# Pyridinethiones; XIII. Alkylation of 1,5-Pentenedione Enolates, New Synthons for the Preparation of 5-Substituted 2(1*H*)-Pyridinethiones

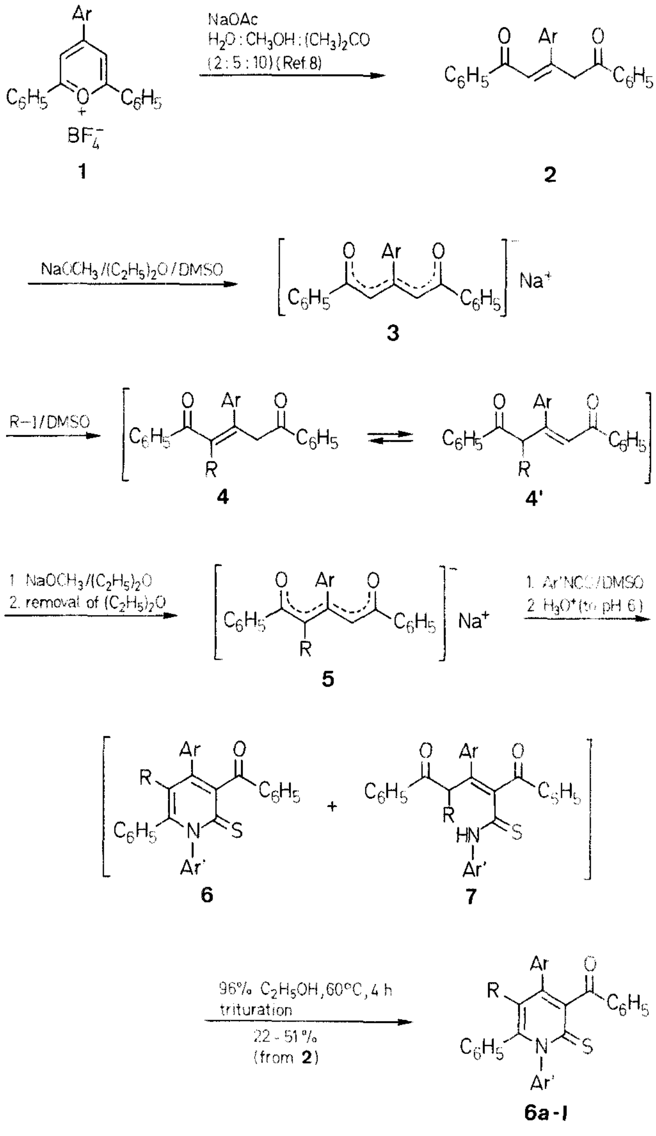
Jan Becher*, Carsten E. Stidsen, Fahmy M. Asaad

Department of Chemistry, University of Odense, DK-5230 Odense M, Denmark

Anions **3** of 1,5-pentenediones can be alkylated to give 2-alkyl-1,5-pentenediones **4**, whose anions **5** react with isothiocyanates to yield the oxoenoles **7**. These cyclize to give the new 5-substituted 2(1*H*)-pyridinethiones **6** in fair yields. Anions of unsymmetrical 1,5-pentenediones yields mixtures of 2(1*H*)-pyridinethiones **9** and **10**.

The glutacondialdehyde anion is an ambident anion, which, depending upon the nature of the electrophile, can react at the carbanion in the C-2 or C-4 position or at oxygen[1].

Deuteration[2] in the glutacondialdehyde enol anion also takes place at C-2 or C-4. Recently, it has been shown that 1,5-pentenediones can easily be deuterated at C-2 and C-4[3]. When treated with catalytic amounts of bases such as triethylamine and deuterium oxide, exchange takes place in the enol anion. Cyclization can then give pyrylium salts deuterated at position 3 or 5. It was previously demonstrated[4] that 1,5-pentenediones derived from 2,4,6-trisubstituted pyrylium salts could be alkylated at the 2-position when treated with methyl iodide in basic solution. Reinvestigation of this reaction[5] showed that 1,3,5-triaryl-1,5-pentenedione enolates reacted in dipolar aprotic solvents with various types of alkyl iodides. These results were in excellent agreement with our previous findings[6], and we have therefore been prompted to investigate the formation of new 5-substituted-2(1*H*)-pyridinethiones *via* alkylation of the stable 1,5-pentenedione enolates. Interestingly, it has been reported that related potassium 1,5-pentenedione enolates cannot be alkylated[7].



