Cycloaddition of Bis[3,3-bis(diethylamino)thioacryloyl] Disulfide with Alkynic Dienophiles: A New Access to 2*H*-Thiopyran-2-thiones

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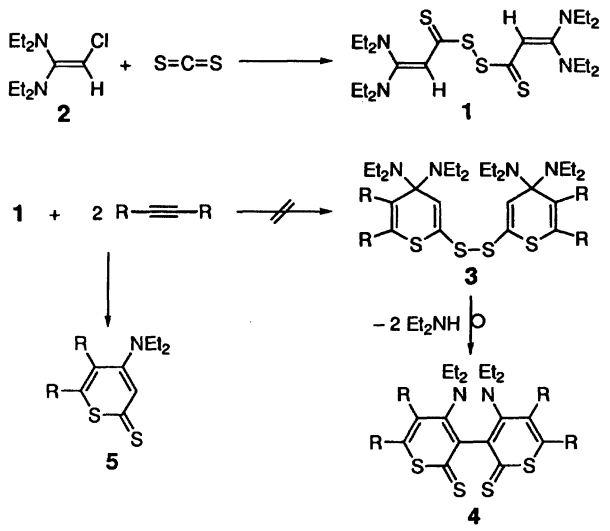
The reaction of bis[3,3-bis(diethylamino)thioacryloyl] disulfide (**1**) with dimethyl acetylenedicarboxylate gave dimethyl 4-diethylamino-2-thioxo-2*H*-thiopyran-5,6-dicarboxylate in 69% yield. Similarly, a series of alkynic dienophiles reacted with **1** to give the corresponding 2*H*-thiopyran-2-thione derivatives in modest-to-reasonable yields. A full experimental description of this 2*H*-thiopyran-2-thione formation is given and a mechanism involving [4+2]cycloaddition followed by homolytic cleavage of the S–S bond is presented.

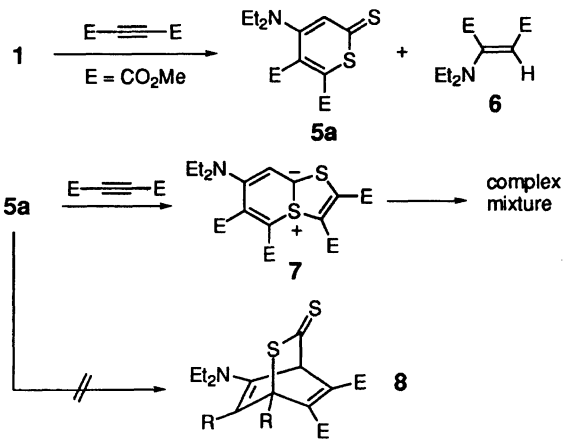
Recently, we reported on an unexpected formation of bis[3,3-bis(diethylamino)thioacryloyl] disulfide (**1**) by the reaction of 1,1-bis(diethylamino)-2-chloroethylene (**2**) with carbon disulfide.[1] It has been known that enamino thioketones[2,3] and enamino dithioesters[2,4] act as a 4π-component toward a variety of dienophiles to give thiopyran derivatives, thereby the thiocarbonyl group participates in a part of the diene system. With this in mind, **1** has been expected to give 4*H*-thiopyranyl disulfides **3** as the initial product upon cycloaddition with two molecules of alkynic dienophiles. Our further expectation was that **3** might undergo a thio-Cope rearrangement[5] to give a hitherto unknown class of compounds, [3,3′-bi-2*H*-thiopyran]-2,2′-dithione **4**, as the final product along with the elimination of two molecules of diethylamine. Although the reaction did not give the expected **4**, it did give 2*H*-thiopyran-2-thiones **5** (Scheme 1). To our knowledge, no report has appeared concerning the synthesis of 2*H*-thiopyran-2-thiones by the cycloaddition of enamino thioketones or dithioesters with dienophiles. We have therefore pursued the synthetic utility of this reaction as a new access to 2*H*-thiopyran-2-thiones, and give here the full experimental details concerning this reaction.



