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ON THE PHOTOCHEMICAL AND THERMAL REACTIONS OF THE CYCLOBUTENE-IRON COMPLEXES INVOLVED IN HETEROATOMIC BICYCLO[3.2.0]HEPTADIENE SYSTEM

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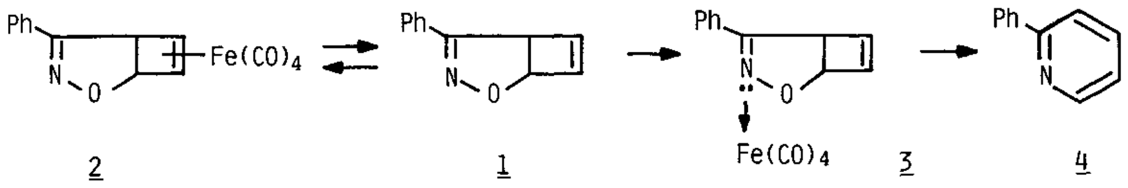
Abstract——Photochemical reaction of tetracarbonyl(6-7-η-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron to give 2-phenylpyridine and 2-formyl-5-phenylpyrrole was studied. Furthermore, photochemical and thermal reactions of tetracarbonyl(6-7-η-2-ethoxycarbonyl-2,3-diazabicyclo-[3.2.0]hepta-3,6-diene)iron were found to undergo decomplexation, N-N bond cleavage leading to 1-(N-ethoxycarbonyl)amino-4-cyano-1,3-butadiene, and dimerization of the cyclobutene moiety incorporating carbonyl group.

The thermal reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (1) (bicyclic 1,2-oxazepine) at high temperature has been reported by Mukai et al. to give 6-phenyl-2-pyridone and 2-formyl-5-phenylpyrrole.[1,2] The unstable 1,2-oxazepine[3] originating from the cyclobutene ring opening of (1) is postulated as the intermediate. In contrast to the cyclobutene-ring opening at high temperature, thermally induced facile rearrangement of tetracarbonyl(3-4-η-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene)iron to tricarbonyl(2-5-η-bicyclo[4.2.0]octa-2,4,7-triene)iron[5] suggests that the iron atom in a suitable system can assist a facile cyclobutene-ring opening.[6] Unsubstituted tricarbonyl(4-7-η-1H-1,2-diazepine)iron has been prepared, although no 1H-1,2-diazepine has been isolated. Thus an attempt to isolate the complexed 1,2-oxazepine seemed interesting. In the previous paper, we reported the preparation

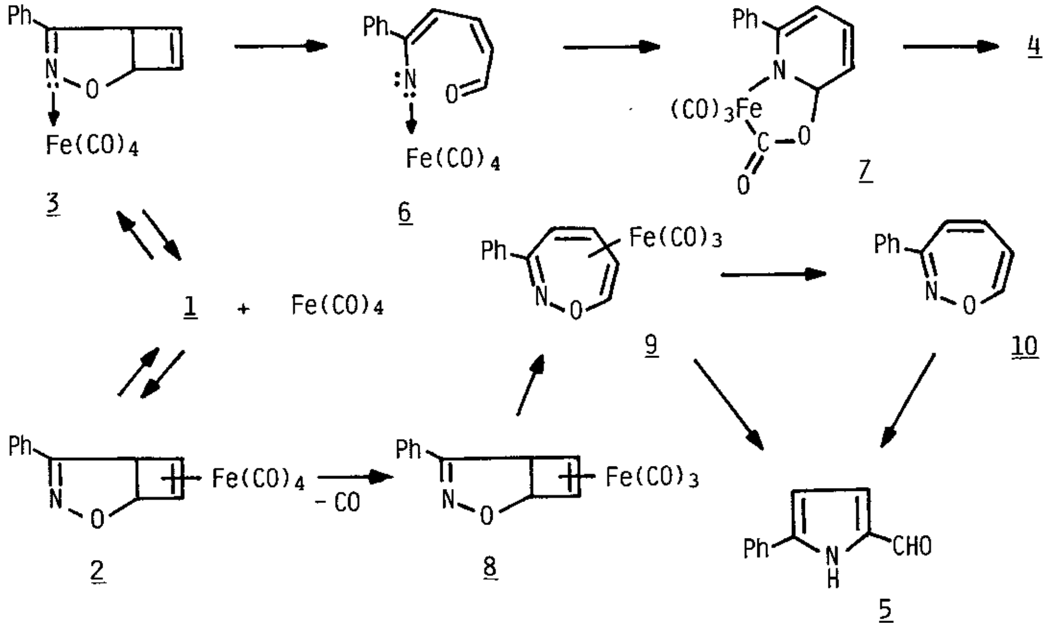


Scheme 1.

