with that of E_{mix} in Figure 4. The new information concerns the reaction pathways which should be rather unsymmetrical for the reactions of 2CPBQ and 3COBQ and symmetrical for 4COBQ.

In conclusion, the present work indicates that the predictions of the chemo- and regioselectivities in the vinylcyclohexene–benzoquinones cycloaddition are strongly dependent on the level of approximation in the use of the PMO equation as well as on the distances between the reaction centers. These difficulties can be overcome if the complete PMO equation is coupled to an "external" description of the early stages of the reactions. We suggest that this description should be provided by evaluating the minimum of the nonbonding energy.

The analysis of three reactions does not allow us to state a theory. The aim of the present work is to analyze the failure of the simplest theoretical approximation in these reactions and to search for an alternative theoretical approach. Further work on a larger set of examples is in course.

Acknowledgment. We thank the Italian C.N.R. (Progetto Finalizzato per la Chimica Fine e Secondaria, Grant No. CT82.00815.03, Grant No. CT83.00298.03) for financial support.

Registry No. 1, 95673-71-5; 2, 95673-72-6; 3, 95673-73-7; 4′, 95673-74-8; 4″, 95673-75-9; methyl 3,4-dihydroxybenzoate, 2150-43-8; methyl 2,3-dihydroxybenzoate, 2411-83-8; 1-vinylcyclohexene, 25168-07-4; 2-carbomethoxy-1,4-benzoquinone, 3958-79-0.

Supplementary Material Available: Final coordinates of the atoms and thermal parameters with their estimated standard deviations for the crystal structure determinations of compounds 1 and 2 (8 pages). Ordering information is given on any current masthead page.

Cationic Carbon-to-Nitrogen Rearrangements in *N*-(Arylsulfonoxy)amines[1]

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A series of *N*-alkyl-*O*-(arylsulfonyl)hydroxylamines was prepared by the reaction of amines with bis(arylsulfonyl) peroxides. In the absence of base, these amine derivatives underwent rearrangement involving the migration of groups from carbon to nitrogen. The migratory tendencies of the groups which rearranged were found to be in the order Ph > H > alkyl > Me. The migratory aptitudes Ph/Me > 72 and *n*-hexyl/Me = 4.2 suggest that these rearrangments are polar in nature and involve electron-deficient nitrogen species. Furthermore the migration of groups was found to be sensitive to the substitution pattern at the migration origin and subject to stereoelectronic control.

The reaction between amines and arylsulfonyl peroxides has been shown to be a convenient way to prepare *N*-(arylsulfonoxy)amines[2,3] (eq 1). These materials undergo

$$2RCH_2NH_2 + (ArSO_2O)_2 \xrightarrow[-78\ °C]{EtOAc} RCH_2NH{-}OSO_2Ar + RCH_2NH_3{}^+ArSO_3{}^- \quad (1)$$

facile biomolecular elimination to imines in the presence of bases.[4] In the absence of base, however, products resulting from carbon-to-nitrogen rearrangements have been observed.[5] The *N*-arylsulfonoxy derivatives of both tritylamines and benzhydrylamines decompose by ionization of the N–O bond that is accompanied by migration of an aromatic group from carbon to nitrogen (eq 2). These systems are highly prone to rearrangment because of the good migrating groups present in these compounds.

$$PhCArRNHOSO_2Ar' \rightarrow PhCR{=}NAr + ArCR{=}NPh \quad (2)$$

R = Ph, H

We wished to determine if carbon-to-nitrogen rearrangement is a general decomposition pathway of *N*-(arylsulfonoxy)amines—even those with poorer migrating groups present—and if so, what structural features influence the products. It was also pertinent to establish whether a polar mechanism is the general decomposition route for *N*-(arylsulfonoxy)amines. To address these issues we prepared a series of *N*-(arylsulfonoxy)amines and studied their decompositions. The results are reported herein.

