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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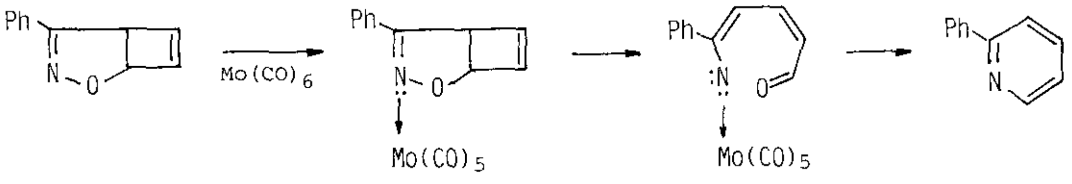
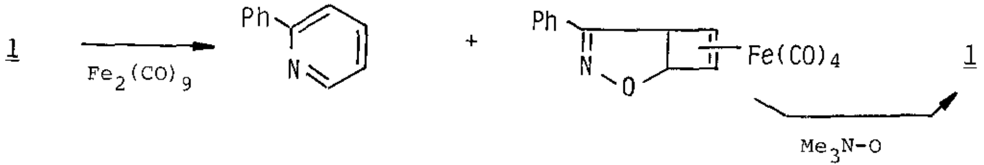
Abstract —— The reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene with [$Fe_2(CO)_9$] afforded tetracarbonyl(η^2-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron along with 2-phenylpyridine. Thermal behavior of the complex and the reaction of the related compounds with [$Fe_2(CO)_9$] giving pyridine derivatives were also studied.

Photosubstitution of group 6A metal carbonyls [$M(CO)_6$] (M=Cr, Mo, and W) has found a wide range of applications, mainly with n-donor ligand.[1] Previously, the [$Mo(CO)_6$]-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 ketovinylnitrene complex 3 as shown below.[2] 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.[3,4] 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.[3,5] The 3-phenyl-1,2-oxazepine, which is derived from the cyclobutene-ring opening, is postulated as the intermediate.[6] In contrast to the cyclobutene-ring opening at high temperature, thermally



1 2 3 4

induced rearrangement of tetracarbonyl(η^2-tricyclo[4.2.0.0^{2,5}]octadiene)iron to tricarbonyl(η^4-bicyclo[4.2.0]octadiene)iron[7] suggests that iron in certain system allows a facile disrotatory cyclobutene-butadiene ring opening to take place.[8] In connection with these facts, it is of interest to study the reaction of cyclobutene system in 1 with [$Fe_2(CO)_9$]. We report here a preparation and the thermal behavior of tetracarbonyl(η^2-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron. The reactions of the related compounds to 1 with [$Fe_2(CO)_9$] are also described. Thermal reaction of 1 with two molar equivalent quantities of [$Fe_2(CO)_9$] in anhydrous benzene for 8 min at 60 °C resulted in the formation of 2-phenylpyridine (4), tetracarbonyl(η^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 n-donor complex 7 (*vide infra*). The pyridine 4 was identified by comparison with the authentic sample,[2] and the structure of 5 was assigned on the basis of the following facts:[9] 5: mp 101-102 °C (decomp); IR ($CHCl_3$), 3100-2900, 2100, 2000, 1435, 1354, 1012, 969, 878 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ 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}C-NMR ($CDCl_3$), δ 56.4, 57.8, 61.5, 90.4, 126.7, 128.8, 130.1, 158.6, 208.5.



