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ENAMINE CHEMISTRY–XXVI[a]

THE [4+2] CYCLOADDITION REACTIONS OF 3-AMINO-1-(4-NITROPHENYL)-PROP-2-ENE-1-THIONE WITH ELECTROPHILIC OLEFINS AND ACETYLENES

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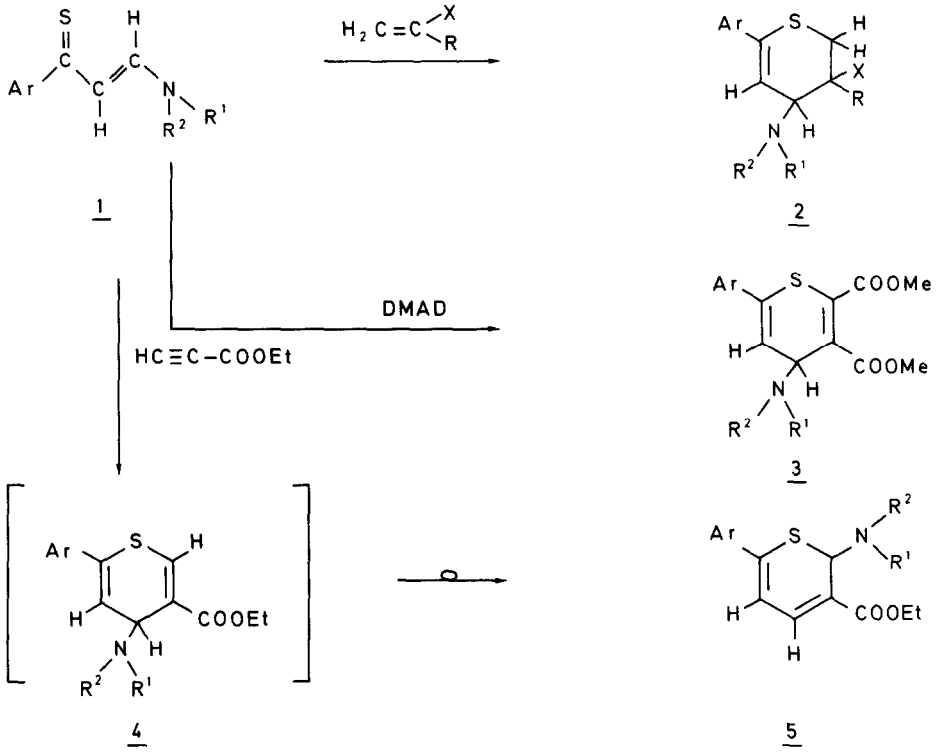
Abstract—Enamino-thiones **1** prepared from the corresponding enaminones by thiation with Lawesson's Reagent, were allowed to react with 2-chloroacrylonitrile and dimethyl acetylenedicarboxylate giving dihydro-2H-thiopyrans, **2**, and 4H-thiopyrans, **3**, respectively. The reaction of **1a** with ethyl propiolate at room temperature afforded 4H-thiopyrans, **4a**, which on standing rearranged to 2H-thiopyran, **5a** (1, 3 amide shift). The reaction of **1b** with ethyl propiolate produced **4b** and **5b**. Some of the ^{13}C NMR data are reported.

Enamino-thiones are known to be useful synthetic intermediates, e.g. in the preparation of thiophenes,[1] thiopyrans[2,3] and isothiazoles.[4,5] Recently, we reported[6] on the [4+2] cycloaddition reactions of 1-aryl-3-amino (N,N-disubstituted)-propene-1-thiones with electrophilic olefins and acetylenes (Scheme 1).

It was not possible to isolate the 4H-thiopyran, **4**, but only the 2H-thiopyran, **5**. In our attempts to isolate intermediates of type **4** we have prepared and reacted some enamino-thiones (Ar = 4-$NO_2C_6N_4$) with electrophilic olefins and acetylenes. This paper reports the results.

RESULTS AND DISCUSSION

Earlier it was shown[7] that enaminones are prepared in excellent yields by Route A[8] (Scheme 2). However, when Ar is equal to 4-nitrophenyl only low yields of the



Ar = C_6H_5, 4-Br-C_6H_4, 4-MeOC_6H_4 ; NR^1R^2 = N⌐⌐ N⌐⌐

X = H, Cl

Scheme 1.

