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THE CHELETROPIC FRAGMENTATION OF HYPERVALENT THREE-MEMBERED THIAHETEROCYCLIC INTERMEDIATES

URI ZOLLER*

Division of Chemical Studies, Haifa University-Oranim
P.O. Kiryat Tivon 36910, Israel

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Abstract: Lithio-imidazolium salts 10, generated *in-situ* from N,N-dimethylimidazolium salts 9, readily undergo sulfonylation with sulfur dioxide, sulfines, N-sulfinylamines, and thiirane. The resulting zwitterionic species 4 fragment thermally to yield the corresponding imidzaolium thione 5 with the hypervalent three-membered thiaheterocyclic intermediates 3 connecting 4 and 5 on the reaction surface.

The non-linear cheletropic fragmentation of these relatively stable hypervalent sulfuranes appears to be general for this class of compounds (3 or 4), and the experimental results are in accord with theoretical considerations.

Introduction and Background

Three-membered thiaheterocycles are a well-known class of compounds[1-3] as are the hypervalent sulfuranes.[4-6] Both classes have been extensively studied and their structural features, chemistry, and reaction mechanisms are well-established.[1-6]

While the whole spectrum of three-membered CCS ring systems (e.g. the sulfur atom at different oxidation states) is known to date, only one of each of the corresponding CNS and NNS ring systems (i.e., thiaziridine dioxides[7] and thiadiaziridine dioxides[8] respectively) have been synthesized, characterized and their chemistry studied thus far.[1-2] On the other hand, thiadioxiranes, thiaoxiranes and thiaoxaziridines having the structure represented by either 1 or 2 are as yet elusive although their existence as intermediates (e.g. 1 a[6,10], 2 b[1,11]) along the reaction coordinate of some chemical transformations has been proposed.[1]


1


2

a. X=Y=O; b. X=CRR,Y=O; c. X=NR,Y=O

Recently, the intermediacy of dithiiranes, the sulfur analoges of 1a (i.e. 1, X=Y=S) has been advocated[12] and considered[13].

Hypervalaent three-membered thiaheterocycles of type 3 not only are not known to date, but even their possible intermediacy has been only very recently invoked.[10]

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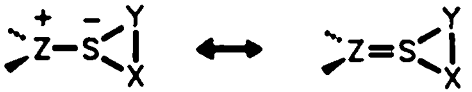
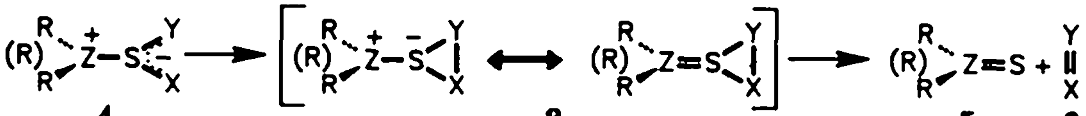
*On sabbatical (1987-1988) at the University of British Columbia, Department of Chemistry, Vancouver, British Columbia, Canada


(i) 3 (Z=C or P) (ii)

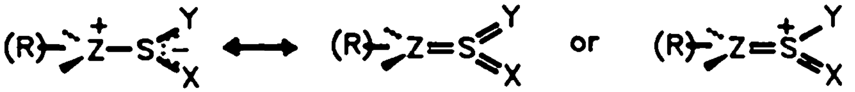
Within the framework of our pursuit of these as yet elusive three-membered thiaheterocycles, we searched for an appropriate reaction sequence along the reaction coordinate of which a) stabilized hypervalent species of type 3 might be formed under relatively mild conditions; b) the fragmentation of 3 will lead to the isolation of characterizable products from which the intermediacy of 3 could be confidently inferred; and c) the mode of fragmentation of the intermediates 3 will provide some insight into the manifestation (and generality) of the principles of conservation of orbital symmetry[14] in hypervalent, thia three-membered ring systems.

We reasoned[10] that an energetically low-lying unoccupied molecular orbital (LUMO) of the π-type attached to sulfur will stabilize a tricoordinate hypervalent sulfurane bonding array 3, provided the latter is potentially capable of being formed from an appropriate precursor. Furthermore, the unique geometric and electronic constraints of such systems should eventually, under mild theromolytic conditions, induce a cheletropic-type fragmentation of the three-membered ring with the concomitant formation of the corresponding thiones and unsaturated systems (i.e. 5 and 6 respectively) as illustrated below:


4 3 5 6

The above expected reverse [n+1] cycloaddition reaction[15] in which the hypervalent three-membered thiaheterocycle 3 is destroyed is of special interest in that the geometric factors require it to take place in a disrotatory, or suprafacial manner.[14] Consequently, this fragmentation must occur by the non-linear cheletropic path (the cyclic transition state contains 4 MOs) similar to the non-linear cheletropic extrusion of sulfur dioxide from thiirrane dioxides which is a symmetry-allowed $[\sigma 2_s + \sigma 2_a]$ reaction.

Since, in principal, three-membered second-row heterocycles constitute parts of potential energy surfaces which also comprise acyclic species[16] (i.e. 3'iii in the case of 3), the intermediacy of the hypervalent three-membered ring 3i as well its relative energy content have some bearing on the question of which one of the structural isomers (i.e. 3ii or 3'iii) constitutes the deepest energy miniumum.


