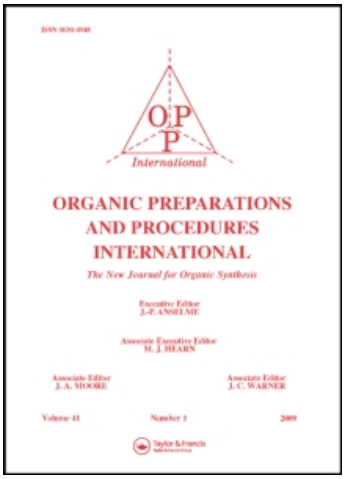

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ONE-POT SYNTHESIS OF 3-FORMYLCHROMONES FROM *bis*-(TRICHLOROMETHYL) CARBONATE/DMF

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ONE-POT SYNTHESIS OF 3-FORMYLCHROMONES FROM *bis*-(TRICHLOROMETHYL) CARBONATE/DMF

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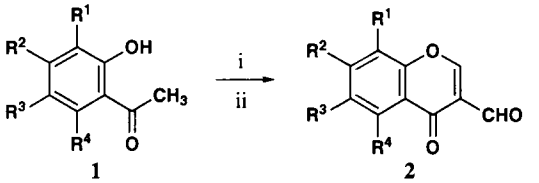
3-Formylchromones possess significant biological activities[1-7] and have been extensively used as versatile building blocks for the synthesis of a large number of heterocyclic systems.[8-18] They contain three electron-deficient sites (C-2, C-4 and the carbonyl carbon atom CHO) susceptible to nucleophilic attack. To our best knowledge, 3-formylchromones have been previously synthesized in low yields from the reaction of 2-formyl-2-hydroxyacetophenones with ethyl orthoformate and acetic anhydride.[19] On the other hand, the synthesis of 3-formylchromones from 2,2-difluoro-4-methylnaphtho-1,3,2-dioxaborin compounds was reported.[20] However, in the case of 2,2-difluoro-4-methylnaphtho-1,3,2-dioxaborin compounds, double formylations occurred. Nohara[21,22] rationalized these results on the basis of prohibition of enolization by 1,3,2-dioxaborin ring formation thus leading to double formylation. Following this strategy, they carried out double formylation of *o*-hydroxyacetophenones derivatives to afford 3-fromylchromones. In recent years, microwave promoted and solid-supported methods for the preparation of 3-formylchromones have been reported in various yields.[23,24] In general, the Vilsmeier synthesis is more convenient than other existing methods. The most traditional reagent involves a combination of $POCl_3$ and DMF. However, some of these methods often suffer from certain drawbacks such as long reaction time, unexpected side-reactions and unsatisfactory yields.

BTC is a stable crystalline solid and shown to be a useful reagent for the synthesis of a large number of organic compounds.[25,26] In light of our success using this reagent,[27] we turned our attention to the much more challenging reactions of the combinations of BTC with other reagents. Herein, we report a new Vilsmeier route for one-pot synthesis of 3-formylchromones using a novel Vilsmeier-type reagent generated *in situ* from BTC and DMF (*Scheme 1*).

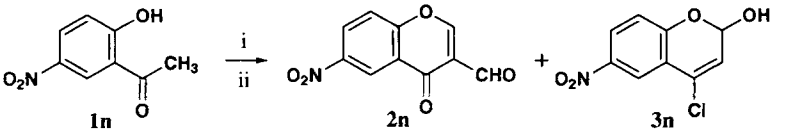


(i) BTC (12 mmol), DMF (72 mmol), 0-5°C, 0.5 h; r.t., 0.5-1 h.
(ii) 0-5°C, then **1** (6 mmol), 0.5 h; r.t., 3-6 h

(a) $R^1 = R^2 = R^3 = R^4 = H$; (b) $R^1 = R^2 = R^4 = H$, R^3=F; (c) $R^1 = R^2 = R^4 = H$, $R^3 = Cl$;
(d) $R^1 = R^2 = R^4 = H$, R^3 = Br; (e) $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$; (f) $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$;
(g) R^1 = Br, $R^2 = R^4 = H$, $R^3 = CH_3$; (h) $R^1 = R^3 = Cl$, $R^2 = R^4 = H$; (i) $R^1 = R^3$ = Br, $R^2 = R^4 = H$;
(j) $R^1 = R^2 = R^4 = H$, R^3 = MeO; (k) $R^1 = R^3 = R^4 = H$, R^2 = MeO;
(l) $R^1 = H$, $R^2 = R^3 = R^4 = F$; (m) R^1, R^2 = *benzo*, $R^3 = R^4 = H$; (n) $R^1 = R^2 = R^4 = H$, $R^3 = NO_2$;
(o) $R^1 = NO_2$, $R^2 = R^4 = H$, $R^3 = CH_3$; (p) $R^1 = R^2 = R^4 = H$, R^3 = OH;