Scheme 1.

Results and Discussion

First, we have investigated the reaction of **1** with dimethyl acetylenedicarboxylate (DMAD). Thus, a solution of DMAD (4 molar amounts) in CH_2Cl_2 was added dropwise to a solution of **1** in CH_2Cl_2 at 0 °C over a period of 15 min. The original light-yellow solution turned dark red immediately upon the addition of DMAD. A workup of the mixture, after being stirred at 0 °C for 2 h and at room temperature for 1 h, gave dimethyl 4-diethylamino-2-thioxo-2*H*-thiopyran-5,6-dicarboxylate (**5a**) in 39% yield along with dimethyl diethylaminomaleate (**6**) in 29% yield (Run 1) (Scheme 2). In spite of much effort, no other products could be isolated in a pure, identifiable form. The structure of **5a** was determined spectroscopically, and that of **6** by an independent

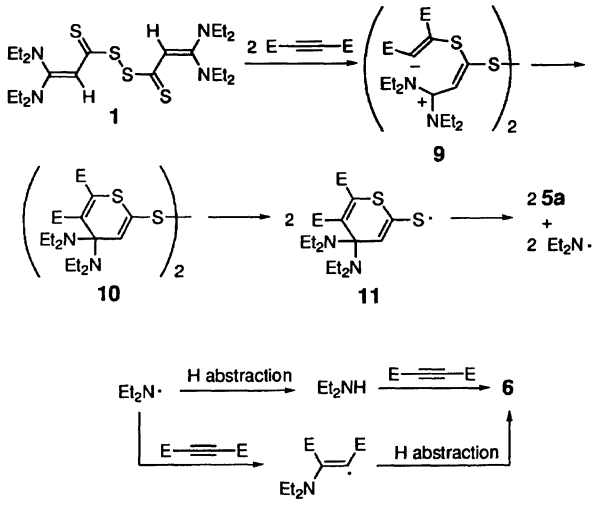


Scheme 2.

synthesis;[6] the reaction of diethylamine with DMAD gave a mixture of **6** and dimethyl diethylaminofumarate in the ratio 85 : 15. The reaction was carried out under a variety of conditions in order to improve the yield of **5a** and to elucidate the mechanism of its formation. The results are summarized in Table 1. The use of ether and tetrahydrofuran (THF) as the solvent resulted in a slight increase in the yields of **5a** and **6** (Runs 2 and 3). A rapid addition of DMAD at 0 °C also increased the yield of **5a** to 57% (Run 4). In this case, even the use of 2 molar amounts of DMAD also gave **5a** in 57% yield along with the recovery of the starting disulfide **1** in 8% yield, though **6** was formed with a decreased yield (12%) (Run 5).

As described above, the yield of **5a** could not exceed 57%. This can probably be ascribed to the subsequent reaction of **5a** with DMAD. Actually, separate experiments monitored by ^{1}H NMR revealed that the reaction of **5a** with DMAD took place even below 0 °C to give a very complex mixture from which no pure products could be isolated, though no reaction occurred below −20 °C. On the other hand, the reaction of **1** with DMAD was found to proceed even at −20 °C. Thus, when the reaction was carried out at about −25 °C in order to suppress the reaction of **5a** with DMAD, the yield of **5a** was improved to 69% (Run 6). To our knowledge, no cycloaddition of 2*H*-thiopyran-2-thiones with alkynes has been reported. As for the reaction of **5a** with DMAD, a 1,3-dipolar cycloaddition leading to a ylide intermediate **7** seems to be operative. The decomposition of the ylide **7**, which does not possess any pathway leading to thermally stable products, would bring about the formation of a very complex mixture. If the [2+4]cycloaddition leading to **8** takes place, a more simple mixture may be formed, even if **8** is not isolable.

