

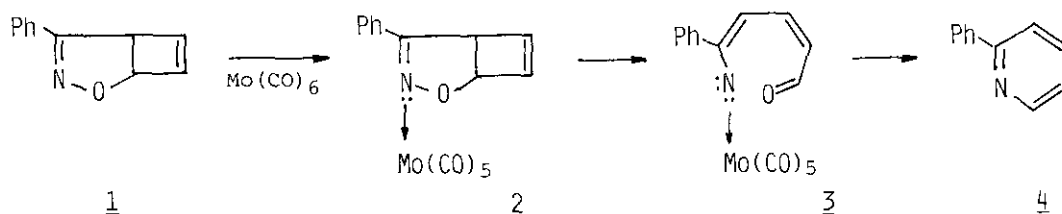
NONACARBONYLDIIRON-INDUCED REACTION OF 2-OXA-3-AZABICYCLO-  
[3.2.0]HEPTA-3,6-DIENE SYSTEM. PREPARATION AND THERMAL  
BEHAVIOR OF THE CYCLOBUTENE-IRON COMPLEX

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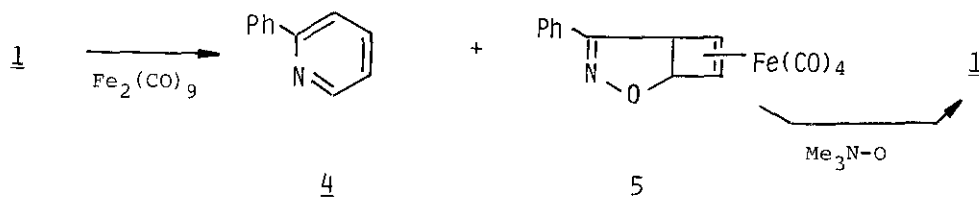
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**Abstract** — The reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene with  $[\text{Fe}_2(\text{CO})_9]$  afforded tetracarbonyl( $\eta^2$ -4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron along with 2-phenylpyridine. Thermal behavior of the complex and the reaction of the related compounds with  $[\text{Fe}_2(\text{CO})_9]$  giving pyridine derivatives were also studied.

Photosubstitution of group 6A metal carbonyls  $[\text{M}(\text{CO})_6]$  ( $\text{M}=\text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$ ) has found a wide range of applications, mainly with  $n$ -donor ligand.<sup>1</sup> Previously, the  $[\text{Mo}(\text{CO})_6]$ -induced reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (**1**) under thermal conditions has been shown to undergo the N-O and C-1-C-5 bond cleavage to give 2-phenylpyridine, via a postulated  $n$ -donor ligand complex **2** and a ketovinyl-nitrene complex **3** as shown below.<sup>2</sup> The N-O and C-1-C-5 bond cleavage of **1** stands in contrast to the photochemical reaction of **1** giving a reactive intermediate of 3-(3-phenyl-2H-azirin-2-yl)acrylaldehyde studied by Mukai and his coworkers.<sup>3,4</sup> On the contrary, the thermal reaction of **1** at high temperature has been shown to give 6-phenyl-2-pyridone and 1-formyl-2-phenylpyrrole.<sup>3,5</sup> The 3-phenyl-1,2-oxazepine, which is derived from the cyclobutene-ring opening, is postulated as the intermediate.<sup>6</sup> In contrast to the cyclobutene-ring opening at high temperature, thermally



induced rearrangement of tetracarbonyl( $\eta^2$ -tricyclo[4.2.0.0<sup>2,5</sup>]octadiene)iron to tricarbonyl( $\eta^4$ -bicyclo[4.2.0]octadiene)iron<sup>7</sup> suggests that iron in certain system allows a facile disrotatory cyclobutene-butadiene ring opening to take place.<sup>8</sup> In connection with these facts, it is of interest to study the reaction of cyclobutene system in 1 with  $[\text{Fe}_2(\text{CO})_9]$ . We report here a preparation and the thermal behavior of tetracarbonyl( $\eta^2$ -4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron. The reactions of the related compounds to 1 with  $[\text{Fe}_2(\text{CO})_9]$  are also described. Thermal reaction of 1 with two molar equivalent quantities of  $[\text{Fe}_2(\text{CO})_9]$  in anhydrous benzene for 8 min at 60 °C resulted in the formation of 2-phenylpyridine (4), tetracarbonyl( $\eta^2$ -4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron (5), and the remainder being unreacted starting material in 21, 11, and 34% yields, respectively. The product 5 was recrystallized from hexane solution upon cooling to -78 °C. The formation of the pyridine 4 could be explained by an intervention



