diazirines were removed under vacuum as they formed and sequentially passed through a drying trap containing NaOH pellets and a second trap cooled to -30 °C. They were collected in a third trap (-78 °C) containing 2 mL of solvent. The chloroisopropyldiazirine **8b**, obtained in 49% yield from **3b**, was identical (IR and NMR) with the authentic material[15] obtained by standard Graham oxidation[2] of **1b**. The methoxychlorodiazirine **8c**, obtained from **3c**, was trapped in isobutene and permitted to decompose at 25 °C (sealed tube) to afford the known[16] isobutene adduct of methoxychlorocarbene in 43% overall yield.

These results indicate that the dichloroamidines **3** are likely precursors of the diazirines **8**, as suggested by Graham.[2] Moreover, control experiments with *N*-chloro- and *N,N,N'*-trichloroamidines (series **a** and **b**) show that none of these amidine derivatives afford **8** under nonoxidative Graham conditions. Preliminary experiments indicate that **3b** and **3c** can be converted to 3-azido-3-isopropyldiazirine and 3-bromo-3-methoxydiazirine, respectively, upon treatment with aqueous NaOH saturated with NaN_3 or NaBr. The new diazirines are formed as mixtures, however, with the appropriate 3-chlorodiazirine present and *dominant* in each case.

Diazirinium Ions. The final stage of Graham's mechanism remains unclear. On the assumption that **3** does afford **6** (in analogy[2] to the Neber rearrangement), how is **6** converted to **8**? Intervention of a free diazirinium ion (**7**), for which recent ab initio calculations indicate thermodynamic instability,[17] seems quite unlikely. Moreover, we have failed to obtain evidence for the ionization of **8** to **7**, despite the suggestion that diazirinium ion "formation under solvolytic conditions is not unreasonable".[2] Thus, treatment of **8c** (or methoxybromodiazirine) with $AgNO_3$, $AlBr_3$, SbF_5/SO_2, H_2SO_4, $AlCl_3$, AgF, or FSO_3H at various temperatures and with several methods of spectroscopic or chemical monitoring failed to provide evidence for diazirinium ions as spectroscopic entities or as chemical intermediates. Several related experiments failed with methylchlorodiazirine (our work) and with phenylhalodiazirines.[18]

The suggestion[2] that **6** affords **8** by an addition-elimination reaction with X^- is also difficult to accept. If this were so, we would expect nearly complete interception of **6** by added "foreign" anions. However, our experience with the conversion of **3** to **8** is that N_3^- or Br^-, although supplied in ~20-fold excess, compete poorly with the chloride initially present in **3**.

Our current working hypothesis is that **6** is a high-energy species which, in aqueous solution, is exothermically converted to **8** via an *intimate ion pair* (**7**, X^-) in which return of the "original" anion is favored over capture of a "foreign" anion. There is a clear analogy here to the interconversion of isomeric 3-chloro-1-azirines, which may well proceed via azirinium cation-chloride anion pairs.[19] We are vigorously exploring numerous mechanistic and synthetic ramifications of the present work.

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Registry No. **1a**·HCl, 1670-14-0; **1b**·HCl, 22007-68-7; **1c**·HCl, 5329-33-9; **2a**, 40078-03-3; **2b**, 79499-48-2; **2c**, 19224-53-4; **3b**, 79499-49-3; **3c**, 79499-50-6; **8b**, 29648-80-4; **8c**, 4222-27-9.

Supplementary Material Available: Tables I-III containing the fractional coordinates, temperature parameters, bond distances, and bond angles of **2a** from the X-ray experiments (5 pages). Ordering information is given on any current masthead.

