The thermal energy gain by the anion addition to the bent alkyne provides enough excess energy to allow the rearrangement, whereas in the case of the relaxed alkyne decomposition to the starting material is more favorable. The transition state for addition is located very early at an O–C distance of 3.0 Å with the bent alkyne and much later at 2.0 Å with the relaxed alkyne. Alkyne bending therefore not only eliminates the activation barrier but also increases the probability for the addition of strong nucleophiles. The stability of the intermediates N and N′ indicates that intermolecular protonation by hydrogen abstraction from solvent molecules is more likely than the unfavorable intramolecular 1,3-hydrogen shift.

The overall conclusion of this study is that cis bending of alkynes, as in cyclic alkynes, most effectively reduces the activation barrier for nucleophilic addition. Considerable charge separation in the transition structure for water addition predicts a strong solvent effect for such reactions. The absence of any activation barrier for the addition of hydroxide ions explains the lack of selectivity found in the reaction of benzyne with strong nucleophiles.[34-38] In contrast to the nucleophilic addition, the electrocyclic addition of olefins to alkynes is only partly affected by cis bending of the alkyne unit. With bent alkynes the formation of the first C–C bond becomes the rate-determining step, and the ring-closure reaction to the cyclobutyl ring is greatly accelerated relative to linear alkynes. This explains very nicely the tendency of cyclic alkynes to undergo 2 + 2 cycloaddition reactions at all (compared to the pronounced polymerization behavior of linear alkynes); it also accounts for the increase in stereospecifity of 2 + 2 cycloaddition reactions of cyclic alkynes observed with decreasing ring size. Electron correlation is not important for the nucleophilic addition reactions but essential for a reasonable description of the forbidden cycloaddition. The flexible wave function of the biradicaloid twixtyl in the 2 + 2 cycloaddition reaction makes the nature of this intermediate extremely environment dependent. In polar solvents the intermediate may have a zwitterionic nature, but in unpolar solvents or in the gas phase the ground state is predicted to be biradicaloid. We also think that MNDOC represents a very valuable extension of the MNDO method which greatly expands the applicability of this semiempirical approach.

Acknowledgment. This work was supported by NSF Equipment Grant CHE-82-14313. We thank Bob McDowell for assistance with the operation of the VAX 11/750 computer system.

Registry No. OH^-, 14280-30-9; acetylene, 74-86-2; ethylene, 74-85-1; water, 7732-18-5; benzyne, 462-80-6.

Ionization of *N*-Arylsulfonyloxy Amines: The Nitrenium Ion Question[1]

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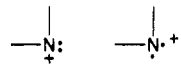
Abstract: The solvolyses of the *p*-nitrobenzenesulfonoxy derivatives of 2-methyl-2-octylamine, (**7**), 1-methylcyclohexylamine, (**8**), and 4,7,7-trimethyl-2-azabicycloheptane (**10**) and the *m*-(trifluoromethyl)benzenesulfonoxy derivative of dibenzylamine, (**9**) gave high yields of carbon-to-nitrogen rearrangement products. No parent amines were produced, even in the presence of heavy-atom solvents. The results, when compared to data from the literature, suggest that competing reaction pathways lead to rearranged or hydrogen abstraction products in the solvolysis of compounds with leaving groups attached to nitrogen.

Reaction intermediates involving positively charged, electron-deficient nitrogen atoms, nitrenium ions, have been a subject of considerable interest and some controversy.[2] Nitrenium ions are divalent nitrogen cations, which are isoelectronic with carbenes, and can exist in either a singlet, **1**, or triplet, **2**, spin state. Central

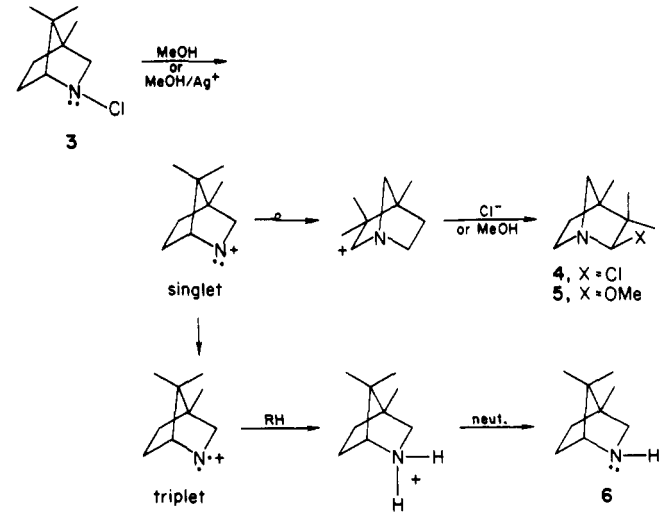


1 **2**

to the debate is the question of the spin state of nitrenium ions produced solvolytically in solution from compounds having leaving groups attached to nitrogen. While spin conservation requires that the first-formed ion is a singlet, the triplet state is the ground state,[3] and intersystem crossing to the triplet state has been used to explain some of the products of solvolysis.

Specifically, the formation of parent amine, **6**, from the solvolysis of chloramine, **3**, has been interpreted as evidence for the formation of a discrete nitrenium ion, which underwent intersystem crossing to the triplet. The triplet, being a 1,1 diradical, abstracted hydrogen from the solvent to give an ammonium salt and, upon neutralization, the parent amine, (Scheme I). Chloramine, **3**, is a well studied, but not unique, example of this behavior.[4] Of

Scheme I



(1) Taken in part from the Ph.D. Thesis of A.K. submitted to the Graduate School of New Mexico State University, December 1983.

