

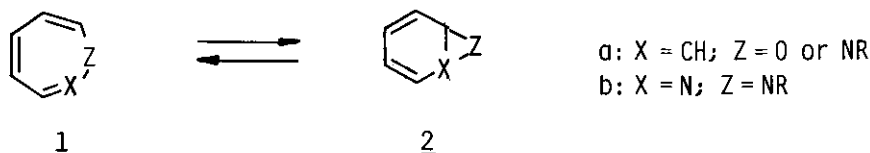
ON THE REACTION OF 1-ETHOXYCARBONYL-1H-1,2-DIAZEPINE WITH
MOLYBDENUM AND IRON CARBONYL COMPLEXES

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Abstract—The reaction of 1-ethoxycarbonyl-1H-1,2-diazepine (3) with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ resulted in the N-N bond cleavage of the seven-membered ring to give dienaminocarboxaldehyde 4 and dienaminonitriles, 5 and 6. On the other hand, the reaction of 3 with $[\text{Fe}_2(\text{CO})_9]$ or with $[\text{Fe}(\text{CO})_5]$ afforded 4 and 6, or 2-(ethoxycarbonylamino)pyridine and N,N'-di(2-pyridyl)urea, in addition to $[\text{diene}]\text{-Fe}(\text{CO})_3$ complex.

The valence tautomeric equilibrium of heteroepine (1a)-arene oxide or arene 1,2-imine (2a) generally lies on the side of 1a. It was theoretically shown that protonation or coordination on the lone pair electron of the hetero atom of 1a-2a strengthen the C-C bond of the three-membered ring of 2a so as to shift the equilibrium to the side of 2a.^{1,2} Previously, we have shown that the $\text{BF}_3 \cdot \text{OEt}_2$ - or metal carbonyl-induced reaction of phenyl-substituted 1,3-oxazepines gives novel pyridones or pyridine and/or pyrrole derivatives via an O-coordinated pyridine-2,3-oxide.^{4,5} On the other hand, 1H-1,2-diazepine (1b) has been shown to rearrange to N-iminopyridinium ylides on treatment with acid.^{6,7} This rearrangement, coupled with the thermal isomerization of 1b to 1H-1,3-diazepine and 2- or 6-aminopyridine derivatives,⁸ constitutes the main evidence for existence of 2b. The reaction of 1H-1,2-diazepines and iron carbonyls has generally led to $[\text{diene}]\text{-Fe}(\text{CO})_3$ complexes as the only isolated products.⁴ The exception is the reaction of 1-arenesulfonyl-1H-1,2-diazepines with $[\text{Fe}_2(\text{CO})_9]$. In this reaction, iron coordination occurs on N-2 atom



to undergo the ring contraction giving pyrrole derivatives.⁹ In connection with these results and our previous studies,^{4,5} we describe here the novel reactions of 1-ethoxycarbonyl-1H-1,2-diazepine (3) induced by molybdenum or iron carbonyl complexes.

The reaction of 3⁴ with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$, which is prepared by heating $[\text{Mo}(\text{CO})_6]$ in MeCN,¹⁰ at room temperature in anhydrous or in moist acetonitrile afforded dienecarboxaldehyde 4, *trans*, *cis*-dienaminonitrile 5, and *trans*, *trans*-dienaminonitrile 6 (Scheme 1 and Table 1). The structure of 4 was deduced on the basis of the physical data, although the stereochemistry is not explicitly defined. The products 5 and 6 were identified by comparison of the spectral data with those of authentic samples.¹¹

The N-N bond cleavage of 3 to give 4, 5 and 6 is explained by the mechanistic pathways depicted in Scheme 1. The thermal reaction of 3 with the metal carbonyl is considered to result in the formation of the complex 7, formation of which is similar to the $[\text{Mo}(\text{CO})_6]$ - or $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ -induced reaction of isoxazoles to give (β -oxo vinyl)nitrene intermediate.¹² Then, the N-N bond cleavage occurs in 7 to give the complexed nitrene intermediate 8. An intermediate similar to 8 has also been suggested in the ring contraction of 1-arenesulfonyl-1H-1,2-diazepines with $[\text{Fe}_2(\text{CO})_9]$ to give pyrrole derivatives.⁹ Thus, the facile N-N bond cleavage of 7 to give 8 seems to be plausible.