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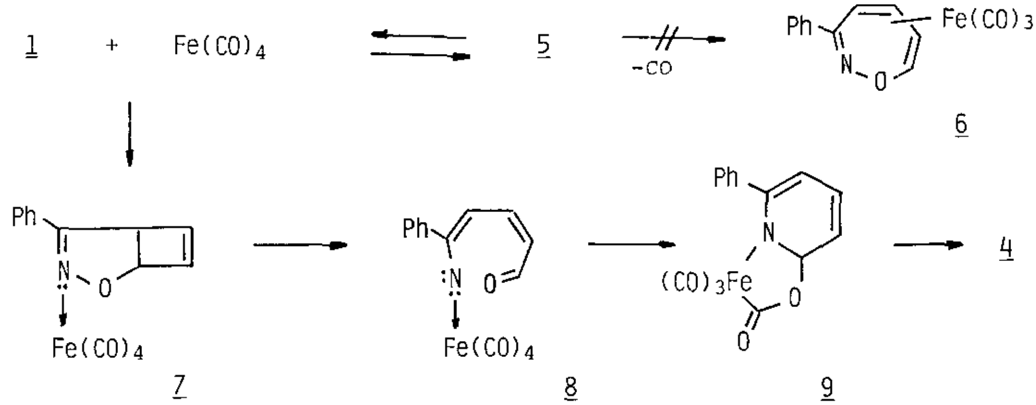
In the comparison of the NMR spectra of 1[10] and 5, particularly noteworthy are the chemical shifts of the hydrogens on the cyclobutene double bond and the carbon absorption at the C-4 position. In the case of 1, the key proton absorptions were seen at δ 6.08 and δ 6.66. In the case of 5, however, these proton absorptions appeared at the higher field of δ 3.98 and δ 4.25. This phenomenon is observed also in ^{13}C-NMR spectra. Although the four carbon absorptions (δ 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 δ 139.1 and δ 145.6 in the case of

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

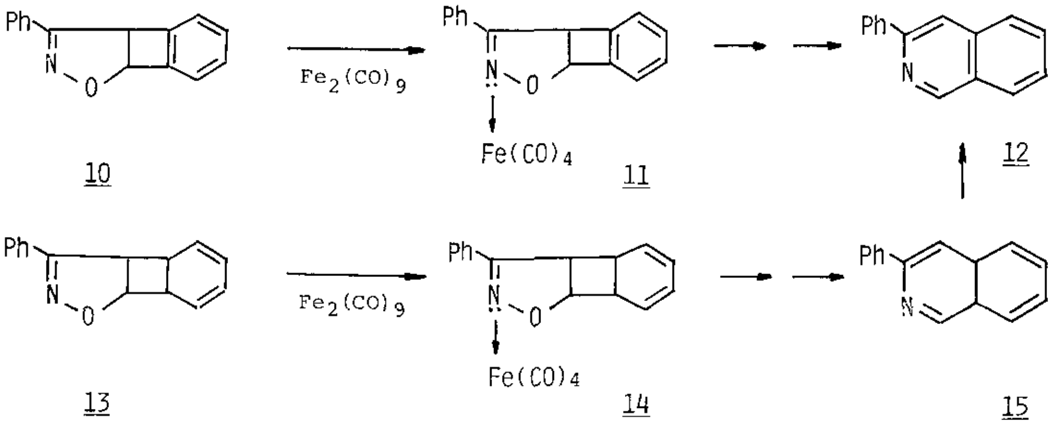
The complex 5 in a solid state is stable and survived for 4 weeks in a refrigirator, however, it was converted to 1 and 4 in 64 and 10% yields respectively when heated at 60 °C in anhydrous benzene, indicating that the equilibrium between 1 and 5 could exist in solution at 60 °C. An expected disrotatory 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 [Fe(CO)$_4$] unit could bind to the nitrogen atom of the regenerated 1 giving 7, which is similar to the postulated complex 2.[2] The [Fe$_2$(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.[13] 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 π-d electron from the iron to the π* 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.[2,14] Thus the [Fe(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 [Fe$_2$(CO)$_9$] were heated at 60 °C for 5 h. Thus the complex 7 giving 4 could be generated directly from 1 with [Fe$_2$(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)[15] and its dihydrogenated compound 13[16] contain no labile cyclobutene double bond complexing with [Fe(CO)$_4$] unit. However 13 contains a diene moiety which has a possibility of giving a complex with [Fe(CO)$_3$] unit.[8] The reaction of 10 with two molar equivalent amounts of [Fe$_2$(CO)$_9$] at 60 °C for 3 h afforded 3-phenylisoquinoline (12)[2] 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 [Fe$_2$(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-[Fe(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 arize from the postulated n-donor complex 11 or 14.



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