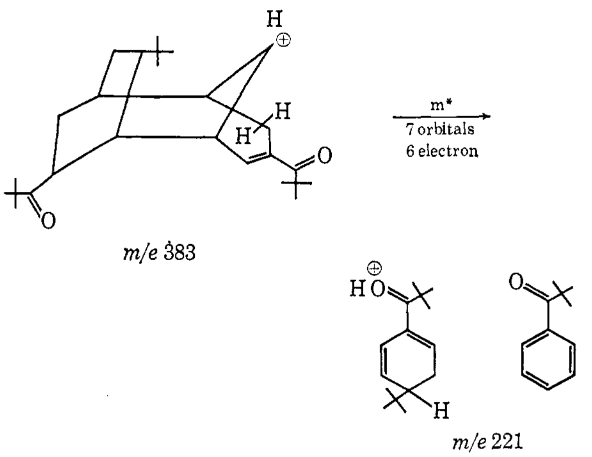
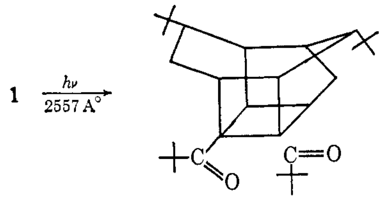


(3)

cyclooctadienyl anion to, after hydrolysis, *cis*-bicyclo[3.3.0]oct-2-ene.[8]

Compound **1** undergoes an irreversible transformation in the solid state in sunlight over 2 weeks in Pyrex or in pentane solution irradiated for 5 min at 2557 Å (medium-pressure mercury lamp) to **6**, mp 146–147.5°. Compound **6** has no double bonds, and its positive ion mass spectrum is very similar to that of **1**. This result determines the stereochemistry of the double bonds in **1** and excludes structures in which intramolecular 2 + 2 photoprocesses are geometrically impossible.



6

The sequence of reactions from methyl benzoate to **7** is a fast, efficient route to pentacyclic compounds.

Acknowledgment. This research was supported by Air Force Office of Scientific Research Grant 253-65 and National Science Foundation Grant GP-8567.

[8] P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965); L. H. Slaugh, *ibid.*, **32**, 108 (1967); R. B. Bates and D. A. McCombs, *Tetrahedron Letters*, 977 (1969).

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A Stable Complex of Heptafulvene

Sir:

Many unstable organic species have been isolated as metal complexes, including trimethylenemethane,[1] norbornadienone,[2] and certain sesquifulvalene and calicene systems.[3] Heptafulvene is a conjugated, nonbenzenoid hydrocarbon which is nonisolable and stable only in dilute solution at −170°;[4] only a few moderately stable monosubstituted derivatives have been reported.[5,6] We here report the preparation of the first stable transition metal derivative of unsubstituted heptafulvene, prepared by a method previously used to generate ethylene and propylene complexes.[7] This complex may prove to be a convenient source of heptafulvene for the further investigation of its reactions and properties.

Modification of an earlier preparation of 7-(carbethoxy)cycloheptatriene,[4] using G.E. 250-W infrared heat lamps and a room-temperature workup, gave the desired ester in 35% yield with up to 95% isomeric integrity. Inverse addition of $LiAlH_4$ at 0° to the ester in diethyl ether afforded a 90% yield of 7-(hydroxymethyl)-cycloheptatriene, apparently identical with that recently prepared by another route.[8] Reaction with benzenesulfonyl chloride at 0° in γ-collidine gave the corresponding ester (I) as a heat-sensitive oil;[9] the methylene group appears as a doublet in the nmr spectrum (τ 5.85, $J = 6$ Hz, CCl_4), confirming retention of the 7-substituted cycloheptatriene skeleton.

Addition under nitrogen of sodium π-cyclopentadienyliron dicarbonyl to I in dry, degassed tetrahydrofuran at −70°, warming to room temperature, removal of solvent, and chromatography on neutral alumina yielded 45% of the σ-bonded C_8H_9Fe-π-$Cp(CO)_2$ (II) as an air-sensitive orange-yellow liquid. Its nmr spectrum is characteristic of the 7-substituted cycloheptatriene skeleton: τ 3.45 (t, H_γ), 3.95 (m, H_β), 4.85 (four-line m, H_α), 5.38 (s, H_{Cp}), 8.20 (m, CH and CH_2), in the ratio 2:2:2:5:3 (CS_2). The infrared spectrum displayed strong absorptions at 1953 and 2008 cm^{-1} (CS_2), characteristic of σ-alkyl-π-cyclopentadienyliron dicarbonyl complexes.[7]

