## Reaction of Diiron Nonacarbonyl with Benzvalene. Fragmentation, Rearrangement, and Hydrogen Transfer

Sir:

Recent work has demonstrated strikingly the manifold reactions of the vinylcyclopropyl group in polycyclics with metal carbonyls.[1a-c] Benzvalene (1) offers an interesting substrate for this reaction because it possesses the structural prerequisites for either $\sigma-\pi$ allyl complexation as with semibullvalene[1a,c] or ferretane formation as with dibenzosemibullvalene.[2] These processes correspond to cleavage of one of the four equivalent σ bonds (a) or insertion into the one unique σ bond (b), respectively.

Reaction of benzvalene (1)[3] in Et_2O–C_6H_6 at 50°
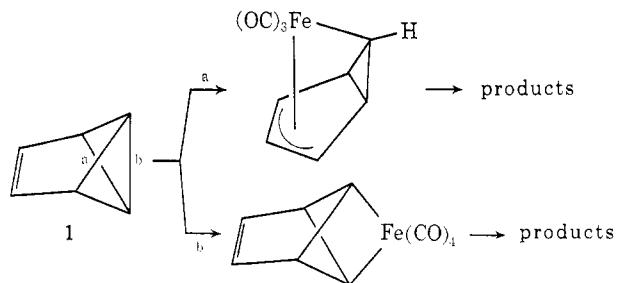
under nitrogen with a twofold excess of diiron nonacarbonyl for 4 hr followed by chromatographic separation on alumina yielded hexacarbonylfulvenediiron (2),[5] *trans*-di-μ-carbonyl-dicarbonyldi-π-cyclopentadienyldiiron (3), *cis*-di-μ-carbonyl-dicarbonyldi-π-cyclopentadienyldiiron (4),[8] and di-μ-carbonyl-dicarbonyldi-π-methylcyclopentadienyldiiron (5) of unknown configuration. The yield ratio of 2, 3 + 4, and 5 is 2:1:1 with 20% total yield. Also a very small amount of the

(1) (a) R. M. Moriarty, C.-L. Yeh, and R. C. Ramey, *J. Amer. Chem. Soc.*, 93, 6709 (1971); (b) R. M. Moriarty, C.-L. Yeh, K.-N. Chen, and R. Srinivasan, *Tetrahedron Lett.*, 5325 (1972); (c) R. Aumann, *Angew. Chem.*, 84, 583 (1972).

(2) R. M. Moriarty, K.-N. Chen, C.-L. Yeh, J. L. Flippen, and J. Karle, *J. Amer. Chem. Soc.*, 94, 8944 (1972).

(3) Benzvalene (1) was prepared by the method of Katz, *et al.*[4] It was codistilled with ether and benzene and its purity was assessed by means of nmr, δ (ppm) 2.06 (2 H), 3.76 (2 H), 5.85 (2 H). Since pure benzvalene is explosive no attempt to remove either the ether or the benzene was made. Importantly and *critical* to the results reported is the fact that absolutely no cyclopentadiene was present as a contaminant. This was ascertained by the absence of nmr absorption due to cyclopentadiene and double checked by the addition of cyclopentadiene to the benzvalene–ether–benzene solution and determination of the nmr of this system.

(4) T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, 93, 3782 (1971).

(5) Compound 2 is a known compound, mp ~135° dec, lit.[6] 140° dec. The X-ray structure of 2 has been determined.[7]

(6) E. Weiss, W. Hübel, and R. Merenyi, *Chem. Ber.*, 95, 1155 (1962).

(7) J. Meunier-Piret, P. Piret, and M. Van Meersche, *Acta Crystallogr.*, 19, 85 (1965).

