thereby raise the carbonyl frequency.[18] Pure inductive effects seem to be of negligible importance, because equatorial α-methoxyl groups in cyclohexyl systems raise the carbonyl frequency by *ca.* 8–11 cm^{-1} over the unsubstituted compound, while axial methoxyl groups have little or no effect on the position of absorption. The effect appears to be smaller, however, than the effect of equatorial halogens, which raise the carbonyl frequency by *ca.* 20–25 cm^{-1} relative to the axial or the unsubstituted ketones. The raising of the carbonyl frequency finds its origin in the destabilization of the polar contribution to the ketone ground state by a simple electrostatic repulsion of the similarly charged ends of the carbonyl and ether oxygen dipoles. Thus the ether dipole induces a decrease in the polarity in the carbonyl and *vice versa; i.e.*, it induces the partial negative charge on the carbonyl oxygen back toward the geometric center of the carbon–oxygen double bond. This, in effect, increases the double-bond character; the bond is therefore strengthened, and the bond-stretching frequency increases.

It is clear from Table III that just as in 2-methoxycyclohexanone ($\Delta\nu_{C=O} = +9$ cm^{-1} relative to cyclohexanone) and its derivatives, the heterocyclic ketones reveal dipole–dipole interactions by their raised car-

Table III. Carbonyl Stretching Frequencies in 1–2% Solution[a]

	Values of $\nu_{C=O}$ (cm^{-1}) (first row) and $10^3\Delta\ \nu/\nu^b$ (second row)					
Compound	n-C_6H_{14}	C_6H_{12}	CCl_4	CH_3-$C{\equiv}N$	CH_2-Cl_2	$CHCl_3$
 [c]	1726	1724 0.1	1719 0.4	1709 1.0	1708 1.0	1705 1.2
	1728	1727 0.06	1720 0.5	1714 0.8	1711 1.0	1711 1.0
 (1c)	1731	1730 0.06	1726 0.3	1721 0.6	1719 0.7	1717.5 0.8
 (2c)	1736	1734 0.1	1730 0.4	1727 0.5		1724 0.7
	1732	1730 0.1	1728 0.2		1724 0.5	1723 0.5
 (6c)	1769.5	1768 0.1	1765.5 0.2	1762 0.4		1761.5 0.5

[a] The estimated accuracy of the data is >±1 cm^{-1}. [b] $\Delta\nu/\nu \equiv (\nu_{n\text{-hexane}} - \nu_{solvent})/\nu_{n\text{-hexane}}$. [c] Data of L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959), give observed values for cyclohexanone: 1725 (n-hexane), 1718 (carbon tetrachloride), 1709 (acetonitrile), 1704 (chloroform) cm^{-1}.

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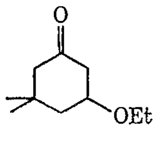
(16) R. B. Turner, *et al.*, *J. Am. Chem. Soc.*, **90**, 4315 (1968).

(17) R. M. Moriarty, C. R. Romain, and T. O. Lovett, *ibid.*, **89**, 3927 (1967).

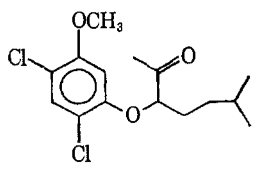
(18) S. S. Stradling and D. S. Tarbell, *J. Org. Chem.*, **29**, 1170 (1964), and references therein.

bonyl frequencies relative to the nonoxygenated parent compounds. Thus, the carbonyl frequency of 4-ketotetrahydropyran (**1c**) is raised by 7 cm^{-1} relative to cyclohexanone in CCl_4 (+12 cm^{-1} in chloroform), while for 3-ketotetrahydrofuran (**6c**) the frequency is raised by *ca.* 17 cm^{-1} (CCl_4) relative to cyclopentanone. These correlate well with the observed slow rates of solvolysis of the corresponding brosylates, and are consistent with the concept that dipolar electrostatic repulsions are the cause in both cases. The carbonyl frequency of 4-methoxycyclohexanone is practically the same as that of cyclohexanone. Similarly, the frequency of 5,5-dimethyl-3-ethoxycyclohexanone (**11**) is somewhat lower, while that of 3-(2,4-dichloro-5-methoxyphenoxy)-6-methyl-2-heptanone (**12**) is the same as cyclohexanone and acetone.[19] These examples serve to supplement further the already extensive literature data which show that dipole and not inductive effects are the important factors responsible for raising the carbonyl frequency.



