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Applications of Baylis–Hillman chemistry: one-pot convenient synthesis of functionalized (1*H*)-quinol-2-ones and quinolines

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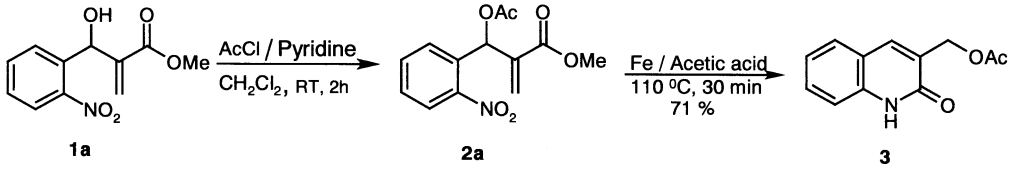
Abstract—A simple synthesis of functionalized (1*H*)-quinol-2-ones and quinolines from the Baylis–Hillman adducts, i.e. alkyl 3-hydroxy-2-methylene-3-arylpropanoates and β-hydroxy-α-methylene-β-arylalkanones, respectively, has been described.

The (1*H*)-quinol-2-one moiety, often referred to as a carbostyril moiety, is an important structural unit present in many biologically active molecules.[1–5] Also the quinoline framework constitutes an integral part of several natural products, many of which possess interesting physiological properties.[6,7] Due to their interesting and important biological properties a number of methods are reported in the literature for the synthesis of (1*H*)-quinol-2-one and quinoline derivatives with different substitution profiles and in fact, development of new and efficient methods for the preparation of these important molecules still continues to be an interesting and attractive area of research in synthetic organic chemistry.[8–13] In continuation of our interest in heterocyclic molecules,[14,15] we herein report a simple and facile one-pot synthesis of functionalized (1*H*)-quinol-2-one and quinoline derivatives using Baylis–Hillman adducts.

In recent years, the Baylis–Hillman carbon–carbon bond forming reaction has become increasingly important because it is an atom economical reaction and provides an unique class of attractive densely functionalized molecules, whose applications in a multitude of synthetic organic transformations have been well documented in the literature.[16–23] During our on-going research program on heterocyclic chemistry, we required 3-acetoxymethyl-(1*H*)-quinol-2-one and their derivatives. Recently Kaye and co-workers have reported an interesting transformation of the Baylis–Hillman adducts derived from 2-nitrobenzaldehyde, into quinoline derivatives via catalytic hydrogenation using Pd/C.[24] More recently Kim and co-workers have described an attractive synthesis of 3-ethoxycarbonyl-4-hydroxyquinoline *N*-oxides via the treatment of Baylis–Hillman adducts of various 2-nitrobenzaldehydes with trifluoroacetic acid.[25] Subsequently Kim has also reported a general synthesis of 3-quinolinecarboxylic acid esters from the Baylis–Hillman adducts derived from *o*-halobenzaldehyde *N*-tosylimines.[26]

It occurred to us that it would be useful if we could directly convert acetates of Baylis–Hillman adducts, derived from 2-nitrobenzaldehydes, into the required 3-acetoxymethyl-(1*H*)-quinol-2-one and their derivatives by treatment with an appropriate reagent, if possible in a one-pot operation. In this direction we first examined application of Fe/acetic acid[27] for the transformation of methyl 3-acetoxy-3-(2-nitrophenyl)-2-methylenepropanoate (**2a**), obtained from methyl 3-hydroxy-3-(2-nitrophenyl)-2-methylenepropanoate (**1a**) via the treatment with acetyl chloride/pyridine,



1a **2a** **3**

Scheme 1.

