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Hexacarbonylmolybdenum-induced Reaction of Isoxazoles. Cycloaddition of Isoxazoles with Acetylenic Esters and Related Reactions[1)]

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In the presence of hexacarbonylmolybdenum, substituted isoxazoles undergo a cycloaddition reaction with dimethyl acetylenedicarboxylate across the C-4–C-5 bond to give 3,4-bis(methoxycarbonyl)pyridine derivatives. In a similar cycloadition of isoxazoles with methyl propiolate, 4-(methoxycarbonyl)pyridine derivatives were also obtained. The β-carbon atom of methyl propiolate could intervene in the bonding with the C-5 position of the isoxazoles regioselectively. A mechanism involving a complexed 2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene derivative and the subsequent N–O and C-1–C-5 bond cleavage leading to a complexed (β-keto vinyl)nitrene intermediate is proposed for the formation of pyridine derivatives. In order to clarify the mechanistic aspect, the reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene and its related compounds were also studied to give pyridine derivatives.

An isoxazole ring system has been the subject of an extensive investigation for its useful synthetic transformations. Its photochemical[2)] and thermal[3] reactions have been shown to isomerize to the corresponding ketoazirine derivatives. The catalytic hydrogenation of isoxazoles to β-amino enones is widely applicable in synthesis.[4)] Previously, we showed that [$Fe(CO)_5$], [$Fe_2(CO)_9$], and [$Mo(CO)_6$] effect the reductive cleavage of the N–O bond of substituted isoxazoles to give β-amino enones under mild conditions in the presence of water.[5)]

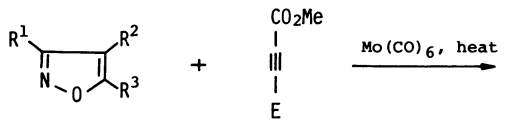
In contrast to these ring cleavage reactions, the cycloaddition of simple isoxazoles with olefins or acetylenic esters has not been accomplished,[6)] although the heterodiene system of 2,1-benzisoxazole derivatives has been shown to undergo a Diels-Alder reaction with *N*-phenylmaleimide,[7)] benzyne,[8)] and dimethyl acetylenedicarboxylate.[9)] The Diels-Alder reaction of 2,1-benzisoxazole with maleic anhydride has been shown to give only a starting material,[10)] although in a previous paper the reaction was reported to proceed.[11)]

This paper describes a [$Mo(CO)_6$]-induced cycloaddition of 3,5-disubstituted isoxazoles (**1a—f**) with acetylenic esters across the C-4–C-5 bond and the subsequent elimination of an oxygen atom to give pyridine derivatives, albeit, in low yields. Furthermore, [$Mo(CO)_6$]-induced reactions of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (**17**) and its related compound, **18** and **22**, were also studied to assess the mechanistic aspect of the above-mentioned cycloaddition reaction.

Results and Discussion

A benzene solution of isoxazoles **1a—f**, dimethyl acetylenedicarboxylate (DMAD), and [$Mo(CO)_6$] was refluxed for an adequate period to give the pyridine derivatives **2a—f**, as shown in Scheme 1. The reaction conditions and the yields of the products are summarized in Table 1 (Entries 1—6). The yields of the pyridines are rather poor and each of the reactions was accompanied by the formation of hexamethyl benzenehexacarboxylate (**4**) (10—20% yield based on DMAD used) and a mixture of more than three compounds. The latter mixture seemed to contain no methoxycarbonyl group and could not be separated. Thus, the structures have not been elucidated. Compound **4** could possibly be derived from [$Mo(CO)_6$]-induced trimerization of DMAD.[12)]

A similar reaction of isoxazoles **1a,d,e** with methyl propiolate (MP) afforded the pyridine derivatives **3a,d**. No pyridine bearing a methoxycarbonyl group at the 3-position could be detected. This fact clearly indicates that the β-carbon atom of MP connects regioselectively with the C-5-carbon atom of the isoxazole ring. In this case, the trimerization of MP was not observed. Since the thermal treatment of the isoxazole **1a** with DMAD in refluxing benzene afforded no adduct and **1a** was recovered quantitatively, [$Mo(CO)_6$] is indispensable for the present reaction.



