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Synthesis of 6-acyl-5,8-quinolinediols by photo-Friedel–Crafts acylation using sunlight

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ABSTRACT

Synthesis of acyl-5,8-quinolinediols using sunlight was investigated. Photo-Friedel–Crafts acylation of quinoline-5,8-dione and aldehyde afforded the corresponding 6-acyl-5,8-quinolinediols regioselectively in moderate to good yields. The compounds have a variety of potential applications.

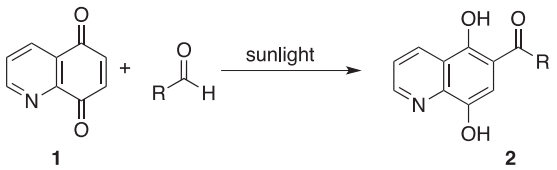
Introduction

Sunlight drives numerous chemical reactions that are essential for life on earth. It is a unique natural resource that can provide an endless supply of renewable and clean energy. Consequently, solar radiation has attracted rising attention in the scientific community. In synthetic organic photochemistry, artificial UV light has been used predominantly, but reactions driven by sunlight have been explored in recent years.

1,4-Quinones have been studied as substrates for many years due to their great abilities as electron acceptors. Actually, the first reaction of 1,4-benzoquinone and aldehydes to obtain acylhydroquinones was reported in 1891.[1] In this Letter the reaction was exposed to sunlight over several months. However, the reaction has not received much attention for more than a century. Over the last decade this photo-Friedel–Crafts acylation has drawn renewed attention from a few research groups.[2–5] Mattay and Oelgemöller began to reinvestigate this reaction using sunlight, and more recently, the Valderrama group reported heteroaromatic acylation.[6] As evidenced by recent reports about the solar reaction of 1,4-benzo- and 1,4-naphthoquinones with aldehydes, this synthetic methodology has been in the spotlight.

These reported acylation results encouraged us to investigate the application of the solar driven reaction using quinoline-5,8-dione **1** (Eq. 1). The initial investigation under artificial light with 1 and *n*-butanal was reported in 1988,[7] however, the products were a mixture of quinone and acylated quinolinediols as regioisomers with low yield, and the reaction needs to be improved. The products, 6-acyl-5,8-quinolinediols **2**, are very interesting: a number of bioactive compounds bearing quinoline moieties are widely found in nature and have received much attention given their diversity in biological activities.[8] In particular, 8-hydroxyquinolines exhibit bioactivities, such as antifungal,[9] anticancer,[10] and HIV-1 replication inhibitors,[11] and are very useful as important key intermediates for pharmaceuticals. 8-hydroxyquinolines are also used as a bidentate chelating reagent, and the complexes with aluminium(III) have been found to be organic light-emitting diodes.[12]

Herein we report the synthesis of 6-acyl-5,8-quinolinediols by photo-Friedel–Crafts acylation of quinoline-5,8-dione using sunlight as the energy source (Eq. 1).



1 2 (1)

Results and discussion

Quinoline-5,8-dione **1** was synthesized from 8-hydroxyquinoline with phenyliodine diacetate (PIDA) in one-step.[13] First, we examined the reaction in a 35 mL Pyrex sealable reaction tube with a 20 mL benzene solution of 1 mmol of quinoline-5,8-dione **1** and

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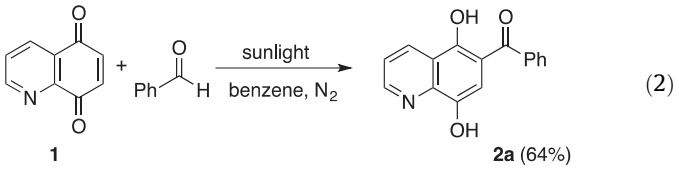
10 mmol of benzaldehyde. The solution was degassed with nitrogen to avoid any oxidation reaction by oxygen. The reaction tube was sealed and placed on the roof of our research building for exposure to direct sunlight.[14] The corresponding 6-benzoyl-5,8-quinolinediol **2a** was obtained in 64% yield after 5 days (Eq. 2).

