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Solvent-free and room temperature synthesis of thiochromans in the presence of a catalytic amount of iodine

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Abstract: Iodine catalyzed cyclocondensation of α, β-unsaturated aldehydes with arenethiols afford the corresponding 2-substituted-4-(arylthio)thiochromans in good yield under solvent-free and room temperature conditions. The present protocol offers advantages over the conventional methods reported using mineral acids in terms of reaction time, easy work up and mild conditions.

Keywords: Thiochromans; α, β-unsaturated aldehydes; arenethiols; iodine; solvent-free; room temperature.

1. Introduction

Thiochroman skeleton continue to attract considerable attention due to their presence in variety of biologically active compounds[1-8] and also they serve as useful synthetic intermediates by virtue of their reactivity towards a wide variety of reagents. Several methods have been reported for their synthesis[9-15] and most popular among them being classical Claisen rearrangement of allyl phenyl sulfides[16-25] and acid-catalyzed intramolecular cyclocondensation of thiol and β -arylthio aldehyde in turn obtained from reaction of arylthiol and α, β-unsaturated aldehyde under basic conditions.[26] This two step transformation has been extended to one pot procedure involving generation of arylthio ethers by Michael addition of arylthiol to conjugated system followed by electrophilic cyclization of carbenium intermediate generated in situ in the presence of Bronsted or Lewis acids. This one pot procedure has been reported with variety of reagents such as H_2SO_4,[27,28] *p*-TSOH,[26] trifluoroacetic acid,[29] nanosized sulfated SnO_2 dispersed in the micropores of Al-pillared clay,[30] iodine,[31] $SnCl_4$,[22] tungstophosphoric acid,[32] montmorillonite KSF[33] and Na_2CO_3/SiO_2-PPA/SiO_2.[34] The synthetic utility of these methods may, however, be considerably limited because of the use of corrosive protic acids or expensive Lewis acids, high temperatures, prolonged reaction times, multi-step reactions, etc. Michael addition of thiols to unsaturated systems to form carbon-sulphur bond is a key reaction in organic synthesis and has been well studied under a variety of conditions. Molecular iodine a versatile catalyst has been used to effect a wide array of synthetic transformations and been reported to catalyze smooth 1,4 addition of thiols to unsaturated systems. Iodine has been studied for cyclocondensation of thiophenol with cinnamaldehyde and the reaction requires about 16 hrs in dichloromethane.[30] However, the utility of this catalyst has not been explored in detail by varying solvents or under neat

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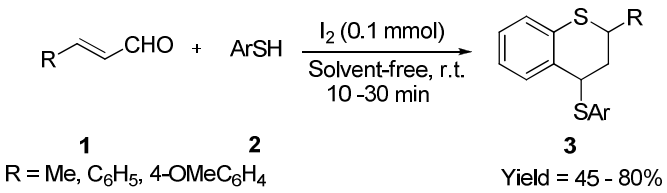
conditions for synthesis of thiochroman skeleton and here in we describe facile one pot synthesis of substituted thiochromans using molecular iodine as catalyst at room temperature under solvent free conditions. Reactions carried out under solvent-free conditions have received immense popularity in recent years. The mild reaction conditions, short reaction times, occasional enhanced selectivity and clean products are salutary features of this approach.

2. Results and discussion

A mixture of α, β-unsaturated aldehyde and arenethiol in the presence of catalytic amount of iodine was stirred at room temperature under neat conditions (Scheme 1). The reaction was followed by TLC and the reaction proceeded to completion in 30 minutes to afford the corresponding thiochroman in moderate to good yield.

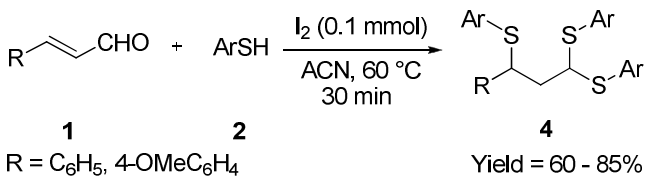


Scheme 1. Iodine catalyzed cycloaddition of α, β-unsaturated aldehyde with arenethiols under solvent free conditions.