(2) (a) Gassman, P. G. *Acc. Chem. Res.* **1970**, *3*, 26. (b) Abramovich, R. A.; Jeyaraman, R. In "Azides and Nitrenes", Scriven, E. F. V., Ed.; Academic Press: New York, 1984, p 297. (c) Lwowski, W. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, p 327; (d) Abramovich, R. A. In "Organic Reactive Intermediates"; McManus, S., Ed.; Academic Press: New York, **1973**, p 181.

(3) Lee, S. T.; Morokuma, K. *J. Am. Chem. Soc.* **1971**, *63*, 6863.

0002-7863/85/1507-4731$01.50/0

further note is that the yield of parent amine increased dramatically when heavy-atom solvents were present, so much that **6** became nearly the sole product in the presence of chloroform or bromoform. Increased intersystem crossing due to a heavy-atom effect[5] was used to explain this change in product distribution.[2a]

Another interpretation of these results is that there are multiple reaction pathways followed by chloramines. When there is the potential for facile rearrangement, then a two-electron nitrenium ion route obtains. However, the usual route involves either homolysis of the N–Cl bond (which may be silver assisted) or heterolysis in the opposite sense to give a chloronium ion.[6]

A variety of studies have been reported and rationalized on the basis of singlet/triplet nitrenium ions[7] or ionic/free radical partitioning,[8] and there is no clear consensus as to whether triplet nitrenium ions are produced in solvolytic reactions.

One obvious problem is the use of chloramines as starting materials due to their many modes of decomposition[9] and to the uncertainty as to the role of silver ions often used to promote the reaction.[6,8] The use of acyloxy leaving groups offers no apparent solution,[4] and *N*-sulfonyloxy amines have been largely inaccessible due to their instability.[4b,4d,10]

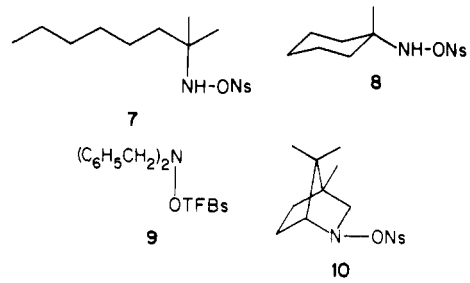
We have found that arylsulfonyloxy leaving groups can be attached efficiently to the nitrogen of amines via the reaction of amines with arylsulfonyl peroxides[11] (eq 1). These compounds undergo very facile ionization, thereby providing superior solvolysis precursors for probing the spin state of the derived nitrenium ions. We wish to report results from the solvolyses of several *N*-arylsulfonyloxy amines which suggest that triplet nitrenium ions are not involved in these reactions.

$$2RNH_2 + (ArSO_2O)_2 \rightarrow RNH{-}OSO_2Ar + RNH_3{}^+ArSO_3{}^- \quad (1)$$

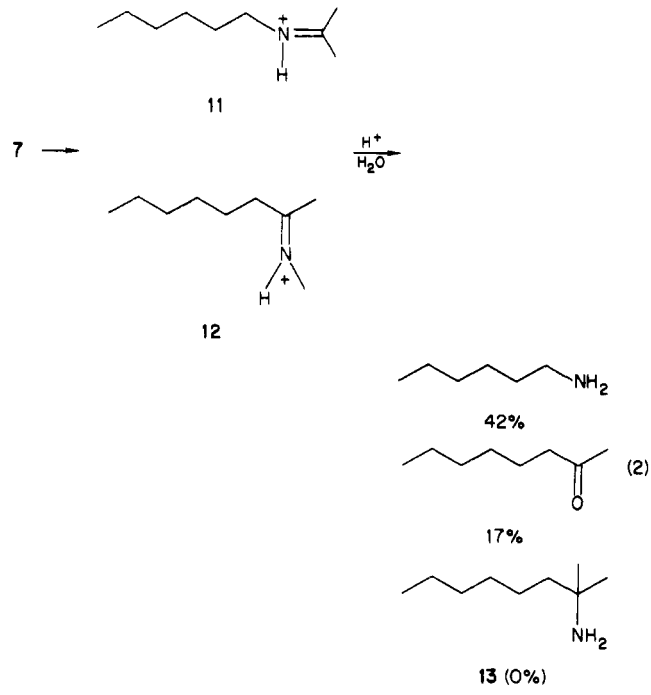
Ar = 4-$NO_2C_6H_4$-, 3-$CF_3C_6H_4$-

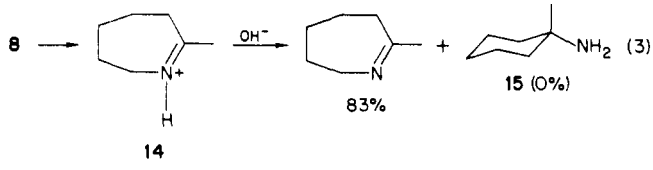
Results

N-Arylsulfonyloxy derivatives **7**, **8**, and **10** were prepared from the corresponding amine and *p*-nitrobenzenesulfonyl peroxide at −78 °C according to eq 1. Derivative **9** was prepared similarly with *m*-(trifluoromethyl)benzenesulfonyl peroxide. Passage of the reaction solution through a cold silica gel column and evaporation of the solvent at low temperature gave **7**, **8**, and **9** as unstable solids. Adducts **7**–**9** were insufficiently stable to permit complete characterization, however, the identity of these materials is well-founded.[11] All were isolated as single components (TLC) that oxidized iodide to iodine. All gave low-temperature ^{1}H NMR spectra that were consistent with the assigned structure, but different than the starting materials (see Experimental). Compound **9** was particularly revealing since the low-temperature ^{1}H NMR spectrum showed the benzylic protons as an AB quartet due to slow inversion of nitrogen bonded to the arylsulfonyloxy oxygen.[12] This quartet reversibly collapsed to a singlet at room temperature. Compound **10** decomposed upon solvent removal and thus solutions of **10** that were homogeneous by TLC were used.



