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# Co(III)DMG Complex Catalyzed Allylation of 1,3-Dicarbonyl Compounds with Allylic Alcohols

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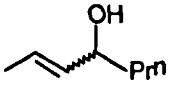
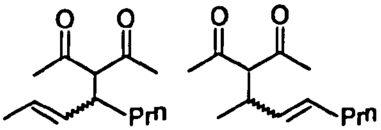
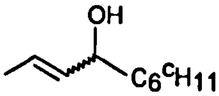
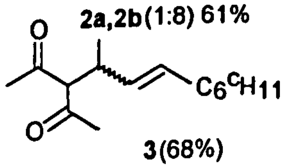
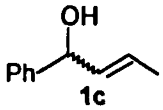
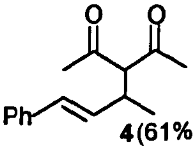
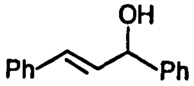
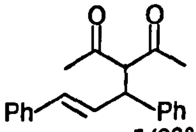
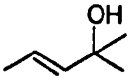
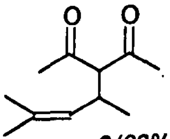
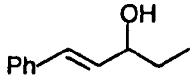
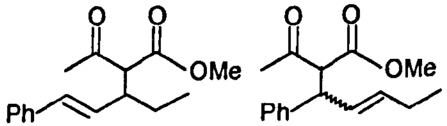
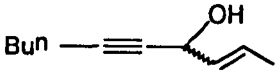
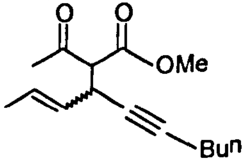
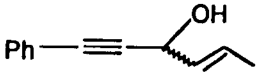
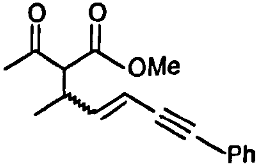
**Abstract:** *Co(III)DMG, [ Co(III)DMG is Co(DH)(DH$_2$)Cl$_2$, where DH is monoanion of dimethylglyoxime ], complex catalyses the allylation of 1, 3-dicarbonyl compounds with allyl alcohols in good yields. These reactions are highly regioselective as compared to the corresponding Co(II) catalyzed transformation using allyl acetates.*

Recent studies from our group has demonstrated[1] that CoCl$_2$ acts as an excellent catalyst in the allylation of 1,3-dicarbonyl compounds with allyl acetates. These allylations have advantage over the corresponding Pd catalyzed[2] reaction because it does not require the mandatory formation of anion prior to reaction with allyl acetate. We now show that Co(III)DMG complex acts as an efficient catalyst in the allylation of 1,3-dicarbonyl compounds with allyl alcohols. A preliminary account of these findings are described below.

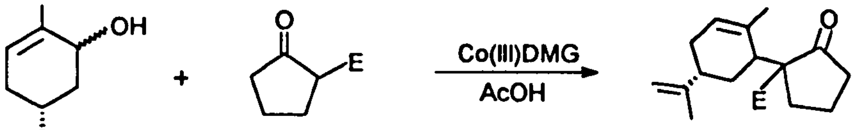
Typically, allyl alcohol (10 mmol), 1,3-dicarbonyl compound (12 mmol) & Co(III)DMG complex[3] (5 mol%) are taken in AcOH (15mL) and the resulting mixture is heated at 80°C for 8-10 h. Removal of acetic acid followed by bicarbonate workup affords a residue which is chromatographed over silica gel to give allylated products. Thus secondary allyl alcohols **1a-1d**, can be used to allylate 2,4-pentanedione to give predominantly[4] one regioisomer (Table 1, entry 1-4). Similarly tertiary allylic alcohol **1e** also reacts to give mainly one regioisomer (Table 1, entry 5). In a similar fashion methylacetoacetate can also be allylated regioselectively with allylic as well as acetylenic alochols **1g** & **1h** to give **7a,7b,8a** & **9** respectively as the main products (Table 1, entry 6-8). No reaction product arising due to the attack at triple bond is observed for alcohols **1g** & **1h**. The cyclic keto

**Table-1:Co(III)DMG Catalyzed Allylation of Allylic Alcohols With 1,3-Dicarbonyl Compounds**

| Entry | Allyl Alcohol | 1,3-Dicarbonyl compound* | Product(s) (Yield)$^{a,b}$ |
|---|---|---|---|
| 1. |  **1a** | 1 |  **2a,2b**(1:8) 61% |
| 2. |  **1b** |  |  **3**(68%) |
| 3. |  **1c** |  |  **4**(61%) |
| 4. |  **1d** |  |  **5**(63%) |
| 5. |  **1e** |  |  **6**(63%) |
| 6. |  **1f** | 2 |  **7a,7b**(1:9)(64%) |
| 7. |  **1g** |  |  **8a**(53%) |
| 8. |  **1h** |  |  **9**(56%) |

*a) Isolated Yield. b) Ratio was determined from $^1$H-NMR of the crude reaction mixture.*