Scheme 1

Much effort was made to develop a suitable ratio of *o*-hydroxyacetophenone/BTC/DMF using 1,2-dichloroethane as solvent. After screening a variety of ratios, a 1:2:8 ratio of *o*-hydroxyacetophenone/BTC/DMF was determined to be suitable to generate the desired 3-formylchromone in good yields. When other *o*-hydroxyacetophenones were tested under these conditions, in most cases the desired 3-formylchromones were obtained in good yields without by-products formation. Unexpected results occurred when a substituted *o*-hydroxyacetophenone bearing a strong electron-withdrawing group (e.g., NO_2 at C-5) was used. The desired chromone **2n** was obtained accompanied by the unexpected by-product **3n** in 70% total yield (**2n/3n** = 7:3) (*Scheme 2*).



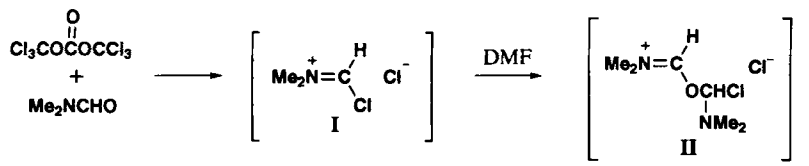
(i) BTC (6 mmol), DMF (24 mmol), 0-5°C, 0.5 h; r.t., 0.5-1 h.; (ii) 0-5°C, then **1n** (3 mmol), 0.5 h; r.t., 6 h

Scheme 2

The structure of **3n** was confirmed by ^1H, ^{13}C NMR and MS. This novel observation prompted us to investigate the mechanism by carrying optimization studies with 5-nitro-2-hydroxyacetophenone (**1n**). It was found that the ratio of **2n/3n** increased significantly when more DMF was used. Based on this result, the ration of **1n**/BTC/DMF was changed to 1:2:12, with **2n** being obtained in 88% yield with only a small amount of **3n**. On the other hand, when that ratio was applied to *o*-hydroxyacetophenone, the yield was improved only slightly [81% (1:2:8); 84% (1:2:12)] and further increase of the DMF ratio had little effect on the yield. So the optimal molar ratio of this reaction should be *o*-hydroxyacetophenones/BTC/DMF = 1:2:12. The solvent effect and reaction time were also investigated. A series of solvents were tested to optimize the reaction conditions. When diethyl ether or toluene was used, the reaction proceeded slowly and gave low yields. Good yields were obtained in 1,2-dichloroethane or DMF and 1,2-dichloroethane was

chosen as the solvent. To confirm the optimal ratio and extend the scope of this reaction, a wide range of substituted and structurally diverse *o*-hydroxyacetophenones were subjected to this reaction under the same conditions. As summarized in *Table 1*, a variety of substituted 3-formylchromones were obtained in good to excellent yields.