and thermal reaction of tetracarbonyl(6-7-η-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron (2).[8] In that paper, it was suggested that the complex (2) underwent decomplexation-complexation sequences leading to (3) and subsequent N-O bond cleavage followed by deoxygenation gave 2-phenylpyridine (4). We report here a photochemical reaction of (2). Furthermore, the photochemical and thermal reaction of tetracarbonyl(6-7-η-2-ethoxycarbonyl-2,3-diazabicyclo[3.2.0]hepta-3,6-diene)iron (12) were examined to clarify a general behavior of the cyclobutene-iron complexes involved in the heteroatomic bicyclo[3.2.0]heptadiene system.

Photochemical reaction of (1) with $[Fe(CO)_5]$ resulted in the formation of cyclobutene-iron complex (2),[8] 2-phenylpyridine (4), 2-formyl-5-phenylpyrrole (5), and the starting material in 7, 9, 6, and 58% yields, respectively. The photoirradiation of (1) in the absence of $[Fe(CO)_5]$ under the present conditions caused no reaction and the starting material was recovered in 92% yield. The fact that the independent irradiation of (2) afforded (4) and (5) in 35 and 21% yields, suggests that both the products are derived from the complex (2).

The present reactions can be explained in terms of the mechanism in Scheme 2, though this mechanism is speculative since no intermediate has been isolated. The transient formation of (1) during the photoreaction of (2) was detected by TLC. Therefore, the formation of (4) from (2) suggested the involvement of the complex (3) as in the reaction of (2) under the thermal conditions (cf. Scheme 1). The facile N-O

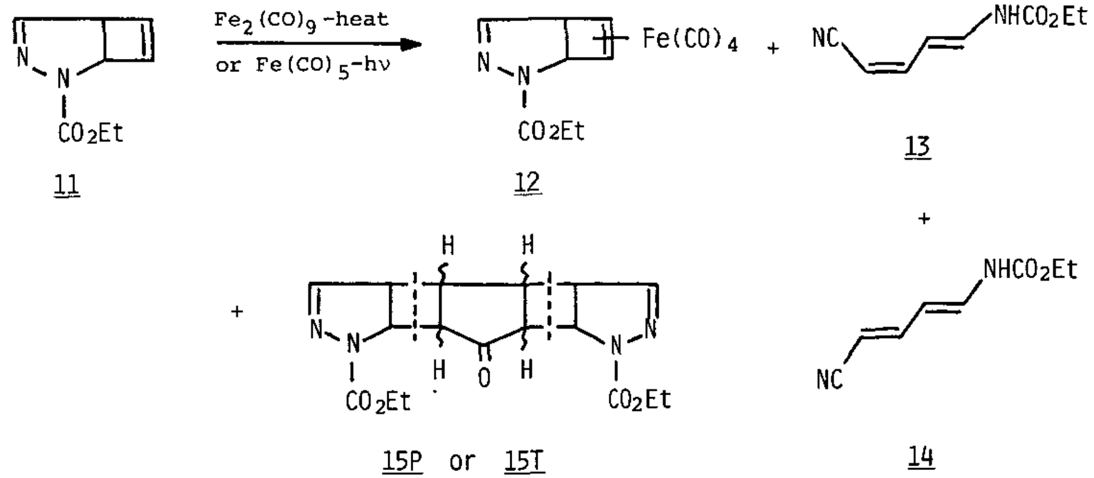


Scheme 2.

and C-1-C-5 bond cleavage of the isoxazoline moiety[9] in (3) is expected to give (6) and then (7), which undergoes decomplexation to give (4).[10]

Several derivatives of (6) have also been postulated in the cycloaddition reaction of isoxazoles with acetylenic esters to give pyridine derivatives,[10,11] excepting that the 1,2,4,5-tetraphenyl-substituted derivative of (6) gives several pyrroles.[12] In consideration of these facts and the behavior of (6), which gives only (4),[8] no formation of (5) via (6) seems to occur. One of the possible pathway for the formation of (5) is a photoinduced decarbonylation of (2) leading to (8) and subsequent cyclobutene-ring opening to give the complexed 1,2-oxazepine (9). The N-O bond cleavage of (9) or decomplexed 1,2-oxazepine (10)[1,2] possibly affords (5). For further confirmation of the cyclobutene-ring opening, the preparation and reaction of tetracarbonyl(6-7-η-2-ethoxycarbonyl-2,3-diazabicyclo[3.2.0]hepta-3,6-diene)-iron (12) was examined. The results and the reaction conditions are summarized in Table 1. The photochemical reaction of 2-ethoxycarbonyl-2,3-diazabicyclo[3.2.0]-hepta-3,6-diene (11)[13] with $[Fe(CO)_5]$ resulted in the formation of the complex (12), trans, cis-1-(N-ethoxycarbonyl)amino-4-cyano-1,3-butadiene (13), a mixture of carbonyl-incorporated dimerization products (15P), and the starting material (11) (entry 1). However, thermal reaction of (11) in the presence of $[Fe_2(CO)_9]$ resulted in the formation of the complex (12), trans, trans-1-(N-ethoxycarbonyl)amino-4-cyano-1,3-butadiene (14), and a mixture of dimerization products (15T), in addition to the starting material (11).