[a]Part XXV: S. Carlsson and S.-O. Lawesson, *Tetrahedron* **38**, 413 (1982).

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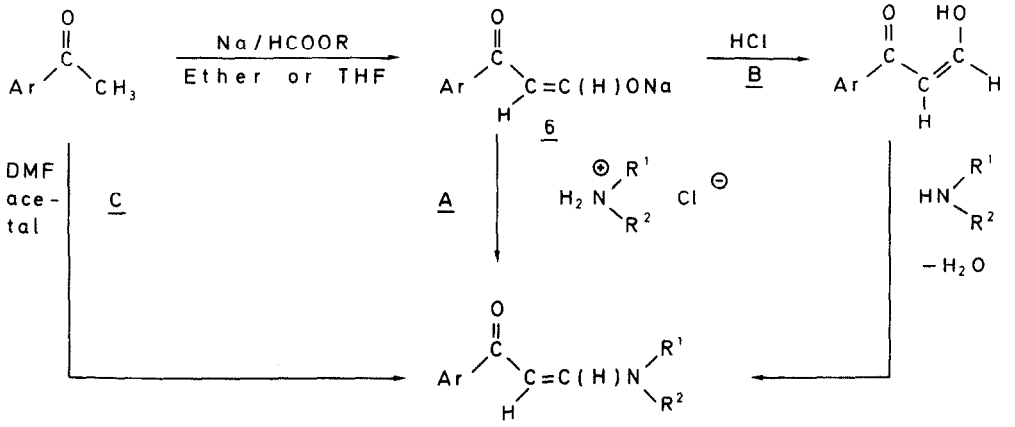
desired enaminones, **7**, are obtained. Alternatively,[9] Route B is used and it gives high yields of enaminones from the sodium salt, **6**. For $R^1 = R^2 = CH_3$ the best method to prepare **7c** is by Route C.[10–12]

In the ^{1}H NMR spectrum of **2a** the hydrogens at C(2) show an AB structure and shifts at δ_A 3.37 and δ_B 3.70 (J_{HH} = 13.5 Hz).[14] A doublet is observed at δ 3.90 (J = 5.8 Hz) and δ 6.25 (J = 5.8 Hz) assigned to the hydrogens



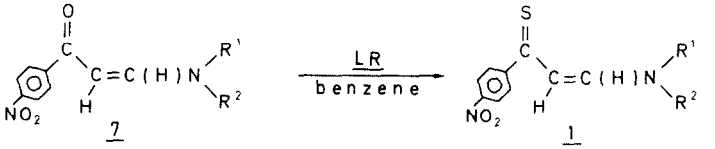
Scheme 2

The prepared enaminones **7** are allowed to react with 2, 4-bis(4-methoxyphenyl)-1, 3, 2, 4-dithiadiphosphetane 2,4-disulfide, Lawesson's Reagent (**LR**), in benzene at room temperature giving the corresponding enamino-thiones, **1**, in high yields (Scheme 3). The compounds **7** and **1** are characterized by means of ^{1}H NMR, ^{13}C NMR, IR, UV and MS. The configuration of the double-bond is E for **7a**, **7c**, **1a** and **1c** (^{1}H NMR $J_{H^2H^3} > 11$ Hz), but two rotamers around the C(1)–C(2) bond are observed (E-s-E $\rightleftharpoons$ E-s-Z). Compounds **7b** and **1b** exist in equilibrium between E-s-Z and Z-s-Z depending on the solvent (^{1}H NMR, $CDCl_3$): < 5% E-s-Z; (DMSO): ≈ 50% E-s-Z.

at C(4) and C(5), respectively. The ^{1}H NMR spectrum of **2b** shows a singlet for the hydrogens at C(2) (δ 3.65). Two doublets at δ 4.60 and 5.96 (J = 4.0 Hz) are observed for the hydrogens at C(4) and C(5), respectively. In MS the base peak, for both **2a** and **2b**, is m/e 244 (M^+-Cl-amine), while M^+ and M^+ – amine are not observed. The assignment of the ^{13}C NMR spectra[15] (Table 1) for **2a** and **2b** is made by off resonance decoupled spectra.