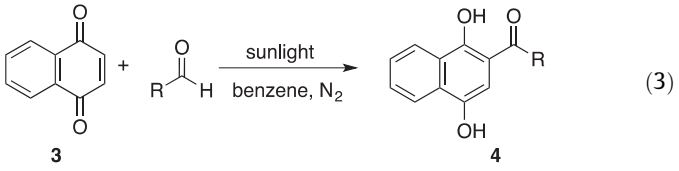


(2)

Photo-dimerization was reported with 1,4-benzoquinone,[15] however, in our experiment, no photo-dimerization product was observed. We also tried reactions in various solvents including: *t*-BuOH and *t*-BuOH/acetone, and benzene gave us the best yields.

Then, we investigated the substrate scope in the same condition. The results were summarized in Table 1. The acylation took place regioselectively; only at 6-position, not at 7 position. The structure was determined by NMR techniques including HMBC proton carbon correlations.[16] We used both aromatic and aliphatic aldehydes, and the products were obtained in good yields. However, when we used *p*-chloro- and *p*-nitrobenzaldehyde, the reactions did not proceed even after 10 days. The reaction with *p*-bromobenzaldehyde afforded the product in 12% yield (entry 6). This indicates that electron withdrawing group on the benzene ring of benzaldehyde hindered the reaction. The mechanism of the photoacylation has been reported and the photoaddition is initiated by hydrogen abstraction from the aldehyde moiety to the triplet excited quinone.[3,17] Low yields in our case can be explained by electron withdrawing groups inhibiting hydrogen abstraction from aldehydes.

The position of methoxy group on the benzene ring affects the yield (Table 1, entries 3–5). We also tried the reactions of these three aldehydes with 1,4-naphthoquinone **3**, and the tendency is the similar (Eq. 3, Table 2). Steric hindrance may be the reason for varying the yields.



(3)

Table 1
Solar-Friedel–Crafts acylation with quinoline-5,8-dione[18]

Entry	RCHO	Product	Time (in days)	Yield (%)
1	Ph	**2a**	5	64
2	*p*-MeC_6H_4	**2b**	4	58
3	o-$MeOC_6H_4$	**2c**	4	41
4	*m*-$MeOC_6H_4$	**2d**	4	45
5	*p*-$MeOC_6H_4$	**2e**	5	47
6	*p*-BrC_6H_4	**2f**	4	12
7	Me	**2g**	4	67
8	Et	**2h**	5	71
9	*i*-Pr	**2i**	4	68
10	C_7H_{15}	**2j**	4	60
11	$C_{11}H_{23}$	**2k**	4	62

Table 2
Solar-Friedel–Crafts acylation with naphthoquinone

Entry	RCHO	Product	Time (in days)	Yield (%)
1	o-$MeOC_6H_4$	**4a**	4	50
2	*m*-$MeOC_6H_4$	**4b**	5	51
3	*p*-$MeOC_6H_4$	**4c**	4	72

Conclusion

We demonstrated the synthesis of 6-acyl-5,8-quinolinediols by photo-Friedel–Crafts acylation of quinoline-5,8-dione with aldehyde using sunlight. The operation for this reaction is very simple and easy to perform. Currently, we are working on their applications and carrying out the reactions in more environmentally friendly conditions.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04.021.

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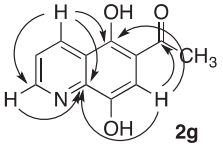

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18. General procedure for synthesis of 7-acyl-5,8-quinolinediols.
In a 35 mL Pyrex sealable reaction tube, a solution of 1 mmol of the quinone and 10 mmol of the aldehyde with 20 mL benzene is prepared and degassed with nitrogen. The reaction tube is then sealed and placed on the roof for exposure to direct sunlight. A magnetic stir plate was used to allow constant mixing/stirring of the solution. The reaction mixture was then checked by TLC. Column Chromatography using ethylacetate/hexanes mixture as the eluent afforded the desired products.