N-Sulfonyloxy amines are known to undergo smooth cationic carbon-to-nitrogen rearrangement.[13] Thus **7** dissolved in methanol or chloroform gives a mixture of iminium salts **11** and **12** (quantitative by NMR) which upon hydrolysis yields *n*-hexylamine (42%) and 2-octanone (17%) from *n*-hexyl and methyl migration, respectively (eq 2). Examination of the reaction mixture before and after hydrolysis showed no parent 2-methyl-2-octylamine (**13**) was produced. Likewise, **8** rearranged to the ring-expanded iminium salt **14** (quantitatively by NMR), which upon neutralization gave 2-methylazacyclohept-1-ene (83%),[14] (eq 3). Again careful examination of the reaction mixture before and after neutralization showed no parent amine **15** present. Thus primary nitrenium ion precursors give no evidence of hydrogen abstraction products, even in the presence of heavy-atom solvents.





(4) (a) Reference 2a. (b) Gassman, P. G.; Hartman, G. D. *J. Am. Chem. Soc.* **1973**, *95*, 449. (c) Gassman, P. G.; Campbell, G. A.; Frederick, R. C. *Ibid.* **1972**, *94*, 3884. (d) Biehler, J.-M.; Fleury, J.-P. *Tetrahedron*, **1971**, *27*, 3171. (e) Kovacic, P.; Lowery, M. R.; Roskos, P. D., *Tetrahedron* **1970**, *26*, 529. (f) Wasserman, H. H.; Adickes, H. W.; DeOchao, O. E. *J. Am. Chem. Soc.* **1971**, *93*, 5586. (g) Rautenstrauch, V. *J. Chem. Soc. D* **1969**, 112.

(5) (a) Murrell, J. N. "The Theory of Electronic Spectra of Organic Molecules"; John Wiley and Sons: New York, 1963, pp 294–300. (b) Kasha, M. *J. Chem. Soc.* **1952**, 71. (c) Anastassiou, A. S. *J. Am. Chem. Soc.* **1968**, *88*, 2322.

(6) (a) Edwards, O. E.; Vocelle, D.; ApSimon, J. W. *Can. J. Chem.* **1972**, *50*, 1167. (b) Edwards, O. E.; Bernath, G.; Dixon, J.; Paton, J. M.; Vocelle, D. *Ibid.* **1974**, *52*, 2123. (c) Bastable, J. W.; Hobson, J. D.; Riddell, W. D. *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2205.

(7) (a) DeRosa, M.; Haberfield, P. *J. Org. Chem.* **1981**, *46*, 2639. (b) Hiyama, T.; Kiode, H.; Nozaki, T. *Bull. Chem. Soc. Jpn.* **1978**, *48*, 2918. (c) Freeman, J. P.; Janiga, E. *J. Org. Chem.* **1974**, *39*, 2663. (d) Carey, F. A.; Hayes, L. J. *Ibid.* **1973**, *38*, 3107. (e) Paul, D. F.; Haberfield, P. *Ibid.* **1976**, *41*, 3170. (f) Mokotoff, M.; Sprechner, R. F. *Tetrahedron* **1974**, *30*, 2623.

(8) (a) Schell, F. M.; Ganguly, R. N. *J. Org. Chem.* **1980**, *45*, 4069. (b) Furstoss, R.; Tadayoni, R. *Ibid.* **1977**, *42*, 2844. (c) Furstoss, R.; Tadayoni, R.; Waegell, B. *Nouv. J. Chim.* **1977**, *1*, 167. (d) Tadayoni, R.; Lacrampe, J.; Jeuman, A.; Furstoss, R.; Waegell, B., *Tetrahedron Lett.* **1975**, 735. (e) Potts, K. T.; Kutz, A. A.; Nachod, F. C., *Tetrahedron* **1975**, *31*, 2171.

(9) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639.

(10) See Gassman and Granrud (Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498) for a recent example.

(11) Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34.

(12) Griffith, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4089. Brois, S. L. *Ibid.* **1970**, *92*, 1079.

(13) (a) Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2364. (b) Hoffman, R. V.; Cadena, R.; Poelker, D. J. *Tetrahedron Lett.* **1978**, 203.

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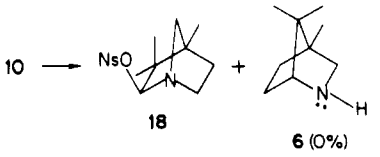
Dibenzylamine adduct **9** was decomposed in dichloromethane, and the reaction mixture was treated with aqueous sodium hydroxide and extracted with dichloromethane. Only *N*-benzylidenebenzylamine, (**16**) and small amounts of benzaldehyde and benzylamine from its hydrolysis were identified. Acid hydrolysis gave benzaldehyde (58%) (eq 4). No dibenzylamine (**17**)

$$\mathbf{9} \rightarrow C_6H_5CH{=}N\overset{+}{C}HCH_2C_6H_5 \xrightarrow{OH^-} C_6H_5CH{=}NCH_2C_6H_5 \xrightarrow[H_2O]{H^+} C_6H_5CHO \quad (4)$$

16 58%

was detected before or after hydrolysis. If dibenzylamine was added to the solvolysis reaction, it was recovered completely. Thus if any dibenzylamine were produced in the solvolysis, it would have been detected.

