overlapping triplets, 4 H). The integration of the *t*-butyl group is low and is probably a result of the partial decomposition of the product. The presence of the sharp singlet does indicate a *t*-butyl group and the rest of the spectrum is similar to that of 5-bromopentanol.

Gas Phase Pyrolysis of *t*-Butylperoxy 6-Bromohexanoate (2).—Quantities of 0.4 g of per ester were decomposed in the gas phase at 300 and 250°. The flow rate of nitrogen through the column was 100 ml/min which led to a residence time of 10 sec at the high temperature. Nmr spectra of the products showed the major components to be 1-bromopentane and acetone. A significant amount of tars was formed. Analysis of the products by glpc showed no cyclopentane. To ensure that the column temperature was not high enough to remove a bromine from 2, 1-bromopentane was subjected to the same pyrolysis conditions. Greater than 95% of the 1-bromopentane was recovered.

Kinetic Studies.—The rates of decomposition of per esters 2 and 3 were followed by the infrared method of Bartlett and Hiatt.[8] Aliquots of stock solutions of per ester in cyclohexane were placed in constricted test tubes, sealed without degassing, heated for measured intervals, quenched by cooling, and stored at 0° until measurement. The rate was followed by observing the decrease in transmittance of the carbonyl band. Constants were calculated as described by Bartlett and Hiatt.[8]

Acknowledgment.—We thank Dr. Roy W. King and Dr. T. H. Kinstle for assistance in obtaining some of the nmr and mass spectra and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Nucleophilic Reactivity of the Carbon–Carbon Double Bond. VI. The Use of Urea as a Base in Acetolysis Reactions

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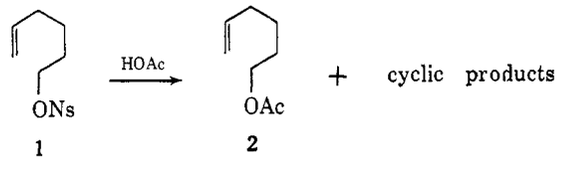
In the study of acetolysis reactions where it is necessary to neutralize the strong acid liberated, urea possesses certain advantages over sodium acetate as a base to be added to the solution. It is (a) too weakly nucleophilic to superpose a displacement reaction on the solvolysis, (b) not basic enough to give rise to acetate ions, yet (c) basic enough to neutralize sulfonic acids. Being an uncharged base urea produces no initial salt effect upon solvolytic reactions. On the other hand, the product solution containing the conjugate acid of urea is somewhat more acidic than pure acetic acid, and there is a class of sensitive substrates which it does not adequately protect against acid-catalyzed reactions.

When an alkyl arenesulfonate is solvolyzed in a nonbasic solvent, a strong arenesulfonic acid is produced. In many cases, the products and reactants are not stable to such a strong acid and are rearranged or transformed to tars by cationic polymerization. By addition of a sufficiently strong base to the reaction solution, the sulfonic acid produced is converted to an inert sulfonate salt, and thus the products and reactants are protected from the strong acid. The most commonly used base in acetolysis has been sodium or potassium acetate.[2] However, these acetates, good nucleophiles, can affect the product composition through direct displacement and can affect the rate both by this mechanism and by a kinetic salt effect. Because product studies are often run at relatively high solute concentrations, the correlation of product information with rate information is impaired.

An example is found in the study of double-bond participation in the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate[3] (1). The acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate is 1.6 times as fast as that of



1 2

n-hexyl *p*-nitrobenzenesulfonate. This means that, if the relative rate constant for the unassisted solvolysis is 1.0, then that for the assisted reaction is 0.6. Thus, if the cyclohexyl cation is obtained from the assisted reaction, then one should obtain (0.6) (100)/(1.6) = 37% cyclic products, since the solvolysis of cyclohexyl arenesulfonates gives no acyclic products. Correction for the inductive effect of the double bond raises this estimate.[3,4] However, with sodium acetate as the base, only 18% cyclic products are obtained. This could mean that the k for the unassisted reaction is not equal to that of the saturated analog, that there are different salt effects on the unassisted and assisted reaction, that the assisted reaction does not lead to a true cyclohexyl cation and therefore does not give cyclic products exclusively, or that a considerable amount of direct displacement by the acetate ion gives more open acetate. Calculations based upon this last interpretation[3] have afforded reasonable agreement between the expectations based upon rates and the product compositions observed. As a further check on this interpretation and in search of improved practice for future solvolysis studies, it appeared desirable to use a nonnucleophilic base so that no S_N2 reaction between the substrate and base would occur. We have sought a poorly nucleophilic base which would be weak enough not to be protonated by acetic acid, but strong enough to be protonated by the sulfonic acid. This type of base would not displace the arenesulfonate itself, it would not give rise to an equivalent of acetate ions, yet it would preserve the products from attack by the sulfonic acid. Urea appeared as a promising candidate.