When treating **1a** and **1b** with dimethyl acetylenedicarboxylate in benzene at room temperature 4H-thiopyrans, **3**, are formed in quantitative yields (Scheme 5).

The general mass fragmentation patterns of **3** are as described earlier.[6] In the ^{1}H NMR spectra a difference



a: $R^1R^2 = -(CH_2)_4-$

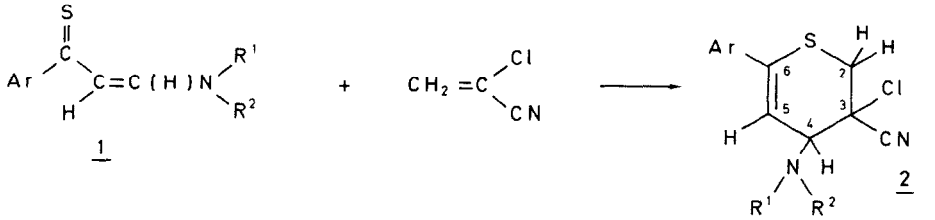
b: $R^1 = H$, $R^2 = C_6H_5$

c: $R^1 = R^2 = CH_3$

Scheme 3.

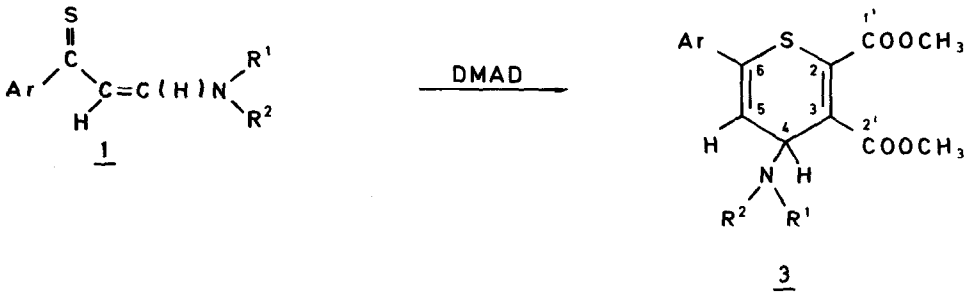
The enamino-thiones, **1a** and **1b**, in benzene at room temperature undergo a [4 + 2] regiospecific cycloaddition reaction with 2-chloroacrylonitrile, a ketene equivalent,[13] giving the dihydro-2H-thiopyrans **2** (Scheme 4) in quantitative yields.

between **3a** and **3b** is observed for the coupling constant between H(4) and H(5) (ΔJ = 0.5 Hz). This effect is also reflected in the ^{13}C NMR spectra (assigned as described earlier, Table 1) where C(1'), C(2) and C(4) shift at lower field for **3b** than for **3a**. Hydrogen bonding is not observed for **3b** in the ^{1}H NMR spectrum.



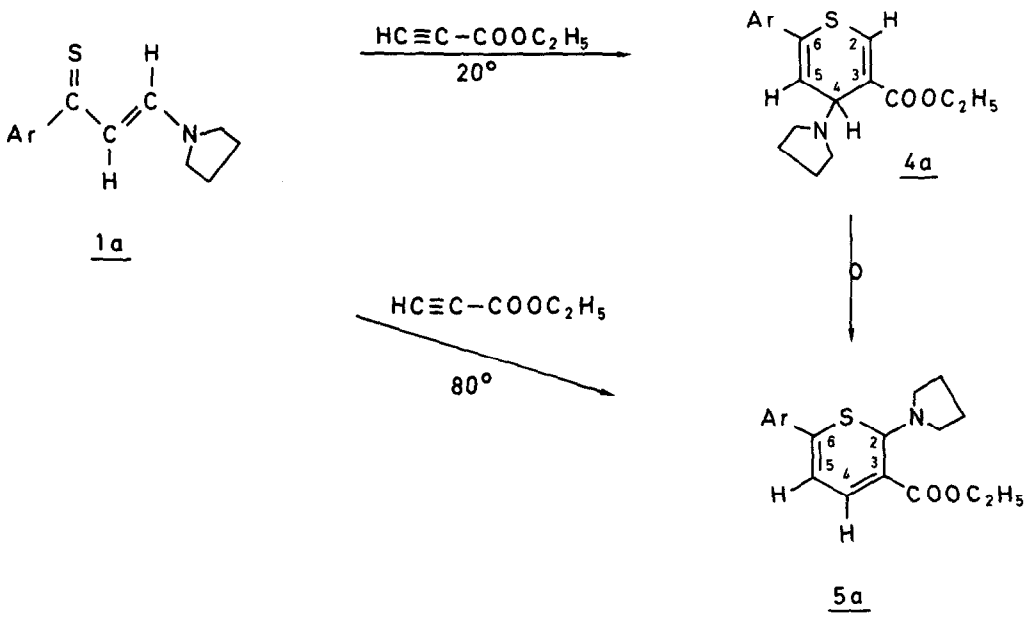
Ar = 4-nitrophenyl; a: $R^1R^2 = -(CH_2)_4-$; b: $R^1 = H$, $R^2 = C_6H_5$

