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ARTICLE

Efficient and selective iron-mediated reductive Claisen rearrangement of propargyloxyanthraquinones to anthrafurandiones in ionic liquids

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Abstract: An efficient and rapid method is described for the reductive Claisen rearrangement of different propargyloxyanthraquinones to anthra[1,2-b]furan-6,11-diones for first time using iron powder in a mixture of two ionic liquids, namely 1-methylimidazolium tetrafluoroborate [Hmim]BF_4 and 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl. The present method is able to execute single or double Claisen rearrangements of 1,4- or 1,5-bispropargyloxyanthraquinones selectively, so that the desired anthra(mono)furandiones or anthra(bis)furandiones are produced, respectively, as the major product.

Key words: propargyloxyanthraquinone, Claisen rearrangement, anthrafurandione, iron, ionic liquid.

Résumé : Le présent article est le premier à décrire une méthode efficace et rapide pour effectuer le réarrangement de Claisen de différentes propargyloxyanthraquinones en anthra[1,2-b]furan-6,11-diones par voie réductrice en présence de poudre de fer dans un mélange de liquides ioniques, à savoir le tétrafluoroborate de 1-méthylimidazolium ([Hmim]BF_4) et le chlorure de 1-benzyl-3-méthylimidazolium ([Bzmim]Cl). Cette méthode permet d'exécuter sélectivement un réarrangement de Claisen unique ou double de 1,4-bispropargyloxyanthraquinones ou de 1,5-bispropargyloxyanthraquinones pour produire respectivement les anthra(mono)furandiones ou anthra(bis)furandiones désirées comme produit majoritaire. [Traduit par la Rédaction]

Mots-clés : propargyloxyanthraquinone, réarrangement de Claisen, anthrafurandione, fer, liquide ionique.

Introduction

Anthraquinone derivatives are considered an important group in organic chemistry due to their applications in various fields such as preparation of photochemical and colorimetric sensor systems[1] and the dye industry (e.g., textile dyestuff),[2] as well as their anti-inflammatory,[3] anticancer,[4–6] antioxidant,[7] antimicrobial, and antiviral[8] properties. Moreover, some anthraquinone derivatives have been extracted from slimming tea,[9] and some others are found in some other plants such as lichens and fungi and even in some insects, forming their colour as natural pigments. However, a narrow choice of reactions is considered for the functionalization of anthraquinones due to inertness of their skeleton to a variety of electrophilic substitution reactions. In this connection, reductive Claisen rearrangement of allyloxyanthraquinones can be used as a known and progressive way for this purpose and introduction of a carbon–carbon new bond onto the structure of anthraquinones.[10] This [3,3] sigmatropic rearrangement has been carried out using various reductants[10] such as dithionate[11] and glucose.[12] However, these reported methods suffer from some disadvantages such as long reaction times, reduction or isomerization of double bond in the rearranged allyl group, and low yields. Also, the use of sodium metabisulfite as a reagent has been reported for performing this rearrangement.[13]

In continuation of our previous work on the reductive Claisen rearrangement of allyloxyanthraquinones with silver/potassium iodide as a reagent in acetic acid,[14] and also with respect to importance of ionic liquids and their applications in organic synthesis as environmentally friendly solvents,[15] we report an efficient and selective method for the reductive Claisen rearrangement of propargyloxyanthraquinones producing anthrafurandiones using iron powder in a mixture of two ionic liquids 1-methylimidazolium tetrafluoroborate [Hmim]BF_4[16] and 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl in short reaction times (Scheme 1). As far as we know, this is the first method for reductive Claisen rearrangement of propargyloxyanthraquinones.

Experimental

Solvents, reagents, and chemicals were obtained from Merck, Fluka, or Aldrich chemical companies. Some substrates and products are known compounds[10,17,18] and were characterized by comparison of their physical or spectral data with authentic samples. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer RXI spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on Brucker Avance 300, 400, and 500 spectrometers. UV–vis spectra were obtained with an Analytik Jena SPECORD 205 spectrometer. Also, elemental analyses were performed using an Elementar vario EL III analyzer. Melting points were determined in open capillary tubes in an Electrothermal 9100 melting point apparatus. Thin layer chromatography (TLC) was carried out on silica gel 254 analytical sheets obtained from Fluka.

