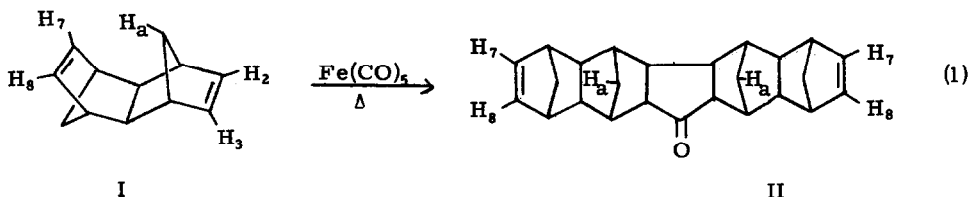


IRON CARBONYL INDUCED COUPLING OF OLEFINS TO CARBON MONOXIDE

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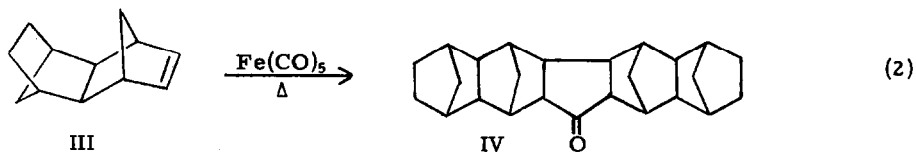
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When neat diene I is treated with a 2:1 molar ratio of $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}(\text{CO})_5$ at 85° in a glass pressure bottle for 12 hours, coupling occurs through the $\Delta^{2,3}$ double bond yielding ketone II. The product is stereochemically pure by TLC on silica gel, and nmr.



$(m/e)^+ = 344$
 70%mp = $271-272.5^\circ$

While the analogous coupling of bicyclo[2.2.1]hepta-2,5-diene was observed¹ as early as 1958, we find that iron carbonyl induced coupling of olefins to carbon monoxide is a general process and synthetically useful. Further, isolated double bonds are reactive, a 1,4 system being unnecessary for reactivity. In the case of norbornadiene coupling, the ketonic product was assigned by nmr spectroscopy² to be the exo-trans-exo isomer. This assignment was confirmed by synthesis³ of all three cis-trans-cis isomers.

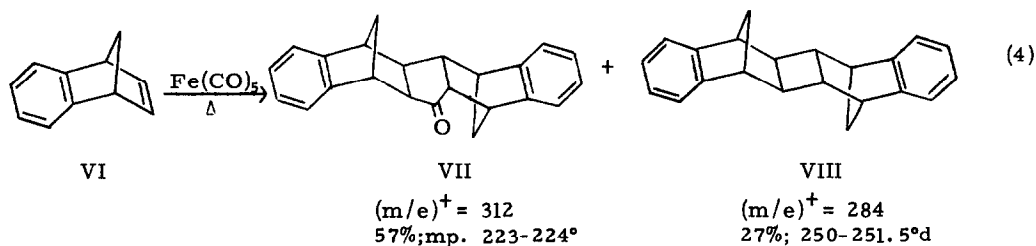


$(m/e)^+ = 348$
 65%mp = 274.5°



Olefin III reacts smoothly to form saturated ketone IV. The identical ketone is formed when two moles of H_2 are absorbed by II. Contrariwise, the $\Delta^{7,8}$ double bond is totally unreactive as illustrated by the lack of reactivity of compound V and the stereochemical purity of product II. These observations are important to our assignment of product stereochemistry.

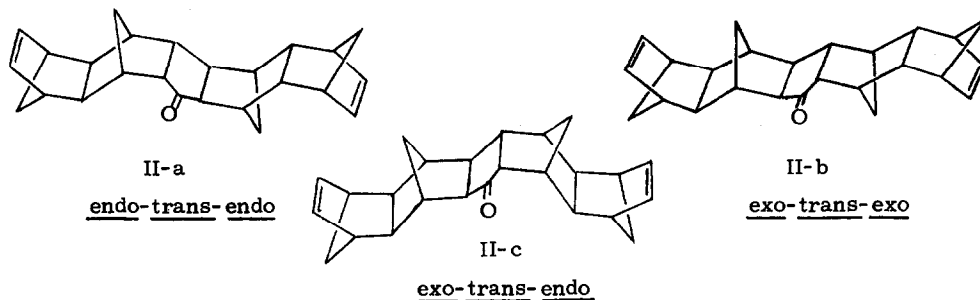
The reaction generates highest yields with strained olefins. Thus while cyclohexene and norbornene each react to give the corresponding ketone, yields are less than 2% using $Fe_2(CO)_9$ as the coupling agent. Nevertheless, the more highly strained bicycloolefin does give the higher yield of these two olefins. Benznorbornadiene reacts with $Fe(CO)_5$ to give a mixture of the corresponding ketone and the previously reported cyclobutane derivative⁷, as illustrated in reaction (4). The stereochemistry of ketone VII is assigned by analogy to II, VIII, and by a complete analysis of the nmr spectrum. The nmr data will be published separately. Once again, yields are in the synthetically useful range. Product separation was accomplished by column chromatography on silica gel.



