Rearrangement Studies on Acylketene *O*-Prop-2-ynyl *S*-Methylmonothioketals

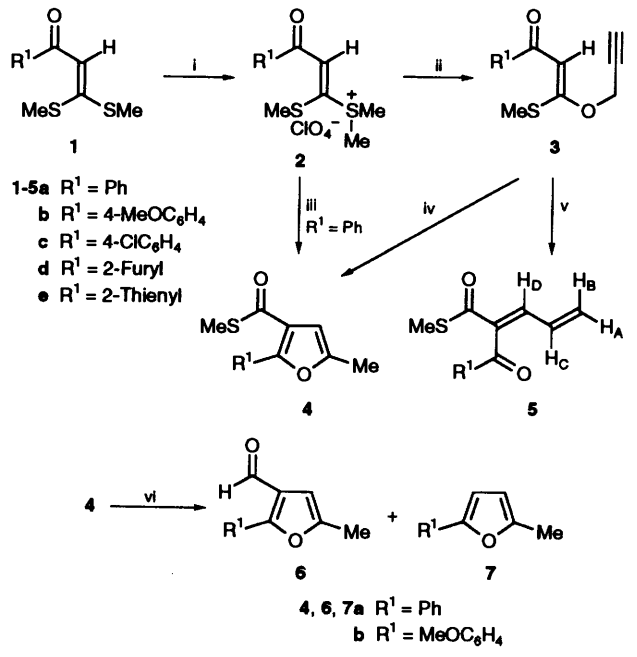
Laxminarayan Bhat, Hiriyakkanavar Ila* and Hiriyakkanavar Junjappa*
Department of Chemistry, North-Eastern Hill University, Shillong – 793 003, Meghalaya, India

Acylketene *O*-prop-2-ynyl *S*-methylmonothioketals **3a–e**, easily obtained through displacement on β-oxosulfonium salts **2a–e** by prop-2-ynol, are shown to undergo facile rearrangement under neutral (toluene–xylene) and basic conditions (K_2CO_3–EtCOMe) to afford the diene esters **5a–e** and the substituted furans **4a–e**, respectively. The probable mechanism for the formation of the various products involving initial Claisen rearrangement of compounds **3a–e** has been described.

The Claisen rearrangement of appropriate prop-2-ynyl ethers has been studied both in aromatic and aliphatic series.[1] Thus, arylpropynyl ethers are reported to give 2*H*-1-benzopyran derivatives when heated in either *N*,*N*-dimethylaniline or DMF.[2] The proposed mechanism involves the 2-allenylphenols as initial intermediates[2] which on subsequent 1,5-hydrogen shift followed by electrocyclic ring closure afford the 2*H*-1-benzopyrans as the final products.[3] In a separate study, 1,3-dimethyl-5-(prop-2-ynyloxy)uracil is shown to undergo facile thermal rearrangement at 130 °C to give a mixture of 1,3,6-trimethyl-6,7-dihydrofuro[3,2-*d*]pyrimidine-2,4-dione and the corresponding 1,3-dimethyl-6*H*-pyrano[3,2-*d*]pyrimidine-2,4-dione.[4] The course of the reaction is shown to depend markedly on the nature of solvent and can be directed to give predominantly either the furopyrimidine (DMF) or the pyranopyrimidine (xylene) or a mixture of both products (DMSO). The authors have proposed an ionic ring closure mechanism for the formation of furopyrimidine involving nucleophilic attack on the activated allene moiety of the 6-allenyl-5-hydroxyuracil intermediate.[4] It is pertinent to note that the benzofuran products have not been reported from thermal Claisen rearrangement of phenylprop-2-ynyl ethers, although they are formed during the base-catalysed ring closure of *O*-allenylphenol.[3a,5] Unlike the aromatic series, few examples of the thermal Claisen rearrangement of vinylprop-2-ynyl ethers to afford allenic carbonyl compounds through a concerted six-membered cyclic transition state are known.[6] This is probably due to the lack of stable functionalised vinylprop-2-ynyl ether precursors required for the study. We have now synthesised acylketene *O*-prop-2-ynyl *S*-methylmonothioketals and studied their rearrangements under different reaction conditions to afford either substituted furans or acyclic conjugated diene esters. The results of the study are presented in this paper.

