

IRON CARBONYL-INDUCED COUPLINGS OF BENZONORBORNADIENES
TO CARBON MONOXIDE :
A REMARKABLE SWITCH IN STEREOSPECIFICITY

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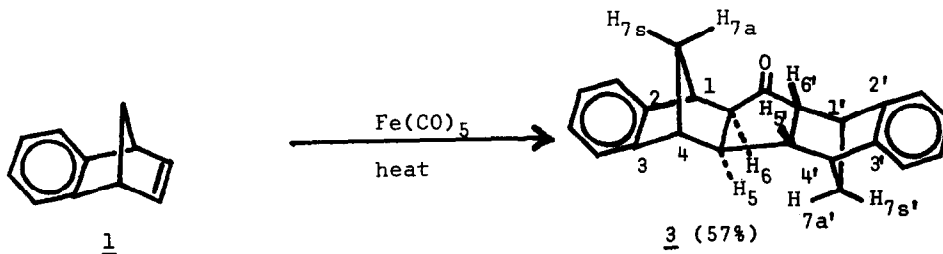
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Recent reports dealing with reactions of strained olefins with iron carbonyls ^{3,4}, prompt us to communicate the results of studies of the corresponding reactions with benzonorbornadiene (1) and with 7,7-dimethoxybenzonorbornadiene (2). The reaction of 1 with a 2:1 molar ratio of Fe₂(CO)₉ or Fe(CO)₅ at 85° in a glass pressure bottle for 12 hr. has been reported to yield the exo-trans-exo ketone, 3³.



The stereochemical assignment for 3 was reported to follow from an analysis of its nmr spectrum, although the details of this analysis have not yet been published³.

In our hands, the reaction of 1 with excess Fe(CO)₅, allowed to reflux overnight under dry nitrogen in di-n-butyl ether solution, afforded 3, m.p.

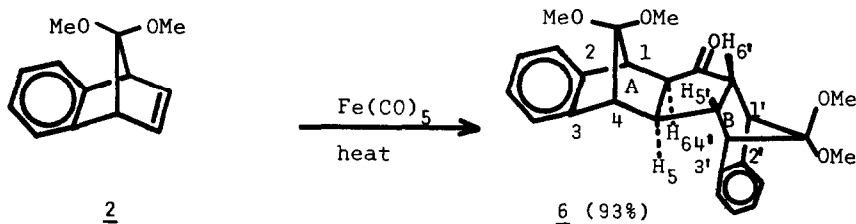
228.6 - 229.7⁵ (lit.³ m.p. 223 - 224°). Analysis⁵ (LAOCOON III)⁶ of the cyclopentanone protons of 3 revealed $J_{5,6} = J_{5',6'} = 7.1$ Hz and $J_{5,5'} = 0$. The magnitudes of these coupling constants are indicative of the cis-relationship of the 5,6 (and 5',6') protons and of the trans-relationship of the 5,5' protons, respectively⁷. The fact that the 5(5') and 6(6') protons are endo to the benzonorbornene ring is indicated by $J_{1,6} = J_{1',6'} = J_{4,5} = J_{4',5'} < 0.8$ Hz.^{8,9}

Double irradiation of the 5(5') and of the 6(6') protons revealed the expected long range ("W-letter") coupling $J_{5,7_s} = J_{5',7_{s'}} = J_{6,7_s} = J_{6',7_{s'}} =$ ca. 1 Hz. The observation of this stereospecific long-range coupling in 3 permitted our assigning the relative chemical shifts for H_{7_s} (H_{7_s} ,) and H_{7_a} (H_{7_a} ,), corresponding to multiplets centered at $\delta = 1.35$ and 1.70, respectively. Our conclusion that the anti-bridge proton absorptions (H_{7_a} and H_{7_a} ,) lie at higher field than do the corresponding syn-bridge proton absorptions (H_{7_s} and H_{7_s} ,) is in accord with generalizations which have been forwarded previously to account for the observed chemical shifts of bridge protons in norbornenes⁸ and in benzonorbornenes⁹.