Results

A series of amines were converted to their corresponding *N*-(*m*-(trifluoromethyl)phenylsulfonoxy) (OTFBs) derivatives by reaction with *m*-(trifluoromethyl)benzenesulfonyl peroxide in ethyl acetate solvent. They were purified by low-temperature silica gel chromatography. Adducts **1**, **4**, **6**, and **7** were sufficiently stable to be isolated whereas adducts **2**, **3**, **5**, and **8** could not be isolated in pure form. Consequently they were generated, purified, and used in situ.

Ethyl acetate or chloroform solutions of adducts **1–8** decomposed slowly at room temperature to give rearranged products (eq 3). The progress of the reaction was monitored by thin-layer chromatography and by testing for the presence of adduct, which gave a positive starch/iodine

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

(2) (a) Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34. (b) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 5687. (c) Hoffman, R. V.; Cadena, R. *Ibid.* **1977**, *99*, 8226.

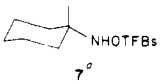
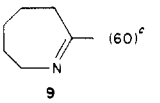
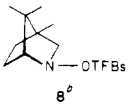
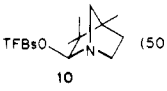
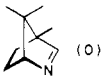
(3) For other attempts to prepare these materials, see: (a) Berlin, A. Y.; Shchukina, M. N.; Sayanova, E. D. *Zh. Obshch. Khim.* **1944**, *14*, 249. (b) Gassman, P. G.; Hartman, G. D. *J. Am. Chem. Soc.* **1973**, *95*, 449. (c) Boche, G.; Mayer, N.; Bernheim, M.; Wagner, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 687. (d) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498, 2448.

(4) (a) Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2183. (b) Hoffman, R. V.; Cadena, R. *Ibid.* **1977**, *99*, 8226. (c) Hoffman, R. V. *Ibid.* **1976**, *98*, 6702.

(5) (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.

0022-3263/85/1950-1859$01.50/0

Table I. Products of Rearrangement of (*N*-Arylsulfonoxy)amines 1–8

starting amine	adduct	product	migrating group	hydrolysis product (% yield[d])
benzylamine	$PhCH_2NHOTFBs$ (1[a])	$PhN{=}CH_2$	Ph	aniline (4)
		$PhCH{=}NH$	H	benzaldehyde (56)
α-methylbenzylamine	$PhCH(CH_3)NHOTFBs$ (2[b])	$PhN{=}CHCH_3$	Ph	aniline (72)
		$PhC(CH_3){=}NH$	H	acetophenone (6)
		$PhCH{=}NCH_3$	CH_3	benzaldehyde (0)
benzhydrylamine	$Ph_2CHNHOTFBs$ (3[b])	$PhCH{=}NPh$	Ph	benzaldehyde (95)
		$Ph_2C{=}NH$	H	benzophenone (0)
tert-butylamine	$(CH_3)_3CNHOTFBs$ (4[a])	$(CH_3)_2C{=}NCH_3$	CH_3	acetone (56)
2-octylamine	$n\text{-}C_6H_{13}CH(CH_3)NHOTFBs$ (5[b])	$n\text{-}C_6H_{13}C(CH_3){=}NH$	H	2-octanone (62)
		$n\text{-}C_6H_{13}N{=}CHCH_3$	$n\text{-}C_6H_{13}$	*n*-hexylamine (0)
		$n\text{-}C_6H_{13}CH{=}NCH_3$	CH_3	heptanal (0)
2-methyl-2-octylamine	$n\text{-}C_6H_{13}C(CH_3)_2NHOTFBs$ (6[a])	$n\text{-}C_6H_{13}N{=}C(CH_3)_2$	$n\text{-}C_6H_{13}$	*n*-hexylamine (41)
		$n\text{-}C_6H_{13}C(CH_3){=}NCH_3$	CH_3	2-octanone (17)
1-methylcyclohexylamine	 7[a]		alkyl ring	 9
		$c\text{-}C_6H_{10}{=}NCH_3$	CH_3	cyclohexanone (0)
4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane	 8[b]		alkyl ring	 10
			H	 11

[a] The *N*-sulfonoxyamine was isolated. [b] The *N*-sulfonoxyamine was generated and used in situ. [c] Products were analyzed without hydrolysis of the reaction mixture. [d] Yields are for isolated yields measured by gas chromatography and are averages for several runs.

test. After decomposition was complete, the structures and distributions of the iminium products were determined by hydrolysis of the reaction mixture and gas chromatographic analysis of the carbonyl and amine components that were produced. The results are collected in Table I.