Independent photoirradiation of the complex (12) afforded a mixture of dimerized



Scheme 3.

Table 1. Thermal and Photochemical Reactions of (11) and (12).[a]

		Reaction Conditions		Products (Yield/%)				
Entry	Compound	$h\nu$ or heat	Time/h	(11)	(12)	(13)	(14)	(15P,T)
1	(11)[b]	$h\nu$	110	20	37	2	--	30
2	(11)[c]	heat, 50 °C	0.5	27	47	--	1	1
3	(12)	$h\nu$	20	21	9	2	--	46
4	(12)	heat, 80 °C	0.5	63	--	4	--	6

a. Reactions were carried out in benzene solution. b. In the presence of two molar equivalent amounts of $[Fe(CO)_5]$. c. In the presence of two molar equivalent amounts of $[Fe_2(CO)_9]$.

products (15P) as the main product, along with (13), decomplexed compound (11), and the starting material (12) (entry 3). In contrast, thermal reaction underwent decomplexation to give (11) in high yield (entry 4). In these reactions, no tricarbonyl(4-7-η-1-ethoxycarbonyl-1H-1,2-diazepine)iron (20)[14] was obtained.

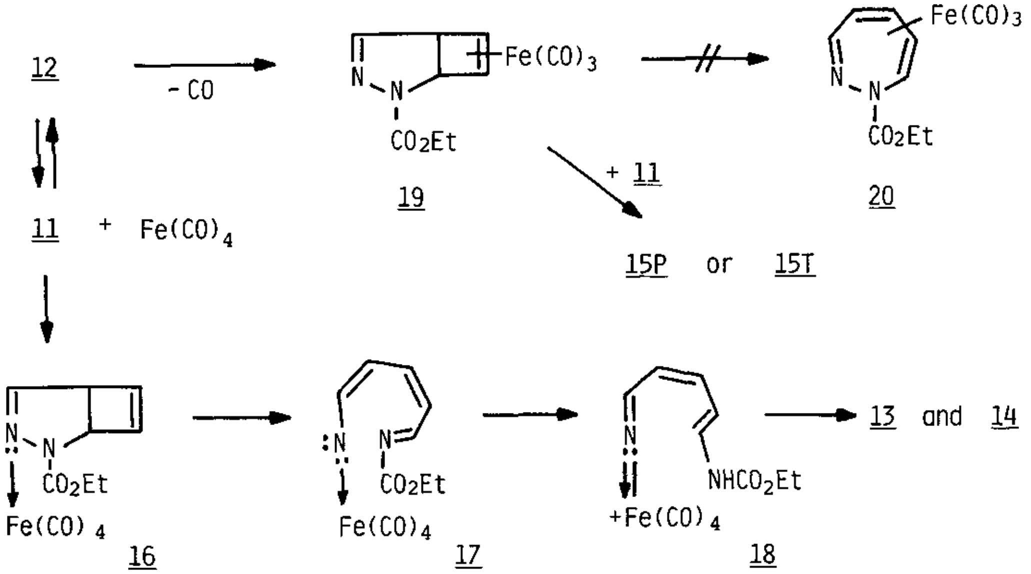
The structures of (13) and (14) were identified by comparison of the physical data with those in the literature.[15] The complex (12) undergoes decomplexation gradually. Therefore, the satisfactory elemental analyses and mass spectral data were not obtained. However, the spectral data are satisfactory for the proposed structure (12). The chemical shifts of the protons on the cyclobutene double bond in (11) and (12) are noteworthy. In the case of (11), the key proton absorptions were observed at δ 6.11 and 6.33. In the case of (12), however, these proton absorptions appeared at the high field (δ 3.76-4.26). The proton absorptions at C-4 of both (11) and (12) appear almost same field. These features and the comparison of the spectral characteristics of (1) and (2) clearly indicate that the cyclobutene double bond is bonded to the $[Fe(CO)_4]$ unit in (12).