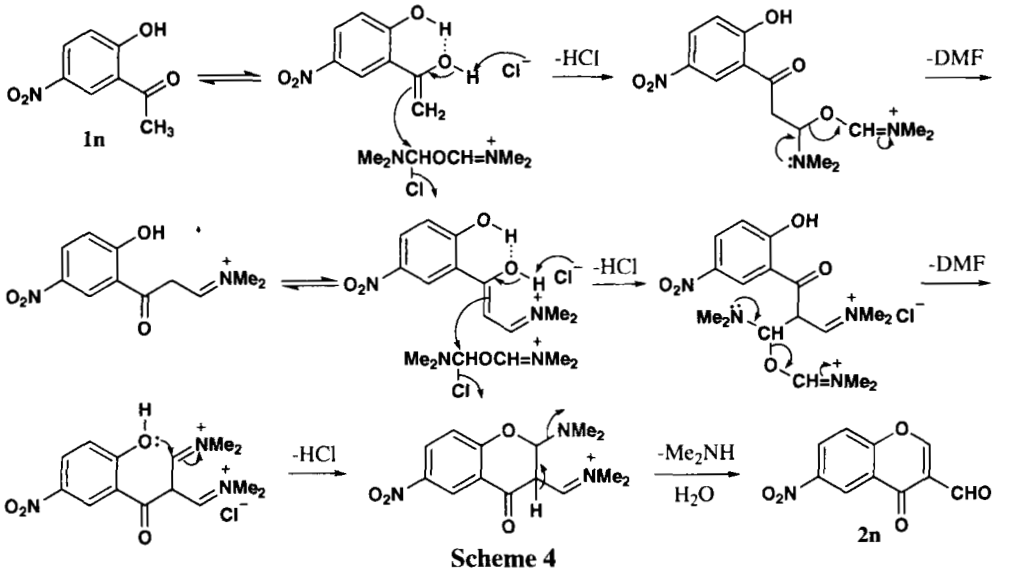
Generally speaking, *o*-hydroxyacetophenones containing either electron-withdrawing or electron-donating groups give the desired products in satisfactory yields. However, *o*-hydroxyacetophenones bearing OMe group at the C-4 or C-5 position (e.g., 4-methoxy or 5-methoxy-2-hydroxyacetophenone), proceeded in relatively lower yields (*Table 1, Entries 10, 11*). Nohara[21,22] proposed that the formylation on the benzene ring and formation of the tarry material led to this result, but these by-products were not detected by the present method. They also claimed that *o*-hydroxyacetophenones carrying one more OH group (e.g., 2,5 or 2,4-dihydroxyacetophenone) gave the desired hydroxy chromones in poor yields. Nevertheless, when 2,5-dihydroxyacetophenone was subjected to the present conditions, to our delight, pure 6-hydroxychromone was isolated successfully in moderate yield (70%). On the other hand, attempts to prepare 5,7-dihydroxy-3-formylchromones from 2,4,6-trihydroxyacetophenone were unsuccessful. It has been assumed[28] that the presence of several hydroxy groups significantly lowers the acidity of the methyl hydrogen of the acetyl group thus favoring ring formylation and polycondensation of the intermediates. It is generally accepted that in the structure of *o*-hydroxyacetophenones, an *o*-hydroxy group forms a hydrogen bond with the acetyl group, similar to dioxaborin ring system.[21,22] In 1996, Rajanna reported another possible sequence of this reaction,[29] but the detailed mechanism is still uncertain. According to Rivero *et al.*,[25c] the Vilsmeier-type reagent generated *in situ* from BTC and excess DMF, is adduct **II**, which is less reactive than adduct **I** (*Scheme 3*).



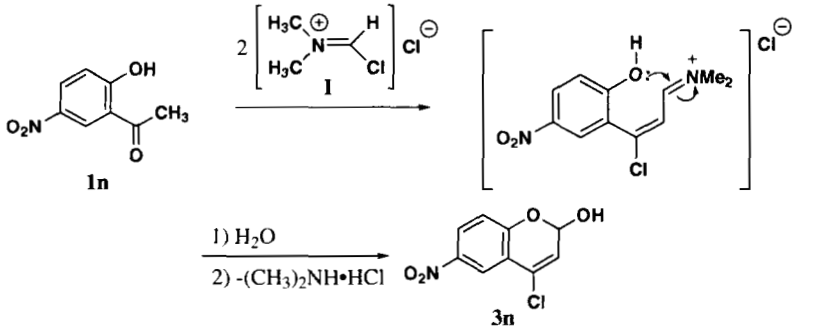
Formation of **I** and the less active adduct **II**

Scheme 3

Based on our results, we suggest a mechanism for the formation of **2n** (*Scheme 4*) and the possible rationalization for the formation of **3n** (*Scheme 5*). Since hydrogen bonding should be weaker in 1,2-dichloroethane compared with using DMF as solvent, O-alkylation or C-alkylation may take place in the corresponding enol intermediate of *o*-hydroxyacetophenones. Under these conditions (**1n**/BTC/DMF = 1:2:8), 5-nitro-2-hydroxyacetophenone underwent partial chloroformylation to yield **3n** after hydrolysis; thus the reaction of 5-nitro-2-hydroxyacetophenone and adduct **I** led to a mixture of **2n** and **3n** (*Scheme 5*). When a larger excess DMF is used (**1n**/BTC/DMF = 1:2:12), 5-nitro-2-hydroxyacetophenone reacted with the less active adduct **II** to afforded the main product **2n** contaminated with a small amount **3n** (*Scheme 4*).



Scheme 4



Possible rationalization for the formation of **3n** (**1n**/BTC/DMF = 1:2:8)

Scheme 5

In summary, we have developed a mild and efficient Vilsmeier route to the synthesis of 3-formylchromones from *o*-hydroxyacetophenones in good to excellent yields.