The rearrangement of *tert*-butylamine adduct **4** proceeded quantitatively (NMR) to the iminium salt of *N*-isopropylidenemethylamine. Addition of water gave acetone, which was converted to its 2,4-DNP derivative (56%). Thus even poorly migrating methyl groups can rearrange to nitrogen in these decompositions.

A variety of migratory patterns were noted in the other substrates. The N–OTFBs derivatives of 2-octylamine (**5**) and benzylamine (**1**) gave mainly products of hydrogen migration. Adduct **5** gave 2-octanone (62%, H migration) but no heptanal (methyl migration) or hexylamine (*n*-hexyl migration). Adduct **1** yielded benzaldehyde (56%, H migration) and a small amount of aniline (4%, phenyl migration). Only phenyl rearrangment was noted for **3**.

α-Methylbenzylamine adduct **2** gave products of both hydrogen migration (acetophenone, 6%) and phenyl migration (aniline, 72%), but no methyl migration was detected. However, *n*-hexyl migration (*n*-hexylamine, 41%) and methyl migration (2-octanone, 17%) were competitive in **6**.

For cyclic compound **7** only ring expansion to azacycloheptene **9** occurred, while norbornyl-type rearrangement occurred exclusively in **8**.

Discussion

The collective results demonstrate that carbon-to-nitrogen rearrangement is a fundamental decomposition pathway of *N*-(arylsulfonoxy)amines. A variety of groups migrate effectively. In all cases, an iminium ion is the first-formed rearrangment product (eq 3). Since these

$$R_1CR_3R_3NHOTFBs \xrightarrow{\leq 25\ ^\circ C} R_2R_3C{=}\overset{+}{N}HR_1 + R_1R_2C{=}\overset{+}{N}HR_3 + R_1R_3C{=}\overset{+}{N}HR_2 \quad (3)$$

products are relatively unstable,[6] the yields of hydrolysis products are somewhat variable. However, the rearrangements of **4** and **7** were monitored by ^1H NMR, and they were found to proceed cleanly and quantitatively. Thus side reactions of the iminium products prior to or during hydrolysis probably give rise to less than quantitative yields of hydrolysis products. Where the iminium product is relatively stable, as in adduct **3**, excellent yields are obtained.

From the product mixtures it is seen that a migration preference of Ph > H ≫ *n*-alkyl > Me holds. From the product data for **2** and **6**, migratory aptitudes were calculated to be Ph > 72, H ≈ 10–12, *n*-alkyl = 4.2, Me = 1.0. From a sampling of migratory aptitudes reported for various rearrangement reactions (Table II) it is seen that migratory aptitudes found for the rearrangements of *N*-(arylsulfonoxy)amines are similar in magnitude to those found for other cationic migrations to carbon (entry 3) and nitrogen (entry 5) but somewhat lower than that for migration to oxygen (entry 4). A nitrene mechanism can be excluded due to the nonselectivity observed for this mechanistic alternative (entries 1, 2). From these comparisons and previous data on the Steiglitz rearrangement of *N*-(arylsulfonoxy)tritylamines and -benzhydrylamines,[5] it is concluded confidently that concerted, cationic rearrangement is the general mode of decomposition in these amine derivatives.

Besides the Steiglitz rearrangement,[12] the most well-

(6) Merenyi, R. In "Iminium Salts in Organic Chemistry"; Bohme, H., Viehe, H. G., Eds.; Wiley: New York, 1976; pp 23–26.
(7) Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.
(8) Montgomery, F. C.; Saunders, W. H., Jr. *J. Org. Chem.* **1976**, *41*, 2368.
(9) (a) Magee, P. S. Ph.D. Dissertation, University of California at Los Angeles, 1955. (b) Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 883.
(10) Hedaya, E.; Winstein, S. *Ibid.* **1967**, *87*, 1661.
(11) Abramovitch, R. A.; Court, J.; Kyba, E. P. *Tetrahedron Lett.* **1972**, 4059.
(12) Smith, P. A. S. In "Molecular Rearrangements"; deMayo, P., Ed.; Wiley-Interscience: New York, 1963; Part 1, pp 457–567.