1

2: E = CO_2Me
3: E = H

4

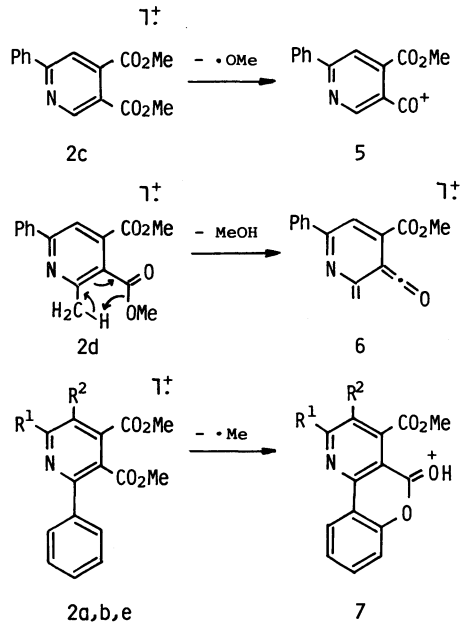
1 and 2: a, $R^1=R^3=Ph$, $R^2=H$; b, $R^1=R^2=R^3=Ph$; c, $R^1=Ph$, $R^2=R^3=H$; d, $R^1=Ph$, $R^2=H$, $R^3=Me$, e, $R^1=Me$, $R^2=H$, $R^3=Ph$; f, $R^1=4\text{-}ClC_6H_4$, $R^2=R^3=H$.
3: a, $R^1=R^3=Ph$, $R^2=H$; d, $R^1=Ph$, $R^2=h$, $R^3=Me$.

Scheme 1.

Table 1. Reaction of isoxazoles **1a—f** with acetylenic esters[a] in the presence of $[Mo(CO)_6]$[b]

Entry	Isoxazole	Acetylenic Ester	Reaction Time/h	Pyridine (Yield/%)
1	**1a**	DMAD[c]	24	**2a** (28)
2	**1b**	DMAD	24	**2b** (22)
3	**1c**	DMAD	24	**2c** (16)
4	**1d**	DMAD	24	**2d** (26)
5	**1e**	DMAD	10	**2e** (12)
6	**1f**	DMAD	20	**2f** (11)
7	**1a**	MP[c]	24	**3a** (19)
8	**1d**	MP	20	**3d** (21)
9	**1e**	MP	10	**3d** (19)

a) 2.0 Molar equivalent of acetylenic ester to **1** was used. b) 1.0 Molar equivalent of $[Mo(CO)_6]$ to **1** was used. c) DMAD: dimethyl acetylenedicarboxylate; MP: methyl propiolate.



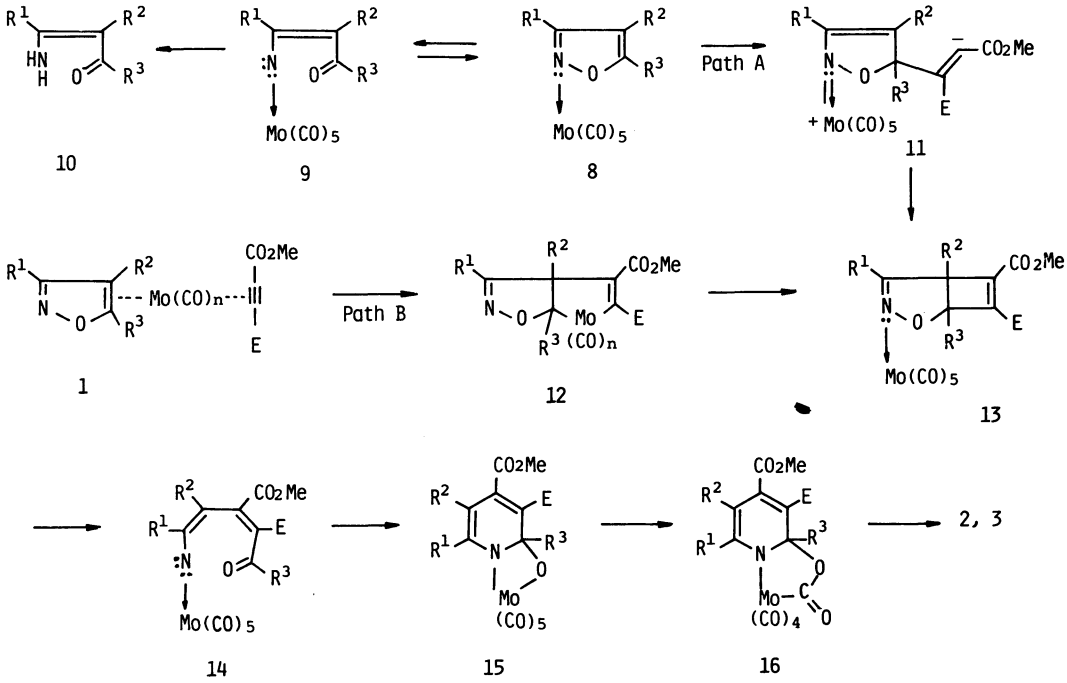
Scheme 2.

