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Organic Electrosynthesis: A Promising Alternative Methodology for the Synthesis of Nanosized Particles of Pyrans

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An electrochemical strategy is presented herein for the synthesis of pyran nanoparticles by an electro-generated base from a propanol anion in a one-pot, three-component reaction. This reaction includes the condensation of isatin or an aromatic aldehyde, ethyl acetoacetate, and malononitrile in propanol in the presence of sodium bromide as an electrolyte in an undivided cell. The effects of current, temperature, solvent, time and anode type were studied. The optimized current and temperature is 20 mA cm^{-2} and 25 °C for the synthesis of spiropyrans nanoparticles, and is 40 mA cm^{-2} and 50 °C for producing nanosized particles of 4*H* pyrans. The formation of propanol anions on the surface of the cathode-generated malononitrile anion proceeded by Knoevenagel condensation which is followed by a Michael addition and ended by the intramolecular ring-closing strategy. The products were characterized after purification using infrared spectroscopy (IR), ^{1}H and ^{13}C nuclear magnetic resonance, scanning electron microscope (SEM), and dynamic light scattering (DLS). The proposed method produces pyran nanoparticles directly from initial compounds in a safe and mild condition.

Keywords: Electrochemical synthesis, Nanoparticles, Pyran, Malononitrile

INTRODUCTION

Heterocyclic compounds have useful pharmacological and biological properties, such as cytotoxic [1], antitubercular [2], neuroprotective [3], antifungal [4], antimicrobial [5], antiviral [6], antioxidant and tyrosinase inhibitory properties [7]. Multi component reactions (MCRs) are effective methods for the production of diverse chemical libraries of drug-like molecules in heterocyclic scaffolds. MCRs increase the efficiency by combining several operational steps without changing the reaction conditions or isolating the intermediates [8]. Previously, pyrans were produced in the presence of catalysts such as piperidine [9], triethylamine [10], K_2CO_3 [11], Mg/La [12], PEG1000-DAIL/EM [13], nano ZnO [14], $SnCl_2$/nano SiO_2 [15], $ZnFe_2O_4$ [16] and nano magnesium oxide [17]. 4*H*-pyrans and pyran-annulated heterocyclic scaffolds represent a "privileged" structural motif that is well distributed in naturally occurring compounds with a broad range of significant biological activities, including anticancer [18], cytotoxic [19], anti-HIV [20], anti-inflammatory [21], antimalarial [22], antimicrobial [23], antihyperglyce-mic and antidyslipidemic activities [24]. They can also play an anti-neurodegenerative role in disorders like Alzheimer's, Parkinson's, and Huntington's disease [25] and many more [26].

Although there are methods available for the synthesis of different pyrans, their technical complexity, general use of heating, expensive catalyst or organic solvents with toxic properties limit the significant synthetic potential of these methods [11-17,27,28]. There is still a high demand for facile and simple procedures for the preparation of pyran derivatives using a cheap and readily available catalyst, although several methods have been reported for the

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synthesis of these compounds [29-34]. Over the last couple of years, considering the fact that the society is about to develop environmentally compatible processes, organic electrosynthesis has been introduced as one of the methodologies to fulfill several important criteria needed for this issue.

There are several characteristics making the electrochemical production of organic compounds less polluting compared to classical methods; these include high material utilization, application of mild reaction conditions, lower amount of energy required, ease of reaction control, less hazardous processes due to the reduced waste production, and the ability to perform a wide range of multi component reactions [35-37]. Due to the importance of the synthesis of this compound and the disadvantages of previously reported synthetic routes, this article is presented to consider the electrosynthesis of pyran nanoparticles in one step. Previously, the production of nanosized particles of organic compounds required two stages: the first for the synthesis, and the other for the fabrication of the nanosized particles [38-42].

EXPERIMENTAL

Apparatus and Reagents

Constant-current coulometry and preparative electrolysis were performed using a SAMA potentiostate/galvanostate (Isfahan, Iran). The electrolysis cell was equipped with an iron cathode (5 cm^2) and a magnesium anode (5 cm^2). NMR spectra were recorded on a Bruker DRX-300 Avance instrument. The IR spectra were recorded on a Bruker IFS-66 FT-IR spectrophotometer. Scanning electron microscopy (SEM) was run with an axl30 scanning electron micro analyzer (Philips, Netherlands) at an acceleration voltage of 20.0 kV. The melting point of the products was obtained using an electro thermal melting point apparatus (UK), 9200. All the compounds were commercially available, obtained from Merck, and used without further purification.

Preparation of Nanosized Particles of Ethyl-2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (4a)

For synthesis of nanoparticles of spiropyran (4a), a mixture of 1 mmol ethylacetoacetate (1), malononitrile (2), isatin (3) and NaBr (0.05 g, 0.5 mmol) in anhydrous propanol (25 ml) was used. The mixture was stirred and electrolyzed in an undivided cell equipped with an iron cathode (5 cm^2) and magnesium anode (5 cm^2) at room temperature, under constant current density of 20 mA cm^{-2} (I = 100 mA). After the completion of the reaction (monitored by thin-layer chromatography, ethyl acetate/*n*-hexane 1:1), the solvent was evaporated under reduced pressure, and then 20 ml ethanol (80%) was added to the reaction mixture. The resulting solid was separated by centrifugation.

