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# Co(III)DMG-Catalyzed Synthesis of Allylamides from Allyl Alcohols and Acetonitrile

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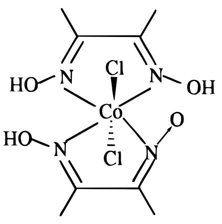
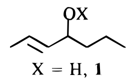
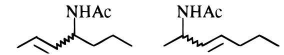
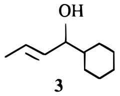
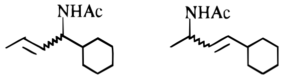
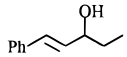
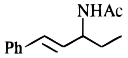
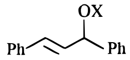
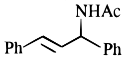
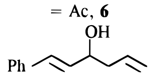
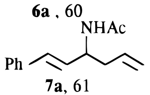
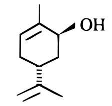
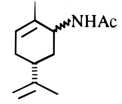
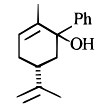
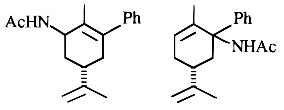
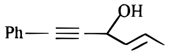
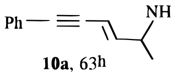
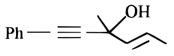
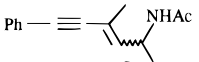
A recent study from our group has demonstrated[1] that cobalt(II) chloride catalyzes the conversion of allylic alcohols to the corresponding allylic amides in acetonitrile medium. This conversion requires the presence of acetic anhydride or acetic acid (Scheme 1, eq 1, path a), as no amide formation is observed in their absence and the allylic alcohols are recovered as a mixture of regioisomers (Scheme 1, eq 1, path b). A careful study of this reaction revealed that allylamide formation is occurring via allyl acetates that are formed by cobalt-catalyzed acylation[2] with acetic acid or acetic anhydride. These results clearly establish that acetic anhydride or acetic acid plays an important role during the cobalt(II)-catalyzed formation of allylic amides from the corresponding alcohols or acetates. In contrast to these observations, we now demonstrate that Co(III)DMG complex[3] (Chart 1) efficiently catalyzes the conversion of allyl alcohol to the corresponding allylamide[4] in the absence of acetic acid or acetic anhydride (Scheme 1, eq 1, path c). A brief account of these findings is described below.

**Chart 1**



**Co(III)DMG**

**Table 1. Co(III)DMG-Catalyzed Amidation of Allylic Alcohols in the Presence of Nitrile**

| Entry | Allylic Alcohol | Products (%Yield)[a] |
|---|---|---|
| 1 | <br>X = H, **1**<br>= Ac, **2** | <br>**1a , 1b** (1:3)[b,d], 67<br>**2a , 2b** (1:3)[b,d], 63 |
| 2 | <br>**3** | <br>**3a , 3b** (1:1)[b,d], 51 |
| 3 | <br>**4** | <br>**4a**, 58 |
| 4 | <br>X = H, **5**<br>= Ac, **6** | <br>**5a** , 58<br>**6a** , 60 |
| 5 | <br>**7** | <br>**7a**, 61 |
| 6 | <br>**8** | <br>**8a**[c,e] , 58 |
| 7 | <br>**9**[f] | <br>**9a, 9b** (1:1.25)[b,c], 57 |
| 8 | <br>**10** | <br>**10a**, 63[h] |
| 9 | <br>**11** | <br>**11a**, 62, (1:2)[g] |

[a] Isolated yield. [b] The ratio for the regioisomers was determined by the chemical shift of methyl signals in $^1$H NMR. [c] A mixture of diastereomers was obtained. [d] The ratio of *E*:*Z* was found to be nearly 1 in these cases. The chemical shift of the olefinic proton in the *E* alkene was upfield compared to the corresponding *Z* alkene. [e] Carveol (**8**) was obtained after purification as a single *anti* diastereomer from sodium borohydride reduction of optically pure (−)-carvone. [f] The isomer ratio of this alcohol (obtained from carvone) could not be determined as the crude alcohol was used. [g] The *E*:*Z* ratio was determined by NMR. [h] Obtained mainly as the *E* isomer.