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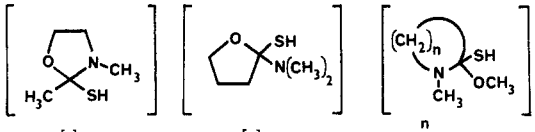
Breakdown of Hemiorthothioamide Tetrahedral Intermediates Derived from *O,N*-Dimethyllactamium Tetrafluoroborates[1,2]

Summary: The sulfhydrolytic cleavage of *O,N*-dimethylbutyrolactamium and *O,N*-dimethylvalerolactamium tetrafluoroborates involves C-N scission under kinetic control (61 °C, NaSH, Ac_2O, $CHCl_3$) but C-O cleavage under thermodynamic control (27 °C, NaSH, acetone).

Sir: We recently reported that hemiorthothioamide intermediates [**1**] and [**2**] derived from *anti*- and *syn*-imidates, respectively, undergo preferential cleavage of the C-N bond (rather than the C-O bond), under kinetic control (-78 °C, NaSH, acetone).[3] We hereby report on the breakdown of hemiorthothioamide tetrahedral intermediates [**3**] and [**4**], generated in aprotic solvents acetone and chloroform from NaSH and *O*-methyl derivatives of lactams **5** and **6**, respectively, at temperatures between -78 and 61 °C. The sulfhydrolytic breakdown for [**3**] and [**4**]



is presented in Scheme I and the results are summarized in Table I.

The reaction of **5** with NaSH in acetone at room temperature (75 min), gave thiolactam **11** exclusively (% C-N cleavage/% C-O cleavage = 7/11 = 0:100; Table I, entry 1).[4] Even at -78 °C, the sulfhydrolysis in acetone followed

(15) R. A. Moss and R. C. Munjal, *J. Chem. Soc., Chem. Commun.*, 775 (1978).
(16) R. A. Moss and W.-C. Shieh, *Tetrahedron Lett.*, 1935 (1978).
(17) K. Krogh-Jespersen, *Tetrahedron Lett.*, 4553 (1980).
(18) B. B. Wright and M. S. Platz, Central and Great Lakes Regional American Chemical Society Meeting, Dayton, OH, May 20, 1981, Abstract 247.
(19) J. Ciabattoni and M. Cabell, Jr., *J. Am. Chem. Soc.*, **93**, 1482 (1971); A. Padwa, T. J. Blacklock, P. H. J. Carlsen, and M. Pulwer, *J. Org. Chem.*, **44**, 3281 (1979).

(1) The Chemistry of Tetrahedral Intermediates. 7. For part 6, see: Kaloustian, M. K.; Khouri, F. *Tetrahedron Lett.* **1981**, *22*, 413-416; part 5, Kaloustian, M. K.; Khouri, F. *J. Am. Chem. Soc.* **1980**, *102*, 7579-7581.
(2) (a) Presented at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 25, 1980; ORG 76. (b) Taken in part from the Ph.D. Dissertation of R. B. Nader, Fordham University, 1980.
(3) Kaloustian, M. K.; Aguilar-Laurents de Gutierrez, M. I.; Nader, R. B. *J. Org. Chem.* **1979**, *44*, 666-668.