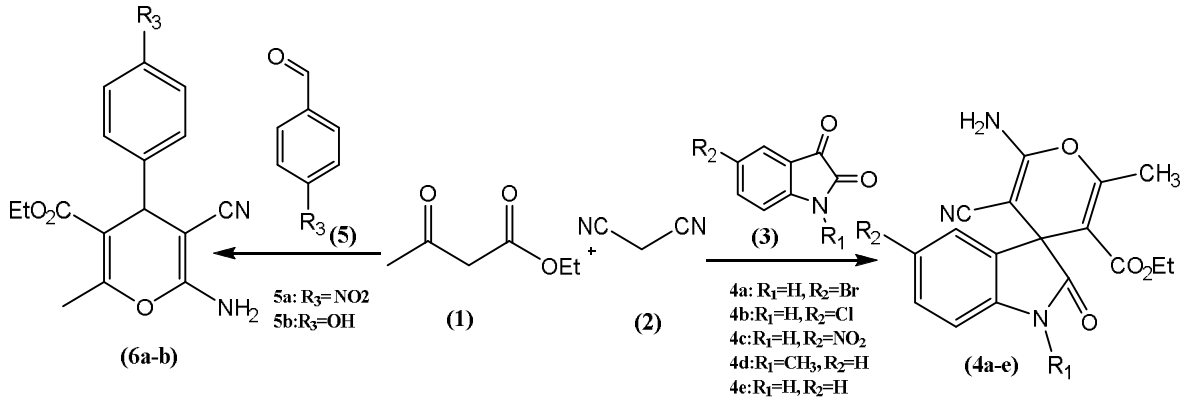
Characteristics of the Selected Products

Ethyl-2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxo-spiro[indoline-3,4'-pyran]-5'-carboxylate (4a). Dark brown; Yield 90%; M. p.: 254-256 °C; IR (KBr): ν = 3335 (NH), 3317 (NH), 2207 (CN), 1710 (C=O), 1703 (C=O), 1654, 1476, 1418, 1380, 1282, 1222, 1073; ^{1}H NMR (DMSO-d_6): δ = 0.83 (t, 3H, J = 6.8 Hz, CH_3), 2.33 (s, 3H, CH_3), 3.81 (q, 2H, J = 6.9 Hz, CH_2), 6.77 (m, 1H, Ar-H) , 7.23-7.34 (m, 2H, Ar-H, 2H, NH_2), 10.57 (br.s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ = 13.5, 19.2, 49.6, 56.3, 60.8, 104.1, 111.7, 113.9, 117.8, 126.7, 131.7, 137.6, 141.8, 159.3, 160, 164.8, 178.7. Anal. Calcd. for $C_{17}H_{14}BrN_3O_4$: C, 50.51; H, 3.49; N, 10.4%. Found: C, 50.82; H, 3.36; N, 10.32%.

Ethyl-2'-amino-3'-cyano-1,6'-dimethyl-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (4d)

Light brown; Yield 96%; M. p.: 212-214 °C; IR (KBr): ν = 3360 (NH), 3174 (NH), 2199 (CN), 1710 (C=O), 1697 (C=O), 1370, 1287, 1073 ; ^{1}H NMR (DMSO-d_6): δ = 0.72 (t, 3H, *J* = 6.7 Hz, CH_3), 2.33 (s, 3H, CH_3), 3.13 (s, 3H, CH_3), 3.71-3.72 (m, 2H, CH_2), 6.96-7.07 (m, 2H, ArH), 7.09-7.17 (m, 1H, ArH), 7.20 (br.s, 2H, NH_2), 7.27-7.34 (m, 1H, ArH). ^{13}C NMR (DMSO-*d6*): δ = 13.1, 18.5, 26.4, 48.4, 56.1, 60.1, 104.4, 108.1, 117.2, 122.5, 123.0, 128.7, 133.7, 143.4, 158.8, 158.9, 164.2, 176.9. Anal. Calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38%. Found: C, 63.76; H, 5.01; N, 12.33%.

Ethyl-2'-amino-3'-cyano-6'-methyl-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (4e). Dark brown; Yield 92%; M. p.: 256-258 °C, IR (KBr): 3482 (NH), 3223 (NH), 3156 (NH); 2191 (CN), 1701 (C=O), 1691 (C=O), 1381, 1288, 1211, 1072; ^{1}H NMR (DMSO-*d_6*): δ = 0.85 (t, 3H, *J* = 7.2 Hz, CH_3), 2.39 (s, 3H, CH_3), 3.83 (q, 2H, *J* = 6.6



Scheme 1. Formation of pyrans

Hz, CH_2), 6.82 (m, 1H, Ar-H), 7.2-7.22 (m, 3H, Ar-H), 7.26 (br.s, 2H, NH_2), 10.58 (br.s, 1H, NH). ^{13}C NMR (DMSO-*d6*): δ = 13.5, 19.4, 49.6, 55.5, 61, 103.4, 110, 117.6, 119.6, 126.5, 136.4, 142.9, 149, 159.4, 161, 164.6; 179.6. Anal. Calcd. for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92%. Found: C, 62.84; H, 4.58; N, 12.97%.