The structures of the pyridines were established by their spectral properties (NMR, IR, MS, and in part UV) and by a comparison of the physical data (mp and bp) with those of the authentic specimens. Only the pyridines, **2a** and **2f**, are new compounds. A comparison of their mass spectra revealed the position of the substituents. The main fragmentation pathways of the pyridines are illustrated in Scheme 2. The pyridine **2c** gives the ion **5** with *m/z* 240 (M^+-31), which is derived from the elimination of the MeO group. This fragmentation pattern is generally observed for compounds **2a—f** and **3a,d**. On the other hand, **2d** gives the ion **6** with *m/z* 253 (M^+-32), in addition to an ion with *m/z* 254 (M^+-31). The ion **6** indicates a loss of a methanol molecule through a general "ortho" effect. However, the spectrum of **3d**, which has a methoxycarbonyl group at the 4-position, did not exhibit the corresponding ion of M^+-32. Furthermore, **2a**, **2b**, and **2e**, all of which have a phenyl group adjacent to the methoxycarbonyl group at the 3-position, exhibit an ion of M^+-15 along with an ion of M^+-31. The former ion would be derived from a loss of a methyl group to give the ion **7**, which is stabilized by the phenyl group.[13] The mass spectrum of **3a** did not exhibit the corresponding ion of M^+-15. A comparison of the mass spectral data of the new pyridines with those typical fragmentations and the reaction sequences of the present reaction (*vide infra*) revealed the structure of **2a** and **2f** unequivacally.

Possible mechanistic pathways for the formation of the pyridines are outlined in Scheme 3. An initial complexation of the isoxazole to $[Mo(CO)_6]$ would give the n-donor complex **8**,[5] which has been shown to undergo an N–O bond cleavage to give the complexed nitrene intermediate **9**, collapsing to the corresponding β-amino enone **10** in the presence of water.[5] The factor allowing the facile N–O bond cleavage of **8** could be attributed to the delocalization of the p-d electron from molybdenum to the π* orbital of the isoxazole.[5] The addition reaction of several β-amino enones with DMAD has been shown to give no pyridines.[14] Furthermore, the β-amino enone, which is derived from the isoxazoles **1a**, did not undergo a reaction with DMAD under the present conditions. In the presence of DMAD or MP, **8** may undergo cycloaddition to give complex **13** *via* **11** (Path A). In the case of MP, the C-5-atom of the isoxazole in **8** seems to attack the more electron-deficient β-carbon atom of MP to afford **13** (E=H) (Path A). The regioselectivity affording **3a,d**, which have a methoxycarbonyl group at the 4-position, originate at this stage.

