The undeuterated compound was synthesized and injected in exactly the same manner within the same hour for proper comparison between it and the deuterated ether. Freshly fractionated 2-propanol was used for each run.

Calculation of Rate Constants. The nonlinear least-squares computer program of Lietzke[18] was used to fit the data to the equation

$$y = a_0\{1 - \exp[-k(t + b)]\}$$

where y is the concentration (conductivity), t is the time, and the following three parameters were adjusted by the program to give the best least-squares fit to the equation: k, the rate constant; a_0, the infinity point; and b, the "time error." Use of this program has been discussed by Collins.[19] The assumption of a linear relationship between conductance (as read from the bridge) and HCl concentration was shown to be valid within our experimental error over the concentration range used (*ca.* 10^{-13} *M*) by comparison with the literature[2] and by construction of a calibration line[2] for the very poorly ionizing solvent, dioxane–methanol (83.3:16.7).

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Medium Effects. I. Solvolysis of 5-Hexenyl *p*-Nitrobenzenesulfonate in Acetic Acid–Nonhydroxylic Solvent (20:80) Mixtures[1a,b]

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Abstract: Acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate in the presence of the base urea has been previously shown to lead to open (55%) and cyclic (45%) products. These two sets of products may be considered to be the result of (a) external nucleophilic attack by the solvent, acetic acid, to give open product and (b) internal nucleophilic attack by the olefin to give cyclic products. Products of the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in media composed of acetic acid–nonhydroxylic solvent (20:80) and urea were determined. Yields of cyclic materials from the solvolysis of other 5-hexenyl sulfonates in some of these media were also determined. These results are analyzed and discussed with respect to solvent nucleophilicity.

One of the most important and least understood ways to influence a chemical reaction is by solvent variation. Physical organic chemists have paid much attention to the empirical correlation of solvent effects on rates and equilibria through linear free energy relationships.[2,3] Numerous parameters such as *Y* values and *Z* values have been developed. All of these parameters with the exception of Swain's equation, eq 1,[4]

$$\log (k/k^0) = c_1d_1 + c_2d_2 \tag{1}$$

measure "solvent polarity" exclusively. Swain's equation when applied to the reaction of nucleophiles with neutral substrates contains nucleophilic and electrophilic terms and the notation given by eq 2 is used. However,

$$\log (k/k^0) = sn + s'e \tag{2}$$

when applied to solvolysis reactions, Swain points out that these terms may not measure nucleophilic and electrophilic reactivity of the solvent and in order to avoid the implication that it does, he changes the notation to that of eq 1.

Nucleophilicity is concerned with the rate that a given substrate undergoes a certain nucleophilic reaction.[4] Thus if substance A is more nucleophilic than substance B, A will undergo a nucleophilic reaction faster than B will undergo this reaction.

The term "solvent nucleophilicity" is a rather vague term, and its meaning is complicated by the fact that a change of solvent changes the medium. It is therefore impossible to talk about "solvent nucleophilicity" in a given medium as one can do with "anion nucleophilicity." Nevertheless, the term "solvent nucleophilicity" should have some meaning since many of the characteristics of anions, such as basicity and solvation, which affect "anion nucleophilicity" are also present in solvents.

In order to discuss "solvent nucleophilicity," we propose the following definition: "solvent nucleophilicity"

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[1] (a) Based on work by M. P. Doyle in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University. (b) Preliminary communication, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 94-O. (c) U. S. Public Health Service Fellow, 1966–1967. (d) National Science Foundation College Teacher Research Participant, Summer, 1965.