Ethyl-6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (6a). Dark brown; Yield 90%; M. p.: 177-179 °C, IR (KBr): ν = 3433 (NH), 3322 (NH), 2190 (CN), 1680 (C=O), 1689 (C=O), 1343; ^{1}H NMR (DMSO-d_6): δ = 1.02 (t, 3H, *J* = 7.2 Hz, CH_3), 2.35 (s, 3H, CH_3), 3.96 (q, 2H, *J* = 7.2 Hz, CH_2), 4.47(s, 1H, CH), 7.10 (s, 2H, NH_2) , 7.44 (d, 2H, J = 8.7 Hz, Ar-H), 8.20 (d, 2H, J = 8.7 Hz, Ar-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.1, 18.8, 39.2, 56.6, 60.8, 106.5, 119.7, 124.2, 129.0, 146.8, 153.0, 158.4, 159.0, 165.5. Anal. Calcd. for $C_{16}H_{15}N_3O_5$: C, 58.36; H, 4.59; N, 12.76%. Found: C, 58.23; H, 4.46; N, 12.79%.

Ethyl-6-amino-5-cyano-4-(4-hydroxyphenyl)-2-methyl-4H-pyran-3-carboxylate (6b). White yellow; Yield 83%; M. p.: 185-187 °C, IR (KBr): ν = 3402 (NH), 3327 (NH), 3221; 2190 (CN), 1673 (C=O), 1667 (C=O), 1646, 1530; ^{1}H NMR (DMSO-d_6): δ = 1.02 (t, 3H, *J* = 5.3 Hz, CH_3), 2.33 (s, 3H, CH_3), 3.94 (q, 2H, *J* = 6.8 Hz, CH_2), 4.51 (s, 1H, CH), 7.07 (br.s, 2H, NH_2), 7.62-7.66 (m, 2H, Ar-H), 7.96 (s, 1H, OH), 8.07-8.12 (m, 2H, ArH).^{13}C NMR (DMSO-*d6*): δ = 13.6, 16.3, 56.2, 60.3, 106.2, 119.3, 121.7, 121.9, 130.1, 134.2, 147.3, 147.7, 157.6, 158.6, 165.0. Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33%. Found: C, 63.91; H, 5.44; N, 9.27%.

RESULTS AND DISCUSSION

Herein, the synthesis of nanosized particles of pyrans (4,6) was reported, following to the other nanoparticles such as 3-hydroxy-3-(1*H*-indol-3-yl) indolin-2-one [43], 2-amino-pyranes [44], 2-amino-4*H*-chromenes [45], spirooxindoles [46], and phthalazines [47] synthesized before, *via* a green one-pot three-component reaction including ethylacetoacetate (1), malononitrile (2) and isatin (3) or aldehyde (5). Electrical current was applied as an efficient catalyst under mild conditions that resulted in good and excellent yields (Scheme 1).

In order to optimize the synthesis conditions, several factors such as current, anode type, time, solvent and temperature were investigated (Tables 1 and 2).

It is shown in Table 1 that the best conditions for minimizing the synthesis time and maximizing the production yields of spiropyrans nanosized particles are dry propanol at a current density of 20 mA cm^{-2} (I = 100 mA, electrode surface = 5 cm^2) at 25 °C. In the same manner, Table 2 shows that the optimized condition for producing nanosized particles of 4*H* pyrans is dry propanol at a current density of 40 mA cm^{-2} (I = 200 mA, electrode surface = 5 cm^2) at 50 °C. To examine the scope and generality of this protocol, various isatins or aldehydes were employed in the next experiments (Table 3).

SEM micrographs of template-synthesized nanoparticles obtained from powder are shown in Fig. 1. The average particle size, DSEM, is <100 nm. Existence of Mg^{2+} in the

Table 1. Comparison of the Effect of Different Temperatures, Time and Currents on the Reaction of Ethylacetoacetate (1), Malononitrile (2) and Isatins (3a) to Obtain Spirooxindole Derivative (4a)

Entry[a]	Current (mA)	Temperature (°C)	Time (min)	Electricity passed (F mol^{-1})	Yield (%)[b]
1	50	50	150	4.7	62
2	50	25	360	11.2	84
3	50	50	360	11.2	80
4	100	50	120	7.5	63
5	100	50	360	22.3	79
6	100	25	150	9.3	80
7	100	25	300	18.7	90
8	100	25	360	22.4	90
9	200	25	360	44.8	83
10	200	50	300	37.3	81
11	400	25	360	89.5	80
12	600	25	360	134.3	80

For all the reactions, 0.5 mmol of NaBr, an iron cathode (5 cm^2), and *n*-propanol as solvent were used. [a]Magnesium (5 cm^2) was used as the anode. [b]Isolated yields based on ethylacetoacetate.

