

Figure 1. ^{13}C Fourier transform magnetic resonance spectra of pyrrolnitrin: (A) from C-13 natural abundance; (B) from D,L-tryptophan-alanine-3- ^{13}C .

data for nitrobenzene made the cmr analysis of all carbons except C-2 and C-5 of pyrrolnitrin facile. The most important assignments were the signals for C-3 (111.7 ppm) and C-4 (115.3 ppm) of the pyrrole ring. These assignments were confirmed by checking the effect of reduction of the nitro group. The signal at 111.7 ppm was almost unchanged, whereas the signal at 115.3 ppm was shifted to 118.7 ppm in the spectrum of aminopyrrolnitrin (IX).² Finally, in the spectrum of the biosynthetic pyrrolnitrin- ^{13}C (cf. Figure 1) the signal at 111.7 ppm showed significant enrichment, indicating that C-3 of the pyrrole ring originates from C-3 of the tryptophan side chain.

This conclusion is in agreement with the results of chemical degradations of radioactive pyrrolnitrin samples from earlier feeding experiments. Pyrrolnitrin obtained from tryptophan-alanine-3- ^{14}C ³ (3140 dpm/ μmol) was subjected to a modified permanganate oxidation¹⁰ yielding 3-chloro-2-nitrobenzoic acid (IV) (6.7 dpm/ μmol) which contained only 0.21% of the label. Formylation¹¹ of pyrrolnitrin- ^{14}C , ^3H ($T/^{14}\text{C} = 2.34$) obtained biosynthetically from DL-tryptophan-alanine-3- ^{14}C -2- ^3H ³ gave the aldehyde V (Scheme I) ($T/^{14}\text{C} = 0.23$) with loss of most of the tritium. Direction of the formylation was confirmed by Ag_2O oxidation¹² of a

(10) H. Imanaka, M. Kousaka, G. Tamura, and K. Arima, *J. Antibiot., Sect. A*, **18**, 207 (1965).

(11) K. Hattori and M. Hashimoto, Japanese Patent 4152 (1967); *Chem. Abstr.*, **67**, 32585U (1967).

(12) K. Hattori and M. Hashimoto, Japanese Patent 181 (1967); *Chem. Abstr.*, **66**, 55379Y (1967).

nonlabeled sample of the aldehyde to the known carboxylic acid VI.¹³

These results establish the labeling pattern of the pyrrole ring of pyrrolnitrin, showing that C-3 of the tryptophan side chain becomes C-3 of the antibiotic and that tryptophan is a direct and specific precursor of pyrrolnitrin. This is important in view of a recent report¹⁴ on the incorporation of δ -aminolevulinic acid-4- ^{14}C into the pyrrole ring of the antibiotic. Finally, the results rule out the aforementioned rearrangement process involving a 1,2-aryl shift.

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(13) K. Tanaka, K. Kariyone, and S. Umio, *Chem. Pharm. Bull.*, **17**, 622 (1969).

(14) H. Imanaka, M. Ajisaka, K. Hattori, G. Tamura, and K. Arima, *Abstracts, 4th International Fermentation Symposium, Kyoto, Japan, 1972*, p 135.

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Ferretane. A New Ring System from the Reaction of Diiron Nonacarbonyl and Dibenzosemibullvalene

Sir:

Previously it was reported that reaction of semibullvalene with diiron nonacarbonyl yields a $\text{C}_8\text{H}_8 \cdot \text{Fe}(\text{CO})_3$ complex which possesses the bicyclo[3.2.1]octyl ring system with π -allyl and σ bonding of the $\text{Fe}(\text{CO})_3$ unit to the carbocyclic framework.¹ We now find that reaction of dibenzosemibullvalene (1)^{2a,b} with diiron nonacarbonyl follows a dramatically different pathway, namely, the iron atom inserts into a σ bond of the three-membered ring to yield a four-membered ring containing iron bonded by two $\text{Fe}-\text{C}$ σ bonds.³

(1) R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971).