Results and Discussion

We have reported a general route for acylketene *O*,*S*-ketals through nucleophilic displacement on β-oxovinylsulfonium salts (obtained from the respective α-oxoketene dithioketals) by various alcohols and phenols.[7] A similar strategy was employed for the synthesis of *O*-prop-2-ynyl *S*-methylmonothioketals **3** (Scheme 1). Thus, when the sulfonium salt **2a** was treated with prop-2-ynol in the presence of potassium carbonate in ethyl methyl ketone at room temperature, work-up of the reaction mixture afforded compound **3a** in 76% yield (Scheme 1). However, when the same reaction mixture was refluxed, the product isolated (58%) was characterised as the *S*-methyl furan-3-carbothioate **4a** which was also obtained in an improved yield (84%) when the *O*-prop-2-ynyl ketal **3a** was refluxed in ethyl methyl ketone in the presence of K_2CO_3. The regiochemistry of compound **4a** was further confirmed by its reductive



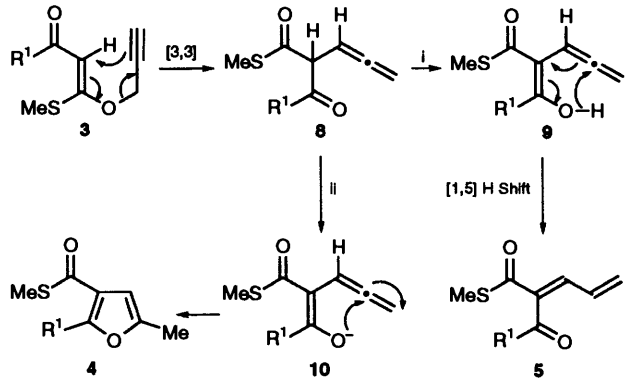
Scheme 1 *Reagents and conditions:* i (*a*) Me_2SO_4, heat, 3 h, (*b*) $HClO_4$, diethyl ether, room temp.; ii, $HC{\equiv}CCH_2OH$, K_2CO_3, EtCOMe, room temp.; iii, $HC{\equiv}CCH_2OH$, K_2CO_3, EtCOMe, reflux, 4 h; iv, K_2CO_3, EtCOMe, reflux, 3–6 h; v, toluene, reflux, 1–2 h or xylene, reflux, 15–30 min; vi, Raney nickel, EtOH, room temp., 10 h

desulfurisation with Raney nickel to afford the corresponding furan-3-carbaldehyde **6a** and the 3-unsubstituted furan **7a** in 46 and 34% yields, respectively (Scheme 1). The other substituted *O*,*S*-ketals **3b–c** and the furans **4b–c** were similarly obtained from the corresponding sulfonium salts **2b–c** in good yields under identical conditions. When the α-furoylsulfonium salt **2d** was subjected to displacement by prop-2-ynyl at room temperature, the reaction mixture afforded the *O*,*S*-ketal **3d** (66%) along with a smaller amount of the furan **4d** (11%), while the α-thienoylsulfonium salt **2e**, under identical conditions, yielded the furan **4e** as the major product (65%) together with *O*,*S*-ketal **3e** in poor yield (12%). Reductive desulfurisation of compound **4b** with Raney nickel also afforded the mixture of furan-3-carbaldehyde **6b** and the 3-unsubstituted furan **7b** in 48 and 36% yields, respectively (Scheme 1).

The *O*,*S*-ketals **3a–e** were found to be stable at room temperature, although in refluxing toluene or xylene, they underwent facile rearrangement to give exclusively one product, characterised as the diene esters **5a–e** (isolated as single stereoisomers) on the basis of both spectral and analytical data (Scheme 1). No other products, such as dihydropyran or its

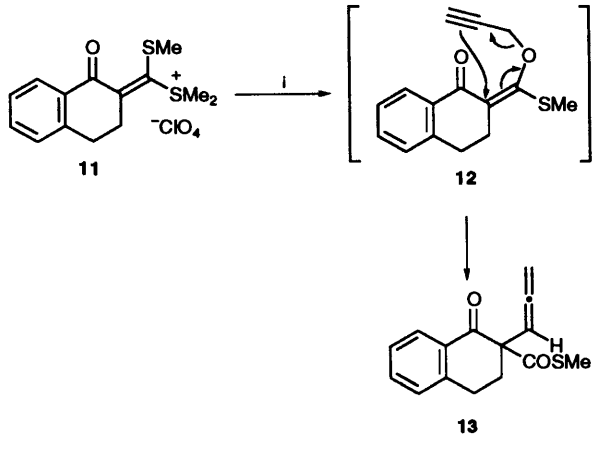
dimer, were isolated from the reaction mixture. Attempted isomerisation of compound **3a** in polar solvents like DMF or DMSO (anhydrous or aqueous) gave only an intractable mixture of products, whereas in refluxing pyridine, the furan **4a** was isolated in poor yield, along with a complex reaction mixture.

The probable mechanism for the formation of the furan **4** or the diene ester **5** from the *O,S*-ketals **3** is shown in Scheme 2.



