

Cobalt (II) Catalysed Allylation of 1,3-Dicarbonyl Compounds with Allyl Acetates

Beena Bhatia, M.Madhava Reddy and Javed Iqbal*
Department of Chemistry, Indian Institute of Technology,
Kanpur - 208 016, INDIA

Abstract: *An efficient allylation of various 1,3-dicarbonyl compounds can be achieved with allyl acetates in the presence of catalytic cobalt (II) chloride in 1,2-dichloroethane.*

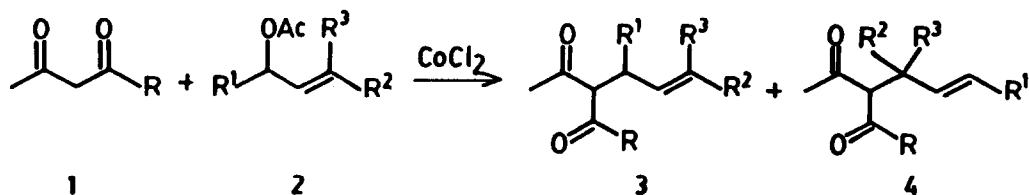
Palladium catalysed allylation of 1,3-dicarbonyl compounds with allyl acetates has emerged as an outstanding transformation¹ in the domain of synthetic organic chemistry. The versatility of this methodology is clearly evident from the widespread use that it enjoys² in the contemporary organic synthesis. These allylations are conducted on the preformed π -allyl palladium complex under basic conditions using stabilised anions derived from 1,3-dicarbonyl compounds. We now present an operationally simple and efficient route to allylations which can be performed using neutral 1,3-dicarbonyl compounds and allyl acetates in the presence of catalytic amount of cobalt (II)chloride.

Treatment of allyl acetates **2** with methyl acetoacetate **1a** in the presence of cobalt (II)chloride (5 mol%) in 1,2-dichloroethane at 70° C for 8-12 h afforded the allylated products³ in good yields. These allylations can also be carried out with acetylacetone **1b** and ethyl-2-oxocyclopentanecarboxylate **1c** in moderate to good yields. The regiochemistry of the allylation depends upon the structure of the allyl acetates and most of the reactions afforded one of the regioisomer as the major product (Table 1). Acetylacetone and cyclic 1,3-dicarbonyl compound **1c** exhibited a high regiochemistry and provided the allylated products in good chemical yields.

The reaction with diene acetate **2d** is quite regioselective and this selectivity seems to depend upon the nature of the 1,3-dicarbonyl compounds. Thus methyl acetoacetate **1a** gave the linear alkylated product **4g**, whereas acetylacetone **1b** and cyclic ketoester **1c** afforded the branched alkylated products **3i** and **5a** respectively as the major regioisomer in good yields (Table 1 and scheme 1). These reactions result into the formation of small amounts of the corresponding regioisomer and interestingly no eliminated or oligomeric products were observed under these conditions.

The reaction between enyl acetate **2e** and methyl acetoacetate **1a** afforded an equal mixture of regioisomers (Table 1, entry 8) whereas acetylacetone **1b** and the cyclic ketoester **1c** underwent highly regioselective alkylation to provide the branched products **4j** (Table 1, entry 10) and **5b** (scheme 1) respectively as the major regioisomer in excellent yields. The corresponding regioisomers from the reaction involving **1c** were obtained in minor amounts whereas no regioisomer was observed in the case of acetylacetone **1b**. It is

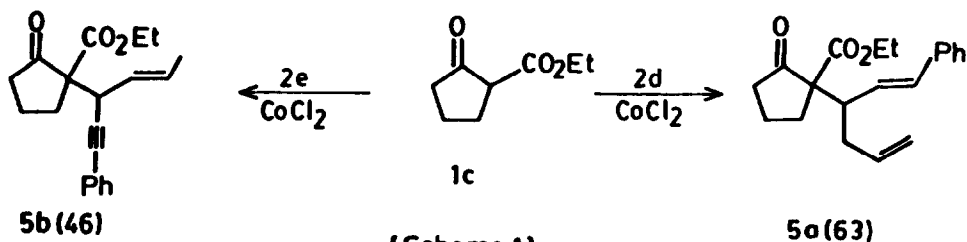
Table 1: Cobalt Chloride Catalysed Reaction of 1,3-Dicarbonyl Compounds with Allyl Acetates