Table 2. Comparison of the Effect of Different Temperatures, Solvents, Anodes and Currents on the Reaction of Ethylacetoacetate (1), Malononitrile (2) and 4-Nitrobenzaldehyde (3b) to Obtain 4*H*-pyran Derivative (6b)

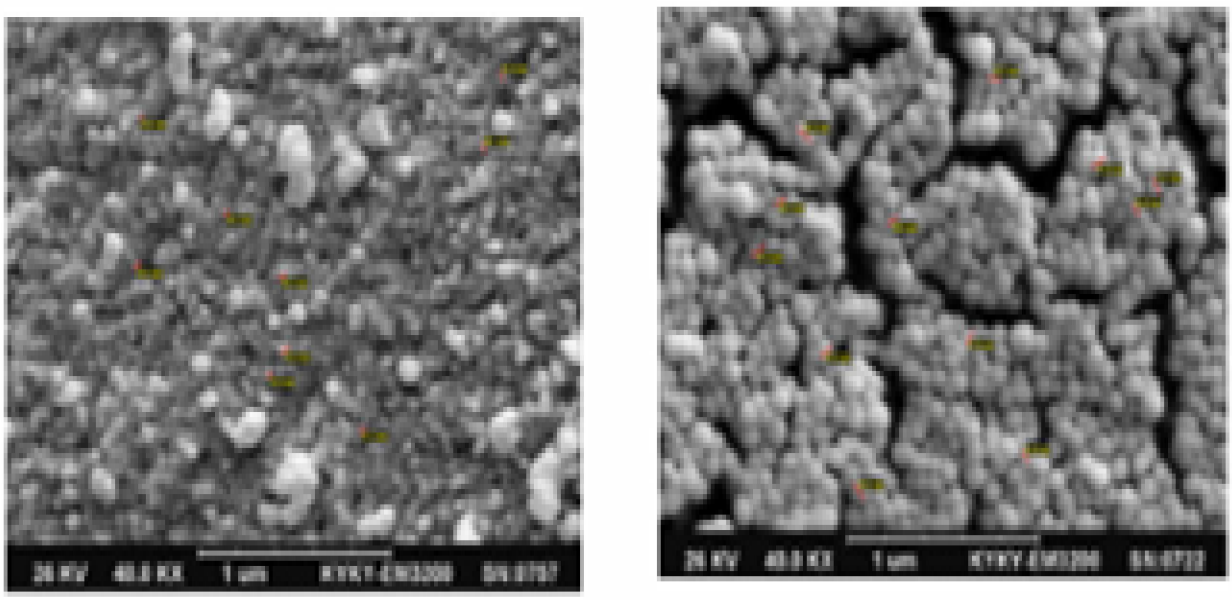
Entry	Current (mA)	Temperature (°C)	Time (min)	Electricity passed (F mol^{-1})	Solvent	Yield (%)[c]
1[a]	100	25	150	9.3	Propanol	83
2[a]	100	50	90	5.6	Propanol	92
3[a]	200	50	45	5.6	Propanol	95
4[a]	200	50	135	8.4	Ethanol	79
5[b]	50	25	>3h	>5.6	Ethanol	30
6[b]	50	50	>3h	>5.6	Ethanol	Side product
7[b]	100	25	>3h	>11.2	Propanol	44
8[b]	100	50	200	12.4	Propanol	70

For all the reactions, 0.5 mmol of NaBr, and an iron cathode (5 cm^2) were used. [a]Magnesium (5 cm^2) and [b]Graphite (5 cm^2) were used as the anode. [c]Isolated yields based on ethylacetoacetate.

Table 3. Results Obtained from the Reaction of a Series of Representative Ethylacetoacetate, Malononitrile, Aldehyde or Isatin to Obtain Nanoparticles of Pyrans (4,6)[a]

Compound[b]	R_1	R_2	R_3	Yield (%)	Time (min)	IR (cm^{-1}) CN(ν), CO(ν)	M.p. (°C)	Lit. M.p. (°C)
4a	H	Br	-	90	80	2207, 1703	254-256	262-264[48]
4b	H	Cl	-	96	80	2206, 1705	264-266	277-278[48]
4c	H	NO_2	-	82	60	2207, 1723	248-250	251-252[49]
4d	CH_3	H	-	96	90	2199, 1710	212-214	214-216[50]
4e	H	H	-	92	100	2191, 1701	256-258	260-261[49]
6a	-	-	4-Nitro	90	90	2199, 1690	177-179	174-177[51]
6b	-	-	4-OH	83	60	2190, 1673	185-187	175-176[51]

[a]For all the reactions, 0.5 mmol of NaBr, an iron cathode (5 cm^2) and a magnesium anode (5 cm^2) were used at 25 °C for compound (4) and 50°C for compound (6). [b]Isolated yields based on ethyl acetoacetate.



(a) **(b)**

Fig. 1. SEM images of nanoparticles of a) Ethyl-2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate(4a), and b)6-Amino-5-cyano-2-methyl-4-(4-nitro-phenyl)-4*H*-pyran-3-carboxylic acid ethyl ester (6a).