(8) Compounds 3 and 4 were obtained as a mixture by chromatography of the crude reaction mixture. The infrared spectra of *trans*-di-μ-carbonyl-dicarbonyldi-π-cyclopentadienyldiiron (3), mp 150° dec, lit. 146° dec,[9] and the cis isomer 4, mp 150° dec, lit. 146° dec,[9] have characteristic differences in the C≡O stretching frequency region of the infrared spectra. The cis isomer uniquely possesses bands at 1766, 1801, 1933, and 1975 cm⁻¹. The pure cis isomer was obtained by repeated crystallization at −78° from ethyl acetate. In the present study the structure of the cis isomer was established by a single-crystal X-ray analysis. The study was only carried out to a point where the structure was established unequivocally since a complete report on its structure has already been published.[9] Compound 5 has mp 99–100°, lit.[10] 98–99°. The presence of trace amounts of di-μ-carbonyl-dicarbonyl-π-methylcyclopentadienyl-π-cyclopentadienyldiiron was indicated by mass spectral analysis of a chromatographic fracton from the crude reaction product which contained predominantly 5. Peaks at m/e 368, 340, 312, and 121 (C_5H_5Fe) are indicative. Thus far this compound has not been isolated in crystalline form.

configuration unknown
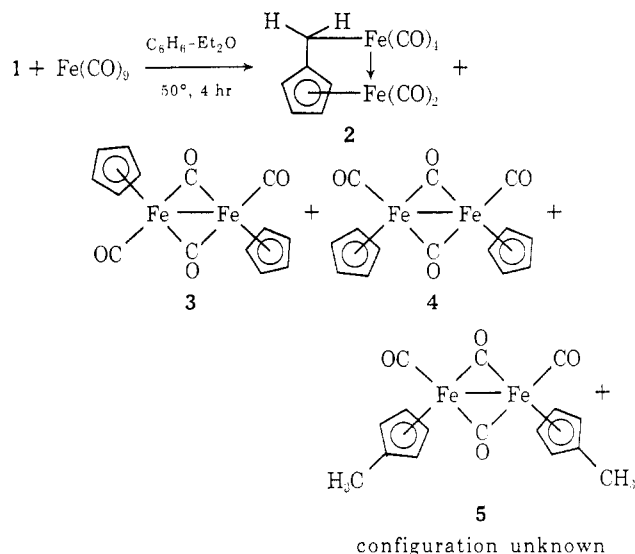
mixed cyclopentadienyl complex di-μ-carbonyl-dicarbonyl-π-methylcyclopentadienyl-π-cyclopentadienyldiiron was indicated by mass spectral analysis.[8]

Formation of 3 and 4 involves an unprecedented loss of CH from the C_6H_6 starting material. Formation of 5 requires a reduction step and this accounts for the overall stoichiometry ($2C_6H_6 \rightarrow C_5H_5 + C_6H_7 + C$). Complex 2 results from a 1,2-hydrogen migration for which ample precedent exists.[11] The following mechanistic pathway represents a working hypothesis for rationalization of this complex series of reactions.

The salient feature of this mechanism is that the C_6H_6, C_6H_7, and C_5H_5 products may derive from two different initial intermediates. Sequence $1 \rightarrow 6 \rightarrow 7$
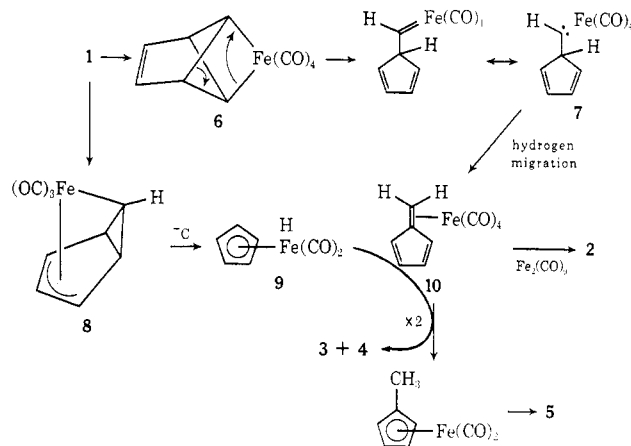
involves ferretane formation;[2] subsequent bond reorganization in what is formally a nonallowed $2 + 2$ retrocycloaddition or an allowed $2 + 2 + 2$ retrocycloaddition yields the carbene complex 7. 1,2-Hydrogen migration ($7 \rightarrow 10$) is a well known reaction of carbenes.[12] The sequence $1 \rightarrow 8 \rightarrow 9$ is basically a cycloelimination of carbon preceded by hydrogen migration to yield 9 which has been postulated already as an intermediate in the formation of 3 and 4 from cyclopenta-

(9) R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, 3068 (1970).