(2) (a) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965); (b) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(3) Compound 2 was obtained as yellow crystals, mp 143° dec, in 25% yield by chromatography on silica gel (*Anal.* Calcd for $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Fe}$: C, 64.54; H, 3.23. Found: C, 64.80; H, 3.40) and it showed $\text{C}=\text{O}$ absorption at 1980–2080 cm^{-1} . The nmr spectrum possessed the same overall appearance as dibenzosemibullvalene, but all resonances were shifted from their positions in the starting material: δ (ppm) 3.04 (H_a , d, 2 H), 4.55 (H_b , H_c , m, 2 H), 7.00 (aromatic protons, m, 6 H), 7.25 (H_d , m, 2 H). The mass spectrum showed the parent molecular ion $\text{C}_{16}\text{H}_{12}\text{Fe}(\text{CO})_3^+$ at m/e 372 and $\text{C}_{16}\text{H}_{12}\text{Fe}(\text{CO})_3^+$ at m/e 344; $\text{C}_{16}\text{H}_{12}\text{Fe}(\text{CO})_2^+$, 316; $\text{C}_{16}\text{H}_{12}\text{Fe}(\text{CO})^+$, 288; $\text{C}_{16}\text{H}_{12}\text{Fe}^+$, 260; and $\text{C}_{10}\text{H}_{12}^+$, 204. Compound 4 had mp 158° dec, $\nu(\text{C}=\text{O})$ 1900–1935 cm^{-1} .

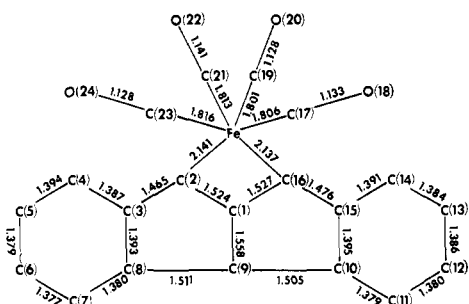


Figure 1. Bond lengths for dibenzosemibullvaleneiron tetracarbonyl.

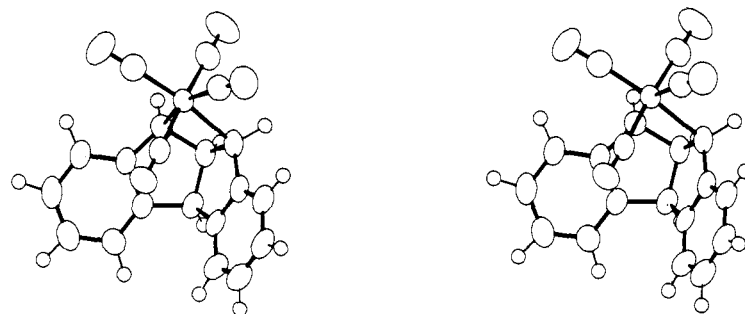
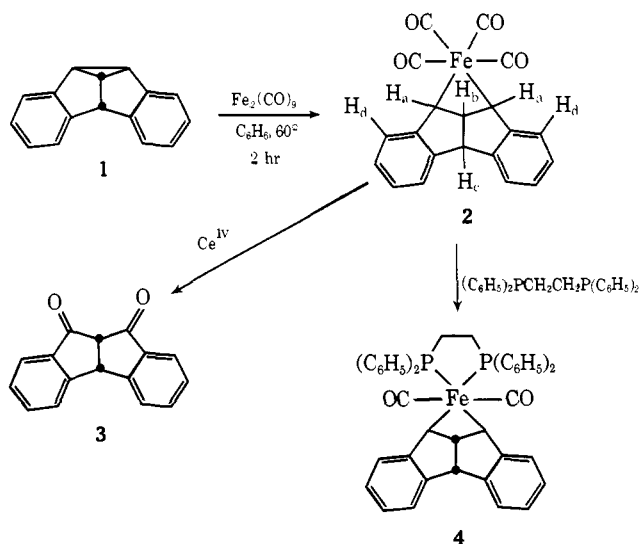


