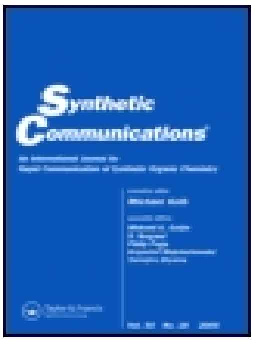

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Regioselective radical addition of 3-oxopropanenitriles with terminal dienes promoted by cerium(IV) ammonium nitrate and manganese(III) acetate

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ABSTRACT
Radical addition of 3-oxopropanenitriles to 1,3-butadiene derivatives promoted by $(NH_4)_2Ce(NO_2)_6$ and $Mn(OAc)_3$ afforded 5-ethenyl-4,5-dihydrofuran-3-carbonitriles in low to good yields. These dihydrofurans were characterised by IR, ^{1}H-NMR, ^{13}C-NMR and HRMS spectra. All radical additions performed via CAN and $Mn(OAc)_3$ were occurred on the terminal double bond on dienes. A mechanism for the formation of the dihydrofurans was proposed.

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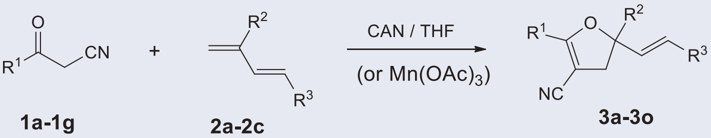
KEYWORDS
Cerium(IV) ammonium nitrate; dihydrofuran; radical addition

GRAPHICAL ABSTRACT



Introduction

Substituted dihydrofurans are significant class of compounds, since they show a wide range of biological activities and form the basic structure of many natural products and medicinal important compounds.[1,2] Attention to synthesis of dihydrofurans obtained by the radical addition of 1,3-dicarbonyls to alkenes mediated by transition metal salts such as $Mn(OAc)_3$[3–8] or $(NH_4)_2Ce(NO_2)_6$ (CAN)[9–12] has increased, due to commercially available and easily synthesized starting materials can be utilized to alter complex reactions in the synthesis of biologically active compounds.

Nishino et al first reported the mechanism and the reaction of acylacetonitriles with alkenes in the presence of $Mn(OAc)_3$.[13,14] Afterwards, we obtained poly functional 4,5-dihydrofuran-carbonitriles by treatment of acylacetonitriles with alkenes and acrylamide derivatives bearing thiophen-2-yl and furan-2-yl groups.[15–20] Moreover, we reported that some 4,5-dihydrofuran-carbonitriles show antibacterial and antifungal activities.[21] In addition of these studies, thus far, our research group has carried out radical

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cyclization of various active methylene compounds with alkenes, alkynes, dienes and acrylamide derivatives.[22–29] $Mn(OAc)_3$ was usually employed as radical oxidant in these reactions. However, very recently we performed an optimization study on the radical addition of 3-oxopropanenitriles to alkenes using CAN in ethereal solvents, resulting in dihydrofurans in high yields on mild condition by CAN/THF system.[30] In the present study, we applied the mentioned method to the reactions of 3-oxopropanenitriles with conjugated dienes promoted CAN/THF and obtained 5-ethenyl-4,5-dihydrofuran-3-carbonitriles as regioselectively. Besides, a comparative study is presented by using MAH and CAN as radical oxidants.

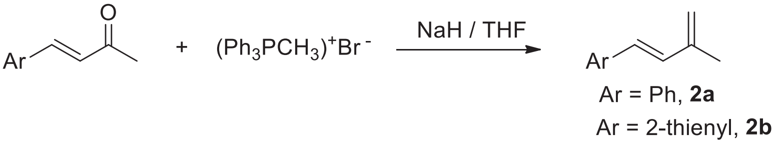
Results and discussions

All 3-oxopropanenitriles (except **1c**) were prepared by treatment of suitable esters and CH_3CN in the presence of NaH/PhMe, according to the literature.[15–20,31] 3-Methyl-1-phenyl-1,3-butadiene **2a**[32,33] and 3-methyl-1-(2-thienyl)-1,3-butadiene **2b**[34] were synthesized by utilizing Wittig reaction of triphenylphosphoniummethyl bromide with benzoylacetone and (*E*)-4-(2-thienyl)but-3-en-2-one, respectively (Scheme 1).