It was of interest to us to extend this study to include a 7,7-disubstituted benzonorbornene to determine the effects of substituents in the bridge position of 1 on the stereochemical course of its reaction with iron carbonyls. Compound (2) was prepared for this purpose in admixture with 7,7-dimethoxybenzonorbornene (4) by dechlorination (Na, tBuOH, THF) of 1,4,5,6-tetrachloro-7,7-dimethoxybenzonorbornadiene (5)¹⁰. This reduction has been reported to afford (2) and (4) as a 1:1 mixture which could only be partially separated by conventional techniques¹⁰. Accordingly, we have not attempted to separate (2) from (4); instead, the mixture obtained from dechlorination of (5) (3.96 g, b.p. 68°/0.2-0.3 mm, lit.¹⁰ b.p. 83-86°/1.5-2.0 mm) was refluxed under nitrogen with $Fe(CO)_5$ (3 ml) in di-n-butyl ether (50 ml) for 3.75 hr. The hot solution was filtered rapidly and the residue was washed several

times with boiling benzene. Concentration of the filtrate and recrystallization of the residue from benzene-hexane afforded ketone (6) as a colorless, microcrystalline solid, m.p. 214-216°. The yield of purified material was 782 mg, (93%, based on the previous assertion¹⁰ that the starting material contained 50% (2) and 50% (4), the latter compound being inert toward $\text{Fe}(\text{CO})_5$)¹¹.

Our assignment of the exo-trans-endo stereochemistry for ketone (6), shown below, is based on nmr evidence obtained in CDCl_3 solution (TMS internal standard) at 300 MHz. The nmr spectrum of (6) displays four distinct methoxyl absorptions at $\delta = 3.01, 3.08, 3.12,$ and 3.36 . Of the six possible stereoisomers for (6), only two (exo-trans-endo and exo-cis-endo) have the symmetry properties required by the observation of four magnetically



nonequivalent methoxyl groups. Computer simulation of the nmr spectrum of (6) revealed the following coupling constants, ($\pm 0.1\text{Hz}$): $J_{1',6'} = 5.2$ and $J_{4',5'} = 4.8$, ($\text{H}_{5'}$ and $\text{H}_{6'}$, exo to benzonorbornene ring B)^{8,9}; $J_{5',6'} = 8.8$, ($\text{H}_{5'}$ and $\text{H}_{6'}$, mutually cis)⁷; $J_{5,6} = 9.2$, (H_5 and H_6 mutually cis)⁷; $J_{1,6} = 0$; $J_{4,5} = 0$, (H_5 and H_6 endo to benzonorbornene ring A)^{8,9}; and $J_{5,5'} = 2.2$ Hz, (H_5 and $\text{H}_{5'}$, mutually trans)⁷. The following long-range couplings are also determined: $J_{4',5} = 0.6$; $J_{6,6'} = 1.2$; $J_{1,4} = 0.6$; $J_{1',4'} = 1.4$.

Additionally, inspection of Dreiding models indicates that H_6 in the exo-trans-endo isomer should be anomalously shielded due to its location relative to the benzene moiety in ring B, but that none of the other protons on the cyclopentanone ring ($\text{H}_{5'}$, H_5 , or H_6 ,) should experience this shielding

effect. This expectation is borne out by the nmr spectrum of 6 which shows the H₆ resonance signal at unusually high field ($\delta = 0.63$) relative to H₅, H₅, and H₆, (which display absorptions at $\delta = 1.70, 3.19$ and 3.46 , respectively).

The exo-trans-endo ketone (6) was the only product isolated from the thermal reaction of (2) with Fe(CO)₅. Thus, we have demonstrated that the stereochemical course of the reaction of benzonorbornadiene with iron pentacarbonyl can be markedly influenced by the presence of substituents in the 7-position of the substrate. We are continuing to study reactions of strained olefins with iron carbonyls with an eye toward delineating their detailed mechanisms. We plan to report the results of these studies shortly.

REFERENCES

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11. Anal. for 6 (C₂₇H₂₈O₅) : Calculated mol. wt. = 432.193661; Found (by high resolution mass spectroscopy), mol. wt. = 432.19355.