

yield. Similar isothiazolones 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).

T. S. Chou,* J. R. Burgdorf, A. L. Ellis
S. R. Lammert, S. P. Kukolja

*The Lilly Research Laboratories, Eli Lilly and Company
Indianapolis, Indiana 46206*

Received October 27, 1973

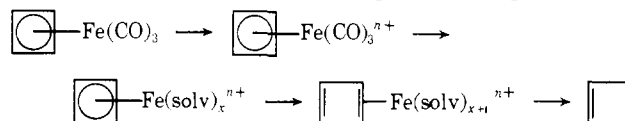
Dihapto Cyclobutadienoid Transition Metal Complexes. The Preparation of η^2 -1,2-Benzocyclobutadiene- η^5 -cyclopentadienyldicarbonyliron Hexafluorophosphate

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

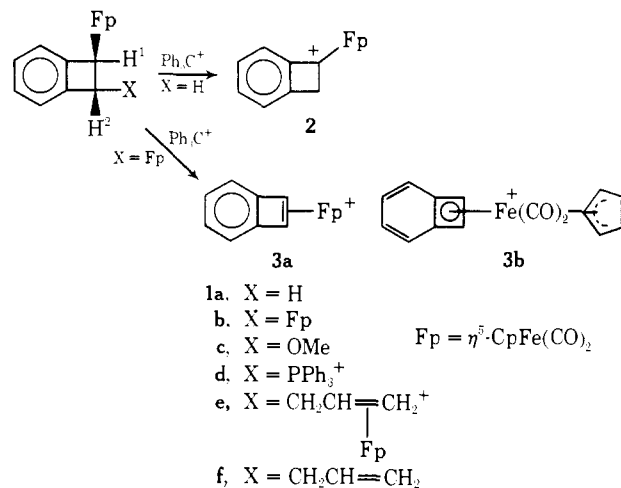
(1) (a) R. H. Grubbs and R. A. Grey, *J. Amer. Chem. Soc.*, **95**, 5765 (1973), and references therein; (b) P. Reeves, T. Devon, and R. Pettit, *ibid.*, **91**, 5888 (1969).

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 metalocarbenium 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° ,



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-

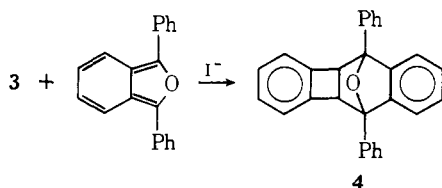
(2) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 200.

(3) A. Sanders, L. Cohen, W. P. Gierring, 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**.

able exotherm at room temperature. Decomposition in solution (MeNO₂, Me₂CO, PhNO₂, SO₂, THF) is very rapid as evidenced by bubbling and darkening of the mixture. Unfortunately, due to its instability or insolubility in appropriate solvents, we have not been able to recrystallize **3** to remove paramagnetic impurities which have thus far thwarted our efforts to obtain an nmr spectrum of **3**. The carbonyl stretching frequencies of **3** (2070 and 2035 cm⁻¹) are typical of cationic olefin complexes of η⁵-cyclopentadienyldicarbonyliron. The overall infrared spectrum of **3** is very similar to that of the related styrene complex, (PhCH=CH₂)Fp⁺PF₆⁻.

The identity of **3** was established by the characterization of a series of trans 1,2-disubstituted benzocyclobutenyl complexes formed by the addition of a variety of nucleophiles to **3**.^{5,6} Thus, **3** is reduced to the known benzocyclobutenyl complex (**1a**) by lithium borohydride in tetrahydrofuran in 20% yield.³ Treatment of **3** with a mixture of methanol and sodium bicarbonate gives an 83% yield of the trans methoxy adduct (**1c**): ir (KBr) 1995, 1940 cm⁻¹ (C=O), nmr (CS₂) τ 6.61 (s, 3, CH₃), 6.00 (d, 1, J_{1,2} = 1.5 Hz, H¹), 5.59 (d, 1, H²), 5.23 (s, 5, Cp), 2.96 (m, 4, Ar). Although **3** is initially sparingly soluble in methylene chloride, it rapidly dissolves in the presence of triphenylphosphine to form, in 82% yield, the trans phosphonium salt (**1d**): ir (hexachlorobutadiene) 2000, 1937 cm⁻¹ (C=O), nmr (CD₃NO₂) τ 5.51 (m, 1, J_{1,2} = 1 Hz, J_{P,H1} = 12 Hz, H¹), 5.03 (m, 1, J_{P,H2} = 5 Hz, H²), 4.95 (s, 5, Cp), 2.74 (m, 19, Ar). Analogously, **3** is readily alkylated by a cold methylene chloride solution of η¹-3-propenyl-η⁵-cyclopentadienyldicarbonyliron to yield 63% of the cationic binuclear complex (**1e**). The neutral trans alkylated complex **1f** is generated in 30% yield by subsequent treatment of **1e** with sodium iodide in acetone: (**1f**) ir (neat) 1995, 1930 cm⁻¹ (C=O), nmr (CS₂) τ 7.60 (m, 2, CH₂-), 6.91 (m, 1, J_{1,2} = 1.8 Hz, H²), 6.29 (d, 1, H¹), 5.33 (s, 5, Cp), 5.00 (m, 2, =CH₂), 4.07 (m, 1, -CH=), 3.02 (m, 4, Ar). Treatment of **3** with a methylene chloride solution of tetra-*n*-butylammonium iodide in the presence of 1,3-diphenylisobenzofuran gives the known Diels-Alder adduct (**4**)⁷ of benzocyclobutadiene in 25% yield and thereby demonstrates the lability of the cyclobutadienoid ligand. At present, we have no evidence to suggest that **3** decomposes by rearrangement to **2**.



