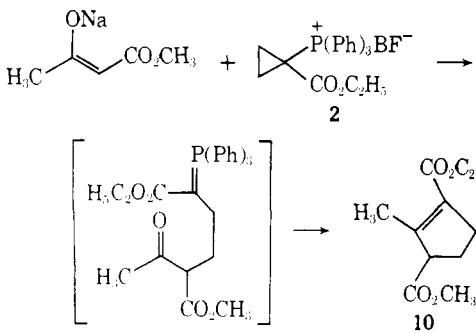

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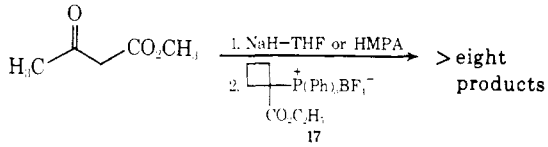
Attempts to utilize homologous reagent **17** in these reactions have been unrewarding.[12]



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Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(11) Thus far, efforts to detect a stabilized ylide intermediate have not been successful; this suggests that ring opening may be the rate limiting step in these reactions.

(12) Carboethoxycyclobutyltriphenylphosphonium fluoroborate (**17**) may be prepared from cyclobutyltriphenylphosphonium bromide[13] by a procedure analogous to the one used for the synthesis of **2** (**17**: 63% yield (mp 162–163°)).

(13) K. V. Scherer, Jr., and R. S. Lunt III, *J. Org. Chem.*, **30**, 3215 (1965).

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Azetidinone Sulfenic Acids. Isolation of Crystalline Sulfenic Acids from Penicillin Sulfoxides and a Study of Their Reactivities

Sir:

It has been 10 years since the sulfenic acid II was postulated as an intermediate in the important thermal rearrangement of penicillin sulfoxide (I) to desacetoxycephalosporin (IV).[1] While some derivatives or salts of sulfenic acids have been made,[2] compounds with this reactive function have defied isolation and in reality have only been known as a transient species. We wish to report the actual crystallization of this key intermediate sulfenic acid, IIa, and the isolation of other sulfenic acids in stable forms.

When the penicillin sulfoxide ester Ia was refluxed in ethyl acetate for 10 min and then evaporated to dryness, a mixture of the sulfoxide Ia and the sulfenic acid IIa was obtained in a 4:1 ratio. Recrystallization from ethyl acetate–ether gave sulfoxide Ia (60%). Evaporation of the filtrate and crystallization from methylene dichloride–cyclohexane yielded the pure sulfenic acid, IIa, mp 152–153° (10%).

The structure IIa was supported by nmr ($CDCl_3$–DMSO-d_6, 1:1) δ 2.0 (3 H, s, vinyl methyl), 5.6 and 5.9 (2 H, d, J = 4.5 Hz, *cis*-azetidinone protons), 5.01 and 5.19 (allylic and methylene protons), 7.25 (1 H, s, exchangeable with D_2O, –SOH);[3] infrared spectrum (KBr, cm^{-1}) showed four carbonyl absorptions, 1779 and 1720 (phthalimido), 1760 (azetidinone), and 1740 (ester), as well as a broad absorption at 3160 (OH) and intense bands at 1179, 1154, and 770 cm^{-1} which we assign to the S–O function; and high resolution mass spectrum, m/e 497 M^+. The crystalline α,β-unsaturated sulfenic acid isomer IIIb, mp 147–149°, was obtained in high yield by hydrolysis (methanol, 0°, 2 hr) of its trimethylsilyl sulfenic ester:[4] nmr ($CDCl_3$–DMSO-d_6) δ 2.22 and 2.33 (6 H, 2s), 5.67 and 5.83 (2 H, 2d, J = 5 Hz), 7.56 (1 H, s, exchangeable with D_2O, –SOH); infrared (5% $CHCl_3$) ν_{max} 3570 cm^{-1} (broad) sulfenic acid –OH.

Other sulfenic acids obtained by removal of the trimethylsilyl protecting function were IIb, amorphous, nmr ($CDCl_3$) δ 7.34 (1 H, s, exchangeable with D_2O, –SOH) and the above crystalline IIa.

A demonstration of the reactive nature of sulfenic acid IIa was obtained when a 50% conversion to penicillin sulfoxide (Ia) occurred (3 hr, 38°, $CHCl_3$ solution) as evidenced by nmr studies. Expected ring closure of the sulfenic acid IIa and IIb to the cephalosporin derivatives IVa and IVb occurred upon treatment with methane sulfonic acid in benzene–dimethylacetamide.[5]

Further evidence supporting the structural assignment of IIa derives from chemical reactions.[6] The oxidation of IIa with sulfuryl chloride (methylene chloride, room temperature) afforded the sulfinyl chloride Va[7] in almost quantitative yield and reaction with methane sulfonic acid (1 equiv, room temperature) gave VIa in a high yield.[8]

When the sulfenic acid IIb was treated with a trace of triethylamine in anhydrous benzene, there was obtained a crystalline isothiazolone derivative, VIIb,[9] in high

(1) 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); R. D. G. Cooper, L. D. Hatfield, and D. O. Spry, *Accounts Chem. Res.*, **6**, 32 (1973).