The bicyclic chloramine derivative **3** has served an important role in designating spin states of nitrenium ions.[2] It was of great interest therefore to examine the *N*-sulfonyloxy analogue **10** under similar conditions. Since adduct **10** could not be isolated as a pure solid, ethyl acetate solutions of **10** that showed a single component by TLC were purified by low-temperature silica gel chromatography. Storage at −20 °C overnight led to decomposition of **10** and the formation of a single product, **10** (48%) (eq 5). Exam-



(5)

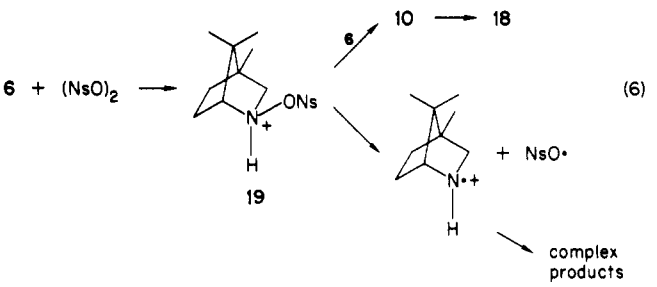
ination of the reaction before and after it was made basic revealed that no parent amine **6** was produced from the ionization of **10**.

If chloroform (1:1 v/v) was added to the adduct solution before rearrangement, only product **18** was obtained (48%), and again, no parent amine **6** was detected. This is very different from the results with the corresponding chloramine which gave 65% of the parent amine in the presence of chloroform.[2] Dilution with methanol did not give any products of methanol capture; only **18** was obtained (40%). This also confirms an earlier observation that solvent polarity has little effect on the partitioning of products.[2]

Control experiments show that adduct **10**, once formed, is stable to the isolation procedure, since repeated passes of solutions of **10** through cold chromatography columns gave no decrease in yield. Furthermore, when the parent amine **6** was added to the adduct solution before rearrangement, it was recovered completely after solvolysis. Thus if parent amine **6** were produced in the solvolysis of **10**, it could have been detected.

When the column used for purification of **10** was washed with methanol, parent amine (44%) was recovered along with a significant quantity of higher molecular weight products. Thus the stoichiometry shown in eq 1 for the formation of adduct **10** holds, and the moderate yields, which are based on starting amine and peroxide, reflect losses in the formation of **10**, not in its subsequent reactions. It appears that adduct **10** rearranges quantitatively to **18**.

The formation of *N*-sulfonyloxy adduct **10** from the secondary amine **6** and *p*-nitrobenzenesulfonyl peroxide is accompanied by side reactions which consume both the amine and the peroxide and give high molecular weight products. Such is not the case for primary amines which give virtually quantitative yields of *N*-sulfonyloxy adducts.[11] Electron transfer from the amine to the peroxide may be more important in the case of secondary amines. Consideration of a two-electron mechanism, however, reveals that the first-formed intermediate from nucleophilic attack of the amine on the peroxide bond gives the protonated adduct **19** (eq 6). Deprotonation of this species gives the *N*-sulfonyloxy adduct **10**. It may be that protonated **19** can undergo competing homolysis of the N–O bond to give free radicals and then undefined reactions. This pathway may be more important for secondary amines than primary amines, since the secondary nitrogen cation radicals obtained are more stable than primary ones.[15] Deprotonation



(6)

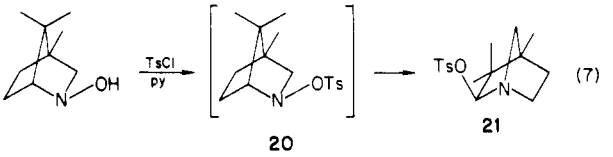
of the first-formed adduct has been previously shown to be a necessary step in the production of *N*-sulfonyloxy amines when competing reactions of the protonated adduct are possible.[13]

Further support for this reaction scenario comes from the observation that if excess amine (100% more than the normal 2 equiv of eq 1) is used, the yield of adduct **10** (and hence the solvolysis product **18**) increased to 71%. The increased amine concentration causes more rapid deprotonation of **19** and a higher yield of adduct **10**.

Discussion

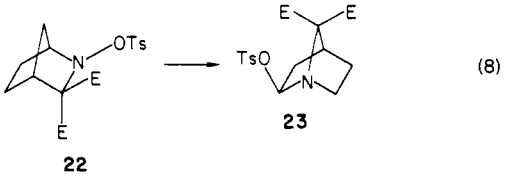
The results presented above indicate that *N*-arylsulfonyloxy amines undergo ionization of the N–O bond accompanied by skeletal rearrangement. No hydrogen abstraction products were found for either the primary or secondary systems investigated. Based on earlier work[13] and the results for **10**, where internal return is the exclusive pathway, it is likely that rearrangement is concerted with leaving group loss, and that products result from the collapse of intimate ion pairs. Since only primary and secondary nitrenium ions are formed, and since nitrenium ions are less stable than the analogous carbenium ions,[16] it is not surprising that development of electron deficiency on nitrogen is accompanied by concerted rearrangement and close association of the anionic leaving group.