Previously, it was suggested that the $[\text{Mo}(\text{CO})_5]$ -complexed 1-phenylvinyl nitrene,

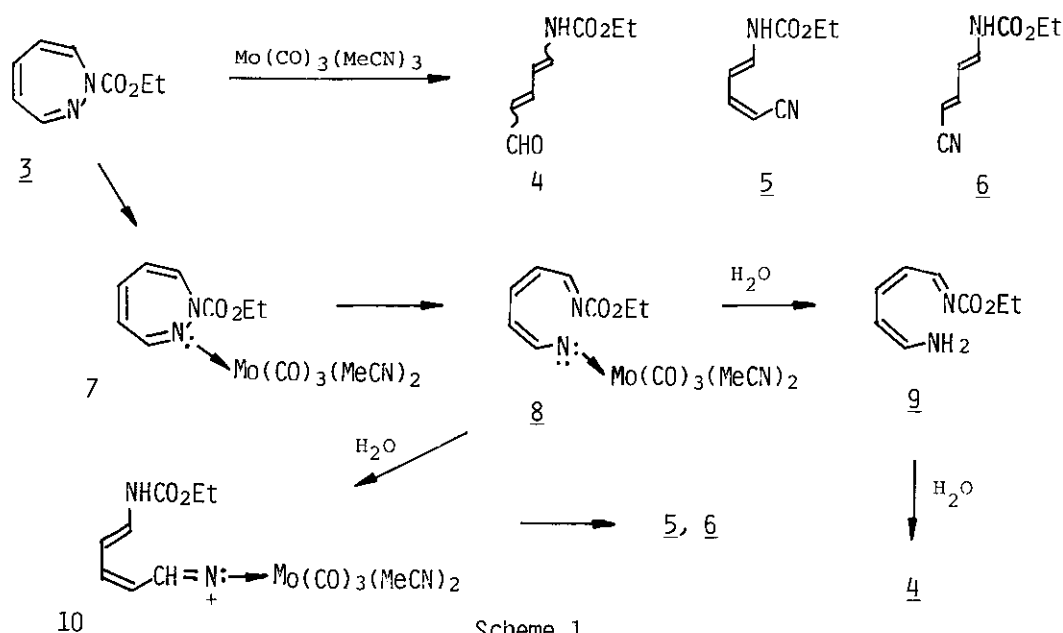


Table 1. Reaction of 1H-1,2-Diazepine 3 with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$.^a

Entry	Solvent	Reaction		Product			Recovery
		conditions	time/h	<u>4</u>	<u>5</u>	<u>6</u>	
1	MeCN	room temp.	1	28	6	—	6
2	MeCN-H ₂ O	room temp.	1	24	1	5	—

a. $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ was prepared from 2.0 molar equivalent amounts of $[\text{Mo}(\text{CO})_6]$.

which derived by heating α -azidostyrene or 3-phenyl-2H-azirine with $[\text{Mo}(\text{CO})_6]$, was reduced to enamine.¹³ Furthermore, $[\text{MoL}_n]$ -complexed (β -oxo vinyl)nitrene has been reduced to the corresponding β -amino enones.¹² On the basis of these facts, the protonation-reduction sequences of the compound 8 in the presence of water or even stray water could give the imine 9, which is hydrolyzed to give the aldehyde 4. Another collapsing pathway for 7 could be the deprotonation-decomplexation sequences to give the nitriles 5 and 6.¹⁴ The complexation of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ to the N-1 atom of 3 is not exemplified in the present reaction.

Similar to the $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ -induced reaction of 3, $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Fe}(\text{CO})_5]$ also causes novel reactions of 3 (Scheme 2 and Table 2). The free or solvated $[\text{Fe}(\text{CO})_4]$ species is generally assumed to be the common reactive intermediate in the thermolysis ($\geq 80^\circ\text{C}$) or photolysis of $[\text{Fe}(\text{CO})_5]$ and the thermolysis of $[\text{Fe}_2(\text{CO})_9]$ ($\geq 20^\circ\text{C}$).¹⁵ Consistent with this theory, photoirradiation of 3 with $[\text{Fe}(\text{CO})_5]$ in benzene afforded [diene]- $\text{Fe}(\text{CO})_3$ complex 11 and the starting material 3 (entry 1). Similarly, the thermal reaction of 3 with $[\text{Fe}_2(\text{CO})_9]$ in a large scale (see Experimental) at room temperature followed by careful workup afforded 11, a trace of 4 and 6, and the starting material 3 (entry 2). The formation of 11 pertains to the general reaction of 1H-1,2-diazepine with iron carbonyls.⁴ However, the formation of 4 and 6 is novel, and this is similar to the reaction in Scheme 1. Thus, the complex 12, which is similar to 7, seems to intervene in the reaction, and it could be decomposed via an intermediate 13.¹⁴ A stray water possibly assists the protonation-reduction sequences of 13 to give 4.