3'iv 3'iii 3'v

The highly reactive sulfenes[17] and the known thiourea dioxides[19] are represented by of 3'aiii (Z=C; X=Y=O), whereas the isolable stable trialkylamine-sulfur dioxide complexes $R_3\overset{+}{N}\text{-}SO_2^{-}$[19] are represented by 3'd iv (Z=N; X=Y=O). The acyclic structural isomers of thiaoxiranes 3b (Z=C; X=CRR; Y=O) and 3c (Z=C; X=NR; Y=O) are unknown today.

A combination of three major aspects of interest and concern are the focus of the study presented herein:

a. Three membered thiaheterocycles, particularly thiadioxiranes, thiaoxiranes and thiaoxaziridines and their thermodynamical stability (σ aromaticity[15] and stability in three-membered ring thiaheterocycles[1]).

b. Hypervalent sulfur incorproated within a tricoordinate hypervalent three-membered ring sulfurane bonding array.

c. Cheletropic extrusion of thiones from hypervalent three-membered thiaheterocycles.

We present evidence that indeed hypervalent three-membered ring systems of type 3 are involved in the transformation 4 → 5 + 6 represented above, and that the nonlinear cheletropic fragmentation path of 3 to 5 + 6 appears to be a general pattern in the thermolysis of these and closely-related systems. Our experimental results will be discussed in terms of

a. the expected formation of the hypervalent species 3 from 4 and their thermodynamic stability;

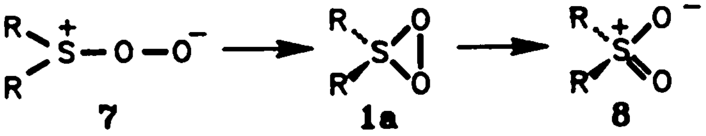
b. the stabilizing effect of the adjacent energetically LUMO of the π-type system on the hypervalent sulfur as well as on the mode of fragmentation of the three-membered ring sulfurane 3;

c. the predicted and the actually observed final products derived from the fragmentation of 3; and

d. the plausible mechanism by which the observed transformations can be accounted for and the nature of the species involved.

Results and Discussion

Strategy: It was shown that persulfoxides 7 which result from the action of singlet oxygen on sulfides[20] or hydrogen peroxide on trialkoxysulfuranes[9] can be ultimately converted (in the absence of oxidizable reagents) into the sulfone 8 possibly via the hypervalent thiadioxirane 1a.[10,21]

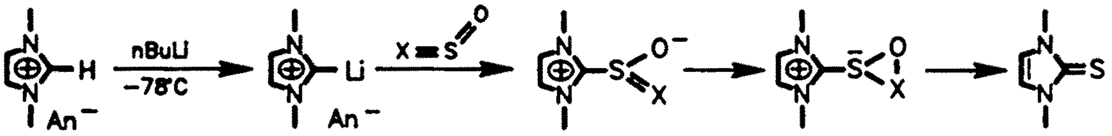


Also it has been reported, that diaminocyclopropenium[22] and dihydrodiazepinium[23] salts may be lithiated followed by electrophilic substitution of the lithiated site.[22]

Similarly lithiation of imidazolium salts 9 should lead to lithiocarbenium ions 10 which would readily undergo SE reactions with electrophiles of type 11 (i.e. sulfur dioxide, sulfines, N-sulfinylamines, and even, probably, thiiranes, the sulfur serving as the electrophilic site to afford 4. We expected that the generated zwitterion species 4a-c should eventually rearrange to give the hypervalent three-membered ring intermediates 3a-c since the latter would be stabilized by the energetically low-lying, unoccupied molecular orbital (LUMO) of the π-type of the imidazolium electron acceptor system adjacent to the hypervalent sulfur. Thermal cheletropic dethionylation of 3 should be facilitated by both the unique stability of the thione 5a and the irreversibility of this fragmentation.

The ultimate result would then be <u>reversal</u> of the transformation 7 → 8 with the intermediacy of 3a-c on the reaction surface connecting 4 and 5, if the lithiated imidazolium ions 10 would be treated with sulfur dioxide,[10] sulfines, and N-sulfinylamines.

The general scheme is shown below:



9 10 11 4a−c 3 5a

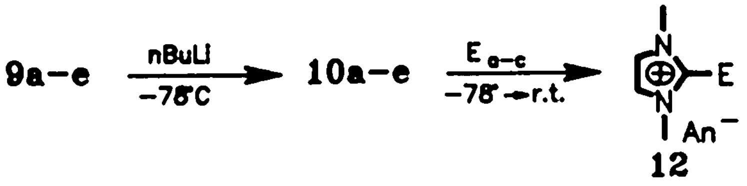
a. An=Br
b. An=CF_3SO_3
c. An=I
d. An=BF_4
e. An=ClO_4

a. X=O
b. X=CR
c. X=NR

Lithio-imidazolium salts 10 and their SE reaction with weak electrophiles: The very hygroscopic starting imidizaolium salts 9a-d were prepared, in practically quantitative yields by the treatment of 1-methylimidazole with an equimolar amount of the alkylating agent (CH_3Br, $CH_3OSO_2CF_3$, CH_3I, $(CH_3)_3O^+BF_4^-$ respectively), and 9e by the exchange of the bromide anion of 9a with the perchlorate anion of sodium perchlorate in methylene chloride solutions (see experimental section).