(2) K. Fries, *Chem. Ber.*, **45**, 2965 (1912); T. C. Bruice and P. T. Markiw, *J. Amer. Chem. Soc.*, **79**, 3150 (1957); W. Jenny, *Helv. Chim. Acta*, **41**, 317, 326 (1958); J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967); B. C. Pal, M. Uzil, D. G. Doherty, and W. E. Cohn, *ibid.*, **91**, 3634 (1969).

(3) The allylic proton is weakly coupled with the trans vinyl proton. Incidentally, the nmr spectrum of IIa is very similar and almost superimposable on the spectrum of the sulfinyl chloride Va reported previously (see ref 7).

(4) The trimethylsilyl ester was obtained by refluxing sulfoxide Ib with 100% excess silylating agents (2:1 molar ratio of trimethylsilyl chloride and hexamethyldisilazane) plus a trace of triethylamine. The trimethylsilyl esters of the β,γ-unsaturated sulfenic acids IIa and IIb were obtained from sulfoxide Ia and Ib, respectively, with the silylating agents only. See T. S. Chou, *Tetrahedron Lett.*, in press.

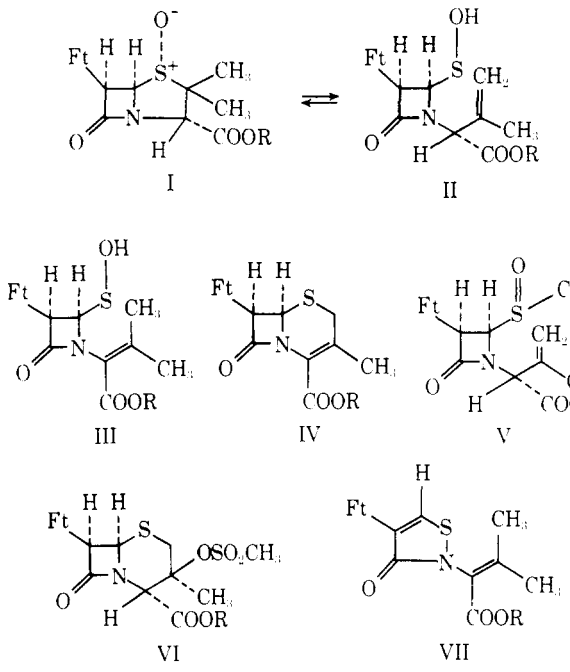
(5) Reference samples of compound IVa (mp 186–188°, $[\alpha]^{26}D$ –7.2° (*c* 1.0, $CHCl_3$)) and compound IVb (mp 176–177°, $[\alpha]^{26}D$ –4.7° (*c* 1.0, $CHCl_3$)) were prepared by procedures described in G. E. Gutowski, B. J. Foster, C. J. Daniels, L. D. Hatfield, and J. W. Fisher, *Tetrahedron Lett.*, 3433 (1971). Compound IVb had been previously prepared, S. Kukolja and S. R. Lammert, *J. Amer. Chem. Soc.*, **94**, 7169 (1972).

(6) Paper to be presented (S. Kukolja) at a Symposium on New Sulfur Chemistry sponsored by the Division of Petroleum Chemistry at the 167th Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1974.

(7) S. Kukolja and S. R. Lammert, *Angew. Chem.*, **85**, 40 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 67 (1973).

(8) The nmr ($CDCl_3$) spectrum of amorphous VIa: δ 1.83 (3 H, s), 3.61 and 3.50 (2 H, abq, J = 15 Hz), 3.56 (3 H, s), 5.38 (2 + 1 H, s), 5.46 (1 H, d, J = 4.5 Hz), 5.65 (1 H, d, J = 4.5 Hz), and 7.50–8.50 Hz (8 H, m, ar H).

(9) The isothiazolone VIIb has a melting point >230° dec, nmr ($CDCl_3$) δ 1.95 (3 H, s), 2.40 (3 H, s), 3.75 (3 H, s), 7.83 (4 H, m), and 8.40 (1 H, s); high resolution mass spectrum shows molecular ion at m/e 358 and a base peak at m/e 299 ($M - CO_2CH_3$). The intense peak at m/e 187 characteristic of a β-lactam compound with a phthalimido side chain is missing.



I II III IV V VI VII

a. R = $CH_2C_6H_4$-*p*-NO_2
b. R = CH_3
Ft = phthalimido

yield. Similar isothiazolines had previously been obtained by direct treatment of penicillin sulfoxides with bases.[10] It appears that abstraction of the sulfenic acid proton is essential in the azetidinone–isothiazolone transformation since it does not occur when the sulfenic acid is protected by the trimethylsilyl function.