Scheme 2 *Reagents and conditions:* i, toluene or xylene, reflux; ii, K_2CO_3, EtCOMe, reflux

The first step involves the Claisen rearrangement of the *O,S*-ketal **3** to the allene intermediate **8** which, under neutral conditions (toluene or xylene), rearranges to the diene ester **5** through enolization and a subsequent 1,5-hydrogen shift in the intermediate **9**. Under basic conditions (K_2CO_3–ethyl methyl ketone), the intermediate **8** undergoes a proton abstraction to give the enolate anion **10**, which on intramolecular ring closure through the nucleophilic attack onto the activated allene moiety, affords the 5-methylfuran **4**. Interestingly, treatment of the sulfonium salt **11** from 3,4-dihydronaphthalen-1(2*H*)-one with prop-2-ynol under the reported conditions, gave the allene intermediate **13** (Scheme 3), thus proving its intermediacy in this rearrangement.



Scheme 3 *Reagents and conditions:* i, $HC{\equiv}CCH_2OH$, K_2CO_3, EtCOMe, room temp.

In conclusion, the newly synthesised acylketene *O*-prop-2-ynyl *S*-methylthioketals **3** are shown to undergo Claisen rearrangement either under basic or neutral conditions to afford novel substituted furans **4** or activated diene esters **5** in high yields. Although benzofurans are reported to be formed in base-catalysed cyclisation of *O*-allenylphenols, to our knowledge this is the first report of the formation of furan derivatives through base induced cyclisation of allenic intermediates formed in prop-2-ynylic Claisen rearrangement of acyclic aliphatic precursors.[8]

Experimental

M.p.s were determined on a Thomas Hoover melting point (Capillary Method) apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer and the ^1H NMR spectra were recorded on Varian EM-390, 90 MHz, Bruker 250 MHz and Gemini-300 MHz spectrometers (tetramethylsilane was used as the internal standard) with *J*-values given in Hz. The mass spectra were recorded on a Jeol JMS-D 300 mass spectrometer. Elemental analysis was performed on a Heraeus CHN-O-Rapid Elemental Analyzer.

General Procedure for the Preparation of Acylketene O-*Prop-2-ynyl* S-*Methyl Monothioketals* **3a–e**.—A stirred suspension of prop-2-ynyl alcohol (1.68 g, 30 mmol) and anhydrous K_2CO_3 (12.42 g, 90 mmol) in anhydrous acetone (or ethyl methyl ketone) (75 cm^3) was refluxed for 3 h. The resulting mixture was cooled to 0–5 °C and the dimethylsulfonium perchlorate salt **2** (10 mmol) was added to it in small portions with stirring. The mixture was further stirred at the same temperature for 2 h and then for a further 5–6 h at room temp. It was then filtered, the filter being washed with acetone (or ethyl methyl ketone) (2 × 25 cm^3) and the filtrate concentrated under reduced pressure. The residue was poured onto crushed ice and extracted with $CHCl_3$ (2 × 100 cm^3). The combined extracts were washed with water (3 × 100 cm^3), dried (Na_2SO_4) and then evaporated to give the crude product **3**, which was purified by crystallisation (chloroform–hexane).

In the case of the sulfonium salts **2d** and **2e**, formation of the *O,S*-ketals **3d** and **3e** was accompanied with the furans **4d** (0.24 g, 11%) and **4e** (1.54 g, 65%), respectively, which were separated by column chromatography over silica gel using hexane–ethyl acetate (98:2) as eluent. A suspension of the sulfonium salt **2a** (3.38 g, 10 mmol), prop-2-ynyl alcohol (1.68 g, 30 mmol) and anhydrous K_2CO_3 (12.42 g, 90 mmol) in anhydrous ethyl methyl ketone (75 cm^3) was refluxed for 4 h to give the furan **4a** (1.34 g, 58%).

3-*Methylthio*-1-*phenyl*-3-(*prop*-2-*ynyloxy*)*prop*-2-*en*-1-*one* **3a**. Pale yellow crystals (1.76 g, 76%); m.p. 99–100 °C; ν_{max}(KBr)/cm^{-1} 3326, 2130, 1621, 1609, 1503 and 1261; δ_H(90 MHz; $CDCl_3$) 2.30 (3 H, s, SMe), 2.60 (1 H, t, *J* 1.5, ≡CH), 4.83 (2 H, d, *J* 1.5, CH_2), 6.55 (1 H, s, =CH), 7.30–7.58 (3 H, m, ArH) and 7.82–8.02 (2 H, m, ArH); *m/z* 232 (M^+, 1%) and 105 (100%) (Found: C, 67.4; H, 5.4. $C_{13}H_{12}O_2S$ requires C, 67.21; H, 5.21%).