Lithiation of the imidazolium salts 9 was easily achieved within a few minutes by treatment of their stirred <u>suspensions</u> in aprotic solvents (methylene chloride, tetrahydrofuran, or diethyl ether) with equimolar amounts of n-butyllithium at -78°C under inert atmosphere. The formation of the lithiated species, to which we assigned the structure depicted in 10, was evident from both the clear homogeneous solutions obtained just after the completion of the addition of the base, and the fast quenching of 10 with weak electrophiles to yield 2-substituted imidazolium salts. It should be noted that except for the triflate imidazolium salt 9b, which is soluble in methylene chloride and THF, all the others (i.e. 9a,c-e) are <u>insoluble</u> in aprotic solvents. Significantly, the solutions of the resulting organometallic species 10, remained homogeneous on allowing the reaction temperature to reach up to about -40°C. Neither suspension of 9a in diethyl ether nor of 9e in THF afforded clear homogeneous solutions after being treated with n-Bufi even under high dilution conditions. These observations casted some doubt concerning the use of ether as a solvent or imidazolium perchlorate salt in the final step of the designed scheme. Quenching of the homogeneous solution of lithiocarbenium ion 10 with D_2O, CH_3Br and Ph_2PCl resulted in an immediate appearance of turbidity and afforded the 2-deuterated (quantitatively), 2-methylated, and 2-phosphinated imidzaolium salts 12a-c respectively as shown below. Recovered started materials 9 were the only other products in these lithium/SE reactions.

The above results set the stage for the crucial part of the designed scheme. In following the same protocol, the treatment of the lithiated species 10 with the electrophilic sulfur dioxide as well as with its C- and N-analogues (i.e. sulfines and N-sulfinylamines



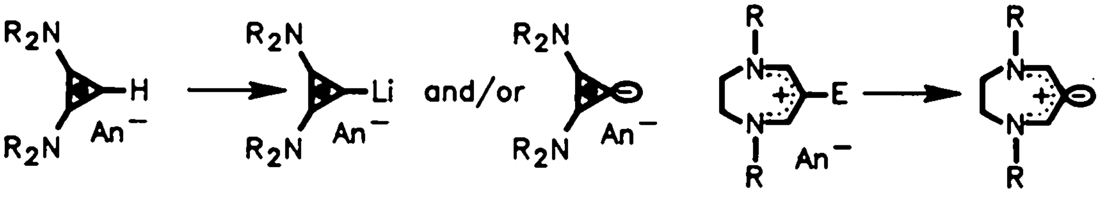
E_a=D_2O a. E=D; An=Br or OTf

E_b=CH_3Br b. E=CH_3; An=Br

E_c=Ph_2PCl c. E=PPh_2; An=Cl

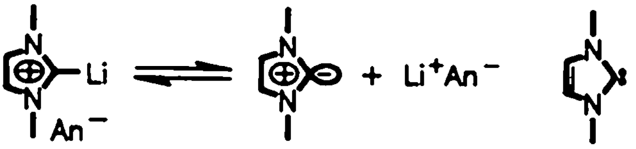
respectively) should lead smoothly to 4a-c which, in turn, are expected to give 5a via the intermediacy of the hypervalent three-membered ring sulfuranes 3a-c (see above).

On the nature of the lithiocarbenium ion 10: Diaminocyclopropenium[22] and dihydroazepinium[23] salts (13 and 15 respectively) are electronically similar to the imidazolium salts 9. It has been postulated that an onium ion 14b is formed as an intermediate in a number of reactions[24] and that a similar onium-anion species (i.e. 16) is formed in the vinamidium system 15 .[25] In addition, a short-lived carbene was produced from the N-methylbenzthiazolium salt.[26]



13 14a 14b 15 16

Therefore, both 10a and 10b as well as the carbene 10c should be considered as possible structures of the lithiated imidazolium species 10 in the aprotic solvent solutions:



10a 10b 10c

Clearly, under our reaction conditions, no "free" onium-anion species of type 10b is present since its formation would be accompanied by precipitation of the corresponding molar equivalents of LiAn (e.g. An = Br, OTf, I, etc.) which are insoluble in the solvent media-methylene chloride or tetrahydrofuran (LiOTf, however, is soluble in THF). Since the suspensions of the imidazolium salts 9 turned into clear homogeneous solutions on lithiation, we must conclude that in our case the lithiated imidazolium species are more likely to be 10a. This is in accord with analogous lithiated species (i.e. 14a) suggested as the . actual intermediates in similar reactions performed on the diaminocyclopropenium system[22,27] and in contrast to the "free" onium-anion 16 proposed[25] in the dihydrodiazepinium series

The turbidity immediately developed within the clear cold homogeneous solutions of

10a following the addition of the electrophiles is a result of the insolubility of both the 2-substituted products (i.e. 12a-c) as well as the released LiAn salts in the organic solvents. In the case of the triflate 9b in THF, the developed turbidity is due solely to the product, since $LiOT_f$ is soluble in THF. Similar protonations[22], alkylations[22] and phosphinations[24], under comparable reaction conditions, gave similar results. This supports the validity of the proposed structures 10a and 14a for the lithiocarbenium ion species. A contribution of a carbene structure (10c) is highly unlikely since on theoretical grounds this would require a considerable loss of resonance stability and on experimental grounds this would require the obtaining of the corresponding tetraminoethylene dimer.[26,28] No dimers (e.g. 24) could be detected in our hands in the treatment of salts 9 with BuLi under a variety of reaction conditions.