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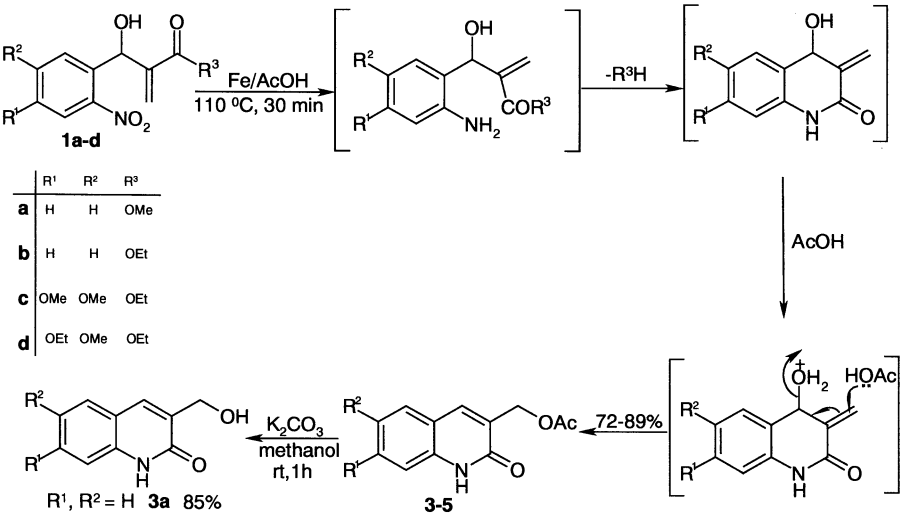
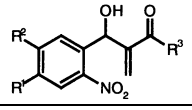


Scheme 2.

into the required 3-acetoxymethyl-(1*H*)-quinol-2-one (**3**). Interestingly, we found that treatment of methyl 3-acetoxy-3-(2-nitrophenyl)-2-methylenepropanoate (**2a**) with Fe/acetic acid at 110°C for 30 min provided 3-acetoxymethyl-(1*H*)-quinol-2-one (**3**) in 71% isolated yield (Scheme 1).

At this stage we envisioned that the treatment of methyl 3-hydroxy-3-(2-nitrophenyl)-2-methylenepropanoate (**1a**) directly with Fe/acetic acid might provide the desired 3-acetoxymethyl-(1*H*)-quinol-2-one (**3**) due to the presence of acetic acid, which might provide the desired acetoxy substitution. We have indeed obtained the desired product **3** in 77% yield when we treated methyl 3-hydroxy-3-(2-nitrophenyl)-2-methylenepropanoate (**1a**) with Fe/acetic acid at 110°C for 30 min, after usual work-up and crystallization from chloroform and hexanes (1:1). This is a very encouraging result in the sense that the reaction directly provides the desired 3-acetoxymethyl-(1*H*)-quinol-2-one, as acetic acid also acts as a source for the acetoxy group. We then successfully transformed a representative class of Baylis–Hillman adducts (**1b–d**), derived from the corresponding *ortho*-nitrobenzaldehydes and alkyl acrylates, into 3-acetoxymethyl-(1*H*)-quinol-2-one derivatives (**3–5**) (Scheme 2, Table 1).

Table 1. Synthesis of functionalized (1*H*)-quinol-2-ones and quinolines



Substrate	R^1	R^2	R^3	Product[a]	Yield (%)[b]	Mp (°C)
1a	H	H	OMe	**3**[c]	77	167–169
1b	H	H	OEt	**3**[c]	89	167–169
1c	OMe	OMe	OEt	**4**	72	177–178
1d	OEt	OMe	OEt	**5**	87	182–183
1e	H	H	Me	**6**[c]	63	94–95
1f	H	H	Et	**7**	83	–
1g	OMe	OMe	Me	**8**	56	97–98

All reactions were carried out on a 1 mmol scale of Baylis–Hillman adducts (**1a–g**) with iron (6 mmol) in the presence of acetic acid (5 mL) at reflux for 30 min. The products (**3–5**) were obtained as golden yellow crystalline solids after usual work-up followed by crystallization (chloroform and hexanes, 1:1) and the products (**6** and **8**) were obtained as brown crystalline solids after usual work-up followed by column chromatography (silica gel, 30% EtOAc in hexanes) and crystallization (chloroform and hexanes, 2:3). The compound **7** was obtained as brown liquid after column chromatography (silica gel, 30% EtOAc in hexanes).