A probable mechanism for the formation of **5a** is shown below (Scheme 3). The first step should involve a [2+4]-cycloaddition of **1** with 2 molecules of DMAD, yielding a 4*H*-thiopyran-2-yl disulfide **10**, which proceeds via a stepwise mechanism involving a zwitterion intermediate **9**. The S–S bond of this type of disulfides is known to undergo thermal dissociation into sulfanyl radicals.[7] Thus, **10** would undergo thermal dissociation to give the radical **11**, but not the thio-Cope rearrangement leading to **4** (R = CO_2Me); this is due to the sterically unfavorable transition state leading



Scheme 3.

to a rearranged product. Then, the radical **11** extrudes the diethylamino radical to give **5a** as the final product. The thus-formed diethylamino radical would abstract a hydrogen atom from the solvent to give diethylamine, which then adds to DMAD to give the adduct **6**; alternatively, **11** may add to DMAD to give the vinyl radical, which abstracts a hydrogen atom from the solvent to give **6**. The fact that the reaction in ether and THF (better hydrogen-atom donors) gave **6** in better yields than that in CH_2Cl_2 may support this hypothesis. In addition, the fact that the reaction in the presence of 2,6-di-*t*-butyl-4-methylphenol as the hydrogen atom donor in CH_2Cl_2 gave **6** in increased yield (64%) (Run 7) may favor the former mechanism.

We next have investigated the reaction of **1** with a variety of alkynic dienophiles in order to understand the scope and limitation of this 2*H*-thiopyran-2-thione formation. The results are summarized in Table 2. The reaction conditions for the reaction to take place depended on the electronic factors of the dienophiles. The reaction of **1** with dibenzoylacetylene, carrying two electron-withdrawing groups in THF, took place even at about −20 °C to give the 2*H*-thiopyran-2-thione **5b** (Run 1) (Scheme 4). The reactions of **1** with methyl propiolate and 3-butyn-2-one, activated by one electron-withdrawing group, proceeded at room temperature

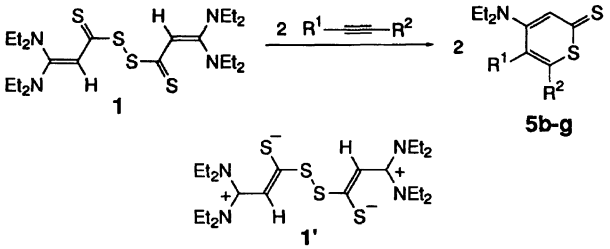
Table 1. Reaction of **1** with DMAD under Various Conditions

Run	DMAD (mol amounts)	Method[a]	Solvent	Temperature[b]	Yield (%)	
					5a	**6**
1	4.0	A	CH_2Cl_2	0 °C, 2 h, r. t., 1 h	39	29
2	4.0	A	Et_2O	0 °C, 2 h, r. t., overnight	49	46
3	4.0	A	THF	0 °C, 2 h, r. t., 1 h	48	40
4	4.0	B	THF	0 °C, 2 h, r. t., 1 h	57	41
5	2.0	B	THF	0 °C, 2 h, r. t., 1 h	57[c]	12
6	2.2	B	THF	−25 °C, 3 h, r. t., 1 h	69	24
7	4.0	A[d]	CH_2Cl_2	0 °C, 2 h, r. t., 1 h	40	64

a) For A, dropwise addition of a solution of DMAD to a solution of **1**, while for B, addition of neat DMAD at one stroke with a syringe to a solution of **1**. b) In most cases, consumption of **1** is nearly complete without warming to room temperature (^{1}H NMR analyses). c) With recovery of **1** in 8% yield. d) In the presence of 2,6-di-*t*-butyl-4-methylphenol (4 mol amounts).

