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Synthesis of 4*H*-[1,3]dithiolo[4,5-*b*]pyrroles through the reaction of benzoyl isothiocyanate and dialkyl acetylenedicarboxylates in the presence of Ph_3P

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Abstract—Benzoyl isothiocyanate reacts with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine in a mechanistically novel reaction to afford highly substituted dialkyl 2-(benzoylimino)-5-phenyl-4*H*-[1,3]dithiolo[4,5-*b*]pyrrole-4,6-dicarboxylates with double insertion of the isothiocyanate. The reaction proceeds via a carbon to nitrogen migration of an alkoxycarbonyl group.
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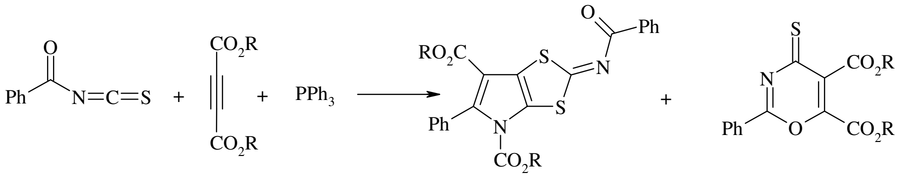
The family of poly-sulfur–nitrogen heterocycles includes highly stable aromatic compounds that display physicochemical properties with relevance in the design of new materials, especially those relating to molecular conductors and magnets, which are currently under intense investigation.[1] Derivatives of sulfur heterocycles such as thiophene and 1,3-dithiole have been widely explored as new materials because of their superconducting and optical and electronic switching properties.[2] The synthesis of some 2-imino-1,3-benzodithiols have been reported.[3,4]

As part of our current studies on the development of new routes in heterocyclic synthesis,[5] we describe the reaction between benzoyl isothiocyanate and dialkyl acetylenedicarboxylates in the presence of triphenylphosphine (Ph_3P), in one-pot, to afford dialkyl 2-(benzoylimino)-5-phenyl-4*H*-[1,3]dithiolo[4,5-*b*]pyrrole-4,6-dicarboxylates, with double insertion of the isothiocyanate, and dialkyl 2-phenyl-4-thioxo-4*H*-1,3-oxazine-5,6-dicarboxylates in a 3:1 ratio (Scheme 1).

The reaction proceeded spontaneously in CH_2Cl_2 and was complete within a few hours. The ^1H and ^{13}C NMR spectra of the crude products clearly indicated the formation[6] of compounds **3** and **4**. When the reaction was carried using two equivalents of **1**, the yield of **3** was increased. The structures of **3** and **4** were



1

2	R
a	Me
b	Et
c	^{t}Bu

3

4

3, 4	R	Yield (%) of **3**	Yield (%) of **4**
a	Me	38	10
b	Et	40	8
c	^{t}Bu	35	10

Scheme 1.

Keywords: Acetylenic ester; Benzoyl isothiocyanate; Intramolecular Wittig reaction; Dithiolopyrrole; Oxazine.

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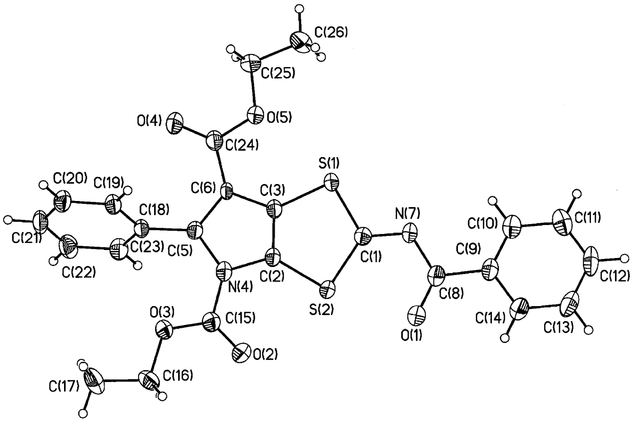


Figure 1. X-ray crystal structure (ORTEP) of **3b** (arbitrary numbering).

deduced from their elemental analyses and their IR, ^{1}H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m*/*z* values.

Unambiguous evidence for the structure of **3b** was obtained from single-crystal X-ray analysis.[7] An ORTEP diagram of **3b** is shown in Figure 1. There are two molecules of **3b** in the unit cell, which are arranged in a centrosymmetric manner (see Fig. 2). The fused dithiolopyrrole system is nearly planar, but the phenyl group attached to the pyrrole moiety is twisted by 65.5°.