0022-3263/81/1946-5050$01.25/0

Scheme I

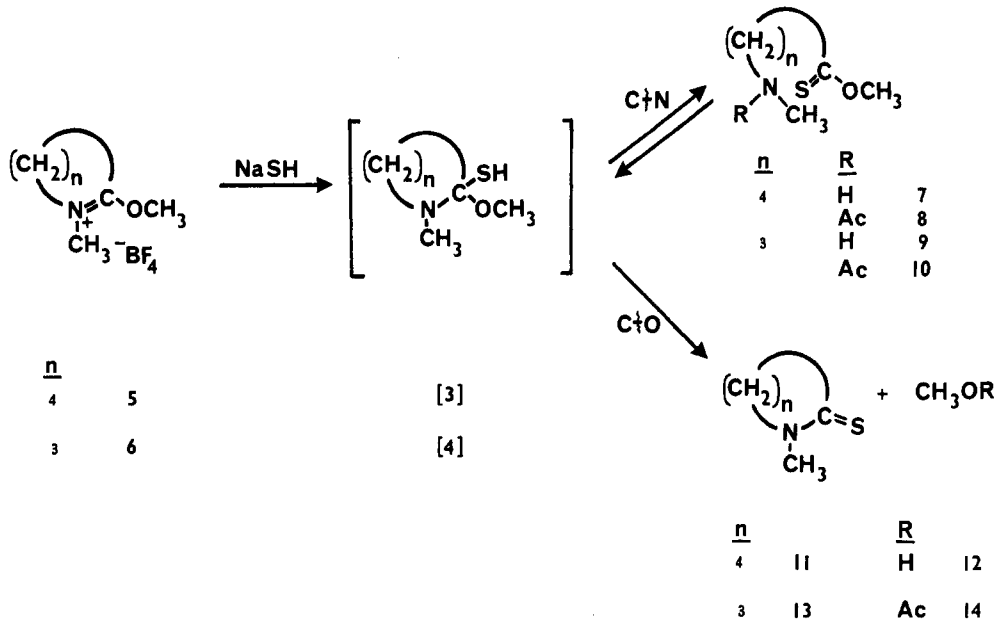


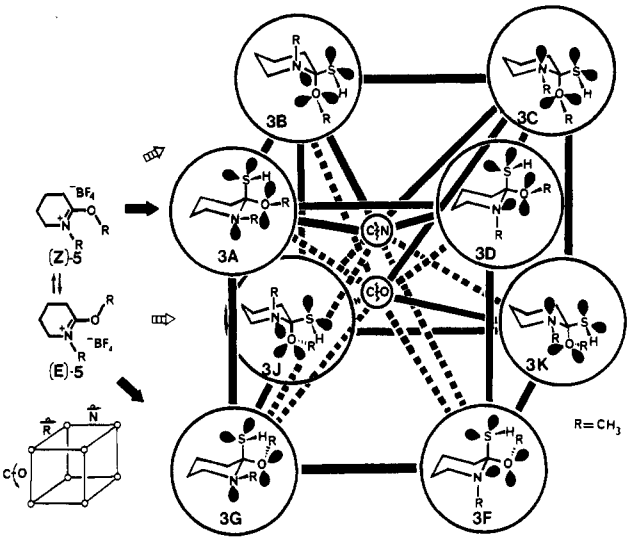
Table I. Sulfhydrolysis of *O,N*-Dimethyllactamium Salts[a]

imidate salt	entry	T, °C	trapping procedure	% C-N cleavage	% C-O cleavage	% overall yield
5	1	27		0	100	99
	2	-78	A[b]	5	95	70
	3	61[c]	A	80	20	71
	4	27	B[d]	87	13	56
	5	-78	B	92	8	64
	6	61[c]	B	100	0	70
6	7	27		0	100	100
	8	-78	A	8	92	94
	9	27	B	72	28	50
	10	-78	B	83	17	87
	11	61[c]	B	95	5	69

[a] Solvent acetone (except where noted). [b] Procedure A: AcCl/py is added *after* the reaction of imidate salt with NaSH is complete. [c] Solvent chloroform [d] Procedure B: Ac_2O is added to the imidate salt *prior* to the addition of NaSH.

by trapping with excess acetyl chloride afforded predominantly thiolactam **11** (8/11 = 5:95; Table I, entry 2). When lactamium salt **5** was heated at reflux in anhydrous chloroform, followed by treatment with NaSH, one could still observe, by TLC, only thiolactam **11** (100% C–O cleavage). However, when the hot chloroform reaction mixture was quenched to −78 °C and acetylated subsequently, the molar percent ratio 8/11 increased to 80:20 (Table I, entry 3). When the sulfhydrolyses in acetone were carried out in the presence of acetic anhydride, the 8/11 ratio further increased to 87:13 at 27 °C (Table I, entry 4) and 92:8 at −78 °C (Table I, entry 5); in refluxing chloroform with preadded acetic anhydride, the sulfhydrolysis led to a 8/11 ratio of 100:0 (100% C–N cleavage; Table I, entry 6).[5] The *N,O*-dimethylpyrrolidonium fluoroborate (**6**) behaved in all respects in a manner similar

