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ORIGINAL PAPER

Synthesis of oxoindolin-3-ylidene-1,3-dithioles

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Abstract An efficient and one-pot synthesis of 2-(2-oxoindolin-3-ylidene)-1,3-dithiole-4,5-dicarboxylates by a three-component condensation reaction of isatins, carbon disulfide and dialkyl acetylendicarboxylates in the presence of Bu_3P is reported. Reaction of carbon disulfide and dialkyl acetylene dicarboxylates with acenaphthylene-1,2-dione, ninhydrine and pyrimidine-tetraone resulted in the formation of 2-(2-oxoacenaphthylen-1(2*H*)-ylidene)-1,3-dithiole-4,5-dicarboxylates, 2-(1,3-dioxo-1*H*-inden-2(3*H*)-ylidene)-1,3-dithiole-4,5-dicarboxylates and 2-(2,4,6-trioxotetrahydropyrimidin-5(6*H*)-ylidene)-1,3-dithiole-4,5-dicarboxylates, respectively, in the same conditions.

Keywords Isatin · Oxindole · Oxoindolin-3-ylidene-1 · 3-dithiole · 1,3-Dithiole

Introduction

The heterocyclic indole and indoline ring system is a widely distributed structural framework present in a number of pharmaceuticals and natural products [1], and some of indolines, oxindole derivatives, have shown high biological activities. Oxindoles are known to possess antibacterial, antiprotozoal, and anti-inflammatory activities and are also patented as progesterone receptors agonists [2–5]. The varied biological activities of oxindole derivatives have attracted the synthetic chemists to a number of synthetic strategies [6–10]. Therefore, the development of methodologies using novel reagents with greater efficiency, simpler operational procedure, milder reaction condition, higher yield of products coupled with potential bioactivity is in demand.

Derivatives of sulfur heterocycles such as thiophene and 1,3-dithiole have been widely explored as new materials because of their superconducting optical and electronic switching properties [11]. 1,3-Dithiol-2-ylidenes have attracted much attention as building blocks for electronic materials due to their highly electron-donating properties [12, 13]. Therefore, due to the importance of 1,3-dithioles, various methods have been reported for the synthesis of 1,3-dithiole derivatives [12–22].

Despite of continuous research for the synthesis of heterocyclic indoline ring system and polysulfur heterocycle derivatives, only a limited number of indoles fused polysulfur heterocycles have been reported [23]. Therefore, as part of our program aimed at developing new methodologies for the preparation of heterocycles [24–31], we report here an efficient synthesis of 2-(2-oxoindolin-3-ylidene)-1,3-dithiole-4,5-dicarboxylates **4** via a three-component reaction of dialkyl acetylenedicarboxylate **1**, carbon disulfide **2** and isatins **3** in the presence of tributylphosphine based on Wittig reaction (Scheme 1).

Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz, respectively. ^1H and ^{13}C NMR spectra were obtained on solutions in DMSO-d_6. IR spectra were recorded using an FTIR apparatus. Elemental analyses were performed using a Heracus CHN-O-Rapid analyzer. The chemicals used in this work were

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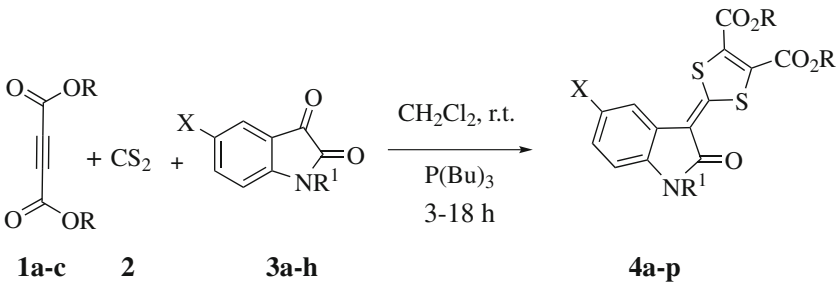
Scheme 1 Synthesis of oxoindolin-3-ylidene-1,3-dithioles **4**



purchased from Fluka and Merck and were used without purification.