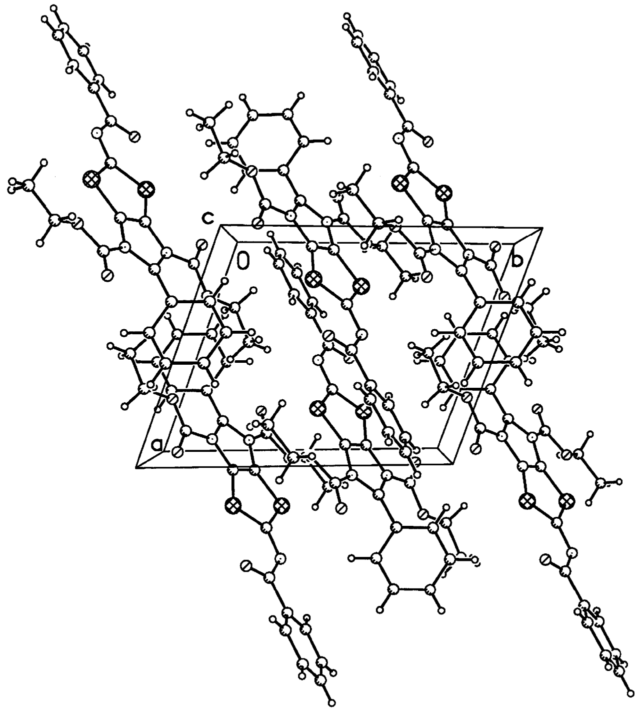
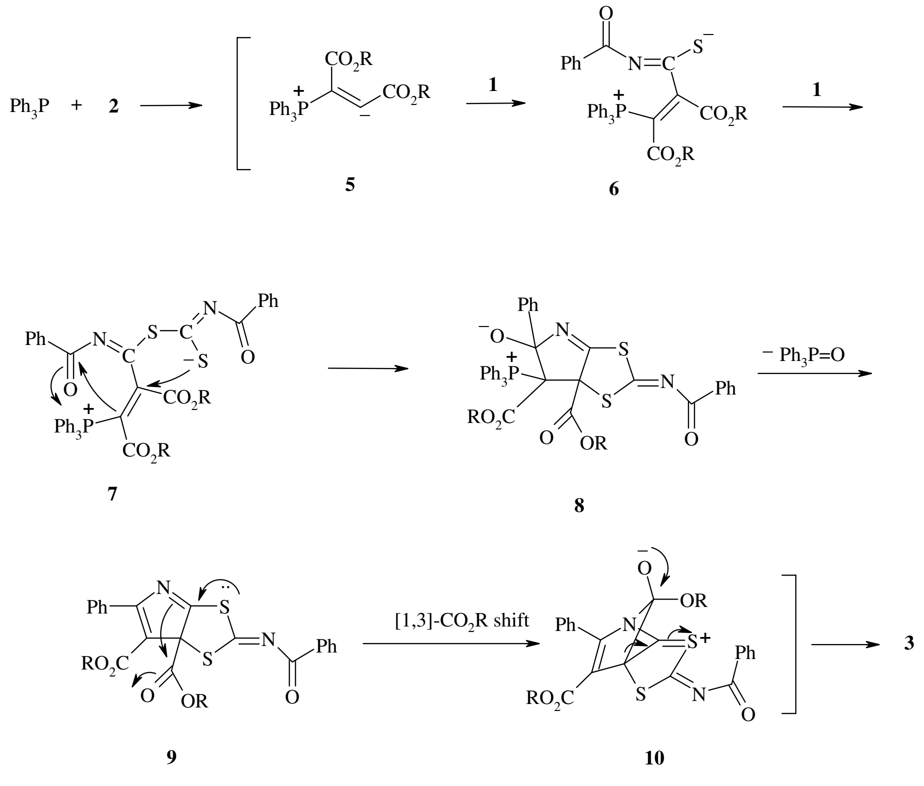
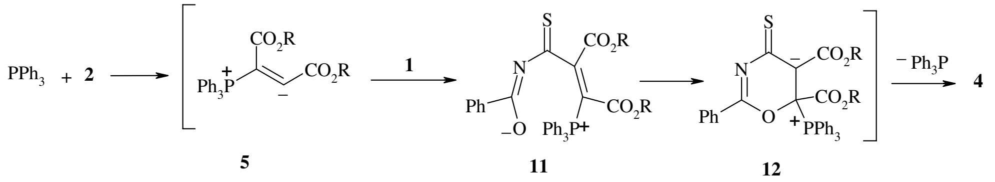


Figure 2. Crystal packing of **3b**.