Hypervalent three-membered sulfuranes and their fragmentation: The results of the experiments in which the lithiated salts 10 were treated with sulfur dioxide[10], sulfines, and N-sulfinylamines are summarized in Table 1.

Table 1. Yields of Imidazole Thione (5a) in Sulfonylation of Lithiated N,N-dimethylimidazalium Salts 10a,b.

Entry	Starting Salt	Sulfonylating Agent	Solvent	Reaction Time (hours)	Yield of 5a (%)	Other Products Isolated (or identified)
1[10]	9a	sulfur dioxide	$(C_2H_5)_2O$	20	36.8	9a(a), O_2[10]
2[10]	9a	sulfur dioxide	CH_2Cl_2 or THF	>12	trace	9a
3[10]	9b or 9e	sulfur dioxide	CH_2Cl_2 or THF	>12	0	9b or 9e
4	9a	Fluorenethione-S-oxide(b) (17)	CH_2Cl_2	5	33.7	18, 19, 9a
5	9a	Fluorenethione-S-oxide(b) (17)	CH_2Cl_2	28	40.5	18(c), 19(c), 9a
6	9b	Fluorenethione-S-oxide(b) (17)	THF	18	26.2	18, 19, 9b
7	9b	Fluorenethione-S-oxide(b) (17)	THF	96	60.9	18(d), 19(d), 9b
8	9b	Di-t-butyl-thione-S-oxide(b)	THF	19	trace	9b
9	9b	N-sulfinyl-p-toluene-sulfonamide(e)	THF	15	21.1	
10	9b	N-sulfinyl-p-toluene-sulfonamide(e)	THF	24	24.9	9b, p-TSAm(f)(h)
11	9b	N-sulfinyl aniline(e)(g)	THF	100	2.3	9b, aniline
12	9a	Thiirane	CH_2Cl_2	18	7.0	9a
13	9b	Thiirane	THF	20	2.4	9b

(a) At no time did the reaction mixture become homogeneous in this entry.[10]
(b) Sulfine
(c) Yields: 18-18.8%; 19-16.6% (based on the fluorenethione-S-oxide used).
(d) Yields: 18-34%; 19-43% (based on the fluorenethione-S-oxide used).
(e) N-sulfinylamine
(f) Para-toluenesulfonamide
(g) Anilinethionyl chloride
(h) The hydrolyzed starting sulfonylating agents.

Significantly, in each of the runs associated with the transformations 4a-c → 5a, the recovered starting imidazolium salt 9 complimented almost to quantitative yield (based on 9) the yields of the thione 5a. The origin of the other products obtained and identified is the electrophilic counterpart.

SCF-MO calculations revealed that the lowest energy mode of decomposition of species of type 4 is dissociation into the singlet carbene-sulfur dioxide complex lying only a few kcal above the bound sulfur dioxide.[10] Consequently, the equilibrium of 10 and 11 (sulfur dioxide or sulfine, or N-sulfinylamine) with 4 accounts for the isolation of substantial amounts of the starting imidazolium salts 9 after the work-up at the end of the long-time duration sulfonylation-thionation reactions (e.g. 10 ⟶ 5a).

The fact that thione 5a and the recovered starting imidazolium salt 9 appear to be the only products originated in 9 in the transformation 9 → 10 → 4 → [3] → 5 strongly suggests that:

a) *the yield of 5a is actually the ultimate conversion percentage of both 9 and 3 to 5a under the reaction conditions employed;*

b) *the hypervalent three-membered thiaheterocycle 3 is indeed the intermediate connecting 4 and 5 on the reaction surface;*

c) *the stabilizing effect of the LUMO of the imidazolium π-system on the adjacent incipient hypervalent sulfur is considerable enough to facilitate the rearrangement of 4 to 3;*

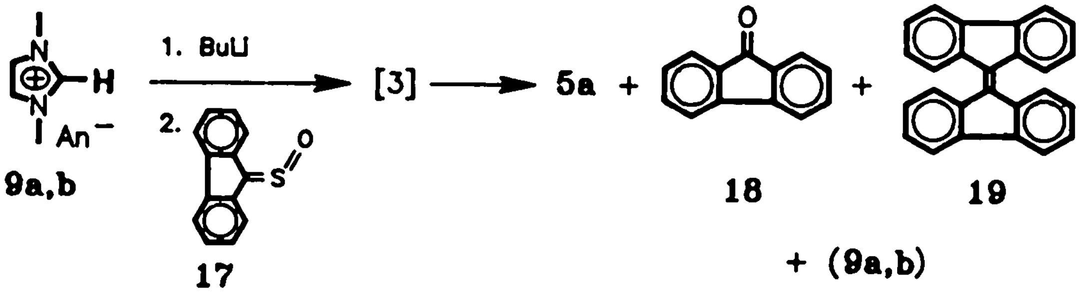
d) *once formed, the three-membered ring sulfurane 3 has a life-time sufficient (before collapsing back to the highly resonance-stabilized acyclic switterionic isomer 4) for undergoing a cheletropic fragmentation leading to 5a; and*

e) *the thermally-allowed cheletropic fragmentation of 3 to give 5a is energetically the most favored one available to this intermediate in its ground state.*