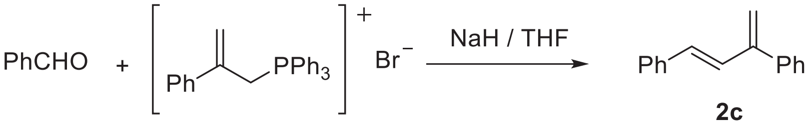
Moreover, 1,3-diphenyl-1,3-butadiene **2c** was obtained from the Wittig reaction of benzaldehyde and triphenyl(2-phenylallyl)phosphonium bromide which was prepared from the reaction of 2-phenylallyl bromide and triphenylphosphine.[35–37] 2-Phenylallyl bromide was obtained from allylic bromination of 2-phenylpropene by NBS in CCl_4[38–41] (Scheme 2). All dienes were freshly prepared before used in the radical addition reactions.

All radical reactions between 3-oxopropanenitriles and conjugated dienes were performed using $Mn(OAc)_3$/AcOH and CAN/THF as single electron generator and all results are displayed in Table 1 and Table 2.

As seen in Table 1, treatment of 3-phenyl-3-oxopropanenitrile **1a** with 3-methyl-1-phenyl-1,3-butadiene **2a** in the presence of $Mn(OAc)_3$/AcOH gave 5-ethenyl-4,5-dihydrofuran-3-carbonitrile **3a** in 53% yield, whereas the product **3a** was obtained in 75% yield by using CAN/THF system. Similarly, radical addition of 4-Me-phenyl (**1b**) and 4-Cl-phenyl (**1c**) substituted 3-oxopropanenitriles to diene **2a** in the presence of CAN formed corresponding dihydrofurans **3b** (53%) and **3c** (60%), respectively. In the reaction of 3-(2-thienyl)-3-oxopropanenitrile **1d** with diene **2a,** yield of product **3d** when



Scheme 1. Synthesis of dienes **2a** and **2b**.



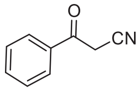
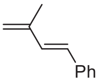
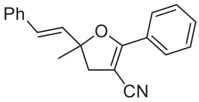
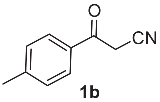
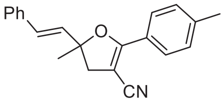
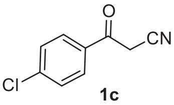
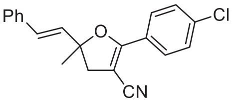
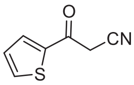
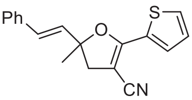
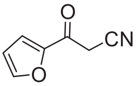
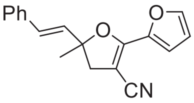
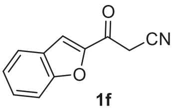
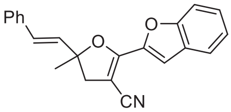
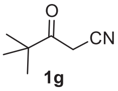
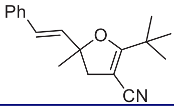
Scheme 2. Synthesis of 1,3-diphenyl-1,3-butadiene **2c**.

employed $Mn(OAc)_3$ (59%) was obtained more than when used CAN (40%) (Entry 4). However, dihydrofurans **3e** and **3f** were produced from the radical addition of 3-(2-furyl) (**1e**) and 3-(2-benzofuryl)-3-oxopropanenitriles (**1f**) to diene **2a** promoted by CAN, respectively. Also, dihydrofuran **3g** (30%) was obtained in low yield by the reaction of 4,4-dimethyl-3-oxopentanenitrile **1g** and **2a**.

When CAN was used as radical oxidant in the reaction of 3-oxopropanenitriles (**1a, 1d, 1e**) with 3-methyl-1-(thiophen-2-yl)-1,3-butadiene **2b,** neither formed (isolable product) any product nor trace dihydrofuran was observed in TLC (Entries 1–3, Table 2). However, we achieved to obtain dihydrofuran-3-carbonitriles **3h–3j** in low yields by the radical addition of diene **2b** with 3-oxopropanenitriles (**1a**, **1e** and **1d**, respectively) mediated by $Mn(OAc)_3$ (Table 2). According to these results, it is clear that no (or any trace of) product could be obtained when thiophen-2-yl group was substituted to either 3-oxopropanenitrile or diene.