[a] All the products **3–8** gave satisfactory IR, ^{1}H NMR (200 MHz), ^{13}C NMR (50 MHz) spectral data and elemental analyses.

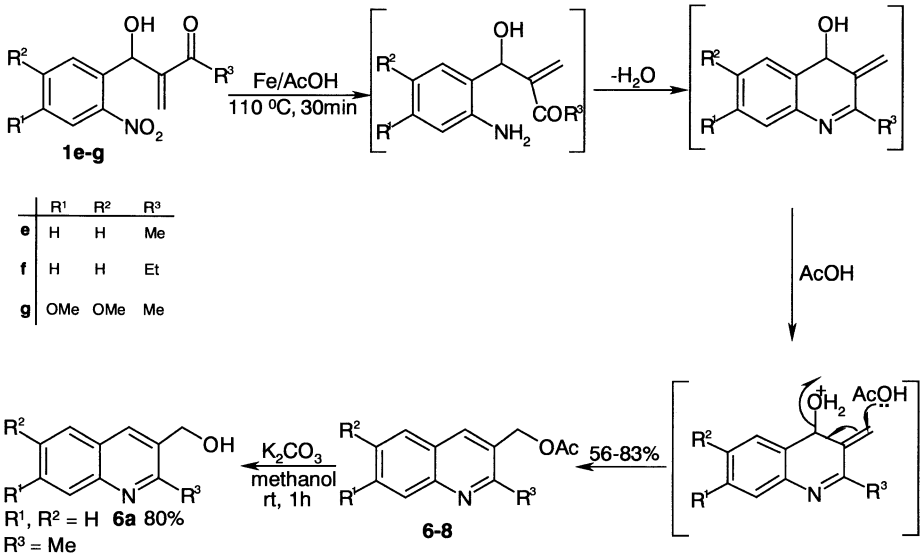
[b] Isolated yields of the pure products (for **3–5** after crystallization, for **6** and **8** after column chromatography followed by crystallization, for **7** after column chromatography).

[c] Structure was also confirmed by mass spectral analysis.

With a view to understanding the generality of this reaction, we have extended the same strategy to 4-hydroxy-4-(2-nitrophenyl)-3-methylenebutan-2-one (**1e**), the Baylis–Hillman adduct derived from 2-nitrobenzaldehyde and methyl vinyl ketone. Thus, the treatment of 4-hydroxy-4-(2-nitrophenyl)-3-methylenebutan-2-one (**1e**), with Fe/acetic acid at 110°C for 30 min provided the desired 3-acetoxymethyl-2-methylquinoline (**6**) in 63% isolated yield after usual work-up followed by column chromatography and crystallization from chloroform and hexanes (2:3). Encouraged by this successful result, we have prepared representative 3-acetoxymethylquinoline derivatives (**7**, **8**) from the Baylis-Hillman adducts (**1f**, **g**), obtained from the substituted appropriate 2-nitrobenzaldehydes and alkyl vinyl ketones (Scheme 3, Table 1). A plausible mechanism for the formation of 3-acetoxymethyl-(1*H*)-quinol-2-one derivatives and 3-acetoxymethylquinoline derivatives from the corresponding Baylis–Hillman adducts is described in Schemes 2 and 3.

We have also prepared the interesting allylic alcohols, 3-hydroxymethyl-(1*H*)-quinol-2-one (**3a**) and 3-hydroxymethyl-2-methylquinoline (**6a**), via the treatment of 3-acetoxymethyl-(1*H*)-quinol-2-one (**3**) and 3-acetoxymethyl-2-methylquinoline (**6**), respectively, with aqueous potassium carbonate/methanol (Schemes 2 and 3).

