ISSN: 0974 - 7516 Volume 12 Issue 1

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 12(1), 2016 [011-015]

Microwave-assisted catalyst-free reduction of some arylidenmalononitriles under solvent-free conditions

Bagher Mohammadi*, Hamed Kazemi

Department of Chemistry, Payame Noor university, P. O. Box 19395-3697, Tehran, (IRAN)

E-mail: bagher.mohammadi@yahoo.com

ABSTRACT

This work described the reduction of some benzylidenmalonoitrile derivatives to form appropriate arylemalononitriles*via* a simple reaction between arylidenmalonoitriles and malononitrile in the presence of Na_2CO_3. This reaction took place under microwave irradiation and solvent-free conditions in good to excellent yields.

INTRODUCTION

The reduction of carbon-carbon double bonds is one of the fundamental reactions in organic chemistry and plays a key role in the manufacturing of a wide variety of bulk and fine chemicals. So far, several synthetic methods have been reported for the reduction of carbon-carbon double bonds. The most common synthetic approaches involve uses of some catalysts such as homogeneous or heterogeneous catalysts. Recently some olefins reducing are reported in many articles[1-7]. Some important reports are included: use of polymer-supported Hantzsch 1,4-dihydropyridine ester for the reduction of electron-withdrawing conjugated olefins ester[8], Hydrogenation of olefins using Hantzsch ester catalyzed by palladium on carbon[9] Sodium borohydride has been traditionally used as a reducing agent for reducing a few electron-deficient alkenes without any catalyst[10] and catalyst free chemoselective reduction of the carbon-carbon double bond in conjugated alkenes with Hantzsch esters in water[11]. Typically, either a metal-containing catalyst or a complex reducing reagent is needed to obtain the target product in acceptable yield and selectivity[12-16]. Chemo selective reduction of α,β-unsaturated ketones and nitriles by Using of iodotrichlorosilane II[17]. Hydrogenation of olefins can be achieved readily with molecular hydrogen in many cases, but transfer hydrogenation methods using suitable donor molecules such as formic acid or alcohols are receiving increasing attention as possible synthetic alternatives as they require no special equipment[18]. Some organic hydride compounds such as N,Ndimethylbenzimidazolidine (DMBI), 2-phenylbenzimidazoline (PBI) and 2-phenylbenzothiazoline (PBT) use as hydride donors, to reduce electron-deficient olefins and α,β-unsaturated ketones[19]. And hence several reagents have been utilized for this purpose[20-22].

The majority of the mentioned methods suffered from many problems about catalysts, solvents or reducing agents. Some problems involved the handling of potentially hazardous gaseous hydrogen and also the toxicity, price and accessibility of other reducing agents[6,23,24].

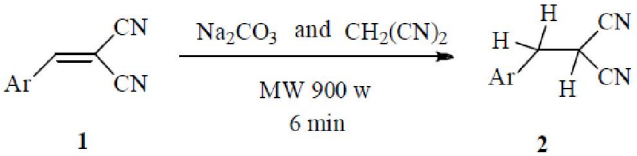
Full Paper

In recent years High-speed synthesis by microwaves has interested a considerable amount of tendency. Using a microwave oven in microwave-assisted organic synthesis (MAOS), not only reduces chemical reactions times from hours to minutes and increases the yield, but also can change the mechanism of some reactions, and improves reproducibility. Therefore, many researchers are already using MAOS as a foremost part technology for rapid Preformation of reactions for the efficient synthesis of new chemicals[25-32].