While this work is the most detailed to date on the reactions of aliphatic *N*-arylsulfonyloxy amines, our results are consistent with the observation of Gassman that the attempted preparation of *N*-tosyloxyamine **20** returned only the rearranged **21**[4b] (eq 7).



(7)

Biehler and Fleury also showed that several *N*-tosyloxy[2.2.1]-azabicyclic compounds **22** (E = electron withdrawing group) give moderate yields of the analogous rearrangement products, **23** (eq 8).[4d] Several examples of comparable behavior are known for



(8)

solvolysis of bicyclic chloramines where rearrangement is accompanied by large amounts of internal return.[2a,17]

In order to place our results in perspective with results from the solvolyses of other compounds with leaving groups attached to nitrogen, a collection of data from the literature is shown in Table I. We have largely selected results from bicyclic substrates for several reasons: (a) the largest group of comparable data is available in this series, (b) the products of cationic rearrangement are quite distinct from those of other processes, and (c) they

(15) Hull, L. A.; Davis, G. T.; Rosenblatt, D. H.; Mann, C. K. *J. Phys. Chem.* **1969**, *73*, 2142.
(16) Tietz, R. F.; McEwen, W. E. *J. Am. Chem. Soc.* **1958**, *77*, 4007.
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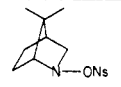
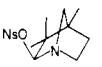
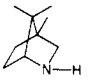
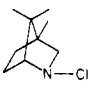
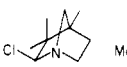
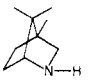
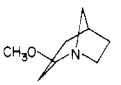
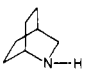
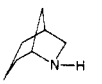
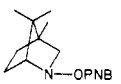
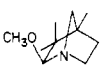
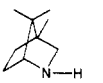
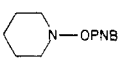
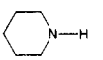
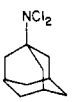
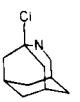
Table I. Products from the Solvolyses of Various Amine Derivatives

entry	substrate	conditions	rearranged products (%)		H-abstraction product (%)	total yield (%)	ref
1.		$EtOAc/CHCl_3$					
	10		71[a]		0	71	this work
2.	$(C_6H_5CH_2)_2NOTFBs$	CH_2Cl_2	$C_6H_5CH{=}NCH_2C_6H_5$		$(C_6H_5CH_2)_2NH$		
	9		58		0	58	this work
3.		CH_3OH					
	3		59	20	7	86	17
4.	3	CH_3OH/Ag^+	78	8	4	92	17
5.	3	$CH_3OH/CHCl_3$	4	1	63	68	22
6.		CH_3OH					
	24		11		20	31	23
7.	24	CH_3OH/Ag^+	60		0	60	23
8.		CH_3OH					
	25		"trace"		"major"		23
9.	25	CH_3OH/Ag^+	9		36	45	23
10.		CH_3OH/Ag^+					
	26		25[b]		50	75	8a
11.	26	C_6H_5/Ag^+					
			92		3	95	8a
12.		CH_3OH					
	27		15.3		13.4	29[c]	4b
13.		CH_3OH					
					71[c]	71	4b
14.		$CH_2Cl_2/AlCl_3$					
			70–80			70–80	24

[a] Yield based on starting amine and peroxide. This is the only product observed. [b] This is assigned as a product of rearrangement followed by oxidation. [c] Products from the methanolysis of the *p*-nitrobenzoyl group are not included.

provide rigid structures that highlight structural features.

As a starting point, it is generally agreed that rearranged products result from a spin-paired, electron-deficient nitrogen intermediate generated by ionic cleavage of the nitrogen-leaving group bond.[2,4,6-8] Leaving group, solvent, and structure all appear to have important influences on the facility of the rearrangement process.

Leaving Groups. In the azabicyclo[2.2.1] system, the yield of rearranged products varies directly with the leaving ability of the group attached to nitrogen, and varies from 100% (–ONs, entry 1) to 15% (–OPNB, entry 12). The chloramine lies between these extremes (entry 3), but adding silver ion increased the leaving ability of chlorine and hence the amount of rearrangement (entry 4). Aluminum chloride also serves to make chlorine a better leaving group (entry 14).

Solvent. The solvent profoundly influences the amount of rearrangement, but the data are often contradictory. Schell has found that a change from methanol to benzene increases the amount of rearrangement (entries, 10, 11).[8a] In other cases, a decrease in solvent polarity causes a decrease in rearrangement (entries 3, 5). In our work, little change is seen in several different solvents. Thus solvent polarity may not be the major factor, but the solvent does play a role. It may be that the chemical properties of the solvent (acidity, basicity, and abstractable hydrogens) are important also, but the data are not sufficient to permit meaningful speculation.

Structural Factors. A factor which we find to be important in determining the ease of rearrangement is stereoelectronic features in the solvolysis precursor. It is crucial that a migrating group be antiperiplanar to the departing leaving group in order to anchimerically assist the ionization. This requirement in *N*-arylsulfonyloxy amines is discussed elsewhere,[18] and the data in Table I show that it is generally important. For several bicyclic chloramines solvolyzed in methanol (entries 3, 6, 8), rearrangement yields decrease 79%, 11%, and <1%. In the presence of silver ion, the same series gives 86%, 60%, and 9% rearrangement (entries

(18) Hoffman, R. V.; Kumar, A. *J. Org. Chem.* **1985**, *50*, 1859.