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(2) See, as an early example, S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1153 (1952), and many other cases included in Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(3) (a) E. M. Nicholson, Ph.D. Thesis, Harvard University, 1965; (b) P. D. Bartlett, E. M. Nicholson, and R. Owyang, *Tetrahedron*, in press.

(4) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965).

TABLE I
VAPOR PHASE CHROMATOGRAPHIC ANALYSIS

Sample	Carbowax 20 M[a]	Ucon 50 HB 2000[b]	Diisododecyl phthalate[c] A	Diisododecyl phthalate[c] B	β,β'-Oxydipropionitrile[d]	Glyceryl tripropionate[e]
1,5-Hexadiene	2.80					
Unknown hydrocarbon	3.20					
Methylenecyclopentane	4.25	7.4	2.9		6.20	5.40
1-Methylcyclopentene	4.25	7.4	2.9		5.60	5.10
Cyclohexene	5.60	9.2	3.6	2.55	8.0	6.45
Unknown acetate I	15.8					
1-Methylcyclopentyl acetate	16.2					
Unknown acetate II	16.8					
5-Hexenyl acetate	17.5			11.1		
Cyclohexyl acetate	18.1			13.6		
Cyclopentylcarbinyl acetate	18.1			14.4		
5-Hexen-1-ol	18.3					
n-Amyl acetate (standard)	14.3			5.60		

[a] Five-foot 20% Carbowax 20 M (60–80 mesh) on Chromosorb P operated at 60° for 7 min, then programmed at 10°/min; injection temperature 180°, detector temperature 310°, flow 47%, 60-psi pressure. [b] Five-foot 20% Ucon 50 HB 2000 (60–80 mesh) on Chromosorb P operated at 65°; injection temperature 180°, detector temperature 310°, flow 47%. [c] Six-foot 20% diisodecyl phthalate (60/80 mesh) on Chromosorb P: (A) operated at 78°, injection temperature 180°, detector temperature 310°, flow 47%; (B) operated at 150°, injection temperature 200°, detector temperature 260°, flow 42%. [d] β,β'-Oxydipropionitrile (20%, 60–80 mesh) on Chromosorb P operated at 41°; injection temperature 177°, detector temperature 260°, flow 54%. [e] Glyceryl tripropionate (20%, 60–80 mesh) on Chromosorb P operated at 92°; injection temperature 110°, detector temperature 245°, flow 45%.

TABLE II
PRODUCTS OF ACETOLYSIS OF 5-HEXENYL *p*-NITROBENZENESULFONATE
(100°, 12 hr)

NaOAc, *M*	Urea, *M*				 [a]	Unknown hydrocarbon	Unknown acetate I	Unknown acetate II
	0.210	46.1	26.0	11.2	0.92	0.79	0.33	0.57
	0.236	42.7	24.4	11.4	0.89	0.76	0.31	0.55
0.252		69.4	13.2	5.4	0.72	0.26	0.32	0.28
0.296		72.0	10.5	4.4	0.38	0.36	0.26	0.37

[a] Not resolved from  .

Experimental Section

Materials, equipment, and kinetic measurements have been previously described.[4] The preparation of 5-hexenyl and cyclohexyl *p*-nitrobenzenesulfonates were previously reported.[4] The salts, bases, *p*-toluenesulfonic acid, cyclohexene, and 1-methylcyclohexene were reagent-grade materials used without further purification. 1-Methylcyclohexyl acetate was prepared by the acetylation of the corresponding alcohol.[3a]