Typically, heating the allyl alcohols in acetonitrile in the presence of Co(III)DMG complex (5 mol %) at 80 °C for 12−14 h afforded the corresponding allylamides in good yields. According to this protocol, the allyl alcohol **1** underwent transformation to give a 1:3 mixture of regioisomers of the corresponding allylamide (Table 1, entry 1). Similarly, the cyclohexyl allylic alcohol **3** afforded a 1:1 mixture of the corresponding allylic amides in moderate yields (Table 1, entry 2), whereas the aromatic allylic alcohols **4** and **5** (Table 1, entries 3 and 4) could be transformed to the corresponding amides in good yields. The diene alcohol **7** underwent conversion to the corresponding amide as the only regioisomer (Table 1, entry 5). The cyclic allylic alcohol **8** *anti*-carviol, from carvone was transformed to the corresponding amides as 1:1.7 mixture of diastereomers; however, no attempt was made to separate them (Table 1, entry 6). Similarly, the tertiary alcohol **9** derived from carvone underwent smooth transformations to a 1:1.25 mixture of regioisomers, and each regioisomer was found to be a mixture of diastereomers. Interestingly, the ene−yne secondary and tertiary **10** and **11** alcohols underwent complete rearrangement to give the corresponding amide in good yields (Table 1, entries 8 and 9). It is noteworthy that these reactions could also be performed in acetic acid medium using a stoichiometric amount of acetonitrile in comparable yields. The regiochemistry of amidation here does not change to any significant extent compared to the transformation conducted in acetonitrile medium. We were unable to form the amide from allyl alcohol **12**. However, the corresponding acetate **13** underwent amidation to afford a 1:1.7 mixture of the regioisomers in good yields (eq 2). It is also interesting to note that $CoCl_2$ did not catalyze amide formation from the allyl acetate **13**. In view of these observations, it is evident that $CoCl_2$- and Co(III)DMG-catalyzed amidation reactions are oc-

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(1) Mukhopadhyay, M.; Reddy, M. M.; Maikap, G. C.; Iqbal, J. *J. Org. Chem.* **1995**, *60*, 2670.

(2) Iqbal, J.; Srivastava, R. R. *J. Org. Chem.* **1992**, *57*, 2001.

(3) Co(III)DMG complex was prepared according to the known procedure: Costa, G.; Tauzher, G.; Puxeddu, A. *Inorg. Chim. Acta* **1969**, *3*, 45. There is no detailed structural information available on this complex. The proposed structure incorporates an undefined stereochemistry of oxime anion.

(4) For some recent syntheses of allylamide and amines see: (a) Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1448. (b) Helquist, P.; Connell, R. D.; Akermark, B. *J. Org. Chem.* **1989**, *54*, 3359. (c) Buchwald, S. L.; Watson, B. T.; Wannamakar, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