4, 7, 9). Since these systems all involve the same leaving groups, solvent, and a secondary nitrogen reaction center, the disparate results are probably due to increasingly poor geometry for rearrangement. Examination of models illustrates this trend. Likewise, the [3.2.1] system in entry 10 gives efficient rearrangement because the migrating group is well-disposed geometrically for migration. Open-chain systems (entries 14, 2) are able to achieve antiperiplanar geometry by rotation.

The other type of product often found in these solvolyses is the parent amine. Two mechanistic explanations for this product currently constitute the basis of the debate about nitrenium ions. Ionization followed by intersystem crossing to a triplet nitrenium ion is one explanation for this product, while homolysis of the leaving group is a second scenario. In either case an unpaired electron species is produced which abstracts hydrogen to give the parent amine. The hydrogen-abstracting species cannot be a simple nitrogen-centered free radical since these species have been shown to give chemistry distinct from that found in solvolysis.[19] Likely alternate candidates are protonated or metal-complexed nitrogen cation radicals.

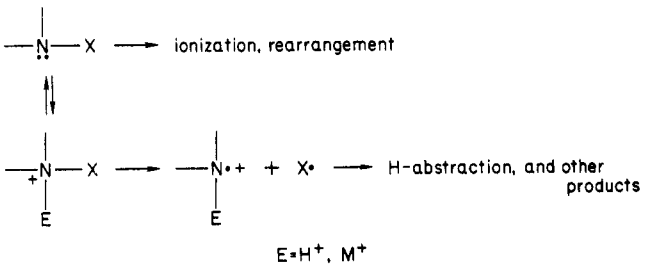
The difference between these two mechanisms is that the singlet–triplet mechanism branches to rearrangement or H-abstraction products after the ionization step, whereas the homolysis mechanism (H-abstraction) occurs in competition with ionization (rearrangement). From the data in Table I, it can be argued that ionization does not lead to hydrogen-abstraction products. Since a free singlet nitrenium is required for intersystem crossing,[2a] substrates with the best leaving groups are expected to more readily yield free nitrenium ions and thus higher yields of hydrogen abstraction.[4b] It is seen that the best leaving groups yield no hydrogen-abstraction products, while poorer leaving groups give the highest yields of such products.

In the second place our data and others[17,18] indicate that the ionic cleavage of the leaving group is anchimerically assisted by a rearranging group. It seems quite reasonable to expect that such a concerted reaction would not lead to unpaired electron intermediates and no parent amine products. Thus if hydrogen abstraction products result from an ionization step, then there must be two competetive ionization processes—one of which is concerted with rearrangement, the other of which is not concerted and leads to free nitrenium ions and intersystem crossing. It seems unlikely that the ionization would take two distinct courses, particularly since the concerted one appears to be of lower energy. It is less likely that substrates with poorer leaving groups would increasingly favor the higher energy pathway.

If triplet nitrenium ions do not appear to be likely intermediates to account for the parent amine product, what then are likely candidates? Since aminyl free radicals have been ruled out experimentally,[19] the best candidate is a protonated or metalated nitrogen radical cation, **24**, which has been postulated by several workers.[4c,8a,20] Work on the Hofmann–Loffler reaction[21] illustrates that the nitrogen–chlorine bond is considerably labilized toward homolysis by protonation. Our work on the preparation of **10** shows that a protonated *N*-arylsulfonyloxy amine decomposes readily, perhaps by homolysis. Thus in protic solvents, protonation or hydrogen bonding to nitrogen in the reactant could lead to homolysis of the leaving group competing with its ionization.

Realizing that the best leaving groups (–ONs) are also the most electron withdrawing, ionization is favored (entries 1,2). The lowered basicity of the nitrogen in these substrates precludes protonation and subsequent homolysis of the leaving group. The poorest leaving group ($-O_2CR$) decreases the basicity of nitrogen the least, so protonation and homolysis are favored while ionization is minimized (entries 12, 13). A chloride leaving group falls between these extremes. While ionization can be the major pathway (entry 3), the partitioning appears to be quite sensitive to structural and environmental influences. Where structural features slow the concerted rearrangement, the competing homolysis pathway becomes increasingly predominant. The solvent may also influence the partitioning of products by its acidity or leveling ability. Oxygenated solvents may moderate the effect of acidic byproducts and thereby reduce protonation of nitrogen and favor ionization.

Scheme II



There is some experimental evidence to indicate that protonation of nitrogen can influence the partitioning in these reactions. Gassman reported that while the solvolysis of chloramine **3** gives largely rearranged products from ionization (entries 3, 4), an excess of hydrogen chloride catalyzes the decomposition of **3** to give only the parent amine **6**.[26] We have carried out the solvolysis of bicyclic **10** in the presence of methanesulfonic acid (2 equiv) and observed a slight decrease in yield to 48%, but no parent amine was detected in the product. Dibenzylamine derivative **9** in the presence of methanesulfonic acid (2 equiv) gave a dark product mixture that contained only 10% rearranged products, but again no parent amine was detected. Furthermore, the presence of acid did not give a noticeable increase in the rate of decomposition of these materials.

These results suggest that chloramines, in the presence of acid, are protonated on nitrogen and give a large proportion of homolysis. It also seems that *O*-sulfonylhydroxylamines are muct less basic, so protonation of nitrogen and homolysis of the N–O bond are not important. The role of acid in these decompositions is different. Perhaps the greater acidity of the mixture influences the ion pairing between the leaving group and the organic cation formed upon ionization.

The addition of silver ion to chloramine solvolyses can be interpreted in the same way if it is recognized that silver(I) can complex with either nitrogen or chlorine. The latter leads to ionization, and the former gives a silver complexed radical cation. Scheme II summarizes these competing pathways.