| 6 | Ar | Ar' | R |
|---|---|---|---|
| **a** | $C_6H_5$ | $C_6H_5$ | $CH_3$ |
| **b** | $C_6H_5$ | $4\text{-}CH_3O-C_6H_4$ | $CH_3$ |
| **c** | $C_6H_5$ | $4\text{-}Cl-C_6H_4$ | $CH_3$ |
| **d** | $4\text{-}Cl-C_6H_4$ | $C_6H_5$ | $CH_3$ |
| **e** | $4\text{-}Cl-C_6H_4$ | $4\text{-}CH_3O-C_6H_4$ | $CH_3$ |
| **f** | $4\text{-}Cl-C_6H_4$ | $4\text{-}Cl-C_6H_4$ | $CH_3$ |
| **g** | $4\text{-}CH_3O-C_6H_4$ | $C_6H_5$ | $CH_3$ |
| **h** | $C_6H_5$ | $C_6H_5$ | $CH_2C_6H_5$ |
| **i** | $C_6H_5$ | $4\text{-}CH_3O-C_6H_4$ | $CH_2C_6H_5$ |
| **j** | $C_6H_5$ | $4\text{-}Cl-C_6H_4$ | $CH_2C_6H_5$ |
| **k** | $4\text{-}Cl-C_6H_4$ | $4\text{-}CH_3O-C_6H_4$ | $CH_2C_6H_5$ |
| **l** | $4\text{-}Cl-C_6H_4$ | $4\text{-}F-C_6H_4$ | $CH_2C_6H_5$ |

$^1H$-NMR spectra revealed that the initial product obtained in the alkylation of 1,3,5-triphenyl-1,5-pentenedione with methyl iodide was a mixture of 2-and 4-methyl-1,5-pentenediones. Treatment of this mixture with base allows the isolation of a single isomer: 2-Methyl-1,3,5-triphenyl-1,5-pentenedione.

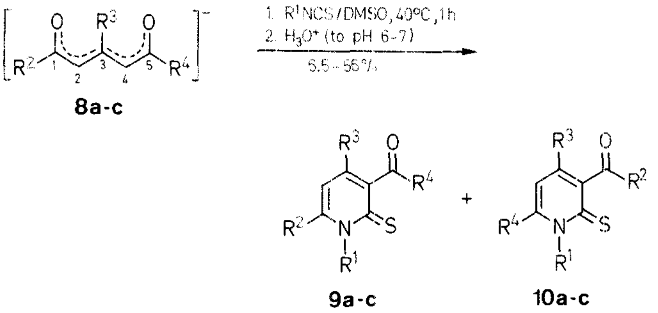
In general, the alkylated 1,5-pentenedione **4**/**4'** need not be isolated; the ether solution obtained is dried and treated with sodium methoxide to give the anion **5**. Removal of solvent *in vacuo* is followed by reaction of **5** with an aryl isothiocyanate in dry DMSO.

Addition of water to the reaction mixture precipitated a mixture of compounds composed of the cyclized product **6** as well as the non cyclic thioamide **7**. The $^1H$-NMR spectrum of the reaction mixture of **6h** and **7h** ($R = CH_2C_6H_5$) for example clearly showed both a OH and a NH resonance. Trituration of this crude reaction mixture promotes cyclization resulting in acceptable overall yields of the thiones **6**.

This result with easy formation of the 2(1*H*)-pyridinethiones **6** was a surprise to us since unsymmetrical anions of 1,5-pentenediones such as **8a** gave only a low total yield, 6.5%, of thiones **9a**/**10a** (17:3) beside a number of unidentified products.