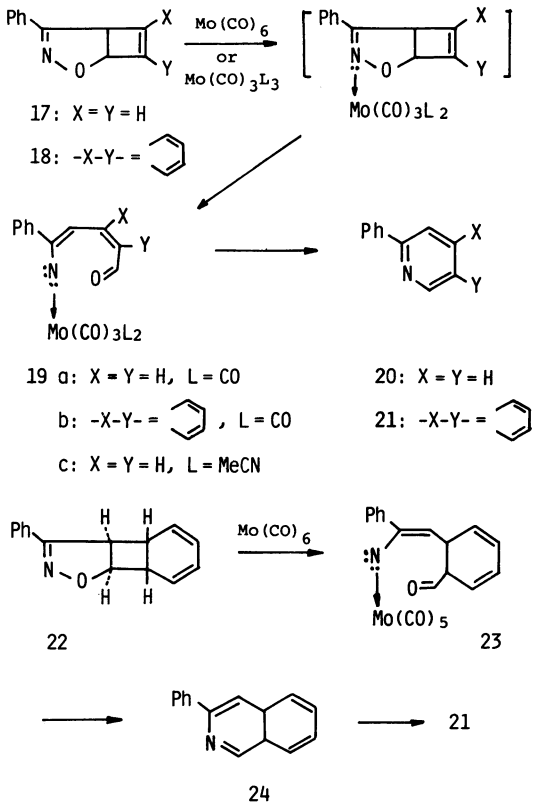
On the other hand, $[Mo(CO)_6]$-induced cyclobutane formation has been proposed for the reaction of 3-phenyl-2*H*-azirines with DMAD.[15] In some cases, $[Mo(CO)_6]$ has also been used for the metathetic reaction of acetylenes.[16] Therefore, an alternative mechanistic possibility may be a [2+2] cross-cycloaddition between **1** and an acetylenic ester to give **13** *via* a metallacycle such as **12** (Path B). Considering the facile n-donor complexation[5] of the isoxazole with $[Mo(CO)_6]$ species as well as the regioselectivity giving **3a,d**, Path A seems to be plausible over Path B.

It has been shown that the N–O and C-4–C-5 bond cleavage of 3,5-disubstituted isoxazolines afford the corresponding aldehydes and the complexed nitrene intermediate in the presence of $[Fe(CO)_5]$, $[Fe_2(CO)_9]$,[17] or $[Mo(CO)_6]$.[18] In a similar fashion, **13** would give the complexed nitrene intermediate **14**. The cyclization of **14** to produce **15** and the following ligand migration gives **16**, which collapses to afford the pyridines **2** or **3**.[19]



Scheme 3.

In order to study the possible intervention of complexes such as **13** and **14**, we investigated the reaction of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene (**17**) and its benzoannelated compound **18** with $[Mo(CO)_6]$. As shown in Scheme 4, the reaction of **17** or **18** in refluxing benzene gave 2-phenylpyridine (**20**) or 3-phenylisoquinoline (**21**) in a 76 or 65% yield, respectively. A complexed nitrene intermediate, such as **19a,b** (cf. **14**), which could be derived from the cleavage of the N–O and C-1–C-5 bonds of an isoxazoline moiety, would also be a reasonable intermediate in the transformations. Thus, the intermediacy of **13** and **14** in Scheme 3 seems to be plausible. The $[Mo(CO)_6]$-induced cleavage of **17** is very similar to the photochemical N–O and C-1–C-5 bond-cleavage of **17** to give 3-(3-phenylazirin-2-yl)acrolein.[20] This fact also suggests the delocalization of the p-d electron from molybdenum to the π^* orbital of the C=N–O moiety of the complexed **17**.[17] The *in situ* preparation of $[Mo(CO)_3(MeCN)_3]$,[21] and the subsequent reaction with **17** at an ambient temperature gave **20** in a 76% yield. This fact may suggest that the ligand-exchange reaction of $[Mo(CO)_3(MeCN)_3]$ with **17** proceeds under mild conditions as compared to that of $[Mo(CO)_6]$ with **17**. The N–O bond cleavage of the complexed **17** and the subsequent ring-annelation occurs even at ambient temperature.

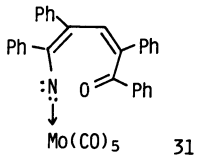


Scheme 4.