Typical procedure for the conversion of 1-hydroxyanthraquinone (3) to 1-(prop-2′-ynyloxy)anthraquinone (1)

Dry potassium carbonate (4.5 mmol, 0.62 g) was added to a flask containing a solution of **3** (2.23 mmol, 0.50 g) in DMF (30 mL). The reaction mixture was stirred at 90 °C for 15 min. Then, propargyl bromide (4.5 mmol, 0.48 mL) was added and the stirring was continued about 30 min. Propargyl bromide (2 mmol, 0.21 mL) was

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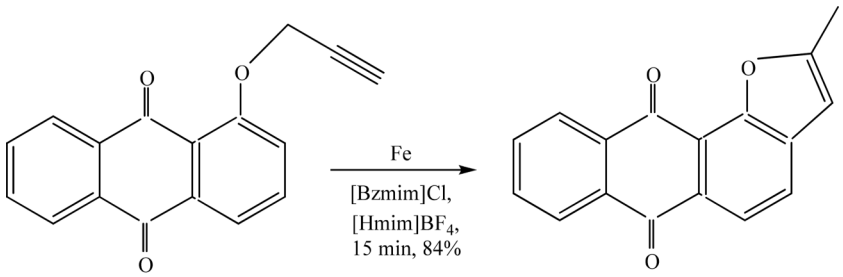
Scheme 1. Iron-mediated reductive Claisen rearrangement of 1-(prop-2′-ynyloxy)anthraquinone (**1**) to 2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (**2**) in a mixed ionic liquids [Hmim]BF_4 and [Bzmim]Cl.



(1) (2)

added again and the stirring was continued until TLC showed the completion of the reaction after 15 min. The reaction mixture was filtered and the residue was washed with hot DMF (10 mL). The product was precipitated after addition of distilled water (30 mL) to the filtrate and then filtered. **1** was obtained after washing of precipitate with water (2 × 20 mL) and crystallization from acetone as yellow needles in 95% yield (0.55 g); mp = 218–220 °C (lit.[18a] 219–220 °C).

Typical procedure for the reductive Claisen rearrangement of 1 to 2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (2)

Iron powder (2 mmol, 0.11 g) was added to a flask containing a solution of two ionic liquids [Hmim]BF_4 (0.85 g) and [Bzmim]Cl (2.50 g) and **1** (1 mmol, 0.26 g) in an oil bath at 160 °C. The reaction mixture was stirred until TLC showed the completion of the reaction (15 min). The reaction mixture was cooled to room temperature and then filtered after addition of CH_2Cl_2 (2 × 20 mL). The organic layer was washed with water (50 mL), saturated $NaHCO_3$ (40 mL), and brine (40 mL). **2** was obtained after evaporation of organic solvent and column chromatography of crude mixture on silica gel 60 using n-hexane:ethyl acetate (30:1) as eluent in 84% yield (0.22 g) together with **3** in 5% yield (0.011 g).

Data

1-Methoxy-4-(prop-2′-ynyloxy)anthraquinone (6)

Bright yellow needles; mp = 170–172 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.58 (s, 1H), 4.04 (s, 3H), 4.90 (s, 2H), 7.36–7.38 (d, 1H, J = 9.2 Hz), 7.54–7.57 (d, 1H, J = 9.2 Hz), 7.74 (s, 2H), 8.19 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.93, 58.60, 76.53, 78.43, 119.30, 119.50, 122.76, 125.00, 126.46, 126.54, 133.35, 133.50, 134.05, 134.28, 151.52, 155.52, 178.82, 183.35 ppm; IR (KBr): 3260 (s), 3014 (w), 3005 (w), 2950 (w), 2850 (w), 2132 (m), 1667 (s), 1587 (s), 1441 (s), 1314 (s), 1282 (s), 1239 (s), 965 (s), 742 (s) cm^{-1}; UV (MeOH), λ_{max} (log ε): 280 (4.07), 415 (4.09) nm; Anal. Calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.10. Found: C, 73.27; H, 3.74.

1-Hydroxy-8-(prop-2′-ynyloxy)anthraquinone (11)

Bright yellow needles; mp = 163–165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.64 (s, 1H), 5.00 (s, 2H), 7.32–7.34 (d, 1H, J = 8.00 Hz), 7.54–7.56 (d, 1H, J = 8.00 Hz), 7.64–7.68 (m, 1H), 7.78–7.82 (m, 2H), 8.06–8.08 (d, 1H, J = 7.60 Hz), 12.93 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 57.22, 77.09, 77.34, 117.02, 118.95, 120.52, 121.28, 124.82, 126.64, 133.38, 134.32, 135.52, 136.01, 158.72, 162.52, 182.55, 188.75 ppm; IR (KBr): 3432 (br), 3265 (m), 3080 (w), 2925 (s), 2856 (m), 2120 (w), 1673 (m), 1641 (s), 1582 (m), 1455 (s), 1264 (s), 1096 (s), 1020 (s), 803 (s), 710 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 210 (3.78), 225 (3.90), 255 (4.58), 270 (4.51), 390 (3.67) nm; Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.59. Found: C, 72.53; H, 3.34.