**Table 1.** Spectral Data for 5-Alkyl-3-benzoyl-2-thioxo-1,2-dihydropyridines [5-Alkyl-3-benzoyl-2(1*H*)-pyridinethiones]**6**

| Product **6** | IR (KBr) $\nu(C=O)$ [$cm^{-1}$] | UV ($C_2H_5OH$) $\lambda$[nm] (log $\varepsilon$) | $^1H$-NMR ($CDCl_3/TMS_{int}$) $\delta$[ppm] |
|---|---|---|---|
| **a** | 1674 | 248 (4.44)<br>295 (4.17)<br>399 (3.93) | 1.65 (s, 3H); 7.0–8.0 (m, 20H) |
| **b** | 1673 | 247 (4.36)<br>293 (4.11)<br>399 (3.82) | 1.60 (s, 3H); 3.75 (s, 3H); 6.8–8.2 (m, 19H) |
| **c** | 1673 | 248 (4.38)<br>294 (4.10)<br>402 (3.84) | 1.61 (s, 3H); 7.1–7.9 (m, 19H) |
| **d** | 1673 | 249 (4.37)<br>294 (4.12)<br>402 (3.84) | 1.60 (s, 3H); 7.1–7.9 (m, 19H) |
| **e** | 1671 | 248 (4.45)<br>289 (4.21)<br>402 (3.88) | 1.59 (s, 3H); 3.68 (s, 3H); 6.6–7.9 (m, 18H) |
| **f** | 1670 | 250 (4.40)<br>294 (4.14)<br>404 (3.85) | 1.60 (s, 3H); 6.9–7.9 (m, 18H) |
| **g** | 1673 | 248 (4.33)<br>296 (4.25)<br>398 (3.86) | 1.65 (s, 3H); 3.70 (s, 3H); 7.0–8.0 (m, 19H) |
| **h** | 1674 | 248 (4.40)<br>296 (4.15)<br>398 (3.87) | 3.50 (s, 2H); 6.6–8.0 (m, 25H) |
| **i** | 1674 | 246 (4.37)<br>296 (4.17)<br>400 (3.82) | 3.50 (s, 2H); 3.70 (s, 3H); 6.5–8.0 (m, 24H) |
| **j** | 1673 | 248 (4.33)<br>297 (4.19)<br>400 (3.88) | 3.50 (s, 2H); 6.5–8.0 (m, 24H) |
| **k** | 1670 | 247 (4.38)<br>296 (4.16)<br>401 (3.81) | 3.50 (s, 2H); 3.70 (s, 3H); 6.8–8.2 (m, 23H) |
| **l** | 1672 | 248 (4.36)<br>296 (4.15)<br>400 (3.85) | 3.45 (s, 2H); 6.6–7.9 (m, 23H) |

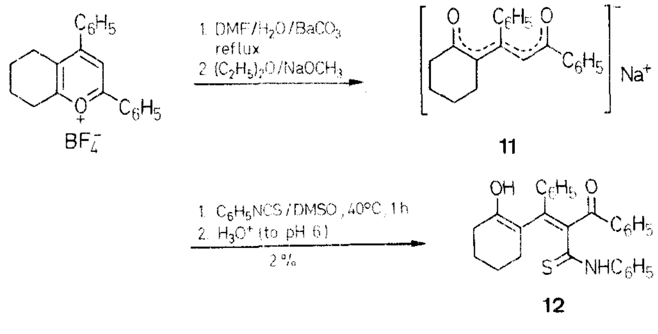


| Compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **8a/9a** | $C_6H_5$ | $CH_3$ | $SCH_3$ | $C_6H_5$ |
| **10a** | $C_6H_5$ | $C_6H_5$ | $SCH_3$ | $CH_3$ |
| **8b/9b** | $C_6H_5$ | $C_6H_5$ | $C_6H_5$ | 4-Cl-$C_6H_4$ |
| **10b** | $C_6H_5$ | 4-Cl-$C_6H_4$ | $C_6H_5$ | $C_6H_5$ |
| **8c/9c** | 4-$CH_3O$-$C_6H_4$ | $C_6H_5$ | $C_6H_5$ | 4-Cl-$C_6H_4$ |
| **10c** | 4-$CH_3O$-$C_6H_4$ | 4-Cl-$C_6H_4$ | $C_6H_5$ | $C_6H_5$ |