There remain many questions concerning the details of these reactions; however, Scheme II provides a framework consistent with current observations. It would be very helpful if appropriate nitrogen cation radicals were investigated and their place in this scheme ascertained.

Experimental

Proton magnetic resonance spectra were taken on a JEOL PS-100 instrument with Me_4Si as the internal reference and chloroform as the solvent. Carbon-13 NMR spectra were taken on a Varian XL-200 spectrometer. Infrared spectra were recorded neat for liquids and as KBr disks for solids on a Perkin-Elmer 283B spectrometer. Mass spectra were recorded on a Hitachi RMU-6E instrument. Gas chromatography was performed on either a Varian Model 920 or a Hewlett-Packard 5890 gas chromatograph. Columns used in this study were the following: (A) 6 mm × 2.5 m 5% QF-1 on Anachrome ABS support, carbonyl products, (B) 6 mm × 3 m Carbowax 20 M–2% KOH on Anachrome ABS support, amine products, (C) 0.53 mm × 10 m fused silica column, Alltech Assoc, temperature programmed, all products. Thin-layer chromatography utilized Eastman chromatogram sheets of silica gel with fluorescent indicator. Melting points are uncorrected. Elemental analysis was performed by Micanal, Tuscon, AZ.

(19) Gassman, P. G.; Uneyama, K.; Hahnfeld, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 647.
(20) See footnote 8, ref 19.
(21) Wolff, M. E. *Chem. Rev.* **1963**, *63*, 55.
(22) Gassman, P. G.; Cryberg, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 5176.
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(26) Footnote 7, ref 19.

Preparations of 2-methyl-2-octylamine (**13**), 1-methylcyclohexylamine, (**15**), and 4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane (**6**) have been detailed previously.[18] Dibenzylamine was purchased from Aldrich, *p*-Nitrobenzenesulfonyl peroxide (PNBSP)[27] and *m*-(trifluoromethyl)-benzenesulfonyl peroxide (TFBSP)[28] were prepared by the literature methods.

Preparation of *O*-Arylsulfonylhydroxylamines. Adducts **7–10** were prepared by the general procedure described earlier.[18] Briefly, the appropriate amine and arylsulfonyl peroxide were reacted at −78 °C for several hours. The reaction mixture was filtered and eluted through a short column of silica gel which was cooled by dry ice. Removal of the solvent in vacuo at low temperature furnished the pure adducts.

***O*-(*p*-Nitrobenzenesulfonyl)-*N*-(2-methyl-2-octyl)hydroxylamine (7)** was obtained as a pale yellow solid that showed a single spot upon TLC analysis (chloroform) and gave a positive test for active oxygen (KI—acetic acid). The NMR spectrum [δ 0.88 (singlet superimposed on broad triplet, 9 H, methyl H's), 1.2 (m, 10 H, CH_2 H's), 5.5 (br s, 1 H, N–H), 8.26 (a (AA'BB'), 4 H, aromatic H's)] is consistent with the structure of **7**, and the methyl signals distinguish it from starting materials or products. Adduct **7** begins to decompose in the NMR probe after several minutes. Other structural characterizations were not possible due to this instability.

***O*-(*p*-Nitrobenzenesulfonyl)-*N*-(1-methylcyclohexyl)hydroxylamine (8)** was obtained as a pale yellow solid that showed a single spot by TLC and gave a positive active oxygen test. The NMR spectrum [δ 0.92 (s, 3 H, CH_3), 1.32 (br m, 10 H, ring H's), 5.0 (br s, 1 H, N–H), 8.28 (AA'Bb' q, 4 H, aromatic H's)] is consistent with the structure, and the methyl singlet distinguishes it from both the reactants and the rearranged products. Adduct **8** begins to decompose in the NMR probe after several minutes. Other structural characterizations were not possible due to this instability.

***O*-(*m*-(Trifluoromethyl)benzenesulfonyl)-*N*,*N*-dibenzylhydroxylamine (9)** was obtained as a white solid that showed a single spot upon TLC analysis and gave a positive test for active oxygen. The low-temperature (−60 °C) NMR spectrum [δ 4.10 (AB q, 4 H, benzylic H's), 7.12 (m, 10 H, C_6H_5 H's), 8.0–7.3 (m, 4 H, −TFBs H's)] is consistent only with the indicated structure. Warming of the sample caused collapse of the AB quartet to a singlet at δ 4.10δ. Recooling gave back the quartet which is indicative of relatively slow inversion of nitrogen carrying an oxygen substituent.[12] Further characterization was not possible due to the instability of **9**.

***N*-(*p*-Nitrobenzenesulfonyloxy)-4,7,7-trimethyl-2-azabicyclo[2.2.1]-heptane (10)** could not be obtained in a pure form, since attempted solvent removal gave only decomposition products. Cold solutions of **10**, obtained after elution through silica gel, showed a single component by TLC that was distinct from the starting materials and gave a positive active oxygen test. These solutions of **10** were utilized in the rearrangement studies.