[2] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

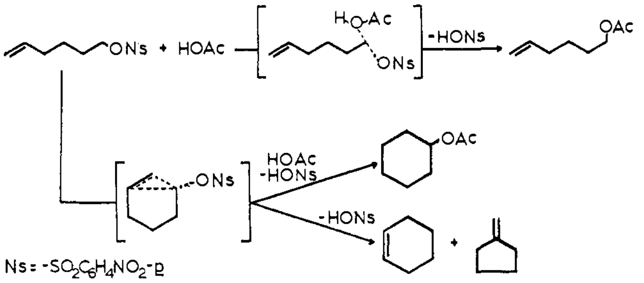
[3] (a) E. A. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press Inc., New York, N. Y., 1966; (b) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, 4, 29 (1965); (c) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[4] (a) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 75, 141 (1953); (b) C. G. Swain and R. B. Mosely, *ibid.*, 77, 3731 (1955); (c) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 77.

is a measure of the tendency of a solvent to attack as a nucleophile some electron-deficient center relative to the tendency of a standard nucleophile to undergo a standard nucleophilic reaction in that solvent. Since one might expect a different order of solvent nucleophilicities with each different class of reactions (such as attack on alkyl arenesulfonates or halides, attack on carbonyl compounds, etc.),[3c] one must restrict each set of nucleophilicities to a certain type of reaction. In order for "solvent nucleophilicity" to be a useful general term and measurable, it should be independent of the substrate at least for a certain type of reaction. In other words, if solvent A is more nucleophilic than solvent B, solvent A should attack any substrate of a certain class in a nucleophilic fashion faster than solvent B. In order for this situation to exist, both ground-state and transition-state changes must be relatively independent of the substrate.

Several workers have recently shown[5,6] that olefins can assist the solvolysis of arenesulfonates. For example, acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate was 1.7 times faster than that of its saturated analog and gave cyclic products,[5c,6a,7] both observations supporting anchimeric assistance by the olefin. The mechanism of the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate in the presence of urea may be written as shown in Chart I.[7] Urea must be used as the base to neutralize the arenesulfonic acid instead of the usual alkali metal acetate since the added acetate ion enters into an SN2 reaction with the primary *p*-nitrobenzenesulfonate.[7] Solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate may be viewed as two competitive nucleophilic reactions: (a) external nucleophilic attack by the hydroxylic solvent, acetic acid,[8] which leads to acyclic material; and (b) internal nucleophilic attack by the olefin, which leads to cyclic materials.

Chart I



A measure of the ratio of cyclic to open products from the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate offers the possibility of being a sensitive measure of the relative solvent nucleophilicity of a solvent mixture toward attack on alkyl arenesulfonates or halides. The internal olefin should be an excellent standard nucleophile since it is nonpolar and should thus not be highly solvated. Because the olefin is nonpolar, its nature should not change much from solvent to solvent. Moreover, the low solvation of the olefin suggests that the energy needed to bring about the conformational changes in going from the open-chain ground state to the cyclic transition state should be independent of solvent changes. Thus the cyclization reaction should be a good standard nucleophilic reaction. Since the substrate is in both ground states, any change in the ground-state free energies must reflect a change in the solvent nucleophilicity. However, the ratio of cyclic to open products will measure solvent nucleophilicity only if the transition states of both reactions are affected in a similar manner by solvent changes. If this condition exists, solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in a solvent mixture that is more nucleophilic than acetic acid should lead to less cyclic materials and vice versa.

In this study, we have measured the yields of the products of the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate and other 5-hexenyl derivatives in binary solvent mixtures which are composed of 20% acetic acid and 80% nonhydroxylic solvent. The changes in the yields of these products are analyzed and discussed with respect to solvent nucleophilicity.

Results

In Table I are presented the data from the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in media composed of 20% acetic acid and 80% other solvent. In no case were we able to recover greater than 90% of the theoretical yield of products. One possible product, 1,5-hexadiene, was not formed while three unidentified products were observed by gas–liquid partition chromatography (glpc) in less than 2% total yield. Solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in 98% formic acid for 3 hr at 90° led to 95% total recovery of products.[9] Thus, the longer reaction time in acetic acid must lead to side reactions of the reactants or products. Since there was little difference in total recovery when 5-hexenyl *p*-nitrobenzenesulfonate was solvolyzed in acetic acid for 12 (Table II) or 50 hr (Table I), a side reaction of the starting material seems most likely.