In conclusion, we have successfully synthesized 3-acetoxymethyl-(1*H*)-quinol-2-one derivatives and 2-alkyl-3-acetoxymethylquinoline derivatives from the Baylis–Hillman adducts derived from alkyl acrylates and alkyl vinyl



Scheme 3.

ketones, thus demonstrating the efficacy of Baylis–Hillman adducts in organic synthesis.

1. Experimental

1.1. General

Melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-FT-IR model 5300 spectrometer using samples as neat liquids or as KBr plates. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuterochloroform ($CDCl_3$) or in DMSO-d_6 on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS, δ=0) as internal standard. Mass spectra were recorded on a micromass VG 7070H instrument. Elemental analyses were recorded on a Perkin–Elmer 240C-CHN analyzer. All the required Baylis–Hillman adducts (**1a**–**d**) were obtained via the reaction between alkyl acrylates and the corresponding *ortho*-nitrobenzaldehydes in the presence of catalytic amount of DABCO. Similarily the allylic alcohols (**1e**–**g**) were obtained by the coupling of (m)ethyl vinyl ketone with the corresponding *ortho*-nitrobenzaldehydes under the catalytic influence of DABCO in THF as a solvent.[17,18,28]

1.1.1. 3-(Acetoxymethyl)-(1*H*)-quinol-2-one (3) [from methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate (2a)]. To a stirred solution of methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate (**2a**) (1 mmol, 0.279 g) in acetic acid (5 mL) at 110°C electrolytic iron powder (6 mmol, 0.335 g) was added and stirring continued for 30 min at the same temperature. The reaction mixture was cooled to room temperature and acetic acid removed under reduced pressure. The reaction mixture was diluted with ethyl acetate (15 mL), stirred for 2 min and filtered to remove iron impurities. The insoluble iron residue was washed with ethyl acetate (2×10 mL) and combined with the filtrate. Ethyl acetate was removed and the solid obtained crystallized from chloroform and hexanes (1:1) to provide 3-(acetoxymethyl)-(1*H*)-quinol-2-one (**3**) in 71% yield (0.153 g), as golden yellow crystals. Mp: 167–169°C; IR (KBr):1622, 1664, 1730, 2800–3200 (multiple bands) cm^{-1}; ^{1}H NMR: 2.17 (s, 3H), 5.21 (s, 2H), 7.18–7.62 (m, 4H), 7.85 (s, 1H), 11.39 (b, 1H); ^{13}C NMR: δ 21.06, 61.54, 116.10, 119.71, 122.87, 127.67, 127.92, 130.72, 138.25, 138.55, 163.25, 170.86; MS (*m/z*): 217 (M^+); Analysis calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45; found: C, 66.26; H, 5.12; N, 6.52.

1.1.2. 3-(Acetoxymethyl)-(1*H*)-quinol-2-one (3) [from methyl 3-hydroxy-2-methylene-3-(2-nitrophenyl)propanoate (1a)]. To a stirred solution of methyl 3-hydroxy-2-methylene-3-(2-nitrophenyl)propanoate (**1a**) (1 mmol, 0.237 g) in acetic acid (5 mL) at 110°C electrolytic iron powder (6 mmol, 0.335 g) was added and stirring continued for 30 min at same temperature. The reaction mixture was cooled to room temperature and acetic acid removed under reduced pressure. Then the reaction mixture was diluted with ethyl acetate (15 mL) and stirred for 2 min and filtered to remove iron impurities. The insoluble iron residue was washed with ethyl acetate (2×10 mL). The filtrate and washings were combined. Ethyl acetate was removed and the solid obtained was crystallized from chloroform and hexanes (1:1) to provide 3-acetoxymethyl-(1*H*)-quinol-2-one (**3**) in 77% yield (0.167 g), as golden yellow crystals. Mp: 167–169°C. Spectral data (IR, ^{1}H and ^{13}C NMR) of this molecule are identical with that of the molecule prepared from methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate.

