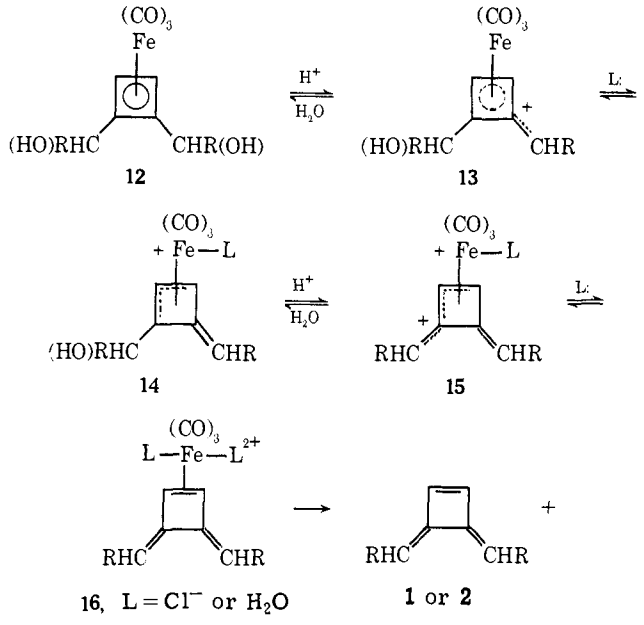
Scheme I



$$FeL_2(aq)^{2+} + 3CO(g)$$

to hydrocarbon, hydrated ferrous chloride, and carbon monoxide.[13] The overall result is an internal disproportionation in which the elements of H_2O_2 or a functional equivalent are transferred to iron.

Reaction of carbonium fluoroborate **7a** with DBN may proceed in an analogous manner at an early stage. The fact that product does not appear until at least 1 equiv of base has been added is consistent with initial coordinate saturation of iron. The role of additional base in leading to **1**, *i.e.*, deprotonation–decomplexation or possibly attack at an α carbon followed by 1,4 elimination–decomplexation, is not clear at this point.

Extension of the aforementioned approaches to other cyclobutadienoid systems is currently under study.

Acknowledgment. We thank the National Science Foundation for support of this work (GP-13368).

(13) Breakdown of **16** finds analogy in the hydrolytic instability of tetracarbonyliron dichloride: (a) W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928); (b) A. Mittasch, *Angew. Chem.*, 41, 827 (1928); (c) W. Hieber and G. Bader, *Z. Anorg. Allgem. Chem.*, **190**, 193 (1930). Gas evolution was observed in the reaction of both diols.

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Reversible Interconversions of Penam and Cepham Systems *via* a Common Thiiranium Ion Intermediate[1]

Sir:

The thermal cleavage of the S_1–C_2 bond in penicillin sulfoxide (**1**) and the existence of the resulting sulfenic acid **2** (X = OH) are well documented.[2–6] Our interest in monocyclic azetidinone sulfenyl chlorides[7] prompted us to investigate the possibility of utilizing the sulfenic acids for the preparation of sulfenyl chlorides **2** (X = Cl).

The sulfenic acid **2** (X = OH), prepared by thermolysis of penicillin sulfoxide (**1**), is converted to the sulfenyl chloride **2** (X = Cl) with thionyl chloride and triethylamine in boiling carbon tetrachloride. This highly reactive intermediate instantly cyclizes to two stable products **3** and **4** in the ratio of *ca.* 3:4. After chromatography on silica, the major component is recrystallized as colorless needles, mp 109–112°, $[\alpha]D$ +265.6° (MeCN). Structure **4** is assigned to the major component on the basis of spectral properties and is substantiated by independent synthesis from methyl 7-phthalimido-3-hydroxy-3-methylcepham-4-carboxylate (**5**) and thionyl chloride.[8] Unsuccessful dehydrochlorination in the presence of triethylamine indicates the synclinal conformation[10] of chlorine and the H-4 in **4**.[11] Additional evidence for this conformation is the absence of an internal nuclear Overhauser effect (NOE) between the proton at C_4 and the 3-methyl group.

The second product, mp 166–167°, $[\alpha]D$ −221° (MeCN), has distinctive ir, nmr, and mass spectra and the structure **3** is established on the basis of spectral data. The stereochemistry of **3** is assigned by measuring an NOE. Irradiation of the methyl protons (116 Hz) increases the intensity of the H-3 singlet at 286 Hz by 13.1%; consequently, the observed relaxation of H-3 is due to the β methyl protons and the configuration at C-2 is as shown by **3**.