Due to the interesting chemistry of olephine reduction, the development of synthetic methods enabling easy access to the reduced organic compounds is desirable. As part of our studies on the development of efficient and straightforward microwave assisted methods to prepare organic compounds from readily available building blocks, a simple and efficient method to reduce some benzilidenmalonoitrile derivatives with unexpected reducing factor malononitrile in the presence of Na_2CO_3 is reported here in this study. We unexpectedly found that a mixture of arylidenmalonoitriles and malononitrile in the presence of Na_2CO_3 under microwave irradiation affords arylemalononitriles2 in good to excellent yields (Scheme 1, TABLE 1)

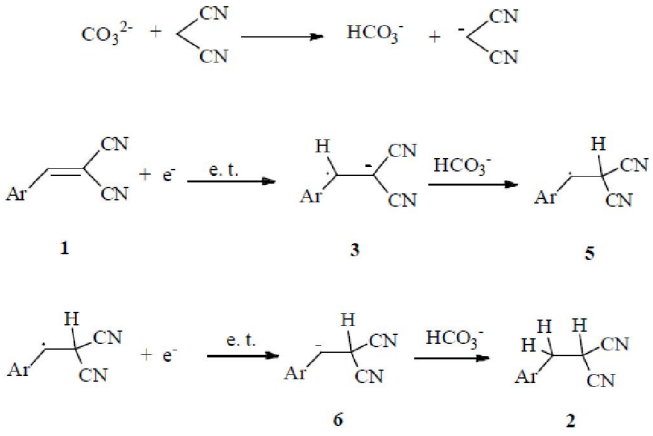
EXPERIMENTAL

All arylaldehydes and malononitrile were obtained from Merck (Germany), and were used without further purification. benzylidenemalononitrile was prepared by mixing arylealdehydes and malononitrile in water solution with catalytic amount of triethylamine. Melting points were measured on a lectrothermal 9100 apparatus. ^1H and ^{13}C NMR spectra were measured with Bruker DRX-250 AVANCE (at 250.1 and 62.5 MHz) spectrometer using $CDCl_3$ solvent with TMS as an internal standard. Chromatography columns were prepared from Merck silica gel 60 meshes. The experiments were performed using a microwave oven (ETHOS 1600, Milestone) with a maximum power of 900 W specially designed for organic synthesis.



1 2

Scheme 1 : Reduction of arilidenmalononitrile's carbon-carbon double bond



Scheme 2 : Proposed mechanism for the reduction of arilidenmalononitrile's carbon-carbondouble bond

General procedure for the preparation of benzylmalonoitriles2

The reactions were carried out by first mixing benzylidenemalononitrile (154 mg, 1 mmol), malononitrile (198 mg, 3 mmol), and sodium carbonate (0.212 mg, 2 mmol), then the mixture was irradiated in a sealed 5 ml vial at 900 W for 6 minutes. ^1H NMR analysis of the reaction mixtures clearly indicated formation of benzylmalonoitrile2. The residue was purified by column chromatography using petroleum ether-ethyl acetate (4:1) as eluent. The solvent was removed and the product was obtained as colorless crystals. The characterization data of the compounds are given below.

RESULT AND DISCUSSION

Characterization data of some of the compounds: 2-benzylmalononitrile (2a); White crystals. mp = 86-87 °C. IR (KBr): 3036, 2914, 2256, 1495, 1454, 1074, 1030, 748 and 702 cm^{-1}. ^1H NMR (250.1 MHz, $CDCl_3$): δ = 3.28 (d, *J* = 7.3 Hz, 2 H, CH_2,), 3.90 (t, *J* = 7.0 Hz, 1 H, CH), 7.26-7.40 (m, 5 H, 5 CH). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 132.9 (C), 129.32 (2 CH), 129.15 (2 CH), 128.84 (CH), 112.16 (2CN), 36.71 (CH_2), 25.03 (CH).

2-(4-Methylbenzyl)malononitrile (2b); White crystals. mp = 79-80 °C IR (KBr): 3033, 2920, 2256, 2225 (Ca"N), 1915, 1516,815, 790 and 708 cm-1.^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3,), 3.27 (d, 2 H, CH_2), 3.89(t, 1 H, CH), 7.36-7.75 (m, 4 H, 4CH). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 131.2 (C), 130.9 (2 CH), 129.83 (2 CH), 123.19 (CH), 111.25 (2CN), 35.8 (CH2), 25.11 (CH).