Scheme II



to that of the six-membered analogue (Table I, entries 7–11).[6]

The results of the trapping experiments may be rationalized in terms of Deslongchamps' stereoelectronic theory[7] as applied to the conformational cube[8] in SchemeII. Accordingly, the C–N cleavage products (**7** or **8**) can form only through conformers [**3A**]–[**3D**] (upper floor)[9] but not from conformers [**3F**], [**3G**], [**3J**], [**3K**] (lower floor),[9]

(4) Thiolactam **11**: yellowish oil; R_f 0.76 ($CHCl_3$–CH_3CN, 5:1 v/v); IR (film) 1520, 1330, 1220, 1085 cm^{-1}; NMR ($CDCl_3$) δ 1.58–2.08 (4 H, m, ring methylenes), 3.00 (2 H, t, J = 6.0 Hz, $CH_2C{=}S$), 3.32–3.56 (5 H, m, NCH_3 and NCH_2).

(5) Amido thioester **8**: pale yellow oil; R_f 0.45 ($CHCl_3$–CH_3CN, 5:1, v/v); IR (film) 1630, 1440, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.40–1.95 (4 H, br s, CH_2CH_2), 2.10 (3 H, s, CH_3CO), 2.75 (2 H, t, $CH_2C{=}S$), 2.90 and 2.98 (3 H, 2 s, NCH_3), 3.37 (2 H, t, CH_2N), 4.07 (3 H, s, OCH_3). Anal. Calcd for $C_9H_{17}NO_2S$: C, 53.17; H, 8.43. Found: C, 53.01; H, 8.33.

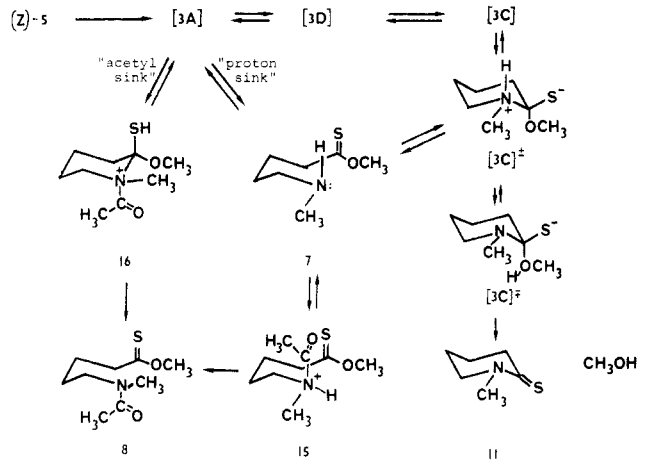
(6) Thiolactam **13**: pale yellow oil; R_f 0.72 ($CHCl_3$–CH_3CN, 5:1, v/v); IR (film) 1520, 1300, 1105 cm^{-1}; NMR ($CDCl_3$) δ 2.07 (2 H, quintet, J = 7 Hz, CCH_2C), 2.99 (2 H, t, J = 7 Hz, $CH_2C{=}S$), 3.24 (3 H, s, NCH_3), 3.78 (2 H, t, J = 7 Hz, CH_2N). Amido thioester **10**: yellowish oil; R_f 0.36 ($CHCl_3$–CH_3CN, 5:1, v/v); IR (film) 1640, 1440, 1405, 1270, 1195 cm^{-1}; NMR ($CDCl_3$) δ 1.78–2.33 (m) and 2.01 (s) (5 H, CCH_2C and CH_3CO, respectively), 2.72 (2 H, m, $CH_2C{=}S$), 2.91 and 2.99 (3 H, 2 s, NCH_3), 3.16–3.56 (2 H, m, CH_2N), 4.07 (3 H, s, OCH_3).