EXPERIMENTAL SECTION

Mps were obtained on an Electrothermal melting-point apparatus and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet Avatar 370 spectrophotometer. ^{1}H NMR spectra were determined on a Varian Mercur plus-400 spectrometer in $CDCl_3$ or DMSO using TMS as internal standard. ^{13}C NMR spectra were measured on a Varian Mercur plus-400 spectrometer using DMSO as the solvent. MS (EI) spectra were acquired on a Finnigan Trace DSQ spectrometer. ESI-MS spectra were obtained on a Agilent LCQ/Advantage mass spectrometer. HRMS were measured on a Bruker APEX III spectrometer. The progress of the reaction was monitored by TLC. The starting *o*-hydroxyacetophenones **1** were prepared according to the literature.[30]

Typical Procedure.- BTC (3.6 g, 12 mmol) in $ClCH_2CH_2Cl$ (20 mL) was added dropwise to a solution of DMF (7.2 mL, 72 mmol) in $ClCH_2CH_2Cl$ (10 mL) immersed in an ice-water bath. The mixture was stirred for 20 minutes, then the ice-water bath was removed. The reaction temperature was raised to 20°C with stirring continued for an additional 0.5-1 h to obtain the Vilsmeier reagent. Substituted *o*-hydroxyacetophenone **1** (6 mmol) in $ClCH_2CH_2Cl$ (15 mL) was added dropwise to the mixture at 0-5°C, and the resulting reaction mixture was heated to room temperature. After completion of the reaction [monitored by TLC(ethyl acetate-cyclohexane-acetic acid = 50:50:1)], the mixture was poured into ice-water with stirring for 1-1.5 h. The organic layer was separated and the aqueous layer extracted with $ClCH_2CH_2Cl$ (20 mL x 2). The combined organic layer was washed successively with 10% $NaHCO_3$ (20 mL x 2) and brine (20 mL x 3). After condensation, the crude product was purified by column chromatography (ethyl acetate/cyclohexane = 2:1) to obtain the pure product.

Table 1. Preparation of 3-Formylchromones with BTC/DMF in 1,2-Dichloroethane[a]

Entry	Product	Time (h)	Yield[b] (%)	mp (°C) (*lit.* mp)	IR (cm-1)	^{1}H NMR (δ)
1	**2a**	4	87	154-155 (154[31])	3059, 2867, 1694, 1650	7.50–7.56 (m, 2 H, ArH), 7.75–7.79 (m, 1 H, ArH), 8.31 (d, 1 H, *J* = 8.0 Hz, ArH), 8.56 (s, 1 H, 2-H), 10.40 (s, 1 H, CH=O)
2	**2b**	4	81	157 (157-158[32])	3069, 2857, 1698, 1655	7.47–7.51 (m, 1 H, ArH), 7.56–7.59 (m, 1 H, ArH), 7.94–7.96 (m, 1 H, ArH), 8.56 (s, 1 H, 2-H), 10.38 (s, 1 H, CH=O)
3	**2c**	4	82	163-164 (163-165[32])	3079, 2859, 1694, 1658	7.52 (d, 1 H, *J* = 8.4 Hz, ArH), 7.71 (d, 1 H, *J* = 8.8 Hz, ArH), 8.27 (s, 1 H, ArH), 8.54 (s, 1 H, 2-H), 10.37 (s, 1 H, CH=O)
4	**2d**	4	86	186 (186[31])	3072, 2861, 1692, 1656	7.45 (d, 1 H, *J* = 8.8 Hz, ArH), 7.84 (d, 1 H, *J* = 8.4 Hz, ArH), 8.41 (s, 1 H, ArH), 8.54 (s, 1 H, 2-H), 10.36 (s, 1 H, CH=O)
5	**2e**	4	85	170 (171[31])	3082, 2855, 1695, 1655	2.50 (s, 3 H, CH_3), 7.44 (d, 1 H, *J* = 8.4 Hz, ArH), 7.56 (d, 1 H, *J* = 8.0 Hz, ArH), 8.08 (s, 1 H, ArH), 8.54 (s, 1 H, 2-H), 10.39 (s, 1 H, CH=O)
6	**2f**	4	82	170-171 (170-172[31])	3062, 2869, 1692, 1655	2.52 (s, 3 H, CH_3), 7.31-7.33 (m, 2 H, ArH), 8.18 (d, 1 H, *J* = 8.0 Hz, ArH), 8.52 (s, 1 H, 2-H), 10.39 (s, 1 H, CH=O)
7	**2g**	4	88	144-145 (145[3])	3060, 2866, 1709, 1645	2.48 (s, 3 H, CH_3), 7.80 (s, 1 H, ArH), 8.03 (s, 1 H, ArH), 8.58 (s, 1 H, 2-H), 10.37 (s, 1 H, CH=O)

Table 1. Continued...