General procedure for the preparation of oxoindolin-3-ylidene-1,3-dithioles

To a magnetically stirred solution of carbon disulfide (1 mmol) and tributylphosphine (1 mmol) in CH_2Cl_2 (5 mL) for 0.5 h were added isatin (1 mmol) and dimethyl acetyenedicarboxylate (1 mmol) at room temperature. The mixture was finally stirred for 2.5 h. After completion of the reaction (TLC), the reaction mixture was filtered off and the residue was washed with ether (10 mL) to afford the pure product **4**.

Dimethyl 2-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4a**) Orange powder (0.35 g, yield 98%). MP 229–231 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,017, 1,741, 1,713. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.96 (6H, s, 2CH$_3$), 6.99–7.40 (4H, m, H–Ar), 8.15 (1H, s, NH). Anal. Calcd for $C_{15}H_{11}NO_5S_2$: C, 51.57; H, 3.17; N, 4.01. Found: C, 51.46; H, 3.11; N, 3.94. (Due to the very low solubility of product **4a**, we were unable to obtain the ^{13}C NMR spectrum).

Dimethyl 2-(1-methyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4b**) Orange powder (yield 94%); mp 237–239 °C, lit.[16] mp 242–244 °C. IR (KBr) (ν_{max}/cm^{-1}): 1,715, 1,672. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.33 (3H, s, CH$_3$), 3.87 (6H, s, 2CH$_3$), 7.06–7.30 (4H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 26.4, 54.3, 109.0, 110.2, 120.8, 121.2, 122.3, 127.4, 129.3, 135.9, 140.6, 146.6, 159.3, 160.1, 164.8. Anal. Calcd for $C_{16}H_{13}NO_5S_2$: C, 52.88; H, 3.61; N, 3.85. Found: C, 52.74; H, 3.69; N, 3.77.

Dimethyl 2-(1-ethyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4c**) Yellow powder (yield 85%); mp 158–160 °C. IR (KBr) (ν_{max}/cm^{-1}): 1,718, 1,674. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.15 (3H, t, $^3J_{HH}$ = 7.01 Hz, CH$_3$), 3.75–3.80 (2H, m, CH$_2$), 3.87 and 3.88 (6H, s, 2CH$_3$), 7.08–7.24 (4H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 13.5, 54.3, 54.3, 108.9, 110.2, 120.9, 121.3, 122.1, 127.3, 129.2, 136.0, 139.5, 146.5, 159.3, 160.1, 164.4. Anal. Calcd for $C_{17}H_{15}NO_5S_2$: C, 54.10; H, 4.01; N, 3.71. Found: C, 54.19; H, 4.92; N, 3.61.

Dimethyl 2-(1-benzyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4d**) Yellow powder (yield 91%); mp 178–179 °C. IR (KBr) (ν_{max}/cm^{-1}): 17.16, 1,654. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.81(3H, s, CH$_3$), 3.89(3H, s, CH$_3$), 4.99 (2H, s, CH$_2$), 7.01–7.29 (9H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 43.2, 54.4, 109.6, 109.8, 121.0, 121.4, 122.5, 127.3, 127.7, 127.8, 129.1, 129.5, 136.0, 137.1, 139.5, 147.6, 159.3, 160.1, 164.9. Anal. Calcd for $C_{22}H_{17}NO_5S_2$: C, 60.12; H, 3.90; N, 3.19. Found: C, 60.03; H, 3.83; N, 3.12.

Dimethyl 2-(5-bromo-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4e**) Yellow powder (yield 83%); mp 285–287 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,446, 3,127, 1,756, 1,666. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.80 and 3.87 (6H, s, 2CH$_3$), 6.84–7.73 (3H, m, H–Ar), 10.98 (1H, s, NH). Anal. Calcd for $C_{15}H_{10}BrNO_5S_2$: C, 42.07; H, 2.35; N, 3.27. Found: C, 42.18; H, 2.29; N, 3.16.