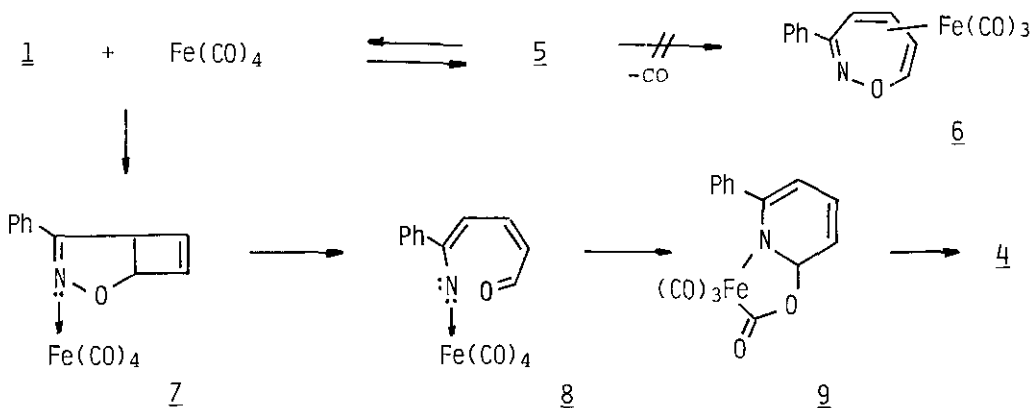
of the  $\pi$ -donor complex 7 (*vide infra*). The pyridine 4 was identified by comparison with the authentic sample,<sup>2</sup> and the structure of 5 was assigned on the basis of the following facts:<sup>9</sup> 5: mp 101-102 °C (decomp); IR ( $\text{CHCl}_3$ ), 3100-2900, 2100, 2000, 1435, 1354, 1012, 969, 878  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  3.98 (1H, d,  $J=3.4$  Hz), 4.25 (1H, dxd,  $J=3.4, 2.1$  Hz), 4.35 (1H, d,  $J=4.2$  Hz), 5.42 (1H, dxd,  $J=4.2, 2.1$  Hz), 7.0-7.70 (5H, m);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  56.4, 57.8, 61.5, 90.4, 126.7, 128.8, 130.1, 158.6, 208.5.

In the comparison of the NMR spectra of 1<sup>10</sup> and 5, particularly noteworthy are the chemical shifts of the hydrogens on the cyclobutene double bond and the carbon absorption at the C-4 position. In the case of 1, the key proton absorptions were seen at  $\delta$  6.08 and  $\delta$  6.66. In the case of 5, however, these proton absorptions appeared at the higher field of  $\delta$  3.98 and  $\delta$  4.25. This phenomenon is observed also in  $^{13}\text{C-NMR}$  spectra. Although the four carbon absorptions ( $\delta$  56.4, 57.8, 61.5, and 90.4) of the cyclobutene moiety of 5 were not assigned distinctly, two of these signals would correspond to the carbons on the cyclobutene double bond. These two signals appeared at the lower field of  $\delta$  139.1 and  $\delta$  145.6 in the case of

1.<sup>10</sup> The carbon absorption of the C-4 position of 5 appeared at  $\delta$  158.6, which is almost the same as that of 1 ( $\delta$  158.9). These facts clearly indicate the cyclobutene double bond is bonded to the  $[\text{Fe}(\text{CO})_4]$  unit.<sup>11</sup> Furthermore, a treatment of 5 with a large excess of trimethylamine oxide in benzene at an ambient temperature afforded 1 in 72% yield.<sup>12</sup> Thus the structure of 5 seems to be assessed.

The complex 5 in a solid state is stable and survived for 4 weeks in a refrigerator, however, it was converted to 1 and 4 in 64 and 10% yields respectively when heated at 60 °C in anhydrous benzene, indicating that the equilibrium between 1 and 5 could exist in solution at 60 °C. An expected disrotatory ring-opening giving the complexed 3-phenyl-1,2-oxazepine (6) was not observed.