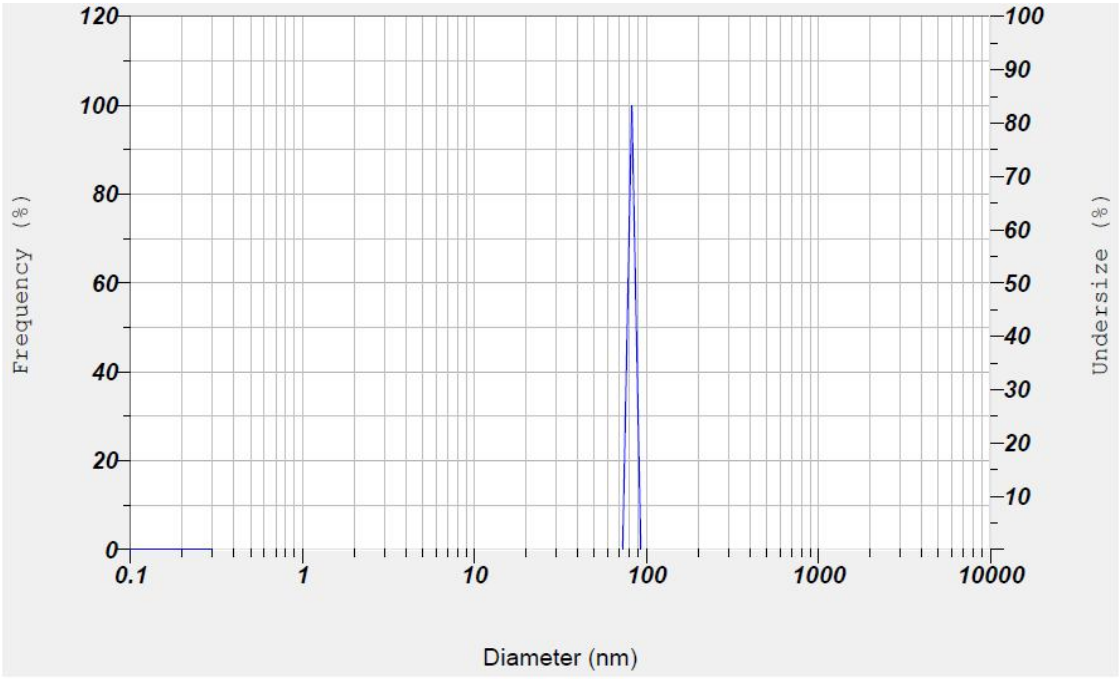


Fig. 2. Particle size distribution diagram of nanoparticles of 6-amino-5-cyano-2-methyl-4-(4-nitro-phenyl)-4*H*-pyran-3-carboxylic acid ethyl ester.

solution may prevent the aggregation of the products and nanoparticles formation. [44]

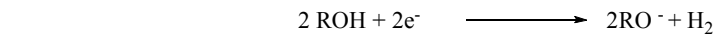
Particle size distribution diagram of product 4a is shown in Fig. 2. The mean radii of nanoparticles are 77.5 ± 0.1 nm. Considering the above results and strong literature review [52,53], the mechanism of the proposed method is as follows: an alkoxide anion is formed on the surface of the cathode by deprotonation of an alcohol. The subsequent reaction taking place between the alkoxide anion and malononitrile gives rise to the malononitrile anion. Knoevenagel condensation of the malononitrile anion with isatin (3) or aldehyde (5) occurs through the elimination of water and the formation of derivative intermediates (7 or 8) (Scheme 2).

Subsequently, the condensation of enol (1) with 7 or 8 leads to intermediate 9 or 10, in which the nucleophilic oxygen group attacks the cyano moiety and products (4, 6) are formed (Schemes 3, 4) [44]. The structure of the compounds (4, 6) were deduced from ^{1}H NMR, ^{13}C NMR and IR spectral data. Despite the loss of magnesium electrode during the reaction, this electrode was used as anode due to advantages such as shorter reaction time, higher yield, and production of nontoxic Mg^{2+}.