**Table 2.** Spectral Data for 3-Acyl-2-thioxo-1,2-dihydropyridines[3-Acyl-2(1*H*)-pyridinethiones] **9** and **10**

| Product | IR (KBr) $\nu$(C=O) [$cm^{-1}$] | UV ($C_2H_5OH$) $\lambda$ [nm] (log $\varepsilon$) | $^1$H-NMR ($CDCl_3/TMS_{int}$) $\delta$ [ppm] |
|---|---|---|---|
| **9a** | 1668 | 249 (4.30),<br>285 (4.50),<br>387 (3.90) | 2.12 (s, 3H); 2.43 (s, 3H); 6.56 (s, 1H); 7.21 (d, 2H, $J$ = 6 Hz); 7.40-7.54 (m, 6H); 7.98 (d, 2H, $J$ = 6 Hz) |
| **10a** | 1700 | 245 (3.72),<br>290 (4.01),<br>395 (3.44) | 2.47 (s, 3H); 2.68 (s, 3H); 6.58 (s, 1H); 7.03-7.10 (m, 5H); 7.18-7.26 (m, 5H) |
| **9b** | 1673 | 260 (4.50),<br>283 (4.35),<br>407 (3.85) | 6.79 (s, 1H); 7.19-7.46 (m, 17H); 7.78 (m, 1H); 7.93 (s, 1H) |
| **10b** | 1672 | 250 (4.53),<br>285 (4.39),<br>410 (3.92) | 6.74 (s, 1H); 7.14-7.42 (m, 17H); 7.85-7.97 (m, 2H) |
| **9c** | 1670 | 257 (4.56),<br>285 (4.39),<br>407 (3.89) | 3.70 (s, 3H); 6.77 (s, 1H); 6.83-7.92 (m, 18H) |
| **10c** | 1670 | 253 (4.58),<br>280 (4.45),<br>407 (3.95) | 3.73 (s, 3H); 6.73 (s, 1H); 6.85-7.95 (m, 18H) |

CNDO/2 calculations[10] on the anion **8a** showed the electron density $p_{HOMO}^{C-2} = 0.324e$ and $p_{HOMO}^{C-4} = 0.307e$. This relatively small difference explains the formation of both isomers **9a** and **10a**, albeit in low yields. A much better result was obtained with a "nearly symmetrical" anion **8b**; the total yield here was 56% of a 1:1 mixture of the thiones **9b** and **10b**.



In another experiment the enol anion **11** derived from the corresponding pyrylium salt resulted in isolation of the noncyclic thioamide **12** in low yield (2%), along with a number of unidentified products.

Microanalyses were carried out by Mr. Preben Amsler, NOVO A/S, Bagsvaerd, Denmark. IR spectra were obtained on a Perkin-Elmer 580; UV spectra were obtained on a Varian CARY 219; $^1$H- and $^{13}$C-NMR spectra were obtained on a Joel FX 60 Q; MS spectra were obtained on a Varian MAT 311 A. Melting points are uncorrected and were obtained with a Büchi apparatus. Yields are given for recrystallized analytical pure products.

**5-Alkyl-3-benzoyl-1,4-diaryl-6-phenyl-2-thioxo-1,2-dihydropyridines [5-Alkyl-3-benzoyl-1,4-diaryl-6-phenyl-2(1*H*)-pyridinethiones] 6; General procedure:**

The required 1,3,5-triaryl-1,5-pentenediones **2** is prepared from the appropriate 2,4,6-triaryl-pyrylium tetrafluoroborates **1** as described by Fischer and Herrmann[8].