Table II. Migratory Aptitude Data for Selected Rearrangements

entry	system	migratory aptitudes							ref
		Me	Et	*n*-Pr	*n*-C_6H_{13}	*i*-Pr	H	Ph	
1	$Ph(CH_3)CHN_3$	1					0.7	0.7	7
2	(*n*-Pr)(Et)(Me)CN_3	1		1.05					8
3	$(CH_3)_2CRCH_2OTs$	1				5.3		335	9
4	$(CH_3)_2CROOPNB$	1	45					1.1×10^5	10
5	$(CH_3)_2ArC—N{=}O$	1						<160	11
6	$Ph(CH_3)(H)CNHOTFBs$	1					~10–12[a]	>72	*b*
7	(*n*-C_6H_{13})$(CH_3)_2CNHOTFBs$	1			4.2				*b*

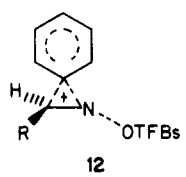
[a] The migratory aptitude for hydrogen is quite variable and depends heavily on the system under investigation. [b] This work.

known reactions that involve migration of a group from carbon to electron deficient nitrogen are the Beckmann rearrangment of oximes and Schmidt reaction of carbonyl compounds with hydrogen azide. However, these two reactions are not good models for the present system since migratory ratios depend heavily on the configuration of migration precursors, not on electronic factors.[12]

Further examination of the results in Table I leads to the conclusion that structural effects at the migration origin are also important in determining migratory aptitudes.[13] Comparison of compounds **1**, **2**, and **3** are instructive since the Ph:H migration ratio changes from 4:56 to 72:6 to >95:1 for this series. Likewise in the rearrangement of **5**, migratory aptitudes of H:*n*-hexyl ≈ 10:4 predict a mixture of products. Instead only H migration is detected; thus H:*n*-hexyl > 62. These changing ratios are consistent with the notion that the electronic character of the migrating group is not the sole factor that determines migratory aptitudes.[13]

This seems quite reasonable since during the migration, charge is developed on the N terminus, the migrating group, *and* the migration origin. Features that help stabilize developing positive charge at the migration origin also contribute to the stability of the transition state for migration.

This influence is clearly demonstrated in the series **1**, **2**, and **3** where the N terminus is a primary nitrogen, the leaving group is the same, and only phenyl or hydrogen migrates. Differences in these systems are related to the ability of groups at the migration origin that do not migrate to stabilize positive charge. The transition-state structures for phenyl, **12**, and hydrogen, **13**, migration illustrate that



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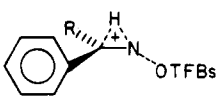


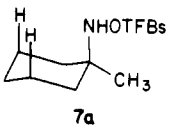
13

phenyl migration in **1**, R = H, leads to positive charge at the origin on a primary carbon while hydrogen migration leads to positive charge at the origin on a benzylic carbon. This large difference in stabilization of charge at the migration origin leads to preferential hydrogen migration and masks the normally higher mobility of the phenyl group. Substitution at the origin in **2**, R = methyl, and **3**, R = Ph, results in increasing stabilization of charge at the origin, and the inherently greater migratory mobility of phenyl over hydrogen is increasingly manifested.

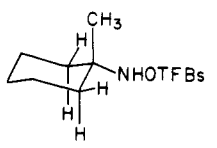
The same argument is applicable to **6** wherein hydrogen migration proceeds via a tertiary migration origin, while *n*-hexyl migration gives a secondary migration origin. A single product from H migration is formed, rather than a mixture.

The results for **7** and **8** (Table I) suggest that rearrangements in *N*-(arylsulfonoxy)amines can also be influenced by the stereoelectronic disposition of the migrating groups. Cyclohexyl adduct **7** gave only ring-expanded **9**; no methyl migration was detected. Furthermore bicyclic adduct **8** delivered only rearranged **10**; no hydrogen migration of imine **11**[14] could be detected. From the migratory aptitudes of groups determined in **2** and **6**, mixtures of rearranged products are expected.