Blank reaction carried out in the absence of iodine as catalyst did not yield any product and led to recovery of starting materials under identical conditions. Thus it is apparent that molecular iodine is required to bring about 1,4 addition followed by dehydrative cyclization. In order to test the scope and limitation of this transformation catalysed by iodine, a variety of substituted arene thiols were treated with aliphatic and aromatic unsaturated aldehydes and the results are presented in Table 1. The reaction seems to be sensitive to electronic and steric factors as is obvious from the observation that crotonaldehyde undergoes smooth reaction compared to cinnamaldehyde and yields suffered with sterically hindered thiophenols. It is worth mentioning that naphthalene derivatives undergo facile reaction to afford the corresponding thiochroman in good yield.

Further the reaction was studied in different solvents such as acetonitrile and dichloromethane. The reaction with aliphatic systems such as crotonaldehyde proceed as expected and yield the corresponding thiochromans while cinnamaldehyde and p-methoxy cinnamaldehyde under go reaction with thiophenol to afford the corresponding thioacetal. Same reaction carried out in acetonitrile at 60 °C for 30 minutes gave trisubstituted product[33]. The reaction with benzyl thiol irrespective of the conditions yield trisubstituted adduct and no trace of cyclic product was observed (Scheme 2).

Thus the present study reveals that optimum yields of thiochromans are obtained under neat conditions at room temperature. Although the details of the mechanism still remain ambiguous, the reaction may proceed through allylic cationic intermediates generated in situ.



Scheme 2. Iodine catalyzed protective addition of α, β-unsaturated aryl aldehyde with arenethiols in acetonitrile

Table 1. Reaction of aldehydes with arenethiols in the presence of catalytic amount of I_2

Product	R	Ar	Time (min.)	Yield (%)[a]
3a	Me	C_6H_5	10	66
3b	Me	4-ClC_6H_4	15	59[b]
3c	Me	4-BrC_6H_4	15	63[b]
3d	Me	4-MeC_6H_4	15	58[b]
3e	Me	2, 4-MeC_6H_3	20	47
3f	Me	3, 5-ClC_6H_3	20	45[b]
3g	Me	2-$C_{10}H_7$	30	80[b]
3h	C_6H_5	C_6H_5	15	68
3i	C_6H_5	4-ClC_6H_4	15	80[b]
3j	C_6H_5	4-MeC_6H_4	15	-
3k	4-$OMeC_6H_5$	C_6H_5	15	70

[a]Yields refer to isolated pure products. The products were characterized by ^{1}H NMR and ^{13}C NMR spectral data.
[b]Minimum amount of dichloromethane was used for dissolution.

3. Conclusion

In conclusion, the present method is a very simple, one-pot reaction, which is carried out at ambient temperature under mild and solvent less conditions using iodine (I_2) as an effective, homogeneous, readily available and low cost catalyst. This method is a green protocol for the synthesis of thiochromans.

4. Experimental

All melting points were determined on an electrothermal Gallenkamp apparatus. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Gemini Spectrometer 300 and 400 MHz respectively. IR spectra were recorded on Nicolet Fourier Transform spectrometer. Mass spectra were obtained on a 7070H or VG Autospec Mass spectrometer using LSIMS technique. Thin-layer chromatography (TLC) was performed on GF-25U (Anal. Tech) plates and silica gel glass-backed plates. Routine column chromatography was conducted using silica gel 100-200 mesh.

General procedure:

The α, β-unsaturated aldehyde (1 mmol), thiophenol (2.5 mmol) and iodine (0.1 mmol) were mixed together and stirred at room temperature for 10–30 min. After completion of the reaction (monitored by TLC), ice cold saturated 5% sodium thiosulphate solution (5 mL) was added and extracted with dichloromethane (3 x 15 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporation of solvents under the reduced pressure afforded corresponding thiochromans (47-80%). The pure products were obtained by chromatography on 100-200 mesh silica gel (petroleum ether) or (petroleum ether/ ethyl acetate 98: 2).

2-methyl-4-(phenylthio)thiochroman (3a)[32-34]**:** Colorless oil, yield 66%, IR (neat) Vmax/cm^{-1} 693, 747, 904, 1018, 1084, 1441, 1473, 1580, 2857, 2920, 2962, 3063. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (3H, d, J = 6.8Hz), 1.85 (1H, m), 2.10 (1H, m), 3.60 (1H, m), 4.73 (1H, dd, J = 8.8Hz, 5.6Hz), 7.21-7.33 (6H, m), 7.43-7.75 (3H, m). EI MS: *m/z* (rel.abund.%) 273 (M^+, 100), 163 (M^+, 60%).