In order to determine an approximate half-life for the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in the binary solvent mixtures, we solvolyzed hexyl *p*-nitrobenzenesulfonate in several of these solvents for a period of less than one half-life. The approximate half-lives in hours for the solvolysis of hexyl *p*-nitrobenzenesulfonate in 20% acetic and 80% inert solvent are 2 for acetic acid, 16 for triacetin, 18 for γ-butyrolactone, 13 for methyl benzoate, 10 for ethyl stearate, 13 for phenyl ether, 12 for carbon tetrachloride, 18 for benzonitrile, 15 for nitrobenzene, 40 for triphenyl phosphite, 10 for hexamethylphosphoramide, 14 for tris(tetrahydrofurfuryl) phosphate, 9 for sulfolane, 10 for methyl phenyl sulfone, 15 for 1,4-butanesultone, and 16 for benzene.

In Table II are presented the results of solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in binary solvent mixtures for 12 hr, which was usually a period of approximately one half-life or less. Comparison of the cyclohexene to cyclohexyl acetate ratios at 12 and 50 hr shows that no significant interconversion of these products take place over a 50-hr period.

In Table III the yields of cyclic products from the solvolysis of various 5-hexenyl sulfonates in several sol-

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[7] W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, 32, 150 (1967).

[8] A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, 79, 6233 (1957).

[9] Unpublished results of W. S. Trahanovsky and M. P. Doyle.

Table I. Solvolysis of 5-Hexenyl *p*-Nitrobenzenesulfonate at 100° in Acetic Acid–Solvent (20:80) Mixtures[a]

				Anal.,[b] %					
Solvt no.	Solvent[c] (no. of runs)	Reaction time, hr	% recovery[d]	1-Methylcyclopentene	A, cyclohexene	B, cyclohexyl acetate	5-Hexyl acetate	% cyclic / % open product	A/B
1	Acetic acid (4)	50	90	0.9	13.2	31.1	54.8	0.83	0.42
				Esters					
2	Triacetin (2)	50	78	0.9	14.0	19.1	66.0	0.51	0.73
3	γ-Butyrolactone (2)	50	47	0.6	15.0	18.6	65.6	0.52	0.81
4	Methyl benzoate (2)	50	83	0.8	18.6	9.4	71.2	0.40	1.98
5	Ethyl stearate (2)[e]	40	78	0.4	8.0	8.8	82.8	0.21	0.91
				Ethers					
6	Ethyl ether (2)	48	77	0.1	8.4	0.9	90.6	0.10	9.3
7	Benzyl ether (2)	50	74	0.4	16.2	8.6	74.8	0.34	1.88
8	*p*-Methylanisole (2)[f]	50	78	0.6	16.0	5.6	77.8	0.29	2.86
9	Phenyl ether (2)	50	81	1.0	16.5	14.2	68.3	0.46	1.16
10	Phenyl sulfide (2)	50	68	0.9	19.8	12.3	67.0	0.49	1.61
11	Tetrahydrofuran (2)	50	34	1.2	7.5	4.4	86.9	0.15	1.70
				Halides					
12	Carbon tetrachloride (3)	50	89	0.4	7.4	7.8	84.4	0.18	0.95
13	Chloroform (2)	50	74	0.6	24.8	13.0	61.6	0.62	1.90
14	1,1,2,2-Tetrachloroethane (2)	50	83	1.1	38.8	12.4	47.7	1.10	3.13
15	*o*-Dichlorobenzene (2)	50	89	0.9	17.0	13.4	68.7	0.46	1.27
16	Trichloroethylene (2)	50	60	0.5	9.6	9.8	80.1	0.25	0.98
				Ketones					
17	Acetophenone (2)	50	71	0.9	11.9	11.0	76.2	0.31	1.08
18	Benzil (2)[g]	50	30	0.6	13.8	72.3	13.3	6.51	0.19
				Nitriles					
19	Acetonitrile (2)	50	42	1.0	31.7	13.3	54.0	0.85	2.38
20	Benzonitrile (2)	50	56	2.0	25.5	15.0	57.5	0.74	1.70
				Nitro compounds					
21	Nitromethane (2)	50	59	0.7	59.7	19.7	19.7	4.02	3.03
22	Nitrobenzene (2)	50	86	2.2	39.6	18.7	39.5	1.53	2.12
				Phosphorus compounds					
23	Triphenyl phosphite (4)	50	41	4.2	74.4	5.9	15.5	5.46	12.6
24	Hexamethylphosphoramide (2)	53	69	0	0	36.4	63.6	0.57	0
25	Trimethyl phosphate (2)[h]	50	27	0	0	11	89	0.12	0
26	Triphenyl phosphate (2)	50	68	0.8	19.2	13.5	66.5	0.50	1.42
27	Tris(tetrahydrofurfuryl) phosphate (1)	50	57	0.1	9.9	6.3	83.7	0.19	1.57
				Sulfur compounds					
28	Sulfolane (2)	40	66	1.6	48.8	12.6	37.0	1.70	3.87
29	Butyl sulfone (2)[i,j]	53	81	0.6	20.9	11.8	66.7	0.49	1.77
30	Methyl phenyl sulfone (2)[i]	50	74	2.4	38.6	18.8	40.2	1.49	2.05
31	Vinyl sulfone (2)	53	80	1.2	44.2	16.4	38.2	1.62	2.70
32	1,4-Butanesultone (3)	50	60	1.5	39.9	38.5	20.1	3.97	1.04
33	Dimethyl sulfoxide (2)[k]	50	45	0	0	0	100	0	...
				Miscellaneous solvents					
34	Benzene (4)	50	84	0.2	15.4	8.9	75.5	0.32	1.73
35	Furan (2)	50	77	0.5	11.6	11.8	76.1	0.31	0.98
36	N,N-Dimethylformamide (2)	50	51	0	0	25.1	74.9	0.33	0
37	Tripentyl borate (2)[l]	50	45	0.4	10.8	10.8	78.0	0.28	1.00
38	Pyridine N-oxide (1)	12	39	*m*	7.3	0	92.7	0.08	...