11

1714 cm^{-1} (CCl_4)



12

1718 ± 1 cm^{-1} (CCl_4)

Perhaps the most significant feature of the data is the fact that 3-ketotetrahydropyran (**2c**) also shows a raised carbonyl frequency relative to both cyclohexanone and 4-ketotetrahydropyran (**1c**) in all of the solvents examined.

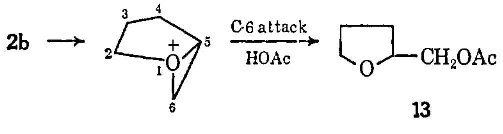
From the data of Table III it is clear that the interaction between the ether and carbonyl dipoles is even stronger in the 3-keto than in the 4-keto heterocycle, the carbonyl frequency being consistently 4–6 cm^{-1} higher in the former than in the latter. This result shows that the transannular dipolar repulsions are present (as expected) in each of the three heterocyclic compounds, and renders very unlikely the possibility that the dipole effect is absent in the solvolysis of 3-tetrahydropyranyl brosylate (**2b**).

A similar conclusion is reached upon examination of the relative solvent shifts of the carbonyl frequencies. The generally observed phenomenon, that the carbonyl frequency of a given compound is lowered by increasing the polarity of the solvent, is a result of the increased polarization of the carbonyl group from the increasing solvent stabilization of the ionic contribution to the resonance hybrid.[20] The more polar the carbon–oxygen bond the less its double-bond character, and therefore the stretching frequency is increasingly lowered. Thus, the cyclohexanone absorption is shifted from 1726 cm^{-1} in the nonpolar solvent *n*-hexane down to 1705 cm^{-1} in chloroform. On the other hand, dipolar destabilization of the ionic contribution to the carbonyl by the ether oxygen dipole counteracts solvent stabilization to some extent. Therefore, for compounds in which a dipolar interaction is present, the solvent shift will be *less* than if there were no such effect; *i.e.*, the dipolar raising of the carbonyl frequency relative to a model compound will be paralleled by a reduced sensitivity of the carbonyl group to solvent polarity. Presumably, the stronger the dipolar interaction the smaller will be the relative solvent frequency shift. For example, with 4-ketotetrahydropyran (**1c**) the carbonyl absorption drops from 1731 cm^{-1} in *n*-hexane to only 1717.5 cm^{-1} in chloroform, a shift of only slightly more than half that of cyclohexanone. Again, from the data in Table III it is apparent that the frequency shift is even less for 3-ketotetrahydropyran (**2c**) than for 4-ketotetrahydropyran, indicating that dipolar destabilizing interactions are significant for both compounds. The solvent frequency shift for 3-ketotetrahydrofuran (**6c**) is even smaller yet, dropping only 8 cm^{-1} in going from hexane to chloroform.

From the fact that a fairly strong dipolar interaction is indicated in 3-ketotetrahydropyran, it would be expected that the solvolysis of 3-tetrahydropyranyl brosylate (**2b**) should also reveal the rate-retarding dipole effect as a significantly reduced acetolysis rate constant. As discussed above, however, a rate reduction is not observed. The observed rate is approximately that expected in the absence of the dipole effect as estimated by considering only the inductive effect of the oxygen atom β to the leaving group; the rate is *faster* than that of the 4-tetrahydropyranyl derivative whereas it should be more than a power of ten slower; and the rate is unexpectedly much faster than that of the corresponding five-membered ring compound (**6b**). The most reasonable explanation of this enhanced reactivity of 3-tetrahydropyranyl brosylate is that it solvolyzes with anchimeric assistance by the ether oxygen, as shown above (structure **10**). Further evidence that the rate enhancement by **10** is real comes from the fact that **2b** undergoes acetolysis at virtually the same rate as *trans*-2-methoxycyclohexyl brosylate,[21] in which case there is good evidence for neighboring methoxyl group participation.[8,22] If there were no rate enhancement in the heterocyclic compound **2b**, it would have been expected to solvolyze considerably more slowly than the 2-methoxycyclohexyl derivative.