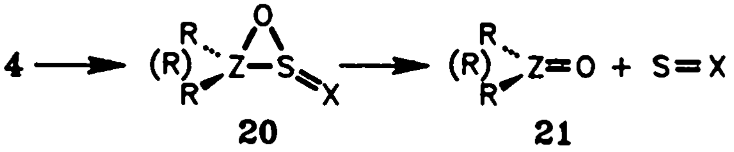
We do not have as yet any direct evidence about the relative "steady state" concentrations of 4 and 3 (e.g. $\longrightarrow [4] \rightleftharpoons [3] \longrightarrow$) within the overall set of equilibria prevailing in the multistep transformation of 9 to 5a. We did establish, however, that the kinetics of the fragmentation of species of type 4 (e.g. 4 d: R=NH_2, Z=C, X=Y=O; and 4e: R=n-Butyl, Z=C, X=Y=O) is of the first order with composites of $k_1=1.0\times10^{-4}$[10] (in CD_3CN; 45°C) and $k_1=1.2\times10^{-4}$(in DMSO-d_6; 85°C) for 4 d and 4 e respectively. These results indicate that the hypervalent three-membered thiaheterocycles 3 enjoy considerable thermodynamic stability which can be accounted for in terms of the δ aromaticity[15] largely confined to molecules with three-membered rings including three-membered ring heterocycles (e.g. thiranes, oxiranes, aziridines). Indeed, the latter resemble cyclopropane in exhibiting unexpected stability combined with unusual chemical behaviour.[15]

Inspection of Table 1 reveals three important aspects associated with the described transformations: they are highly solvent-dependent (entries 1,2). They are time-dependent (entries 4,5; 6,7; 9,10). In the case of the sulfine 17, an additional product (i.e. 19) is being formed, on top of the thione 5a, and the expected product 18 which result as a consequence of the cheletropically extruded thione. Also some recovered starting imidazolium salt 9(a,b) is obtained.

The remarkable solvent effect being most pronounced in the case of the sulfur dioxide as the sulfonylating agent[10], can be rationalized (speculatively as yet) in terms of stabilized, solvated organo-lithium species in ether, compared with the competitive reaction of the lithium reagent with the solvent in methylene chloride[29] and the acid-base type THF:SO_2 complex in tetrahedrofuran. This observed solvent-dependency could be expected, however, since strong solvent effects in electrophilic reactions[31] and, particularly, the sensitivity of many reactions of sulfur dioxide to the solvent used is well-documented.[32] Both time-dependency and the salt's anion-type dependency of the yields of thione 5a can be accounted for in terms of the cyclization (4 → 3) and fragmentation (3 → 5 + 6) rates and the relative solubility of both salts 9 and 10 in the solvent media respectively.

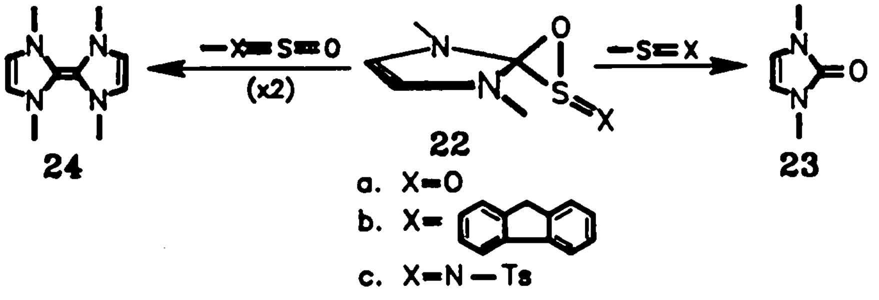


As we previously reported[10], thiourea dioxides (i.e. 4 : R=NR$_2$; Z=C, X=Y=O) and phosphine sulfide-S-dioxides (i.e. 4: R=Aryl & N-alkyl; Z=P; X=Y=O) yield on thermolysis the corresponding ureas and thioureas and the phosphine oxides and phosphine sulfides respectively. The intermediacy of a three-membered sultine 20 was proposed[10] to account for the formation of both ureas 21a and phosphine oxides 21b in these transformations.



a. R=NH$_2$ or NHR; Z=C; X=O
b. R=Aryl or N(alkyl)$_2$; (R)=N(alkyl)$_2$; Z=P

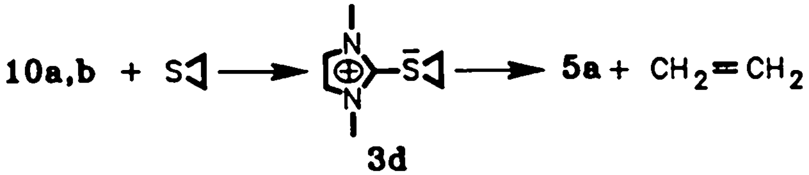
Analogous spiro three-membered ring intermediates in the case of the sulfonylated imidazolium species, (e.g. 21a-c) are highly unlikely. Indeed, neither 2-imidazolone 23 (as a result of the extrusion of S=X from 22) nor the tetraamino ethylene 24 (the expected product in case of the cheletropic fragmentation of 22) could be detected in the sulfonylations of 10 with sulfur dioxide, sulfine 17, or N-sulfinylamines.



a. X=O
b. X=
c. X=N—Ts

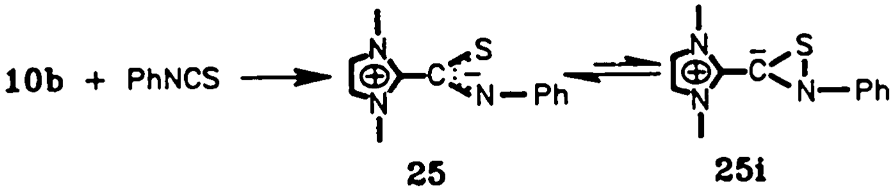
We must conclude, therefore, that the origin of bisfluorenylidene (19b) is clearly not 22b. This means that 19 was formed either from the unreacted sulfine 17 or from the sulfurane 3b (or from both).