The IR spectra of (15P) and (15T) are very similar to each other. However, a slight defference on the IR spectra between (15P) and (15T) may suggest the different ratio of isomers in (15P) and (15T). The ^{1}H-NMR spectrum of (15P) suggests the existence of cyclopentanone and pyrazoline moieties as well as the cyclobutene moiety. The repeated separation of (15P) through TLC afforded a pure isomer (15), the spectral data of which are very similar to those of (15P) and (15T).

The analytical data as well as the spectral data of (15) are satisfactory for proposed structure such as (15P) or (15T). However, the detailed structure of (15) is not assigned distinctly.

The present results indicate that the complexation-decomplexation sequences of [Fe(CO)$_4$] unit allow the equilibrium between (11) and (12) under thermal conditions or under photoirradiation. Furthermore, [Fe(CO)$_4$] unit seems to bind to the nitrogen atom of (11) to give (16), which is similar to the postulated complex (3). The N-N bond cleavage of (16) to give (17) and subsequent reduction can afford (18).[9] The nitrene complexes similar to (17) have been postulated in the nonacarbonyldiiron-induced reaction of 1-tosyl- and 1-benzenesulfonyl-1H-1,2-diazepines to give pyrrole derivatives.[16] However, the expected pyrrole derivative was not obtained in the present reactions. The deprotonation-decomplexation sequences result in the formation of (13) or (14). This process is a minor process (Table 1), and the N-N bond in (16) seems to be strong as compared with the N-O bond in (3). The main reaction pathway for (12) under photoirradiation involves decarbonylation to give (19), which further reacts with (11) to give (15P).[17] Under the thermal conditions, decarbonylation of (12) to give (19) and then (15T) becomes a minor process and (12) seems to give (11) mainly.

In the reaction of (12), the cyclobutene-ring opening was not observed, and the decomplexation and dimerization predominated. On the contrary, the dimerization in (2) was not detected at all. Further confirmation of the postulated 1,2-oxazepine species such as (9) and (10) leading to (5) is still necessary.



Scheme 4.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H-NMR (60 MHz) and ^{13}C-NMR (22.5 MHz) spectra were recorded on a Hitachi R-24 and JEOL JNM-FX90Q spectrometer, respectively, and chemical shifts were given in ppm (δ) relative to internal Me_4Si standard. Mass spectral studies were conducted using Shimadzu GCMS-QP-1000 spectrometer. The photoirradiations otherwise mentioned were carried out using Rayonet photoreactor (RPR-100) fitted with RPR-350 nm lamps through Pyrex filter. All of the melting points are uncorrected.

Preparation of 3-Phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (1) with Pentacarbonyliron

A solution of (1) (171 mg, 1 mmol) and $[Fe(CO)_5]$ (392 mg, 2 mmol) in anhydrous benzene (20 ml) was irradiated under nitrogen atmosphere. The reaction mixture was filtered through Celite to remove insoluble material. The filtrate was concentrated and the residue was separated by TLC on silica gel using benzene as developer to give the complex (2) (24 mg, 7%), 2-phenylpyridine (4)[8] (14 mg, 9%), and 2-formyl-5-phenylpyrrole (5)[2] (10 mg, 6%), in addition to unreacted starting material (1) (100 mg, 58%). For (2): IR ($CHCl_3$), 3100-2900, 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), 7.0-7.7 (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; MS, m/z (rel intensity), 283 (M^+-56, 1), 155 (100). Anal. Calcd for $C_{15}H_9NO_5Fe$: C, 53.13; H, 2.67; N, 4.13. Found: C, 53.36; H, 2.85; N, 4.05.

Photoirradiation of (1) in the Absence of Pentacarbonyliron

A solution of (1) (87 mg, 0.5 mmol) in anhydrous benzene (10 ml) was irradiated for 48 h under nitrogen atmosphere. After the solvent was evaporated, the residue was purified by TLC on silica gel using benzene as developer to give 83 mg (92%) of the unreacted starting material (1).

Photoirradiation of Tetracarbonyl(6-7-η-4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene)iron

A solution of (2) (95 mg, 0.28 mmol) in anhydrous benzene (20 ml) was irradiated for 22 h under nitrogen atmosphere. After the reaction mixture was concentrated, the residue was separated by TLC on silica gel using benzene as developer to give (4) (15 mg, 35%) and (5) (10 mg, 21%).