1-(4-*Methoxyphenyl*)-3-*methylthio*-3-(*prop*-2-*ynyloxy*)*prop*-2-*en*-1-*one* **3b**. Pale yellow crystals (2.04 g, 78%); m.p. 113 °C; ν_{max}(KBr)/cm^{-1} 3255, 2126, 1620, 1510, 1268 and 1174; δ_H(90 MHz; $CDCl_3$) 2.30 (3 H, s, SMe), 2.65 (1 H, t, *J* 1.5, ≡CH), 3.82 (3 H, s, OMe), 4.82 (2 H, d, *J* 1.5, CH_2), 6.59 (1 H, s, =CH), 6.99 (2 H, d, *J* 9, ArH) and 7.99 (2 H, d, *J* 9, ArH); *m/z* 262 (M^+, 41%) and 135 (100) (Found: C, 64.4; H, 5.65. $C_{14}H_{14}O_3S$ requires C, 64.10; H, 5.38%).

1-(4-*Chlorophenyl*)-3-*methylthio*-3-(*prop*-2-*ynyloxy*)*prop*-2-*en*-1-*one* **3c**. Pale yellow crystals (2.0 g, 75%); m.p. 95–96 °C; ν_{max}(KBr)/cm^{-1} 3225, 2129, 1625, 1480 and 1242; δ_H(90 MHz; $CDCl_3$) 2.32 (3 H, s, SMe), 2.73 (1 H, t, *J* 1.5, ≡CH), 4.88 (2 H, d, *J* 1.5, CH_2), 6.59 (1 H, s, =CH), 7.49 (2 H, d, *J* 9, ArH) and 7.93 (2 H, d, *J* 9, ArH); *m/z* 266 and 268 (M^+, 4 and 2%), 219 (78) and 139 (100) (Found: C, 58.8; H, 4.4. $C_{13}H_{11}ClO_2S$ requires C, 58.53; H, 4.16%).

1-(2-*Furyl*)-3-*methylthio*-3-(*prop*-2-*ynyloxy*)*prop*-2-*en*-1-*one* **3d**. Pale yellow crystals (1.46 g, 66%); m.p. 101–102 °C; ν_{max}(KBr)/cm^{-1} 3235, 2125, 1622, 1594, 1538, 1268 and 1210; δ_H(90 MHz; $CDCl_3$) 2.32 (3 H, s, SMe), 2.72 (1 H, t, *J* 1.5, ≡CH),

4.85 (2 H, d, *J* 1.5, CH_2), 6.48–6.63 (2 H, m, =CH and 4-H furyl), 7.19 (1 H, d, $J_{5,4}$ 1.5, 5-H furyl) and 7.58 (1 H, br s, 3-H furyl); a small M^+ peak was observed at *m/z* 222 but was too small for the exact mass spectrum to be measured, 197 (17%), 175 (17) and 95 (100) (Found: C, 59.7; H, 4.7. $C_{11}H_{10}O_3S$ requires C, 59.44; H, 4.54%).

3-*Methylthio*-3-(*prop*-2-*ynyloxy*)-1-(2-*thienyl*)*prop*-2-*en*-1-*one* **3e**. Pale yellow crystals (0.28 g, 12%); m.p. 85–86 °C; ν_{max}(KBr)/cm^{-1} 3250, 2128, 1620, 1500, 1410, 1358, 1268 and 1160; δ_H(90 MHz; $CDCl_3$) 2.28 (3 H, s, SMe), 2.71 (1 H, t, *J* 1.5, ≡CH), 4.81 (2 H, d, *J* 1.5, CH_2), 6.46 (1 H, s, =CH), 7.13 (1 H, apparent dd, separation 5 and 3.5, 4-H thienyl), 7.56 (1 H, br d, separation 5, 5-H thienyl) and 7.68 (1 H, br d, separation 3.5, 3-H thienyl); *m/z* M^+ (238) was not observed, 193 (2%), 191 (11) and 111 (100) (Found: C, 55.7; H, 4.5. $C_{11}H_{10}O_2S_2$ requires C, 55.44; H, 4.23%).

General Procedure for the Preparation of S-*Methyl* 2-*Aryl*-5-*methylfuran*-3-*carbothioates* **4a–e**.—A suspension of acylketene *O*-prop-2-ynyl *S*-methyl monothioketal **3** (10 mmol) in ethyl methyl ketone (25 cm^3) and K_2CO_3 (4.15 g, 30 mmol) was refluxed for 3–6 h (monitored by TLC). The reaction mixture was filtered, the filter washed with ethyl methyl ketone (2 × 25 cm^3) and the combined filtrates were concentrated. The residue was dissolved in chloroform (50 cm^3) and the solution washed with water (3 × 100 cm^3), dried (Na_2SO_4) and evaporated to give the crude product, which was purified by column chromatography over silica gel using hexane as eluent.