The fact that thiirane too, like sulfur dioxide and its C- and N- analogues react with lithiated imidazolium salts to give thione 5a (albeit in small yields) under the same reaction conditions, is strong support for the sequence 10 → 4 → 3 → 5 depicted above. The hypervalent thiirane 3d, formed directly by the nucleophilic attack on the lithiocarbenium ion 10 on the sulfur atom of the thiirane, fragments cheletropically to yield the observed thione 5a and ethylene.



In this reaction, as in the cheletropic loss of carbon monoxide form cyclopropanones[33] and the cheletropic fragmentations of 3a-c, stereochemical information on the extrusion process is lacking. However, for the related reverse process, the stereospecific combination of singlet carbenes with olefins to give cyclopropanes, semiemperical calculation yield results in concordance with the analysis of non-linear cheletropic process.[34]

Interestingly, the reaction of the phenyl isothiocyanate with 10b afforded the betaine 25 (analogous to 4c) under the same reaction conditions (see experimental section) which led to the thione 5a in all the other reactions studied.



The cyclization of 25 to its interesting - as yet unknown - three- membered ring isomer 25i, may provide a system suitable, in principle, for cheletropic fragmentation analogous to that of the hypervalent three-membered thiaheterocycles 3. Apparently, the mild conditions applied (-78° → r.t.) are not sufficient for overcoming the energy barrier to a cheletropic fragmentation which would result in obtaining the high-energy species diazolium methylide and thianitroso benzene as the primary products.

At the theoretical molecular orbital level (MINDO/3 with geometry-energy optimization) the orbital correspondence for the fragmentation of a singlet hypervalent substituted thiadioxirane 1a to dioxygen and thione (3 → 5 + 6; X=Y=O) is described below (Fig. 1).[10]

Along this fragmentation reaction coordinate a singlet-triplet crossing occurs. Indeed, an external heavy atom effect was found in the thermolysis of both n-butylthiourea dioxide and dimethylamino diphenylphosphine sulfide-S-dioxide.[10]

In taking all the experimental evidence and theoretical considerations into account, the following general mechanism is suggested for the thermolytic cheletropic fragmentation of imidazolim sulfinates 4a-c, thiourea dioxides, phosphine sulfide-S-dioxides, and imidazolium-hypervalent thiiranes (3d).

The key role of hypervalent three-membered ring sulfuranes in the transformation 3 → 5 is apparent.

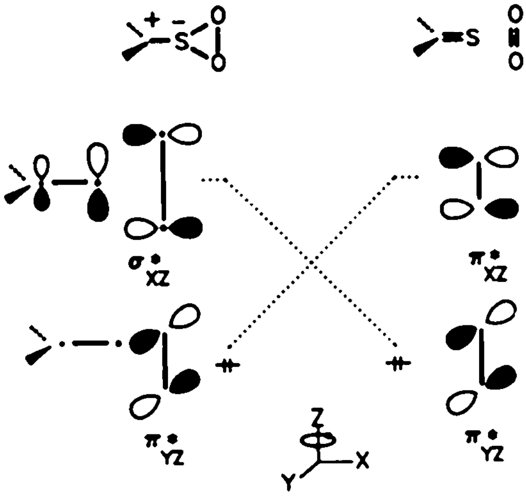
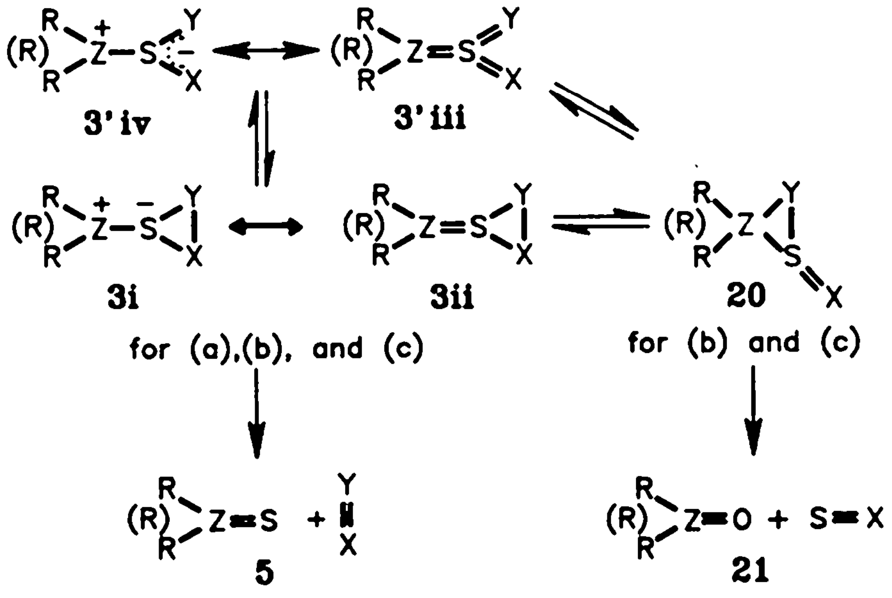


Figure 1: Orbital correspondence for the fragmentation of a hypervalent thiadioxirane to dioxygen.