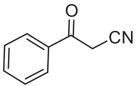
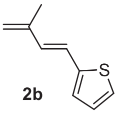
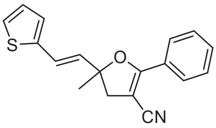
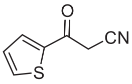
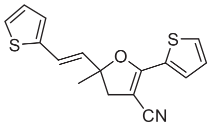
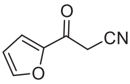
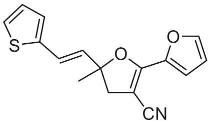
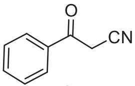
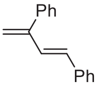
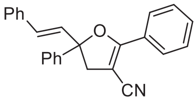
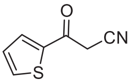
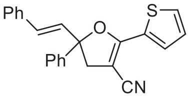
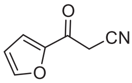
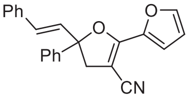
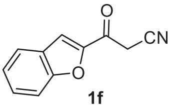
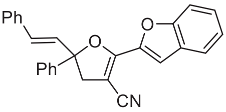
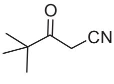
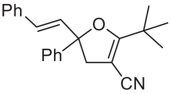
Reaction of 1,3-diphenyl-1,3-butadiene **2c** with **1a** promoted by CAN in THF afforded 4,5-dihydrofuran-3-carbonitrile **3k** (82%) in a very good yield (Entry 4). Also,

Table 1. Synthesis of 5-ethenyl-4,5-dihydrofuran-3-carbonitriles (**3a**–**3g**).

Entry	3-oxopropanenitrile	diene	dihydrofuran	Product and yield (%)[a]
1	 **1a**	 **2a**		**3a**, 75 (53)[b]
2	 **1b**	**2a**		**3b**, 53
3	 **1c**	**2a**		**3c**, 60
4	 **1d**	**2a**		**3d**, 40 (59)[b]
5	 **1e**	**2a**		**3e**, 61
6	 **1f**	**2a**		**3f**, 58
7	 **1g**	**2a**		**3g**, 30

[a]Yield of isolated product based on the amount of diene.
[b]Yields in the brackets were obtained by using $Mn(OAc)_3/AcOH$, the other products were obtained by CAN.

Table 2. Synthesis of 5-ethenyl-4,5-dihydrofuran-3-carbonitriles (**3h**–**3o**).

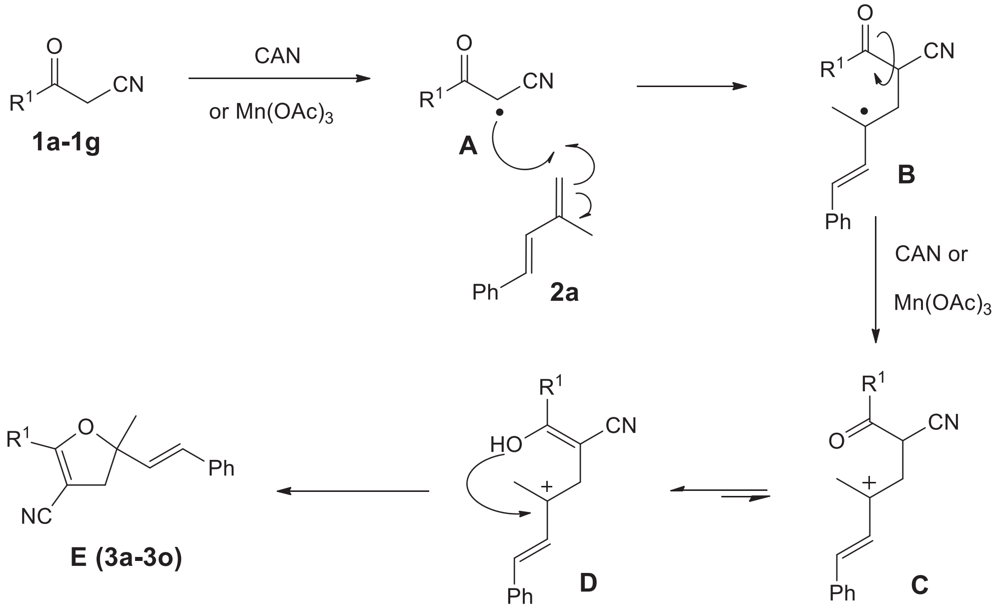
Entry	3-oxopropanenitrile	diene	dihydrofuran	Product and yield (%)[a]
1	 **1a**	 **2b**		**3h**, -- (56)[b]
2	 **1d**	**2b**		**3i**, -- (44)[b]
3	 **1e**	**2b**		**3j**, -- (46)[b]
4	 **1a**	 **2c**		**3k**, 82
5	 **1d**	**2c**		**3l**, -- (88)[b]
6	 **1e**	**2c**		**3m**, 60
7	 **1f**	**2c**		**3n**, 69
8	 **1g**	**2c**		**3o**, 46