Product Studies.—The product studies of the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate were carried out by adding 5 ml of acetic acid, with or without sodium acetate, to weighed amounts of 5-hexenyl *p*-nitrobenzenesulfonate, base, and/or salt. The mixture was heated to help dissolve the solids and transferred to a constricted test tube which was then sealed. After the solution had been held at a given temperature for a period of time usually greater than 10 half-lives (12 hr at 100° unless stated otherwise), the tube was cooled and opened. A quantity of amyl acetate (*ca.* 20 mg) was weighed into the tube. Then 10 ml of water was added to the acetic acid solution, and it was extracted with 5 ml of pentane. The pentane solution was washed with saturated sodium bicarbonate and water, dried over magnesium sulfate, and filtered. The composition of the pentane solution was determined by gas phase chromatography using experimentally determined thermal conductivities of the products relative to amyl acetate. The amount of amyl acetate added being known, the absolute yield of each product was calculated. The total yield of recovered products was always 70–90%. Table I lists the retention times of each product on one or more of five columns.

Results

The products of the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate in the presence of various bases and salts are presented in Table II, and in Table III are shown the products of acetolysis of cyclohexyl *p*-nitrobenzenesulfonate under the same conditions except that the time required for essentially complete solvolysis is less for this more reactive substrate. As in the previous work[3] the relative amounts of cyclohexene and cyclohexyl acetate are very different from the two starting materials, but they do not depend upon whether urea or sodium acetate is used as the base. On the other hand, the fraction of cyclic material from 5-hexenyl *p*-nitrobenzenesulfonate is about twice as great with the use of urea as it is with the use of sodium acetate. This is consistent with the view that competing displacement is important with sodium acetate and unimportant with urea. Especially striking in

TABLE III
PRODUCTS OF ACETOLYSIS OF
CYCLOHEXYL *p*-NITROBENZENESULFONATE
(100°, 2 hr)

Starting material, *M*	NaOAc, *M*	Urea, *M*	Products,[a] % 		
0.1016	0.220		0	18.6	70.0
0.1026	0.220		0	20.4	69.3
0.1036		0.228	0	18.9	68.4
0.0982		0.222	0	19.4	70.0

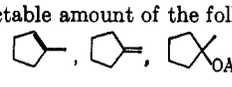
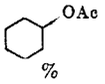
[a] No detectable amount of the following were found. 

Table II is the presence of about 1% of a five-membered ring product not detected in previous work which is methylcyclopentene, the transformation product of methylenecyclopentane. This peak in the chromatogram was carefully looked for in the product from cyclohexyl *p*-nitrobenzenesulfonate and was shown to be absent. In Table IV is the per cent of cyclohexene

TABLE IV

THE CONVERSION OF CYCLOHEXENE TO CYCLOHEXYL ACETATE IN ACETIC ACID SOLUTIONS CONTAINING *p*-TOLUENESULFONIC ACID AND UREA OR ACETAMIDE AT 100°

Base	Acid	Time, hr	Cyclohexene, %	 %
0.2 *M* urea	0.1 *M* TsOH·H_2O	89	93.3	6.9
0.15 *M* acetamide	0.1 *M* TsOH·H_2O	1	90.5	9.5
0.15 *M* acetamide	0.1 *M* TsOH·H_2O	10.5	56.9	43.1
0.15 *M* acetamide	0.1 *M* TsOH·H_2O	17	52.1	47.9

and cyclohexyl acetate in acetic acid solutions containing *p*-toluenesulfonic acid and a base after being held at 100° for certain periods of time. In Table V are similar data for 1-methylcyclohexene and 1-methylcyclohexyl acetate. Table VI reports a series of product runs in which only the three main products, cyclohexene, cyclohexyl acetate, and 5-hexenyl acetate, were determined. The ratios of cyclized to uncyclized product seen here are an index of the amount of competing displacement reaction.

Discussion

Initially in our search for a poorly nucleophilic base that is weak enough not to be protonated by acetic acid but strong enough to be protonated by an arenesulfonic acid, we made use of some acid–base equilibrium constants in acetic acid obtained by Kolthoff and Bruckenstein.[5] From these data, a base having a pK_a of *ca.* 0.5 in water seemed likely to meet these requirements. From the product studies of the acetolysis of 0.1 *M* 5-hexenyl *p*-nitrobenzenesulfonate at 100° shown in Table II, it is seen that the percents of cyclohexyl products are the predicted 36–38% using urea as the base, but only 15–19% using sodium acetate. That urea meets the first requirement of being nonnucleophilic is clearly supported by the high yield of normal acetolysis products. The second requirement of not giving rise to an equivalent of acetate ions is shown to be met by the substantial difference in product compositions between solutions containing equivalent amounts of sodium acetate and of urea and the greater amounts of apparent displacement product in the former case. That these differences are not salt effects has been shown in a number of related cases. Sodium or lithium perchlorate increases the cyclization product through its effect upon direct ionization and decreases the proportion of displacement products.[3] The stronger base, 2,6-lutidine, substituted for sodium acetate, did not decrease the amount of direct displacement product. All these results indicate that the discrepancy between products and rates when sodium acetate is used as the base is due largely to a concurrent SN2 reaction by acetate ion.

