

Ultrasound Assisted Nitratobis (Triphenyl phosphine) Copper (I) catalyzed Addition of Organocadmium Reagents to α , β -Unsaturated Cyanoester

Ashok S. Pise^a, Arvind S. Burungale^b, Ramesh B. Gawade^b, Santosh S. Devkate^b, Sunil D. Jadhav^c and Shripad M. Patil^a

^aDepartment of Chemistry, Dada Patil Mahavidyalaya, Karjat, Ahmednagar, Maharashtra, India

^bDepartment of Chemistry, S. M. Joshi College Hadapsar, Pune, Maharashtra, India

^cDepartment of Chemistry, Mahatma Phule Mahavidyalaya, Panvel, Raigad, Maharashtra, India

ABSTRACT

Treatment of α , β -unsaturated cyanoester with phenyl cadmium bromide, derived from dilithium tetrachloro cadmium (Li_2CdCl_4) and Grignard reagent in the presence of 10 mol % of Nitratobis (Triphenyl phosphine) Copper (I) i.e. $\text{Cu}(\text{PPh}_3)_2\text{NO}_3$ catalyst afforded chemoselective conjugated product in high yields.

Keywords : Conjugate addition, Cyanoester, Cu (I) catalyst, Grignard reagent, Ultrasound irradiation.

I. INTRODUCTION

Loomis et al was first time introduced the ultrasound irradiation in aqueous medium.¹ Luche & co-workers was developed ultrasound mediated conjugate addition reactions under aqueous conditions.²⁻³ The copper (I) catalyzed allylic substitution has generated a great deal of interest in recent years. For allylic substitutions a broad range of organometallic compounds such as organolithium, Grignard and organozinc have been used.⁴⁻⁹ The conjugate addition of n-butyl and phenyl manganese bromide to trans-cinnamaldehyde and allylic bisacetate has been reported.¹⁰⁻¹¹ The copper catalyzed substitution reactions of acylal with organomanganese reagent has been reported.¹² A conjugate addition of nucleophiles and indole to unsaturated carbonyl compounds in acidic or basic or Lewis acid catalyst were developed.¹³⁻¹⁵ Recently, different varieties of catalysts such as ZnCl_4 ,¹⁶ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$,¹⁷ $\text{NaAuCl}_2 \cdot 2\text{H}_2\text{O}$,¹⁸ $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI on silica gel,¹⁹ $\text{PdCl}_2(\text{CH}_3\text{CN})_2$,²⁰ InBr_3 ,²¹ GaI_3 ,²² SmI_3 ,²³ AuCl_3 ,²⁴ $\text{Cu}(\text{OTf})_2$ immobilized in ionic liquid,²⁵ and Mg, THF, NH_4Cl ,²⁶⁻²⁸ are used in conjugate addition.

Most of the reported methods suffer from the serious drawbacks such as involvement of expensive reagents, acidic conditions, longer reaction time, environmental pollution and moderate yields. In the present work, we have investigated the conjugate addition of organo cadmium reagent with α , β -unsaturated cyanoester compounds in the presence of Nitratobis (Triphenyl phosphine) Copper (I) under conventional and ultrasound conditions.

II. METHODS AND MATERIAL

The melting points and boiling points of compounds are uncorrected. are determined by in a open capillary tube. The IR spectra were recorded on a Shimadzu Miracle 10 ATR instrument. The ¹H NMR spectra were obtained on a Varian Mercury YH-300 MHz with CDCl_3 as the solvent. Sonication was performed in an Ultrasonic Cleaner with frequency 33 KHz and a normal power of 250 W. The reaction progress are checked by TLC using pet. ether/ethyl acetate

as the mobile phase. The spots were visualized using UV cabinet. Crude products were purified by column chromatography using pet. ether/ethyl acetate as a solvent.

Procedure for preparation of Nitratobis (Triphenyl phosphine) Copper (I) :

0.04 mol PPh₃ (10.5 gm) and Cu(NO₃)₂·3H₂O (0.01mol, 2.45 gm) was added to 100 ml hot CH₃OH. Immediately, Cu(II) dissolves and white suspension formed. This suspension was refluxed for 10 min. and cooled to ambient temperature. After filtration, washed with ether, ethanol and dried. Recrystallization from methanol gave colourless solid.

M.P. 232°C, Soluble in DMF, CHCl₃, CH₂Cl₂, CH₃CN and THF.

IR:(ν,) 3047, 2924, 1538, 1479, 1464, 1384, 1295, 1096, 810, 741, 693 cm⁻¹.

Procedure for preparation of cyanoesters :

Cyanoesters were prepared from substituted aromatic aldehyde (1 mmol), ethylcyanoacetate (2.6 mmol), glycine (0.7 mmol) and 2 gm silica gel. The content was mixed thoroughly and taken in 50 ml borosil beaker. The beaker was placed in Al₂O₃ bath and reaction mixture was irradiated for 20 min. Crude product was obtained and purified by column chromatography.