Scheme 4.



Ar = 4-nitrophenyl; a: R^1R^2 = -$(CH_2)_4$-; b: R^1 = H, R^2 = C_6H_5

Scheme 5.



Scheme 6.

Table 1. ^{13}C NMR data for the thiopyrans 2, 3, 4, 5 (δ vs TMS)

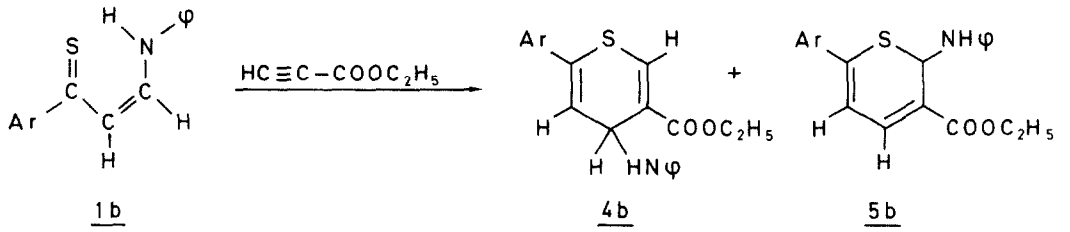
Comp. \ ass.	C(2)	C(3)	C(4)	C(5)	C(6)	C(1')	C(2')
2a	34.77	55.95	63.92	116.62	134.04	117.71+	-
2b*	35.52	59.13	58.72	119.57	133.66	118.03+	-
3a	133.28	125.16	54.72	118.73	132.85	163.91	166.60
3b	142.21	127.02	69.16	114.87	135.60	171.11	166.01
4a	143.27	119.90	50.75	120.54	133.28	165.01	-
5a	61.40	116.69	133.05	117.74	144.21	166.80	
5b	52.54	118.54	133.12	118.54	142.95	165.66	

*d_6-$(CH_3)_2CO$; + CN

When allowing enamino-thiones to react with ethyl propiolate 4H-thiopyrans are formed,[6] but they rearrange to the more stable 2H-thiopyrans. Earlier[6] we were not able to isolate the 4H-thiopyrans, but for **1**, Ar = p-nitrophenyl this is possible. The product from **1a** and ethyl propiolate, **4a**, is formed in quantitative yields at room temperature. When the reaction is performed at 80° (Scheme 6) only **5a** is isolated.

Compound **4a** is unstable and rearranges on storage, even at −20°. It is characterized by means of MS, ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR shifts are found at δ 4.95 (J = 6.2 Hz), δ 6.35 (J = 6.2 Hz) and δ 7.83 (s) for the thiopyran ring, in accordance with those of **2a**. The assignment of the ^{13}C NMR spectrum (Table 1) is made by off resonance decoupled spectra. Compound **5a** was characterized as described earlier.[6]

Also **1b** was allowed to react with ethyl propiolate. The reactions is very slow at room temperature, but at 80° **1b** is consumed in 1 h and the reaction mixture consists of both **4b** and **5b** (Scheme 7)



1b 4b 5b

Ar = 4-nitrophenyl

Scheme 7.