Due to very low solubility of the products **4e–i**, we cannot report the ^{13}C NMR data for these products.

Dimethyl 2-(5-nitro-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4f**) Yellow powder (yield 86%); mp 280–282 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,184, 1,716, 1,685. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.88 and 3.89 (6H, s, 2CH$_3$), 6.77–8.08 (3H, m, H–Ar), 11.45 (1H, s, NH). Anal. Calcd for $C_{15}H_{10}N_2O_7S_2$: C, 45.68; H, 2.56; N, 7.10. Found: C, 45.79; H, 2.63; N, 7.01.

Dimethyl 2-(5-bromo-1-ethyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate **(4g)** Orange powder (yield 65%); mp 290–291 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,446, 2,931, 1,754, 1,664. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.08 (3H, bs, CH$_3$), 3.64 (2H, bs, CH$_2$), 3.83 (6H, bs, 2CH$_3$),6.92–7.21 (3H, m, H–Ar Anal. Calcd for $C_{17}H_{14}BrNO_5S_2$: C, 44.74; H, 3.09; N, 3.07. Found: C, 44.62; H, 3.02; N, 3.19.

Dimethyl 2-(1-methyl-5-nitro-2-oxoindolin-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4h**) Yellow powder (yield

75%); mp >300 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,101, 3,028, 1,753, 1,721, 1,669. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.80 (3H, s, CH_3), 3.89 (6H, s, $2CH_3$), 7.26–8.16 (3H, m, H–Ar). Anal. Calcd for $C_{16}H_{12}N_2O_7S_2$: C, 47.05; H, 2.96; N, 6.86. Found: C, 46.92; H, 2.88; N, 6.76.

Diethyl 2-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4i**) Yellow powder (yield 93%); mp 220 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,231, 2,975, 1,732, 1,665. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.27–1.29 (6H, bs, $2CH_3$), 4.31–4.33 (4H, bs, $2CH_2$), 6.93–7.27 (4H, m, H–Ar), 10.84 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.1, 63.6, 110.2, 111.2, 121.5, 121.7, 121.8, 127.5, 129.3, 135.9, 139.5, 145.9, 159.0, 159.7, 163.6, 166.4. Anal. Calcd for $C_{17}H_{15}NO_5S_2$: C, 54.10; H, 4.01; N, 3.71. Found: C, 54.01; H, 4.10; N, 3.63.

Diethyl 2-(1-methyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4j**) Yellow powder (yield 90%); mp 169 °C. IR (KBr) (ν_{max}/cm^{-1}): 2,965, 2,923, 1,732, 1,707, 1,669. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.30–1.35 (6H, m, $2CH_3$), 3.27 (3H, s, CH_3), 4.33–4.40 (4H, m, $2CH_2$), 7.09–7.39 (4H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.0, 14.1, 14.2, 26.4, 63.6, 108.9, 110.1, 120.8, 121.1, 122.2, 127.3, 129.4, 135.9, 140.5, 146.5, 158.9, 159.6, 164.7. Anal. Calcd for $C_{18}H_{17}NO_5S_2$: C, 55.23; H, 4.38; N, 3.58. Found: C, 55.11; H, 4.31; N, 3.50.

Diethyl 2-(1-benzyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4k**) Yellow powder (yield 85%); mp 210 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,420, 2,981, 1,737, 1,720, 1,674. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.30 (6H, t, $^3J_{HH} = 7.12$ Hz, $2CH_3$), 4.29–4.37 (4H, m, $2CH_2$), 4.96 (2H, s, CH_2Ph), 6.97–7.28 (9H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.1, 14.2, 43.2, 63.6, 109.5, 109.8, 121.0, 121.3, 122.4, 127.2, 127.7, 129.0, 129.6, 135.9, 137.1, 139.5, 147.4, 158.9, 159.6, 164.9. Anal. Calcd for $C_{24}H_{21}NO_5S_2$: C, 61.65; H, 4.53; N, 3.00. Found: C, 61.72; H, 4.57; N, 2.94.