Preparation of 2-Ethoxycarbonyl-2,3-diazebicyclo[3.2.0]hepta-3,6-diene (11)

A solution of 1-ethoxycarbonyl-1H-1,2-diazepine (1.94 g, 12 mmol) in methanol (400 ml) was irradiated with RPR-300 nm lamps for 79 h under argon atmosphere. After the solvent was evaporated, the residue was purified by column chromatography on silica gel using benzene-ethyl acetate (1/1) as eluent to give 1.76 g (88%) of (11), which exhibited the following spectral data:[13] ^{1}H-NMR ($CDCl_3$), δ: 1.33 (3H, t, J=7.2 Hz), ca. 4.07 (1H, m), 4.25 (2H, q, J=7.2 Hz), 5.02 (1H, dxd, J=4.0, 2.0 Hz), 6.11 (1H, dxd, J=2.5, 1.0 Hz), 6.33 (1H, dxd, J=2.5, 2.0 Hz), 6.93 (1H, d, J=1.4 Hz).

Photoreaction of (11) with Pentacarbonyliron

A solution of (11) (166 mg, 1 mmol) and [$Fe(CO)_5$] (392 mg, 2 mmol) in anhydrous benzene (20 ml) was irradiated for 110 h under nitrogen atmosphere. The reaction mixture was filtered through Celite to remove insoluble material. The filtrate was concentrated and the residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) as developer. The first band from the TLC plates gave 4 mg (2%) of (13). The second band from the TLC plates contained the complex (12) (123 mg, 37%): oil; IR ($CHCl_3$), 2989, 2102, 2015, 1994, 1694, 1589, 1429, 1388, 1355, 1146 cm^{-1}; ^{1}H-NMR (acetone-d_6), δ: 1.31 (3H, t, J=7.1 Hz), 3.76-4.26 (3H, m), 4.23 (2H, q, J=7.1 Hz), 4.83 (1H, broad d, J=3.4 Hz), 7.00 (1H, broad s). The third band from the TLC plates contained 33 mg (20%) of unreacted starting material (11). The forth band from the TLC plates gave 62 mg (34%) of a mixture of dimerized product (15P): IR ($CHCl_3$), 1731, 1700, 1590, 1430, 1385, 1354, 1147 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ: 1.33 (6H, broad t, J=7.1 Hz), 2.90-3.79 (6H, m), 4.09-4.57 (6H, m), 6.80-7.20 (2H, m). Repeated separation of the mixture by TLC afforded a pure sample of (15), which exhibited the following physical data: mp 146-148 °C; IR ($CHCl_3$), 1726, 1704, 1588, 1429, 1388, 1357, 1153 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ: 1.33 (6H, t, J=7.0 Hz), 2.94-3.71 (6H, m), 4.10-4.52 (6H, m), 7.08 (2H, d, J=1.9 Hz); MS, m/z (rel intensity), 362 (M^+, 0.5), 68 (100). Anal. Calc for $C_{17}H_{20}N_4O_5$: C, 56.66; H, 5.59; N, 15.55. Found: C, 56.28; H, 5.21; N, 15.26.

Thermal Reaction of (11) with Nonacarbonyldiiron

A solution of (11) (220 mg, 1.32 mmol) and [$Fe(CO)_5$] (963 mg, 2.65 mmol) in anhydrous benzene (10 ml) was heated at 50 °C for 0.5 h under nitrogen atmosphere. The reaction mixture was then filtered through Celite to remove insoluble material. The filtrate was concentrated and the residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) to give (14) (3 mg, 1%), the complex (12) (208 mg, 47%), unreacted starting material (11) (60 mg, 27%), and a mixture of dimerized products (15T) (2 mg, 1%): IR ($CHCl_3$), 1728, 1702, 1589, 1432, 1388, 1354, 1146 cm^{-1}.

Photochemical Reaction of the Complex (12)

A solution of (12) (210 mg, 0.63 mmol) in anhydrous benzene (20 ml) was irradiated for 20 h under nitrogen atmosphere. After the reaction mixture was filtered through Celite, the filtrate was concentrated. The resulting residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) to give (13) (2 mg, 2%), unreacted (12) (15 mg, 9%), decomplexed compound (11) (18 mg, 21%), and a mixture of dimerized products (15P) (52 mg, 46%).

Thermal Reaction of the Complex (12)

A solution of (12) (200 mg, 0.6 mmol) in anhydrous benzene (7 ml) was heated under reflux for 0.5 h under nitrogen atmosphere. After the evaporation of the solvent, the residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) to give (13) (4 mg, 4%), decomplexed product (11) (63 mg, 63%), and a mixture of dimerized products (15T) (7 mg, 6%), which was identified by comparison with the IR spectrum.

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