Table 2. Reactions of **1** with Various Alkynic Dienophiles

Run	R^1	R^2	Conditions	Thiopyrans	Yield/%
1	COPh	COPh	THF, −25 °C, 5 h, r. t., 1 h	**5b**	39
2	CO_2CH_3	H	THF, r. t., overnight	**5c**	47
3	$COCH_3$	H	THF, r. t., overnight	**5d**	60
4	$CO_2CH_2CH_3$	Ph	Dioxane, refl., 15 h	**5e**	53
5	$COCH_3$	Ph	Dioxane, refl., 8 h	**5f**	58
6	$CO_2CH_2CH_3$	CH_3	Bu_2O, refl., 2 h	**5g**	32



Scheme 4.

to give the corresponding 2*H*-thiopyranthiones **5c** and **5d**, respectively (Runs 2 and 3). Although, in these cases, the formation of two positional isomers was possible, the sole isomers (**5c** and **5d**) were formed. This selectivity is easily explained by the fact that **1** is a highly polarized species and that the canonical structure **1′** predominantly contributes to the ground state of **1**, as previously reported.[1] The reactions of **1** with ethyl phenylpropiolate, 4-phenyl-3-butyn-2-one, and ethyl 2-butynoate required higher temperatures to give the corresponding adducts **5e**—**g**, respectively, probably because of electronic and steric reasons. Phenylacetylene and diphenylacetylene did not react with **1** in refluxing dioxane, **1** being recovered in good yields. An angle-strained cycloalkyne, cyclooctyne, also failed to react with **1**, while benzyne, generated by thermolysis of 2-carboxybenzenediazonium chloride, gave a complex mixture from which no pure products could be isolated.

Alkenic dienophiles, such as tetramethyl ethylenetetracarboxylate and dimethyl maleate, failed to react with **1**, while the reaction with tetracyanoethylene gave a complex mixture.

Experimental

^1H and ^{13}C NMR spectra were determined on a JEOL EX-270 spectrometer (270 MHz for ^1H NMR and 76.8 MHz for ^{13}C NMR) with TMS as an internal standard. The mass spectra were obtained on a Shimadzu QP-1000 spectrometer operating at 70 eV; IR spectra were obtained on a Hitachi 270-30 spectrophotometer. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER for carbon, hydrogen, and nitrogen.

Reaction of Bis[3,3-bis(diethylamino)thioacryloyl] Disulfide (1) with Dimethyl Acetylenedicarboxylate (DMAD). Two representative procedures are given below.

(a) In CH_2Cl_2. To a stirred solution of 246 mg (0.5 mmol) of **1** in 20 ml of CH_2Cl_2 was added dropwise a solution of 245 μl (2 mmol) of DMAD in 10 ml of CH_2Cl_2 at 0 °C over a period of 15 min. The original light-yellow solution turned dark red immediately. After stirring at 0 °C for 2 h and then at room temperature for 1 h, the mixture was evaporated under reduced pressure to give a dark-brown oil. Chromatographic separation of the oil on a column of silica gel with ether as the eluent gave 121 mg (39%) of dimethyl 4-diethylamino-2-thioxo-2*H*-thiopyran-5,6-dicarboxylate (**5a**) and 62 mg (29%) of dimethyl diethylaminomaleate (**6**).

5a: Dark-red plates (from ether); mp 94—95 °C; ^1H NMR (270 MHz, $CDCl_3$) δ = 1.22 (6H, t, J = 7.0 Hz, $\underline{CH_3}CH_2$), 3.36 (4H, q, J = 7.0 Hz, $CH_3\underline{CH_2}$), 3.87 (3H, s, CH_3OCO), 3.90 (3H, s, CH_3OCO), 7.17 (1H, s, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.2 (q), 46.1 (t), 53.5 (q), 53.8 (q), 123.4 (d), 127.8 (s), 146.1 (s), 151.9 (s), 161.6 (s), 165.7 (s), 194.0 (s); IR (KBr) 1738 (C=O), 1564, 1466, 1448, 1260, 972 cm^{-1}; MS (EI, 70 eV) *m/z* 315 (M^+). Found: C, 49.49; H, 5.41; N, 4.18; S, 20.38%. Calcd for $C_{13}H_{17}NO_4S_2$: C, 49.50; H, 5.43; N, 4.44; S, 20.33%.