Diethyl 2-(5-bromo-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4l**) Yellow powder (yield 80%); mp 220 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,231, 2,981, 1,734, 1,680. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.24–1.32 (6H, m, $2CH_3$), 4.30–4.37 (4H, m, $2CH_2$), 6.87–7.34 (3H, m, H–Ar), 10.97 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.2, 16.0, 63.6, 63.7, 66.2, 85.6, 109.8, 112.0, 113.4, 123.3, 123.7, 129.6, 130.1, 135.6, 138.4, 148.8, 158.9, 159.5, 166.1, 173.0. Anal. Calcd for $C_{17}H_{14}BrNO_5S_2$: C, 44.74; H, 3.09; N, 3.07. Found: C, 44.65; H, 3.01; N, 3.12.

Diethyl 2-(5-nitro-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4m**) Yellow powder (yield 80%); mp >300 °C dec. IR (KBr) (ν_{max}/cm^{-1}): 3,237, 2,975, 1,727, 1,681. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.31 (6H, t, $^3J_{HH} = 6.96$ Hz, $2CH_3$), 4.31–4.35 (4H, m, $2CH_2$), 7.02–8.10 (3H, m, H–Ar), 11.49 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.1, 63.7, 63.8, 108.7, 109.9, 115.5, 119.9, 121.7, 123.6, 130.4, 135.8, 141.9, 144.6, 150.9, 158.6, 159.1, 163.8, 166.5. Anal. Calcd for $C_{17}H_{14}N_2O_7S_2$: C, 48.33; H, 3.34; N, 6.63. Found: C, 44.23; H, 3.25; N, 6.59.

Di-tert-butyl 2-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4n**) Yellow powder (yield 89%); mp >300 °C. dec IR (KBr) (ν_{max}/cm^{-1}): 3,179, 2,970, 1,727, 1,666. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.53 (18H, bs, $6CH_3$), 6.92–7.31 (4H, m, H–Ar), 10.84 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 27.9, 85.4, 110.2, 121.5, 121.8, 121.9, 127.4, 130.2, 136.5, 139.4, 146.0, 157.9, 158.5, 166.4. Anal. Calcd for $C_{21}H_{23}NO_5S_2$: C, 58.18; H, 5.35; N, 3.23. Found: C, 58.24; H, 5.47; N, 3.29.

Di-tert-butyl 2-(1-methyl-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4o**) Orange powder (yield 85%); mp >300 °C dec. IR (KBr) (ν_{max}/cm^{-1}): 2,944, 2,860, 1,729, 1,680. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.52 (18H, bs, $6CH_3$), 3.23 (3H, s, CH_3), 7.08–7.33 (4H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.0, 23.8, 23.9, 24.0, 24.1, 26.4, 27.1, 27.9, 85.4, 108.9, 109.8, 120.9, 121.2, 122.2, 127.3, 130.4, 136.3, 140.5, 146.7, 157.8, 158.4, 164.9. Anal. Calcd for $C_{22}H_{25}NO_5S_2$: C, 59.04; H, 5.63; N, 3.13. Found: C, 58.92; H, 5.54; N, 3.04.

Di-tert-butyl 2-(5-bromo-2-oxo-1,2-dihydro-3H-indol-3-ylidene)-1,3-dithiole-4,5-dicarboxylate (**4p**) Yellow powder (yield 79%); mp >300 °C dec. IR (KBr) (ν_{max}/cm^{-1}): 3,190, 2,986, 1,721, 1,672, 1,627. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.53 (18H, bs, $6CH_3$), 6.87–7.36 (3H, m, H–Ar), 10.98 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 27.9, 85.6, 109.5, 112.0, 113.3, 123.3, 123.8, 129.5, 130.9, 136.3, 138.3, 148.9, 157.9, 158.2, 166.2. Anal. Calcd for $C_{21}H_{22}BrNO_5S_2$: C, 49.22; H, 4.33; N, 2.73. Found: C, 49.14; H, 4.39; N, 2.84.