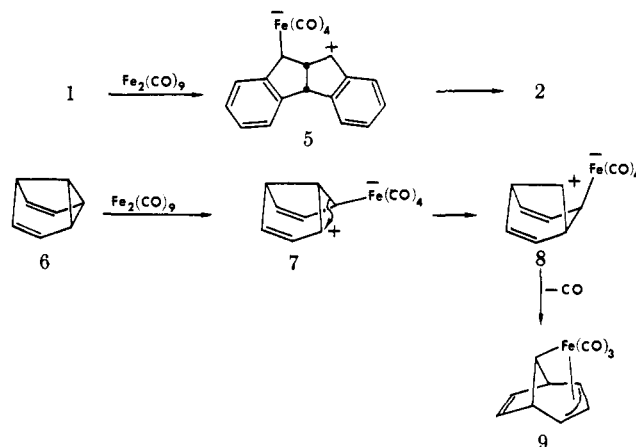
Figure 2. The stereoconfiguration of **2** including the position of the hydrogen atoms.



The infrared, nuclear magnetic resonance, and mass spectra of **2** were consonant with the proposed structure.³ Oxidative decomposition of **2** with ceric ammonium nitrate in alcohol-water yielded the β -diketone 3,4,7,8-tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene (**3**) which was compared with an authentic sample.⁴ Reaction of **2** with 1,2-bis(diphenylphosphino)ethane yielded **4**.³

In spite of the presence of two Fe-C σ bonds, **2** shows impressive chemical stability. Treatment with concentrated hydrochloric acid at 80° for 3 days gave no reaction. Attempted reduction with lithium aluminum hydride in ether at reflux for 24 hr yielded no reaction. Also, the compound was completely unreactive toward sodium borohydride.

The stability of **2** is probably kinetic in origin, that is, there are no normal metal-alkyl decomposition pathways available such as β elimination or carbon-carbon σ bond rearrangement for its decomposition.⁶ Furthermore, its formation can also be rationalized on a similar basis. Intermediate **5** can do little else but close to **2** while in the case of semibullvalene (**6**) the analogous intermediate **7** can and does rearrange to **8**



which ultimately yields the observed product **9**.

The stereoconfiguration of **2** was established by X-ray single-crystal analysis. Intensity data were collected on an automatic diffractometer. The unit cell dimensions are $a = 9.36$, $b = 18.36$, and $c = 9.82$ Å and $\beta = 106.0^\circ$, space group $P2_1/n$. The structure was solved using the symbolic addition procedure for centrosymmetric crystals⁷ and refined to a final R factor of 4.4%.

Bond lengths are shown in Figure 1 and the stereo-configuration including the position of the hydrogen atoms is shown in Figure 2.

The dibenzosemibullvalene portion of the molecule is composed of two planar segments; atoms C(1)-C(9), planar to within ± 0.075 Å, and atoms C(9)-C(16) plus C(1), planar to within ± 0.033 Å. The angle between the two planes is 61.5° . The ferretane ring is planar to within ± 0.013 Å. A detailed description of the crystal structure will be published elsewhere. The Fe-C σ -bond lengths of 2.141 and 2.137 Å are close to the related Fe-C σ -bond lengths in: $\pi(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-C}_5\text{H}_5$, 2.11 ± 0.02 Å;⁸ $(\text{OC})_2\text{Fe}(\pi\text{-C}_5\text{H}_4\text{CH}_2)\text{-Fe}(\text{CO})_3$, 2.12 Å;⁹ $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-CH}_2\text{COOH}$, $2.06 \pm \sim 0.02$ Å;¹⁰ tetracarbonylacrylonitrileiron, 2.09 and 2.10 Å;¹¹ and 1,5-cyclooctadienebis(iron tetracarbonyl), 2.14 and 2.15 Å.¹²

(7) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(8) M. J. Bennett, Jr., F. A. Cotton, A. Davidson, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(9) J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Crystallogr.*, **19**, 85 (1965).

