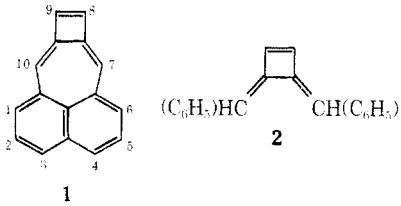
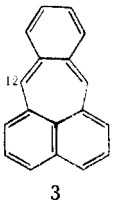
Generation of Dimethylenecyclobutenes from Cyclobutadieneiron Tricarbonyl Complexes. Synthesis of Cyclobutadienopleiadiene and α,α'-Diphenyldimethylenecyclobutene

Sir:

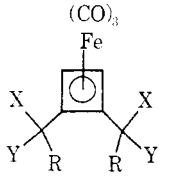
Our interest in the synthesis of fused-ring cyclobutadienoid systems from cyclobutadieneiron tricarbonyl complexes[1,2] has led us to examine the general problem posed when processes other than simple decomplexation are required for generation of systems which cannot be depicted formally as cyclobutadienes. For example, conversion of a vicinal diacylcyclobutadieneiron tricarbonyl to the corresponding dimethylenecyclobutene requires substituent manipulation in conjunction with decomplexation. We wish to report a solution to this problem with the conversion of diketones **4a** and **4b** to hydrocarbons **1** and **2**, and to describe some properties of **1**, cyclobutadienopleidaiene (CBP), the cyclobutadienoid analog of benzopleiadiene (**3**).[3,4]

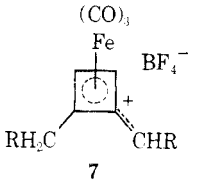


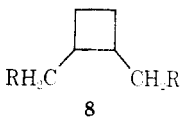


a, R,R = 

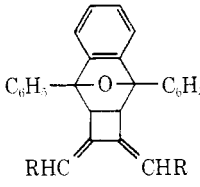
b, R = C_6H_5

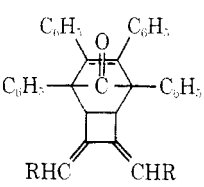


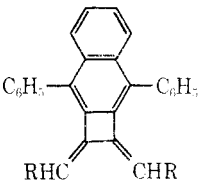




4, X,Y = C=O
5, X = Y = H
6, X = H; Y = OH







As a tactical approach, we envisaged sequential hydride–proton removal from **5a** to give **1** or a complex derivative. Treatment of **5a**, obtained *via* reduction (BH_3–BF_3–THF) of diketone **4a**,[2,5] with trityl fluoroborate in dichloromethane produced the violet, crystalline fluoroborate **7a**, mp 186° dec. Reaction of the latter with excess 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)[6] in dichloromethane then led directly to **1**. An alternate and more convenient approach was discovered when it was observed that simply shaking diol **6a**, mp 184–189° dec (obtained by the reduction of **4a** with B_2H_6),[7] in a concentrated aqueous HCl–THF mixture for a few minutes also afforded **1**.

CBP (**1**) was obtained as moderately stable yellow plates which slowly darken during storage in the cold and which decompose at ~70° to form a red, apparently polymeric material. The stability of the compound contrasts markedly with that of **3**, which is fleeting except at low temperatures and rapidly undergoes ($_{\pi}4_s + {}_{\pi}4_s$) dimerization across positions 7 and 12.[3] In view of the distinction between **1** and **3** as quinodimethane derivatives of cyclobutadienoid and benzenoid systems, respectively, the qualitative divergence in behavior is not surprising.

The structure of **1** (*m/e* 202) is supported by (a) the pmr spectrum [$\delta_{TMS}^{CDCl_3}$ 6.27 (s, 2 H, H_7 and H_{10}), 7.08 (s, 2 H, H_8 and H_9),[8] and 7.32–7.66 (ABC m, 6 H, aromatic, δ 7.27, 7.27, 7.56; J = 7.6, 7.6, and 1.8, Hz)],[9] (b) oxidation ($KMnO_4$–$NaIO_4$–K_2CO_3) to 1,8-naphthalic anhydride, and (c) reduction (H_2–Pd/C) to the hexahydro derivative **8a**, mp 85–88°. The compound also forms a picrate, dec range 160–170°, from which it can be recovered by alumina chromatography.