In the ^{1}H NMR spectrum the characteristic two doublets at δ 4.80 and 6.30 of the thiopyran ring and also two lowfield NH hydrogens are observed. Compound **5b** was characterized by means of MS, ^{1}H NMR, ^{13}C NMR and microanalyses.

Similar 4H- → 2H-thiopyran rearrangements have been observed for hydrogen,[16] catalyzed by thiopyrylium cations, and benzyl,[17] catalyzed by HCl.

EXPERIMENTAL

^{1}H NMR, ^{13}C NMR and MS are obtained as described earlier.[6] Coupling constants are given as |J|. M.p.'s are uncorrected. Microanalyses were carried out by Løvens Kemiske Fabrik, DK-2750 Ballerup (Microanalytical Laboratory). The exact mass spectra were obtained on a Varian MAT 311A by electron impact (70 eV) and using the direct insertion system. 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, Lawesson's Reagent (*LR*), is commercially available from Fluka AG, CH-9470 Buchs 1.

Preparation of enaminones **7**. 0.25 Mol (41.25 g) of 4-nitroacetophenone and 0.375 mol (22.5 g) of methyl formate in 100 ml THF were added dropwise (vigorous stirring) to 0.25 mol (13.5 g) $NaOCH_3$ in 100 ml anhydrous and redistilled THF (N_2). The solvent was evaporated after 2 h and the sodium salt **6** was isolated in 90% yield.

Route A. To the sodium salt, **6**, dissolved in C_2H_5OH, was added pyrrolidinium chloride or anilinium chloride giving **7a** (8%) or **7b** (20%), respectively.

Route B. The sodium salt, **6**, was dissolved in H_2O and acidified with dilute HCl, followed by extraction with CH_2Cl_2. The solvent was evaporated yielding 95% crude product, 4-nitrobenzoylacetaldehyde. 30 mmol (5.79 g) of the latter and 30 mmol (2.13 g) pyrrolidine in 100 ml benzene were refluxed for 3 h with a Dean-Stark water-separator, yielding, after evaporation of the solvent and recrystallization from CH_2Cl_2/petroleum, 60% of 1-(4-nitrophenyl)-3-(1-pyrrolidinyl)-propen-1-one, **7a**. M.p. 137°. MS: *m/e* 246 (M^+). ^{1}H NMR ($CDCl_3$): 1.8–2.1 (4H, m), 3.25 (2H, m), 3.55 (2H, m), 5.55* (1H, d, J 12 HZ), 7.92* (1H, d, J 12 Hz), 7.86 (2H, d, J 9 HZ), 8.13 (2H, d, J 9 Hz). [*Using DMSO (d_6) as solvent the signals for H(2) and H(3) are broadened and shifted 0.2 and 0.1 ppm downfield, respectively.] ^{13}C NMR ($CDCl_3$): δ 24.81 (CH_2), 46.97 (CH_2–N), 52.40 (CH_2–N), 92.50 (C(2)), 123.00 (C(3')), 128.00 (C(2')), 145.87 (C(1')), 148.57 (C(4')), 150.64 (C(3)), 185.27 (C(1)).

3-Anilino-1-(4-nitrophenyl)-propen-1-one **7b**. The same procedure (Route B) as used for **7a**. Yield 70%, m.p. 172–173° (CH_2Cl_2/petroleum). MS: *m/e* 268 (M^+). ^{1}H NMR ($CDCl_3$): δ 5.95 (1H, d, J 8 Hz), 6.90–7.50 (5H, m), 7.55 (1H,dd, J 8 and 13 Hz), 8.00 (2H, d, J 9 Hz), 8.25 (2H, d, J 9 Hz), 12.5 (broad). ^{1}H NMR (DMSO (d_6)): δ 6.16 (0.5 H, d, J 7.8 Hz), 6.42 (0.5H, d, J 12.2 Hz), 7.0–7.5 (5H, m), 7.9–8.4 (5H, m), 10.6 (0.5H, d, J 13 Hz), 12.25 (0.5H, d, J 13 Hz).