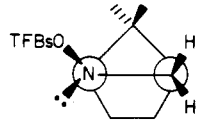
One explanation for the observed selectivities is that there is a strong requirement for an antiperiplanar orientation between the migrating group and the leaving group. In either conformer of **7**, peri interactions of the *N*-arylsulfonoxy group with the 3,5-protons in **7a** or the 2,6-



7a



7e



8

protons in **7e** enforce an antiperiplanar relationship of the ring bonds, which causes them to migrate preferentially. In contrast, the acid-promoted decomposition of 1-alkyl-1-cyclohexyl azides gives products of both ring expansion and alkyl migration.[15] Thus *N*-(arylsulfonoxy)amines appear to be quite sensitive to stereoelectronic factors when they are present in the molecule.

Likewise for compound **8**, it is seen that the 1,6-bond is favorably disposed to migrate whereas the endo 3-proton makes a dihedral angle of 120° with the departing leaving group. Thus again, stereoelectronic requirements override normal migratory preferences.

These data clearly emphasize that there is certain danger in comparing migratory aptitudes from different reactions as a way to reliably distinguish mechanistic alternatives. In order for such comparisons to be valid, different systems should have comparable structure at the migration origin and should not be stereoelectronically constrained. Differences in migratory aptitude are especially pronounced for hydrogen. As seen above, the phenyl:hydrogen migration ratio and the hydrogen:alkyl migration ratio vary widely. The migratory aptitude of hydrogen is known to vary unpredictably.[13] The migration of hydrogen often leads to a different cation type (primary, secondary, or

(13) For an excellent discussion of this factor, see: March, J. A. "Advanced Organic Chemistry", 2nd Ed.; McGraw-Hill: New York, 1977; pp 969–971. See also ref 12, pp 473–475.

(14) Gassman, P. G.; Uneyama, K.; Hahnfeld, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 647.

(15) (a) Lakritz, J. Ph.D. Thesis, University of Michigan, 1960, cited in ref 12, p 474. (b) For other examples of the Schmidt reaction, see: Boyer, J. H.; Canter, F. C.; Hamer, J.; Putney, R. K. *J. Am. Chem. Soc.* **1956**, *78*, 325. Boyer, J. H.; Canter, F. C. Ibid. **1955**, *77*, 3287. Yukawa, Y.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **19578** *78*, 1049. Fikes, L. E.; Shechter, H. *J. Org. Chem.* **1979**, *44*, 741. This reaction is not completely understood so migratory aptitude data may not be strictly comparable to those determined in this study.

tertiary) at the migration origin than migration of carbon-containing groups. Thus structural features at the migration origin are much more important for hydrogen migration, and the inherent migratory ability of hydrogen is masked.

If these factors are kept in mind, the valid use of migratory aptitudes as mechanistic probes depends mostly on their magnitudes, not on their specific order.

Conclusions

Amines can be converted readily to their *N*-arylsulfonoxy derivatives. These materials undergo smooth skeletal rearrangement to iminium products by a concerted, cationic process that has distinct electronic requirements at the migration origin and is subject to stereoelectronic control in appropriate substrates. This reaction provides a new general method to easily functionalize the nitrogen atom of amines in such a way that nitrogen is the reaction center for subsequent cationic transformations.

Experimental Section

Proton magnetic resonance spectra were taken on a JEOL PS-100 instrument using Me_4Si or DSS (aqueous solution) as the internal reference. 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 an Aerograph A90-P3 instrument with thermal conductivity detectors and helium carrier gas. Columns used in this study were as follows: (A) 6 mm × 2.5 m, 5% QF-1 on Anachrome ABS support, carbonyl products, and (B) 6 mm × 3 m, Carbowax 20M–2% KOH on Anachrome ABS support, amine products. Thin-layer chromatography utilized Eastman chromatogram sheets of silica gel with fluorescent indicator. Melting points are uncorrected.