6-chloro-4-(4-chlorophenylthio)-2-methylthiochroman (3b)[30]**:** Pale yellow oil, yield 59%, IR (neat) Vmax/cm^{-1} 695, 750, 902, 1015, 1089, 1446, 1472, 1589, 2855, 2927, 2960, 3065. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (3H, d, J = 6.6Hz , 1.82-2.08 (2H, m), 3.43-3.48 (1H, m), 4.62 (1H, dd, J =

9.0Hz, 5.2Hz), 7.22-7.38 (7H, m). EI MS: *m/z* (rel.abund.%) 342 (M^+, 100), 344 (M^+, 66), 197 (M^+ , 50), 199 (M^+, 17).

6-bromo-4-(4-bromophenylthio)-2-methylthiochroman (3c)[29] **:** Colorless oil, yield 63%, IR (neat) Vmax/cm^{-1} 690, 750, 920, 1025, 1090, 1436, 1462, 1582, 2850, 2922, 2967, 3063. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (3H, d, J = 6.6Hz), 1.87-2.01 (2H, m), 3.51-3.57 (1H, m), 4.63 (1H, dd, J = 9.4Hz, 5.7Hz), 7.15 (2H, d, J = 8.4), 7.27-7.46 (5H, m). EI MS: *m/z* (rel.abund.%) 430 (M^+, 50), 432 (M^+, 100), 241 (M^+, 50), 243 (M^+, 48).

2,6-dimethyl-4-(p-tolylthio)thiochroman (3d)[26,30,32,34]**:**Pale yellow oil, yield 58%, IR (neat) Vmax/cm^{-1} 685, 750, 920, 1030, 1090, 1440, 1458, 1582, 2850, 2922, 2967, 3063. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (3H, d, J = 6.7Hz), 1.82-1.85 (1H, m), 1.98-2.01 (1H, m), 2.33 (3H, s), 2.35 (3H, s), 3.51-3.54 (1H, m), 4.63 (1H, dd, J = 11.6Hz, 6.4Hz), 7.03-7.19 (7H, m). EI MS: *m/z* (rel.abund.%) 301 (M^+, 100), 177 (M^+, 45%).

4-(2,4-dimethylphenylthio)-2,6,8-trimethylthiochroman (3e): Pale yellow oil, yield 47%, IR (neat) Vmax/cm^{-1} 680, 750, 900, 1030, 1080, 1440, 1455, 1582, 2850, 2922, 2967, 3059. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (3H, d, J = -6.6Hz), 1.98-2.10 (1H, m), 2.14-2.20 (1H, m), 2.81-2.36 (12H, m), 3.45-3.58 (1H, m), 4.55 (1H, dd, J = 11.6Hz, 6.4Hz), 6.84-7.10 (3H, m), 7.12 (1H, d, J = 10.4Hz), 7.35 (1H, d, J = 10.4Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 20.8, 20.9, 21.0, 21.4 41.1, 43.4, 55.7, 127.0, 127.1, 129.8, 129.9, 131.1, 131.2, 133.3, 133.4, 133.5, 137.1, 137.7, 140.2. EI MS: *m/z* (rel.abund.%) 329 (M^+, 100), 191 (M^+, 55). Anal. Calcd. For $C_{18}H_{20}S_2$ (328.53) C, 73.12; H, 7.36; S, 19.52. Found C, 73.02; H, 7.46; S, 19.42%.

5,7-dichloro-4-(3,5-dichlorophenylthio)-2-methylthiochroman (3f): Pale yellow oil, yield 45%, IR (neat) Vmax/cm^{-1} 695, 800, 902, 1020, 1070, 1435, 1472, 1585, 2860, 2935, 2952, 3055. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (3H, d, J = 8.8Hz), 1.87-2.12 (2H, m), 3.41-3.56 (1H, m), 4.90-4.97 (1H, m), 7.20-7.33 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 41.8, 42.4, 56.6, 129.0, 129.1, 129.3, 131.6, 131.9, 133.6, 134.4, 134.4, 134.5, 134.5. EI MS: *m/z* (rel.abund.%) 411 (M^+, 80), 413 (M^+, 100), 231, (M^+, 60), 233 (M^+, 40). Anal. Calcd. For $C_{16}H_{12}Cl_4S_2$ (410.20) C, 46.85; H, 2.95; S, 15.63. Found C, 46.69; H, 3.05; S, 15.49%.