(10) M. L. Green, J. K. P. Ariyaratne, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).

(11) A. R. Luxmore and M. R. Truter, *Proc. Chem. Soc.*, 466 (1961).

(12) C. Krüger, *J. Organometal. Chem.*, **22**, 697 (1970).

(4) 3,4,7,8-Tetrahydro-3,4-dioxo-1,2,5,6-dibenzopentalene was synthesized by treatment of 1-oxo-3-phenyl-2-indanylglyoxylic acid with polyphosphoric acid. The reported melting point is 259°.⁵ In our hands the material showed mp 243-244° and the material obtained by Ce^{IV} oxidation of **2** had mp 243-244°. Furthermore, the two compounds had identical infrared spectra and mass spectra.

(5) W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, *J. Chem. Soc.*, 4026 (1957).

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y., 1972, pp 756-761.

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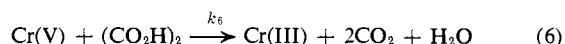
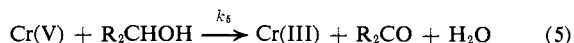
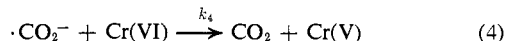
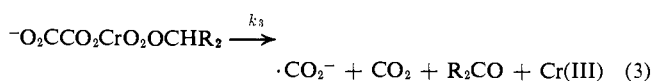
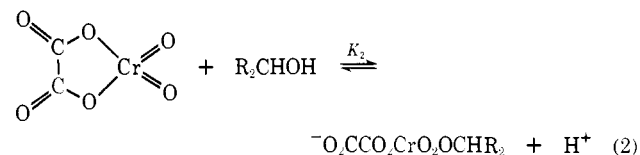
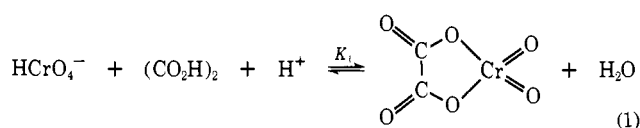
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Three-Electron Oxidations. III. The Chromium(V) Oxidation Step¹

Sir:

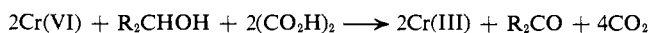
In the first paper of this series, we proposed the following mechanism (Scheme I) for the chromic acid co-

Scheme I

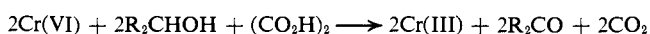


oxidation of oxalic acid and isopropyl alcohol.²

Chromium(V) produced in reaction 4 can react either with isopropyl alcohol (reaction 5) or with oxalic acid (reaction 6).³ If all chromium(V) formed in reaction 4 reacted with oxalic acid, the total stoichiometry of the reaction would be



If, on the other hand, all chromium(V) reacted with isopropyl alcohol, the following stoichiometry would result



Thus, depending on the concentration of oxalic acid and isopropyl alcohol in the reaction system, the ratio of CO₂:acetone should vary between 4:1 and 1:1, provided that the reactivity of chromium(V) toward the two substrates is of comparable magnitude.

Table I and Figure 1 give the dependence of the CO₂:acetone ratio as a function of the isopropyl alco-

(1) Part II: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, in press.

(2) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

(3) Actually, at least two different chromium(V) species can be formed, depending on whether the ·CO₂ radical reacts with free chromic acid or with the chromic acid-oxalic acid complex. As there is sufficient reason to believe that chromium(V) is sufficiently long lived to permit the establishment of a new equilibrium between chromium(V) and the components of the solution, it is not necessary to consider each species separately.