Compound **2** (0.01 mol) is dissolved in dry dimethylsulfoxide (25 ml, 25°C). A solution of sodium methoxide [from sodium (0.25 g, 0.011 mol) in dry methanol (5 ml)] is added, followed by the alkyl iodide (0.011 mol). After stirring for 30 min (25°C), the reaction mixture is added to an ether/water mixture (500 ml ether/50 ml water), whereupon the ether phase is washed with water and dried with sodium sulfate. To this ether solution is added with stirring a solution of sodium methoxide [from sodium (0.25 g, 0.011 mol) in dry methanol (5 ml)] followed by concentration *in vacuo*. The dry residue is dissolved in dry dimethylsulfoxide (25 ml), the required arylisothiocyanate (0.011 mol) is added, and the mixture stirred for 2 hours (40°C). The reaction mixture is then added to water (500 ml, 0°C), and the resultant mixture saturated with sodium chloride and treated with 1 molar hydrochloric acid (to pH = 6). The precipitate is isolated, washed with water and triturated with 96% ethanol (25 ml, 60°C) for 4 hours. The resulting suspension was filtered hot and the yellow crystals recrystallized from toluene. Crude yields ~90%.

*3-Benzoyl-5-methyl-2-thioxo-1,4,6-triphenyl-1,2-dihydropyridine[3-Benzoyl-5-methyl-1,4,6-triphenyl-2(1H)-pyridinethione]* **6a**:
The general method gave **6a** as yellow crystals: yield 2.1 g (45%); m.p. > 260°C.

MS: *m/e* (rel. int., %) = 457 (41), 428 (100), 352 (12), 105 (10), 77 (40).

| | | | | |
|---|---|---|---|---|
| $C_{31}H_{23}NOS$ | calc. | C 81.37 | H 5.07 | N 3.06 |
| (457.6) | found | 81.76 | 5.13 | 3.00 |

*3-Benzoyl-4,6-diphenyl-1-(4-methoxyphenyl)-5-methyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-4,6-diphenyl-1-(4-methoxyphenyl)-5-methyl-2(1H)-pyridinethione]* **6b**:
The general method gave **6b** as yellow crystals: yield 1.1 g (22%); m.p. > 260°C.

MS: *m/e* (rel. int., %) = 487 (60), 458 (100), 243.5 (13), 105 (14), 77 (28).

| | | | | |
|---|---|---|---|---|
| $C_{32}H_{25}NO_2S$ | calc. | C 78.82 | H 5.17 | N 2.87 |
| (487.6) | found | 78.96 | 5.19 | 2.68 |

*3-Benzoyl-1-(4-chlorophenyl)-4,6-diphenyl-5-methyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-1-(4-chlorophenyl)-4,6-diphenyl-5-methyl-2(1H)-pyridinethione]* **6c**:
The general method gave **6c** as yellow crystals; yield: 3.3 g (33%); m.p. > 260°C.

MS: *m/e* (rel. int., %) = 491 (45), 462 (100), 386 (10), 105 (21), 77 (38).

| | | | | |
|---|---|---|---|---|
| $C_{31}H_{22}ClNOS$ | calc. | C 75.67 | H 4.51 | N 2.85 |
| (492.0) | | 75.76 | 4.50 | 2.68 |

*3-Benzoyl-4-(4-chlorophenyl)-1,6-diphenyl-5-methyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-4-(4-chlorophenyl)-1,6-diphenyl-5-methyl-2(1H)-pyridinethione]* **6d**:
The general method gave **6d** as yellow crystals; yield: 2.4 g (48%); m.p. > 260°C.

MS: *m/e* (re. int., %) = 491 (46), 462 (100), 386 (10), 105 (21), 77 (38).

| | | | | |
|---|---|---|---|---|
| $C_{31}H_{22}ClNOS$ | calc. | C 75.67 | H 4.51 | N 2.85 |
| (492.0) | found | 75.48 | 4.56 | 2.77 |

*3-Benzoyl-4-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-methyl-6-phenyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-4-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-methyl-6-phenyl-2(1H)-pyridine-thione]* **6e**:
The general method gave **6e** as yellow crystals; yield: 1.5 g (29%); m.p. > 260 °C.

*MS: m/e (rel. int., %) = 521 (64), 492 (100), 260.5 (7), 105 (20), 77 (37).*

| | | | | |
|---|---|---|---|---|
| $C_{32}H_{24}ClNO_2S$ | calc. | C 73.62 | H 4.63 | N 2.68 |
| (522.1) | found | 73.53 | 4.66 | 2.61 |

*3-Benzoyl-1,4-bis (4-chlorophenyl)-5-methyl-6-phenyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-1,4-bis (4-chlorophenyl)-5-methyl-6-phenyl-2(1H)-pyridinethione]* **6f**:
The general method gave **6f** as yellow crystals; yield: 1.7 g (32%); m.p. > 260 °C.