Entry	Dicarbonyl compound	Allyl acetate ^d	R	R ¹	R ²	R ³	Isolated Yield ^a (%)	Selectivity	
								Regio(3:4) ^b	Stereo(E:Z) ^c
1	1a	2a	OMe	Et	Me	H	29	(3a:4a)30:70	60:40
2		2b	OMe	Me	Me	Me	27	(3b:4b)90:10	-
3		2c	OMe	Et	Ph	H	55	(3c:4c)25:75	90:10
4	1b	2a	Me	Bu ⁿ	Me	H	38	(3d:4d)20:80	70:30
5		2b	Me	Me	Me	Me	35	(3e:4e)100:0	-
6		2c	Me	Pr ⁿ	Ph	H	67	(3f:4f)90:10	100:0
7	1c	2d	OMe	CH ₂ =CH-CH ₂ -	Ph	H	53	(3g:4g)35:65	-
8		2e	OMe	Me	Ph-C≡C-	H	26	(3h:4h)50:50	95:5
9	1b	2d	Me	CH ₂ =CH-CH ₂ -	Ph	H	64	(3i:4i)70:30	-
10		2e	Me	Me	Ph-C≡C-	H	55	(3j:4j)20:80	-

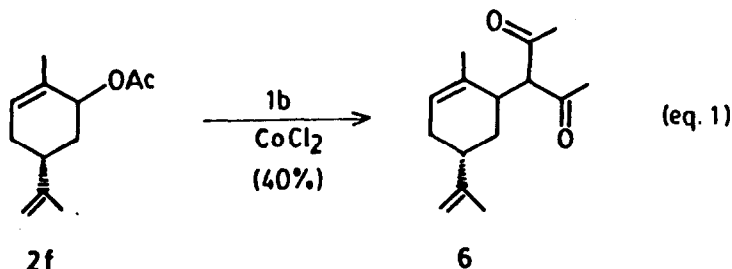
(a) Isolated yield of the mixture of regioisomers. (b) Ratio was determined from the ¹H-NMR of the crude mixture of regioisomers. (c) Ratio of the geometrical isomers of the major regioisomer. (d) All the acetates were a mixture of *E* : *Z* isomers with predominantly *E* (~80%) stereochemistry.

noteworthy that the reaction with acetylacetone 1b is highly regioselective and it exhibits the opposite regiochemistry as compared with that of methyl acetoacetate 1a (Table 1, entries 3, 6, 7 and 9). Interest-

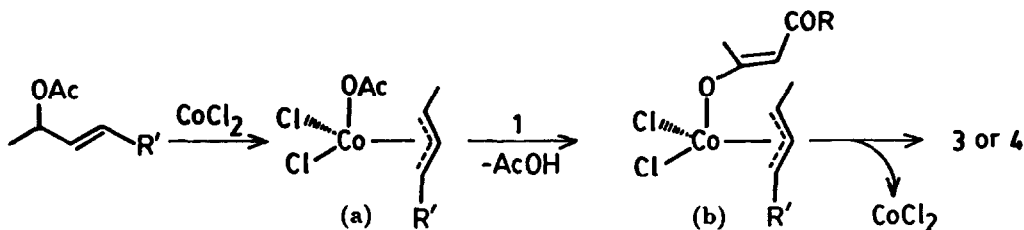


(Scheme 1)

ingly, methyl acetoacetate **1a** failed to react with a diastereomeric mixture of carvovyl acetate **2f** whereas, acetylacetone **1b** readily afforded the trans diastereomer **6** as the major product (eq. 1).



The mechanism for this reaction is presently unclear however, these results may be accounted for based on the following mechanistic rationale (scheme 2). The interaction of cobalt (II) with allyl acetate may provide⁴ a π -allyl cobalt complex (a) which subsequently reacts with 1,3- dicarbonyl compounds via a redox process to give a cobalt-enolate (b). The later species may undergo an intramolecular carbon-carbon bond formation to afford the allylated product. We have earlier proposed a similar model⁵ for the reaction of vinyl ethers with methyl acetoacetate. The high regioselectivity in the case of acetylacetone, which will



(Scheme 2)

readily form an enolate, may be arising due to this intramolecular reaction.

We have demonstrated that cobalt (II)chloride catalysed allylation of 1,3- dicarbonyl compounds can be performed under very simple and mild conditions and thus this methodology provides a formidable alternative to similar transformations achieved by other metal catalyst.