Dreiding models, including the hydrogen atoms, clearly demonstrate that of the six isomers of II having cis-fused rings, only those shown in figure 1 are sterically possible. The three isomers having cis geometry about the bond opposite the carbonyl function all show severe carbon-carbon repulsion. Of the three remaining isomers (figure 1), II-b, the exo-trans-exo form, possesses minimal hydrogen-hydrogen repulsion and is expected to be the thermodynamically stable product.

Figure 1

Sterically Allowed Isomers of Ketone II

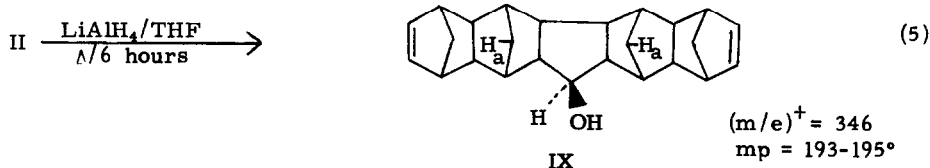


Comparison of the nmr spectra of III and V, Table I, demonstrates that the $\Delta^{2,3}$ double bond is the active linkage in reaction (1). This is the least hindered of the two double bonds as the $\Delta^{7,8}$ bond is directly opposed to the H_a bridge proton. The nmr spectrum of olefin I shows a high field resonance at 0.95 δ assigned⁴ to the H_a proton. Resonances at 6.17 δ and 5.99 δ were assigned to the $H_{2,3}$ and $H_{7,8}$ protons respectively. Ketone II shows a doublet resonance at 0.39 δ which integrates for two protons and is assigned to the H_a protons, while the $H_{7,8}$ protons appear at 5.19 δ . The nmr spectra of III and V confirm the assignments of resonances observed in the olefinic region of hydrocarbon I and of the nature of the olefinic resonance in the spectrum of ketone II.

Table I
Nuclear Magnetic Resonance Spectral Data

Compound	Triplet Olefinic Resonance δ (ppm)	Doublet High Field Resonance δ (ppm)
I	5.99(J=2.0 Hz) 6.17(J=1.6 Hz)	0.95(J=8.5 Hz)
II	5.91(J=3.0 Hz)	0.39(J=10.8 Hz)
III	6.18(J=1.6 Hz)	-----
V	5.87(J=1.5 Hz)	0.52(J=9.5 Hz)
IX	5.91(J=2.0 Hz)	0.30(J=10.2 Hz) 0.53(J=10.0 Hz)

Isomers II-a and II-b have C_2 axes of symmetry and may each form but one alcohol, while isomer II-c may form two isomeric alcohols. Treatment of II with $LiAlH_4$ in refluxing THF, reaction (5), leads to an alcohol indicated by TLC on silica gel to be a single product. The hindered nature of the carbonyl group is suggested by the unusually strenuous conditions needed to bring about reduction.



The nmr spectrum of alcohol IX is best interpreted as arising from a single, homogeneous product. A broad triplet centered at 0.40 δ at 60 MHz was shown to be due to the fortuitous overlap of two doublets by use of the shift reagent⁵ $Eu(fod)_3$. This pair of doublets is resolved at 90 MHz, as indicated in Table I, and is assigned to the H_a protons in IX. The carbinol methine proton appears as a doublet of doublets centered at 3.77 δ ($J_{cis} = 9.2$ Hz, $J_{trans} = 3.5$ Hz).

Addition of the shift reagent $\text{Eu}(\text{fod})_3$ to ketone II does not cause further splitting of the high field doublet at 0.39 τ thus lending credence to our interpretation of the nmr data as indicating a symmetric ketone. The olefinic resonance does split into an AB pattern due to the enhanced difference between the "back" and "front" of the molecule. A complete analysis of the 90 MHz nmr spectrum of II, to be published separately, leads us to the conclusion that II-b illustrates the correct stereochemistry. As II-b is expected to be the thermodynamically stable product, we cannot speak to whether thermodynamics or kinetics is the controlling feature of the mechanism.

Nevertheless, product II-b is consistent with exo attack on the olefin by an iron complex to form a tricarbonylbisolefiniron(O) intermediate in which the olefins are both in the basal plane of the trigonal bipyramid and antiparallel to one another. Oxidative coupling⁶ followed by migratory insertion and elimination completes the sequence to the observed stereochemical product. Alternative geometries of the bisolefin intermediate lead to products which are not observed. A similar sequence may be written with one olefin axial and the other basal. Exo attack on the $\Delta^{7,8}$ double bond of I leads to a high energy intermediate due to the resultant interaction between the H_a and the $\text{H}_{7,8}$ protons. Thus this mode of attack is kinetically unimportant. Cyclobutane derivative VIII may be regarded as an intermediate of an olefin metathesis reaction wherein full isomerization is blocked. We are investigating this possibility further.

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