*MS: m/e (rel. int., %) = 525 (40), 496 (100), 111 (12), 105 (21), 77 (42).*

| | | | | |
|---|---|---|---|---|
| $C_{31}H_{21}Cl_2NOS$ | calc. | C 70.72 | H 4.02 | N 2.66 |
| (526.5) | found | 70.56 | 4.05 | 2.53 |

*3Benzoyl-1,6-diphenyl-4-(4-methoxyphenyl)-5-methyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-1,6-diphenyl-4-(4-methoxyphenyl)-5-methyl-2(1H)-pyridinethione]* **6g**:
The general method gave **6g** as yellow crystals; yield: 2.5 g (51%); m.p. > 260 °C.

*MS: m/e (rel. int., %) = 487 (46), 458 (100), 235 (13), 105 (12), 77 (34).*

| | | | | |
|---|---|---|---|---|
| $C_{32}H_{25}NO_2S$ | calc. | C 78.83 | H 5.17 | N 2.87 |
| (487.6) | found | 78.78 | 5.15 | 2.82 |

*3-Benzoyl -5-benzyl-2-thioxo-1,4,6-triphenyl-1,2-dihydropyridine-[3-Benzoyl-5-benzyl-1,4,6-triphenyl-2(1H)-pyridinethione]* **6h**:
*The general method gave* **6h** *as yellow crystals; yield: 2.3 g (43%);* m.p. > 260 °C.

MS: *m/e* (rel. int., %) = 533 (50), 504 (100), 105 (13), 91 (22), 77 (30).

| | | | | |
|---|---|---|---|---|
| $C_{37}H_{27}NOS$ | calc. | C 83.27 | H 5.10 | N 2.62 |
| (533.7) | found | 83.45 | 5.15 | 2.57 |

*3-Benzoyl-5-benzyl-4,5-diphenyl-1-(4-methoxyphenyl)-2-thioxo-1,2-dihydropyridine[3-Benzoyl-5-benzyl-4,6-diphenyl-1-(4-methoxyphenyl)-2(1H)-pyridinethione]* **6i**:
The general method gave **6i** as yellow crystals; yield: 2.2 g (39%); m.p. > 260 °C.

MS.: *m/e* (rel. int., %) = 563 (89), 534 (100), 105 (13), 91 (25), 77 (19).

| | | | | |
|---|---|---|---|---|
| $C_{38}H_{29}NO_2S$ | calc. | C 80.97 | H 5.19 | N 2.48 |
| (563.7) | found | 81.22 | 5.27 | 2.36 |

*3-Benzoyl-5-benzyl-1-(4-chlorophenyl)-4,6-diphenyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-5-benzyl-1-(4-chlorophenyl)-4,6-diphenyl-2(1H)-pyridinethione]* **6j**:
The general method gave **6j** as yellow crystals; yield: 2.0 g (35%); m.p. > 260 °C.

MS: *m/e* (rel. int., %) = 567 (59), 538 (100), 105 (16), 91 (25), 77 (20).

| | | | | |
|---|---|---|---|---|
| $C_{37}H_{26}ClNOS$ | calc. | C 78.22 | H 4.61 | N 2.47 |
| (568.1) | found | 78.26 | 4.66 | 2.34 |

*3-Benzoyl-5-benzyl-4-(4-chlorophenyl)-1-(4-methoxyphenyl)-6-phenyl-2-thioxo-1,2-dihydropyridinethione[3-Benzoyl-5-benzyl-4-(4-chlorophenyl)-1-(4-methoxyphenyl)-6-phenyl-2(1H)-pyridine-thione]* **6k**:
The general method gave **6k** as yellow crystals; yield: 1.4 g (24%); m.p. > 260 °C.