When II was treated with trityl salts ($(C_6H_5)_3C^+BF_4^-$, $(C_6H_5)_3C^+PF_6^-$, or $(C_6H_5)_3C^+SbF_6^-$) in methylene chloride at 0°, a deep red product formed immediately. Triphenylmethane could be isolated in nearly quantitative yields. The tetrafluoroborate and hexafluorophosphate salts were not readily crystallized; the hexafluoroantimonate derivative was an air-stable, nonhygroscopic dark red crystalline salt (III or IV), mp 98–100° (recrystallized from CH_2Cl_2-Et_2O). *Anal.* Calcd for $C_{15}H_{13}FeO_2SbF_6$: C, 34.8; H, 2.51; Fe, 10.80. Found: C, 35.1; H, 2.57; Fe, 10.68. Its nmr spectrum showed a peak, theoretically an $A_2B_2C_2$ multiplet, at τ 2.20, a sharp singlet at 4.73, and a sharp singlet at 6.51, in the ratio 6:5:2 (acetone-d_6).[10] The carbonyl groups of the product absorbed at 1986 and 2033 cm^{-1} in the infrared (CH_2Cl_2).[11] The nearly equivalent chemical shifts appearing in this case at τ 2.20 are frequently observed in symmetrical fully conjugated seven-membered rings,

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[1] G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).

[2] J. M. Landesberg and J. Sieczkowski, *ibid.*, **90**, 1655 (1968).

[3] M. Cais and A. Eisenstadt, *ibid.*, **89**, 5468 (1967).

[4] W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

[5] (a) 8-Vinylheptafulvene has been synthesized: D. Bertelli, C. Golino, and D. Dreyer, *J. Am. Chem. Soc.*, 86, 3329 (1964). (b) The nmr spectra of several heptafulvenes have recently been analyzed: D. Bertelli, T. Andrews, and P. Crews, *J. Am. Chem. Soc.*, **91**, 5286 (1969).

[6] (a) 8-Cyanoheptafulvene: M. Oda and Y. Kitahara, *Chem. Commun.*, 352 (1969); (b) 8-formyl and 8-carbethoxyheptafulvenes: M. Oda and Y. Kitahara, *Chem. Ind.* (London), 920 (1969).

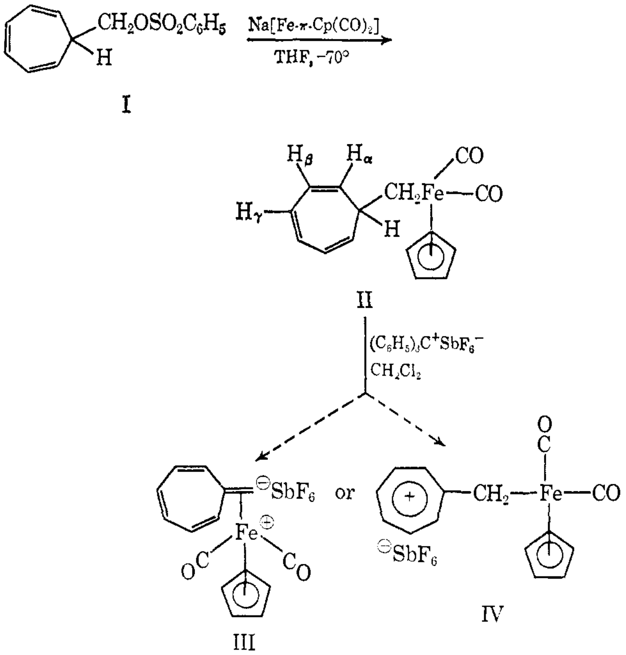
[7] M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963), and references contained therein.

[8] G. D. Sargent, N. Lowry, and S. Reich, *J. Am. Chem. Soc.*, **89**, 5985 (1967).

[9] The benzenesulfonate must be kept at temperatures lower than 15° to avoid spontaneous exothermic decomposition.

[10] No change was observed in the spectrum upon lowering the temperature to −60°.

[11] A small amount (<5%) of an unidentified impurity was present in all of our samples of this complex. The impurity exhibited a singlet in the nmr at τ 4.1 and weak carbonyl absorptions in the infrared at 2075 and 2128 cm^{-1}.



