at a refluxing temperature if a small amount of aqueous fluoroboric acid was added.

The infrared data of the hydrazone type complexes obtained are given in Table I. The ν(C=N) band of the complex derived from benzaldehyde is considerably lower than those of the complexes derived from acetone and propionaldehyde. This is explained by the resonance effect of the phenyl group. We are presently investigating the reactivities of these hydrazone type complexes, especially their reduction to hydrazine derivatives.

References and Notes

(1) Part 4: T. Tatsumi, H. Tominaga, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, **114**, C27–C29 (1976).
(2) J. Chatt, A. J. Pearman, and R. L. Richards, *Nature (London)*, **253**, 39–40 (1975).
(3) Y. G. Borodko, L. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1178 (1972); J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074–2082 (1974); J. M. Manriquez, R. D. Sanner, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 3042–3044 (1976).
(4) A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organomet. Chem.*, **84**, C11–C12 (1975); V. W. Day, T. A. George, and S. D. A. Iske, *J. Am. Chem. Soc.*, **97**, 4127–4128 (1975); V. W. Day, T. A. George, S. D. A. Iske, and S. D. Wagner, *J. Organomet. Chem.*, **112**, C55–C58 (1976).
(5) R. Ben-Shoshan, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, **112**, C9–C10 (1976).
(6) E. E. van Tamelen, and H. Rudler, *J. Am. Chem. Soc.*, **92**, 5253–5254 (1970); J. Chatt, G. A. Heath, and G. J. leigh, *J. Chem. Soc., Chem. Commun.*, 444–445 (1972); T. Tatsumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, **14**, 2530–2534 (1975).
(7) P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 509 (1976).
(8) M. Hidai, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, in press.
(9) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 1392 (1969).

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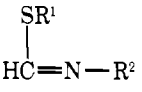
Received July 27, 1976

Azetidin-2-oxo-4-thiones. Novel Thermolytic Products of β-Lactam Sulfoxides

Sir:

The thermal rearrangement of penicillin sulfoxides to deacetoxycephalosporin,[1] as well as that of similar β-lactam sulfoxides, provides a useful tool for the chemical interconversion of β-lactam antibiotics.[2] This rearrangement involves the intermediacy of sulfenic acids. As part of our studies on β-lactams related to penicillins and cephalosporins[3] we have investigated the thermolysis of the β-lactam sulfoxides **7** and **8**. We report herein an unusual rearrangement of these sulfoxides to the corresponding azetidin-2-oxo-4-thiones **11** and **12** which are thiomalonic acid imides, a hitherto unreported class of compounds.

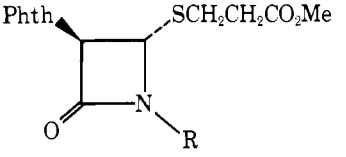


1, R^1 = Me; R^2 = $C(CO_2Me)=CMe_2$
2, R^1 = $CH_2CH_2CO_2Me$; R^2 = $C(CO_2Me)=CMe_2$
3, R^1 = Me; R^2 = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$
4, R^1 = $CH_2CH_2CO_2Me$; R^2 = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$

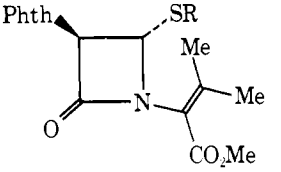
Treatment of the thioformimidate **2**, obtained by warming the thioformimidate **1**[4] and methyl 3-mercaptopropionate, with phthaloylglycyl chloride gave the trans β-lactam **5** (mp 92–93 °C, 56%).[5] Similarly, **3**, prepared by S-methylation (MeI, NaH in toluene) of *O-tert*-butyl-*N*-thioformyl-*d,l*-serine *tert*-butyl ester, was converted through **4** into the β-lactam **6** which consisted of a 1:1 mixture of two trans diastereoisomers.[5]