General procedure for Copper Catalyzed organocadmium reagent with cyanoester :

Conventional method: Li₂CdCl₄ (5ml, 1M) in tetrahydrofuran (10 ml) was added in 100 ml round bottom flask, which was previously flushed

with dry nitrogen. Then phenyl or butyl magnesium bromide (1.4 M, 5 mmol, 3.5 ml) was added at 0°C. The mixture turned into clear yellow brown solution and after being stirred for 20 min. at 0°C, 10 mol % Cu(PPh₃)₂NO₃ in THF (2 ml) was added and the whole mixture was stirred for 1 hour and then 5 mmol cyanoester in 5 ml THF was added and stirred the content 3 to 5 hours. The mixture was poured into 1 M HCl and extracted with ether (3x20ml). Purification of the products by silica gel column chromatography gave a pure product.

Ultrasound: All contents were placed in an ultrasonic bath for the periods indicated in Table-2 at 0 to 10°C and worked up as described above.

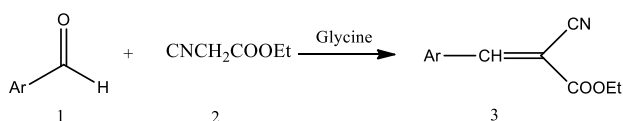
Spectral data of Products:

4f: Yellow liquid, IR (ν cm⁻¹) 3030 (Aromatic C-H), 2230 (-CN), 1738 (-COO), 1595, 1489 (Aromatic C=C), ¹HNMR (300 MHz, CDCl₃) δ 1.07 (t, CH₃ J=7, Hz, 3H), 3.7 (s, CH₃), 4.1(q,CH₂), 4.2(d, CH, J=7 Hz), 4.7(d, -CH. J=7 Hz) 6.8-7.74 (m, 9 H, ArH) ppm.

4c: Red colour viscous oil, IR (ν cm⁻¹) 3020 (Aromatic C-H), 2233 (-CN), 1745,(-COO) 1590, 1485 (Aromatic C=C), ¹HNMR (300 MHz, CDCl₃) δ 1.1 (t, CH₃ J=7, Hz, 3H), 4.1(q,CH₂), 4.3(d, CH, J=8 Hz), 4.9(d, -CH. J=7 Hz) 7.2-8.1 (m, 9 H, ArH) ppm.

4d: Red colour viscous oil, IR (ν cm⁻¹) 3030 (Aromatic C-H), 2240 (-CN), 1742,(-COO), 1595, 1489 (Aromatic C=C), ¹HNMR (300 MHz, CDCl₃) δ 1.1 (t, CH₃ J=7, Hz, 3H), 4.2(q,CH₂), 4.3(d, CH, J=7 Hz), 4.9(d, -CH. J=7 Hz) 7.2-8.2 (m, 9 H, ArH) ppm.

III. RESULTS AND DISCUSSION



Scheme 1. Synthesis of cyanoester

Entry	Substate	Ethylcyano acetate/mmo l	Glycine /mmol	Yield, %	M.P. /°C
a	C ₆ H ₅ CHO	2.6	0.7	84	52
b	4-CH ₃ C ₆ H ₄ CHO	2.6	0.7	89	88

Table: 2. Copper catalyzed conjugate addition of organo cadmium reagent under conventional and ultrasound conditions

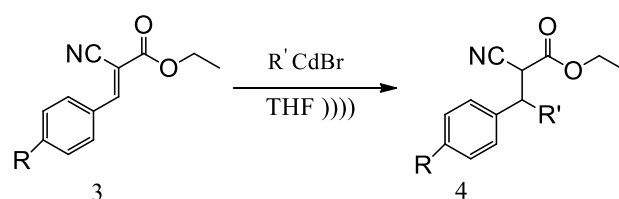
Entry	R'	Cu (I) 10 mol %	Solvent	Conventional conditions		Ultrasound irradiation	
				Time, hrs.	Yield, %	Time, min.	Yield, %
3f	Bu	Cu(PPh ₃) ₂ [NO ₃]	THF	5.0	69	37	90
3b	Bu	Cu(PPh ₃) ₂ [NO ₃]	Et ₂ O	4.5	70	35	87
3b	Ph	Cu(PPh ₃) ₂ [NO ₃]	THF	4.5	69	34	84
3e	Bu	Cu(PPh ₃) ₂ [NO ₃]	THF	4.0	72	28	88
3e	Ph	Cu(PPh ₃) ₂ [NO ₃]	Et ₂ O/THF	4.0	65	30	88
3f	Ph	Cu(PPh ₃) ₂ [NO ₃]	THF	5.0	69	35	83
3c	Ph	Cu(PPh ₃) ₂ [NO ₃]	THF	4.0	74	25	91
3d	Ph	Cu(PPh ₃) ₂ [NO ₃]	THF	4.0	72	27	93
3c	Bu	Cu(PPh ₃) ₂ [NO ₃]	Et ₂ O	4.5	80	28	89

From the table 2 – We have found that using ultrasonic irradiation, the reaction time was shortened from 5 hours to 25 min. In addition the yield of product was improved by 10-20% in comparison with those obtained by the conventional method. The yield of final product was slightly reduced by electron donating substituents.