S-*Methyl* 5-*methyl*-2-*phenylfuran*-3-*carbothioate* **4a**. Colourless viscous liquid (1.94 g, 84%); ν_{max}(neat)/cm^{-1} 1675, 1558, 1550, 1380, 1228 and 1166; δ_H(250 MHz; $CDCl_3$) 2.29 (3 H, d, *J* 1.5, Me), 2.36 (3 H, s, SMe), 6.45 (1 H, d, *J* 1.5, 4-H), 7.33–7.42 (3 H, m, ArH) and 7.91–7.96 (2 H, m, ArH); δ_C(62.8 MHz; $CDCl_3$) 11.57 (SMe), 13.09 (Me), 107.52 (4-C furyl), 121.32 (3-C furyl), 127.66, 127.96, 129.08 and 129.59 (phenyl CH), 129.64 (1-C phenyl), 151.24 (2-C furyl), 152.84 (5-C furyl) and 186.46 (CO); *m/z* 232 (M^+, 20%), 185 (100) and 105 (57) (Found: C, 67.4; H, 5.4. $C_{13}H_{12}O_2S$ requires C, 67.21; H, 5.21%).

S-*Methyl* 2-(4-*methoxyphenyl*)-5-*methylfuran*-3-*carbothioate* **4b**. Colourless viscous liquid (2.30 g, 88%); ν_{max}(neat)/cm^{-1} 1679, 1620, 1505 and 1268; δ_H(90 MHz; $CDCl_3$), 2.29 (3 H, s, Me), 2.33 (3 H, s, SMe), 3.76 (3 H, s, OMe), 6.47 (1 H, s, 4-H), 6.95 (2 H, d, *J* 9, ArH) and 8.02 (2 H, d, *J* 9, ArH); *m/z* 262 (M^+, 42%) and 217 (100) (Found: C, 64.3; H, 5.6. $C_{14}H_{14}O_3S$ requires C, 64.10; H, 5.38%).

S-*Methyl* 2-(4-*chlorophenyl*)-5-*methylfuran*-3-*carbothioate* **4c**. Colourless crystals (2.28 g, 86%); m.p. 60–61 °C (from diethyl ether–hexane); ν_{max}(KBr)/cm^{-1} 1678, 1562, 1495, 1383, 1280 and 1175; δ_H(250 MHz; $CDCl_3$) 2.32 (3 H, d, *J* 1.5, Me), 2.39 (3 H, s, SMe), 6.47 (1 H, d, *J* 1.5, 4-H), 7.35 (2 H, d, *J* 9, ArH) and 7.91 (2 H, d, *J* 9, ArH); *m/z* 266 and 268 (M^+, 11 and 4%), 219 (100) and 139 (37) (Found: C, 58.6; H, 4.3. $C_{13}H_{11}ClO_2S$ requires C, 58.53; H, 4.16%).

S-*Methyl* 2-(2-*furyl*)-5-*methylfuran*-3-*carbothioate* **4d**. Colourless viscous liquid (1.97 g, 89%); ν_{max}(neat)/cm^{-1} 1663, 1610, 1535, 1374, 1265 and 1174; δ_H(90 MHz; $CDCl_3$) 2.29 (3 H, s, Me), 2.37 (3 H, s, SMe), 6.33–6.56 (2 H, m, 4-H and 4′-H furyl), 7.51 (1 H, br s, 5′-H furyl) and 7.63 (1 H, br d, separation 3, 3′-H furyl); *m/z* 222 (M^+, 5%), 174 (100) and 94 (48) (Found: C, 59.7; H, 4.8. $C_{11}H_{10}O_3S$ requires C, 59.44; H, 4.54%).

S-*Methyl* 5-*methyl*-2-(2-*thienyl*)*furan*-3-*carbothioate* **4e**. Pale yellow viscous liquid (2.16 g, 91%); ν_{max}(neat)/cm^{-1} 1662, 1620, 1569, 1508, 1425, 1392, 1260, 1219 and 1173; δ_H(300 MHz; $CDCl_3$), 2.35 (3 H, d, *J* 1.5, Me), 2.45 (3 H, s, SMe), 6.46 (1 H, d, *J* 1.5, 4-H), 7.10 (1 H, dd, $J_{4,5}$ 5 and $J_{4,3}$ 3.5, 4-H thienyl), 7.39 (1 H, dd, $J_{5,4}$ 5 and $J_{5,3}$ 1.2, 5-H thienyl) and 8.04 (1 H, dd, $J_{3,4}$ 3.5 and $J_{3,5}$ 1.1, 3-H thienyl); δ_C(75 MHz; $CDCl_3$) 11.73 (SMe), 13.41 (Me), 107.18 (4-C furyl), 119.71 (3-C furyl), 127.49, 127.58, 128.14 (thienyl CH), 131.79 (2-C thienyl), 148.82 (2-C furyl), 150.99 (5-C furyl) and 185.99 (CO); *m/z* 238 (M^+, 34%), 191 (100) and 111 (33) (Found: C, 55.7; H, 4.4. $C_{11}H_{10}O_2S_2$ requires C, 55.44; H, 4.23%).

