

INTRAMOLECULAR TRAPPING OF CYCLOBUTADIENE

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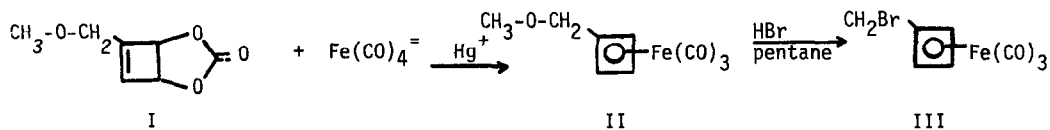
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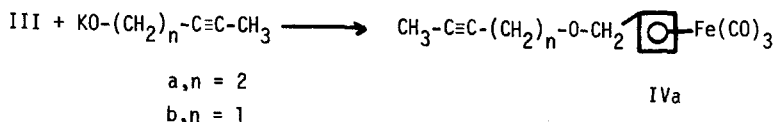
Cyclobutadiene generated from cyclobutadieneiron tricarbonyl has proven to be a useful intermediate in organic synthesis.<sup>1</sup> We now have evidence that cyclobutadiene will react in an intramolecular fashion with attached dienophiles. Since cyclobutadiene is a high energy, reactive molecule,<sup>2</sup> this reaction opens up new pathways to highly strained ring systems. In order to explore the possibility of this reaction, cyclobutadieneiron tricarbonyl with pendant acetylene groups were prepared and oxidatively decomposed.

Propargyl methyl ether was photochemically added to vinylene carbonate to yield methoxymethyl-3,4-carbonyldioxycyclobutene (I) in 22% yield. This carbonyldioxycyclobutene reacted with disodium tetracarbonylferrate (-2) to produce methoxymethylcyclobutadieneiron tricarbonyl (II) in 25% yield.<sup>3</sup>

Treatment of a pentane solution of II (b.p. 50-55%/.2mm, nmr ( $\delta$ ) 3.4, 3.76, 4.12, 4.20, singlets, 3:2:1:2) with 48% hydrobromine acid gave a quantitative yield of bromomethylcyclobutadieneiron tricarbonyl III.<sup>4</sup>

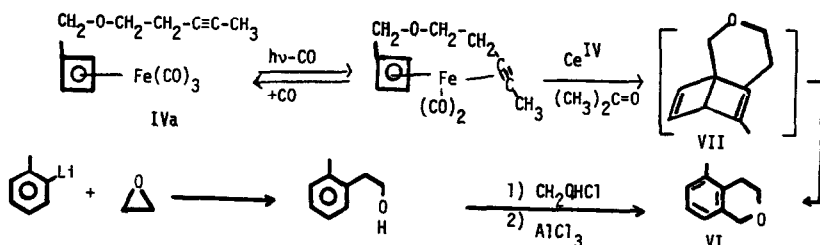


The very reactive bromomethyl moiety can serve as a link for attachment of a variety of reactive function groups. For example, potassium 3-pentyne-1-oxide reacted with III to produce IVa (n.m.r. ( $\delta$ ) 4.2 (s), 4.6 (s), 3.85 (s), 3.6 (t), 2.4 (m), 1.75 (t), 2:1:2:2:2:3) in a near



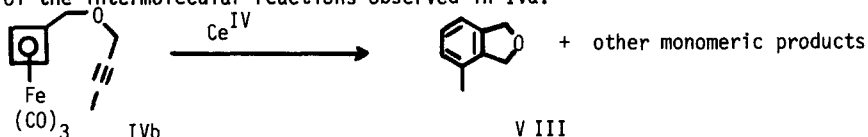
quantitative yield.

Direct ceric ion oxidation of IVa gave a mixture of organic products. However, photolysis of IVa in pentane gave an intermediate metal complex (V is a suggested structure) which slowly gave back IVa on standing under 40 psi of carbonmonoxide. The crude photolysis mixture gave an 83% yield of a C<sub>10</sub> (VI) organic compound on ceric ion oxidation. This C<sub>10</sub> compound (VI) was identified as 5-methyl isochroman by comparison to an authentic sample.<sup>5</sup> The following is a proposed scheme for the reaction.<sup>6,7</sup>



The 7-methyl isomer of VI was prepared from p-bromotoluene<sup>5</sup> and none of this isomer could be detected in the reaction mixture.

The 2-butyne ether complex (IVb)<sup>8</sup> gave high yields of C<sub>9</sub> compounds on direct ceric ion oxidation. Apparently the shorter chain increased the rate of intramolecular reaction and prevented some of the intermolecular reactions observed in IVa.



The major C<sub>9</sub> product from this reaction was 4-methylphthalan (VIII) (50% yield). The other products from this reaction are under investigation.

#### REFERENCES

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8. All the iron complexes showed a parent peak and the characteristic consecutive loss of 28 m/e.