IV. CONCLUSION

In conclusion, the mild condition was described for the preparation of conjugative addition products. The advantages of ultrasound in

c	3-NO ₂ C ₆ H ₄ CHO	2.6	0.7	91	137
d	4-NO ₂ C ₆ H ₄ CHO	2.6	0.7	84	170
e	4-ClC ₆ H ₄ CHO	2.6	0.7	82	87
f	4-OCH ₃ C ₆ H ₄ CHO	2.6	0.7	78	86



Scheme 2. Conjugate addition of R' group.

chemical reactions, shortened reaction time and higher yields of products were obtained.

V. ACKNOWLEDGMENTS

The author thanks the Central Instrumentation Facility, Savitribai Phule, Pune University and DST-FIST sponsored Central Instrumentation Laboratory, Dada Patil Mahavidyalaya Karjat Dist. Ahmednagar for the spectral analysis.

VI. REFERENCES

- [1]. W. Richards, Loomis A. J. *Am. Chem. Soc.* (1927), 49, 3086.
- [2]. J. L. Luche *J. Chem. Society, Chem. Comm.* (1992), 798-799.
- [3]. J. L. Luche *Synthetic Communication*, (1991), 21, 643-651.
- [4]. A. Commercon, M. Bourgain, M. Delaumeny, J. F. Normant & J. Villieras, (1975), 16, 3837.
- [5]. P. Barsantai, V. Calo, L. Lopez, G. Marchese, F. Naso & G. Pesce, *J. Chem Soc. Chem Commun*, (1978), 1085.
- [6]. C. C. Tseng, S. D. Paisley and H. L. Goering, *J. Org. Chem*, (1986), 51, 2884.
- [7]. J. E. Backvall, M. Sellen and B. Grant, *J. Am. Chem. Soc.* (1990), 112, 6615.
- [8]. J. E. Backvall, E. S. M. Persson and A. Bombrun, *J. Org. Chem*, (1994), 59, 4126.
- [9]. E. S. M. Persson, M. Van Klaveren, D. M. Grove and J. E. Backvall, *Chem Eur J.* (1995), 1, 351.
- [10]. M. B. Deshmukh, S. D. Jadhav, A. R. Mali, A. W. Suryawanshi, P. V. Anbhule, S. S. Jagtap and S. A. Deshmukh, *Synth. Commn*, (2005), 35, 2967.
- [11]. M. B. Deshmukh, S. D. Jadhav, A. R. Mali, A. W. Suryawanshi, P. V. Anbhule, *J. Chem Res.*
- [12]. M. B. Deshmukh, S. D. Jadhav, and S. V. Kadam, *Indian Journal of Chemistry*, (2007), 46B, 989-994.
- [13]. W. J. Houlihan, *Indoles*, (John Wiley and Sons Inc, New York) 1972.
- [14]. Ji-Tai Li, Zhi-Ping Lin and Cai Tong Liu, *Indian Journal of Chemistry*, (2008), 47B, 283-290.
- [15]. D. Kanwar, R. Rani J. Agarwal and R. K. Peddinti, *Indian Journal of Chemistry*, (2010), 49B, 1290-1299.
- [16]. V. Kumar, S. Kaur and S. Kumar, *Tetrahedron Lett*, (2007), 47, 7001.
- [17]. P. Armugam and P. T. Perumal, *Chem Lett*, (2006), 35, 632.
- [18]. A. Arcadi, G. Bianchi, M. Chiarini, F. Marinelli, *Synlett*, (2004), 944.
- [19]. G. Bartoli, M. Bartolacci, M. Bosco, G. Foglia, A. Giuliani, E. Marcantoni L. Sambri and E. Torregiani, *J. Org. Chem.* (2003), 68, 4594.
- [20]. W. J. Li, X-F Lin, J. Wang G-L Li and Y-G Wang, *Synlett*, (2006), 2003.
- [21]. M. Bandini, P. G. Cozzi, M. Giacomini, P. Melchiorre, S. Selva and A. Umani-Ronchi, *J. Org. Chem*, (2002), 67, 3700.
- [22]. Z. H. Huang, J. P. Zou and W. Q. Jiang, *Tetrahedron Lett*, (2006), 47, 7965.
- [23]. Z-P. Zhan, R-F Yang and K. Lang, *Tetrahedron Lett*, (2005), 46, 3839.
- [24]. Z. Li, Z. Shi & C. He, *J. Organomet. Chem*, (2005), 5049)
- [25]. J. S. Yadav B, V. S. Reddy G. Baishya, K.V. Reddy and A. V. Narsaiah, *Tetrahedron Lett*, (2005), 61, 9541.
- [26]. C. A. M. A. Hug and A. R. Naresh Raj, , *Indian Journal of Chemistry*, (2013), 52B, 1451-1454.
- [27]. S. Kotha and R. Ali, *Indian Journal of Chemistry*, (2016), 55B, 1099-1106.
- [28]. E. Korkusuz and I. Yildirim, *Indian Journal of Chemistry*, (2017), 56B, 152-159.