Benzylamine, benzhydrylamine, *tert*-butylamine, and α-methylbenzylamine were all purchased from Aldrich Chemical Co. Solvents were reagent grade and were used as received.

2-Octylamine was prepared from 2-octanone by conversion to the oxime,[16] which was reduced with sodium in ethanol.[17]

2-Methyl-2-octylamine was prepared from 2-octanone by the following two-step sequence. 2-Octanone was reacted with methylmagnesium bromide to give 2-methyl-2-octanol,[18] which was converted to 2-methyl-2-octylamine by the Ritter reaction with HCN.[19]

1-Methylcyclohexylamine was prepared from cyclohexanone by the same methyl Grignard addition[18] and Ritter reaction[19] sequence as described for 2-methyl-2-octylamine.

4,7,7-Trimethyl-2-azabicyclo[2.2.1]heptane was prepared by the route outlined by Gassman.[20]

Preparation of OTFBs Derivatives of Amines. The procedure described earlier[2] was used with slight modification. To a stirred solution of the amine (4 mmol) in ethyl acetate (30 mL) at −78 °C under nitrogen was added *m*-(trifluoromethyl)-phenylsulfonyl peroxide[21] (2.1 mmol). The flask was flushed with nitrogen, stoppered, and stirred at −78 °C. A silica gel column (230–400 mesh, EM Reagents) that was 4 cm high was prepared in a sintered-glass funnel (3-cm diameter). The silica gel was washed with ethyl acetate (25 mL); suction filtration was used to wet and pack it. A disk of filter paper was placed on top of the column, and the funnel was wrapped in aluminum foil, and cooled with dry ice held in contact with a second layer of foil. After 2 h of stirring, the reaction mixture was vacuum filtered through the silica gel column into a receiver cooled in a dry ice bath. Additional cold (−78 °C) ethyl acetate (40 mL) was eluted through the column. This procedure gave solutions of adducts 1–8 that were pure by TLC (silica gel, chloroform).

Adducts **1**, **4**, **6**, and **7** could be isolated as solids by removal of solvent at low temperature (−30 °C) and high vacuum (<0.1 torr). Adducts **1** and **4** were reported earlier.[2] The low-temperature NMR spectrum of **6** is as follows: δ 0.88 (br s, 9 H, methyl H), 1.16 (m, 10 H, methylene H), 5.32 (br, 1 H, NH), 7.6–8.25 (m, 4 H, aromatic H). Adduct **7**: δ 0.92 (s, 3 H, methyl H), 1.32 (br m, 10 H, ring methylene H), 5.0 (br, 1 H, NH), 7.6–8.25 (m, 4 H, aromatic H). Both **6** and **7** were insufficently stable to obtain further spectral characterization or elemental analysis. However, they showed only a single component by TLC analysis (silica gel, chloroform) and exhibited chromatographic behavior different from any of the starting materials; no extraneous absorptions (other than traces of solvent) were observed in the NMR, and they were >85% pure by iodometric titration. These materials can be stored at −78 °C for long periods, but storage at −20 °C (freezer) led to some decomposition after several days.

Adducts **2**, **3**, **5**, and **8** underwent rearrangement upon attempted solvent removal and therefore purified solutions were employed without isolation.

Rearrangments of Adducts 1–3, 5, and 6. A solution of the adduct in ethyl acetate was stirred at room temperature until no adduct was detected (typically overnight) by iodometric analysis (KI–HOAc). The solvent was removed by rotary evaporation at room temperature, and aqueous acid (2.5 M HCl, 60 mL) was added to the residue. The mixture was steam-distilled until 35 mL of distillate was collected. The steam distillate was treated with saturated sodium bicarbonate (10 mL) and extracted with methylene chloride (2 × 10 mL). The organic extract was dried (magnesium sulfate) and analyzed for carbonyl components by gas chromatography on column A after addition of a suitable internal standard. The acidic aqueous residue from the steam distillation was basified with potassium hydroxide (pH >14), and extracted with methylene chloride (3 × 10 mL); the organic extracts were dried (potassium carbonate) and analyzed for amine components by VPC on column B after addition of a suitable standard. The results are found in Table I. Products were identified by comparison of VPC retention times and NMR spectra with those of authentic compounds that were obtained commercially (Aldrich).

