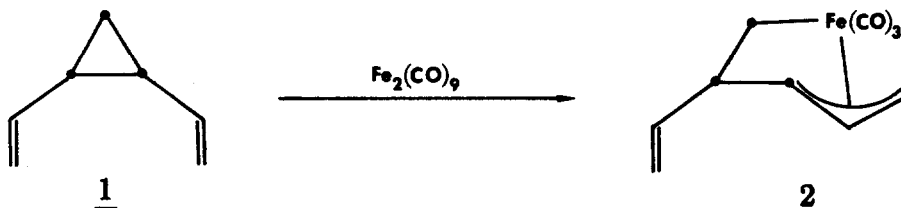


REACTION OF DIIRON NONACARBONYL WITH BRIDGED POLYCYCLICS
CONTAINING THE VINYL CYCLOPROPANE GROUP

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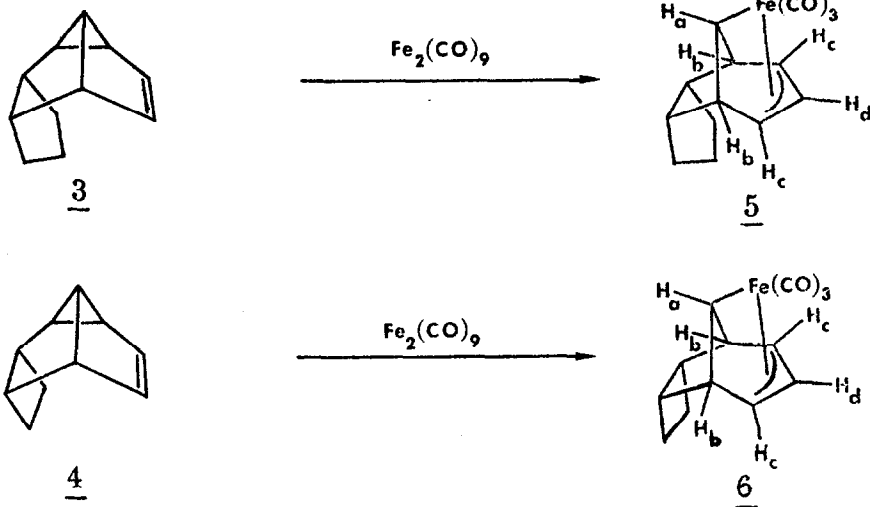
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Recently it has been shown that the divinylcyclopropyl system present in bullvalene¹, semibullvalene^{2,3}, homosemibullvalene³, tetracyclo [4.4.0.0^{5,7}.0^{2,10}] deca-3, 8-diene⁴, and barbaralone^{3,5} react with diiron nonacarbonyl in the sense 1 + 2. The essential feature in 2 is the presence of a carbon-iron σ -bond and a π -allyl system attached to the Fe(CO)₃ unit.



However, the vinylcyclopropane system in substituted cyclopropylstyrenes reacts with iron pentacarbonyl to yield diene- $\text{Fe}(\text{CO})_5$ complexes, although an intermediary σ -bonded π -allyl complex has been proposed as a likely precursor of the diene- $\text{Fe}(\text{CO})_5$ complex.⁶

These results caused our attention to be directed towards 3⁷ and 4⁸ since these compounds incorporate the basic feature of a vinylcyclopropyl system within a rigid tricyclic ring system, but they lack the additional double bond present in semibullvalene.



3,6-endo-Tetracyclo [5.3.0^{2,10}.0^{3,6}] decene-8 (3) upon reaction with excess $\text{Fe}_2(\text{CO})_9$ in benzene at reflux for 1 hour under nitrogen yielded 5 (m.p. 51-52.5° from pentane) in 75% yield. Under the same conditions 3,7-endo-tetracyclo [6.3.0.0^{2,11}.0^{3,7}] undecene-9 (4) afforded 6 (oil, solidifies below 20°) in 80% yield. The structures are based upon their composition, respectively: calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{Fe}$, C, 57.35; H, 4.41, found C, 57.59; H, 4.41; calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Fe}$, C, 58.74; H, 4.89, found, C, 58.60; H, 4.87. The C=O stretching frequency for 5 occurred at 1983 and 2054 cm^{-1} , and 1982 and 2050 cm^{-1} for 6.