Dimethyl 2-(2-oxoacenaphthylen-1(2H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**8a**) Orange powder (yield 96%); mp 198 °C. IR (KBr) (ν_{max}/cm^{-1}): 17.15, 1,669. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.88 and 3.90 (6H, s, $2CH_3$), 7.41–8.14 (6H, m, H–Ar). Anal. Calcd for $C_{19}H_{12}O_5S_2$: C, 59.36; H, 3.15. Found: C, 59.43; H, 3.08. (Due to very low solubility of the product **8a**, we cannot report the ^{13}C NMR data for this product).

Diethyl 2-(2-oxoacenaphthylen-1(2H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**8b**) Yellow powder (yield 94%);

mp 164 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,425, 1,718, 1,653. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.23–1.30 (6H, m, 2CH$_3$), 4.29–4.33 (4H, m, 2CH$_2$),7.18–8.02 (6H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.0, 14.1, 63.5, 63.7, 118.6, 119.2, 122.2, 124.7, 128.5, 128.8, 128.9, 129.0, 129.2, 130.0, 131.8, 132.4, 132.6, 132.7, 135.5, 135.7, 145.9, 158.8, 159.6, 187.5. Anal. Calcd for $C_{21}H_{16}O_5S_2$: C, 61.15; H, 3.91. Found: C, 61.04; H, 3.86.

Di-tert-butyl 2-(2-oxoacenaphthylen-1(2H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**8c**) Yellow powder (yield 85%); mp >300 °C. IR (KBr) (ν_{max}/cm^{-1}): 3,425, 1,720,1,674, 1,612. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.57 (18H, s, 6CH$_3$), 7.48–8.13 (6H, m, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 28.1, 85.5, 119.3, 122.2, 124.8, 128.6, 129.0, 130.3, 131.9. Anal. Calcd for $C_{25}H_{24}O_5S_2$: C, 64.08; H, 5.16. Found: C, 63.98; H, 5.08.

Dimethyl 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**9a**) Yellow powder (yield 80%); mp >300 °C. IR (KBr) (ν_{max}/cm^{-1}): 1,706, 1,664. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.89 (6H, s, 2CH$_3$), 7.77 (4H, bs, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 54.5, 122.9, 134.7, 135.2, 140.2, 159.5, 186.9. Anal. Calcd for $C_{16}H_{10}O_6S_2$: C, 53.03; H, 2.78. Found: C, 53.11; H, 2.71.

Diethyl 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**9b**) Yellow powder (yield 72%); mp >300 °C dec. IR (KBr) (ν_{max}/cm^{-1}): 3,430, 2,981, 1,725, 1,659. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.30 (6H, t, $^3J_{HH}$ = 7.09 Hz, 2CH$_3$), 4.34 (4H, q, $^3J_{HH}$ = 7.07 Hz, 2CH$_2$), 7.74 (4H, bs, H–Ar), 11.49 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.1, 63.8, 115.6, 122.9, 134.7, 135.2, 140.1, 159.0, 162.0, 186.9. Anal. Calcd for $C_{18}H_{14}O_6S_2$: C, 55.37; H, 3.61. Found: C, 55.29; H, 3.36.

Di-tert-butyl 2-(1,3-dioxo-1H-inden-2(3H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**9c**) Yellow powder (yield 70%); mp >300 °C. IR (KBr) (ν_{max}/cm^{-1}): 2,986, 2,928, 1,718, 1,715, 1,672. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.55 (18H, s, 6CH$_3$), 7.80 (4H, bs, H–Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 27.9, 85.9, 122.9, 135.2, 135.5, 140.2, 157.8, 187.0. Anal. Calcd for $C_{22}H_{22}O_6S_2$: C, 59.17; H, 4.97. Found: C, 59.23; H, 4.89.

Dimethyl 2-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(6H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**10a**) Cream powder (yield 91%); mp 210 °C. IR (KBr) (ν_{max}/cm^{-1}): 1,737, 1,716, 1,701. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.31 (3H, s, CH$_3$), 3.90 (3H, s, CH$_3$) ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.5, 23.8, 28.3, 54.4, 136.4, 150.5, 159.7, 160.7, 173.2. Anal. Calcd for $C_{13}H_{12}N_2O_7S_2$: C, 41.93; H, 3.25; N, 7.52. Found: C, 41.85; H, 3.33; N, 7.60.