*MS: m/e (rel. int., %) = 597 (84), 568 (100), 105 (12), 91 (18), 77 (13).*

| | | | | |
|---|---|---|---|---|
| $C_{38}H_{28}ClNO_2S$ | calc. | C 76.30 | H 4.72 | N 2.34 |
| (598.2) | found | 76.50 | 4.96 | 2.18 |

*3-Benzoyl-5-benzyl-4-(4-chlorophenyl)-1-(4-fluorophenyl)-6-phenyl-2-thioxo-1,2-dihydropyridine[3-Benzoyl-5-benzyl-4-(4-chlorophenyl)-1-(4-fluorophenyl)-6-phenyl-2(1H)-pyridinethione]* **6l**:
The *general method gave* **6l** *as yellow crystals; yield: 2.5 g (42%),* m.p. > 260 °C.

MS: *m/e* (rel. int., %) = 585 (45), 556 (100), 105 (24), 91 (30), 77 (28).

| | | | | |
|---|---|---|---|---|
| $C_{37}H_{25}ClFNOS$ | calc. | C 75.82 | H 4.30 | N 2.39 |
| (586.1) | found | 76.13 | 4.35 | 2.32 |

### 2-Benzoyl-3,*N*-diphenyl-3-(2-hydroxycyclohexenyl)-thiopropenamide; 12:

2,4-Diphenyl-5,6,7,8-tetrahydro-1-benzopyrylium tetrafluoroborate[9] (3.74 g, 0.01 mol) is dissolved in dimethylformamide (30 ml) and water (25 ml) and heated to reflux, whereupon the mixture is added to a refluxing suspension of barium carbonate (6 g, 0.03 mol) *in water (30 ml). Reflux is continued for 5 minutes followed by rapid* cooling and extraction with ether (3 × 200 ml). The ether phase is washed with water and dried with sodium sulfate. To the dry ether solution is added a solution of sodium methoxide [from sodium (0.25 g, 0.011 mol) in dry methanol (5 ml)] and the mixture concentrated *in vacuo*. The dry residue is dissolved in dry dimethylsulfoxide (25 ml), whereupon phenylisothiocyanate (1.5 g, 0.011 mol) is added, and the mixture stirred for 1 hour at 40 °C. The reaction mixture is added to water (500 ml, 0 °C) and treated with 1 molar hydrochloric acid (to pH 6). Extraction with ether *(3 × 150 ml), drying with sodium sulfate and concentration in vacuo* gave an orange oil. Chromatography by PTLC (silica gel, eluent $CHCl_3/CH_3OH$, 33:1) yields orange crystals of the title compound; yield: 77 mg (2%); m.p. 172–173 °C.

MS: *m/e* (rel. int., %) = 439 (14), 406 (100), 105 (70).

IR (KBr): $\nu$ = 3700–3100 (OH, NH); 1670 cm$^{-1}$ (C=O).

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 2.08 (br., 4H, $CH_2$); 2.75 (br., 2H, $CH_2$); 3.23 (br., 2H, $CH_2$); 7.25–8.29 ppm (m, 15$H_{arom}$).

$^{13}$C-NMR ($CDCl_3$/TMS): $\delta$ = 25.84 ($CH_2$); 26.94 ($CH_2$); 30.65 ($CH_2$); 162.34 (=C–OH); 171.35 (C=S); 197.60 ppm (C=O).

| | | | | |
|---|---|---|---|---|
| $C_{28}H_{25}NO_2S$ | calc. | C 76.51 | H 5.73 | N 3.19 |
| (439.6) | found | 75.93 | 5.72 | 3.10 |

### 3-Acyl-2-thioxo-1,2-dihydropyridines[3-Acyl-2-(1*H*)-pyridinethiones] 9 and 10; General Procedure:

The required 1,3,5-trisubstituted-1,5-pentenedione enolate **8** is prepared according to a previously reported method[6].

To a solution of the enolates **8** (0.01 mol) in dry dimethylsulfoxide (25 ml) is added arylisothiocyanate (0.011 mol), and the mixture stirred for 1 hour at 40 °C. The reaction mixture is then cooled to room temperature, added to ice-cold water (500 ml), and the mixture *stirred for 30 minutes. The aqueous phase is saturated with sodium* chloride and treated with 1 molar hydrochloric acid (to pH 6–7). Extraction with ether (3 × 150 ml), drying with sodium sulfate and concentration *in vacuo* gives a brown-orange oil. Chromatography by PTLC (silica gel, eluent $CHCl_3$, developed 3 times) with isolation of the orange bands yielded yellow-orange crystals of **9** and **10**.