Rearrangement of 4. A chloroform solution of **4** (2 mmol) was stirred at room temperature until iodometric analysis showed no **4** remained. (It was shown earlier by NMR that **4** gives the *N*-methyliminium salt of acetone quantitatively under these conditions.[2]) Several drops of water were added, and after the mixture was stirred for 30 min, a solution of 2,4-DNPH (2.6 mmol) in ethanol (40 mL) was added followed by concentrated HCl (0.2 mL). The mixture was warmed on the steam bath (1 min) and stirred at room temperature (15 min), and the solvents were removed in vacuo. Chromatography of the residue (silica gel, benzene) gave the 2,4-DNP derivative of acetone (56%), mp 123–124 °C (lit.[22] mp 126 °C).

Rearrangement of 7. 1-Methylcyclohexylamine adduct **7** (1 mmol) was dissolved in either chloroform or ethyl acetate (25 mL) and stirred until the starting material was gone (36 h). The solvent was removed by rotary evaporation, and the residue was treated with 5% aqueous sodium hydroxide and extracted with methylene chloride (3 × 15 mL). Drying and evaporation of the solvent gave 2-methylazacycloheptene (60%) which was identical by IR and NMR with an authentic sample prepared by the procedure of Sommers.[23]

In another experiment, aqueous HCl was added to the reaction after removal of the solvent. The mixture was steam-distilled, and the distillate was worked up and analyzed as above. No cyclohexanone was detected in the products.

Rearrangement of 8. 4,7,7-Trimethyl-2-azabicyclo[2.2.1]-heptane adduct **8** was prepared and purified in ethyl acetate solution. After decomposition of the adduct was complete at −20

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°C (overnight), the solvent was removed, the residue was basified with 20% sodium hydroxide, and the mixture was extracted with ether. The ether extract was dried (sodium sulfate) and analyzed by gas chromatography for imine **11**. None was detected. The ether was removed to give a yellow solid, which was identified as rearranged **10** (50%).[24]

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(24) Full characterization of this material has been reported: Hoffman, R. V.; Kumar, A.; Buntain, G. A. *J. Am. Chem. Soc.*, submitted for publication.

Registry No. 1, 80953-41-9; 2, 96040-82-3; 3, 96040-83-4; 4, 85462-15-3; 5, 96040-84-5; 6, 96040-85-6; 7, 96040-86-7; 8, 96040-87-8; 9, 3338-03-2; 10, 96040-89-0; 11, 62150-62-3; $PhCH_2NH$, 100-46-9; $PhCH(CH_3)NH_2$, 98-84-0; Ph_2CHNH_2, 91-00-9; *t*-$BuNH_2$, 75-64-9; $CH_3(CH_2)_5CH(NH_2)CH_3$, 693-16-3; $CH_3(CH_2)_5C(CH_3)_2NH_2$, 2626-63-3; $PhN{=}CH_2$, 100-62-9; $PhCH{=}NH$, 16118-22-2; $PhN{=}CHCH_3$, 6052-11-5; $PhC(CH_3){=}NH$, 13280-20-1; $PhCH{=}NCH_3$, 622-29-7; PhCH=NPh, 538-51-2; $Ph_2C{=}NH$, 1013-88-3; $(CH_3)_2C{=}NCH_3$, 6407-34-7; *n*-$C_6H_{13}C(CH_3){=}NH$, 64030-07-5; *n*-$C_6H_{13}N{=}CHCH_3$, 96040-88-9; *n*-$C_6H_{13}CH{=}NCH_3$, 6898-71-1; *n*-$C_6H_{13}N{=}C(CH_3)_2$, 32838-32-7; *n*-$C_6H_{13}C(CH_3){=}NCH_3$, 18641-72-0; c-$C_6H_{10}{=}NCH_3$, 6407-35-8; $CH_3(CH_2)_5C(O)CH_3$, 111-13-7; $CH_3(CH_2)_5C(CH)_3{=}NOH$, 7207-49-0; $CH_3(CH_2)_5C(CH_3)_2OH$, 628-44-4; MeMgBr, 74-83-9; 1-methylcyclohexanamine, 6526-78-9; cyclohexanone, 108-93-0; 4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane, 18715-80-5.