(7) (a) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463–2490. (b) *Pure Appl. Chem.* **1975**, *43*, 351–378. (c) *Heterocycles* **1977**, *7*, 1271–1317.

(8) As shown in the lower left-hand corner, "left-right" interconversions correspond to nitrogen inversion, "front-back" ones refer to six-membered ring flip, whereas "up-down" transformations indicate rotation about the C–O bond. In the cube, solid lines designate stereoelectronically allowed interconversions, whereas dashed ones denote disallowed transformations.

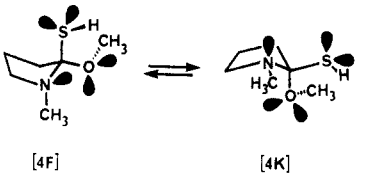
(9) Conformers [**3A**]–[**3D**] define the "upper floor" of the cube; [**3F**], [**3G**], [**3J**], and [**3K**] constitute the "lower floor".

Scheme III



whereas the C–O cleavage products (**11** + **12**, or **11** + **14**) may arise from conformers [3C] (upper floor) or [3K] (lower floor). It appears that over the −78–27 °C range, the kinetically preferred course of the sulfhydrolysis reaction of **5**, in acetone, is through the upper pathway (*Z*)-**5** → [**3A**] → **7**. Owing to the highly reactive nature of **7** (C≠N), little or none of **7** is trapped (as **8**) (Table I, entries 1, 2), since it rapidly rearranges through the irreversible[10] **7** (C≠N) → [3C] → **11** + **12** (C≠O) pathway.[11] In the presence of acetylating agent,[12] **7** is efficiently trapped (87–92%; Table I, entries 4, 5), possibly through the **7** → **15** → **8** route (Scheme III). In solvent chloroform, the rearrangement of **7** to **11** through the **7** → [**3C**]$^{\pm}$ → [3C]$^{\mp}$ → **11** + **12** route[13] appears to be sluggish even at 61 °C. It is not surprising that in the less polar solvent chloroform (as contrasted to acetone), both the formation of [**3C**]$^{\pm}$ from **7** (Scheme III), as well as the [**3C**]$^{\pm}$ → [3C]$^{\mp}$ transformation through an already-unfavorable N→O proton transfer, are both adversely affected.[13] Thus, in effect, the lifetime of **7** is prolonged, and at 61 °C, 80% of it can be trapped as the acetyl derivative **8** (Table I, entry 3).[14] In the presence of *preadded* acetic anhydride,[12] one isolates only **8** (100% C–N cleavage); the formation of **8** may well proceed through the interception of [**3A**] by way of the [**3A**] → **16** → **8** pathway (Scheme III).

For the sulfhydrolysis of **5**, under conditions of kinetic control, it is the upper (i.e., (*Z*)-**5** → [**3A**] → ...) pathway that consumes **5** through its less stable but more reactive (*Z* conformer (Scheme II).[15] This kinetic pathway involves exclusive C–N cleavage of [**3A**] and is favored in the presence of an "acetyl sink", even at the *highest* temperature studied. Under similar conditions, the sulfhydrolysis of **6** involves the dominant (rather than exclusive) cleavage of the C–N bond (**10**:**13** = 95:5; Table I, entry 11). Here, the analogous (*E*)-**6** → [**4G**] → [**4F**] → [**4K**] → **13** + **14** pathway may gain in importance, since the six-ring inversion ([**3F**] → [**3K**]) is replaced by a facile five-ring pseudorotatory motion [**4F**] → [**4K**].[16]



These results underscore the role of stereoelectronic effects in the breakdown of hemiorthothioamide tetrahedral intermediates derived from conformationally heterogeneous imidates and headed toward an acetyl sink in relatively nonpolar media.

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Registry No. **3**, 79568-46-0; **4**, 79568-47-1; **5**, 19964-07-9; **6**, 79568-48-2; **7**, 79568-49-3; **8**, 79568-50-6; **9**, 79568-51-7; **10**, 79568-52-8; **11**, 13070-07-0; **13**, 10441-57-3.