*6-Benzoyl-5,8-quinolinediol (**2a**)*
Mp = 176–178 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.39 (s, 1H), 8.93 (dd, J = 4.1, 1.6 Hz, 1H), 8.82 (dd, J = 8.2, 1.6 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 7.60–7.58 (m, 2H), 7.56–7.51 (m, 3H), 7.27 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.26, 156.3, 151.70, 143.46, 141.98, 137.92, 133.70, 131.86, 130.27, 128.98, 128.43, 121.60, 120.82, 119.8, 112.82, 109.48. IR (neat, cm^{-1}) ν_{max} 3319, 3074 (OH), 1734 (C=O), 1613, 1578, 1502, 1405, 1323, 1298 (C–O), 1241, 1214, 1028, 663.

*6-(4-Methylbenzoyl)-5,8-quinolinediol (**2b**)*
Mp = 187–189 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.43 (s, 1H), 8.92 (dd, J = 4.1, 1.6 Hz, 1H), 8.81 (dd, J = 8.2, 1.6 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.6 (s, 1H), 7.55–7.53 (m, 1H), 7.32 (d, J = 7.4 Hz, 2H), 7.30 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.95, 156.07, 151.57, 143.40, 142.67, 141.86, 135.18, 133.65, 129.28, 129.08, 121.52, 120.76, 112.94, 109.62, 21.6. IR (neat, cm^{-1}) ν_{max} 3315 (OH), 2923 (CH), 1636 (C=O), 1604, 1590, 1576, 1494, 1324, 1288, 1236, 1208, 1178, 1043, 657.

*6-(2-Methoxylbenzoyl)-5,8-quinolinediol (**2c**)*
Mp = 151–153 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.48 (s, 1H), 8.91 (dd, J = 4.2, 1.6 Hz, 1H), 8.81 (m, 1H), 8.77 (dd, J = 1.2, 4.2 Hz, 1H), 7.47 (m, 1H), 7.41–7.32 (m, 3H), 6.97 (s, 1H), 6.95 (d, J = 8.2 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.15, 156.34, 155.69, 151.53, 147.99, 143.47, 142.13, 133.70, 131.97, 128.60, 121.39, 120.69, 114.16, 111.47, 109.62, 55.63. IR (neat, cm^{-1}) ν_{max} 3330 (OH), 3075, 2837 (CH), 1721 (C=O), 1645, 1598, 1502, 1401, 1329, 1299, 1284, 1191, 1180, 1075, 651.

*6-(3-Methoxylbenzoyl)-5,8-quinolinediol (**2d**)*
Mp = 147–149 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.4 (s, 1H), 8.94 (dd, J = 4.1, 1.6 Hz, 1H), 8.82 (dd, J = 8.2, 1.6 Hz, 1H), 8.77 (dd, 1H), 7.56 (m, 1H), 7.49–7.42 (m, 2H), 7.30 (s, 1H), 7.24 (s, 1H), 7.14 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.09, 159.65, 156.31, 151.72, 148.27, 143.48, 142.02, 139.15, 133.72, 129.46, 121.46, 120.75, 117.97, 113.81, 112.86, 109.52, 55.49. IR (neat, cm^{-1}) ν_{max} 3504, 3341 (OH), 2923 (CH), 1737 (C=O), 1632, 1583, 1400, 1346, 1302, 1180, 1118, 1095, 653.

*6-(4-Methoxylbenzoyl)-5,8-quinolinediol (**2e**)*
Mp = 157–159 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.33 (s, 1H), 8.92 (d, J = 2.4 Hz, 1H), 8.8 (m, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.61 (s, 1H), 7.54 (m, 1H), 7.33 (s, 1H), 7.01 (d, J = 9.1 Hz, 2H), 3.9 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.78, 162.91, 155.82, 151.48, 148.22, 143.37, 141.74, 133.64, 131.70, 131.26, 121.53, 120.80, 113.80, 109.61, 108.92, 55.52. IR (neat, cm^{-1}) ν_{max} 3164 (OH), 3076 (CH), 2935, 2845 (CH), 1738 (C=O), 1594, 1501, 1404, 1318, 1242, 1190, 1119, 1025, 670.