Oxidation of the 4-carbomethoxyethylthio-β-lactam **5** with *m*-chloroperbenzoic acid in $CHCl_3$ at −35 °C gave the corresponding sulfoxide **7** (mp 156–157 °C, 98%): NMR δ ($CDCl_3$) 2.10 (s, Me), 2.31 (s, Me), 2.7–3.0 (m, SCH_2CH_2CO), 3.65 (s, OMe), 3.87 (s, OMe), 5.4 (d, J = 2.5 Hz, azetidinone 4-H), 6.05 (d, J = 2.5 Hz, azetidinone 3-H), and 7.7–8.0 (m, aromatic H); ν_{max} (film), 1790, 1775, 1735, and 1725 cm^{-1}. A similar oxidation of **6** (CH_2Cl_2, −40 °C) afforded the sulfoxide **8** (79%) as a mixture of the two trans isomers separated by chromatography. NMR of one isomer: δ ($CDCl_3$) 1.21 (s, O-*t*-Bu), 1.54 (s, O-*t*-Bu), 2.86 (m, $SCH_2CH_2CO_2$), 3.62 (s, OMe), 3.6–3.9 (m, $CHCH_2O\text{-}t\text{-}Bu$), 4.76 (t, $NCHCO_2$), 5.49 (d, J = 2.5 Hz, azetidinone 4-H), 6.02 (d, J = 2.5 Hz, azetidinone 3-H), and 7.8 br (m, aromatic); NMR of the other isomer, δ ($CDCl_3$) 1.21 (s, O-*t*-Bu), 1.53 (s, O-*t*-Bu), 2.87 (m, $SCH_2CH_2CO_2$), 3.60 (s, OMe), 4.10 (d, $CHCH_2O\text{-}t\text{-}Bu$), 4.79 (t, $NCHCO_2$), 5.30 (d, J = 2 Hz, azetidinone 4-H), 6.15 (d, J = 2 Hz, azetidinone 3-H), and 7.9 br (m, aromatic).

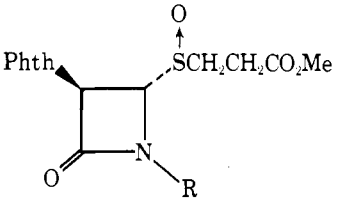
Sulfoxides bearing a hydrogen substituent at a β-carbon atom are thermolyzed to olefins and sulfenic acids.[6] This process which involves a C to O hydrogen shift is facilitated when the migrating hydrogen atom is made more acidic.[7,8] It was therefore anticipated that thermolysis of the unsymmetrical sulfoxide **7** should give the corresponding β-lactam 4-sulfenic acids **9** and methyl acrylate. This prediction was corroborated by trapping the sulfenic acid with dihydropyran according to Barton's procedure.[9] Thus, heating (80–85 °C, sealed tube) **7** in dihydropyran with $AlBr_3$ as catalyst for 20 h gave the dihydropyranyl derivative **10** (71%); NMR δ ($CDCl_3$) 1.5–2.0 (m, dihydropyran $=CCH_2CH_2-$), 2.08 (s, Me), 2.30 (s, Me), 3.8–4.1 (m, dihydropyran OCH_2), 3.83 (s, OMe), 5.40 (d, J = 3 Hz, azetidinone H), 5.51 (d, J = 3 Hz, azetidinone H), 6.75 br (s, dihydropyran vinylic H), and 7.8–8.0 (m, aromatic); ν_{max} ($CHCl_3$) 1785, 1765, 1730, and 1720 cm^{-1}.



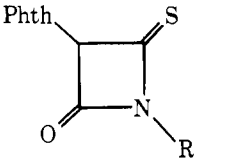
5, R = $C(CO_2Me)=CMe_2$
6, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$



9, R = OH
10, R =



7, R = $C(CO_2Me)=CMe_2$
8, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$