We were interested in synthesizing deacetoxycephalosporin (**7**) from **4**. Since the clinal conformation of **4** is not favorable for the 1,2-elimination reaction, other possibilities for olefin formation were studied. One approach was an attempt to change the configuration at C_3 by nucleophilic displacement which should result in the more favorable periplanar conformation of the groups involved in elimination.[11] When **4** is treated with silver acetate in acetic acid for 5 min, a mixture of **6**, **7**, and **8** in the ratio of *ca.* 3:1:3 is obtained in almost quantitative yield. The structures of these compounds are established by ir and nmr spectra as well as by comparison with authentic samples.[12]

(1) Azetidinone Antibiotics. V. Part IV: S. Kukolja and S. R. Lammert, *Croat. Chem. Acta*, 423 (1972).

(2) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Amer. Chem. Soc.*, **85**, 1896 (1963); **91**, 1401 (1969).

(3) R. D. G. Cooper and F. L. José, *ibid.*, **92**, 2575 (1970); R. D. G. Cooper, *ibid.*, **92**, 5010 (1970).

(4) D. H. R. Barton, F. Comer, D. G. T. Greig, G. Lucente, P. G. Sammes, and W. G. E. Underwood, *Chem. Commun.*, 1059 (1970); D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *ibid.*, 1683 (1970).

(5) D. H. R. Barton, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, B. E. Looker, and W. G. E. Underwood, *ibid.*, 1137 (1971); D. H. R. Barton, F. Comer, D. G. T. Greig, P. G. Sammes, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *J. Chem. Soc. C*, 3540 (1971).

(6) D. O. Spry, *J. Amer. Chem. Soc.*, **92**, 5006 (1970).

(7) S. Kukolja, *ibid.*, **93**, 6267 (1971); S. Kukolja and S. R. Lammert, *Croat. Chem. Acta*, 44, 299 (1972).

(8) Compound **5**, mp 194–195°, is obtained according to ref 9.

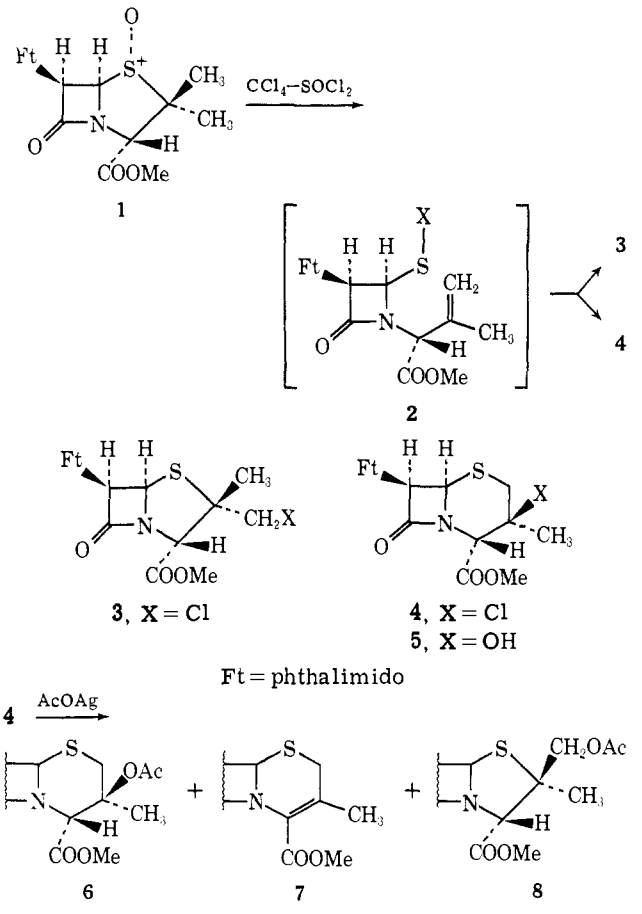
(9) G. E. Gutowski, B. J. Foster, C. J. Daniels, L. D. Hatfield, and J. W. Fisher, *Tetrahedron Lett.*, 3433 (1971).

(10) W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960); R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966); see especially pp 386 and 406.

(11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 689.

(12) Compound **8** was oxidized to the corresponding sulfoxide, which is identical with the sample described by Spry.[6] Methyl 3-methyl-3-cephem-7-phthalimido-4-carboxylate (**7**), mp 167–168°, is identical with a substance made from 7-aminodeacetoxycephalosporanic acid and *N*-carbethoxyphthalimide followed by esterification with diazomethane. The characteristic AB pattern (J_{gem} = 15 Hz) of the C_2 methylene protons of **6** suggests a cephalosporin structure, but firm proof is obtained by the synthesis of **6**, mp 146–147°, from **5** and acetic acid in the presence of fluorosulfuric acid.