1-Methoxy-8-(prop-2′-ynyloxy)anthraquinone (13)

Golden needles; mp = 170–172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.53–2.55 (t, 1H, J = 2.39 Hz), 4.01 (s, 3H), 4.93–4.94 (d, 2H, J = 2.39 Hz), 7.29–7.32 (d, 1H, J = 8.38 Hz), 7.47–7.51 (dd, 1H, J = 8.37, 1.01 Hz), 7.62–7.68 (m, 2H), 7.82–7.85 (dd, 1H, J = 7.69, 1.02 Hz), 7.89–7.92 (dd, 1H, J = 7.67, 1.08 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.50, 57.27, 77.16, 78.02, 118.02, 118.95, 120.26, 121.09, 123.82, 125.10, 133.55, 134.02, 134.71, 134.82, 157.09, 159.46, 182.56, 183.78 ppm; IR (KBr): 3265 (m), 3015 (w), 2921 (m), 2851 (w), 2132 (w), 1667 (s), 1588 (s), 1465 (w), 1442 (w), 1315 (s), 1282 (s), 1240 (s), 965 (s), 742 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 288 (3.66), 382 (4.25) nm; Anal. Calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.10. Found: C, 72.81; H, 3.74.

1-Hydroxy-5-(prop-2′-ynyloxy)anthraquinone (17)

Orange needles; mp = 155–157 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.58–2.60 (t, 1H, J = 2.4 Hz), 4.94–4.95 (d, 2H, J = 2.4 Hz), 7.23–7.79 (m, 5H), 8.03–8.06 (m, 1H), 12.45 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.14, 76.97, 77.54, 115.51, 119.40, 120.63, 121.02, 122.45, 123.10, 134.76, 134.84, 135.43, 136.95, 158.17, 161.96, 181.46, 188.32 ppm; IR (KBr): 3427 (br), 3234 (s), 3006 (w), 2925 (s), 2856 (m), 2116 (w), 1654 (m), 1634 (m), 1602 (m), 1587 (m), 1454 (m), 1284 (s), 1263 (s), 1240 (s), 1072 (m), 705 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 290 (3.87), 402 (4.28) nm; Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.59. Found: C, 72.75; H, 3.24.

1,5- Bis(prop-2′-ynyloxy)anthraquinone (19)

Bright yellow needles; mp = 257–259 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.56–2.58 (t, 2H, J = 2.37 Hz), 4.94 (d, 4H, J = 2.35 Hz), 7.43–7.46 (d, 2H, J = 8.39 Hz), 7.69–7.75 (t, 2H, J = 7.9 Hz), 7.96–7.98 (d, 2H, J = 7.77 Hz) ppm; ^{13}C NMR (DMSO, 75 MHz): δ 56.55, 78.65, 79.05, 119.36, 119.56, 120.73, 135.16, 136.84, 157.02, 181.20 ppm; IR (KBr): 3236 (s), 3014 (w), 2924 (w), 2856 (w), 2115 (w), 1666 (s), 1585 (s), 1458 (m), 1442 (m), 1278 (s), 1261 (s), 1241 (s), 1072 (m), 983 (s), 704 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 290 (3.43), 376 (3.92) nm; Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.79. Found: C, 75.29; H, 3.50.

2-Methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (2)

Yellow needles; mp = 191–193 °C (lit.[19a] 192–193 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.65 (s, 3H), 6.55 (s, 1H), 7.78–7.86 (m, 3H), 8.20–8.23 (d, 1H, J = 8.1 Hz), 8.30–8.34 (m, 2H) ppm.

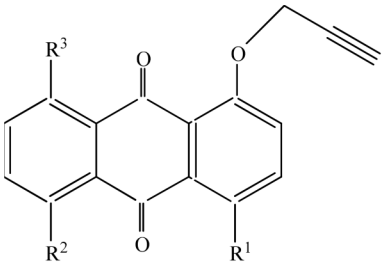
5-Methoxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (7)

Yellow needles, mp = 225–228 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.63 (s, 3H), 4.08 (s, 3H), 6.46 (s, 1H), 7.39 (s, 1H), 7.73–7.80 (m, 2H), 8.24–8.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.77, 56.91, 102.97, 109.14, 117.35, 118.93, 126.19, 127.14, 132.77, 133.07, 134.07, 134.99, 137.52, 146.98, 156.80, 163.25, 182.70, 183.35 ppm; IR (KBr): 3071 (w), 2923 (w), 2861 (w), 1667 (s), 1591 (m), 1567 (m), 1467 (s), 1255 (s), 1234 (s), 984 (s), 725 (s) cm^{-1}; UV (MeOH), λ_{max} (log ε): 255 (3.76), 280 (3.69), 410 (3.35) nm; Anal. Calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.10. Found: C, 73.81; H, 4.00.