2-(4-Chlorobenzyl)malononitrile (2d); White crystals. mp = 91–92 °C IR (KBr): 3045, 2922, 2259, 2219, 2211 (Ca"N), 1596, 1495, 1411, 1290, 848 and 796 cm^{-1}. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.25 (d, J = 6.6 Hz, 2 H, CH_2), 3.91 (t, *J* = 6.6 Hz,1 H, CH), 7.27 (d, *J* = 8.1 Hz, 2H, 2CH), 7.39 (d, *J* = 8.1 Hz, 2H, 2CH). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 135.1 (C), 131.2 (2 CH), 130.04 (2 CH), 128.86 (CH), 111.53 (2CN), 35.32 (CH_2), 24.57 (CH).

2-(4-Nitrobenzyl)malononitrile (2e). White crystals.mp = 153-155 °C IR (KBr): 3029, 2944, 2241, 2214, 2208 (Ca"N), 1592, 1495, 1438, 1299, 842 and 857 cm-1. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.42 (d, *J* = 6.7 Hz, 2 H, CH_2), 4.08 (t, *J* = 6.6 Hz, 1 H, CH), 7.55 (d, *J* = 9.1 Hz, 2H, 2CH), 8.29 (d, *J* = 9.1 Hz, 2H, 2CH). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 145.2 (C), 145.1 (2 CH), 130.47 (2 CH), 124.56 (CH), 111.46 (2CN), 36.12 (CH_2), 24.23 (CH).

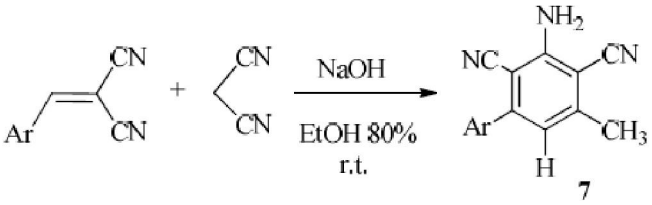
2-(4-Bromobenzyl)malononitrile (2f). White crystals.mp = 138-140 °C IR (KBr): 3031, 2946, 2240, 2215, 2205 (Ca"N), 1589, 1498, 1436, 1298, 840 and 856 cm^{-1}. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.32 (d, J = 7.1 Hz, 2 H, CH_2), 3.98 (t, *J* = 7.1 Hz, 1 H, CH), 7.38 (d, *J* = 6.1 Hz, 2H, 2CH), 7.49 (d, *J* = 7.2 Hz, 2H, 2CH). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ = 132.4 (C), 131.1 (2 CH), 130.43 (2 CH), 124.12 (CH), 112.44 (2CN), 36.18 (CH_2), 24.67 (CH).

The structure of compounds 2a-d was deduced from their melting points, elemental analysis, and high-field ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of 2a exhibited a sharp doublet at δ = 3.29 ppm due to the methylen grope, a triplet at δ = 3.91 ppm for the metheine group, along with characteristic signals for five aromatic H atoms. The 1H-decoupled ^{13}C NMR spectrum of 2a showed 7 distinct resonances in agreement with the structure of the product. ($C_{10}H_8N_2$, C: 76.90; H: 5.16; N: 17.94)

The mp values, elemental analyses, and spectral data of compounds 2a-d, were also in good agreement with those of authentic samples[20].

Arylidenmalononitrile and malononitrile undergo a simple reaction; produce Arylmalononitriles2a-d in 77-86% yields. This reaction carried out in the presence of sodium hydroxide, at solvent free and microwave irradiation conditions (Scheme 1, TABLE 1).