1.1.3. 3-(Acetoxymethyl)-(1*H*)-quinol-2-one (3) [from ethyl 3-hydroxy-2-methylene-3-(2-nitrophenyl)propanoate (1b)]. The reaction of ethyl 3-hydroxy-2-methylene-3-(2-nitrophenyl)propanoate (**1b**) with Fe/acetic acid (following a similar procedure as mentioned for the reaction of the allyl alcohol (**1a**) with Fe/acetic acid) provided 3-(acetoxymethyl)-(1*H*)-quinol-2-one (**3**) in 89% yield as golden yellow crystals. Mp: 167–169°C. Spectral data (IR, ^{1}H and ^{13}C NMR) of this molecule are identical with that of the molecule prepared from methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate.

1.1.4. 3-(Acetoxymethyl)-6,7-dimethoxy-(1*H*)-quinol-2-one (4). Colorless crystals. Yield: 72%; mp: 177–178°C; IR (KBr): 1620, 1658, 1745, 2800–3400 (multiple bands) cm^{-1}; ^1H NMR: δ 2.14 (s, 3H), 3.93 (s, 3H), 3.99 (s, 3H), 5.18 (s, 2H), 6.79 (s, 1H), 6.96 (s, 1H), 7.79 (s, 1H), 11.71 (b, 1H); ^{13}C NMR: δ 21.02, 56.06, 56.23, 61.51, 98.04, 107.67, 113.00, 124.04, 134.23, 138.51, 145.88, 152.64, 163.20, 170.85; Analysis calcd for $C_{14}H_{15}NO_5$: C, 60.65; H, 5.45; N, 5.05; found: C, 60.41; H, 5.48; N, 5.00.

1.1.5. 3-(Acetoxymethyl)-7-ethoxy-6-methoxy-(1*H*)-quinol-2-one (5). Golden yellow crystalline solid. Yield: 87%; mp: 182–183°C; IR (KBr): 1624, 1662, 1741, 2750–3200 (multiple bands) cm^{-1}; ^1H NMR: δ 1.54 (t, 3H, J=6.8 Hz), 2.15 (s, 3H), 3.92 (s, 3H), 4.21 (q, 2H, J=6.8 Hz), 5.19 (s, 2H), 6.75 (s, 1H), 6.96 (s, 1H), 7.78 (s, 1H), 10.92 (b, 1H); ^{13}C NMR: δ 14.58, 21.04, 56.38, 61.63, 64.93, 99.15, 108.56, 113.08, 124.32, 134.49, 138.71, 146.40, 152.45, 163.30, 170.85; Analysis calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81; found: C, 62.12; H, 5.84; N, 4.85.

1.1.6. 3-(Acetoxymethyl)-2-methylquinoline (6). To a stirred solution of 4-hydroxy-3-methylene-4-(2-nitrophenyl)butan-2-one (**1e**) (1 mmol, 0.221 g) in acetic acid (5 mL) at 110°C electrolytic iron powder (6 mmol, 0.335 g) was added and stirring was continued for 30 min at same temperature. The reaction mixture was cooled to room temperature and acetic acid was removed under reduced pressure. Then the reaction mixture was diluted with ethyl acetate (15 mL) and stirred for 2 min, filtered to remove iron impurities. The insoluble iron residue was washed with ethyl acetate (2×10 mL). The filtrate and washings were combined. Ethyl acetate was removed and the residue thus obtained was purified by column chromatography (silica gel, 30% EtOAc in hexanes) followed by crystallization (chloroform and hexanes (2:3)) to afford 3-(acetoxymethyl)-2-methylquinoline (**6**) in 63% yield (0.135 g), as brown crystals. Mp: 94–95°C; IR (KBr): 1620, 1738 cm^{-1}; ^1H NMR: δ 2.16 (s, 3H), 2.76 (s, 3H), 5.29 (s, 2H), 7.45–7.56 (m, 1H), 7.66–7.85 (m, 2H), 8.03 (d, 1H, J=8.2 Hz), 8.09 (s, 1H); ^{13}C NMR: δ 20.85, 22.84, 63.85, 126.05, 126.63, 127.46, 127.67, 128.40, 129.66, 136.01, 147.42, 157.73, 170.58; MS (*m*/*z*): 215 (M^+); Analysis calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51; found: C, 72.49; H, 6.05; N, 6.58.