Although the evidence for an enhanced solvolysis rate of **2b** seems clear, an estimate of the exact magnitude of the rate acceleration is less clear, because it is difficult to estimate accurately what the solvolysis rate would be in the absence of participation. Several rough estimates have been made, but are not described in detail. They agree that the rate enhancement in **2b** due to the ether oxygen participation is a factor of 25–50.

If the oxonium ion **10a** is a discrete intermediate, solvent attack on such a species could occur at carbons C-2, C-5, and/or C-6 and could, therefore, yield rearranged products. For example, attack of acetic acid



13

10a

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[19] Compounds **11** and **12** were prepared by Dr. L. C. Brannigan of this laboratory.

[20] Table III; also L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1965, pp 389–409.

[21] The acetolysis rate constant for *trans*-2-methoxycyclohexyl brosylate at 85° is 2.44×10^{-5} sec^{-1} (calculated from the data of ref 8), compared to 2.47×10^{-5} sec^{-1} for **2b** (Table I).

[22] S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943).

at C-6 of **10a** would yield tetrahydrofurfuryl acetate (**13**). An examination of the products from the acetolysis of 3-tetrahydropyranyl brosylate (**2b**) revealed that no **13** was formed, however; the only detectable acetate in the reaction mixture was the unrearranged substitution product 3-tetrahydropyranyl acetate. Although no definitive conclusions concerning the nature of the intermediate can be drawn from this result (since attack at C-5 could conceivably be the sole mode of decomposition of **10**), it may suggest that a better formulation of the solvolysis intermediate (or transition state) might be the partially bonded or intramolecularly solvated structure **10b**.

This type of 1,3-transannular participation has been observed previously in simple monocyclic compounds, although not in oxygen heterocycles. For example, the 3-substituted four-, five-, and six-membered ring heterocyclic sulfides all exhibit remarkably large neighboring group rate accelerations, being as large or larger than those of β-chloroethyl sulfides.[23] Similarly, weak stabilization by the π electrons of the exocyclic methylene group has been postulated in the solvolytic transition state of 3-methylenecyclohexyl tosylate.[23] This is, of course, analogous to the homoallylic participation observed in the solvolysis of 3-cholesteryl derivatives.[24] Transannular participation has been inferred from rearrangement products obtained from 3-chloropiperidines[25] and from tetrahydrofurfuryl tosylate.[26] The present work appears to be the only evidence for participation in the 3-tetrahydropyranyl derivatives.

Suitable stereochemical studies should show whether solvolysis of **2b** involves intermediates (or transition states) of type **10**.

Experimental Section

4-Hydroxytetrahydropyran (1a). 1,3-Butanediol diacetate, prepared from the diol and acetic anhydride, was distilled from *p*-toluenesulfonic acid through a 25-cm column packed with glass beads (head temperature below 135°). The resulting 3-butenol acetate (allylcarbinyl acetate) and acetic acid were neutralized by dropwise addition of a saturated potassium carbonate solution and then saponified by aqueous sodium hydroxide at room temperature. Distillation gave 3-butenol, bp 110–113°, $n^{21}\text{D}$ 1.4215, in 41% yield from the diol; lit.[27] bp 114°, $n^{20}\text{D}$ 1.4213. The refractive index and ir spectrum were identical with those of a sample prepared by the sequence allyl bromide → allyl cyanide → 3-butenoic acid → 3-butenol. Treatment of 15 g of 3-butenol[28] with 18.5 ml of 35% formaldehyde and 2.5 ml of concentrated sulfuric acid at 80° for 15 hr yielded after work-up and distillation 6.7 g of 4-hydroxytetrahydropyran, which contained, as indicated by refractive index and ir spectrum, about 6–7% of 3-butenol. A sample purified by distillation had $n^{21}\text{D}$ 1.4597, which compares favorably with the reported value. The *p*-nitrobenzoate melted at 68–68.5°; lit.[29] 69°.

