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Preliminary communication

IRON TRICARBONYL COMPLEX OF A *syn*-7 METHOXYNORBORNENE

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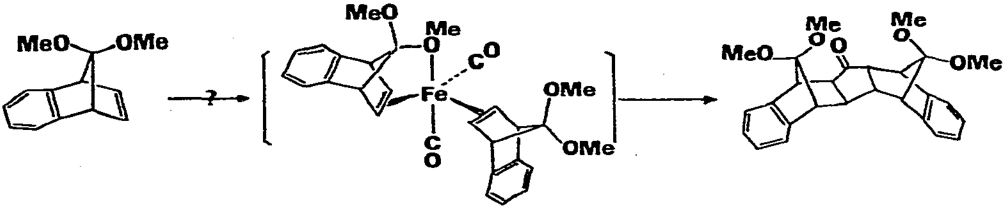
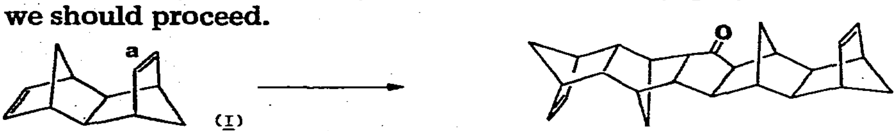
Summary

An iron tricarbonyl complex of a *syn*-7-methoxynorbornene has been prepared; this compound, in which an ether oxygen is coordinated to the metal, is an unusually stable intermediate in the cyclopentanone synthesis reaction.

Strained and reactive olefins form cyclopentanones upon reaction with iron carbonyls [1]. The reaction is highly stereoselective: with norbornenes, *exo—trans—exo* adducts result if the bridge C-7 is unsubstituted; presence at C-7 of a *syn*-methoxy substituent leads to *exo—trans—endo* adducts [2] (eq. 1). This was attributed to coordination to iron by oxygen during the course of the reaction [1,3]. We were encouraged to attempt the isolation of such an intermediate by the observation that 7,7-dimethoxybenzonorbornadiene forms a stable $Cr^0(CO)_4$ complex in which the metal is wedged in between the olefinic and oxygen ligands [4]. However, since this substrate is highly reactive in the carbonylation reaction [1], it would only be possible to trap the corresponding $Fe(CO)_3$ intermediate by working at very low temperatures [5]. A report by Weissberger [6] that the olefinic bond a in I is unreactive with respect to cyclopentanone formation (eq. 2) indicated to us the way we should proceed.



(1)



(I)

(2)

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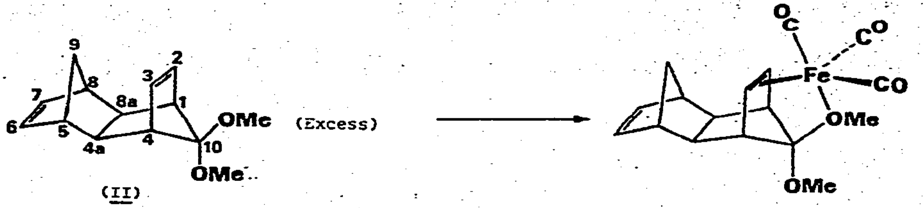
Compound II was made by a published procedure [7]. Its reaction with half a molar equivalent of $Fe(CO)_5$ in refluxing toluene for two days results in formation of a good yield of the desired $Fe(CO)_3$ complex (eq. 3), which was purified by column chromatography (silica gel/hexane) under argon. The orange crystals which are very air-sensitive, analyze correctly for $C_{17}H_{18}O_5Fe$. The mass spectrum shows intense peaks at *M*, *M*−CO, *M*−2CO, *M*−3CO (base peak), *M*−$Fe(CO)_3$, $Fe(CO)_3^+$, and $C_5H_6^+$ (*retro* Diels—Alder). This complex is decomposed to the starting olefin by reaction with methanolic $FeCl_3$. Complexing of the double bond a is evident from the PMR spectrum, which shows an upfield shift of 2.44 ppm and from the CMR spectrum (Table 1). Noteworthy is the shift for the bridge H-9 protons, which is diagnostic of deformation accompanying iron complexation. The shielding at C-1 and the deshielding at C-10 are also relevant.



(3)

TABLE 1

		1	2	4a	5	6	9	10	MeO
^1H	olefin	2.52	5.95	2.18	2.69	6.15	2.55, 0.99		3.1, 3.0
	complex	1.82	3.51	2.21	2.87	6.27	3.16, 1.27		2.98, 2.98
^{13}C	olefin	41.5	133.1	42.2, and	43.5	140.5	31.6	51.3	49.0, 46.4
	complex^a	37.9	117.1	42.2, and	43.5	140.2	29.9	61.2	50.9, 44.8

^{a}CO: 213.8 ppm (singlet at −40°C).

The IR spectrum has carbonyl absorptions at 2044s, 1996w and 1953vs, consistent with either C_{2v} or C_s symmetry. We favor the latter, either a trigonal bipyramid (TBP) or a square pyramid. The geometry of II favors the TBP. Numerous theoretical [8] and experimental [9] studies indicate for the d^8 TBP the apicophilicity of *n*-donors and a basal perpendicular orientation of π-acceptors.

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