6: Colorless oil, bp 110—120 °C/1 mmHg (bulb-to-bulb distillation), (1 mmHg = 133.322 Pa); ^1H NMR (270 MHz, $CDCl_3$) δ = 1.18 (6H, t, J = 7.3 Hz, $\underline{CH_3}CH_2$), 3.18 (4H, q, J = 7.3 Hz, $CH_3\underline{CH_2}$), 3.63 (3H, s, CH_3OCO), 3.93 (3H, s, CH_3OCO), 4.61 (1H, s, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.6 (q), 44.8 (t), 50.5 (q), 52.7 (q), 82.7 (d), 153.7 (s), 166.0 (s), 168.3 (s). These NMR data agreed in all respects with those of an authentic sample prepared by an independent synthesis.

(b) In THF at −25 °C. To a solution of 246 mg (0.5 mmol) of **1** in 20 ml of THF cooled at −30 °C was added DMAD (123 μl, 1 mmol) at one stroke with a syringe. The mixture was stirred at about −25 °C for 3 h and at room temperature for 1 h. A workup in the same manner as described above gave 216 mg (69%) of **5a** and 52 mg (24%) of **6**.

Independent Synthesis of Dimethyl Diethylaminomaleate (6). DMAD (1.42 g, 10 mmol) was added to a solution of 1.46 g (20 mmol) of diethylamine in 20 ml of ether at room temperature. After stirring for 3 h, the mixture was evaporated under reduced pressure to give a red oil, which was distilled to give a mixture of **6** and dimethyl diethylaminofumarate in the ratio 85 : 15 as a colorless oil, bp 105—115 °C/1 mmHg (bulb-to-bulb distillation). Spectroscopic properties of **6** thus prepared agreed with those obtained by reaction of **1** with DMAD. Dimethyl diethylaminofumarate; ^1H NMR (270 MHz, $CDCl_3$) δ = 1.13 (6H, t, J = 7.0 Hz, $\underline{CH_3}CH_2$), 3.34 (4H, q, J = 7.0 Hz, $CH_3\underline{CH_2}$), 3.65 (3H, s, CH_3OCO), 3.81 (3H, s, CH_3OCO), 5.05 (1H, s, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 13.2 (q), 46.5 (t), 50.8 (q), 52.8 (q), 93.1 (d), 150.0 (s), 165.9 (s), 168.2 (s).

4-Diethylamino-5,6-dibenzoyl-2*H*-thiopyran-2-thione (5b). A solution of dibenzoylacetylene[8] (234 mg, 1 mmol) in 3 ml of THF was added to a solution of 246 mg (0.5 mmol) of **1** in 20 ml of THF at −20 °C. The mixture was stirred at that temperature for 5 h and then at room temperature for 1 h. The same workup as that of **5a** gave 160 mg (39%) of **5b**: dark red plates (from CH_2Cl_2/hexane); mp 175.3—176.0 °C; ^1H NMR (270 MHz, $CDCl_3$) δ = 1.01 (6H, t, $\underline{CH_3}CH_2$), 3.25 (4H, q, $CH_3\underline{CH_2}$), 7.27 (1H, s, vinyl H), 7.39 (4H, d/d, J = 7.3/6.8 Hz, phenyl), 7.58 (2H, t, J = 6.8 Hz, phenyl), 7.69 (2H, d, J = 7.3 Hz, phenyl), 7.76 (2H, d, J = 7.3 Hz, phenyl); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.0 (q), 46.3 (t), 121.5 (d), 128.7

(d), 129.3 (d), 129.9 (d), 134.3 (d), 134.5 (s), 134.8 (d), 153.8 (s), 153.3 (s), 158.0 (s), 189.5 (s), 192.6 (s), 192.9 (s); IR (KBr) 1658 (C=O), 1552, 1470, 1452, 1246, 962 cm^{-1}. Found: C, 67.76; H, 5.33; N, 3.37%. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44%.