The formation of Arylmalononitriles probably involves electron transfer process and reduction reaction. Since malononitrile anion was an accessible particle in some reactions[33-35], it seems that malononitrile anion be an efficient electron rich moiety in the reaction mixture which can transfer electron/electrons to the electron acceptor moiety. A possible mechanism is proposed in Scheme 2. The first step may involve an electron transfer process from malononitrile anion to Arylmalononitriles to form 2-benzylmalononitrile radical anion 3 which can achieve one H^+ from HCO_3^- and form 2-benzylmalononitrile radical 5, then electron transfer and H^+ attraction processes take place again to produce 2-benzylmalononitrile 2 in good to excellent yields (Scheme 2).



7

Scheme 3 : Synthesis of 3-aryl-2,6-dicyano-5-methylanilines 7 at room temperature

TABLE 1 : Synthesis of compounds 2a-f

2	Ar	Mp°C	Yield[a] %
a	Ph	86-87	85
b	4-MeC6H4	79-80	77
c	4-MeOC6H4	90-91	82
d	4-ClC6H4	91-92	86
e	4-NO2C6H4	153-155	80
f	4-BrC6H4	138-140	78

a Isolated yields

Full Paper

It is Interesting that when this reaction took place in other conditions such as use of sodium hydroxide instead of sodium carbonate, at room temperature rather than microwave irradiation and in ethanol as solvent then 2,6-dicyanoanilines 7 were formed[36] (Scheme 3).

CONCLUSION

The reported method offers a simple reaction for the reduction of some arylidenmalononitriles under microwave irradiation and solvent-free conditions. The use of cheap, readily available starting materials and mild reaction conditions, good yields of the products and short reaction times, catalyst free and solvent free conditions are the main advantages of this method. Catalysts are often expensive, their separation and reuse troublesome has many problems. We have developed herein a simple and catalyst free method for the synthesis of potentially interesting arylemalononitriles.

ACKNOWLEDGEMENT

I gratefully acknowledge the financial support from the Research Council of Payame Noor University (PNU), Tehran-Iran.