Route C. 3-N,N-Dimethylamino-1-(4-nitrophenyl)-propen-1-one **7c**. To 10 mmol of 4-nitroacetophenone, dissolved in 20 ml CH_3CN were added 10 mmol of dimethylformamide-dineopentylacetal in 5 ml CH_3CN. The mixture was refluxed until the 4-nitroacetophenone was consumed (TLC, 2h), followed by evaporation of the solvent. The black, dry residue was dissolved in hot C_2H_5OH and H_2O was added, whereby **7c** precipitated. Yield 70% (C_2H_5OH), m.p. 150°.[3] MS: *m/e* 228 (M^+). ^{1}H NMR ($CDCl_3$): δ 3.00 (3H, s, broad), 3.15 (3H, s, broad), 5.65 (1H, d, J 12.2 Hz), 7.80 (1H, d, J 12.2 Hz), 7.95 (2H, d, J 9 Hz), 8.20 (2H, d, J 9 Hz). ^{13}C NMR ($CDCl_3$): δ 37.43 (CH_3), 45.28 (CH_3), 91.92 (C(2)), 123.35 (C(3')), 128.35 (C(2')), 146.12 (C(1')), 148.98 (C(4')), 155.22 (C(3)), 185.84 (C(1)).

General procedure for preparation of enaminothiones **1**. To 10 mmol of **7** dissolved or suspended in 50 ml anhydrous benzene were added 5 mmol (2.02 g) of *LR* at room temp. When **7** was consumed (TLC) the solvent was evaporated and the residue dissolved in CH_2Cl_2 followed by treatment with 1% NaOH (25 ml). After separation and evaporation of the solvent the crude mixture was filtered through a column.

1 - (4 - Nitrophenyl) - 3 - (1 - pyrrolidinyl) - propene - 1 - thione **1a**. Reaction time 1 h. Column chromatography: Al_2O_3, 75% CH_2Cl_2/petroleum as eluent. Yield 70% m.p. 172°. ^{1}H NMR ($CDCl_3$): δ 1.75–2.30 (4H, m), 3.45 (2H, m), 3.80 (2H, m), 6.50 (1H, d, J 11.5 Hz, broad), 7.50–8.30 (4.3H, m), 8.65 (0.7H, d, J 11.5 Hz, broad). ^{13}C NMR ($CDCl_3$): 24.51 (CH_2), 48.29 (CH_2–N), 53.59 (CH_2–N), 113.56 (C(2)), 122.58 (C(3')), 127.29 (C(2')), 147.44 (C(4')), 153.05 (C(3')), 153.49 (C(3)), 208.53 (C(1)). Mass spectrum calc. for $C_{13}H_{14}N_2O_2S$ *m/e* 262.0776, found: *m/e* 262.0776.

3-Anilino-1-(4-nitrophenyl)-propene-1-thione **1b**. Reaction time 6 h. Column chromatography: SiO_2, 75% CH_2Cl_2/petroleum as eluent. Yield 90%, m.p. 167°. ^{1}H NMR ($CDCl_3$): δ 6.60–7.50 (5H, m), 6.70 (1H, d, J 7.8 Hz), 7.85 (1H, dd, J 7.8 and 13 Hz), 7.80 (2H, d, J 9 Hz), 8.20 (2H, d, J 9 Hz), 15.5 (1H, broad). ^{1}H NMR (DMSO (d_6)): δ 6.85 (0.5H, d, J 7.5 Hz), 7.10 (0.5H, d, J 12 Hz), 7.10–7.60 (5H, m), 7.70–8.30 (4.5H, m), 8.45 (0.5H, dd, J 7.5 and 13 Hz), 11.25 (0.5H, broad), 15.25 (0.5H, d, 13 Hz). Mass spectrum calc. for $C_{15}H_{12}N_2O_2S$ *m/e* 284.0620, found: *m/e* 284.0602.

3-N,N-Dimethylamino-1-(4-nitrophenyl)-propene-1-thione **1c**. Reaction time 1 h. Column chromatography: Al_2O_3, 75% CH_2Cl_2/petroleum as eluent. Yield 80%, m.p. 142°. ^{1}H NMR ($CDCl_3$): δ 3.10 (3H, s), 3.30 (3H, s, broad), 6.58 (1H, d, J 11 Hz, broad), 7.60–8.20 (4.4H, m), 8.35 (0.6H, d, J 11 Hz). ^{13}C NMR ($CDCl_3$): δ 38.67 (CH_3), 46.45 (CH_3), 111.82 (C(C2)), 123.11 (C(3')), 127.78 (C(2')), 147.92 (C(4')), 153.55 (C(1')), 158.10 (C(3)), 210.79 (C(1)). Mass spectrum calc. for $C_{11}H_{12}N_2O_2S$ *m/e* 236.0620, found: *m/e* 236.0627.