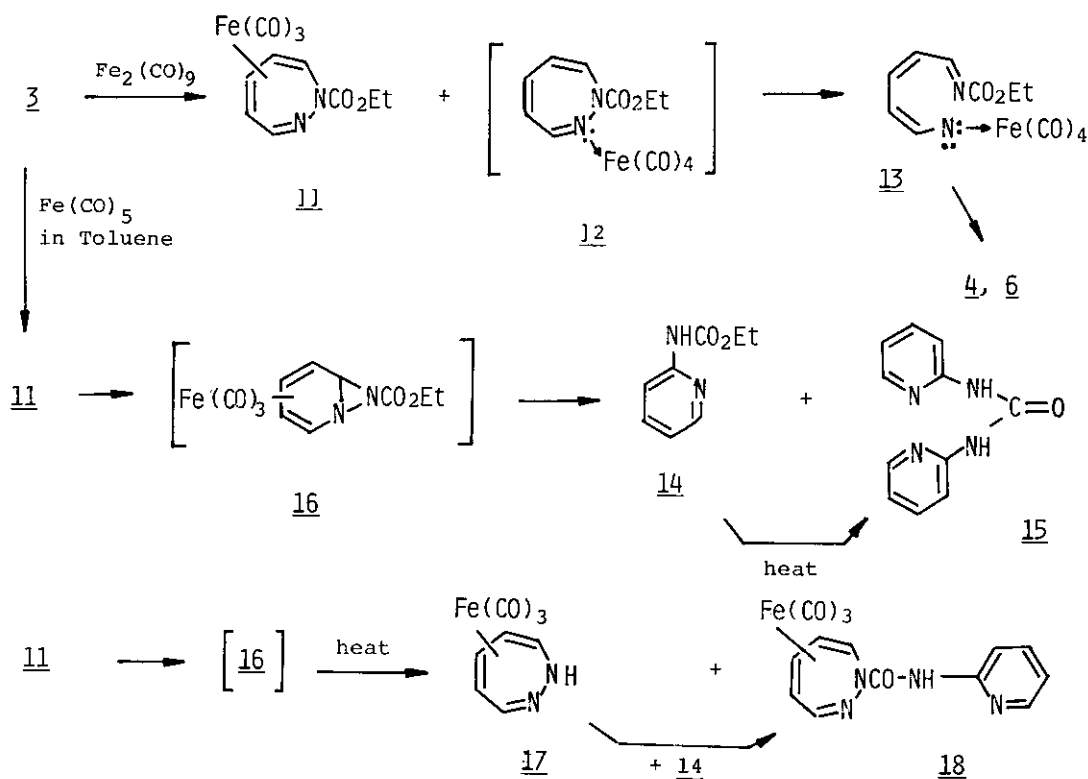
Thermal reaction of 3 with $[\text{Fe}(\text{CO})_5]$ under reflux in benzene could not afford 11, and 3 was recovered (entry 3). However, the reaction of 3 with $[\text{Fe}(\text{CO})_5]$ in toluene under reflux afforded 11, 2-(ethoxycarbonylamino)pyridine (14),¹⁶ N,N'-di(2-pyridyl)urea (15),¹⁷ and the starting material 3 (entry 4). In the entries 1 and 4, the compound 4 or 6 was not isolated probably because of the small scale of the

Table 2. Reaction of 1H-1,2-Diazepine 3 with Iron Carbonyl Complexes.

Entry	Solvent	Reaction			<u>4</u>	<u>6</u>	<u>11</u>	<u>14</u>	<u>15</u>	Recovery
		conditions ^a	time/h							
1	Benzene	A	42	—	—	60	—	—	16	
2	Benzene	B	40	2	1	66	—	—	1	
3	Benzene	C	24	—	—	2	—	—	93	
4	Toluene	C	24	—	—	2	24	33	35	
5	Toluene	D	24	—	—	—	—	—	98	

a. A: 2.0 Molar equivalent amounts of $[\text{Fe}(\text{CO})_5]$ was used under photoirradiation. B: 2.0 Molar equivalent amounts of $[\text{Fe}_2(\text{CO})_9]$ was used at room temperature. C: 2.0 Molar equivalent amounts of $[\text{Fe}(\text{CO})_5]$ was used under reflux. D: Heated under reflux in the absence of iron carbonyl complex.

reactions. Since the compound 3 is stable under reflux in toluene (entry 5), therefore the $[\text{Fe}(\text{CO})_5]$ is indispensable in the present reaction (entry 4). A possible explanation for the formation of 14 is depicted in Scheme 2. The valence isomerization of 11 possibly gives 16 at high temperature in toluene. The N-N bond clea-



Scheme 2.

vage of 16 and proton-migration followed by decomplexation gives 14. Independent thermal reaction of 14 in toluene under reflux afforded 15. Thus, the formation of 15 is rationalized.