The ^{1}H NMR spectrum of **3a** exhibited two single sharp resonances due to the methoxy (δ 3.75 and 3.87 ppm) protons along with resonances (δ 7.38–8.36 ppm) for the aromatic protons. The ^{13}C NMR spectrum of **3a** showed 18 distinct resonances in agreement with the proposed structure. The ^{1}H and ^{13}C NMR spectra of **3b** and **3c** were similar to those of **3a** except for the alk-



Scheme 2.



Scheme 3.

oxy moiety, which exhibited characteristic signals with appropriate chemical shifts.

The ^{1}H NMR spectrum of **4a** showed two singlets for the methoxy (δ 3.99 and 4.08 ppm) protons along with resonances (δ 7.50–8.31 ppm) for the aromatic protons. The ^{13}C NMR spectrum of **4a** showed 12 distinct resonances. The ^{1}H and ^{13}C NMR spectra of **4b** and **4c** were also similar to those of **4a** differing only in the nature of the alkoxy groups.

Although the mechanistic details of the reaction are not known, a plausible rationalization may be advanced to explain the product formation. Presumably, the zwitterionic intermediate[8] **5** formed from Ph$_3$P and dialkyl acetylenedicarboxylate adds to benzoyl isothiocyanate to furnish intermediate **6**, which then adds to another molecule of benzoyl isothiocyanate to produce **7**. This intermediate undergoes cyclization to furnish the fused structure **9** by the elimination of Ph$_3$PO. The pyrrole derivative **9** rearranges to the final product by a carbon to nitrogen carboxyl transfer via the tricyclic intermediate **10** (Scheme 2).

Formation of compound **4** involves addition of the zwitterionic intermediate **5** to benzoyl isothiocyanate to produce **11**. Cyclization of intermediate **11** and subsequent elimination of Ph$_3$P from **12** leads to **4** (Scheme 3).

In conclusion, we have revealed a novel transformation involving benzoyl isothiocyanate, dialkyl acetylenedicarboxylate, and Ph$_3$P that proceeds through a carbon to nitrogen migration of an alkoxycarbonyl group affording dialkyl 2-(benzoylimino)-5-phenyl-4*H*-[1,3]-dithiolo[4,5-*b*]pyrrole-4,6-dicarboxylates. The present procedure carries the advantage that not only is the reaction performed under neutral conditions but also the reactants can be mixed without any prior activation or modification.