The **brosylate 1b**, prepared from brosyl chloride and dry pyridine overnight at 0°, melted after two crystallizations from methanol, at 74–76°. *Anal.* Calcd for $C_{11}H_{13}BrO_4S$: C, 41.13; H, 4.08. Found: C, 41.25; H, 4.11.

3-Hydroxytetrahydrofuran[30] **(6a)** was converted to the brosylate in the usual way; it melted at 72.5–73° after one crystallization from ether–petroleum ether (bp 30–60°). *Anal.* Calcd for $C_{10}H_{11}BrO_4S$: C, 39.10; H, 3.61. Found: C, 39.34; H, 3.60.

3-Hydroxytetrahydropyran (2a) was prepared in 34% yield by hydroboration of dihydropyran with external generation of diborane;[31] it was obtained with bp 85–90° (15 mm), $n^{25}\text{D}$ 1.4560. In addition to the desired product, a small amount of what was tentatively identified (on the basis of nmr and ir spectra) as 4-pentenol was also formed.

When the reaction was carried out by the generation of diborane (from boron trifluoride etherate and sodium borohydride) in the reaction vessel, the yield was only about 5%. The low yields even with the external generation method are probably due to the presence of boron trifluoride, which is known[32] to catalyze the elimination of β-alkoxyorganoboranes. Vpc analysis of the distilled 3-hydroxytetrahydropyran showed a single symmetrical peak, on a 25% Ucon polar column at 160°. The nmr spectrum (neat, τ) showed the hydroxyl singlet at 5.40, 1 H; a 5-H multiplet at 6.0–7.0 (protons on carbon attached to oxygen); and a 4-H multiplet at 8.0–8.9 (methylene protons). The reported boiling point is 88° (18 mm).[33]

The **brosylate 2b** melted, after recrystallization from pentane–ether, at 66.5–67°. *Anal.* Calcd for $C_{11}H_{13}BrO_4S$: C, 41.13; H, 4.08. Found: C, 41.01; H, 4.27.

The **tosylate**, obtained analytically pure, is an oil. The **acetate** had bp 78° (14 mm), $n^{26}\text{D}$ 1.4386. *Anal.* Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.38; H, 8.43.

4-Hydroxytetrahydrothiopyran (3a)[34] was obtained by lithium hydride reduction of the ketone.[35]

The **tosylate 3b** melted at 92–93° and gave a satisfactory carbon–hydrogen analysis; the reported melting point is 90–91°.

5-Methoxy-2-penten-1-ol and 5-Methoxy-1-penten-3-ol.[36] In a 500-ml flask was fused about 2–3 g of zinc chloride. After cooling with protection from moisture, the flask was fitted with a Dry Ice condenser and a gas inlet tube. About 100 g of 1,3-butadiene was then introduced into the cooled flask, followed by the slow addition of 69 g of chloromethyl ether. The mixture was stirred at reflux temperature under the Dry Ice condenser for 11 hr and allowed to stand an additional 8 hr at −10°. The flask was then allowed to come to room temperature. Ether (150 ml) was added and the solution washed with water (three 50-ml portions). After drying, the ether was removed and the residue (*ca.* 120 g) was distilled. The fraction boiling at 50–74° (16 mm) was collected. The total yield of the mixture of allylic chlorides was 18.6 g (71% yield), $n^{24}\text{D}$ 1.4462.

The above-prepared isomeric chloromethoxypentenes were refluxed in 300 ml of saturated aqueous potassium carbonate for 18 hr. The mixture was cooled and extracted thoroughly with ether. The extracts were combined, dried, and fractionated. The isomeric alcohols were collected at 76–101° (16 mm), $n^{26}\text{D}$ 1.4444, yield 41.7 g (77%). Vpc (Carbowax) showed 24% 1-ene and 73% 2-ene plus *ca.* 3% of unreacted primary allylic chloride.