Chemically, CBP exhibits characteristic dienophilic reactivity at the cyclobutene double bond. Thus, heating **1** with 2,5-diphenylisobenzofuran or tetraphenylcyclopentadienone in benzene led to the red adducts **9a** [one stereoisomer, mp 260–270° dec] and **10a** [two stereoisomers mp 214–215° and 268–269°], respectively. Dehydration of **9a** (HBr–Ac_2O) afforded the highly extended hydrocarbon **11a** as a purple powder, mp 210–216°.

In analogous fashion, diketone **4b** was converted by the diol route to one of the symmetrical isomers of α,α'-diphenyldimethylenecyclobutene (**2**) [mp 92–94°; $\delta_{TMS}^{CDCl_3}$ 6.17 (s, 2 H) and 7.06–7.60 (m, 12 H)].[10]

Mechanistic considerations for formation of **1** and **2** are speculative at this point, but we suspect that the reactions observed reflect a new facet of the chemistry of tricarbonylcyclobutadienylcarbinyliron cations. In this view, diol breakdown proceeds (Scheme I) by substituent transfer from α,α' positions to iron *via* ambident complex cations **13** and **15**[11] followed by dissociation of the resulting monoeneiron II complex **16**

(1) B. W. Roberts, A. Wissner, and R. A. Rimerman, *J. Amer. Chem. Soc.*, **91**, 6208 (1969).

(2) B. W. Roberts and A. Wissner, *ibid.*, **92**, 6382 (1970).

(3) (a) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965); (b) J. Kolc and J. Michl, *J. Amer. Chem. Soc.*, **92**, 4147, 4148 (1970).

(4) Although **3** is now called pleiadene,[3] the pleiadiene stem is used here to emphasize the structural relationship between **1** and **3**. The proper name of **1** is cyclobuta[5,6]cyclohepta[1,2,3-*de*]naphthalene.

(5) Compositional analyses and spectral properties of all new compounds were in accord with assigned structures.

(6) H. Oediger, H. Kabbe, F. Moller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(7) The product is one of the cis isomers as indicated by the pmr spectrum.

(8) Assignments were established by comparison with the spectrum of **1**-*7,10-d*$_2$. Deuterium was introduced during reduction of **4a** with $NaBD_4$.

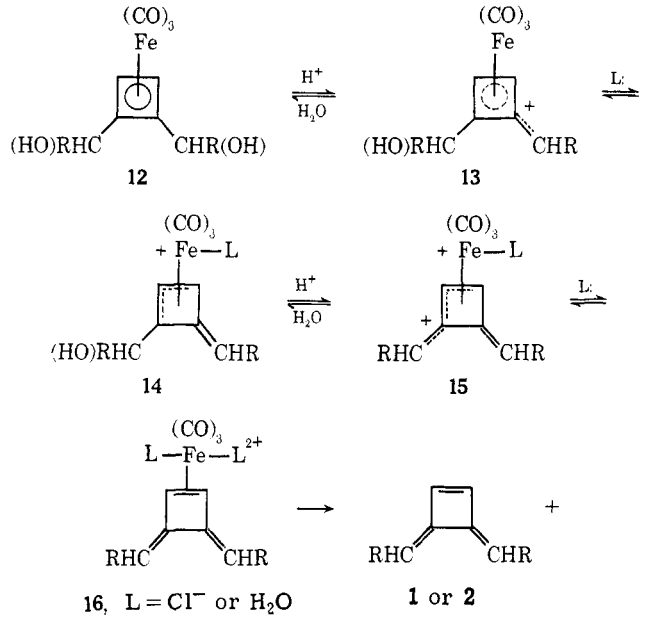
(9) Other spectral data include: ν_{max}^{KBr} 3035, 1590, 1559, 872, 771, and 765 (sh) cm^{-1}; $\lambda_{max}^{dioxane}$ (log ϵ) 241 (4.54), 247 (4.49), 256 (4.56), 268 (sh, 4.14), 278 (4.14), 368 (3.74), 382 (3.81), and 406 nm (3.64).

(10) In preparative work **1** and **2** were obtained in 50 and 28% yields, respectively. Actual yields are considerably higher, however, since the sensitivity of the compounds toward the purification methods used leads to unavoidable loss. In investigative work, solutions of **1** were prepared and employed immediately after decomposition of diol **6a**. Diol yields were 70–80%.

(11) Naphthylcarbinyl and benzylic character will substantially stabilize cations of types **13** and **15**. The exceptional stability of tricarbonylcyclobutadienylcarbinyliron cations is well established[12] and exemplified by **7a**, but we are not aware of any precedent for a cation such as **15**.

(12) (a) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *Tetrahedron Lett.*, 1299 (1966); (b) R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 6688 (1971).

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.