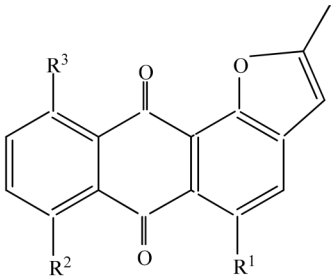
2,5-Dimethyl-7,12-dihydroanthra[1,2-b: 3,4-b′]difuran-7,12-dione (9)

Yellow needles; mp = 295–297 °C (lit.[19c] 296–297 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.681–2.684 (d, 6H, J = 0.78 Hz), 6.647–6.650 (d, 2H, J = 0.89 Hz), 7.75–7.78 (m, 2H), 8.29–8.32 (m, 2H) ppm.

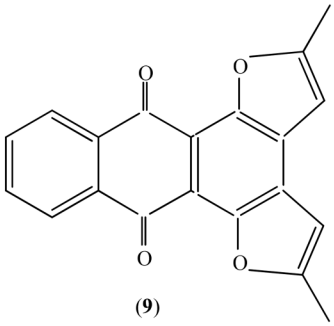
Scheme 2. The propargyloxyanthraquinones used as substrates and the produced anthrafurandiones.



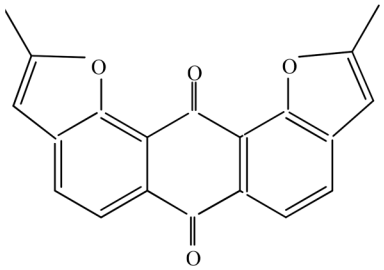
R^1, R^2, R^3= H (**1**)
R^1= OH; R^2, R^3= H (**4**)
R^1= OCH_3; R^2, R^3= H (**6**)
R^1= $OCH_2C{\equiv}CH$; R^2, R^3= H (**8**)
R^1, R^2= H; R^3= OH (**11**)
R^1, R^2= H; R^3= OCH_3 (**13**)
R^1, R^2= H; R^3= $OCH_2C{\equiv}CH$ (**15**)
R^1, R^3= H; R^2= OH (**17**)
R^1, R^3= H; R^2= $OCH_2C{\equiv}CH$ (**19**)



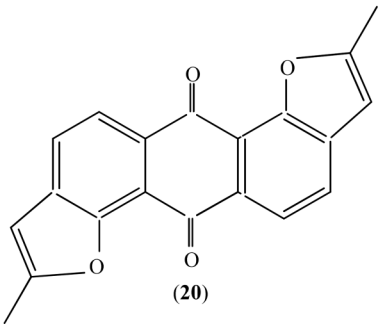
R^1, R^2, R^3= H (**2**)
R^1= OH; R^2, R^3= H (**5**)
R^1= OCH_3; R^2, R^3= H (**7**)
R^1= $OCH_2C{\equiv}CH$; R^2, R^3= H (**10**)
R^1, R^2= H; R^3= OH (**12**)
R^1, R^2= H; R^3= OCH_3 (**14**)
R^1, R^3= H; R^2= OH (**18**)
R^1, R^3= H; R^2= $OCH_2C{\equiv}CH$ (**21**)



(**9**)



(**16**)



(**20**)

2-Methyl-5-(prop-2′-ynyloxy)-6,11-dihydroanthra[1,2-b]furan-6,11-dione (10)

Yellow needles, mp = 247–248 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.65 (s, 3H), 2.70 (s, 1H), 4.96 (s, 2H), 6.51 (s, 1H), 7.59 (s, 1H), 7.76–7.79 (m, 2H), 8.25–8.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.76, 58.33, 76.53, 78.38, 101.98, 103.08, 113.68, 126.28, 126.72, 127.16, 132.80, 133.23, 133.72, 134.10, 134.81, 137.16, 154.21, 163.30, 182.45, 183.09 ppm; IR (KBr): 3386 (m), 3065 (w), 2925 (s), 2855 (m), 2150 (m), 1667 (m), 1592 (m), 1461 (s), 1351 (s), 1230 (s), 1219 (s), 1014 (s), 784 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 295 (4.09), 400 (4.00) nm; Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.79. Found: C, 75.34; H, 3.39.