Decomposition of 7. A solution of **7** (270 mg, 0.7 mmol) in chloroform (10 mL) was stirred at room temperature for 24–30 h until no active oxygen remained. The reaction was hydrolyzed and analyzed as described earlier.[18] By NMR examination of a reaction carried out in chloroform-*d*, the methyl singlet at δ 0.88 disappeared and new methyl signals grew in at δ 2.12 and 2.64 for the syn and anti methyl groups of the *N*-isopropylidene *n*-hexyliminium salt from *n*-hexyl migration. A smaller signal appeared at δ 3.4 which was assigned as the *N*-methyl group of *N*-(2-octylidene)methylamine, the product of methyl migration. Authentic samples were prepared for comparison by a standard method.[25] No methyl signal of the parent amine (δ 1.04) was ever detected in the reaction mixture or in the base fraction after hydrolysis. Yields in methanol were lower than those in chloroform.

Decomposition of 8. A solution of **8** (330 mg, 1 mmol) in chloroform (25 mL) was stirred at room temperature until all the starting material was gone. The reaction yielded 2-methyl-1-azacycloheptene (83%) as described.[18] NMR examination of a reaction in chloroform-*d* showed disappearance of the methyl signal of **8** at δ 0.92 and the growth of a methyl singlet at δ 2.64 of the ring-expanded iminium salt. No parent amine was detected by NMR or gas chromatography before or after neutralization.

Decomposition of 9. A solution of **9** (758 mg, 1.00 mmol) in dichloromethane (70 mL) was stored at −20 °C overnight. The solvent was removed by rotary evaporation, dilute hydrochloric acid (2.5 M, 45 mL) was added to the residue, and the mixture was steam distilled. The steam distillate was extracted with dichloromethane (3 × 25 mL), dried ($MgSO_4$), and analyzed for benzaldehyde (58%) by gas chromatography. The steam distillation residue was basified with sodium hydroxide, extracted with dichloromethane, and dried. Analysis by gas chromatography showed no dibenzylamine present.

In another experiment, the reaction mixture was washed with aqueous sodium hydroxide (10%), dried, and evaporated to a dark oil. Kugelrohr distillation yielded *N*-benzylidenebenzylamine (50%) which was identical with an authentic sample (Aldrich). Small amounts of benzaldehyde and benzylamine were also found, but no dibenzylamine was detected.

Yield were comparable in chloroform, but lower in methanol. The addition of methanesulfonic acid (2 equiv) drastically reduced the yield of rearrangement (10%), but still no dibenzylamine was detected.

Decomposition of 10. A solution of **10**, prepared from **6** (173 mg, 1.24 mmol) and PNBSP (250 mg, 0.62 mmol), in ethyl acetate (55 mL) was passed through a cold silica gel column and eluted further from ether (40 mL). The solution was stored overnight at −20 °C. The solvent was removed at room temperature, and the white solid residue was treated with sodium hydroxide (50 mL, 15%) and extracted with dichloromethane. The organic layer was dried (Na_2SO_4) and evaporated to yield **18** as an orange solid (99 mg, 48%) that had mp 116–120 °C dec. Spectral characterization included IR: ν 2970, 1602 (weak), 1530, 1460, 1347, 1183 cm^{-1}; ^1H NMR δ 0.99 (s, 3 H), 1.03 (s, 3 H), 1.05 (s, 3 H), 1.18 (m, 1 H), 1.71 (m, 1 H), 2.01 (d, 1 H), 2.56 (m, 1 H), 2.62 (d, 1 H), 2.91 (m, 1 H), 4.85 (br s, 1 H), 8.31 (AA'BB' q, aromatic H's); and ^{13}C NMR δ 12.63, 20.47, 22.25, 32.77, 46.54, 50.50, 51.27, 60.67, 107.36, 123.94, 129.23, 144.20, 150.02. Recrystallization from ether–hexane gave an analytical sample. Anal. Calcd for $C_{15}H_{20}N_2O_5S$: C, 52.94; H, 5.88; N, 8.23. Found: C, 53.12; H, 5.98; N, 8.20.

If chloroform (1 vol) was added to the solution of **10**, the yield of **18** was unchanged. Addition of methanol (1 vol) decreased the yield to 40%. Examination of the reaction mixture by gas chromatography before and after workup gave no evidence of parent amine **6**. Deliberate addition of **6** to a solution of **10** showed it to be present quantitatively in the reaction product after neutralization.

The yield of **18** was increased if more than 2 equiv of **6** were used in the preparation of **10**. The following results were found: 2.0 equiv, 48%; 2.5 equiv, 51%; 3.2 equiv, 62%; 4 equiv 71%. Higher amounts were not used since unreacted **6** started to appear in the solution after chromatography. If methanesulfonic acid (2 equiv) was added to the solvolysis reaction, the yield of **18** was reduced to 48% (from 62%), but no parent amine could be detected in the product.

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Registry No. **7**, 96913-38-1; **8**, 96913-39-2; **9**, 96913-40-5; **10**, 96913-41-6; **11**·*p*-$NO_2C_6H_4SO_3^-$, 96913-42-7; **12**·*p*-$NO_2C_6H_4SO_3^-$, 96913-43-8; **18**, 96913-44-9; H_2, 1333-74-0; $CH_3(CH_2)_5C(CH_3)_2NH_2$, 2626-63-3; Ph_2NH, 122-39-4; *p*-$NO_2C_6H_4SO_2OOSO_2C_6H_4$-*p*-$NO_2$, 6209-72-9; *m*-$CF_3C_6H_4SO_2OOSO_2C_6H_4$-*m*-$CF_3$, 35673-10-0; $PhCH_2N{=}CHPh$, 780-26-7; $CH_3(CH_2)_5NH_2$, 111-26-2; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; 1-methylcyclohexylamine, 6526-78-9; 4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane, 18715-80-5; 2-methyl-1-azacyclohept-1-ene, 3338-03-2.

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