(a) $Z=C$; RR=  ; $X=O$ or CR_2 or NR; $Y=O$

(b) $Z=C$; R=NHR; $X=Y=O$

(c) $Z=P$; R=aryl or $N(alkyl)_2$; (R)=$N(alkyl)_2$; $X=Y=O$

Summary

The existence of hypervalent three-membered thiaheterocycles as intermediates on the reaction surface connecting species of type 4 with thiones 5 has been established.

When appropriately substituted (a π-type LUMO adjacent to suflur), these intermediates enjoy sufficent thermodynamic stability (δ-aromatic ?) which enables them to fragment cheletropically to afford the corresponding thiones (or phosphine sulfides). This mode of fragmentation, appears to be a general pattern in the thermolysis of the isologous C- and P- (may be N- too) species of type 3.

Experimental Section

General procedure for the preparation of N,N-dimethylimidazolium salts 9a-d.

The alkylating agent (i.e. CH_3Br, $CH_3OSO_2CF_3$, CH_3I and $(CH_3)_3O^+BF_4^-$) (0.1-1 mol) was added dropwise into a cooled solution (ice bath or cold water) of 1-methylimidazole (8.12 - 81.2 g, 0.1 - 1 mol) in methylene chloride (20 - 40 ml). The mixture was allowed to stir at room temperature over a period of 1/2 - 2 hr after the completion of the addition. The product was isolated either via filtration or after the removal of the methylene chloride under reduced pressure. The yields of the very hygroscopic, colorless imidazolium salts thus obtained are essentially quantitative.

N,N-dimethylimidazolium bromide (9a). M.p. (specially dried), 104-106°C. IR($CHCl_3$): 2960(s), 1574(s), 1173(v.s.), 620(s) cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.29 (broad s, 1H, arom.), 7.86 (d, 2H, arom.), 3.92 (s, 6H, CH_3).

N,N-dimethylimidazolium triflate (9b). The crude salt obtained after the removal of the methylene chloride was purified by dissolving it in a chloroform-ether mixture (3:1 v/v), cooling the solution in an acetone-dry ice bath and decanting the solvent from the colorless precipitate. After repeating this procedure for three times, the precipitate was taken up in methylene chloride, dried ($MgSO_4$), filtered, and the solvent removed to obtain 28.96 g (94.1%, 0.125 mol scale) of 9b. M.p. 34-35.5°C. IR (neat): 3160, 3120(m), 1576(m), 1265(v.s.), 1222, 1160(s), 1029(v.s.), 751(m), 630(v.s.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.68 (br.s, 1H, arom.), 7.39 (d, 2H, arom.), 3.86 (s, 6H, CH_3). This triflate salt is readily soluble in methylene chloride and THF.

N,N-dimethyldiazolium iodide (9c). The quality of the crude salt obtained on a 1 mol scale via the general procedure described above was satisfactory for the subsequent steps.

N,N-dimethylimidazolium tetraborate (9d). This compound is a colorless oil at room temperature. Several attempts to crystallize it failed. ^1H NMR (D_2O): δ 8.65 (br.s, 1H, arom.), 7.49 (d, 2H, arom.), 3.96 (s, 6H, CH_3).

N,N-dimethylimidazolium perchlorate (9e). This salt was prepared by stirring a suspension of N,N-dimethylimidazolium bromide (9a) (8.22 g, 46.4 mmol) and sodium perchlorate (7.68 g, 62.7 mmol) in methylene chloride (200 ml) for 24 hrs. Filtration of the reaction mixture, followed by removal of the solvent under reduced pressure afforded the very hygroscopic perchlorate 9a as a pale yellow oil (5.50 g, 60.3%), which has very low solubility in methylene chloride, THF and other aprotic solvents. IR (neat): 3172, 3135(s), 1582(s), 1180, 1100 (v.s.), 843, 755 (m), 618 (v.s.) cm^{-1}; ^1H NMR (DMSO-d_6): δ 8.99 (br.s, 1H, arom.), 7.63 (d, 2H, arom.), 3.84 (s, 6H, CH_3). Anal. calc. for $C_5H_8ClN_2O_4$: C, 30.55; H, 4.61; N, 14.25; Cl, 18.03. Found: C, 30.33; H, 4.66; Cl, 17.99.

1,2,3-Trimethylimidazolium bromide. Using the procedure described at the outset of this section, the titled compound was obtained in essentially quantitative yield by the treatment of 1,2-dimethylimidazole with methyl bromide. ^1H NMR (D_2O): δ 7.38 (s, 2H, arom.), 3.81 (s, 6H, N-CH_3), 2.64 (s, 3H, CH_3).