[a] [RONs] = 0.1 *M*, [urea] = 0.2 *M*. [b] Relative yield of products. The accuracy of analysis is subject to the analytical method used and is estimated to be within 3% of the reported value of each product. From duplicate runs the precision of analysis was calculated to be well within the accuracy limits. [c] Acetone, 2,4-pentanedione, methyl methanesulfonate, and tetramethyl orthosilicate were also used, but because of interfering side reactions total analysis was not possible. [d] Per cent recovery was based on glpc analysis of the expected solvolysis products. [e] An approximately 0.002 *M* solution of ethyl acetate was produced. [f] Due to the difficulty of separation of solvent from the acetate products, anisole itself could not be used. In anisole the absolute yield of cyclohexene averaged from two runs was 12.8% and that of 1-methylcyclopentene was 0.2%. Assuming a recovery of 78% the relative yields of these two products are 16.4 and 0.3%, respectively, which compares very favorably with the reported values of *p*-methylanisole. [g] A 72.5% solution of benzil. [h] An approximately 0.06 *M* solution of methyl acetate was formed. Nmr spectrum of the solvolysis products after extraction shows no proton resonance attributable to cyclohexene. [i] Density of the solvent assumed to be 1.00. [j] An approximately 0.001 *M* solution of butyl acetate was produced. [k] 5-Hexenal was formed in approximately 15% yield. 5-Hexen-1-ol was found in about 10% yield and approximately 20% of a product believed to be 5-hexenyl methyl sulfide was found. Dimethyl sulfide and methyl acetate were also produced. [l] Less than a 0.002 *M* solution of pentyl acetate was formed. [m] Not analyzed.

Table II. Solvolysis of 5-Hexenyl *p*-Nitrobenzenesulfonate at 100° for 12 hr in Acetic Acid–Solvent (20:80) Mixtures[a]

			Anal.,[b] %					
Solvt no.	Solvent (no. of runs)	% Recovery[c]	1-Methyl-cyclopentane	A, Cyclohexene	B, Cyclohexyl acetate	5-Hexenyl acetate	% cyclic[d] / % open product	A/B[d]
1	Acetic acid (3)	82	1.1	13.8	30.8	54.3	0.84	0.45
3	γ-Butyrolactone (3)	32	1.0	16.6	23.6	58.8	0.70	0.70
5	Ethyl stearate (3)	56	0.6	9.1	13.8	76.5	0.31	0.66
9	Phenyl ether (3)	50	1.4	21.0	19.1	58.5	0.71	1.10
20	Benzonitrile (2)	38	1.8	26.6	19.3	52.3	0.91	1.38
22	Nitrobenzene (3)	57	2.4	44.8	19.3	33.5	1.98	2.32
28	Sulfolane (3)	65	2.8	52.0	14.4	30.8	2.24	3.61