*6-(4-Bromobenzoyl)-5,8-quinolinediol (**2f**)*
Mp = 160–162 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.29 (s, 1H), 8.85–8.79 (m, 2H), 8.52 (m, 1H), 7.94 (d, J = 6 Hz, 1H), 7.63–7.58 (m, 2H), 7.21 (s, 1H), 6.99 (d, J = 6 Hz, 1H), 6.8 (d, J = 6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.0, 151.94, 150.02, 148.32, 133.24, 131.87, 131.72, 130.9, 130.68, 128.84, 123.62, 121.84, 120.88, 109.78, 109.24, 109.12. IR (neat, cm^{-1}) ν_{max} 3294 (OH), 2921 (C–H), 1676 (C=O), 1585, 1501, 1455, 1297, 1069, 1190, 1119, 997, 757.

*6-Acetyl-5,8-quinolinediol (**2g**)*
Mp = 143–145 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.49 (s, 1H), 8.90 (dd, J = 5.7, 1.6 Hz, 1H), 8.75 (dd, J = 9.0, 1.6 Hz, 1H), 7.63 (s, 1H), 7.52 (m, 1H), 7.33 (s, 1H), 2.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 204.27, 154.98, 151.45, 143.88, 142.05, 133.69, 121.59, 120.71, 113.33, 107.04, 27.18. IR (neat, cm^{-1}) ν_{max} 3332 (OH), 3032, 2924 (CH), 1668 (C=O), 1601, 1579, 1501, 1368, 1310, 1234, 1120, 1079, 673.

*6-Propanoyl-5,8-quinolinediol (**2h**)*
Mp = 158–160 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.56 (s, 1H), 8.89 (s, 1H), 8.74 (d, J = 8.2 Hz, 1H), 7.64 (s, 1H), 7.50 (dd, J = 8.2, 6.0 Hz, 1H), 7.36 (s, 1H), 3.07 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ 206.69, 154.85, 151.32, 143.86, 141.92, 133.66, 121.55, 120.82, 112.86, 106.35, 31.56, 8.17. IR (neat, cm^{-1}) ν_{max} 3332 (OH), 2984, 2852 (CH), 1631 (C=O), 1582, 1404, 1378, 1341, 1290, 1236, 1197, 1136, 1082, 651.

*6-(2-Methylpropanoyl)-5,8-quinolinediol (**2i**)*
Mp = 101–103 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.78 (s, 1H), 8.89 (dd, J = 4.2, 1.8 Hz, 1H), 8.75 (dd, J = 8.2, 1.6 Hz, 1H), 7.62 (s, 1H), 7.51 (dd, J = 8.2, 4.1 Hz, 1H), 7.39 (s, 1H) , 3.61–3.55 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.26, 155.82, 151.41, 143.84, 141.97, 133.68, 121.53, 121.00, 111.91, 106.46, 35.51, 30.83, 19.08. IR (neat, cm^{-1}) ν_{max} 3337 (OH), 2988, 2852 (CH), 1629 (C=O), 1603, 1584, 1503, 1402, 1289, 1273, 1202, 1032, 1022, 654.