Furthermore, the evidence for the formation of 14 via 11 was obtained as follows. Thermal reaction of 11 in toluene under reflux for 5 h afforded 17 (16%), 18 (28%), and the starting material 11 (15%) (Scheme 2). The structure of 17 was determined on the basis of the physical data. Since the compound 17 was obtained by heating 14 with 18 in toluene, therefore the formation of 14 is suggested in the reaction of 11. The complex 18 is derived from the reaction of 11 and stray water. The ethoxycarbonyl group is probably eliminated as ethyl carbonate.

In summary, molybdenum coordination occurs at nitrogen atom of 3 to undergo the N-N bond cleavage to give 4, 5, and 6. On the other hand, iron coordination is observed to occur at both diene moiety and nitrogen simultaneously, the latter process is exemplified as a very minor process by the product analysis. The [diene]-Fe(CO)₃ complex 11 could undergo thermal reaction to give the pyridine 14.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-400 spectrometer. The ¹H-NMR spectra were recorded on a Hitachi R-24 (60 MHz) spectrometer, and the chemical shifts were given in ppm (δ) relative to internal SiMe₄ standard. The mass-spectral studies were conducted on a Shimadzu GCMS-QP-1000 spectrometer at 70 eV. All of the reactions were carried out under nitrogen atmosphere. The solvents were dried and purified by the standard methods. All of the melting points are uncorrected.

Reaction of 1-Ethoxycarbonyl-1H-1,2-diazepine (3) with [Mo(CO)₃(MeCN)₃]

A solution of [Mo(CO)₃(MeCN)₃] was prepared from [Mo(CO)₆] (528 mg, 2 mmol) and acetonitrile (3 ml) under reflux for 4 h under nitrogen atmosphere.¹⁰ After the solution was cooled to room temperature, 3 (166 mg, 1 mmol) in acetonitrile (1 ml) was added; the mixture was then stirred for 1 h. After the solvent was evaporated, the residue was dissolved in benzene (10 ml) and filtered through Celite to remove insoluble material. The filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene-ethyl acetate (10/1). The first band from the TLC plates gave 5¹¹ (10 mg, 6%). The second band from the TLC plates gave a mixture of 3 and 4. This mixture was further separated by TLC on alumina using dichloromethane as developer to give 3 (10 mg, 6%) and 4 (47 mg, 28%). For 4: mp 137-138 °C (decomp) (from benzene-hexane); IR (CHCl₃), 3428, 2994, 2824, 2750, 1731,

1683, 1492, 1379. 1291, 1167, 1128. 1044, 986. 867 cm^{-1} ; ^1H -NMR (acetone- d_6), δ : 1.26 (3H, t, $J=7.0$ Hz), 4.25 (2H, q, $J=7.0$ Hz), 5.91-6.38 (2H, m), 7.30-7.65 (2H, m), 9.20-9.52 (1H, broad s), 9.65 (1H, d, $J=8.6$ Hz); MS, m/z (rel intensity), 169 (M^+ , 62), 140 (100). Anal. Calcd for $\text{C}_8\text{H}_{11}\text{O}_3\text{N}$: C, 56.80; H, 6.55; N, 8.28. Found: C, 56.67; H, 6.37; N, 8.16.

Reaction of 3 with $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ in the Presence of Water

A solution of $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ was prepared from $[\text{Mo}(\text{CO})_6]$ (528 mg, 2 mmol) and acetonitrile (3 ml).¹⁰ The solution was cooled to room temperature, and 3 (166 mg, 1 mmol) and water (18 mg, 1 mmol) in acetonitrile (1 ml) was added; the mixture was then stirred for 1 h. Workup similar to that described above and following separation by TLC on silica gel using benzene-ethyl acetate (7/1) was carried out. The first band from the TLC plates gave a mixture, which was further separated by TLC on silica gel using benzene-ethyl acetate (15/1) to give 5 (2 mg, 1%) and 6¹¹ (8 mg, 5%). The second band from the TLC plates gave 4 (41 mg, 24%).