(10) Refluxing of **11** with $NaOCH_3$ in anhydrous methanol followed by treatment with AcCl/pyridine did not yield any of **8**; hence, thiolactam **11** is the thermodynamically favored product.

(11) For the **7** → **11** rearrangement, the sequences **7** → [3C] → **11** + **12** (Scheme II) and **7** → [**3C**]$^{\pm}$ → **11** + **12** (Scheme III) are equivalent. The latter sequence emphasizes the involvement of (partially) charged intermediates; the flow of charge that must accompany the rearrangement is represented here through an arbitrary sequence of fully charged intermediates (depicted in idealized zwitterionic form).

(12) Preadded acetic anhydride serves as an effective source of CH_3CO^+—the trapping species; hence, the entire reaction is led toward an "acetyl sink".

(13) The idealized representations [**3C**]$^{\pm}$ (+ on N, − on S) and [**3C**]$^{\pm}$ (+ on O, − on S) reflect the direction in which + and − charge buildup should occur and does not imply the exact timing of the proton transfer; a gradual change of charges is therefore equally acceptable.

(14) The absence of preadded trapping agent, in effect, corresponds to a "proton sink", and the most likely pathway is **7** → **15** → **8** (Scheme III).

(15) The lower (E)-**5** → [**3G**] → [**3F**] → [**3K**] → **11** + **12** pathway appears to be insignificant.

(16) Pseudorotation in a five-membered ring is a low-energy process [in THF it is 0.16 kcal/mol (cf. Engerholm, G. G.; Luntz, A. C.; Gwinn, W. D. *J. Chem. Phys.* **1969**, *50*, 2446].

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Hydrolysis of Cyclic Thioimidate Tetrafluoroborates at Sub-Zero Temperatures[1,2]

Summary: The hydrolyses of 2-phenyl-*N*-methyl-1,3-thiazolinium and 2-phenyl-*N*-methyl-5,6-dihydro-1,3-thiazinium tetrafluoroborates (**2a** and **2b**, respectively) under kinetic control (NaOH, 15-crown-5, anhydrous *n*-PrCN, Ac_2O, −78 °C) proceed by preferential cleavage of the C–N bond; under thermodynamic control (KOH, EtCN–H_2O, 0 °C for **2a**; KOH, H_2O, 45 °C for **2b**) exclusive C–S bond scission is observed.

Sir: Stereochemical studies on short-lived tetrahedral intermediates of the type $RC(OR')(OH)_2$, $RC(OR')_2OH$, $RC(OR')(NR''_2)OH$, $RC(OR')(NR''_2)SH$, and $RC(OR')_2SH$ have demonstrated that their breakdown is subject to the Deslongchamps effect.[3] We report here on the generation

(1) The Chemistry of Tetrahedral Intermediates. 8. Part 7: Kaloustian, M. K.; Nader, R. B. *J. Org. Chem.* **1981**, *46*, in press. Part 6: Kaloustian, M. K.; Khouri, F., *Tetrahedron Lett.* **1981**, *22*, 413–416.

(2) (a) Presented at the New York Academy of Sciences, New York, NY, June 10, 1980. (b) Taken in part from the M.S. Thesis of Liliane Khouri, Fordham University, 1979.

(3) (a) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463–2490. (b) Deslongchamps, P. *Pure Appl. Chem.* **1975**, *43*, 351–378. (c) Deslongchamps, P. *Heterocycles* **1977**, *7*, 1271–1317 and papers cited therein. (d) Kaloustian, M. K.; Aguilar-Laurents de Gutierrez, M. I.; Nader, R. B. *J. Org. Chem.* **1979**, *44*, 666–668. (e) Kaloustian, M. K.; Khouri, F. *J. Am. Chem. Soc.* **1980**, *102*, 7579–7581.

0022-3263/81/1946-5052$01.25/0