General Procedure for the Demethylthiolation of S-*Methyl* 2-*Aryl*-5-*methylfuran*-3-*carbothioates* **4a** *and* **4b**.—To a stirred solution of the furan **4** (5 mmol) in ethanol (30 cm^3) was added Raney nickel (W-4, ≈5 times by weight) and the reaction mixture was stirred at room temp. for 8–10 h (monitored by TLC). It was then filtered, the filter washed with hot ethanol (2 × 10 cm^3) and the combined filtrates were evaporated on a water bath to furnish a residue, which was then purified by column chromatography over silica gel. Elution with hexane gave first the furan **7** and then the aldehyde **6**.

5-*Methyl*-2-*phenylfuran*-3-*carbaldehyde* **6a**. Colourless thick liquid (0.42 g, 46%); ν_{max}(neat)/cm^{-1} 1683, 1635, 1579, 1510, 1462, 1409 and 1237; δ_H(90 MHz; CCl_4) 2.44 (3 H, s, Me), 6.50 (1 H, s, 4-H), 7.48–7.69 (3 H, m, ArH), 7.86–7.96 (2 H, m, ArH) and 10.28 (1 H, s, CHO); *m/z* 186 (M^+, 100%), 157 (14), 115 (42) and 105 (65) (Found: C, 77.7; H, 5.7. $C_{12}H_{10}O_2$ requires C, 77.40; H, 5.41%).

2-(4-*Methoxyphenyl*)-5-*methylfuran*-3-*carbaldehyde* **6b**. Light yellow crystals (0.51 g, 48%); m.p. 52 °C (from diethyl ether–hexane); ν_{max}(KBr)/cm^{-1} 1656, 1611, 1499, 1443, 1380, 1304 and 1247; δ_H(90 MHz; $CDCl_3$) 2.32 (3 H, s, Me), 3.83 (3 H, s, OMe), 6.50 (1 H, s, 4-H), 7.02 (2 H, d, *J* 9, ArH), 7.73 (2 H, d, *J* 9, ArH) and 10.15 (1 H, s, CHO) (Found: C, 72.4; H, 5.8. $C_{13}H_{12}O_3$ requires C, 72.21; H, 5.60%).

5-*Methyl*-2-*phenylfuran* **7a**. Colourless thick liquid (0.26 g, 34%) (lit.,[9] m.p. 38–39 °C); ν_{max}(neat)/cm^{-1} 1623, 1571 and 1475; δ_H(90 MHz; CCl_4) 2.36 (3 H, s, Me), 5.95 (1 H, d, *J* 3, 4-H), 6.46 (1 H, d, *J* 3, 3-H), 7.10–7.42 (3 H, m, ArH) and 7.46–7.69 (2 H, m, ArH) (Found: C, 83.7; H, 6.6. $C_{11}H_{10}O$ requires C, 83.51; H, 6.37%).

2-(4-*Methoxyphenyl*)-5-*methylfuran* **7b**. Colourless crystals (0.33 g, 36%); m.p. 38–40 °C (from diethyl ether–hexane) (lit.,[9] m.p. 45–46 °C); ν_{max}(KBr)/cm^{-1} 1627, 1542, 1491, 1453 and 1244; δ_H(90 MHz; $CDCl_3$) 2.37 (3 H, s, Me), 3.79 (3 H, s, OMe), 6.10 (1 H, d, *J* 3, 4-H), 6.48 (1 H, d, *J* 3, 3-H), 6.99 (2 H, d, *J* 9, ArH) and 7.71 (2 H, d, *J* 9, ArH) (Found: C, 76.8: H, 6.7. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%).

General Procedure for the Preparation of S-*Methyl* 2-*Aroylpenta*-2,4-*dienethioates* **5a–e**.—A solution of acylketene *O*-prop-2-ynyl *S*-methylmonothioketal **3** (10 mmol) in dry toluene (25 cm^3) was refluxed for 1–2 h (in benzene refluxed for 3–4 h; in xylene for 15–30 min) the reaction being monitored by TLC. The solvent was removed under reduced pressure and the crude product was chromatographed over silica gel using hexane as eluent to give the title compound **5**.