Furthermore, the reaction of **22**, which is a dihydrogenated analogue of **18**, with $[Mo(CO)_6]$ also afforded **21** in a 76% yield. The formation of **21** could be explained by an intervention of the complexed nitrene species **23**, ring-annelation giving **24**, and the subsequent dehydrogenation. Thus, the intramolecular ring-annelation of the complexed nitrene moiety with the carbonyl group, which is located in a preferable

stereochemical situation in compounds such as **14**, **19**, and **23**, seems to be general.

On the contrary, the complexed nitrene **31**, which is similar to **14** or **19a,b**, has been proposed as an intermediate of the $[Mo(CO)_6]$-induced transformation of (*Z*)-2-(3-oxo-1-phenyl)-2*H*-azirine derivative to pyrrole derivatives.[22] The yields of the products have not been mentioned, and no pyridine derivative has been obtained.[22] The steric and/or electronic effect of the benzoyl group in **31** seems to be reflected in the reaction pathway giving pyrrole derivatives. In contrast, the complex **14** or **19** bearing a benzoyl, acetyl, or formyl group could give only a pyridine ring. This fact may suggest that the electron-withdrawing property of the methoxycarbonyl group also affects the reaction pathway. A further confirmation of this point may be necessary.



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Scheme 5.

In conclusion, the $[Mo(CO)_6]$-induced cycloaddition of isoxazoles with acetylenic esters was suggested to give a 2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene skeleton. The N–O and C-1–C-5 bond-cleavage of the ring system was indicated to give the complexed (β-keto vinyl)nitrene intermediate, which collapses to the pyridine ring. The present reaction could also serve as a convenient method for the preparation of a series of [6](2,5)pyridinophane ring system.[23]

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The NMR spectra were recorded on a Hitachi R-24 spectrometer and the chemical shifts are given in ppm (δ) relative to an internal $SiMe_4$ standard. Mass spectral studies were conducted using Hitachi RMU-60 spectrometer. All of the $[Mo(CO)_6]$-induced reactions were carried out under a dry nitrogen atmosphere. Solvents were purified and dried by the standard methods. The isoxazoles **1a**,[24] **1b**,[25] **1c**,[26] **1e**,[27] 2-oxa-3-azabicyclo[3.2.0]hepta-3,6-diene derivatives **17**,[28] and **18**[29] were prepared by methods described in the literature. The isoxazole **1f** was prepared by a procedure similar to that for **1c** and was identified on the basis of physical data.[30] All of the melting points were uncorrected.

Preparation of Isoxazole ***1d.*** To a solution of benzhydroximoyl chloride (1.56 g, 10 mmol) and isopropenyl acetate (3.0 g, 30 mmol) in ether (100 cm^3), triethylamine (5 cm^3) was added over 1 h at 0 °C. After the mixture was stirred for 20 h, it was extracted with ether. The ether extract was dried over $MgSO_4$ and concentrated to give a crude product. This was purified by column chromatography on silica gel to give **1d** (794 mg, 50%); mp 41—42 °C (from hexane) (lit,[31] 42—43 °C); NMR ($CDCl_3$), δ=2.25 (3H, s), 6.10 (1H, s), 7.20—7.40 (3H, m), 7.60—7.80 (2H, m).