3-methyl-1-(naphthalen-2-ylthio)-2,3-dihydro-1H-benzo[f]thiochromene (3g)[26,32]**:** Off white solid, yield 80%, mp 128-130 °C, IR (KBr) Vmax/cm^{-1} 678, 748, 920, 1001, 1084, 1441, 1485, 1590, 2857, 2920, 2962, 3063. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (3H, d, J = 6.8Hz), 2.04 (1H, ddd, J = 2.8Hz, 11.6Hz, 14.4Hz), 2.51 (1H, ddd, J = 2.8Hz, 3.2Hz, 14.0Hz), 4.292-4.34 (1H, m), 5.39 (1H, t, J = 4Hz), 7.19 (1H, d, J = 8.8 Hz), 7.43 (1H, t, J = 8.0Hz), 7.52-7.60 (3H, m), 7.63-7.67 (2H, m), 7.78 (1H, d, J = 8.0Hz), 7.88 (1H, t, J = 8.0Hz), 8.04 (1H, s), 8.31 (1H, d, J = 8.8Hz). EI MS: *m/z* (rel.abund.%) 373 (M^+, 100), 231 (M^+, 56%).

2-phenyl-4-(phenylthio)thiochroman (3h)[31]**:** White solid, yield 68%, mp 101-102 °C, IR (KBr) Vmax/cm^{-1} 691, 751, 901, 1013, 1080, 1445, 1470, 1585, 2855, 2935, 2972. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42-2.47 (2H, m), 4.70-4.71 (1H, m), 5.11 (1H, dd, J = 9.2Hz, 5.6Hz), 7.01-7.05 (1H, m), 7.11-7.16 (1H, m), 7.26-7.37 (8H, m), 7.43 (2H, d, J = 7.6Hz), 7.51 (2H, d, J = 8.0Hz). EI MS: *m/z* (rel.abund.%) 335 (M^+, 100), 225 (M^+, 53).

6-chloro-4-(4-chlorophenylthio)-2-phenylthiochroman (3i)[26,30]**:** Pale yellow oil, yield 80%, IR (neat) Vmax/cm^{-1} 685, 760, 920, 1015, 1085, 1455, 1473, 1595, 2860, 2940, 2969. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44-2.49 (2H, m), 4.71-4.72 (1H, m), 5.13 (1H, dd, J = 9.2Hz, 5.5Hz), 7.22-7.49 (12H, m). EI MS: *m/z* (rel.abund.%) 404 (M^+, 100), 406 (M^+, 66), 259 (M^+, 60), 259 (M^+, 20).

2-(4-methoxyphenyl)-4-(phenylthio)thiochroman (3k): Off white solid, yield 70%, mp 97-99 °C, IR (KBr) Vmax/cm^{-1} 691, 749, 902, 1020, 1082, 1445, 1470, 1582, 2855, 2922, 2960, 3065. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38-2.41 (2H, m), 3.80 (3H, s), 4.69 (1H, t, J = 3.2Hz), 5.05 (1H, t, J = 7.2Hz), 6.87 (2H, d, J = 8.8Hz), 6.99-7.03 (1H, m), 7.09-7.14 (2H, m), 7.26-7.35 (6H, m). ^{13}C NMR (100

MHz, $CDCl_3$): δ 34.7, 39.8, 49.3, 55.2, 114.1, 123.8, 125.8, 127.8, 127.8, 128.9, 129.1, 130.6, 131.5, 132.6, 133.1, 134.2, 134.9, 159.2. EI MS: *m/z* (rel.abund.%) 363 (M^- 100), 253 (M^-, 30). Anal. Calcd. For $C_{22}H_{20}OS_2$ (364.10) C, 72.49; H, 5.53; S, 17.59. Found C, 72.51; H, 5.60; S, 17.42%.

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