(10) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 9, 86 (1959).

(11) C. H. DePuy, V. M. Kobal, and D. H. Gibson, *J. Organometal. Chem.*, 13, 266 (1968).

(12) W. Kirmse, "Carbene Chemistry," Academic Press, New York and London, 1964, pp 53–58.

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diene and Fe(CO)₅.[13] Cycloelimination of carbon is observed in the decomposition of the C₇ carbene of quadricyclane (or norbornadiene) to yield benzene.[14] The driving force in the present reaction **8 → 9 → 3 + 4** is formation of the very stable biscyclopentadienyl complex. We propose that **10** may act as a hydrogen acceptor from **9** and the reduction product dimerizes to yield **5**. Apparently only a very small amount of the π-methylcyclopentadienyldicarbonyliron reacts with π-cyclopentadienyldicarbonyliron to give the mixed bridged complex.

The reason for postulating a different route for the formation of **2, 3 + 4**, and **5** is due to the fact that benzobenzvalene (**11**)[4] yields only the benzofulvene

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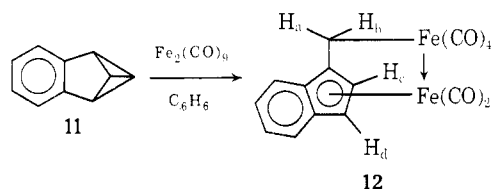
complex **12**[15] upon treatment with diiron nonacarbonyl and no π-indenyl complex analogous to **3, 4,** or **5**.

We interpret this behavior as being due to the fact that formation of a σ–π allyl intermediate analogous to **8** is impossible in the case of **11**. Also relevant to this point is the fact that benzosemibullvalene **13** yields only the σ–π allyl complex **14**.[1b]

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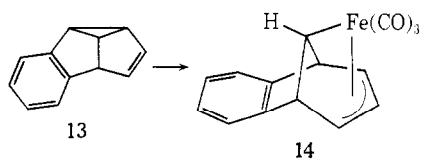
Acknowledgment. Discussion of this work with Dr. R. Aumann, University of Münster, was valuable. The authors also wish to thank Dr. R. Minard of this Department for assistance with the mass spectral work.

(13) H. W. Sternberg and I. Wender, *Chem. Soc., Spec. Publ.,* No. 13, 35 (1959).

(14) P. B. Shevlin and A. P. Wolf, *Tetrahedron Lett.,* 3987 (1970); R. A. Moss, U.-H. Dolling, and J. R. Whittle, *ibid.,* 931 (1971).

(15) Compound 12, mp 118° dec, has ir (C≡O) 1943, 1960–2000, 2060 cm⁻¹; the mass spectrum showed the parent molecular ion at *m/e* 408; other peaks occurred at *m/e* 380, 352, 324, 296, 268, and 240 corresponding to successive loss of CO; nmr showed aromatic absorption δ (relative to Me₄Si) at 7.20 ppm (four proton), H_d 5.66 ppm (d), H_c 3.80 ppm (d, J_{cd} = 2.8 Hz), H_a and H_b centered at 2.21 ppm (q, J_{ab} = 13.1 Hz). *Anal.* Calcd for C₁₆H₈O₆Fe₂: C, 47.06; H, 1.96. Found: C, 47.10; H, 2.03.