I

II

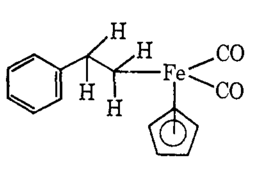
III

IV

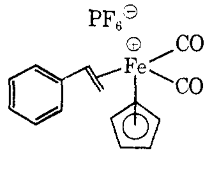
such as those of 8,8-dicyanoheptafulvene (τ 2.8), tropone (τ 3.0), and heptafulvalene (τ 4.2).[5] The downfield shift of the π-cyclopentadienyl proton absorption in the nmr and the shift of the carbonyl bands to higher wavelength following hydride abstraction both indicate more positive charge residing on the iron atom in the product relative to the starting σ complex II; however, the magnitudes of the shifts are not so great as those normally observed for this σ- to π-bonded ligand transformation.[7]

The heptafulvene complex did not form an adduct with tetracyanoethylene on standing at room temperature in solution for several hours, and it was resistant to hydrogenation (unchanged after 24 hr at 25° over Pd–C, 45 psi of H_2). Treatment with $NaBH_4$ gave a mixture of the tautomers of the starting σ complex II;[12] treatment of this mixture with $(C_6H_5)_3C^+SbF_6^-$ regenerated the heptafulvene complex.

Since esters of 7-(hydroxymethyl)cycloheptatriene had been shown to undergo ring contraction on solvolysis,[8] and in order to prepare a model compound for spectral comparison to the heptafulvene complex, σ-(2-phenylethyl)-π-cyclopentadienyliron dicarbonyl (V) was prepared in 80% yield from (2-bromoethyl)benzene and Na[Fe-π-Cp(CO)$_2$]. The product was a yellow, air-stable[13] solid, mp 73–74°, with a cyclopentadienyl proton absorption at τ 5.44 (CS_2), and carbonyl absorptions in the infrared at 1942 and 2000 cm^{-1} (CH_2Cl_2). When $(C_6H_5)_3C^+PF_6^-$ was added to V in CH_2Cl_2, the yellow styrene complex (VI),[13] clearly different from the heptafulvene complex, was immediately precipitated. The nmr absorption of the cyclopentadienyl protons (τ 4.13 in acetone, relative to TMS) and the infrared absorptions of the iron carbonyl groups (2020 and 2062 cm^{-1}, CH_2Cl_2 or Nujol) are as expected for structure VI.[7]



V



VI

The spectral data for the heptafulvene complex fall at positions intermediate between those expected for III and for IV[14] and do not therefore provide clear differentiation between these possibilities. An intermediate structure, such as one based on IV, but having extensive delocalization of positive charge into the iron,[15] may be in best agreement with the available data.[16] Studies are now under way directed toward a resolution of this question as well as to liberation of free heptafulvene from the complex.

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[12] Cais has reported similar results in the reduction of his complexes; see ref 3.

[13] Satisfactory analytical data were obtained for this compound.

[14] The nmr absorption at τ 2.20 indicates considerable shielding of the ring protons as compared to the unsubstituted tropylium fluoroborate at τ 0.86 (G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960)) or to cyanomethyltropylium fluoroborate at τ 0.78.[6]

[15] This may occur through carbon–iron hyperconjugation, or by direct interaction of the metal orbitals with those of the seven-membered ring. For a discussion of these types of metal–carbon interactions, see T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967).

[16] Such an intermediate structure has been observed for a styrene–palladium chloride complex: J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955). We thank a referee for calling this precedent to our attention.

[17] Deceased March 20, 1968.

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Transition-State Geometry of a (2 + 2) Cycloaddition Reaction. Asymmetric Synthesis in a Sulfene–Enamine Condensation[1,2]

Sir:

Although the subject of considerable study since its recognition many years ago, the phenomenon of asymmetric induction[3] has never been applied to the synthesis of four-membered rings, whether carbocyclic or heterocyclic.[4] Recently, interest in the stereochemical consequences of (2 + 2) cycloaddition reactions has been on the increase in view of the interesting predictions provided by the Woodward–Hoffmann rules for such reactions.[5] The present communication describes an example of asymmetric synthesis in the preparation of a thiete 1,1-dioxide and represents a continuation of our studies on the chemical behavior of sulfenes.[6]

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[1] Unsaturated Heterocyclic Systems. LXIX. For the previous paper in this series, see L. A. Paquette, R. W. Houser, and M. Rosen, *J. Org. Chem.*, in press.

[2] Partial financial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant GP-5977) is gratefully acknowledged.

[3] The principle of asymmetric synthesis has recently been reviewed: (a) D. R. Boyd and M. A. McKervey, *Quart. Rev.* (London), **22**, 95 (1968); (b) J. Mathieu and J. Weill-Raynal, *Bull. Soc. Chim. France*, 1211 (1968).

[4] A review of the formation of four-membered heterocycles has recently appeared: L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967.

[5] R. Hoffmann, Abstracts of the Twenty-First National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, 1969, pp 109–129.

[6] L. A. Paquette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, **34**, 2901 (1969); L. A. Paquette and R. W. Begland, *ibid.*, **34**, 2896 (1969); L. A. Paquette and M. Rosen, *J. Am. Chem. Soc.*, **89**, 4102 (1967), and earlier references contained in these papers.