10-Hydroxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (12)

Red needles, mp = 211–214 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.68 (s, 3H), 6.57 (s, 1H), 7.31–7.33 (d, 1H, J = 8.4 Hz), 7.67–7.71 (t, 1H, J = 7.6 Hz), 7.84–7.88 (m, 2H), 8.19–8.21 (d, 1H, J = 8.0 Hz), 12.72 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.71, 103.33, 119.46, 122.52, 124.36, 125.75, 126.44, 126.93, 133.37, 133.95, 136.61, 136.97, 151.88, 162.07, 162.42, 182.42, 188.66 ppm; IR (KBr): 3433 (br), 3083 (w), 2922 (m), 2830 (m), 1669 (s), 1638 (s), 1583 (s), 1481 (s), 1456 (s), 1356 (s), 1286 (s), 1240 (s), 1022 (s), 779 (s), 744 (s) cm^{-1}; UV (MeOH), λ_{max} (log ε): 280 (3.96), 395 (3.39) nm; Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.59. Found: C, 73.64; H, 3.32.

10-Methoxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (14)

Brick red needles; mp = 160–162 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.61 (s, 3H), 4.05 (s, 3H), 6.51 (s, 1H), 7.32–7.34 (d, 1H, *J* = 8.35 Hz), 7.68–7.77 (m, 2H), 7.94–7.96 (d, 1H, *J* = 7.85 Hz), 8.11–8.12 (d, 1H, *J* = 8.05 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.62, 56.49, 103.08, 117.89, 119.58, 121.53, 122.17, 124.83, 128.43, 131.02, 134.70, 135.63, 136.99, 151.93, 160.21, 161.87, 182.41, 183.67 ppm; IR (KBr): 3099 (w), 2924 (s), 2853 (s), 1663 (m), 1583 (m), 1450 (m), 1321 (s), 1302 (s), 1279 (s), 1244 (s), 1111 (m), 740 (w) cm^{-1}; UV (MeOH), λ_{max} (log ε): 294 (3.58), 380 (3.58) nm; Anal. Calcd for $C_{18}H_{12}O_4$: C, 73.97; H, 4.10. Found: C, 72.86, H, 3.74.

2,10-Dimethyl-6,12-dihydroanthra[1,2-b:8,7-b′]difuran-6,12-dione (16)

Yellow needles, mp = 290–291 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.65 (s, 6H), 6.55 (s, 2H), 7.82–7.84 (d, 2H, J = 8.0 Hz), 8.20–8.22 (d, 2H, J = 8.4 Hz) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.66, 103.04, 121.26, 122.02, 125.45, 129.05, 136.74, 151.88, 161.91, 182.35, 183.40 ppm; IR (KBr): 3102 (w), 2996 (w), 2943 (w), 2830 (w), 1697 (m), 1671 (s), 1586 (s), 1439 (s), 1318 (s), 1276 (s), 1234 (s), 1053 (s), 982 (s), 787 (m), 744 (s) cm^{-1}; UV (MeOH), λ_{max} (log ε): 260 (4.00), 290 (4.15), 335 (3.87), 365 (3.96) nm; Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.79. Found: C, 75.39; H, 3.62.

7-Hydroxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (18)

Yellow needles; m p = 210–212 °C; 1H NMR($CDCl_3$, 500 MHz): δ 2.64 (s, 3H), 6.54 (s, 1H), 7.28–7.30 (dd, 1H, J = 8.4, 1.0 Hz), 7.65–7.68 (m, 1H), 7.83–7.84 (m, 2H), 8.19–8.20 (d, 1H, J = 8.15 Hz), 12.74 (s, 1H) ppm; 13C NMR($CDCl_3$, 125 MHz): δ 14.65, 100.93, 103.26, 119.17, 121.85, 124.14, 125.69, 128.80, 133.83, 133.90, 136.47, 137.42, 151.86, 162.37, 162.49, 181.94, 188.79 ppm; IR (KBr): 3439 (s, br), 3099 (w), 2919 (m), 2856 (m), 1671 (m), 1625 (s), 1598 (s), 1579 (m), 1447 (m), 1308 (m), 1278 (s), 1232 (s), 919 (m), 774 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 294 (3.78), 414 (3.68) nm; Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.59. Found: C, 72.54; H, 3.28.

2-Methyl-7-(prop-2′-ynyloxy)-6,11-dihydroanthra[1,2-b]furan-6,11-dione (21)

Bright yellow needles, mp = 170–172 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.58 (s, 1H), 2.63 (s, 3H), 4.96 (s, 2H), 6.52 (s, 1H), 7.49–7.51 (d, 1H, J = 8.25 Hz), 7.72–7.75 (t, 1H, J = 8.55 Hz), 7.81–7.83 (d, 1H, J = 8.05 Hz), 8.05–8.06 (d, 1H, J = 8.3 Hz), 8.15–8.17 (d, 1H, J = 8.1 Hz) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.60, 57.33, 76.70, 77.88, 103.07, 117.29, 120.73, 120.88, 122.23, 122.50, 125.91, 130.82, 134.51, 135.89, 136.22, 151.35, 157.90, 161.55, 182.42, 182.58 ppm; IR (KBr): 3233 (m), 3015 (w), 2923 (s), 2852 (m), 2118 (w), 1670 (m), 1595 (m), 1581 (m), 1443 (w), 1269 (s), 1235 (m), 1040 (m), 926 (w) cm^{-1}; UV (MeOH), λ_{max} (log ε): 298 (2.74), 378 (3.45) nm; Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.79. Found: C, 75.16; H, 3.50.

