The Reaction of (*Z*)-2-(3-Oxo-1-propenyl)-2*H*-azirine Derivative with Molybdenum Carbonyl Complexes

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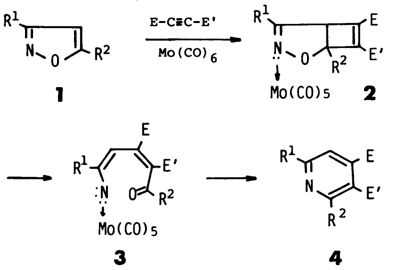
Synopsis. The thermal reaction of (*Z*)-2,3-diphenyl-2-(2,3-diphenyl-3-oxo-1-propenyl)-2*H*-azirine with [Mo$(CO)_6$] or [Mo$(CO)_3$(MeCN)$_3$] was reinvestigated to afford 2,3,5,6-tetraphenylpyridine along with the pyrroles and 1,3-oxazepine derivative. The formation of 1,3-oxazepine was demonstrated to be the purely thermal process. The 1,2,4,5-tetraphenyl-5-oxo-1,3-pentadienylnitrene complex was shown to give the pyridine and the pyrrole derivatives.

It has previously been shown that [Mo$(CO)_6$] effects a reaction of isoxazoles **1** to undergo a novel insertion of acetylenic esters across the C-4–C-5 bond and elimination of an oxygen atom to give pyridine derivatives.[1] Complex **2** and the complexed nitrene **3** were proposed as the intermediates. Independent reaction of 3-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (**5**) with [Mo$(CO)_6$] giving 2-phenylpyridiene (**7**) *via* the nitrene complex **6** (R^1=Ph, R^2=E=E′=H in **3**) supports the proposed mechanism.[1] The facile N–O and C-1–C-5 bond cleavage of the complexed **5** (or **2**) giving **6** (or **3**) is similar to the photochemical reaction of **5** to give 3-(3-phenyl-2*H*-azirin-2-yl)acrylaldehyde,[2] suggesting the delocalization of the p-d electron from the molybdenum atom to the π^* orbital of the C=N–O moiety in the complex such as **2**.[1b,3]



R^1, R^2= Phenyl or Alkyl
E = CO_2Me; E′ = CO_2Me or H

On the contrary, the complexed nitrene **15**, which is similar to **3** or **6**, has been proposed as an intermediate in the reaction of (*Z*)-2-(3-oxo-1-propenyl)-2*H*-azirine derivative **8** with [Mo$(CO)_6$] leading to the 1,3-oxazepine **9** and the pyrroles **10**, **11**, and **12**. The yields of the products are not mentioned, and no pyridine is obtained.[4] We report here the reaction of **8** with [Mo$(CO)_6$] or [Mo$(CO)_3$(MeCN)$_3$] giving 2,3,5,6-tetraphenylpyridine **13**, in addition to the 1,3-oxazepine **9** and the pyrroles **10—12**. The reaction conditions and the yields of the products are summarized in Table 1.

The reaction of **8**[5] with [Mo$(CO)_6$] in tetrahydrofuran (THF) at an ambient temperature, or in boiling benzene, gave the 1,3-oxazepine **9** and the pyridine **13**, along with the pyrroles **10—12** (entry 1 or 3 in Table 1). However, the thermal reaction of **8** without [Mo$(CO)_6$] in THF or in benzene afforded only **9** (entry 2 or 4). Thus **9** seems to have been derived by the purely thermal process which involves a C-2–C-3 bond fission of the azirine ring.[4,5] The reaction of **9** with [Mo$(CO)_6$] under the similar conditions to the [Mo$(CO)_6$]-induced reaction of **8** gave no product, and **9** was recovered quantitatively. Therefore, the pyridine **13** and the pyrroles **10—12** are supposed to be the primary products of the reaction of **8** with [Mo$(CO)_6$].

It has been shown that the ligand exchange of [Mo$(CO)_3$(MeCN)$_3$] with **5** proceeded under mild conditions to afford **7**.[1b] The reaction of **8** with [Mo$(CO)_3$(MeCN)$_3$] (prepared *in situ*, see Experimental) in acetonitrile also proceeded very fast even at an ambient temperature giving the pyrroles **10** and **11** as well as the pyridine **13**, in addition to the small amount of 1,3-oxazepine **9** (entry 5). The purely thermal reaction giving **9** is reduced under these conditions.

The formation of the pyrroles **10—12** is explained as follows. The n-donor complexation of the azirine ring of **8** seems to give the complexed nitrene **15** *via* **14**.[4,7,8] A ring-annelation of **15** and the subsequent decomplexation gives an intermediate **16**. In **16**, the benzoyl migration to the adjacent carbon atom and the subsequent hydrogen migration gives **10**, while benzoyl

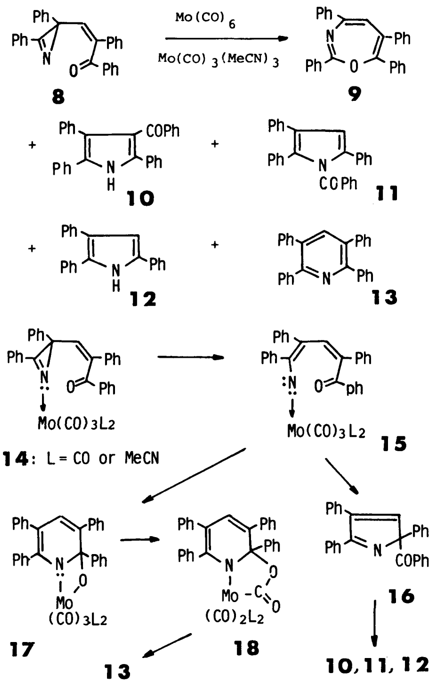
Table 1. Reaction of the azirine **8** in the presence or absence of [Mo$(CO)_6$]