S-*Methyl* 2-*benzoylpenta*-2,4-*dienethioate* **5a**. Yellow viscous liquid (2.18 g, 94%); ν_{max}(neat)/cm^{-1} 1686, 1671, 1620, 1478 and 1232; δ_H(90 MHz; CCl_4) 2.32 (3 H, s, SMe), 5.56 (1 H, dd, J_{AC} 10 and J_{AB} 2, H_A), 5.78 (1 H, dd, J_{BC} 17 and J_{BA} 2, H_B), 6.49 (1 H, ddd, J_{CB} 17, J_{CD} 12 and J_{CA} 10, H_C), 7.42 (1 H, d, J_{DC} 12, H_D), 7.44–7.62 (3 H, m, ArH) and 7.79–8.08 (2 H, m, ArH); *m/z* 232 (M^+, 4%), 185 (70) and 105 (100) (Found: C, 67.4; H, 5.5. $C_{13}H_{12}O_2S$ requires C, 67.21; H, 5.21%).

S-*Methyl* 2-(4-*methoxybenzoyl*)*penta*-2,4-*dienethioate* **5b**. Yellow viscous liquid (2.44 g, 93%); ν_{max}(neat)/cm^{-1} 1681, 1666, 1618 and 1238; δ_H(250 MHz; $CDCl_3$) 2.34 (3 H, s, SMe), 3.86 (3 H, s, OMe), 5.60 (1 H, dd, J_{AC} 10 and J_{AB} 2, H_A), 5.88 (1 H, dd, J_{BC} 16 and J_{BA} 2, H_B), 6.99 (1 H, ddd, J_{CB} 16, J_{CD} 12 and J_{CA} 10, H_C), 7.03 (2 H, d, *J* 9, ArH), 7.44 (1 H, d, J_{DC} 12, H_D) and 7.84 (2 H, d, *J* 9, ArH); δ_C(62.8 MHz; $CDCl_3$) 12.01 (SMe), 56.43 (OMe), 115.2 (5-C), 118.08 (4-C), 130.01, 130.05 (phenyl CH), 132.4 (1-C phenyl), 132.6 (3-C), 140.01 (2-C), 165.57 (4-C

phenyl), 190.68 (phenyl CO) and 193.3 (COSMe); *m/z* 262 (M^+, 4%), 215 (19), 187 (8) and 135 (100) (Found: C, 64.3; H, 5.6. $C_{14}H_{14}O_3S$ requires C, 64.10; H, 5.38%).

S-*Methyl* 2-(4-*chlorobenzoyl*)*penta*-2,4-*dienethioate* **5c**. Yellow viscous liquid (2.42 g, 91%); ν_{max}(neat)/cm^{-1} 1676, 1600, 1498, 1410 and 1222; δ_H(90 MHz; CCl_4) 2.33 (3 H, s, SMe), 5.58 (1 H, dd, J_{AC} 10 and J_{AB} 2, H_A), 5.77 (1 H, dd, J_{BC} 17 and J_{BA} 2, H_B), 6.53 (1 H, ddd, J_{CB} 17, J_{CD} 12 and J_{CA} 10, H_C), 7.45 (1 H, d, J_{DC} 12, H_D), 7.77 (2 H, d, *J* 9, ArH) and 7.91 (2 H, d, *J* 9, ArH); *m/z* 266 and 268 (M^+, 25 and 11%), 219 (22) and 141 (71) (Found: C, 58.8; H, 4.4. $C_{13}H_{11}ClO_2S$ requires C, 58.53; H, 4.16%).

S-*Methyl* 2-*furoylpenta*-2,4-*dienethioate* **5d**. Yellow viscous liquid (1.97 g, 89%); ν_{max}(neat)/cm^{-1} 1678, 1656, 1582, 1479, 1403 and 1224; δ_H(90 MHz; CCl_4) 2.38 (3 H, s, SMe), 5.73 (1 H, dd, J_{AC} 10 and J_{AB} 2, H_A), 5.91 (1 H, dd, J_{BC} 18 and J_{BA} 2, H_B), 6.31–6.82 (2 H, m, H_C and 4-H furyl), 7.30 (1 H, br d, separation 1.5, 5-H furyl), 7.49 (1 H, d, J_{DC} 11, H_D) and 7.81 (1 H, br s, 3-H furyl); *m/z* 222 (M^+, 3%), 175 (66), 147 (17) and 95 (100) (Found: C, 59.7; H, 4.8. $C_{11}H_{10}O_3S$ requires C, 59.44; H, 4.54%).