Results and discussion

First, we selected **1** as a model compound and studied its reductive Claisen rearrangement using iron powder (2 equiv.) in mixed ionic liquids [Hmim]BF_4 and [Bzmim]Cl at 160 °C. Under these conditions, we found that the desired product **2** was produced in 84% yield together with depropargylated product (5%) after only 15 min. It must be noted that the omission of each of these ionic liquids caused the yield of the desired product **2** to decrease to 0%–20%. However, thermal operation of this rearrangement in the absence of iron gave **2** in only 10% yield with concomitant formation of depropargylated product in 50% yield. In addition, reduction of the reaction temperature to 130 °C caused the yield of the product **2** to decrease to 40%. Also, this rearrangement was unsuccessful when potassium chloride KCl was used instead of [Bzmim]Cl. In this case, the starting material (**1**) remained completely intact after 2 h. Then, we applied these conditions for performing the reductive Claisen rearrangement of other structurally different propargyloxyanthraquinones to their corresponding anthrafurandiones (Scheme 2). The results are shown in Table 1. All of these propargyloxyanthraquinones as substrates mentioned in this table were conveniently synthesized from the reaction of the corresponding hydroxyanthraquinones with propargyl bromide in the presence of dry potassium carbonate in DMF as solvent at 90 °C with reaction times up to 2 h.

As shown in Table 1, structurally different anthrafurandiones are synthesized from their corresponding propargyloxyanthraquinones via the present method with short reaction times and in good to excellent yields. Most notable in this table, is that it is possible to carry out reductive Claisen rearrangement of 1,4- or 1,5-bispropargyloxyanthraquinone so that singly or doubly rearranged product is obtained as major product with remarkable selectivity via the controlling of the molar ratio of the reductant or reaction time (Table 1, compare entries 5 with 6 and also 11 with 12).

Table 1. Reductive Claisen rearrangement of propargyloxyanthraquinones with iron in a mixture of two ionic liquids [Hmim]BF_4 and [Bzmim]Cl at 160 °C.

Entry no.	Substrate	Product	Molar ratio AQ:Fe	Time (min)	Yield (%)
1	**1**	**2**	1:2	15	84
		Depropargylated			5
2	**4**	**5**	1:2	5	98
3	**6**	**7**	1:2	10	83
		5			12
4	**8**	**9**	1:2	2	67
		10			15
		5			8
5	**8**	**9**	1:2	6	90
		5			8
6	**8**	**9**	1:1	3	5
		10			72
		5			7
		Doubly depropargylated			5
7	**11**	**12**	1:3	12	73
		Depropargylated			15
8	**13**	**14**	1:2	5	62
		12			8
9	**15**	**16**	1:4	4	73
		Doubly depropargylated			16
10	**17**	**18**	1:2	7	96
11	**19**	**20**	1:0.5	15	81
		21			10
		18			7
12	**19**	**20**	1:0.5	5	23
		21			52
		18			5

Note: The yields are isolated yields. AQ, anthraquinone.