N-methylbenzothiazolium bromide. This salt could be prepared from benzothiazole and methyl bromide by the same procedure that was used for obtaining the midazolium salts 9a-d. The yield, however, was very poor (about 5%). The compound was purified by crystallization from a large amount of methylene chloride. IR (nujol): 1587, 1522, 1440, 1407, 1129, 887, 718 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.54 (s, 1h, hetrarom.), 8.36 (m, 2H, arom.), 7.91 (m, 2H, arom.), 4.37 (s, 3H, CH_3).

General procedure for the lithiation and electrophilic substitution of imidazolium salts

Into a cooled (-78°C) stirred suspension of the imidazolium salt 9 (5 mmol) in exceptionally dried methylene chloride or tetrahedrofuran (35 ml) under an argon atmosphere, n-butyllithium (5.5 mmol; 1.6 M solution in hexane) was added dropwise over a period of five to seven minutes. The suspension turned into a clear solution of 10 after about ten minutesfrom the start of the addition of the lithium base. The homogeneous solution was stirred for an additional 10 to 20 minutes before adding the electrophile or quencher while maintaining the reaction temperature at -78°C during the addition period and for an additional hour afterwards. The reaction temperature was then allowed to reach room temperature gradually. Filtration of the reaction mixture afforded the 2-substituted imidazolium salts 12 which were further purified required.

2-Deuterio-N,N-dimethylimidazolium salts (12a). The deuterated bromide and triflate 12a were obtained in essentially quantitative yield by the quenching of solutions of 10 a,b in methelene chloride and tetrahedrofuran with D_2O. Either just filtration or filtration followed by the removal of the solvent afforded the crude deuterated salts 12a. The NMR spectra of the products revealed only the two aromatic protons at δ 7.86 and 7.39 ppm for the bromide and triflate salts respectively. As expected, the broad peaks of the 2-protons at δ 9.29 and 8.68 respectively were missing.

Trimethylimidazolium bromide (12b). Imidazolium bromide (9a) (1.631 g, 9.2 mmol) was treated with n-BuLi (7.4 ml of 1.6 M solution in hexane) in dry methylene chloride (70 ml) under argon atmosphere as described above. Forty-five minutes later, gaseous methyl bromide was bubbled into the reaction mixture over a period of 20 minutes. Following additional stirring about 1 1/2 hours at room temperature, the colorless precipitate of 12b was filtered from the reaction mixture. The crude product was contaminated with the unreacted (or recovered) starting salt 9a and contained substantial amounts of the solvent. Two consecutive triturations/extractions of the crude 12b separated it from the chloroform-insoluble unreacted salt 9a and the inorganic lithium salt. The yield of pure 12b was 46.6%. Its spectroscopic data were identical to those of an authentic sample.

If sulfur dioxide was bubbled into a homogeneous solution of 10a in methylene chloride followed by the bubbling of gaseous methyl bromide, then no trace of the trimethylimidazolium bromide (12b) could be detected after the usual work up. Only the starting salt 9a was recovered.

2-Diphenylphosphine-N,N-dimethylimidazolium chloride (12c). This salt was prepared via the procedure described above using tetrahydrofuran as solvent.[35]

General procedure for the reaction of lithio-imidazolium salts 10 with sulfines, N-sulfinylamines, and thiirane.

The lithio-salts were prepared *in situ* by the procedure described above in methylene chloride or THF (20 - 50 ml). After allowing the homogeneous solutions to stir for an additional ten minutes at -78°C, one equivalent of the sulfonylating electrophile (i.e. sulfine, N-sulfinylamine, and thiirane), in 5 - 15 mL of the solvent used, was added dropwise over a period of 10 - 20 minutes. The stirring of the reaction mixture was maintained at -78°C for an additional hour, and then the reaction temperature was allowed to reach room temperature. Stirring of the reaction mixture at room temperature was continued over periods of 5 - 100 hours (see Table 1).

Removal of the solvent under reduced pressure was followed by extraction of the residue with ethyl ether, drying, filtering and removal of the ether to afford the thione 5a together with the other reaction products. The yield of 5a was determined by means of NMR integration of the crude product. The pure thione could be obtained by column chromatography on silica gel with methylene chloride as the eluant.

(The unreacted starting imidazolium salts could be recovered).

The specific details of each entry (type of starting salt used, solvent and reaction time) as well as the yields and products obtained are given in Table 1.

Fluoroenethion-S-oxide, di-*t*-butylthione-S-oxide and N-sulfinyl-p- toluenesulfonamide were prepared according to methods described in the literature. N-sulfinyl aniline and thiirane are commercially available.

The reaction of lithio-immidazolium salt 10 with phenyl isothiocyanate.

The isolation of betaine 25. Into the homogeneous solution of 10b prepared as already described from 9b (0.565 g, 2.295 mmol) and n-BuLi (1.70 ml of 1.6 M solution in hexane) in THF (30 ml), was added, dropwise, one equivalent of phenyl isothiocyanate over a period of 30 min. at -78°C. The reaction mixture was allowed to reach room temperature and stirring was continued for an additional 1 1/2 hours. Filtration of the reaction mixture gave yellow solid (0.134 g, 30%) the IR and NMR spectra of which were consistent with that of betaine 25 . IR ($CHCl_3$): 2962(s), 1598, 1583(m), 1494(s), 1447(m), 969(s), 647, 617(m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.54-7.00 (m, 5H, arom.), 6.81 (s, 2H, arom.), 3.88 (s, 6H, CH).

No optimization of the reaction conditions - in order to improve the yields of 25 - has been attempted.

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