Kinetics and Mechanism of the Reactions of *S*-Ethoxycarbonyl *O*-Ethyl Dithiocarbonate with *O*-Ethyl Xanthate and *O*-Ethyl Thiocarbonate Ions

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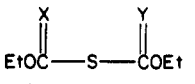
The forward and back reactions of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (**1**) with *O*-ethyl thiocarbonate (**4**) and *O*-ethyl xanthate (**5**) in 95% ethanol are studied kinetically. The back reaction products are bis(ethoxycarbonyl) sulfide (**3**) with **5** and bis(ethoxythiocarbonyl) sulfide (**2**) with **4**, respectively. Compound **1** reacts faster than **2** with **4**, which means that the carbonyl group is more reactive than the thiocarbonyl toward **4**. On the other hand, the reaction of **5** with **1** is faster than that with **3**, which indicates that **5** reacts more readily with the thiocarbonyl than the carbonyl group. Two mechanisms are proposed to account for the kinetics results: one through tetrahedral intermediates (two-step reactions) and the other concerted. The reactions of **4** exhibit $\Delta S^{\ddagger} > 0$, whereas those of **5** show $\Delta S^{\ddagger} < 0$. These ΔS values are explained by a larger solvation of **4** relative to **5** and similar degrees of solvation of transition states and substrates. The observed activation parameters do not allow discrimination between the two mechanisms.

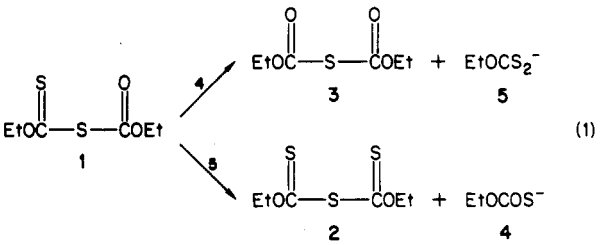
In previous studies we have described the reactions of *S*-ethoxycarbonyl *O*-ethyl dithiocarbonate (**1**) with primary and secondary amines in ethanol.[1] In addition to the carbamates and thiocarbamates formed by attack of the amines at the carbonyl and thiocarbonyl groups of **1**, the formation of bis(ethoxythiocarbonyl) sulfide **2** and bis(ethoxycarbonyl) sulfide **3** was observed. The latter compounds were produced by reactions of **1** with *O*-ethyl thiocarbonate **4** ion and *O*-ethyl xanthate **5** ion, which had been formed by in aminolysis of **1**.



1, X=S, Y=O
2, X=Y=S
3, X=Y=O

4, X=O
5, X=S

In a study of the thiolyses of **1** with **4** and **5** (eq 1) in ethanol at 0 °C, we found that the disappearance of **1** in its reaction with **5** was faster than that with **4**, which suggested that the thiocarbonyl group of **1** was more reactive than the carbonyl toward these ions.[2] However, this comparison is uncertain because **1** was in excess over **4** and **5**, and the reactions were complicated by reverse attack on **1** by the product ions **5** and **4**, respectively.



(1)

In order to shed more light on the reactivities of carbonyl and thiocarbonyl groups toward thioanions, we report in this paper a kinetic study of the reactions of **1** with **4** and **5** in ethanol and also the corresponding reverse steps: the reactions of **3** with **5** and **2** with **4** in the same solvent, where **4** and **5** are in excess over the substrates.

Experimental Section

Materials. The syntheses of **1**,[3] **2**,[4] **3**,[4] the potassium salt of **4**,[5] and the sodium salt of **5**[6] have been described previously. Ethanol (95%) and the chemicals used in the analyses (benzene, hydrochloric acid, sodium carbonate, and methyl caproate) were analytical reagent grade. Ethanolic solutions of **4** and **5** were freshly prepared prior to use.

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