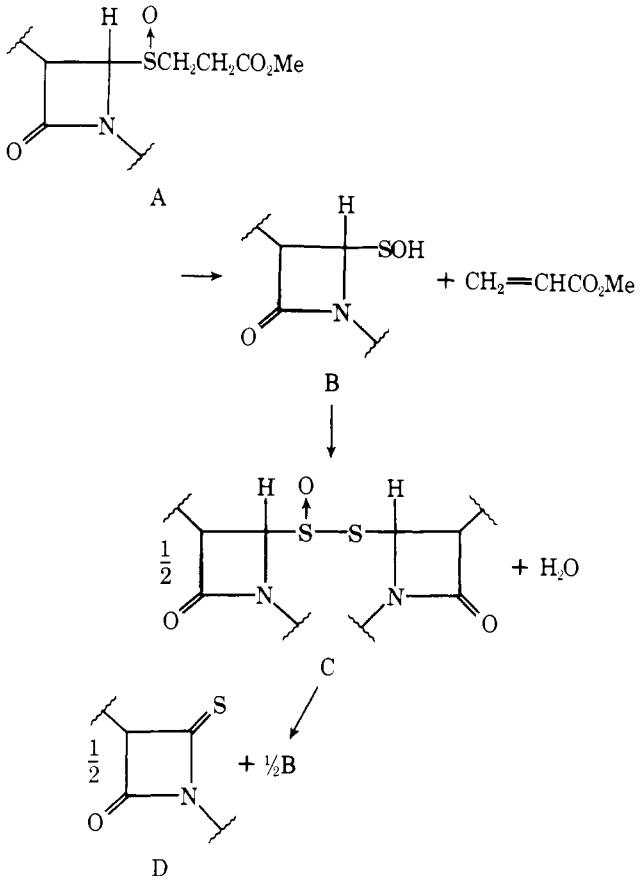


11, R = $C(CO_2Me)=CMe_2$
12, R = $CH(CO_2\text{-}t\text{-}Bu)CH_2O\text{-}t\text{-}Bu$

Phth = phthalimido

However, in the absence of a trapping agent, the sulfenic acid **9**, formed by the thermolysis of the sulfoxide **7** (sealed tube; 80–100 °C in C_6H_6, CCl_4, or $CHCl_3$), gave the azetidin-2-oxo-4-thione **11** (mp 164–167 °C >80%): NMR δ ($CDCl_3$) 2.20 (s, Me), 2.44 (s, Me), 3.80 (s, OMe), 5.97 (s, azetidine H), and 7.8–8.0 (m, aromatic); ν_{max} ($CHCl_3$) 1830, 1780, 1740, and 1730 cm^{-1}; mass spectrum *m/e* (M^+ 358, 330, 299, 203, and 187). A similar thermolysis (105 °C for 24 h) of **8** afforded the azetidin-2-oxo-4-thione, **12**, NMR δ ($CDCl_3$) 1.18 (s, O-*t*-Bu), 1.51 (s, O-*t*-Bu), 4.0 br (m, $CH_2O\text{-}t\text{-}Bu$), 4.85, br (m, $NCHCO_2$), 5.90 (s, azetidine H), 7.88 (m, aro-

Scheme I



matic); ν_{max} ($CHCl_3$) 1830, 1785, and 1730 cm^{-1}; mass spectrum *m/e* (M^+ 446, 390, 334, 203, and 187). Presumably, the formation of these azetidin-2-oxo-4-thiones involves the sequence shown in Scheme I.[10] Methyl acrylate is eliminated from the carbomethoxyethyl sulfoxide A with concomitant formation of the sulfenic acid B which undergoes self-condensation to the thiolsulfinate ester C. Fragmentation of C results in the formation of the azetidin-2-oxo-4-thione D and the sulfenic acid B which is recycled.

Like in the penicillins and in the cephalosporins, the strained four-membered ring in **11** and in **12** is highly substituted by heteroatoms, and as judged from its high C=O stretching frequency, the amide bond lacks the normal amide resonance stabilization to an even more pronounced degree than in the bicyclic β-lactam antibiotics.[11] These structural features are expected to impart to the azetidin-2-oxo-4-thiones a high and versatile chemical activity which is now being investigated.