[a] Yield of isolated product based on the amount of diene.

[b] Yields in the brackets were obtained by using $Mn(OAc)_3$/AcOH, the other products were obtained by CAN.

radical addition of 2-thienyl substituted 3-oxopropanenitrile **1d** to diene **2c** in the presence of $Mn(OAc)_3$ in AcOH produced **3l** in 88% yield. 2-Furyl **(3m)** and 2-benzofuryl **(3n)** substituted 4,5-dihydrofurans were obtained in good yields by the reactions of **1e** and **1f** with **2c** promoted by CAN. Moreover, 4,5-dihydrofuran **3o** (46%) was synthesised in moderate yield.

The mechanism proposed for the radical addition of conjugated dienes **2a**–**2c** with 3-oxopropanenitriles **1a**–**1g** is illustrated in Scheme 3. According to this mechanism, while Ce^{+4} is reduced to Ce^{+3} (or Mn^{+3} is reduced to Mn^{+2}) an α-carbon radical



Scheme 3. Proposed mechanism for the formation of 5-ethenyl-4,5-dihydrofuran-3-carbonitriles (**3a–o**).

A is formed. Then, addition of the radical to the terminal double bond of the diene **2a** forms an allylic radical intermediate **B.** The radical **B** is oxidized to the carbocation **C** by CAN (or $Mn(OAc)_3$), followed by cyclization of **D** to give 5-(2-phenylvinyl)-4,5-dihydrofuran **E.** All radical addition to the dienes occurred on the terminal double bond of the dienes as regioselectively, other adduct products were not observed.

Conclusion

To sum up, we firstly performed the radical addition of 3-oxopropanenitriles **(1a–1g)** to conjugated dienes **(2a–2c)**, leading to the formation of 5-ethenyl-4,5-dihydrofuran-3-carbonitriles **(3a–3o)** in low to good yields. $Mn(OAc)_3$ and CAN were comparatively used as radical oxidant within the reactions. According to these results, we conclude that $Mn(OAc)_3$ can be used effectively in the reactions of 3-oxopropanenitriles with dienes containing thiophen-2-yl group, on the other hand, CAN is rather efficient with the ones excluding thiophen-2-yl containing dienes.

Experimental

3-(4-Chlorophenyl)-3-oxopropanenitrile and other reagents are commercially available and were purchased as highest purity. Melting points were determined on an electrothermal capillary melting point apparatus. IR spectra (ATR) were obtained with a Bruker Tensor-27 400–4000 cm^{-1} range with 2 cm^{-1} resolution. ^{1}H NMR, ^{13}C NMR, spectra were recorded on a Bruker Avance DPX-400 MHz and Varian Oxford NMR300

High performance Digital FT-NMR spectrophotometers. High Resolution Mass Time-of-Flight (TOF) was measured on an Agilent 1200/6210 LC/MS spectrophotometer. $[Mn(OAc)_3]\cdot 2H_2O$ was prepared by electrochemically method according to the literature.[42] Thin-layer chromatography (TLC) was performed on Merck aluminum-packed silica gel plates. Purification of the products was performed by column chromatography on silica gel (Merck silica gel 60, 40–63 mm).