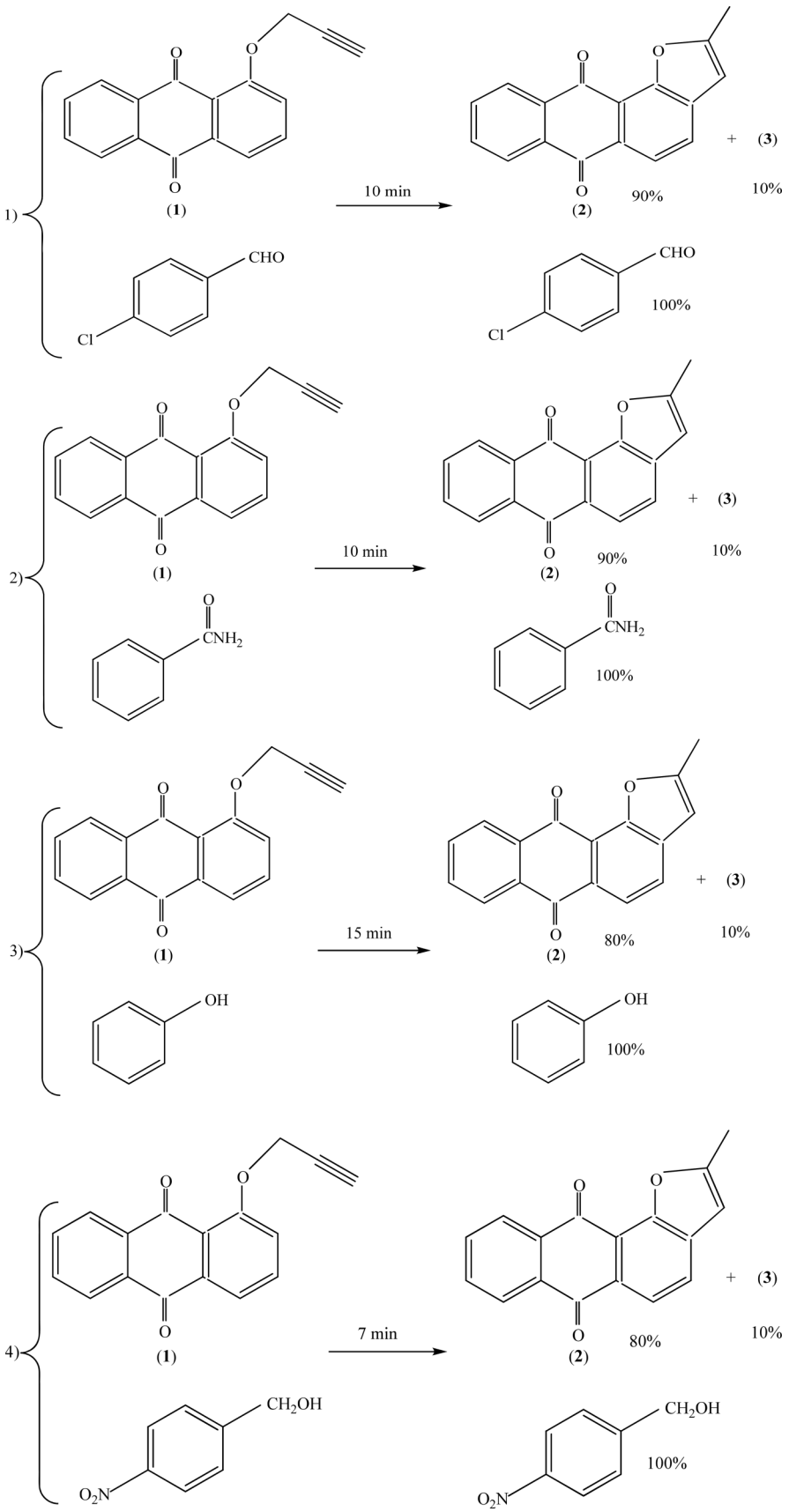
In addition, for obtaining deeper insight into the applicability and other aspects of selectivity of the present method, we examined the possibility of the reductive Claisen rearrangement of propargyloxyanthraquinones in the presence of some other functional groups in different binary mixtures. For this purpose, reductive Claisen rearrangement of **1** was studied in the presence of another compound containing a specified functional group (1:1) using iron powder (2 equiv.) in mixed ionic liquids [Hmim]BF_4 and [Bzmim]Cl at 160 °C. The results and conversion yields of these selective reactions are shown in Scheme 3.

As shown in Scheme 3, this rearrangement can also be carried out in the presence of some other functional groups including aldehydes, carboxylic amides, phenols, and alcohols with excellent selectivity via the present method.