Acknowledgements

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6. Typical procedure for the synthesis of dimethyl 2-(benzoylimino)-5-phenyl-4*H*-[1,3]dithiolo[4,5-*b*]pyrrole-4,6-dicarboxylate (**3a**) and dimethyl 2-phenyl-4-thioxo-4*H*-1,3-oxazine-5,6-dicarboxylate (**4a**): To a stirred solution of benzoyl isothiocyanate (0.32 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.24 mL, 2 mmol) in 10 mL CH$_2$Cl$_2$, a solution of Ph$_3$P (0.52 g, 2 mmol) in 5 mL CH$_2$Cl$_2$ was added dropwise at −10 °C over 10 min. The reaction mixture was then allowed to warm to room temperature and stand for 24 h. Compounds **3a** and **4a** were separated by silica gel column chromatography (Merck 230–400 mesh) using *n*-hexane–EtOAc (5:1) as an eluent.
   Compound **3a**: Light yellow crystals; yield: 0.34 g (38%), mp 125–126 °C. IR ν/cm^{-1} (KBr): 1730 and 1725 (C=O), 1587, 1530, 1425, 1332, 1245. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 3.75$ (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 7.38 (2H, d, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 2CH), 7.44–7.50 (5H, m, 5CH), 7.56 (1H, t, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, CH), 8.36 (2H, d, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 2CH) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 53.3$ (OCH$_3$), 53.8 (OCH$_3$), 127.6 (C), 128.50 (2CH), 128.52 (C), 128.6 (2CH), 130.2 (C), 131.5 (CH), 131.6 (CH), 132.2 (2CH), 132.3 (2CH), 132.6 (C), 133.3 (C), 141.5 (C), 148.3 (C), 159.7 (C), 172.8 (C), 189.9 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 452 (M^{+}, 5), 105 (100), 77 (100). Anal. Calcd for $C_{22}H_{16}N_2O_5S_2$ (452.5): C, 58.40; H, 3.56; N, 6.19. Found: C, 58.46; H, 3.61; N, 6.22.
   Compound **3b**: Light yellow crystals; yield: 0.38 g (40%), mp 150–152 °C. IR ν/cm^{-1} (KBr): 1730 and 1727 (C=O), 1604, 1428, 1308, 1271. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 1.36$ (3H, t, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, CH$_3$), 1.21 (3H, t, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, CH$_3$), 4.20 (2H, q, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, CH$_2$), 4.29 (2H, q, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, CH$_2$), 7.38 (2H, d, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 2CH$_{meta}$), 7.43–7.51 (5H, m, 5CH), 7.57 (1H, t, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, CH$_{para}$), 8.36 (2H, d, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 2CH$_{ortho}$) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 13.6$ (CH$_3$), 14.0 (CH$_3$), 61.0 (OCH$_2$), 65.3 (OCH$_2$), 127.5 (C), 127.6 (2CH), 128.4 (2CH), 128.7 (C), 128.8 (C), 129.1 (CH), 130.1 (2CH), 130.2 (2CH), 131.0 (C), 132.7 (CH), 135.1 (C), 142.8 (C), 148.9 (C), 161.7 (C), 173.5 (C), 190.2 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 480 (M^{+}, 5), 305 (M^{+}, 25), 277 (50), 149 (60), 105 (100), 77 (40), 57 (30). Anal. Calcd for $C_{24}H_{20}N_2O_5S_2$ (480.5): C, 59.99; H, 4.19; N, 5.83. Found: C, 60.81; H, 4.23; N, 5.87.
   Compound **3c**: Pale yellow powder; yield: 0.38 g (35%), mp 182–184 °C. IR, ν/cm^{-1} (KBr): 1730 and 1725 (C=O), 1600,

1425, 1310, 1275. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 1.25$ (9H, s, CMe$_3$), 1.32 (9H, s, CMe$_3$), 7.33 (2H, t, $^3J_{\text{HH}} = 7.1$ Hz, 2CH$_{meta}$), 7.40–7.51 (5H, m, 5CH), 7.61 (1H, t, $^3J_{\text{HH}} = 7.1$ Hz, CH$_{para}$), 8.29 (2H, d, $^3J_{\text{HH}} = 7.1$ Hz, 2CH$_{ortho}$) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 27.9$ (C*Me*$_3$), 28.1 (C*Me*$_3$), 81.2 (O*C*Me$_3$), 81.7 (O*C*Me$_3$), 127.4 (C), 127.7 (2CH), 128.4 (2CH), 128.6 (2CH), 128.8 (C), 130.2 (CH), 130.4 (C), 130.8 (CH), 131.5 (C), 132.2 (CH), 133.9 (CH), 138.9 (C), 142.5 (C), 148.4 (C), 161.5 (C), 171.7 (C), 189.8 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 536 (M$^+$, 5), 105 (100), 77 (100), 51 (20). Anal. Calcd for $C_{28}H_{28}N_2O_5S_2$ (536.6): C, 62.67; H, 5.26; N, 5.22. Found: C, 62.74; H, 5.31; N, 5.28.

Compound **4a**: Pale yellow powder; yield: 0.06 g (10%), mp 115–117 °C. IR, *v*/cm^{-1} (KBr): 1726 and 1677 (C=O), 1586, 1540, 1428, 1334, 1247. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 3.99$ (3 H, s, OCH$_3$), 4.08 (3H, s, OCH$_3$), 7.50 (2H, t, $^3J_{\text{HH}} = 7.5$ Hz, 2CH$_{meta}$), 7.57 (1H, t, $^3J_{\text{HH}} = 7.2$ Hz, CH$_{para}$), 8.31 (2H, d, $^3J_{\text{HH}} = 7.5$ Hz, 2CH$_{ortho}$) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 53.6$ (OCH$_3$), 54.1 (OCH$_3$), 128.5 (2CH), 130.2 (2CH), 133.3 (CH), 133.4 (C), 136.9 (C), 154.6 (C), 159.6 (C=O), 163.8 (C=O), 177.4 (C), 182.2 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 306 (M$^+$+1, 5), 305 (M$^+$, 2), 294 (40), 277 (50), 183 (75), 105 (100), 77 (100). Anal. Calcd for $C_{14}H_{11}NO_5S$ (305.3): C, 55.08; H, 3.63; N, 4.59. Found: C, 55.16; H, 3.67; N, 4.62.