Diethyl 2-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(6H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**10b**) Cream powder (yield 87%); mp 184 °C. IR (KBr) (ν_{max}/cm^{-1}): 2,975, 2,928, 1,733, 1,633. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.30 (6H, t, $^3J_{HH}$ = 7.04 Hz, 2CH$_3$), 3.20 (6H, bs, 2CH$_3$), 4.48 and 4.35 (4H, AB$_q$, $^3J_{HH}$ = 6.98 Hz, 2CH$_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 14.1, 28.3, 63.7, 103.1, 136.4, 150.5, 159.3, 160.7, 173.1. Anal. Calcd for $C_{15}H_{16}N_2O_7S_2$: C, 44.99; H, 4.03; N, 7.00. Found: C, 44.90; H, 4.09; N, 6.91.

Di-tert-butyl 2-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(6H)-ylidene)-1,3-dithiole-4,5-dicarboxylate (**10c**) Cream powder (yield 80%); mp >300 °C. IR (KBr) (ν_{max}/cm^{-1}): 2,975, 2,939, 1,720, 1,717, 1,634. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 1.54 (18H, s, 6CH$_3$), 3.32 (6H, s, 2CH$_3$). Anal. Calcd for $C_{19}H_{24}N_2O_7S_2$: C, 49.99; H, 5.30; N, 6.14. Found: C, 49.83; H, 5.22; N, 6.05. (Due to very low solubility of the product **10c**, we cannot report the ^{13}C NMR data for this product).

Results and discussion

We found that a mixture of dialkyl acetylenedicarboxylate **1**, carbon disulfide **2** and isatins **3** in the presence of tributhylposphine in CH_2Cl_2 at room temperature, afforded oxoindolin-3-ylidene-1,3-dithioles **4** in good yields for 3–18 h. The results are summarized in Table 1.

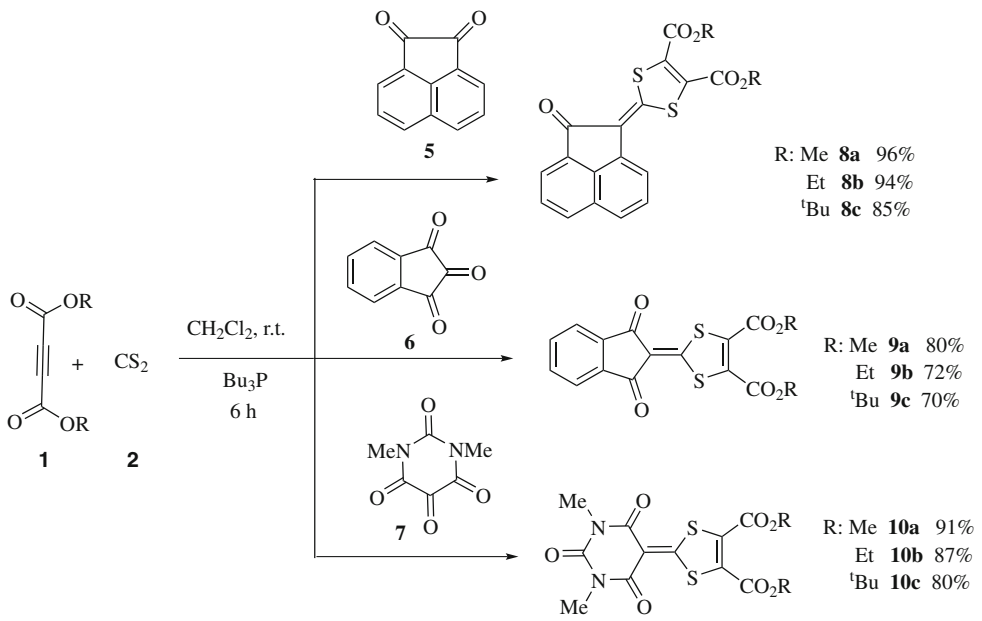
The good yields and purity of products and simplicity of the present procedure makes it an interesting,