** 1 - Acetylacetone, 2 -Methylacetoacetate.*

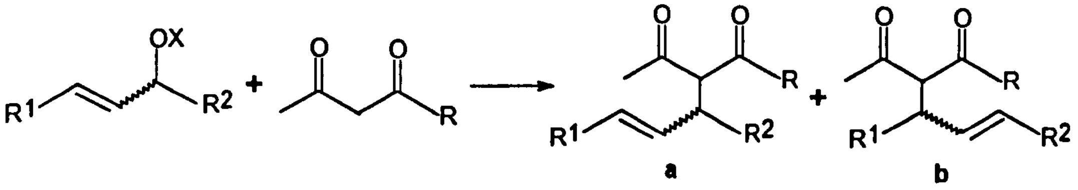


Eq. 1

E=COOEt, 53%

ester can also be allylated with carveol to give a mixture of diastereomers in good yields (Eq. 1). These allylations are more regioselective as compared to the already reported Co(II) catalyzed reaction where allyl acetate is used as the allylating species. It is noteworthy that Co(III)DMG complex also catalyses the allylation of 1,3-dicarbonyl compounds with allyl acetates with same efficiency & chemical yields as exhibited by Co(II)Chloride catalyzed reactions. Co(III)DMG catalyzed allylation with allyl alcohol can be performed in 1,2-dichloroethane or AcOH with equal ease and there is no noticeable difference in the regioselectivity under these conditions. The allylation using allyl alcohols catalyzed by Co(III)DMG are highly regioselective compared to the corresponding Co(II) catalyzed allylation with allyl acetates. It is clearly evident from the results in

**Table -2: Cobalt Catalyzed Allylation of 1,3-Dicarbonyl Compounds. A Comparative Study.**



| Entry | X | R | R1 | R2 | Catalyst[a] | Products, Ratio, Yield[b,c] |
|---|---|---|---|---|---|---|
| 1. | H | Me | Me | $Pr^n$ | Co(III)DMG | 2a:2b(1:8)61% |
| 2. | Ac | Me | Me | $Pr^n$ | $CoCl_2$ | 2a:2b(1:3)68% |
| 3. | H | OMe | Ph | Et | Co(III)DMG | 7a:7b(1:9) 64% |
| 4. | Ac | OMe | Ph | Et | $CoCl_2$ | 7a:7b(1:3) 55% |
| 5. | H | OMe | Me | $\equiv$—$Bu^n$ | Co(III)DMG | 8a(53%) |
| 6. | Ac | OMe | Me | $\equiv$—$Bu^n$ | $CoCl_2$ | 8a:8b(1:1.5) 24% |

*a) Co(II) chloride catalyzed reaction proceeds only in the presence of mol. oxygen.*

*b) Ratio was determined from $^1H$-NMR of the crude reaction mixture. c) Isolated yield.*

Table-2 that the allylation using allyl alcohol **1a** affords the major regioisomer **2b** and the regioselectivity in this case is higher as compared to the corresponding Co(II) catalyzed reaction (Table 2,entry 1 & 2). Similarly allyl alcohol **1f** reacts with methylacetoacetate to afford the regioisomer whose predominance is substantially higher as compared to the similar reaction using Co(II) and the corresponding allyl acetates (Table 2, entry 3 & 4). Similarly, the ene-yne alcohol **1g** reacts with methylacetoacetate to give the regioisomer **8a** as the sole product, whereas the corresponding Cobalt(II) catalyzed reaction with ene-yne acetate gave nearly equal mixture of regioisomers (Table 2, entry 5 & 6). *The reason for difference in regioselectivity of Co(III) catalyzed reaction is not apparent at the moment, however, it is interesting to note that Co(II) catalyzed reaction takes place only in the presence of mol.oxygen.* The presence of latter may coax the Co(II) catalyzed reaction to follow the radical process; whereas the Co(III) catalyzed reaction is likely to proceed via an ionic pathway. Irrespective of the nature of pathway the reaction catalyzed by Co(III) is more regioselective as compared to the corresponding Co(II) catalyzed transformation.

In conclusion Co(III)DMG catalyzed allylation with allyl alcohol provides a formidable alternative to the analogous Co(II) or Pd complex catalyzed[1,2] transformations as the reactions performed under former conditions are highly regioselective and do not require the mandatory formation of an anion or allyl acetates. We are currently pursuing studies to delineate the mechanism of these transformations.

## References and Notes

1.a)Bhatia,B.; Reddy,M.M.; Iqbal,J., *Tetrahedron Lett.*,**1993**, *34*, 6301. b) Maikap,G.C.; Reddy,M.M.; Mukhopadhyay,M.; Bhatia,B.; Iqbal,J., *Tetrahedron*. **1994**, *50*, 9145.

2.a) Trost,B.M.,*Tetrahedron*.**1977**,*33*,2615.b)Trost,B.M.,*Acc.Chem.Res.*,**1980**,*13*, 385. c) *Palladium reagents in organic synthesis*, Heck,R.F.,Academic Press:London, **1985**. d) Godleski,S.A., *Comprehensive Organic Synthesis* , Trost,B.M.,Ed. Pergamon, **1991**, Vol 4, 585.

3.Co(III)DMG complex is prepared according to the known procedure: Costa.G.; Tauzher.G.; Puxeddu.A., *Inorg.Chim.Acta.*, **1969**, *3*, 45.

4.For alkylation of Pentane-2,4-dione through its Co(II) complex see: Vallribera,A.; Marquet,J.; Moreno-Mañas,M.; Cayon,E., *Tetrahedron*. **1993**, *49*, 6437 and references cited therein.

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