The data and reactions recorded above support the intermediacy of a sulfenic acid in the penicillin–cephalosporin rearrangement. These intermediate crystalline sulfenic acids are stable under anhydrous conditions during room temperature storage. Accessibility of this important chemical species now provides an opportunity to study additional properties and reactions of sulfenic acids.

Acknowledgment. We wish to thank Dr. R. T. Rapala for assistance in preparing the manuscript.

(10) A related isothiazolone compound derived from the methyl ester of benzyl penicillin was reported by R. B. Morin, *et al.*, *J. Amer. Chem. Soc.*, **91**, 1401 (1969).

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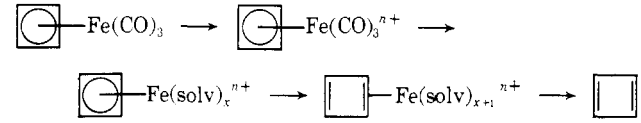
Dihapto Cyclobutadienoid Transition Metal Complexes. The Preparation of η^2-1,2-Benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron Hexafluorophosphate

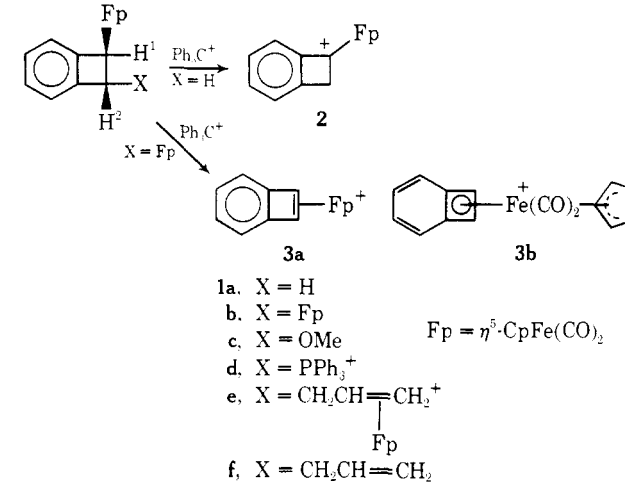
Sir:

Although the free cyclobutadienoid hydrocarbon is thought to be generated by the oxidative degradation of the tetrahapto cyclobutadienoid tricarbonyliron complex, the sequence of chemical events that effect the liberation of the hydrocarbon from the metal remains obscure.[1] We propose that a reasonable mechanism for the oxidative degradation of the iron complexes would involve initial oxidation of the metal, sequential displacement of the ligating carbon monoxides by the solvent molecules, and finally a stepwise detachment of the cyclobutadienoid hydrocarbon proceeding *via* a dihapto cyclobutadienoid complex. Except for an



allusion by Cava and Mitchell that the nickel carbonyl dimerization of benzocyclobutadiene may proceed *via* a bis(η^2-1,2-benzocyclobutadiene)nickel complex,[2] the possible existence of dihapto cyclobutadienoid complexes has received little attention. We now report the preparation and isolation of η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**3**), a complex that may possess the first example of a dihapto cyclobutadienoid ligand.

We initially attempted to generate **3** from the benzocyclobutenyl complex (**1a**) *via* β-hydride abstraction by the triphenylcarbenium ion.[3] Unexpectedly, the metallocarbenium ion (**2**) was formed by α-hydride abstraction. To generate **3** we desired a benzocyclobutenyl complex (**1**) which possessed a good leaving group trans to the iron. A complex possessing a trans methoxy or halo substituent was deemed most desirable; however, the trans binuclear complex (**1b**)[4] was the most available complex of this type, being readily prepared from *trans*-1,2-dibromobenzocyclobutene. Although the iron group had never been observed to function as a leaving group in the formation of a cationic olefin complex, it appeared that oxidative cleavage of one of the metal groups in **1b** would generate **3**. Accordingly, **3** is formed by treating **1b** with a degassed solution of triphenylcarbenium hexafluorophosphate in methylene chloride at −78°, allowing the mixture to warm to 0°,



3a **3b**

1a, X = H
b, X = Fp
c, X = OMe
d, X = PPh_3^+
e, X = $CH_2CH{=}CH_2^+$ (Fp)
f, X = $CH_2CH{=}CH_2$

Fp = η^5-CpFe(CO)$_2$

and filtering to give a 60–70% yield of an orange-red solid. Although solid **3** is stable when kept at −18° and under nitrogen, it rapidly decomposes with a notice-

(1) (a) R. H. Grubbs and R. A. Grey, *J. Amer. Chem. Soc.*, **95**, 5765 (1973), and references therein; (b) P. Reeves, T. Devon, and R. Pettit, *ibid.*, **91**, 5888 (1969).

(2) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 200.

(3) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Amer. Chem. Soc.*, **95**, 5430 (1973).

(4) R. B. King and W. C. Zipperer, *J. Organometal. Chem.*, **38**, 121 (1972). Although not reported by King and Zipperer, we have found that yields of the binuclear complex **1b** are quite variable ranging from 0 to 50%. Benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (**1a**) was often formed in yields up to 30% along with or to the exclusion of **1b**.