General procedure for conjugated dienes (2a–2c)

NaH (22 mmol, in 60% mineral oil) was added to a solution of methyltriphenylphosphonium bromide (21 mmol) (or triphenyl(2-phenylallyl)phosphonium bromide for diene **2c**) in anh. THF. This mixture was kept at 60° C for 2 h, and then the corresponding ketone or aldehyde (20 mmol) was added dropwise under stirring and cooling in ice maintaining the temperature between 0° and 5 °C. The temperature was then rapidly raised to r.t. temperature for 5 h. The THF was then removed under pressure and the residue was extracted with hexane (5 × 20 mL). The organic phase was dried (Na_2SO_4) and concentrated, and the crude product purified by column chromatography (hexane as eluent).

3-Methyl-1-phenyl-1,3-butadiene (2a)[32,33]

^1H NMR (400MHz, $CDCl_3$), δ_H 7.42 (d, $J = 7.2$ Hz, 2H, arom. CH), 7.31 (t, $J = 7.6$ Hz, 2H, arom. CH), 7.24 (t, $J = 7.6$ Hz, 1H, arom. CH), 6.88 (d, $J = 16.0$ Hz, 1H, H_{olef}), 6.53 (d, $J = 16.0$ Hz, 1H, H_{olef}), 5.11 (s, 1H, H_{olef}), 5.07 (s, 1H, H_{olef}), 1.97 (s, 3H, Me).

3-Methyl-1-(thiophene-2-yl)-1,3-butadiene (2b)[34]

^1H NMR (400MHz, $CDCl_3$), δ_H 7.15 (d, $J = 4.4$ Hz, 1H, arom. CH), 6.99–6.96 (m, 2H, arom. CH), 6.71 (d, $J = 16.0$ Hz, 1H, H_{olef}), 6.65 (d, $J = 16.0$ Hz, 1H, H_{olef}), 5.08 (s, 1H, H_{olef}), 5.04 (s, 1H, H_{olef}), 1.94 (s, 3H, Me).

1,3-Diphenyl-1,3-butadiene (2c)[35–37]

^1H NMR (400MHz, $CDCl_3$), δ_H 7.48 (d, $J = 6.4$ Hz, 2H, arom. CH), 7.40–7.15 (m, 8H, arom. CH), 6.63 (d, $J = 12.0$ Hz, 1H, H_{olef}), 6.36 (d, $J = 12.0$ Hz, 1H, H_{olef}), 5.54 (s, 1H, H_{olef}), 5.26 (s, 1H, H_{olef}).

General procedure for synthesis of dihydrofurans using $Mn(OAc)_3$

$[Mn(OAc)_3]\cdot 2H_2O$ (2.5 mmol) in AcOH (10 mL) was heated under N_2 to 80 °C until it dissolved. Thereafter, the soln. was cooled to 60 °C, and a soln. of 3-oxopropanenitrile (1.2 mmol) and conjugated diene (1 mmol) in AcOH (5 mL) was added. The reaction was completed when the initial dark brown solution had disappeared (10–30 min). Afterward, H_2O (20 mL) was added and the mixture extracted with $CHCl_3$ (3 × 20 mL). The combined organic phase was neutralized with sat. $NaHCO_3$ solution, dried

(Na_2SO_4), concentrated and the crude product was purified by column chromatography or preparative TLC (silica gel, hexane/AcOEt as eluent).

General procedure for synthesis of dihydrofurans using CAN

To a solution of 3-oxopropanenitrile (1 mmol) and diene (1.2 mmol) in THF (10 mL) under N_2, a mixture of CAN (2.5 mmol) and $NaHCO_3$ (2.5 mmol) was added at 45 °C. The reaction was completed when the orange colour of CAN had disappeared (10–30 min) or when the 3-oxopropanenitrile spot on TLC had completely vanished. H_2O was added to the solution and the mixture was extracted with $CHCl_3$ (3×20 mL). The combined organic phase was dried (Na_2SO_4) and concentrated and the crude product purified by column chromatography (hexane:AcOEt (5:1) as eluent).

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