(5) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

The possible role of a base in stabilizing products against secondary transformations is thrown into perspective by Tables IV and V in which bases are compared with respect to the slow conversion of cyclohexene to cyclohexyl acetate and the much more rapid conversion of 1-methylcyclohexyl acetate into 1-methylcyclohexene. An acetic acid solution containing urea and *p*-toluenesulfonic acid converts cyclohexene into cyclohexyl acetate only very slowly. A similar mixture containing the slightly weaker base acetamide in place of urea is much more acidic. However, since urea is a weaker base than acetate, its conjugate acid should be a stronger acid than acetic acid. From Table V where the acid-catalyzed conversion of 1-methylcyclohexyl acetate to 1-methylcyclohexene was used as a measure of the relative acidities of the various solutions, it is seen that the reaction is *ca.* 250 times as fast when urea is used as the base instead of sodium acetate. The equilibrium mixture contains less than 5% 1-methylcyclohexyl acetate as shown by the acetamide run and the longer runs with other bases. Thus the use of urea as a base for studying acetolysis products must be attended by a determination of the stabilities of the various products toward the solvolyzing medium. Cyclohexene is stable to the medium for moderate lengths of time. 1-Methylcyclohexyl acetate is not. Methylenecyclopentane is subject to secondary transformations even in the presence of sodium acetate.

In addition to fulfilling the requirements discussed above, urea has the advantage of being an uncharged base and therefore gives rise to no initial salt effects on rates or product ratios. The salt which forms as the acetolysis proceeds can be kept at low concentrations by the choice of conditions. The nonhygroscopic crystalline character of urea makes it technically easy to handle in systematic series of product studies.

In several instances[3,6] the ratio of cyclic to acyclic products in double-bond-assisted solvolysis has been found to correspond to that predicted from the known rate measurements when direct displacement by acetate ion has been corrected for. The use of urea brings about a closer correspondence between the observed product ratios and those predicted from kinetic measurements without the necessity of the correction for direct displacement.

In the course of this study, several other bases were tried but all fell short of being an ideal additive for acetolysis reactions. As mentioned before, 2,6-lutidine is such a strong base that it merely gives rise to an equivalent of acetate ions. On the other hand, acetamide is such a weak base that the sulfonic acid produced is still effective enough to convert cyclohexene into cyclohexyl acetate at a reasonably high rate. In fact, acetic acid containing 0.15 *M* acetamide and 0.10 *M* *p*-toluenesulfonic acid is a slightly acidic medium useful for adding acetic acid to olefins. This mixture is certainly less acidic than the traditional Bertram–Walbaum conditions of sulfuric acid in acetic acid.[7] *p*-Nitroaniline was found to be an awkward base to use, since it gave rise to a voluminous precipitate of *p*-nitroanilinium *p*-nitrobenzenesulfonate. Sodium dihy-

(6) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965).

(7) J. Bertram and H. Walbaum, *J. Prakt. Chem.* (2), **49**, 1 (1894).

TABLE V

THE CONVERSION OF 1-METHYLCYCLOHEXYL ACETATE INTO 1-METHYLCYCLOHEXENE IN ACETIC ACID SOLUTIONS CONTAINING VARIOUS ADDENDS AT 100°