S-*Methyl* 2-*thienoylpenta*-2,4-*dienethioate* **5e**. Yellow viscous liquid (2.04 g, 86%); ν_{max}(neat)/cm^{-1} 1666, 1653, 1538, 1424, 1375, 1258 and 1237; δ_H(90 MHz; $CDCl_3$) 2.38 (3 H, s, SMe), 5.68 (1 H, dd, J_{AC} 10 and J_{AB} 2, H_A), 5.82 (1 H, dd, J_{BC} 18 and J_{BA} 2, H_B), 6.54 (1 H, ddd, J_{CB} 18, J_{CD} 11 and J_{CA} 10, H_C), 7.21 (1 H, apparent dd, separation 5 and 3.5, 4-H thienyl), 7.43 (1 H, d, J_{DC} 11, H_D), 7.72 (1 H, br d, separation 5, 5-H thienyl) and 7.83 (1 H, br d, separation 3.5, 3-H thienyl); *m/z* 238 (M^+, 3%), 190 (86), 163 (19) and 111 (100) (Found: C, 55.7; H, 4.5. $C_{11}H_{10}O_2S_2$ requires C, 55.44; H, 4.23%).

S-*Methyl* 2-*Allenyl*-1-*oxo*-1,2,3,4-*tetrahydronaphthalene*-2-*carbothioate* **13**.—The carbothioate **13** was obtained from the salt **11** according to the general procedure for the preparation of compounds **3a–e** as a yellow viscous liquid (1.75 g, 68%); ν_{max}(neat)/cm^{-1} 2950, 1962, 1690, 1618, 1305 and 1238; δ_H(90 MHz; CCl_4) 2.22 (3 H, s, SMe), 2.52–2.81 (2 H, m, CH_2), 2.82–3.15 (2 H, m, CH_2), 4.98 (2 H, d, *J* 6, HC=C=CH_2), 5.92 (1 H, t, *J* 6, HC=C=CH_2), 7.18–7.64 (3 H, m, ArH) and 8.14–8.20 (1 H, m, ArH); *m/z* 258 (M^+, 8%), 183 (100) and 115 (24) (Found: C, 70.0; H, 5.75. $C_{15}H_{14}O_2S$ requires C, 69.74; H, 5.46%).

Acknowledgements

L. B. thanks CSIR, New Delhi for a Senior Research Fellowship. Financial assistance under the CSIR research scheme is also acknowledged.

References

1 Review: A. Viola, J. J. Collins and N. Filipp, *Tetrahedron*, 1981, **37**, 3765; A. Jefferson and F. Scheinmann, *Quart. Rev. Chem. Soc.*, 1968, **22**, 411.
2 I. Iwai and J. Ide, *Chem. Pharm. Bull.*, 1963, **11**, 1042; J. Hlubucek, E. Ritchie and W. C. Taylor, *Aust. J. Chem.*, 1971, **24**, 2347; J. Hlubucek, E. Ritchie and W. C. Taylor, *Aust. J. Chem.*, 1970, **23**, 1881; R. Gericke and I. Lues, *Tetrahedron Lett.*, 1992, **33**, 1871.
3 J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510; U. Koch-Pomeranz, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 2981; M. R. Attwood, I. Churcher, R. M. Dunsdon, D. N. Hurst and P. S. Jones, *Tetrahedron Lett.*, 1991, **32**, 811.
4 B. A. Otter, S. S. Saluja and J. J. Fox, *J. Org. Chem.*, 1972, **37**, 2858.
5 R. Gaertner, *J. Am. Chem. Soc.*, 1951, **73**, 4400.
6 E. R. H. Jones, J. D. Loder and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180; R. J. D. Evans, S. R. Landor and J. P. Regan, *J. Chem. Soc., Chem. Commun.*, 1965, 397; D. K. Black and S. R. Landor, *J. Chem. Soc.*, 1965, 6784; J. K. Crandall and G. L. Tindell, *J. Chem. Soc., Chem. Commun.*, 1970, 1411.
7 M. L. Purkayastha, M. Chandrasekharam, J. N. Vishwakarma, H. Ila and H. Junjappa, *Synthesis*, 1993, 245.
8 2-Phenyl-3-benzoyl-5-methylfuran has been reported to be formed in the mercuric oxide catalysed cyclisation of 2-benzoyl-1-oxo-1-phenylpent-4-yne, M. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, 1979, 3161.
9 J. P. Girault, P. Scribe and G. Dana, *Bull. Soc. Chim. Fr.*, 1973, 1760.

Paper 4/00769G
Received 8*th February* 1994
Accepted 21*st February* 1994