The mixture of alcohols was carefully distilled through a 90 × 0.5 cm wire spiral-packed, vacuum-jacketed column. The head was heated with a heating coil, and an infrared lamp was employed to prevent column flooding. About 6 hr was required to adjust the boil-up rate, after which three fractions totaling 8–9 ml were collected over 1–1.5 hr: (fraction 1) bp 65–73° (20 mm), $n^{22.9}\text{D}$ 1.4273, which vpc analysis (Ucon polar, 15 ft × 0.25 in. at 160°) and nmr showed to be mainly (82%) 5-methoxy-1-chloro-2-pentene; (fraction 2) bp 74–75° (20 mm), $n^{22.9}\text{D}$ 1.4345, which by nmr and vpc was 5-methoxy-1-penten-3-ol in a purity of ~97%; (fraction 3) bp 75° (20 mm), $n^{22.9}\text{D}$ 1.4345, which by vpc was pure 5-methoxy-1-penten-3-ol. The yield of fractions 2 and 3 was 4.85 g.

The material remaining in the distillation pot was then fractionated through a short Vigreux column: (fraction 4) bp up to 92° (18.5 mm), amounted to less than 1 ml; (fraction 5) bp 92–96° (18.5 mm), $n^{23.1}\text{D}$ 1.4443, yield *ca.* 2 g; (fraction 6) bp 97–100° (18.5 mm), $n^{23.1}\text{D}$ 1.4473, which by vpc contained *ca.* 7% of secondary allylic alcohol, yield 16.6 g; (fraction 7) bp 100° (18.5 mm),

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[23] D. J. Anderson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1960.

[24] S. Winstein and R. Adams, *J. Am. Chem. Soc.*, 70, 838 (1948).

[25] R. D. Reitsema, *ibid.*, 71, 2041 (1949).

[26] D. Gagnaire, *et al.*, *Bull. Soc. Chim. France*, 309, 312 (1961); 721 (1963).

[27] E. Hanschke, *Chem. Ber.*, **88**, 1053 (1955).

[28] A. Juvala, *Ber.*, **63**, 1989 (1930); J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509 (1951).

[29] J. W. Baker, *J. Chem. Soc.*, 296 (1944).

[30] H. Wynberg and A. Bantjes, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 534.

[31] *Cf.* G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[32] D. J. Pasto and C. C. Cumbro, *J. Am. Chem. Soc.*, **86**, 4343 (1964); H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

[33] D. Gagnaire, *Compt. Rend.*, **248**, 420 (1959).

[34] E. Adlerova and M. Protiva, *Collection Czech. Chem. Commun.*, 24, 1268 (1968).

[35] H. M. E. Cardwell, *J. Chem. Soc.*, 715 (1949); E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, 70, 1813 (1948).

[36] W. S. Emerson, G. F. Deebel, and R. I. Longley, Jr., *J. Org. Chem.*, 14, 696 (1949); A. Arbuzow, K. J. Vatsuro, and Y. P. Volkow, *J. Gen. Chem. USSR*, **29**, 2817 (1959).

$n^{23.1}\text{D}$ 1.4478, which by vpc and nmr was pure 5-methoxy-2-penten-1-ol, yield 9.5 g.

The reported[37] values for the primary and secondary allylic alcohols are bp 96–98° (19 mm), $n^{25}\text{D}$ 1.4480, and bp 60–61° (10 mm), $n^{20}\text{D}$ 1.4373, respectively.

1-Methoxy-3-pentanol (4a). A mixture of the isomeric chloromethoxypentenes was treated with sodium acetate to give the mixed acetates, and this mixture was hydrogenated over 5% Pd–C in methanol. The hydrogen uptake was rapid and ceased after the absorption of 1 equiv. The solvent was removed at reduced pressure and the crude ester mixture was saponified with aqueous sodium hydroxide. After ether extraction, drying, and solvent removal, the mixture of alcohols was distilled (short path) and then fractionated through a 90-cm wire spiral column. Only the lower boiling 1-methoxy-3-pentanol was collected, bp 65–70°, $n^{26}\text{D}$ 1.4190. Catalytic reduction of the acetates gave much better results than reduction of the alcohol mixture.