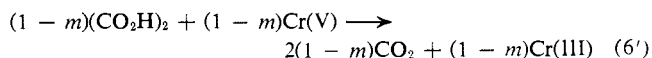
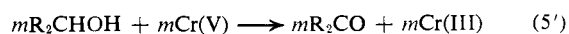
Table I. Effect of Isopropyl Alcohol Concentration on the Ratio of the Products

[<i>i</i> -PrOH], M	[<i>i</i> -PrOH] /[OxH ₂] ^a	Acetone yield, mmol	CO ₂ yield, mmol	CO ₂ : acetone
(A) [Oxalic Acid] = 0.075 M, [Chromium(VI)] = 0.0140 M, [Perchloric Acid] = 0.063 M				
1.56	40.0	0.280	0.285	1.02
0.78	20.0	0.280	0.290	1.04
0.39	10.0	0.234	0.352	1.50
0.195	5.0	0.218	0.408	1.87
0.098	2.5	0.186	0.468	2.52
0.039	1.0	0.156	0.528	3.38
0.0195	0.5	0.150	0.536	3.58
(B) [Oxalic Acid] = 0.15 M, [Chromium(VI)] = 0.0140 M, [Perchloric Acid] = 0.125 M				
2.34	22.94	0.280	0.290	1.04
1.56	15.29	0.250	0.332	1.33
1.17	11.47	0.250	0.350	1.40
0.78	7.64	0.226	0.384	1.70
0.39	3.82	0.198	0.450	2.27
0.195	1.91	0.176	0.490	2.78
0.098	0.95	0.156	0.536	3.44
0.059	0.57	0.134	0.540	4.03
0.039	0.38	0.140	0.540	3.86
(C) [Oxalic Acid] = 0.15 M, [Chromium(VI)] = 0.0157 M, [Perchloric Acid] = 0.63 M				
3.12	22.84	0.310	0.318	1.02
2.34	17.14	0.295	0.320	1.08
1.56	11.42	0.270	0.390	1.45
1.17	8.57	0.266	0.414	1.56
0.78	5.71	0.250	0.464	1.86
0.39	2.85	0.206	0.534	2.59
0.195	1.42	0.200	0.546	2.73
0.078	0.57	0.176	0.610	3.47
0.039	0.28	0.160	0.644	4.03
0.0195	0.14	0.160	0.640	3.99

^a [OxH₂] = concentration of undissociated oxalic acid.

hol:oxalic acid ratio under a variety of conditions.⁴ The analyses were carried out under standard conditions at 25°. Acetone was determined gravimetrically as 2,4-dinitrophenylhydrazone from 20-ml samples of the composition given in Table I. Carbon dioxide was determined from a 2-ml sample manometrically in a Warburg apparatus. *The results show that the CO₂:acetone ratio varies within the predicted range and lend significant additional support to the proposed three-electron oxidation process.*

In order to estimate the relative reactivity of chromium(V) toward the two substrates, reactions 5 and 6 were rewritten to indicate the mole fraction, *m*, of chromium(V) reacting with the isopropyl alcohol



$$m = \frac{k_5[\text{R}_2\text{CHOH}]}{k_5[\text{R}_2\text{CHOH}] + k_6[(\text{CO}_2\text{H})_2]} \quad (7)$$

The total yield of acetone formed by each two molecules of chromium(VI) reduced is therefore 1 + *m*, and

(4) In all substrate ratios given in Table I the cooxidation reaction is by far the most important process taking place. The direct oxidation of isopropyl alcohol accounts for less than 0.5% of the overall reaction, even at the highest alcohol concentration. While the direct oxidation of oxalic acid is more significant, it accounts for a maximum of 16% under the most extreme conditions (lowest alcohol:oxalic acid ratio, last entry in Table I), and is responsible for only 2.7% of the overall reaction containing an equimolar concentration of isopropyl alcohol and of undissociated oxalic acid.