*3-Benzoyl-6-methyl-4-methylthio-1-phenyl-2-thioxo-1,2-dihydropyridine and 3-acetyl-1,6-diphenyl-4-methylthio-2-thioxo-1,2-dihydropyridine[3-Benzoyl-6-methyl-4-methylthio-1-phenyl-2(1H)-pyridinethione* **9a** *and 3-acetyl-1,6-diphenyl-4-methylthio-2(1H)-pyridinethione* **10a**]:
The general method gave **9a** and **10a** as orange crystals; total yield: 0.23 g (6.5%, 17:3); m.p. 252–253 °C, respectively 238–239 °C.

MS: *m/e* (rel. int., %) = **(9a)** 351 (43), 322 (100), 105 (7), 77 (40); **(10a)** 351 (33), 336 (100), 77 (13).

| | | | | |
|---|---|---|---|---|
| $C_{20}H_{17}NOS_2$ | calc. | C 68.37 | H 4.88 | N 3.99 |
| (351.1) | found **(9a)** | 68.44 | 4.78 | 4.04 |

| | | |
|---|---|---|
| HRMS (Peak matching) | calc. | 351.0752 |
| | found **(10a)** | 351.0749 |

*3-(4-Chlorobenzoyl)-2-thioxo-1,4,6-triphenyl-1,2-dihydropyridine and 3-benzoyl-6-(4-chlorophenyl)-1,4-diphenyl-2-thioxo-1,2-dihydropyridine[3-(4-Chlorobenzoyl)-1,4,6-triphenyl-2(1H)-pyridine-thione* **9b** *and 3-benzoyl-6-(4-chlorophenyl)-1,4-diphenyl-2(1H)-pyridinethione* **10b**:
The general method gave **9b** and **10b** as orange crystals; total yield: 2.7 g (56%, 1:1); m.p. 243–244 °C, respectively 263–264 °C.

MS: *m/e* (rel. int., %) = **(9b)** 477 (41), 448 (100), 139 (6), 77 (13); **(10b)** 477 (42), 448 (100), 105 (12), 77 (32).

| | | | | |
|---|---|---|---|---|
| $C_{30}H_{20}ClNOS$ | calc. | C 75.38 | H 4.22 | N 2.93 |
| (478.0) | found **(9b)** | 75.28 | 4.21 | 2.73 |
| | found **(10b)** | 74.75 | 4.05 | 2.91 |

*3-(4-Chlorobenzoyl)-4,6-diphenyl-1-(4-methoxyphenyl)-2-thioxo-1,2-dihydropyridine and 3-benzoyl-6-(4-chlorophenyl)-1-(4-methoxyphenyl)-4-phenyl-2-thioxo-1,2-dihydropyridine[3-(4-Chlorobenzoyl)-4,6-diphenyl-1-(4-methoxyphenyl)-2(1H)-pyridinethione* **9c** *and 3-benzoyl-6-84-chlorophenyl)-1-(4-methoxyphenyl)-4-phenyl-2(1H)-pyridinethione* **10c**]:
The general method gave **9c** and **10c** as orange crystals; total yield: 2.3 g (45%; 2:1); m.p. 270–271 °C, respectively 251–252 °C.

MS: *m/e* (rel. int., %) = **(9c)** 507 (75), 478 (100), 139 (14), 77 (6); **(10c)** 507 (83), 478 (100), 105 (17), 77 (26).

| | | | | |
|---|---|---|---|---|
| $C_{31}H_{22}ClNO_2S$ | calc. | C 73.29 | H 4.36 | N 2.76 |
| (508.0) | found **(9c)** | 72.77 | 4.37 | 2.71 |
| | found **(10c)** | 73.12 | 4.40 | 2.86 |

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A full account of calculations on these anions will be published elsewhere.