Reaction of **1** *with 2-chloroacrylonitrile.* To 2.5 mmol of **1** dissolved in 20 ml benzene were added with stirring at room temp. 2.5 mmol 2-chloroacrylonitrile in 5 ml benzene. When **1** was consumed (1–1.5 h) the solvent was evaporated and ^{1}H NMR spectra were obtained directly on the crude mixture.

3-*Chloro*-3-*cyano*-3,4-*dihydro*-6-(4-*nitrophenyl*-4-(1-*pyrrolidinyl*)-2H-thiopyran, **2a**. Yield quantitative, purity >95%, MS: *m/e* 314 (M^+–Cl), 313 (M^+–HCl). ^{1}H NMR ($CDCl_3$): δ 1.60–1.90 (4H, M), 2.80–3.30 (4H, m), 3.35* (1H, d, J 13 Hz), 3.70* (1H, d, J 13 Hz), 3.90 (1H, d, J 5.4 Hz), 6.05 (1H, d, J 5.4 Hz), 7.55 (2H, d, J 9 Hz), 8.13 (2H, d, J 9 Hz). [*AB spectrum.]

4-*Anilino*-3-*chloro*-3-*cyano*-3,4-*dihydro*-6-(4-*nitrophenyl*)-2H-*thiopyran* **2b**. Yield quantitative, purity >95%. MS: *m/e* 366 (M^+–Cl), 335 (M^+–HCl). ^{1}H NMR ($CDCl_3$): δ 3.65 (2H, s), 3.95 (1H, broad, NH), 4.60 (1H, d, J 4 Hz), 5.96 (1H, d, J 4 Hz), 6.70–7.35 (5H, m), 7.55 (2H, d, J 9 Hz), 8.10 (2H, d, J 9 Hz).

Reactions of **1** *with dimethyl acetylenedicarboxylate (DMAD).* To 2.5 mmol of **1** dissolved in 20 ml benzene were added with stirring at room temp. 3.7 mmol DMAD in 5 ml benzene. After **1** had been consumed (0.25–0.5 h) the solvent was evaporated and ^{1}H NMR spectra were obtained directly from the crude mixture.

2,3-*Dimethoxycarbonyl*-6-(4-*nitrophenyl*-4-(1-*pyrrolidinyl*)-4H-*thiopyran* **3a**. Quantitative yield. MS: *m/e* (ass, % rel. int.) 404 (M^+, 5), 345 (M^+–$COOCH_3$, 100), 334 (M^+–N□, 50), 276 (M^+–128.50). ^{1}H NMR ($CDCl_3$): δ 1.60–1.90 (4H, m), 2.55–2.90 (4H, m), 3.80 (6H, s), 4.95 (1H, d, J 6 Hz), 6.32 (1H, d, J 6 Hz), 7.65 (2H, d, J 9 Hz), 8.22 (2H, d, J 9 Hz).

4-*Anilino*-2,3-*bis*(*dimethoxycarbonyl*)-6-(4-*nitrophenyl*)-4H-*thiopyran* **3b**. Yield quantitative. MS: *m/e* (ass, % rel. int.) 426 (M^+, 5), 424 (M^+–2H, 50), 367 (M^+–$COOCH_3$, 90), 334 (M^+–NHC_6H_5, 10), 276 (M^+–150, 100). ^{1}H NMR ($CDCl_3$): δ 3.82 (6H, s), 5.50 (1H, dd, J 5.5 Hz, J 10 Hz), 6.40 (1H, d, J 5.5 Hz), 6.70–7.30 (5H, m), 7.60 (2H, d, J 9 Hz), 8.18 (2H, d, J 9 Hz).