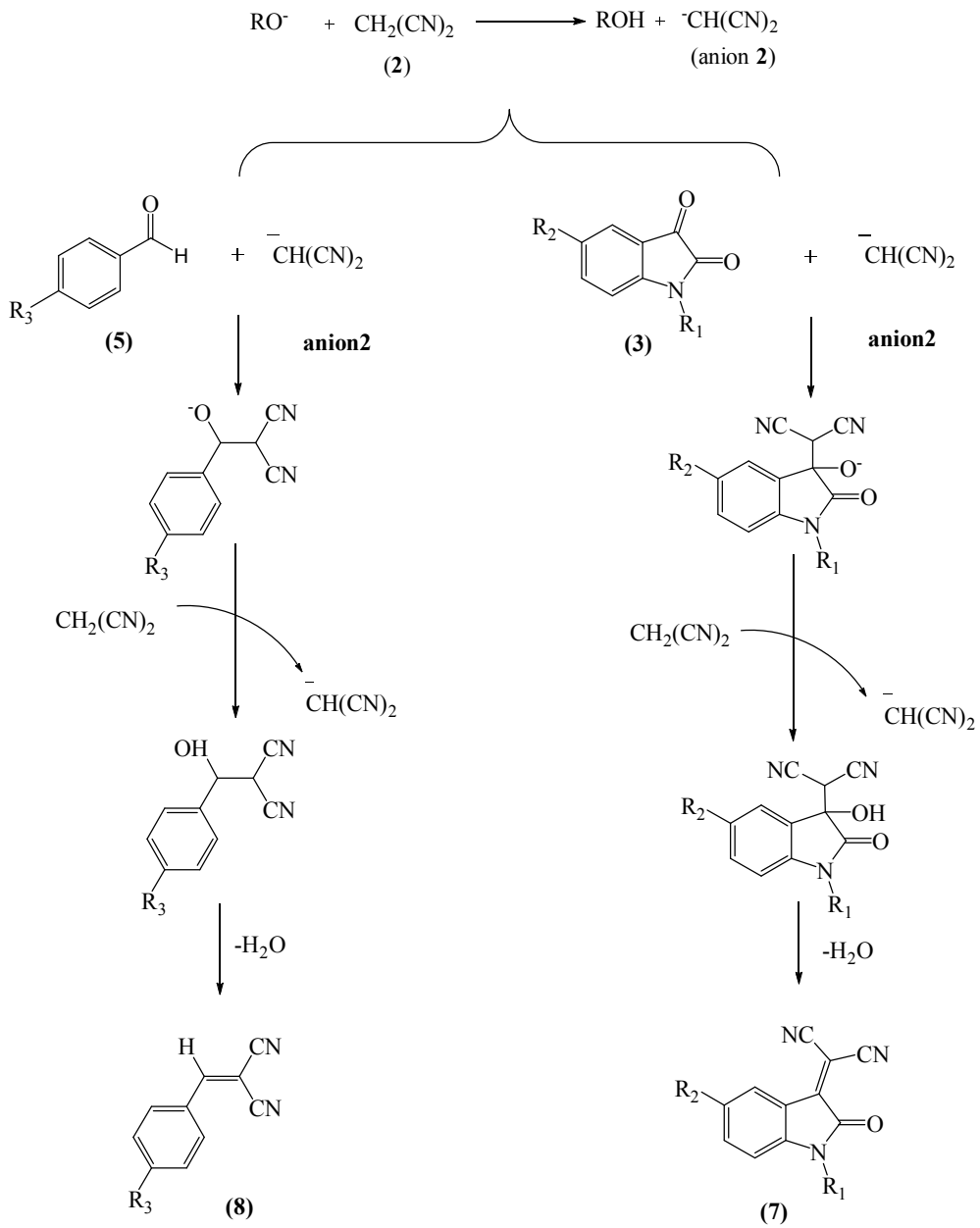
CONCLUSIONS

A pathway was introduced for the synthesis of pyran nanoparticles. The application of electrosynthetic method has some significant advantages. The clean synthesis, one-step reaction, using electricity as an alternative source of energy instead of oxidative reagents, technical feasibility, and high atom economy are of the prominent advantages for this green approach. In addition to using electrosynthesis as a green method and biological properties of pyrans, size reduction is a fundamental unit operation having important applications in pharmacy. Decrease in size, reduction in toxicity, improvement in solubility and bioavailability and enhancement of release provide better formulation opportunities for drugs.

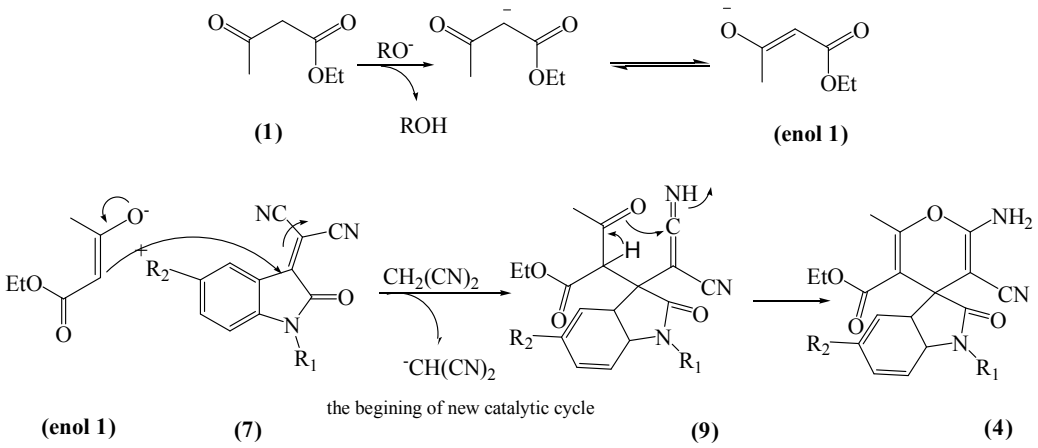
Cathode:



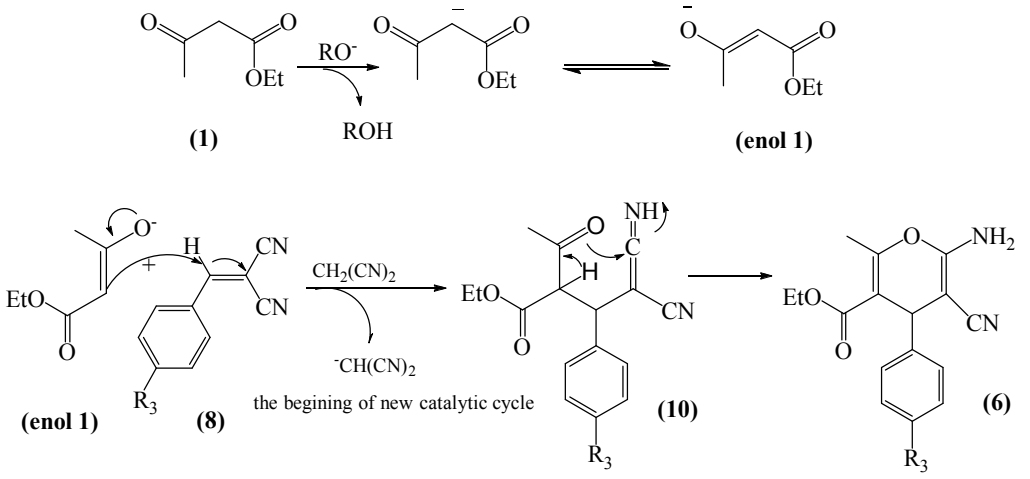
In solution:



Scheme 2. Formation of intermediate 7 and 8



Scheme 3. Formation of the pyrans through intermediate 7



Scheme 4. Formation of the pyrans through intermediate 8

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REFERENCES

[1] A. Zonouzi, R. Mirzazadeh, M. Safavi, S.K. Ardestani, S. Emami, A. Foroumadi, Iran J. Pharm. Res. 12 (2013) 679.

[2] C. Chen, M. Lu, Z. Liu, J. Wan, Z. Tu, T. Zhang, M. Yan, Open J. Med. Chem. 3 (2013) 128.

[3] R. Larget, B. Lockhart, P. Renard, M. Largeron, Bioorg. Med. Chem. Lett. 10 (2000) 835.

[4] T.A. Nakib, V. Bezjak, S. Rashid, B. Fullam, M.J. Meegan, J. Med. Chem. 26 (1991) 221.

[5] N. Mishriky, A.S. Girgis, F.M. Asaad, Y.A. Ibrahim, U.I. Sobieh, N.G. Fawzy, Boll. Chim. 140 (2001) 129.

[6] P.W. Smith, S.L. Sollis, P.D. Howes, P.C. Cherry, I.D. Starkey, K.N. Cobley, H. Weston, J. Scicinski, A. Merritt, A. Whittington, P. Wyatt, J. Med. Chem. 41 (1998) 787.

[7] H.S. Rho, H.S. Baek, J.W. You, S.J. Kim, J.Y. Lee, D.H. Kim, I.S. Chang, Bull. Korean Chem. 28 (2007)