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A New Method for the Synthesis of Epidithiodiketopiperazines

Sir:

The epidithiodiketopiperazine structure is a common functionality in the natural products of the gliotoxin-

sporidesmin class.[1] Although a few simple epidithiodiketopiperazine derivatives have been synthesized,[2] a general method is lacking. Here we report a method which is expected to be generally useful for the synthesis of this functionality, starting from 1,4-dimethylpiperazine-2,5-dione-(*cis* or *trans*)-3,6-dithiol **1a** or **1b**.[2a,b]

Anisaldehyde reacted smoothly with the cis dithiol **1a** in methylene chloride containing boron trifluoride etherate at room temperature, to yield the thioacetal **2**[3] (mp 267–268°) in 80% yield. As expected, the same thioacetal **2** could also be obtained from trans dithiol **1b** under the same conditions in similar yield. The thioacetal **2** is stable under acidic, basic, or reductive conditions.

The thioacetal **2** can be used as a protected precursor of the epidithiodiketopiperazine ring,[4] since **2** can be smoothly cleaved into the epidithiodiketopiperazine **3** and anisaldehyde in two steps: the oxidation of **2** to a sulfoxide with *m*-chloroperbenzoic acid in methylene chloride at 0°, followed by acidic treatment, *e.g.*, BF₃·Et₂O, BCl₃, H₂SO₄, or HClO₄. In the acidic cleavage reaction of the sulfoxide, a facile carbon-sulfur bond fission—note the resonance stabilization of the carbonium ion by the *p*-methoxybenzene ring—is obviously crucial, because the cleavage reaction does not take place in the thioacetals derived from formaldehyde, acetaldehyde, or benzaldehyde (R = H, CH₃, or C₆H₅ in **2**). Related to this point, a smooth and efficient formation of **3** was observed from the di(tetrahydropyranyl) cis dithiol **4**[3] (mp 164–165°) by iodine oxidation in methylene chloride.

One equivalent of butyllithium in THF at −78° generated the monocarbanion at the bridgehead position of **2**.[5] A large difference in the acidity of the two bridgehead hydrogens was observed. Namely, when the monocarbanion was quenched with DCl, only one bridgehead hydrogen was clearly replaced with deuterium (the chemical shifts of H_a and H_b in **2** are 4.88 and 5.03 ppm and only the signal at 4.88 ppm disappeared).

The monoanion was found to react smoothly with primary halides, acid halides, and aldehydes in THF at −78°, to give the monosubstituted thioacetals **5** and a small amount of the disubstituted thioacetals **10**. The monosubstituted thioacetal **5** was a single material, not a diastereomeric mixture, that is again attributed to the difference in the acidity between two bridgehead hydrogens.

In the following case, the identification of the more acidic hydrogen was possible by a chemical method. Namely, the diastereomeric chlorides **6a**[3,6] (mp 212–

(1) Gliotoxin, sporidesmins, aranotins, chaetocins, verticillin A, and chetomin belong to this class.

(2) (a) P. W. Trown, *Biochem. Biophys. Res. Commun.,* **33,** 402 (1968); (b) U. Schmidt, *et al., Angew. Chem.,* **83,** 114 (1971); *Chem. Ber.,* **104,** 1714 (1971); **105,** 625, 635, 3658 (1972); **106,** 165, 396 (1973); (c) T. Hino and T. Sato, *Tetrahedron Lett.,* 3127 (1971); (d) S. G. Svokos and R. B. Angier, *Chem. Abstr.,* **74,** 53845 (1971).

(3) Satisfactory analytical and spectroscopic data were obtained on this compound.

(4) The epidithiodiketopiperazines can be efficiently converted into the thioacetals by sodium borohydride reduction in methanol, followed by an anisaldehyde treatment under acidic conditions.

(5) The monocarbanion is stable at −78°, but decomposes slowly at 0°. The thioacetal 2 decomposed in THF even at −78°, when potassium *tert*-butoxide was used as a base. The dicarbanion, generated from 2 equiv of butyllithium in THF, decomposed into unidentified compounds at −78°.

(6) Y. Kishi, T. Fukuyama, and S. Nakatsuka, *J. Amer. Chem. Soc.,* **95,** 6492 (1973).