[a] See footnote *a*, Table I. [b] Precision of the analysis is within 5% of the reported value of each product. [c] See footnote *d*, Table I. [d] Since the ratios are calculated from the relative yields in an incomplete reaction, any inherent errors in the yields are compounded in these values.

Table III. Yield of Cyclic Products from the Solvolysis of Various 5-Hexenyl Sulfonates at 100° in Acetic Acid and Acetic Acid–Solvent (20:80) Mixtures[a]

	HOAc		HOAc–PhNO$_2$ (20:80)		HOAc–PhH (20:80)	
Leaving group	Cyclic products, %[b]	Reaction time, hr	Cyclic products, %[b]	Reaction time, hr	Cyclic products, %[b]	Reaction time, hr
p-Nitrobenzenesulfonate	45.2	50	60.5	50	24.5	50
	45.7	12	66.5	12	...	...
p-Bromobenzenesulfonate	42.3	36	52.2	72	...	...
p-Toluenesulfonate	33.8	72	32.1	200	...	...
p-Methoxybenzenesulfonate	32.7	72	28.5	200	...	...
Methanesulfonate	30.4	48	33.0	120	13.3	120

[a] These data are obtained from M. P. Doyle and W. S. Trahanovsky, manuscript in preparation. [ROX] = 0.1 *M*, [urea] = 0.2 *M*. [b] Relative yields, not absolute; total recovery was always greater than 80%. See footnotes *b* and *d*, Table I.

Table IV. Solvolysis of 5-Hexenyl *p*-Nitrobenzenesulfonate at 100° in Acetic Acid–Substituted Nitrobenzene (20:80) Mixtures[a]

			Anal.,[b] %					
Solvent[c] (no. of runs)	Reaction time, hr	% recovery[d]	1-Methyl-cyclopentene	A, cyclohexene	B, cyclohexyl acetate	5-Hexenyl acetate	% cyclic / % open product	A/B
Nitrobenzene (2)	50	86	2.2	39.6	18.7	39.5	1.53	2.12
o-Nitrotoluene (2)	50	83	1.5	34.0	15.4	49.1	1.04	2.20
2-Nitro-*m*-xylene (2)	40	87	1.3	30.0	20.4	48.3	1.07	1.47
p-Nitrotoluene (3)	50	87	1.6	38.7	14.1	45.6	1.19	2.74
2,4-Dinitrotoluene (2)	50	78	1.8	34.5	20.5	43.2	1.31	1.68
2,6-Dinitrotoluene (2)	50	80	1.8	29.8	19.7	48.7	1.05	1.51
m-Dinitrobenzene (5)	50	63	2.1	50.1	21.7	26.1	2.83	2.30
1-Chloro-2-nitrobenzene (4)	50	84	1.5	34.4	19.2	44.9	1.23	1.79
1-Chloro-4-nitrobenzene (4)	50	80	1.7	30.6	16.9	50.8	0.97	1.81
o-Nitroanisole (2)[e]	50	77	1.8	44.2	18.0	36.0	1.78	2.46
m-Nitroanisole (3)[f]	50	82	1.1	35.7	14.3	48.9	1.04	2.50
p-Nitroanisole (3)[g]	50	78	1.6	34.3	16.5	47.6	1.10	2.08
2,4-Dinitroanisole (2)[h]	70	80	2.0	38.6	24.8	34.6	1.89	1.56

[a] See footnote *a*, Table I. [b] Relative yield of products. Precision of analysis was generally ±5% of the reported value for solvents which were solids. For liquid solvents see footnote *b*, Table I. [c] Except for nitrobenzene, *o*-nitrotoluene, 2-nitro-*m*-xylene, and *o*-nitroanisole, all the solvents listed in the table were solids at room temperature. [d] See footnote *d*, Table I. [e] No methyl acetate was detected. [f] An approximately 0.05 *M* solution of methyl acetate was produced. [g] Both a 0.02 and a 0.06 *M* solution of methyl acetate were formed in two separate runs. [h] An approximately 0.02 *M* solution of methyl acetate was produced.

vent mixtures are presented. From these results, it is clear that the leaving group does affect the relative amount of cyclization.