REFERENCES

[1] F.Alonso, P.Riente, M.Yus; Tetrahedron, **65**, 10637-10643 **(2009)**.
[2] W.Q.Du, Z.M.Rong, Y.Liang, Y.Wang, X.Y.Lu, Y.F.Wang, L.H.Lu; Chinese Chemical Letters, 23, 773-776 **(2012)**.
[3] M.Heitbaum, R.Froehlich, F.Glorius; Advanced Synthesis & Catalysis, **352**, 357-362 **(2010)**.
[4] Y.Q.Xu, S.L.Yu, Y.Y.Li, Z.R.Dong, J.X.Gao; Chinese Chemical Letters, **24**, 527-530 **(2013)**.
[5] A.Changotra, R.Gupta, S.Paul; Der Pharma Chemica, **6**, (2014).
[6] C.Smit, M.W.Fraaije, A.J.Minnaard; The Journal of organic chemistry, **73**, 9482-9485 **(2008)**.
[7] O.S.Chambyal, S.Paul, T.Shamim, M.Gupta, R.Gupta, A.Loupy; Synthetic Communications, **43**, 656-667 **(2013)**.
[8] J.Che, Y.Lam; Advanced Synthesis & Catalysis, **352**, 1752-1758 **(2010)**.
[9] Q.Liu, J.Li, X.X.Shen, R.G.Xing, J.Yang, Z.Liu, B.Zhou; Tetrahedron Letters, **50**, 1026-1028 **(2009)**.
[10] G.R.A.Adair, K.K.Kapoor, A.L.B.Scolan, J.M.J.Williams; Tetrahedron Letters, **47**, 8943-8944 **(2006)**.
[11] Q.He, Z.Xu, D.Jiang, W.Ai, R.Shi, S.Qian, Z.Wang; RSC Advances, **4**, 8671-8674 **(2014)**.
[12] R.G.Salomon, N.D.Sachinvala, S.R.Raychaudhuri, D.B.Miller, Journal of the American Chemical Society, **106**, 2211-2213 **(1984)**.
[13] B.C.Ranu, S.Samanta; Tetrahedron Letters, **43**, 7405-7407 **(2002)**.
[14] B.Basu, M.M.H.Bhuiyan, P.Das, I.Hossain; Tetrahedron Letters, **44**, 8931-8934 **(2003)**.
[15] B.C.Ranu, S.Samanta; Tetrahedron, **59**, 7901-7906 **(2003)**.
[16] Y.Ren, X.Xu, K.Sun, J.Xu; Tetrahedron: Asymmetry, **16**, 4010-4014 **(2005)**.
[17] S.S.Elmorsy, A.A.S.El Ahl, H.Soliman, F.A.Amer; Tetrahedron Letters, **37**, 2297-2298 **(1996)**.
[18] R.A.Johnstone, A.H.Wilby, I.D.Entwistle; Chemical Reviews, **85**, 129-170 **(1985)**.
[19] D.Xue, Y.C.Chen, X.Cui, Q.W.Wang, J.Zhu, J.G.Deng; The Journal of Organic Chemistry, **70**, 3584-3591 **(2005)**.
[20] Y.S.Feng, C.Y.Yang, Q.Huang, H.J.Xu; Tetrahedron, **68**, 5053-5059 **(2012)**.
[21] J.Kovács, T.D.Todd, J.H.Reibenspies, F.Joó, D.J.Darensbourg; Organometallics, **19**, 3963-3969 **(2000)**.
[22] S.H.Lee, Y.J.Park, C.M.Yoon; Tetrahedron Letters, **41**, 887-889 **(2000)**.
[23] B.C.Ranu, S.Samanta; The Journal of Organic Chemistry, **68**, 7130-7132 **(2003)**.
[24] B.C.Ranu, J.Dutta, S.K.Guchhait; Organic Letters, **3**, 2603-2605 **(2001)**.
[25] V.V.Shinde, S.D.Lee, Y.S.Jeong, Y.T.Jeong; Tetrahedron Letters, **56**, 859-865 **(2015)**.
[26] H.Moghanian, M.Shabanian, H.Jafari, Comptes Rendus Chimie, **15**, 346-349 **(2012)**.
[27] P.Lidström, J.Tierney, B.Wathey, J.Westman; Tetrahedron, **57**, 9225-9283 **(2001)**.
[28] W.Xu, J.Zhou, H.Li, P.Yang, Z.You, Y.Luo; Fuel Processing Technology, **127**, 1-6 **(2014)**.
[29] S.Tu, B.Jiang, Y.Zhang, R.Jia, J.Zhang, C.Yao, F.Shi; Org.Biomol.Chem., **5**, 355-359 **(2007)**.
[30] K.Guo, M.J.Thompson, T.R.Reddy, R.Mutter, B.Chen; Tetrahedron, **63**, 5300-5311 **(2007)**.
[31] R.M.Shaker, A.F.Mahmoud, F.F.Abdel Latif; Journal of the Chinese Chemical Society, **52**, 563-567

(2005).

[32] S.Liu, M.A.Haller, H.Ma, L.R.Dalton, S.H.Jang, A.Y.Jen; Advanced Materials, **15**, 603-607 **(2003)**.

[33] F.J.Smentowski, G.R.Stevenson; The Journal of Physical Chemistry, **74**, 2525-2528 **(1970)**.

[34] C.Gao, X.Tao, Y.Qian, J.Huang; Chemical Communications, 1444-1445 **(2003)**.

[35] C.F.Bernasconi, Jr.R.B.Killion; The Journal of Organic Chemistry, **54**, 2878-2885 **(1989)**.

[36] B.Mohammadi, H.Kazemi, M.Shafieey; Monatshefte für Chemie-Chemical Monthly, **145**, 1649-1652 **(2014)**.