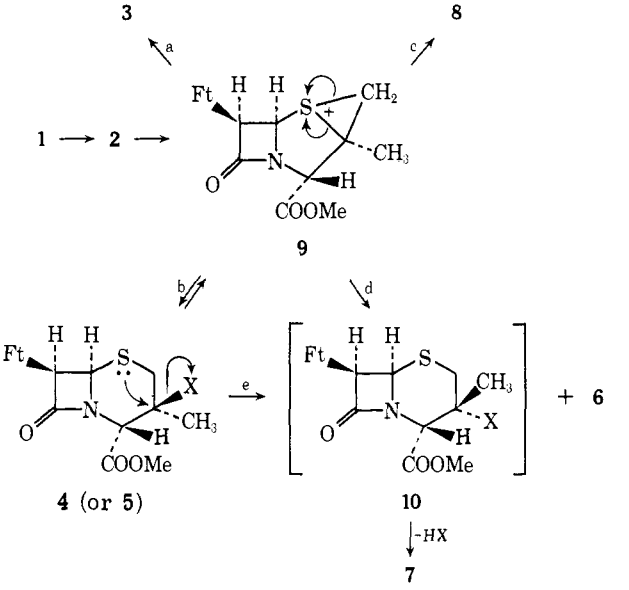
Evidently nucleophilic displacement of the 3-chloro substituent proceeds with both retention and inversion of configuration at C_3 resulting in products **6** and **7** In



addition, the synthesis of **8** from **4** represents the first conversion of a cepham system to a penam system. In order to determine if ring contraction could also be achieved with 3-hydroxycephams, a similar reaction with **5** was investigated. When **5** is heated with thionyl chloride in carbon tetrachloride in the presence of triethylamine, a mixture of **3**, **4**, and **7** in the ratio of *ca.* 1:4:1 is obtained in nearly quantitative yield. The formation of **3** from **5** represents a second example of ring contraction of a cepham to a penam.

Mechanistically the ring contraction of 3-substituted cephams to 2-substituted methylpenicillins is closely related to the ring expansion of penicillin sulfoxides to cephalosporins.[9,13] The intermediacy of **9** has been suggested in the ring expansion reaction,[2-6] and we believe that the ring contraction also occurs *via* **9**. The evidence is presented below in support of the common intermediacy of **9** in both the ring expansion and ring contraction processes.

We propose that the rearrangement of **1** to **3** and **4** *via* **2** (X = OH and Cl) involves initial addition of the sulfenyl chloride grouping to the appropriately positioned olefin to give thiiranium ion **9**.[14] This intermediate in turn undergoes ring opening by nucleophilic attack of chloride ion *via* pathway a and/or b giving **3** and **4**.[15] During ring contraction (**4** → **8** and **5** → **3**) the first step is formation of the carbonium ion which is stabilized by nucleophilic sulfur giving **9**. The episulfonium ion **9** is subsequently opened by anions (pathway a or c) yielding **3** or **8**, as well as the clinal conformer **6** and the periplanar isomer **10** (pathway d).



The latter product is easily transformed to the olefin **7**. An alternate mechanism for the formation of **6** and **10** from **4** can also involve nucleophilic displacement of chloride by acetate (pathway e). Similarly, **4** and **10** (X = Cl) can be formed from **5** by nucleophilic displacement of hydroxyl by chloride.

Acknowledgment. We wish to acknowledge our many helpful discussions with M. Gorman and D. O. Spry of the Lilly Research Laboratories, and Professor E. C. Taylor of Princeton University.

(13) R. R. Chauvette, P. A. Pennington, C. W. Ryan, R. D. G. Cooper, F. L. José, I. G. Wright, E. M. Van Heyningen, and G. W. Huffman, *J. Org. Chem.*, 36, 1259 (1971).

(14) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, 8, 482 (1969), and references therein.

(15) The formation of **3** and **4** can be explained by assuming an intermediate **9** existing in two configurations. The bridging methylene group can be attached to the sulfur from the α or the β face resulting in α or β episulfonium ions. For a detailed discussion, see: R. D. G. Cooper, L. D. Hatfield, and D. O. Spry, *Accounts Chem. Res.*, submitted for publication.

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Stereospecific Reduction of Epoxides with Sodium (Cyclopentadienyl)dicarbonylferrate. A New Route to Cationic Iron–Olefin Complexes

Sir:

We recently reported the preparation of cationic iron–olefin complexes of general constitution h^5-$C_5H_5Fe(CO)_2(olefin)^+$ through an exchange reaction employing the readily available isobutylene complex **1**.[1]

We wish now to report an alternative and facile synthesis of these cations employing epoxides as starting materials. The sequence provides a general method for the synthesis of complexes of this type which are

(1) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).