The **brosylate 4b** was prepared in 50% yield by the usual low-temperature method in pyridine and, after two recrystallizations from hexane at −20°, had mp 52–52.5°. *Anal.* Calcd for $C_{12}H_{17}BrO_4S$: C, 42.73; H, 5.08. Found: C, 42.81; H, 4.84.

1,5-Dimethoxy-2-pentene. To a mixture of 6 g of 61% sodium hydride dispersion in mineral oil in 160 ml of anhydrous ether was added dropwise 16.0 g of 5-methoxy-2-penten-1-ol. When the hydrogen evolution had subsided somewhat, 50 g of methyl iodide was added all at once, and the mixture was stirred and refluxed for 2 days. After cooling, the mixture was filtered and the filtrate fractionated through a short Vigreux column. The ether and excess methyl iodide were removed at atmospheric pressure, and the residue was distilled at 33 mm to give a clear, colorless liquid, bp 74–77°, $n^{26}\text{D}$ 1.4226. The infrared spectrum showed no hydroxy absorption but did show absorptions at 1665 cm^{-1} (weak, olefin stretching) and at 1100 cm^{-1} (strong, C—O stretching). The nmr spectrum (neat, τ) showed a multiplet at 4.42, 2 H (vinyl protons); a doublet at 6.23, $J \cong 4$ cps, 2 H (CH_3OCH_2CH=); a triplet (partially superimposed on the methoxyl absorptions) at 6.67, $J = 6.5$ cps ($-CH_2CH_2OCH_3$); two methoxyl singlets at 6.77 and 6.81, 8 H (total); and a multiplet at 7.75, 2 H (=$CHCH_2CH_2$–). The yield was 10.4 g (58%).

1,5-Dimethoxy-3-pentanol (5a). To a stirred mixture of 26 g of mercuric acetate in 80 ml of water and 80 ml of tetrahydrofuran was added 10.4 g of 1,5-dimethoxy-2-pentene, with stirring for 20 min. The clear solution was cooled in an ice bath and treated with 80 ml of 3 *N* sodium hydroxide, followed by the dropwise addition of 80 ml of 0.5 *N* sodium borohydride in 3 *N* sodium hydroxide. The mixture was allowed to stand overnight and was then filtered and saturated with sodium chloride. The upper layer was separated and the aqueous layer extracted with a total of 400 ml of ether. After drying, the combined organic extracts were concentrated to give 8.8 g of crude product. Distillation afforded 6.3 g of pure 1,5-dimethoxy-3-pentanol, bp 93–94° (11.5 mm), $n^{27}\text{D}$ 1.4281. Vpc analysis on a 5-ft, 25% Ucon polar column at 110° and on a 10-ft, 10% SE-30 column at 175° showed only one symmetrical peak on both columns. The nmr spectrum (neat) showed a quartet for the four methylene protons adjacent to the methine carbon, indicating that the alcohol is the symmetrical 3 isomer rather than the 2 isomer. *Anal.* Calcd for $C_7H_{16}O_3$: C, 56.73; H, 10.88. Found: C, 56.79; H, 11.18.

The **brosylate,** prepared by the usual method in 68% yield, was a low-melting solid, mp *ca.* 20°, $n^{27}\text{D}$ 1.5220. The homogeneity and purity of the ester were indicated by its steady first-order solvolysis rate constant and by the fact that the magnitude of the rate constant relative to that of 1-methoxy-3-pentyl brosylate (**4b**) is consistent only with the 3 isomer (see Discussion). The nmr spectrum is also consistent with the assigned structure. Attempts to prepare solid trityl ether and *p*-nitrobenzoate ester derivatives were unsuccessful. *Anal.* Calcd for $C_{13}H_{19}BrO_5S$: C, 42.51; H, 5.20. Found: C, 42.44; H, 5.01.