Compound **4b**: Pale yellow powder; yield: 0.04 g (8%), mp 110–112 °C. IR, *v*/cm^{-1} (KBr): 1731 and 1672 (C=O), 1583, 1550, 1424, 1324, 1241. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 1.42$ (3H, t, $^3J_{\text{HH}} = 7.1$ Hz, CH$_3$), 1.48 (3H, t, $^3J_{\text{HH}} = 7.1$ Hz, CH$_3$), 4.44 (2H, q, $^3J_{\text{HH}} = 7.1$ Hz, CH$_2$), 4.56 (2H, q, $^3J_{\text{HH}} = 7.1$ Hz, CH$_2$), 7.48 (2H, t, $^3J_{\text{HH}} = 7.6$ Hz, 2CH$_{meta}$), 7.57 (1H, t, $^3J_{\text{HH}} = 7.3$ Hz, CH$_{para}$), 8.32 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, 2CH$_{ortho}$) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 14.0$ (CH$_3$), 14.2 (CH$_3$), 62.8 (OCH$_2$), 63.8 (OCH$_2$), 128.5 (2CH), 130.1 (2CH), 133.2 (CH), 133.6 (C), 136.9 (C), 155.0 (C), 159.2 (C=O), 163.4 (C=O), 177.3 (C), 182.5 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 334 (M$^+$+1, 5), 105 (100), 77 (90), 51 (20). Anal. Calcd for $C_{16}H_{15}NO_5S$ (333.4): C, 57.65; H, 4.54; N, 4.20. Found: C, 57.73; H, 4.57; N, 4.22.

Compound **4c**: Pale yellow powder; yield: 0.08 g (10%), mp 143–145 °C. IR, *v*/cm^{-1} (KBr): 1725 and 1679 (C=O), 1580, 1545, 1425, 1330, 1249. ^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 1.50$ (9H, s, CMe$_3$), 1.60 (9H, s, CMe$_3$), 7.34 (2H, t, $^3J_{\text{HH}} = 7.5$ Hz, 2CH$_{meta}$), 7.56 (1H, t, $^3J_{\text{HH}} = 7.3$ Hz, CH$_{para}$), 8.32 (2H, d, $^3J_{\text{HH}} = 7.5$ Hz, 2CH$_{ortho}$) ppm. ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta = 27.9$ (C*Me*$_3$), 28.4 (C*Me*$_3$), 82.7 (O*C*Me$_3$), 83.6 (O*C*Me$_3$), 128.2 (2CH), 128.8 (2CH), 132.3 (CH), 133.9 (C), 134.2 (C), 160.7 (C), 161.5 (C=O), 162.5 (C=O), 177.8 (C), 186.1 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 389 (M$^+$, 5), 105 (100), 77 (80), 51 (40). Anal. Calcd for $C_{20}H_{23}NO_5S$ (389.5): C, 61.68; H, 5.95; N, 3.60. Found: C, 61.75; H, 6.03; N, 3.65.

7. CCDC-284911 contains the supplementary crystallographic data for **3b** ($C_{24}H_{20}N_2O_5S_2$), $F_{\text{w}} = 480.45$, triclinic, space group P-1, $Z = 2$, $a = 9.1615(18)$ Å, $b = 11.315(2)$ Å, $c = 11.821(2)$ Å, $\alpha = 100.11(3)°$, $\beta = 101.15(3)°$, $\gamma = 106.97(3)°$, $V = 1114.2(5)$ Å^3, $D_{\text{calcd}} = 1.432$ g cm^{-3}, $R = 0.0416$, $R_{\text{w}} = 0.1190$, $0 \leqslant h \leqslant 11$; $-13 \leqslant k \leqslant 13$; $-14 \leqslant l \leqslant 14°$; Mo ($\lambda = 0.71073$ Å), $T = 200(2)$ K. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam. ac.uk.
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