References and Notes

- (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. in *Comprehensive Organic Synthesis*, Trost, B.M., Ed. Pergamon, **1991**, vol 4, 585.
- (a) Trost, B.M.; Verhoeven, T.R., *J. Am. Chem. Soc.*, **1978**, 100, 3435. (b) Trost, B.M.; Godleski, S.A.; Genet, J.P., *J. Am. Chem. Soc.*, **1978**, 100, 3930. (c) Kitagawa, Y.; Itoh, A.; Hashimoto, H.; Yamamoto, H.; Nozaki, H., *J. Am. Chem. Soc.*, **1977**, 99, 3864. (d) Backvall, J.E.; Nystrom, J.E.; Nordberg, R.E., *J. Am. Chem. Soc.*, **1985**, 107, 3676. (e) Connell, R.D.; Rein, T.; Akermark, B.; Helquist, P., *J. Org. Chem.*,

1988, 53, 3845. (f) Fish, P.V.; Reddy, S.P.; Lee, C.H.; Johnson, W.S., *Tetrahedron Lett.*, 1992, 33, 8001. (g) Genet, J.-P.; Thorimbet, S.; Touzin, A.-M., *Tetrahedron Lett.*, 1993, 34, 1159.

3. Allyl acetates **2** (5 mmol) and 1,3- dicarbonyl compound **1** (5 mmol) were heated at 70° C in 1,2-dichloroethane (30 ml) in the presence of catalytic amount of dry cobalt (II)chloride (30 mg) for 8-12 h. Removal of solvent gave a residue which was taken into ethyl acetate and washed successively with saturated solution of sodium bicarbonate (3x15 ml) and water (3x20 ml). Drying ($MgSO_4$) and evaporation of solvent gave a residue which was chromatographed over silica gel to give the products.

4. Cobalt (II) catalysed formation of allyl cation from allyl acetate has been proposed earlier : (a) Nayar, N.K.; Reddy, M.M.; Iqbal, J., *Tetrahedron Lett.*, 1991, 32, 6965. (b) Reddy, M.M.; Iqbal, J., *J. Org. Chem.*, (submitted).

5. Iqbal, J.; Srivastava, R.R., *Tetrahedron Lett.*, 1991, 32, 1663.

6. Some new compounds had the following spectral properties:

4g : 1H NMR($CDCl_3$) δ 7.65-7.15(m, 5H), 5.95-5.25(m, 3H), 5.10(m, 1H), 4.90(m, 1H), 4.05(m, 1H), 3.75(s, 3H), 2.85(m, 2H), 2.15(s, 3H). IR($CHCl_3$, cm^{-1}): ν 1740, 1725, 1625, 1630, 1595, 1490, 1430, 1350.

3i : 1H NMR($CDCl_3$) δ 7.05(s, 5H), 6.15(d, J=18 Hz, 1H), 5.62 (dd, J=6 and 18 Hz, 1H), 5.30(m, 1H), 4.92(bs, 1H), 4.75(m, 1H), 3.50(d, J=8 Hz, 1H), 2.91(m, 1H), 2.45-2.12(m, 2H), 2.0(s, 3H), 1.90(s, 3H).

5a : 1H NMR($CDCl_3$) δ 7.35(m, 5H), 6.35(d, J=18 Hz, 1H), 5.90(dd, J=6 and 18 Hz, 1H), 5.35(m, 1H), 5.05(m, 1H), 4.89(m, 1H), 4.10(q, J= 7 Hz, 2H), 3.21(dt, J=3 and 8 Hz, 1H), 2.65(m, 2H), 2.35-1.80(m, 6H), 1.25(t, J=7 Hz, 3H). IR($CHCl_3$, cm^{-1}): ν 1745, 1720, 1630, 1595, 1490, 1445, 1225.

3h : 1H NMR($CDCl_3$) δ 7.30(m, 5H), 6.05(dd, J=4 and 18 Hz, 1H), 5.85(d, J=18 Hz, 1H), 3.80(s, 3H), 3.48(d, J=7.5 Hz, 1H), 3.15(m, 1H), 2.18(s, 3H), 1.05(d, J= 7.0 Hz, 3H). IR($CHCl_3$, cm^{-1}): ν 2200, 1740, 1700, 1585, 1480, 1430, 1250.

(Received in UK 10 June 1993; accepted 30 July 1993)