References and Notes

(1) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Am. Chem. Soc.*, **85**, 1896 (1963); **91**, 1401 (1969).
(2) (a) R. D. G. Cooper and D. O. Spry, "Cephalosporins and Penicillins. Chemistry and Biology", E. H. Flynn, Ed., Academic Press, New York, N.Y., 1972, p 183; (b) R. D. G. Cooper, L. D. Hatfield, and D. O. Spry, *Acc. Chem. Res.*, **6**, 32 (1973); (c) P. G. Sammes, *Chem. Rev.*, **76**, 113 (1976).
(3) M. D. Bachi and K. J. Ross-Petersen, *J. Chem. Soc., Perkin Trans. 1*, 2525 (1975), and previous papers in the same series.
(4) M. D. Bachi and O. Goldberg, *J. Chem. Soc., Perkin Trans. 1*, 1184 (1974).
(5) All the chiral compounds in this work consist of racemic mixtures; for simplicity only one enantiomer of each pair has been displayed in the formulas.
(6) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).
(7) A. G. W. Baxter, J. Kitchin, R. J. Stoodley, and R. B. Wilkins, *J. Chem. Soc., Chem. Commun.*, 285 (1973); R. J. Stoodley and R. B. Wilkins, *J. Chem. Soc., Perkin Trans. 1*, 1572 (1974).
(8) J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, **8**, 197 (1973).
(9) D. H. R. Barton, D. G. T. Greig, G. Lucente, P. C. Sammes, and M. V. Taylor, *Chem. Commun.*, 1683 (1970); I. Ager, D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, G. H. Hewitt, B. E. Looker, A. Mowatt, C. A. Robson, and W. G. E. Underwood, *J. Chem. Soc., Perkin Trans. 1*, 1187 (1973).
(10) For similar thermolyses of sulfoxides and thiolsulfinate esters see for example (a) J. R. Shelton and K. E. Davis, *J. Am. Chem. Soc.*, **89**, 718 (1967); (b) E. Block, *ibid.*, **94**, 642 (1972).
(11) R. M. Sweet, "Cephalosporins and Penicillins. Chemistry and Biology", E. H. Flynn, Ed., Academic Press, New York, N.Y., 1972, p 280.

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Received July 26, 1976

Extensive Redistribution of Fluorine and Hydrogen in the Reaction of CF_3^+ with SiH_4[1]

Sir:

In a study of the reaction of CF_3^+ with SiH_4 in the gas phase, we have observed a very extensive redistribution of fluorine and hydrogen between carbon and silicon centers which must occur within a single collision complex.

CF_3^+ ions were formed from either CF_4 or CF_3Cl in an electron-impact ion-source, separated from the other ions, that were simultaneously produced, by a quadrupole mass filter, and injected at barycentric energies of 0.3–10 eV into a collision cell containing SiH_4 at a pressure of 1.0×10^{-3} Torr. In related experiments SiH_3^+ ions were formed by electron impact on SiH_4 and reacted with CF_3H in the collision chamber. The ions produced by the collisions were mass analyzed by a second quadrupole mass filter and detected by an electron multiplier. The details of the apparatus have been described previously.[2]

^{28}Si monoisotopic mass spectra for several relative kinetic energies of reactants are shown in Table I, the intensities of all ions having been corrected for contributions due to the naturally occurring ^{29}Si(4.7%) and ^{30}Si(3.1%) isotopes. Identification of the product ions was confirmed by observation of the mass shifts, if any, that resulted when SiH_4 was replaced by SiD_4.

At all three relative kinetic energies of the reactants the predominant product ion is SiH_3^+. On the basis of available thermochemical data[3-5] the only electrically neutral product that is energetically feasible at 1.3 eV is CF_3H and hence the predominant reaction must be written as in eq 1.

$$CF_3^+ + SiH_4 \rightarrow CF_3H + SiH_3^+ \qquad (1)$$

Table I. ^{28}Si Monoisotopic Mass Spectra of $CF_3^+ + SiH_4$ Reaction

		Relative intensity at barycentric energy		
m/e	Ion	1.3 eV	3.2 eV	9.5 eV
12	C^+	—	—	3
13	CH^+	—	0.5	14
14	CH_2^+	—	0.5	3
15	CH_3^+	18	17	3
29	SiH^+	11	24	215
30	SiH_2^+	15	49	150
31	SiH_3^+	1000	1000	1000
33	CFH_2^+	17	*a*	*a*
47	SiF^+	6	12	135
49	SiH_2F^+	69	262	438
50	CF_2^+	40	54	244
51	CF_2H^+	283	307	250
67	$SiHF_2^+$	*b*	*b*	*b*

[a] Definitely present but obscured by isotopic contribution of $^{30}SiH_3^+$. [b] Definitely present but not measurable quantitatively due to proximity of CF_3^+ reactant ion.