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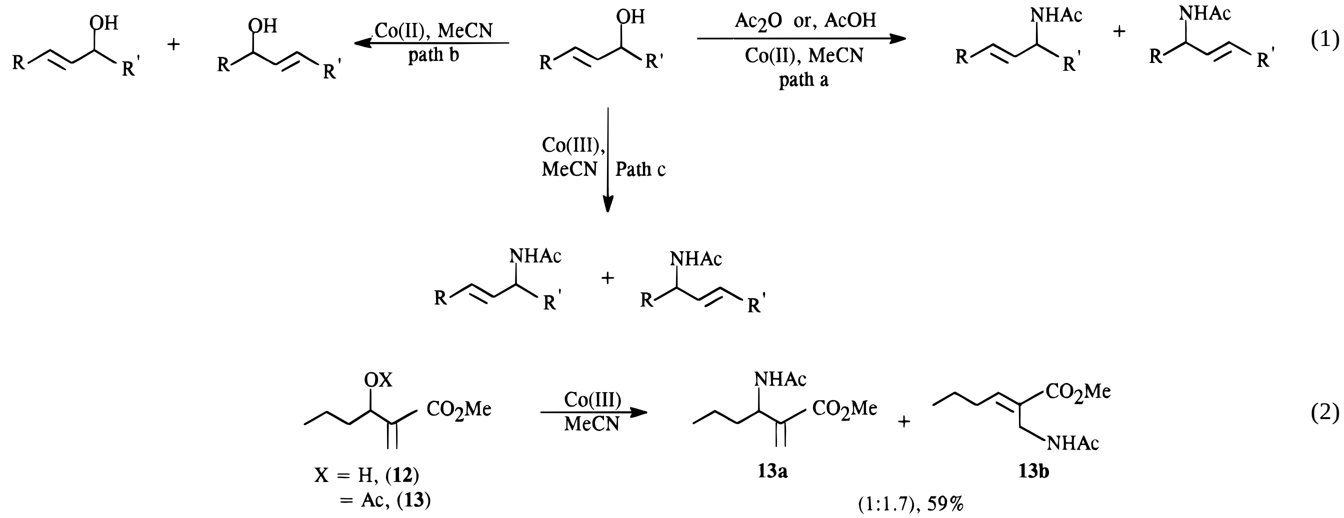
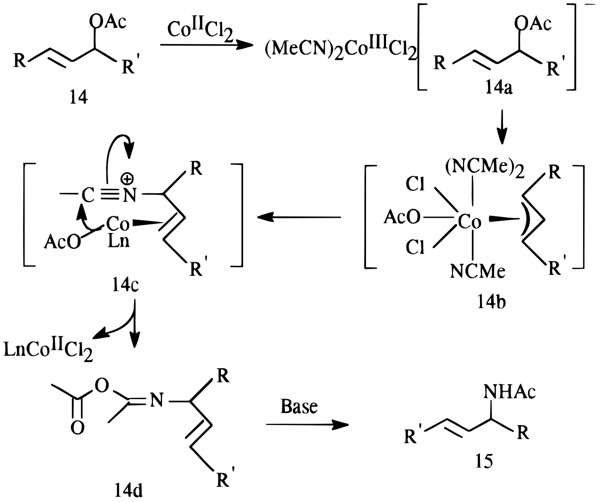
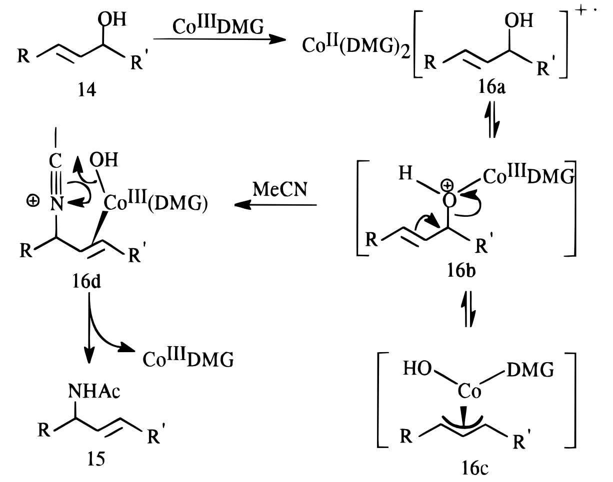
**Scheme 1**



**Scheme 2**



**Scheme 3**



curring via different pathways. It is also noteworthy that Co(III)DMG-catalyzed reactions are not occurring via a [3,3] sigmatropic rearrangement of acetamidate[5] obtained in a Pinner reaction[6] as such a process would lead to a completely rearranged allylic amide that is contrary to our observations.

The preliminary mechanistic exploration based on cyclic voltammetric studies[7] indicates that allyl acetates can easily be reduced in the presence of cobalt(II). This indicates that coordination of cobalt(II) to acetate results in lowering of reduction potential of acetate and the cobalt complexed acetate is easily reduced by an electron transfer from another cobalt(II) species to give a radical anion **14a** (Scheme 2). The latter may form an $\pi$-allyl complex, **14b**, which on attack by acetonitrile may give an intermediate **14c**. An intramolecular attack on **14c** by acetate will afford the imidate ester **14d**, which on base hydrolysis during the workup will afford the allyl amide **15**. On the other hand, Co(III)DMG-catalyzed amidation may be proceeding via a well-known outer-sphere electron-transfer process from allylic alcohol to cobalt(III) to afford a radical cation **16a**, which may exist in equilibrium with **16b** (Scheme 3). An attack by acetonitrile on **16b** or the corresponding $\pi$-allyl complex **16c** will afford **16d**, which on an intramolecular attack of hydroxide will yield the allylamide **15**. This mechanistic proposal seems reasonable as reduction of allyl acetate by cobalt(II) is shown to proceed easily by cyclic voltammetric studies. Similarly, reduction of cobalt(III) by allylic alcohol via an electron-transfer process is very well precedented in literature.[8]

In conclusion, Co(III)DMG-catalyzed amidation offers a viable alternative to the corresponding Co(II)-catalyzed transformation. This methodology has the advantage that it does not require the mandatory formation of allyl acetate prior to the reaction. We are currently persuing studies to delineate the mechanism of Co(II)- and Co(III)-catalyzed amidation reactions.