3-*Ethyoxycarbonyl*-6-(4-*nitrophenyl*)-4-(1-*pyrrolidinyl*)-4H-*thiopyran* **4a**. To a stirred solution of 1.0 mmol **1a** in 15 ml benzene was added at room temp. 1.1 mmol ethyl propiolate in 5 ml benzene. When **1a** was consumed (15 min) the solvent was evaporated and a ^{1}H NMR spectrum was run immediately. Yield quantitative, purity >95%. MS: *m/e* (ass, % rel. int.) 360 (M^+, 2), 315 (M^+–OC_2H_5, 10, 290 (M^+–N□, 60), 287 (M^+–$COOC_2H_5$, 100). ^{1}H NMR ($CDCl_3$): δ 1.30 (3H, t, J 7.2 Hz), 1.50–1.80 (4H, m), 2.45–2.80 (4H, m), 4.25 (2H, q, J 7.2 Hz), 4.95 (1H, d, J 6.2 Hz), 6.35 (1H, d, J 6.2 Hz), 7.57 (2H, d, J 9 Hz), 7.83 (1H, s), 8.15 (2H, d, J 9 Hz). Compound **4a** is unstable. After 8 days at −20° a ^{1}H NMR spectrum shows the **5a** to **4a** ratio of 3:2. Impurities are estimated to be less than 5%.

3-*Ethoxycarbonyl*-6-(4-*nitrophenyl*)-2-(1-*pyrrolidinyl*)-2H-*thiopyran* **5a**. To 1.0 mmol of **1a** dissolved in 15 ml benzene were added at reflux temp. (80°) 1.1 mmol ethyl propiolate. When **1a** was consumed (5 min) two products were obtained, one of which was transformed into **5a** on continued heating. Yield quantitative, purity >95%. MS: *m/e* (ass, % rel. int.) 360 (M^+, 5), 290 (M^+–N□, 15), 287 (M^+–$COOC_2H_5$, 100). ^{1}H NMR ($CDCl_3$): δ 5.78 (1H, s), 6.76 (1H, d, J 7.5 Hz), 7.50 (1H, d, J 7.5 Hz), 7.77 (2H, d, J 9 Hz), 8.18 (2H, d, J 9 Hz). The remaining resonances as for **4a**.

Reaction of **1b** *with ethyl propiolate.* To 1.0 mmol of **1b** suspended in 15 ml benzene were added 1.1 mmol ethyl propiolate at room temp. with stirring. After 2 h two products could be detected, but the major part of **1b** was not consumed. However, by raising the temperature to 80° the reaction was finished within 1 h. The solvent was evaporated and a ^{1}H NMR spectrum was obtained immediately, showing a 3:7 ratio of **4b** to **5b** (overall yield quantitative). By further heating (80°) of the crude mixture only decomposition took place.

4-*Anilino*-3-*ethoxycarbonyl*-6-(4-*nitrophenyl*)-4H-*thiopyran* **4b**. Not pure but obtained as a mixture with **5b**. ^{1}H NMR ($CDCl_3$): δ 4.80 (1H, d, J 6 Hz), 6.30 (1H, d, J 6 Hz), 9.80 (0.5H, broad), 10.15 (0.5H, broad). The remaining resonances are not clearly resolved (6.6–8.4).

2-*Anilino*-3-*ethoxycarbonyl*-6-(4-*nitrophenyl*)-2H-*thiopyran* **5b**. To a $CHCl_3$ solution of the crude reaction mixture was added petroleum ether, whereby **5b** precipitated. M.p. 140–145° (decomp.). MS: *m/e* (ass, % rel. int.) 382 (M^+–COOEt, 20), 290 (M^+–NHC_6H_5, 100). ^{1}H NMR ($CDCl_3$): δ 1.35 (3H, t, J 7 Hz), 3.90 (1H, d, J 11 Hz, broad), 4.32 (2H, q, J 7 Hz), 6.11 (1H, d, J 11 Hz), 7.10 (1H, d, J 6 Hz), 6.70–7.40* (6H, m), 7.56 (1H, d, J 6 Hz), 7.70 (2H, d, J 9 Hz), 8.17 (2H, d, J 9 Hz). [*Integral includes δ 7.10.] Microanalyses: C, H, N, S.

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