All of the aforementioned reactions are typical of cationic olefin complexes of η⁵-cyclopentadienyldicarbonyliron⁸⁻¹¹ and thus strongly support structure **3a**

(5) Trans 1,2-disubstituted benzocyclobutenes are readily characterized by a small coupling ($J_{\text{HH}2} \sim 2$ Hz) between the four-membered ring protons: I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970).

(6) All new compounds gave satisfactory analyses for carbon and hydrogen.

(7) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **27**, 1564 (1962).

(8) L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometal. Chem.*, **25**, 207 (1970).

(9) W. P. Giering, M. Rosenblum, and J. Tancredi, *J. Amer. Chem. Soc.*, **94**, 7170 (1972).

(10) W. P. Giering and M. Rosenblum, *J. Organometal. Chem.*, **25**, C71 (1970).

(11) A. Rosan, M. Rosenblum, and J. Tancredi, *J. Amer. Chem. Soc.*, **95**, 3062 (1973).

possessing a dihapto benzocyclobutadiene ligand. However, in view of the propensity of cyclobutadienoid hydrocarbons to act as tetrahapto ligands¹² and the ability of cationic cyclobutadiene complexes to add nucleophiles to the four-membered ring,¹³ an alternative structure, **3b**, possessing a tetrahapto four-membered ring and a trihapto five-membered ring cannot be excluded as a possibility. We are now attempting to obtain single crystals suitable for an X-ray structure determination to resolve this problem.

Acknowledgment. We gratefully acknowledge the generous support of the Graduate School of Boston University and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(12) P. M. Maitlis and K. W. Eberius in "Nonbenzoid Aromatic Compounds," J. P. Snyder, Ed., Academic Press, New York, N. Y., pp 360-426.

(13) A. Efraty, presented at the 6th International Conference on Organometallic Chemistry, Amherst, Mass., 1973.

A. Sanders, C. V. Magatti, W. P. Giering*

Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received September 10, 1973

Nuclear Magnetic Resonance Spectroscopy Using Flowing Liquids. CIDNP Study of the Oxidation of Isopropyl Alcohol Using Titanous Ion with Hydrogen Peroxide

Sir:

Previously¹ we have reported the use of a flow system to detect the proton nuclear magnetic resonance (nmr) spectrum of a short-lived intermediate formed during the reaction between methoxide ion and 3,5-dinitrobenzene. In the present paper we wish to report the application of this technique to the study of reactions between radicals generated by the oxidation of isopropyl alcohol in H₂O using TiCl₃ plus H₂O₂. In this study we observed enhanced absorption and emission nmr lines indicating non-Boltzmann nuclear spin polarization. The interpretation of this phenomenon is based on a model in which non-Boltzmann nuclear spin polarization occurs as a result of reaction *via* a radical pair.² Details of the theory used to calculate the nuclear spin polarization based on this model have been given previously³ and are not repeated here.

In essence, the experiment consists of mixing an aqueous solution of 0.01 M TiCl₃ plus 0.1 M H₂SO₄ with a solution of 0.1 M H₂O₂ plus 0.3 M isopropyl alcohol. A probe is used which includes two reservoirs which permit the nuclei of the two solutions to come to thermal equilibrium in the magnetic field before they are mixed in a high-pressure mixing chamber and passed through the measuring coils. At suitable flow rates, the absolute signal-noise ratio is appreciably better than that of a stationary sample. In this approach, the flow rates are limited by the capacities of the reservoirs, but these can be maximized by using a probe design in which transmitter and receiver coupling is minimized by time sharing. That the flow system is necessary to obtain good

(1) C. A. Fyfe, M. Cocivera, and S. W. H. Damji, *J. Chem. Soc., Chem. Commun.*, 743 (1973).

(2) For a brief review see R. Lawler, *Accounts Chem. Res.*, **5**, 25 (1972).

(3) M. Tomkiewicz, A. Groen, and M. Cocivera, *J. Chem. Phys.*, **56**, 5850 (1972).