In Table IV are presented the results of solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate in solvent mixtures composed of acetic acid–substituted nitrobenzene (20:80).

Discussion

Because of the low total yields of the four main products (see Table I) and the detection of other unknown products in several cases,[1a,9] we conclude that the solvents γ-butyrolactone, tetrahydrofuran, trichloroethylene, benzil, acetonitrile, benzonitrile, all phosphorus compounds, sulfolane, 1,4-butanesultone, dimethyl sulfoxide, dimethylformamide, tripentyl borate, and pyridine N-oxide are not inert. These solvents interfere with the solvolysis reaction either by competing with acetic acid as a nucleophile, forming derivative products, or by destruction of the products formed.

In Table V the yields of cyclic products in solvent mixtures that give high total recovery of products (>70%)

Table V. Yield[a] of Cyclic Products from the Solvolysis of 5-Hexenyl *p*-Nitrobenzenesulfonate at 100° in Binary Solvent Mixtures Composed of Acetic Acid–Nonhydroxylic Solvent (20:80)[b]

Nonhydroxylic solvents	% cyclic products	Nonhydroxylic solvents	% cyclic products
Ethyl ether	9.4	Phenyl sulfide	33.0
Carbon tetrachloride	15.6	Butyl sulfone	33.3
Ethyl stearate	17.2	Triacetin	34.0
p-Methylanisole	22.2	Chloroform	38.4
Acetophenone	23.8	Acetic acid[c]	45.2
Furan	23.9	1,1,2,2-Tetrachloroethane	52.3
Benzene	24.5		
Benzyl ether	25.2	Methyl phenyl sulfone	59.8
Methyl benzoate	28.8	Nitrobenzene	60.5
o-Dichlorobenzene	31.3	Vinyl sulfone	61.8
Phenyl ether	31.7		

[a] Yields are relative with total recovery being >70%. [b] Reaction time was usually 50 hr. [c] Pure acetic acid.

are given. Since per cent cyclic products/per cent open products is a measure of $k_{\text{assisted}}/k_{\text{unassisted}}$[5c,7] it is seen that $k_{\text{assisted}}/k_{\text{unassisted}}$ varies from 0.104 for ethyl ether to 1.62 for vinyl sulfone. Although a factor of 16 is not a large number, it is significant since it is responsible for changing a reaction from one that leads to largely acyclic materials to one that leads to largely cyclic materials. It can be seen that of the solvents listed in Table V, 1,1,2,2-tetrachloroethane, nitrobenzene, methyl phenyl sulfone, and vinyl sulfone lead to the most cyclization. Compared to acetic acid, nonpolar solvents such as ethyl ether, carbon tetrachloride, ethyl stearate, acetophenone, and benzene substantially increase the amount of 5-hexenyl acetate. *A priori* one might expect that decreasing the concentration of acetic acid by the addition of a nonpolar diluent should decrease the amount of direct displacement instead of increasing it.[10] In fact, inspection of Table V shows that the solvents that lead to the most cyclization are those that are somewhat polar or possess hydrogens that can hydrogen bond. An attractive explanation for this correlation is that these solvents can solvate acetic acid. Solvation of the acetic acid should increase the stability of the ground state that leads to direct displacement (open product). Indeed Arnett has shown that the rate of solvolysis of *t*-butyl chloride in aqueous ethanol mixtures is determined by changes in the stability of the ground state and not of the transition state.[11] However, solvent changes in our system may also alter the relative rates of the two reactions by affecting the transition-state stabilities. As seen in Table III one gets slightly different amounts of cyclic products with different leaving groups. In acetic acid one gets 45% cyclization with the *p*-nitrobenzenesulfonate and only 30% with the methanesulfonate. Moreover, in going from acetic acid to acetic acid–nitrobenzene (20:80), the amount of cyclization increases by a factor of 1.5 for the *p*-nitrobenzenesulfonate but remains almost constant for the methanesulfonate. These differences must be a result of the effect of the leaving group on the relative stabilities of the transition state that leads to open product and the transition state that leads to closed products since the effect of the leaving group on both ground states must be the same. Thus alteration of the solvent may affect the stabilities of these two transition states differently in two ways. First it may alter the stability of these transition states by direct solvation and second it may change the nature of the leaving group (possibly by a strong leaving group–solvent complex) which in turn may change the energies of the transition states.