Entry	Product	Time (h)	Yield[b] (%)	mp (°C) (*lit.* mp)	IR (cm-1)	^{1}H NMR (δ)
8	**2h**	4	93	170 (170-171[33])	3062, 2870, 1699, 1664	7.80 (s, 1 H, ArH), 8.17 (s, 1 H, ArH), 8.60 (s, 1 H, 2-H), 10.35 (s, 1 H, CH=O)
9	**2i**	4	95	177 (177-178[22])	3062, 2895, 1696, 1669	8.10 (d, 1 H, *J* = 2.4 Hz, ArH), 8.36 (d, 1 H, *J* = 2.0 Hz, ArH), 8.60 (s, 1 H, 2-H), 10.35 (s, 1 H, CH=O)
10	**2j**	3	72	158-159 (158[31])	3060, 2844, 1686, 1644	3.93 (s, 3 H, OCH_3), 7.31-7.34 (m, 1 H, ArH), 7.48 (d, 1 H, *J* = 8.8 Hz, ArH), 7.65 (d, 1 H, *J* = 3.2 Hz, ArH), 8.54 (s, 1 H, 2-H), 10.41 (s, 1 H, CH=O)
11	**2k**	3	76	188 (188-190[22])	3060, 2845, 1686, 1644	3.93 (s, 3 H, OCH_3), 7.31-7.34 (m, 1 H, ArH), 7.48 (d, 1 H, *J* = 9.2 Hz, ArH), 7.65 (d, 1 H, *J* = 2.8 Hz, ArH), 8.54 (s, 1 H, 2-H), 10.41 (s, 1 H, CH=O)
12	**2l**[c]	4	82	187-188	3061, 2854, 1693, 1655	7.99-8.03 (m, 1 H, ArH), 8.91 (s, 1 H, 2-H), 10.06 (s, 1 H, CH=O)
13	**2m**	6	89	160 (160-161[34])	3064, 2864, 1701, 1645	7.71-7.79 (m, 2 H, ArH), 7.87 (d, 1 H, *J* = 8.8 Hz, ArH), 7.98 (d, 1 H, *J* = 7.6 Hz, ArH), 8.22 (d, 1 H, *J* = 8.8 Hz, ArH), 8.50-8.52 (m, 1 H, ArH), 8.72 (s, 1 H, 2-H), 10.47 (s, 1 H, CH=O)
14	**2n**	6	91	161 (163[31])	3065, 2865, 1695, 1671	7.74 (d, 1 H, *J* = 9.2 Hz, ArH), 8.58-8.61 (m, 2 H, ArH), 9.16 (d, 1 H, *J* = 2.4 Hz, 2-H), 10.38 (s, 1 H, CH=O)
15	**2o**	6	90	178-179 (180[3])	3060, 860, 1702, 1655	2.59 (s, 3 H, CH_3), 8.22 (d, 1 H, *J* = 2.0 Hz, ArH), 8.37-8.38 (m, 1 H, ArH), 8.59 (s, 1 H, 2-H), 10.37 (s, 1 H, CH=O)
16	**2p**	3	70	235-237 (235-238[35])	3060, 844, 1686, 1644	7.28-7.31 (m, 1 H, ArH), 7.41 (d, 1 H, *J* = 3.2 Hz, ArH), 7.63 (d, 1 H, *J* = 9.2 Hz, ArH), 8.86 (s, 1 H, 2-H), 10.12 (s, 1 H, CH=O)

a) Substrate **1** (6 mmol), BTC (12 mmol) and DMF (7.2 mL, 72 mmol) was used. b) Isolated yields and *o*-hydroxyacetophenones/BTC/DMF = 1:2:12. c) ^{13}C NMR (100 MHz, d_6-DMSO): δ = 103.8, 104.0, 113.0, 120.1, 151.4, 162.8, 165.2, 172.5, 186.6, 187.6. IR (KBr): 3061, 2854, 1693, 1655 cm-1. MS (EI): *m/z* (%) = 229 (M^++1, 30), 200 (100), 174 (56), 158 (48), 146 (58). HRMS-ESI: *m/z* $[M-H]^-$ Calcd. for $C_{10}H_2F_3O_3$: 226.9951. Found: 226.9948.

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