Base	Acid	Time, hr	1-Methylcyclohexene, %	1-Methylcyclohexyl acetate, %
		1	0	100
		24	91.1	8.9
0.2 *M* NaOAc	0.1 *M* TsOH·H_2O	5	45.1	54.9
0.2 *M* NaOAc	0.1 *M* TsOH·H_2O	11	83.4	16.6
0.2 *M* NaOAc	0.1 *M* TsOH·H_2O	15.5	82.4	17.7
0.2 *M* Urea	0.1 *M* TsOH·H_2O	1.5 min	49.1	50.9
0.2 *M* Urea	0.1 *M* TsOH·H_2O	10.0 min	98.5	1.5
0.2 *M* Urea	0.1 *M* TsOH·H_2O	1	94.8	5.2
0.2 *M* Urea	0.1 *M* TsOH·H_2O	2	95.6	4.4
0.2 *M* Acetamide	0.1 *M* TsOH·H_2O	1	98.4	1.6

TABLE VI

PRODUCTS OF THE ACETOLYSIS OF 5-HEXENYL *p*-NITROBENZENESULFONATE IN ACETIC ACID CONTAINING SODIUM ACETATE, UREA, AND SODIUM PERCHLORATE

NaOAc[a,b]	Urea[a]	Temp, °C[c]	Cyclohexene, %	5-Hexenyl acetate, %	Cyclohexyl acetate, %	% cyclohexyl acetate/ % cyclohexene	% cyclic/ % acyclic
	0.2	60	10.4 ± 0.3	69.9 ± 1.0	19.7 ± 0.9	1.9	0.43
0.03	0.2	60	9.7 ± 1.1	66.9 ± 1.7	23.5 ± 2.9	2.4	0.50
0.1	0.1	60	8.2 ± 0.4	77.5 ± 1.9	14.4 ± 1.6	1.8	0.29
0.2		60	4.7 ± 0.3	85.3 ± 2.8	10.3 ± 2.0	2.2	0.18
0.3		60	2.9 ± 0.2	89.6 ± 0.5	6.9 ± 1.1	2.4	0.11
	0.2	100	14.4 ± 0.2	64.6 ± 0.6	21.2 ± 0.4	1.5	0.55
0.03	0.2	100	14.5 ± 0.8	65.4 ± 1.6	20.1 ± 0.7	1.4	0.53
0.1	0.1	100	10.9 ± 0.3	74.8 ± 0.9	14.4 ± 0.8	1.3	0.34
0.2		100	7.1 ± 0.8	80.3 ± 0.8	12.7 ± 1.5	1.7	0.25
0.3		100	5.4 ± 0.4	85.4 ± 0.4	9.0 ± 1.7	1.7	0.17
d	0.2	100	18.3 ± 1.0	60.1 ± 1.0	21.7 ± 0.2	1.2	0.67

[a] In molarity. [b] Two or three runs were made for each determination. [c] Runs at 60° were heated for 22 days. [d] These runs contained 0.2 *M* sodium perchlorate monohydrate.

drogen phosphate monohydrate is also inferior, since it is not very soluble and must be used as a suspended solid.

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p-Nitrosophenol Chemistry. I. Etherification of *p*-Nitrosophenol

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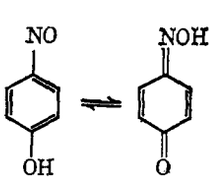
Conversion of *p*-nitrosophenol to its phenolic ethers by reaction with a variety of primary and secondary alcohols is shown to be a superior synthetic method. The equilibrium position in the acid-catalyzed reaction is unfavorable to ether formation but can be shifted toward the ether by use of excess alcohol and by removal of water formed. Careful control of reaction variables has given yields and conversions of ethers up to 98%. This reaction indicates that the recognized activating effect of the nitroso group is enhanced by protonation of *p*-nitrosophenol.

p-Nitrosophenol is a well-known example of tautomerism and is considered to be a mixture of the two forms (I and II).



I II

Although absorption spectra indicate that *p*-nitrosophenol exists predominantly in the quinone oxime form (II) in various solvents[1,2] it undergoes reactions characteristic of both forms. Thus, *p*-nitrosophenol reacts to form the oxime ether in methylation reactions with methyl iodide and alkali and with diazomethane.[3]

(1) L. C. Anderson and M. B. Geiger, *J. Am. Chem. Soc.*, **54**, 3064 (1932); L. C. Anderson and R. L. Yanke, *ibid.*, **56**, 732 (1934).

(2) E. Havinga and A. Schors, *Rec. Trav. Chim.*, **69**, 457 (1950).

(3) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," revised and rewritten by T. W. J. Taylor and W. Baker, Oxford University Press, New York, N. Y., 1937, p 222.