Entry	Reaction Conditions		Time/h	Products (Yield/%)					
	[Mo$(CO)_6$]	Solvent		**8**	**9**	**10**	**11**	**12**	**13**
1	Added[a)]	THF[b)]	65	—	54	39	0.8	0.7	1.3
2	None	THF	65	39	49	—	—	—	—
3	Added[a)]	PhH[c)]	1	—	71	17	1.5	1.7	2.6
4	None	PhH	1	—	99	—	—	—	—
5	Added[d)]	MeCN	0.5	—	3	53	2	—	4

a) 1.0 Molar equivalent amount of [Mo$(CO)_6$] was used. b) Stirred at an ambient temperature. c) Stirred at the refluxing temperature. d) [Mo$(CO)_3$(MeCN)$_3$], prepared from 2.0 molar equivalent amount of [Mo$(CO)_6$], was used at an ambient temperature.

migration to the adjacent nitrogen atom leads to **11**.[4] The attempted reaction of the pyrrole **11** with [Mo(CO)$_6$] in anhydrous or moist benzene gave no **12**, and **11** was recovered quantitatively. Furthermore, **12** was not obtained in the reaction of entry 5 in Table 1. Thus the possibility for the formation of **12** may be ascribed to a stray water-assisted debenzoylation (elimination of benzoyl group as benzoic acid) of the intermediate **16**. The pyridine **13** can be obtained by a cyclization of **15** to give **17**, followed by a ligand migration giving **18**, which would collapse to **13**.[1,8]

In conclusion, the complexed nitrene **15** was shown to give the pyrroles **10**—**12** along with the pyridine **13**, the formation of which was not observed in the previous study.[4] The complexed nitrene **3** or **6** was found to give only pyridine.[1] The steric and/or the electronic effect of the tetraphenyl-substituted derivative, **15**, may be reflected in the pathway giving the pyrroles and the pyridine derivative.



Experimental

All of the reactions were carried out under a dry nitrogen atmosphere. Solvents were purified and dried by the standard methods. All of the melting points were uncorrected.

Reaction of 8 with [Mo(CO)$_6$]. The reaction of **8** (399 mg, 1 mmol) and [Mo(CO)$_6$] (264 mg, 1 mmol) was carried out in 10 cm^3 of THF at an ambient temperature for 65 h, in boiling benzene for 1 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using CCl$_4$ as an eluent to give **9**, **10**, **11**, **12**, and **13** (Table 1, entries 1 and 3). For **9**: mp 138—139 °C (from EtOH) (lit,[5] 146—147 °C). For **10**: mp 198—199 °C (from EtOH) (lit,[5] 200—201 °C). For **11**: mp 152—153 °C (from EtOH) (lit,[9] 154—155 °C). For **12**: mp 137—139 °C (from CCl$_4$) (lit,[10] 137—138 °C). For **13**: mp 228—230 °C (from AcOEt) (lit,[11] 228.5—229.5 °C).

Reaction of 8 with [Mo(CO)$_3$(MeCN)$_3$]. A solution of [Mo(CO)$_3$(MeCN)$_3$] was prepared from [Mo(CO)$_6$] (528 mg, 2 mmol) in 10 cm^3 of acetonitrile under reflux for 4 h[6] After this solution was cooled to an ambient temperature, **8** (399 mg, 1 mmol) was added to the solution, and it was stirred for 0.5 h. A similar workup as described above gave **9**, **10**, **11**, and **13** (Table 1, entry 5).

Reaction of 8 in the Absence of [Mo(CO)$_6$]. A solution of **8** (150 mg, 0.37 mmol) in THF (5 cm^3) was stirred at an ambient temperature for 65 h and the subsequent separation by TLC on silica gel using benzene as the eluent gave **9** and **8**. A similar reaction of **8** (150 mg, 0.37 mmol) in boiling benzene (10 cm^3) for 1 h gave only **9** (Table 1, entries 2 and 4).

Reaction of 1,3-Oxazepine 9. A solution of **9** (100 mg, 0.25 mmol) and [Mo(CO)$_6$] (66 mg, 0.25 mmol) in THF (3 cm^3) was stirred at an ambient temperature for 65 h. After the evaporation of the THF, the residue was purified by TLC on silica gel using benzene as the eluent to recover **9** (89 mg, 89%). A similar reaction of **9** (150 mg, 0.37 mmol) and [Mo(CO)$_6$] (98 mg, 0.37 mmol) in boiling benzene 10 cm^3) for 1 h also gave the unreacted **9** (142 mg, 95%).

Reaction of 11 with [Mo(CO)$_6$]. A solution of **11** (100 mg, 0.25 mmol) and [Mo(CO)$_6$] (66 mg, 0.25 mmol) in 5 cm^3 of anhydrous or moist benzene was refluxed for 1 h. After the evaporation of the benzene, the residue was purified by TLC on silica gel to give **11** in 96% (in anhydrous benzene) or in 94% (in moist benzene).

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