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(5) For rearrangements of allylic imidates see: Overman, L. E. *Acc. Chem. Res.* **1980**, *13*, 218.

(6) For the Pinner reaction see: Compagnon, P. L.; Miocque, M. *Ann. Chim. (Paris)* **1970**, *5*, 23.

(7) Cyclic voltammetry on acetate **14** (R = Ph, R′ = Et) in the presence of CoCl$_2$ in acetonitrile showed an oxidative response at +0.04 V (*vs* saturated calomel electrode in 15 mL of dry acetonitrile) in the form of a catalytic current presumably arising due to the oxidation of this acetate. This oxidative response was not observed in the absence of CoCl$_2$. This observation supports the assumption that addition of CoCl$_2$ lowers the reduction potential of acetate **14** through coordination. The coordination of acetate **14** to cobalt(II) will result in charge transfer to the metal, and this process may facilitate an electron transfer to acetate from another cobalt(II) species.

(8) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.

## Experimental Section

**Materials and Methods.** Acetonitrile, acetic acid, and all other solvents and reagents were purified by the standard procedure before use.[9] $CoCl_2$ was purchased from LOBA India Ltd., Bombay, and dried at 110 °C for 2−3 h before the reaction. The Co(III)DMG complex was prepared according to the literature procedure.[3] Column chromatography was performed using 60−120 mesh (ACME) TLC silica gel or neutral alumina. $^1$H NMR spectra were recorded at 60 and 80 MHz in $CDCl_3$ or $CCl_4$. Chemical shifts are referenced relative to TMS and reported in $\delta$ units. All of the starting allylic alcohols were prepared according to literature procedures and compared with their $^1$H NMR spectra.[1] All of the known amides were characterized by comparison with the literature data.[1]

**General Procedure for the Co(III)DMG-Catalyzed Amidation of Allylic Alcohol/Acetate.** Allylic alcohol/acetate (10 mmol) was added to a solution of Co(III)DMG (5 mol %) in dry acetonitrile (30 mL). The reaction mixture was heated at 80 °C for 12−14 h while the progress of the reaction was monitored by TLC. The solvent was removed in vacuo, and the residue was dissolved in EtOAc (50 mL). The organic layer was washed successively with aqueous $NaHCO_3$ solution (3 × 15 mL), water, and brine (2 × 20 mL). Drying ($Na_2SO_4$) and removal of the solvent yielded a residue that on column chromatography ($SiO_2$) afforded the amides. The ratio of regioisomers was determined by $^1$H NMR of the crude reaction mixture.

The reaction of allyl acetate (**13**)[1,10] (10 mmol) was carried out as described in the general procedure by heating in MeCN and Co(III)DMG (5 mol %) at 80 °C for 11 h to afford **13a** and **13b** as a 1:1.7 regioisomeric mixture.

**Methyl 3-acetamido-2-methylenehexanoate (13a):** $^1$H-NMR ($CDCl_3$) 7.2 (bd, 1H), 6.2 (d, $J = 2.5$ Hz, 1H), 5.6 (d, $J = 2.5$ Hz, 1H), 5.6 (m, 1H), 3.65 (s, 3H), 2.10 (s, 3H), 1.25−1.60 (m, 4H), 0.85 (t, $J = 5.0$ Hz, 3H); IR (thin film) 3280, 2972, 1710, 1640 cm$^{-1}$; FABMS $m/z$ (rel intensity) 199 (28) [M$^+$], 200 (100) [M$^+$ + 1].

**Methyl 2-(methylacetamido)hex-2-enoate (13b):** $^1$H-NMR ($CDCl_3$) 7.2 (bd, 1H), 6.9 (t, $J = 7.0$ Hz, 1H), 4.2 (s, 2H), 3.65 (s, 3H), 1.95 (s, 3H), 1.25−1.60 (m, 4H), 0.85 (t, $J = 5.0$ Hz, 3H); IR (thin film) 3280, 2972, 1710, 1640 cm$^{-1}$.

**Acknowledgment.** MM wishes to thanks the CSIR, New Delhi for senior research fellowship.

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(9) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Vogel, A. I., Ed.; ELBS: England, 1984.

(10) Allyl acetate **13** was prepared from the corresponding alcohol **12** obtained according to the following procedure: Basavaiah, D. *Tetrahedron Lett.* **1986**, *27,* 2031.