Kosower's *Z* values[12] were measured in several of the solvent mixtures in order to determine the effect of "solvent polarity" on the amount of cyclization. However, it was found that the *Z* value for all the mixtures was the same as that for acetic acid.

In conclusion, the cyclic to open products ratio seems to depend on two factors: (a) ground-state changes and (b) transition-state changes. The ground-state changes must be independent of the reaction since both ground states contain the substrate. The correlation of per cent cyclic products with the ability of the added solvent to solvate acetic acid implies that solvation of acetic acid is the prime ground-state change and ground-state changes are more important than transition-state changes. However, the effect of changing the leaving group shows that transition state changes may be as large as ground-state changes. Since the transition state changes are so important, the yield of cyclic to open products from the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate may or may not measure solvent nucleophilicity. It is impossible at present to tell how important the transition-state changes brought about by changing the solvent are.

In Table IV are presented the data for solvent mixtures composed of acetic acid–substituted nitrobenzenes (20:80). It is seen that the relative yields of cyclic products only vary from 50 to 74%, and most of the mixtures result in *ca.* 55% cyclization. Thus the addition of one nitro group to benzene seems to have a large effect, but additional substituents have a small effect. We concluded from this study that nitrobenzene itself is the optimum solvent to use for solvent mixtures of low nucleophilicity. The dinitrobenzene–solvent mixtures that lead to more cyclization are difficult to work with since the dinitrobenzenes are solids at room temperature. Although the *o*-nitroanisole mixture is slightly superior to the nitrobenzene mixture, use of the nitrobenzene mixture is advocated since the increase in cyclization in the *o*-nitroanisole mixture is not that great, nitrobenzene is a more common material that has been used extensively as a solvent, and the methoxy group of the anisole could act as a nucleophile in certain cases.

Solvent mixtures which seem to be less nucleophilic than acetic acid as indicated by the products from the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate may find some use in solvolytic studies since they might permit the study of nucleophilic reactions of nucleophiles that are weaker than acetic acid. These solvent mixtures may also find some use in synthetic organic chemistry in cases where the synthetically useful reaction involves anchimeric assistance.

In future papers, the effects of variation of the leaving groups, the per cent composition of the solvent mixtures,

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(10) More appropriate diluents, such as the hydrocarbons heptane and cyclohexane, were only slightly miscible with acetic acid and for this reason could not be used.

(11) (a) E. M. Arnett, W. G. Bentrude, J. G. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965); (b) E. M. Arnett and D. R. McKelvey, *ibid.*, **87**, 1393 (1965); (c) E. M. Arnett and D. R. McKelvey, *ibid.*, **88**, 5031 (1966).

(12) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

and the hydroxylic component of the mixtures on the products of the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate will be reported.

Experimental Section

Materials and Methods. Equipment has been previously described.[13] Use was made of 6-ft columns of 20% Carbowax 20M on Chromosorb P. Melting points are corrected and boiling points are uncorrected.

Solvents and reagents were usually commercial materials which were purified by distillation or recrystallization if necessary. *p*-Methylanisole was prepared from the corresponding phenol and dimethyl sulfate.[14] Ethyl stearate was prepared from stearic acid and ethanol.[15] Acetates were prepared by standard methods.