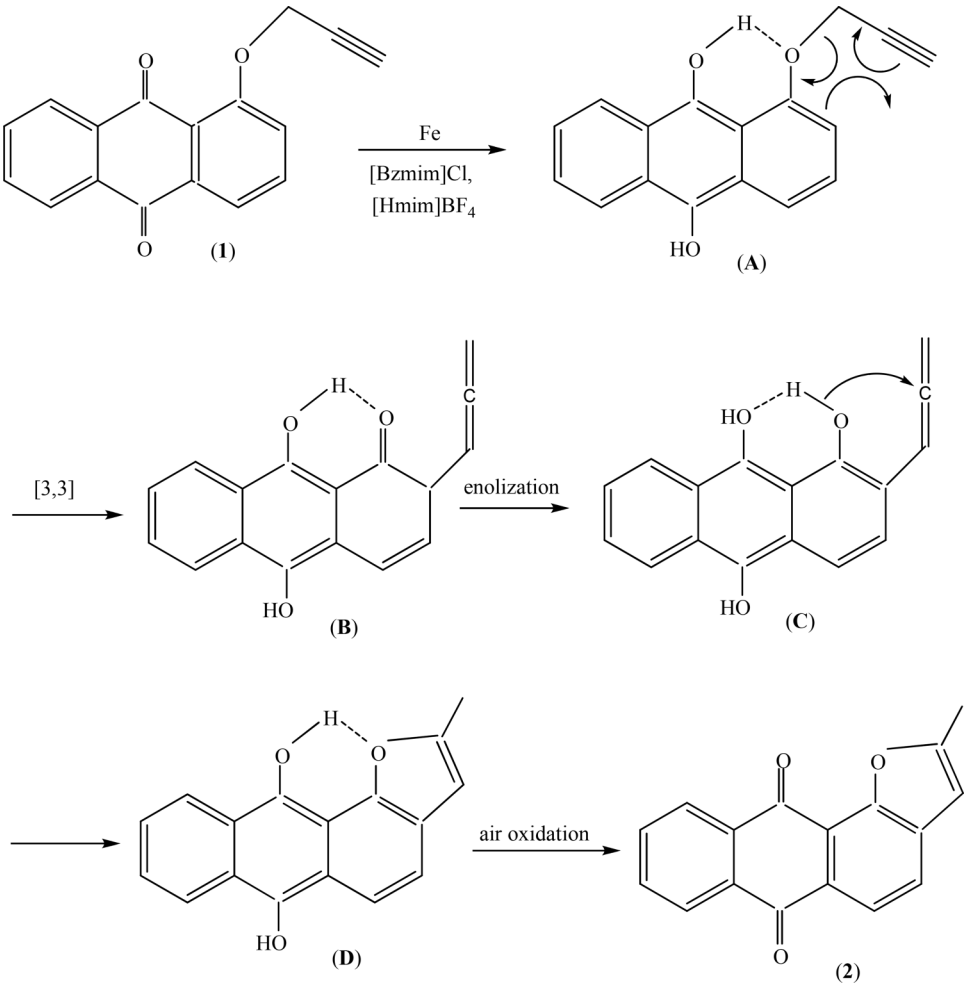
As mentioned above, the Claisen rearrangement of **1** via the present method and in the absence of acidic or chloride containing ionic liquid or Fe powder was unsuccessful; therefore, in these cases the desired **2** was obtained in only 0%–20% yield. With this description, although the exact mechanism of this reaction is not clear, it is suggested that the anthraquinone core is reduced using iron in the presence of [Bzmim]Cl under an acidic condition created by [Hmim]BF_4 to its electron-rich hydroquinone state **A**, which is more active to perform of this rearrangement (Scheme 4).

After this [3,3] sigmatropic rearrangement[19] followed by enolization, the intermediate **C** is formed, which benefits from its intramolecular hydrogen bonding. Then, internal cyclization of this intermediate affords anthrafuran **D**, which is finally converted to the desired product **2** under air oxidation. It seems that [Bzmim]Cl is necessary for facilitating the electron transfer from iron to the anthraquinone core and that [Hmim]BF_4 is necessary

Scheme 3. Various selectivities in the Claisen rearrangement of propargyloxyanthraquinones using iron powder (2 equiv.) in a mixed ionic liquids [Hmim]BF_4 and [Bzmim]Cl at 160 °C.



Scheme 4. The suggested mechanism of the reductive Claisen rearrangement of propargyloxyanthraquinones using Fe, [Bzmim]Cl, and [Hmim]BF_4.



due to its acidic property facilitating this rearrangement. Also, this mixture of ionic liquids acts as environment friendly solvent in the present method. In agreement with this suggested mechanism, we found that this reaction was unsuccessful under N_2 atmosphere. In this condition, the desired product **2** was formed in only 25% yield after 30 min with concomitant formation of **3** in 20% yield.

Conclusions

In conclusion, the present investigation has demonstrated that the use of iron powder in the presence of [Bzmim]Cl under an acidic condition created by [Hmim]BF_4 offers a novel and efficient method for first time for the reductive Claisen rearrangement of propargyloxyanthraquinones to anthrafurandione in moderate to excellent yields in short reaction times. In the cases of 1,4- or 1,5-bispropargyloxyanthraquinones, it is possible to perform single or double Claisen rearrangement selectively by controlling the molar ratio of the reductant or reaction time, so that the desired anthra(mono)furandiones or anthra(bis)furandiones are produced, respectively, as the major product via the present method. Additionally, the present method is able to execute this rearrangement on propargyloxyanthraquinones in the presence of some other functional groups such as aldehydes, carboxylic amides, phenols, and alcohols with excellent selectivity.

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