General Procedure for the Reaction of Isoxazoles ***1a—f*** *with DMAD in the Presence of* $[Mo(CO)_6]$. A solution of isoxazole **1** (2 mmol), DMAD (568 mg, 4 mmol), and $[Mo(CO)_6]$ (528 mg, 2 mmol) in benzene (10 cm^3) was refluxed for an adequate period. To this reaction mixture, hexane (10 cm^3) was added and filtered through Celite to remove insoluble materials. The filtrate was concentrated and the residue was separated by TLC on silica gel using chloroform as the eluent to give the pyridine derivative **2**, along with hexamethyl benzenehexacarboxylate (**4**)[12] (10—20% yield based on DMAD used) and an unidentified mixture (30—40 mg). The reaction times and the yields of the pyridines are summarized in Table 1. The structural proof for the pyridine derivatives **2a—f** were based on the following physical data. 3,4-Bis(methoxycarbonyl)-2,6-diphenylpyridine **2a**: mp 104—105 °C; IR (CCl_4), 1733 cm^{-1}; NMR (CCl_4), δ=3.72 (3H, s), 3.96 (3H, s), 7.20—7.80 (8H, m), 8.00—8.20 (2H, m), 8.17 (1H, s); MS, *m/z* (rel intensity), 347 (M^+, 41), 332 (100), 317 (5), 316 (22). Found: C, 72.91; H, 5.19; N, 4.11%. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03%. 3,4-Bis(methoxycarbonyl)-2,5,6-triphenylpyridine **2b**: mp 221—222 °C (from benzene)(lit,[32-34] 222—223 °C, 231 °C); IR ($CHCl_3$), 1742, 1739 cm^{-1}; NMR ($CDCl_3$), δ=3.57 (3H, s), 3.67 (3H, s), 7.10—7.80 (15H, m); MS, *m/z* (rel intensity), 423 (M^+, 100), 422 (89), 408 (48), 392 (13), 390 (13), 376 (17). 3,4-Bis(methoxycarbonyl)-6-phenylpyridine **2c**: mp 72.5—73 °C (from hexane) (lit,[35] 74 °C); IR ($CHCl_3$), 1731 cm^{-1}; UV (EtOH), λ_{max} (logε), 262 (4.28), 297 (4.33); NMR ($CDCl_3$), 3.96 (3H, s) 3.98 (3H, s), 7.35—7.60 (3H, m), 7.90 (1H, s), 7.95—8.20 (2H, m), 9.13 (1H, s); MS, *m/z* (rel intensity), 271 (M^+, 91), 240 (100), 236 (11), 212 (13). 3,4-Bis(methoxycarbonyl)-2-methyl-6-phenylpyridine **2d**: bp 140—150 °C (bath temp)/13.3 Pa [lit,[36] 175—185 °C (bath temp)/26.6 Pa]; IR ($CHCl_3$), 1743 cm^{-1}; UV (EtOH), λ_{max} (logε), 252 (4.33), 305 (4.24); NMR ($CDCl_3$), δ=2.70 (3H, s), 3.97 (3H, s), 3.98 (3H, s), 7.30—7.60 (3H, m), 7.85—8.20 (2H, m), 8.05 (1H, s); MS, *m/z* (rel intensity), 285 (M^+, 79), 254 (77), 253 (100), 226 (7), 195 (72), 167 (16). 3,4-Bis(methoxycarbonyl)-6-methyl-2-phenylpyridine **2e**: mp 116—117 °C (from CCl_4) (lit,[37] 215—217 °C); IR ($CHCl_3$), 1730 cm^{-1} NMR ($CDCl_3$), δ=2.65 (3H, s), 3.68 (3H, s), 3.88 (3H, s), 7.27—7.77 (5H, m), 7.55 (1H, s); MS, *m/z* (rel intensity), 285 (M^+, 34), 270 (100), 254 (39), 242 (9), 210 (2). 3,4-Bis(methoxycarbonyl)-6-(4-chlorophenyl)pyridine **2f**: mp 118—120 °C (from EtOH); IR ($CHCl_3$), 1724 cm^{-1}: NMR ($CDCl_3$), δ=3.92 (3H, s), 3.96 (3H, s), 7.45 (2H, d, *J*=8.8 Hz), 7.80 (1H, s), 7.95 (2H, d, *J*=8.8 Hz), 9.07 (1H, s); UV (EtOH), λ_{max} (logε), 266 (4.07), 276 (4.19); MS, *m/z* (rel intensity), 307 (M^+, 31), 305 (M^+, 100), 276 (27), 274 (72), 262 (1), 260 (3). Found: C, 58.97; H, 3.86; N, 4.79%. Calcd for $C_{15}H_{12}ClNO_4$: C, 58.93; H, 3.96; N, 4.58%.