471.
[8] L. Weber, Curr. Med. Chem. 23 (2002) 2085.
[9] G.P. Lu, C.A. Cai, J. Heterocycl. Chem. 48 (2011) 124.
[10] V.N. Marshalkin, A.V. Samet, V.V. Semenov, Chem. Heterocycl. Compd. 34 (1998) 1409.
[11] Z. Karimi-Jaberi, B. Pooladian, Sci. World J. 33 (2012) 1945.
[12] N.S. Babu, N.Pasha, K.V. Rao, P.S. Prasad, N. Lingaiah, Tetrahedron Lett. 49 (2008) 2730.
[13] D. Fang, J.M. Yang, H.B. Zhang, C.M. Jiao, J. Ind. Eng. Chem. 17 (2011) 386.
[14] P. Bhattacharyya, K. Pradhan, S. Paul, A.R. Das, Tetrahedron Lett. 53 (2012) 4687.
[15] J. Safaei-Ghomi, R. Teymuri, H. Shahbazi-Alavi, A. Ziarati, Chin. Chem. Lett. 24 (2013) 921.
[16] A. Khazaei, A. Ranjbaran, F. Abbasi, M. Khazaei, A.R. Moosavi-Zare, RSC Adv. 18 (2015) 13643.
[17] M. Babaie, H. Sheibani, Arab. J. Chem. 4 (2011) 159.
[18] J.Y.C. Wu, W.F. Fong, J.X. Zhang, C.H. Leung, H.L. Kwong, M.S. Yang, D. Li, H.Y. Cheung, Eur. J. Pharmacol. 473 (2003) 9.
[19] T. Raj, R.K. Bhatia, A. Kapur, M. Sharma, A.K. Saxena, M.P.S. Ishar, Eur. J. Med. Chem. 45 (2010) 790.
[20] M. Rueping, E. Sugiono, E. Merino, Chem. Eur. J. 14 (2008) 6329.
[21] D.O. Moon, K.C. Kim, C.Y. Jin, M.H. Han, C. Park, K.J. Lee, Y.M. Park, Y.H. Choi, G.Y. Kim, Int. Immunopharmacol. 7 (2007) 222.
[22] V.F. De Andrade-Neto, M.O.F. Goulart, J.F. Da Silva Filho, M.J. Da Silva, M.D.C.F.R. Pinto, A.V. Pinto, M.G. Zalis, L.H. Carvalho, A.U. Krettli, Bioorg. Med. Chem. Lett. 14 (2004) 1145.
[23] L.R. Morgan, B.S. Jursic, C.L. Hooper, D.M. Neumann, K. Thangaraj, B. Leblance, Bioorg. Med. Chem. Lett. 12 (2002) 3407.
[24] A. Kumar, R.A. Maurya, S.A. Sharma, P. Ahmad, A.B. Singh, G. Bhatia, A.K. Srivastava, Bioorg. Med. Chem. Lett. 19 (2009) 6447.
[25] W.O. Foye, Principi di Chemico Farmaceutica, Piccin: Padora, Italy, 1991, p. 416.
[26] Y.L. Zhang, B.Z. Chen, K.Q. Zheng, M.L. Xu, X.H. Lei, X.B. Yaoxue, Chem. Abstr. 96 (1982) 135383e.
[27] A. Shahrisa, Z. Ghasemi, M. Saraei, J. Heterocyclic Chem. 46 (2009) 273.
[28] D. Armesto, W.M. Horspool, N. Martin, A. Ramos, C. Seoane, J. Org. Chem. 54 (1998) 3069.
[29] T.S. Jin, L.B. Liu, T.S. Li, Synth. Commun. 35 (2005) 1859.
[30] R. Ballini, G. Bosica, M.L. Conforti, R. Maggi, A. Mazzacani, P. Righi, G. Sartori, Tetrahedron 57 (2001) 1395.
[31] R. Maggi, R. Ballini, G. Sartori, R. Sartorio, Tetrahedron Lett. 45 (2004) 2297.
[32] R. Ghahremanzadeh, T. Amanpour, A. Bazgir, J. Heterocyclic Chem. 46 (2009) 1266.
[33] A. Bazgir, G. Hosseini, R. Ghahremanzadeh, ACS Comb. Sci. 15 (2013) 530.
[34] L.M. Wang, N. Jiao, J. Qiu, J.J. Yu, J.Q. Liu, F.L. Guo, Y. Liu, Tetrahedron 66 (2010) 339.
[35] B.A. Frontana-Uribe, R.D. Little, J.G. Ibanez, A. Palma, R. Vasquez-Medrano, Green Chem. 12 (2010) 2099.
[36] M. Ameri, A.R Asghari, A. Amoozadeh, H. Daneshinejad, D. Nematollahi, Chin. Chem. Lett. 5 (2014) 797.
[37] D. Nematollahi, A. Amani, E. Tammari, J. Org. Chem. 10 (2007) 3646.
[38] P. Alessi, A. Cortesi, I. Kikic, N.R. Foster, S.J. Macnaughton, I. Colombo, Ind. Eng. Chem. Res. 35 (1996) 4718.
[39] [39] A.C. Cortopassi, P.J. Ferrara, T.M. Wawiernia, J.T. Essel, Int. J. Energetic Mater. Chem. Propulsion 7 (2008) 39.
[40] R. Thakur, R.B. Gupta, Chem. Eng. Commun. 3 (2006) 293.
[41] M. Jaiswal, R. Dudhe, P.K. Sharma, Biotech. 5 (2015) 123.
[42] F. Shakeel, S. Baboota, A. Ahuja, J. Ali, M.S. Faisal, S. Shafiq, Thai J. Pharm. Sci. 32 (2008) 4.
[43] S. Makarem, A.R. Fakhari, A.A. Mohammadi, Monatsh Chem. 143 (2012) 1157.
[44] S. Makarem, A.R. Fakhari, A.A. Mohammadi, Ind. Eng. Chem. Res. 51 (2012) 2200.
[45] S. Makarem, A.A. Mohammadi, A.R. Fakhari, Tetrahedron Lett. 49 (2008)7194.
[46] Z.M. Darvish, B. Mirza, S. Makarem, J. Heterocyclic.

Chem. 54 (2017) 1763.
[47] S. Makarem, A.R. Fakhari, A.A. Mohammadi, Anal. Bioanal. Chem. Res. 2 (2015) 85.
[48] Y. Li, H. Chen, C. Shi, D. Shi, S. Ji, J. Comb. Chem. 12 (2010) 231.
[49] G.D. Wang, X.N. Zhang, Z.H. Zhang, J. Heterocyclic Chem. 50 (2013) 61.
[50] A.A. S.El-Ahl, H. Afeefy, M.A. Metwally, J. Chem. Res. Miniprint 1 (1994) 201.
[51] M. Gupta, M. Gupta, V.K. Gupta, New J. Chem. 39 (2015) 3578.
[52] M.N. Elinson, V.M. Merkulova, A.I. Ilovaisky, D.V. Demchuk, P.A. Belyakov, G.I. Nikishin, Mol. Divers. 14 (2010) 833.
[53] M.N. Elinson, A.I. Ilovaisky, V.M. Merkulova, D.V. Demchuk, P.A. Belyakov, Y.N. Ogibin, G.I. Nikishin, Electrochim. Acta 53 (2008) 8346.