*6-Octanoyl-5,8-quinolinediol (**2j**)*
Mp = 100–102 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.59 (s, 1H), 8.77 (d, J = 4.1 Hz, 1H), 8.62 (d, J = 8.2 Hz, 1H), 7.62 (s, 1H), 7.39 (m, 1H), 7.24 (s, 1H), 2.88 (t, J = 7.5 Hz, 2H), 1.67–1.64 (m, 2H), 1.31–1.13 (m, 8H), 0.77 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.71, 155.04, 151.32, 143.80, 141.92, 133.64, 121.5, 120.83, 112.96, 106.58, 39.01, 31.66, 30.82, 29.27, 29.06, 22.58, 14.01. IR (neat, cm^{-1}) ν_{max} 3343 (OH), 2925, 2852 (CH), 1634 (C=O), 1583, 1503, 1453, 1405, 1267, 1184, 1059, 631.

*6-Dodecanoyl-5,8-quinolinediol (**2k**)*
Mp = 107–109 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.64 (s, 1H), 8.89 (dd, J = 1.6, 3.7 Hz, 1H), 8.75 (dd, J = 9.1, 1.6 Hz, 1H), 7.63 (s, 1H), 7.52–7.49 (m, 1H), 7.36 (s, 1H), 3.00 (t, 2H), 1.77 (m, 2H), 1.43–1.25 (m, 16H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.74, 155.07, 151.33, 143.81, 141.94, 133.66, 121.53, 120.84, 112.98, 106.55, 39.04, 31.88, 31.55, 30.84, 29.58, 29.47, 29.41, 29.31, 24.53, 22.65, 14.06. IR (neat, cm^{-1}) ν_{max} 3349 (OH), 2956, 2852 (CH), 1635 (C=O), 1581, 1505, 1412, 1385, 1342, 1329, 1264, 1235, 1183, 1018, 650.

*1,4-Dihydroxy-2-(2-methoxybenzoyl)-naphthalene (**4a**)*
Mp = 176–178 °C. ^{1}H NMR (600 MHz, CDCl3): δ 13.60 (s, 1H), 8.51 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.2 Hz, 1H), 7.68 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.59 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.48 (ddd, J = 8.4, 7.5, 1.8 Hz, 1H), 7.31 (dd, J = 7.4, 1.7 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 7.01(d, J = 8.2 Hz, 1H), 6.57 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.08, 158.21, 156.39, 142.63, 135.7, 134.12, 132.8, 131.65, 129.9, 128.64, 126.40, 124.68, 121.61, 120.60, 112.85, 111.50, 107.98, 55.75. IR (neat, cm^{-1}) ν_{max} 3288 (OH), 2936, 2836 (CH), 1633 (C=O), 1588, 1507, 1488, 1355, 1240, 1161, 1045, 1023, 659.

*1,4-Dihydroxy-2-(3-methoxybenzoyl)-naphthalene (**4b**)*
Mp = 142–144 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.53 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.70 (t, J = 6.6 Hz, 1H), 7.60 (t, J = 6.6 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.2 (s, 1H), 7.1 (dd, J = 8.2, 2.4 Hz, 1H), 6.88 (s, 1H), 4.90 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.57, 159.56, 158.79, 142.54, 139.52, 130.08, 129.37, 126.59, 126.10, 124.66, 121.71, 121.26, 117.54, 113.76, 111.45, 107.98, 55.49. IR (neat, cm^{-1}) ν_{max} 3325 (OH), 3063, 2988 (CH), 1633 (C=O), 1559, 1508, 1492, 1287, 1240, 1197, 1043, 1029, 661.

*1,4-Dihydroxy-2-(4-methoxybenzoyl)-naphthalene (**4c**)*
Mp = 130–132 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 13.51 (s, 1H), 8.5 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.73–7.68 (m, 3H), 7.59 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 9.1 Hz, 2H), 6.94 (s, 1H), 4.89 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 199.45, 162.58, 158.24, 142.50, 132.20, 131.45, 130.71, 129.78, 129.20, 126.47, 126.15, 124.57, 121.64, 113.67, 111.63, 108.33, 55.47. IR (neat, cm^{-1}) ν_{max} 3465.88 (OH), 3054, 2925 (CH), 1631, 1590, 1511, 1462, 1451, 1418, 1359, 1326, 970, 949, 867, 779, 763, 720.