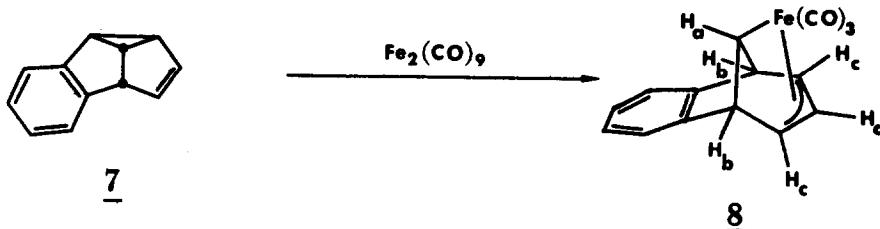
The mass spectrum of each complex showed peaks corresponding to the parent molecular ions and successive loss of one, two and three molecules of CO. The nuclear magnetic resonance spectrum of each agreed well with expectation based upon the proposed structure. The most characteristic features in the spectrum of each complex are the high field resonances corresponding to the proton bound to the carbon bonded to iron atom and the set of three protons comprising the allylic system.

The chemical shifts for the protons in 5 in CDCl_3 relative to TMS (ppm) are $\text{H}_a=0.50$, $\text{H}_b=3.23$, $\text{H}_c=4.33$, $\text{H}_d=4.78$. The protons of the four-membered ring

consist of a complex multiplet centered at 2.00 ppm. The relative intensities are correct and the coupling constants appear to be closely similar to those found for the semibullvalene diiron nonacarbonyl product.² The proton spectrum of 6 was very similar to that of 5: H_a (ppm)=0.85, H_b =2.76, H_c =4.25, H_d =4.60. The higher field position of H_a in 6 relative to 5 is noteworthy but unexplained. Reactions 3 + 5 and 4 + 6 tend to support the concept that the vinylcyclopropane system in general reacts to form a σ -bond π -allyl type complex with diiron nonacarbonyl and this is the final product in cases which rearrangement to a diene: $Fe(CO)_9$ complex cannot occur with facility, e.g. by a 1,2 hydride.

Compounds such as 3 and 4 which incorporate a dihydro-semibullvalene group are readily available from the photochemical 1,3-addition of benzene to strained cyclic olefins^{7,8,9}: therefore a ready synthesis of compounds of the type 5 and 6 can be achieved in two steps.

Finally, benzosemibullvalene reacts in an analogous fashion 7 + 8. Complex 8 was obtained in 75% yield by the reaction of 7 with $Fe_2(CO)_9$ in molar ration 1:2.5 in benzene at reflux under nitrogen for 3 hours.



The structure of 8, m.p. 89.5-90.5°, is based upon its composition: calcd. for $C_{12}H_{10}O_3Fe$, C, 61.22; H, 3.40; found, C, 61.31; H, 3.46, infrared, $C\equiv O$ at $1955-2040\text{ cm}^{-1}$ and the following mass spectral data: $C_{12}H_{10}Fe(CO)_3^+$, m/e 294.3.3%; $C_{12}H_{10}Fe(CO)_2^+$, 266, 17.6%; $C_{12}H_{10}Fe(CO)^+$, 238.14.2%; $C_{12}H_{10}Fe^+$, 210, 28.4%; $C_{12}H_{10}^+$, 154, 100%. The n.m.r. spectrum of 8 (in CS_2) provided strong confirmatory evidence in support of the proposed structure. The

highest field proton (relative to TMS) at 0.75 ppm is due to H_a on the carbon atom σ -bonded to the iron atom. Protons H_c appear at 4.62 ppm and H_d is at 4.12 ppm. The chemical shifts and multiplicity of these three protons comprising the allylic system are very similar to those observed earlier. Protons H_b occur at 3.59 ppm and the aromatic protons appear as a singlet peak at 7.00 ppm. The intensities and peak width at half-height of the multiplets agree with expectation in terms of the number of each proton and expected coupling patterns.²

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