1.1.7. 3-(Acetoxymethyl)-2-ethylquinoline (7). Brown liquid. Yield: 83%; IR (neat): 1624, 1741 cm^{-1}; ^1H NMR: δ 1.44 (t, 3H, J=7.2 Hz), 2.15 (s, 3H), 3.13 (q, 2H, J=7.2 Hz), 5.33 (s, 2H), 7.48–7.62 (m, 1H), 7.71–7.87 (m, 2H), 8.20–8.29 (m, 2H); ^{13}C NMR: δ 13.46, 20.94, 28.70, 63.61, 126.13, 126.59, 127.23, 127.50, 128.40, 129.75, 136.78, 147.41, 162.30, 170.67; Analysis calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; found: C, 73.55; H, 6.66; N, 6.15.

1.1.8. 3-(Acetoxymethyl)-6,7-dimethoxy-2-methylquinoline (8). Brown crystalline solid. Yield: 56%; mp: 97–98°C; IR (KBr): 1620, 1736 cm^{-1}; ^1H NMR: δ 2.14 (s, 3H), 2.70 (s, 3H), 4.00 (s, 3H), 4.03 (s, 3H), 5.25 (s, 2H), 7.03 (s, 1H), 7.37 (s, 1H), 7.94 (s, 1H); ^{13}C NMR: δ 20.96, 22.51, 56.09, 56.19, 64.21, 105.19, 107.44, 122.10, 125.85, 135.09, 144.58, 149.63, 152.85, 155.52, 170.79; Analysis calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09; found: C, 65.26; H, 6.17; N, 5.12.

1.1.9. 3-(Hydroxymethyl)-(1*H*)-quinol-2-one (3a). A mixture of 3-(acetoxymethyl)-(1*H*)-quinol-2-one (**3**) (0.5 mmol, 0.109 g), potassium carbonate (1.5 mmol, 0.207 g) in methanol (2 mL) containing 1 drop of water was stirred at room temperature for 1 h. The reaction mixture was filtered off and the precipitate washed with methanol (4 mL). The combined methanolic solution was concentrated and the crude product obtained subjected to crystallization from methanol at 0°C to provide 3-(hydroxymethyl)-(1*H*)-quinol-2-one (**3a**) as yellow crystals in 85% yield (0.074 g). Mp: 199–200°C; IR (KBr): 1651, 3373 cm^{-1}; ^1H NMR (DMSO-d_6): δ 4.40 (d, 2H, J=5.6 Hz), 5.22 (t, 1H, J=5.6 Hz), 7.11–7.55 (m, 3H), 7.68 (d, 1H, J=7.8 Hz), 7.85 (s, 1H), 11.78 (b, 1H); ^{13}C NMR (DMSO-d_6): δ 58.70, 115.14, 119.53, 121.96, 127.69, 129.53, 133.89, 134.19, 137.90, 161.47; MS (*m*/*z*): 175 (M^+); Analysis calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00; found: C, 68.76; H, 5.15; N, 7.96.

1.1.10. 3-(Hydroxymethyl)-2-methylquinoline (6a). Brown crystals (crystallized from acetonitrile at 0°C). Yield: 80%; mp: 139–141°C; IR (KBr): 1657, 3429 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.60 (s, 3H), 4.69 (s, 2H), 5.45 (b, 1H), 7.48–7.71 (m, 2H), 7.86–7.98 (m, 2H), 8.20 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 22.41, 60.71, 125.84, 126.99, 127.72, 128.11, 128.87, 132.65, 134.54, 146.43, 157.52; Analysis calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09; found: C, 76.12; H, 6.35; N, 8.15.

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