Product Studies. To weighed quantities of the *p*-nitrobenzenesulfonate and urea was added 1.00 ml of acetic acid and 4.00 ml of inert solvent, if it was a liquid at room temperature. When necessary the mixture was warmed slightly to help make it homogeneous and transferred to a constricted tube which was then sealed at atmospheric pressure. After the mixture was heated for a definite period of time, the mixture was cooled and the tube was opened. A measured amount (*ca.* 17 mg) of an internal standard (pentyl acetate),[16] ether, and saturated sodium chloride solution were added, and the ether layer was separated after shaking and washed with saturated sodium chloride solution and saturated sodium bicarbonate solution. The volume of ether was kept small so that no concentration step was necessary prior to glpc analysis. The ethereal solution was dried over anhydrous magnesium sulfate and then passed through a cotton filter into a sample vial. Prior to glpc analysis approximately 0.2 g of anhydrous magnesium sulfate was added to the sample vial to ensure dryness.[17]

If the inert solvent was a solid at room temperature, a weighed quantity equivalent to 4.0 ml of the solid was placed in the constricted tube and the acetic acid solution of the substrate and base was added to the tube. The mixture was treated as above except that after the standard was added, the solid solution plus the tube was placed in a flask fitted with a reflux condenser. Ether was added, and the mixture was heated to reflux for at least 1 hr. After cooling, the ether solution was decanted into a separatory funnel, and the residue was washed four times with ether. The ether solutions were combined and treated as described above.

The yields of the products were determined by glpc. The areas of the product peaks were compared to the area of the standard peak, and the absolute yields of the products based on the average of at least three glpc traces were determined by use of experimentally determined relative thermal conductivity and extraction ratios. Average values for three determinations of the relative thermal conductivity and extraction ratios to pentyl acetate were found to be 0.690 for cyclohexene, 1.400 for hexyl acetate, 1.155 for 5-hexenyl acetate, and 0.894 for cyclohexyl acetate. It was found that these ratios were very close to experimentally determined relative thermal conductivities and thus the relative extraction ratios are *ca.* 1.0. It was also found that these ratios were the same within 2% for extraction from acetic acid, nitrobenzene, and sulfolane. Since these three solvents are very different, it was assumed that these ratios did not vary from mixture to mixture.

Measurement of *Z* values was patterned after the method of Kosower.[12]

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[13] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, 32, 146 (1967).

[14] G. S. Hiers and F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 58.

[15] S. Natelson and S. Gottfried, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 381.

[16] The internal standard was hexyl acetate when tri-*n*-amyl borate was used as the inert solvent.

[17] Without inclusion of this last step, quantitative glpc analysis was almost impossible in some solvent mixtures.

Chain Termination *via* Cumylperoxy Radicals

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Abstract: It is pointed out that the yield of acetophenone per reaction chain initiated in the autoxidation of cumene, or in the chain decomposition of cumene hydroperoxide, can exceed the value of 0.5 which is required by a reaction scheme recently proposed by Traylor and Russell.[1] In the initiated chain decomposition of cumene hydroperoxide at 57°, it is found that the chain length reaches a constant value at considerably lower cumene hydroperoxide concentrations than that required for suppression of acetophenone formation. This behavior can be rationalized if the chain-terminating reactions of methylperoxy radicals are sufficiently slow that under many conditions methylperoxy radicals effectively continue chain propagation.

Recently Traylor and Russell[1] presented convincing arguments that an important chain-terminating reaction in the autoxidation of cumene involved production of methyl radicals by β scission of cumyloxy radicals with subsequent fast termination by reaction of methylperoxy with cumylperoxy radicals. In reducing their ideas to quantitative terms, these authors relied heavily upon the work of Blanchard,[2] who first determined the yield of acetophenone in the oxidation of cumene and thus demonstrated the potential importance of β scission of cumyloxy radicals in the oxidation reaction. The mechanism of Traylor and Russell calls for a maximum yield of one acetophenone per chain-terminating reaction (destruction of two chain-carrying radicals), and they cited Blanchard's results in confirmation of their ideas. Unfortunately, an error of a factor of two was made in transcribing Blanchard's data, which were reported in two sets of units. Under the conditions of his experiments, Blanchard found an

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[1] T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, 87, 3698 (1965).

[2] H. S. Blanchard, *ibid.*, 81, 4548 (1959).