General Procedure for the Reaction of Isoxazoles ***1a, d, e*** *with Methyl Propiolate (MP) in the Presence of* $[Mo(CO)_6]$. A solution of isoxazole **1** (1 mmol), MP (168 mg, 2 mmol), and $[Mo(CO)_6]$ (264 mg, 1 mmol) in benzene (10 cm^3) was refluxed for an adequate period. To this reaction mixture, hexane (10 cm^3) was added and filtered through Celite. The filtrate was concentrated, and the residue was purified by TLC on silica gel using benzene as the eluent to give the pyridine derivative **3**. The reaction times and the yields of the pyridines are summarized in Table 1 (Entries 7—9). The pyridine derivatives **3a,d** are known compounds and were

identified on the basis of the following physical data. 4-Methoxycarbonyl-2,6-diphenylpyridine **3a**: mp 104—105 °C (from hexane) (lit,[38] 104—105.5 °C); IR ($CHCl_3$), 1730 cm^{-1}; NMR ($CDCl_3$), δ=4.05 (3H, s), 7.45—7.68 (3H, m), 8.15—8.40 (2H, m), 8.27 (2H, s); MS, *m/z* (rel intensity), 289 (M^+, 100), 258 (2), 231 (93). 4-Methoxycarbonyl-2-methyl-6-phenylpyridine **3d**: mp 55—57 °C (from hexane) (lit,[39] 59—60 °C); IR (CCl_4), 1733 cm^{-1}; NMR (CCl_4), δ=2.64 (3H, s), 3.89 (3H, s), 7.25—7.45 (3H, m), 7.50 (1H, d, J=1.2 Hz), 7.90—8.10 (2H, s), 7.97 (1H, d, J=1.2 Hz); MS, *m/z* (rel intensity), 227 (M^+, 100), 196 (7), 169 (19) 127 (19).

Reaction of 3-Amino-1,3-diphenyl-2-propenone 10a with DMAD in the presence of [Mo(CO)$_6$]. A solution of **10a** (223 mg, 1 mmol), DMAD (284 mg, 2 mmol), and [$Mo(CO)_6$] (268 mg, 1 mmol) in 10 cm^3 of benzene was refluxed for 24 h. After the evaporation of the solvent, the residue was purified by TLC on silica gel using chloroform as the eluent to give unreacted **10a** (211 mg, 95%).

Reaction of 17 with [Mo(CO)$_6$]. A solution of **17** (171 mg, 1 mmol) and [$Mo(CO)_6$] (264 mg, 1 mmol) in 10 cm^3 of benzene was refluxed for 18 h. To this reaction mixture, hexane (10 cm^3) was added and filtered through Celite. The filtrate was concentrated and the residue was purified by TLC on silica gel using benzene as the eluent to give 2-phenylpyridine (**20**)[40] (118 mg, 76%).

Reaction of 17 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 3 cm^3 of acetonitrile under reflux for 4 h.[20] After this solution was cooled to the ambient temperature, **17** (171 mg, 1 mmol) was added to the solution and it was stirred for 18 h. A workup similar to the one described above gave **20** (117 mg, 76%).

Reaction of 18 with [Mo(CO)$_6$]. A solution of **18** (140 mg, 0.63 mmol) and [$Mo(CO)_6$] (167 mg, 0.63 mmol) in 10 cm^{-3} of benzene was refluxed for 6 h. To this reaction mixture, hexane (10 cm^3) was added and filtered through Celite. The filtrate was concentrated and the residue was purified by TLC on silica gel using benzene as the eluent to give 3-phenylisoquinoline (21) (85 mg, 65%); mp 103—103.5 °C (from hexane); (picrate, mp 196.5—198 °C (from methanol) (lit,[41] mp 102—103.5 °C; picrate, mp 197—199 °C).

Reaction of 22 with [Mo(CO)$_6$]. A solution of **22** (223 mg, 1 mmol) and [$Mo(CO)_6$] (264 mg, 1 mmol) in 10 cm^3 of benzene was refluxed for 22 h. A similar workup followed by TLC on silica gel gave **21** (131 mg, 64%).

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