Reaction of 3 with $[\text{Fe}(\text{CO})_5]$ under Photoirradiation

A solution of 3 (166 mg, 1 mmol) and $[\text{Fe}(\text{CO})_5]$ (392 mg, 2 mmol) in anhydrous benzene (20 ml) was irradiated by Rayonet Photoreactor fitted with RPR-350 lamps through Pyrex filter. After the solvent was evaporated, the residue was dissolved in 6 ml of benzene-hexane (1/1) and filtered through Celite. The filtrate was concentrated and the residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) as developer to give 11⁴ (185 mg, 60%) and 3 (26 mg, 16%).

Reaction of 3 with $[\text{Fe}_2(\text{CO})_9]$ at Room Temperature

A solution of 3 (1.662 g, 10 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (7.276 g, 20 mmol) in anhydrous benzene (70 ml) was stirred for 40 h at room temperature. After the reaction mixture was filtered through Celite, the filtrate was concentrated and the resulting residue was separated by Column chromatography on silica gel. The fraction eluted with benzene-dichloromethane (1/1) gave 11 (1.961 g, 64%). The fraction eluted with dichloromethane was further separated by TLC on silica gel using chloroform as developer to give 6 (9 mg, 1%), 3 (15 mg, 1%), and 4 (32 mg, 2%).

Thermal Reaction of 3 with $[\text{Fe}(\text{CO})_5]$ in Toluene

A solution of 3 (166 mg, 1 mmol) and $[\text{Fe}(\text{CO})_5]$ (392 mg, 2 mmol) in toluene (3 ml) was heated under reflux for 24 h. Workup similar to that described above followed by separation by TLC on silica gel using benzene-ethyl acetate (2/1) as developer afforded 14 (40 mg, 24%): mp 101-102 °C (lit.¹⁶ mp 105 °C), 11 (7 mg, 2%), 3 (58 mg, 35%), and 15 (35 mg, 33%): mp 169-170 °C (lit.¹⁷ mp 174 °C).

Thermal Reaction of 3 in Toluene

A solution of 3 (166 mg, 1 mmol) in toluene (3 ml) was heated under reflux for 20 h. After the toluene was evaporated, the residue was purified by TLC on silica gel using benzene-ethyl acetate (2/1) as developer to give 3 (163 mg, 98%).

Thermal Reaction of 2-(Ethoxycarbonylamino)pyridine 14 in Toluene

A solution of 14 (30 mg, 0.3 mmol) in toluene (3 ml) was heated under reflux for 24 h. After the toluene was evaporated, the residue was separated by TLC on silica gel using benzene-ethyl acetate (5/1) as developer to give 14 (39 mg, 78%) and 15 (7 mg, 22%).

Thermal Reaction of 11 in Toluene

A solution of 11 (306 mg, 1 mmol) in toluene (4 ml) was heated under reflux for 5 h. After the toluene was evaporated, the resulting residue was separated by TLC on silica gel using chloroform as developer to give 11 (45 mg, 15%), 17¹⁶ (65 mg, 28%), and 18 (28 mg, 16%). For 18: mp 136-137 °C (decomp) (from benzene-hexane); IR (CHCl₃), 3360, 2990, 2064, 1986, 1692, 1604, 1578, 1052, 1434, 1294, 1134, 894, 834 cm⁻¹; ¹H-NMR (CDCl₃), δ: 3.33 (1H, dxdxd, J=6.4, 6.0, 1.7 Hz), 4.48 (1H, dxdxd, J=6.4, 4.6, 1.7 Hz), 5.02 (1H, dxd, J=6.4, 1.6 Hz), 6.59 (1H, dxd, J=6.4, 1.6 Hz), 6.79-7.06 (2H, m), 7.64 (1H, dxdxd, J=8.2, 7.1, 1.8 Hz), 7.98-8.30 (2H, m), 9.43-9.65 (1H, broad s); MS, m/z (rel intensity), 326 (M⁺-28, 2), 298 (37), 56 (100). Anal. Calcd for C₁₄H₁₀O₄N₄Fe: C, 47.49; H, 2.85; N, 15.82. Found: C, 47.49; H, 2.84; N, 15.99.

Thermal Reaction of 14 with Tricarbonyl(4-7-η-1H-1,2-diazepine)iron 17 in Toluene

A solution of 14 (83 mg, 0.5 mmol) and 17 (117 mg, 0.5 mmol) in toluene (5 ml) was heated under reflux for 5 h. After the toluene was evaporated, the residue was separated by TLC on silica gel using chloroform as developer to give 14 (40 mg, 48%), 15 (1 mg, 0.4%), 17 (13 mg, 11%), and 18 (78 mg, 44%).

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