Kinetics. The sulfonate ester solutions for the kinetic runs were prepared by dissolving the accurately weighed ester (0.5–0.6 g) in a standard sodium acetate in acetic acid solution in a 50.0-ml volumetric flask at room temperature (25 ± 1°). The anhydrous sodium acetate for the standard solution was either dried at 150° or fused and powdered before use. Reagent grade acetic acid was used without further purification. The initial sodium acetate concentration was determined by titration of an aliquot of the reaction solution to the crystal violet end point with standardized perchloric acid in acetic acid. The reaction solutions were transferred to a 50-ml flask, capped with a rubber serum cap, and placed in the constant-temperature bath at 84.80 ± 0.05° and allowed to come to temperature before the first point was taken. The reactions were followed by withdrawing samples with a syringe, rapidly quenching the reaction by cooling to 0° in an ice bath, and noting the time (electric timer). Then the excess sodium acetate in a measured aliquot (at room temperature) was titrated with standardized perchloric acid in acetic acid from a 5-ml microburet to the crystal violet end point. The rate constants were determined from the integrated first-order rate equation

$$2.303 \ \log \left[\frac{[\text{RX}]_0 - [\text{RX}]_t}{[\text{RX}]_0}\right] = -kt$$

where RX represents the arenesulfonate. The concentrations were generally calculated from the weight of the sulfonate ester and, for the solvolyses which were not inconveniently slow, were checked by the infinity titers. A typical run is presented in Table IV.

Table IV. Acetolysis of 0.03695 *M* 3-Tetrahydropyranyl Brosylate (**5-OBs**) with Added 0.0394 *M* Sodium Acetate at 84.80 ± 0.02°

Time, sec	ml of 0.0485 M^a $HClO_4$/HOAc	[ROBs], *M*	10^5k, sec^{-1}
0	1.565	0.03585	
4370	1.415	0.03225	2.42
8580	1.385	0.02905	2.45
12,570	1.17	0.02625	2.48
17,160	1.06	0.02355	2.44
25,300	0.88	0.01915	2.48
29,790	0.795	0.01705	2.49
37,690	0.68	0.01405	2.49
43,140	0.60	0.01225	2.50

[a] Per 1.979-ml aliquot.

3-Ketotetrahydropyran. To 11.2 g of the alcohol **2a** in 45 ml of ether was added chromic acid solution (11.0 g of sodium dichromate dihydrate plus 8.25 ml of concentrated sulfuric acid, diluted to 55 ml with water) with stirring over 1.5 hr at room temperature. After stirring for an additional 2 hr the ether layer was separated and the aqueous layer twice extracted with ether (75 ml total). The combined ether extracts were washed with saturated sodium bicarbonate and dried over magnesium sulfate overnight. Concentration and distillation gave 3.4 g of ketone, bp 58–64° (11 mm), contaminated with a small amount of alcohol. The structure of the ketone was confirmed by its nmr spectrum, which showed a singlet at τ 6.08 ($-OCH_2C$=O) and a triplet at τ 6.21 ($-OCH_2CH_2$–). The ketone underwent fairly rapid decomposition upon standing at room temperature.

4-Ketotetrahydropyran (1c), prepared as described above, was purified from a small amount of unreacted alcohol by preparative vpc on a 25% Ucon polar column; after purification, the compound had an ir spectrum identical with the published one.[38] The nmr spectrum (CCl_4) showed a triplet at τ 6.12, $J = 6$ cps ($-OCH_2$), and a triplet of equal area at τ 7.63, $J = 6$ cps ($-CH_2C$=O).

3-Ketotetrahydrofuran (6c) was prepared as above and, after purification by preparative vpc, had ir and nmr spectra identical with those reported.[39]

4-Methoxycyclohexanone and the 2-methoxy isomer were prepared by the oxidation of the corresponding alcohols and had the reported properties.

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(37) A. Dudovik and B. Arbuzow, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 541 (1946); *Chem. Abstr.*, 42, 6312 (1948).

(38) S. Olsen and R. Bredoch, *Chem. Ber.*, **91**, 1589 (1958).

(39) J. H. S. Weiland, H. Dÿkstra, and A. B. Pik, *Rec. Trav. Chim.*, **82**, 651 (1963).