Table 1 Synthesis of oxoindolin-3-ylidene-1,3-dithioles **4**

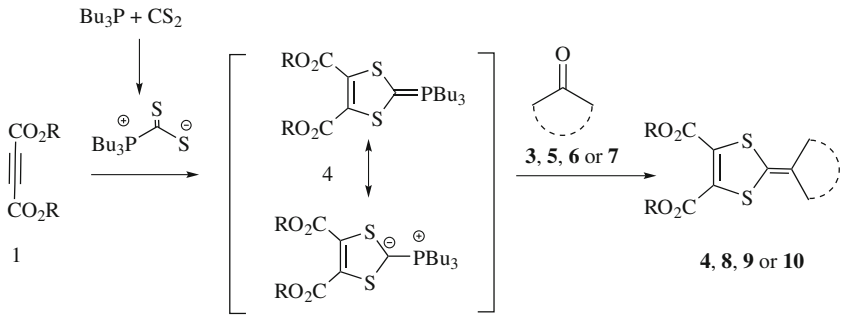
Compound **4**	R	X	R^1	Time (h)	Yield (%)[a]
a	Me	H	H	3	98
b	Me	H	Me	3	94
c	Me	H	Et	3.5	85
d	Me	H	PhCH$_2$	5	91
e	Me	Br	H	13	83
f	Me	NO$_2$	H	12	86
g	Me	Br	Et	15	65
h	Me	NO$_2$	Me	13	78
i	Et	H	H	4	93
j	Et	H	Me	6	90
k	Et	H	PhCH$_2$	7	85
l	Et	Br	H	15	80
m	Et	NO$_2$	H	16	80
n	^{t}Bu	H	H	5	89
o	^{t}Bu	H	Me	8	85
p	^{t}Bu	Br	H	18	79

[a] Isolated yields

Scheme 2 Synthesis of 1,3-dithioles **8**, **9** and **10**



Scheme 3 Proposed mechanism



convenient and acceptable one-pot method for the preparation of functionalized oxoindolin-3-ylidene-1,3-dithioles. In addition, the workup of these very clean reactions involves only a filtration and simple washing step with ether.

As expected, when the isatin **3** was replaced by acenaphthylene-1,2-dione **5**, ninhydrine **6** and 1,3-dimethylpyrimidine-tetraone **7**, 2-(2-oxoacenaphthylen-1(2*H*)-ylidene)-1,3-dithioles **8**, 2-(1,3-dioxo-1*H*-inden-2(3*H*)-ylidene) -1,3-dithioles **9** and 2-(2,4,6-trioxotetrahydropyrimidin-5 (6*H*)-ylidene)-1,3-dithioles **10** were obtained, respectively, in good to excellent yields under the same reaction conditions (Scheme 2). When acenaphthylene-1,2-dione **5** was used, due to sterically hindered, only mono dithiol derivatives **8a-c** were produced and another carbonyl group remained unreacted. Despite several active aldehydes and ketones in 1,3-dithioles synthesis [7–10], utilization of isatins, acenaphthylene-1,2-dione, ninhydrine and pyrimidine-tetraone have not been reported yet.

Compounds **4**, **8**, **9** and **10** are stable solids whose structures were established by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analysis.

We have not established an exact mechanism for the formation of 1,3-dithioles **4**, **8**, **9** and **10**, however, a reasonable possibility is shown in Scheme 3.

Conclusion

In conclusion, we have described a mild, facile and three-component method for the synthesis of oxoindolin-ylidene-1,3-dithioles, oxoacenaphthylen-ylidene-1,3-dithioles, dioxo-inden-ylidene-1,3-dithioles and trioxotetrahydropyrimidin-ylidene-1,3-dithioles using readily available starting materials. Prominent among the advantages of this new method are operational simplicity, good yields and easy work-up procedures employed.

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