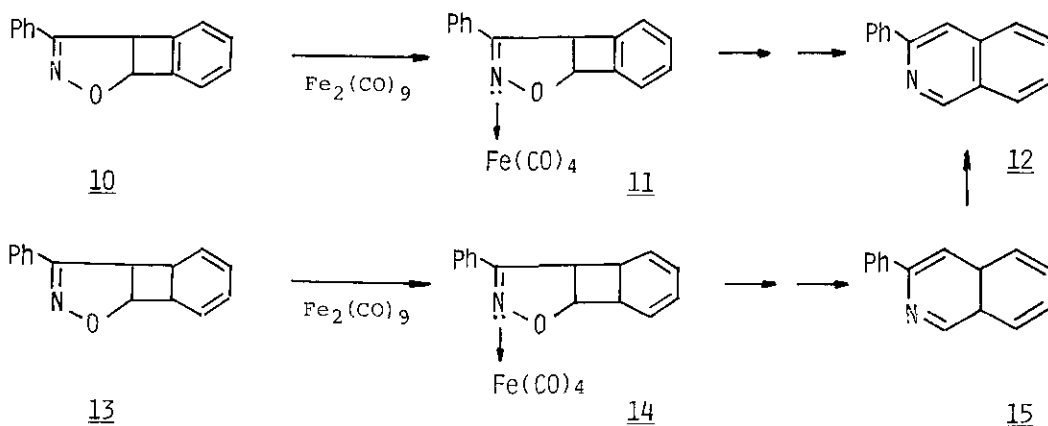
The formation of pyridine 4 from 5 seems to suggest the decomplexed  $[\text{Fe}(\text{CO})_4]$  unit could bind to the nitrogen atom of the regenerated 1 giving 7, which is similar to the postulated complex 2.<sup>2</sup> The  $[\text{Fe}_2(\text{CO})_9]$ -induced N-O and C-4-C-5 bond cleavage of 3,5-disubstituted 2-isoxazoline affording two fragments of aldehydes and the complexed vinylnitrene intermediate has also been shown previously.<sup>13</sup> The protonation and the subsequent reduction of the vinylnitrene complex could occur in protic media to give imine or enamine which collapses to the corresponding ketones. In a similar fashion, the delocalization of  $\pi$ -d electron from the iron to the  $\pi^*$  orbital of the C=N-O moiety would facilitate the N-O and C-1-C-5 bond fission of 7 giving 8 and the subsequent ligand migration could give the pyridine 4 as shown below.<sup>2,14</sup> Thus the  $[\text{Fe}(\text{CO})_4]$ -complexed nitrene moiety was also demonstrated to undergo an intramolecular condensation with the carbonyl function. As expected,



the pyridine 4 was obtained as a sole product in 57% yield when 1 and two molar equivalent quantities of  $[\text{Fe}_2(\text{CO})_9]$  were heated at 60 °C for 5 h. Thus the complex 7 giving 4 could be generated directly from 1 with  $[\text{Fe}_2(\text{CO})_9]$  as well as via 5 in

the reaction of 1. The formation of 4 via 7 is also suggested by the following facts.

6,7-Benzo-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (10)<sup>15</sup> and its dihydrogenated compound 13<sup>16</sup> contain no labile cyclobutene double bond complexing with  $[\text{Fe}(\text{CO})_4]$  unit. However 13 contains a diene moiety which has a possibility of giving a complex with  $[\text{Fe}(\text{CO})_3]$  unit.<sup>8</sup> The reaction of 10 with two molar equivalent amounts of  $[\text{Fe}_2(\text{CO})_9]$  at 60 °C for 3 h afforded 3-phenylisoquinoline (12)<sup>2</sup> in 57% yield. The proposed mechanistic interpretation for the formation of 12 involves a direct formation of the n-donor complex 11, the N-O and C-1-C-5 bond cleavage giving the nitrene complex similar to 8, and the following ring annelation. Similarly the reaction of 13 with  $[\text{Fe}_2(\text{CO})_9]$  at 45 °C for 24 h afforded 12 and the unreacted starting material in 48 and 19% yields, respectively. The reaction sequences, which are similar to that of 10, are also shown. No dihydroisoquinoline 15 was detected at all, indicating a facile dehydrogenation of 15 to 12. Furthermore, no diene- $[\text{Fe}(\text{CO})_3]$  complex of 13 was obtained. This fact suggests the facile n-donor complexation predominates over the complexation to the butadiene unit. Thus the isoquinoline 12 could arise from the postulated n-donor complex 11 or 14.



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