Methyl 4-Diethylamino-2-thioxo-2*H*-thiopyran-5-carboxylate (5c). Methyl propiolate (178 µl, 2 mmol) was added with a syringe to a mixture of 246 mg (0.5 mmol) of **1** in 20 ml of THF at 0 °C. The mixture was stirred at 0 °C for 2 h, at room temperature for 8 h, and then allowed to stand overnight. A workup in the same manner as described above gave 122 mg (47%) of **5c** as a brown viscous oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.26 (6H, t, J = 7.0 Hz, $\underline{CH_3}CH_2$), 3.37 (4H, q, J = 7.0 Hz, $CH_3\underline{CH_2}$), 3.88 (3H, s, CH_3OCO), 7.21 (1H, s, vinyl H), 8.11 (1H, s, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.0 (q), 45.8 (t), 52.8 (q), 120.7 (d), 122.6 (s), 148.2 (d), 151.5 (s), 165.0 (s), 191.2 (s); IR (neat) 1726 (C=O), 1558, 1438, 1242, 1064, 1012, 976 cm^{-1}; MS (EI, 70 eV) *m/z* 257 (M^+). Found: C, 51.25; H, 5.97; N, 5.05%. Calcd for $C_{11}H_{15}NO_2S_2$: C, 51.34; H, 5.87; N, 5.44%.

5-Acetyl-4-diethylamino-2*H*-thiopyran-2-thione (5d). 3-Butyn-2-one (157 µl, 2 mmol) was added with a syringe to a solution of 246 mg (0.5 mmol) of **1** in 20 ml of THF at 0 °C. The mixture was stirred at 0 °C for 2 h, at room temperature for 8 h, and then allowed to stand overnight. A workup in the same manner as described above gave 144 mg (60%) of **5d**: Yellow plates (from ether); mp 101.5—102.2 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.24 (6H, t, J = 7.0 Hz, $\underline{CH_3}CH_2$), 2.51 (3H, s, CH_3CO), 3.35 (4H, q, J = 7.0 Hz, $CH_3\underline{CH_2}$), 7.18 (1H, s, vinyl H), 7.99 (1H, s, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 11.1 (q), 27.0 (q), 45.5 (t), 120.4 (d), 131.4 (s), 145.1 (d), 151.1 (s), 191.5 (s), 194.9 (s); IR (KBr) 1688 (C=O), 1558, 1456, 1246, 968 cm^{-1}; MS (EI, 70 eV) *m/z* 241 (M^+). Found: C, 54.81; H, 6.25; N, 5.64%. Calcd for $C_{11}H_{15}NOS_2$: C, 54.74; H, 6.26; N, 5.80%.

Ethyl 4-Diethylamino-6-phenyl-2-thioxo-2*H*-thiopyran-5-carboxylate (5e). A mixture of ethyl phenylpropiolate (330 µl, 2 mmol) and 246 mg (0.5 mmol) of **1** in 30 ml of 1,4-dioxane was refluxed under nitrogen for 15 h. A workup as described above gave 185 mg (53%) of **5e**: Orange plates (from ether); mp 142.3—143.1 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.83 (3H, t, J = 7.3 Hz, $\underline{CH_3}CH_2OCO$), 1.24 (6H, t, J = 7.0 Hz, $\underline{CH_3}CH_2$), 3.42 (4H, q, J = 7.0 Hz, $CH_3\underline{CH_2}$), 3.85 (2H, q, J = 7.3 Hz, $CH_3\underline{CH_2}OCO$), 7.24 (1H, s, vinyl H), 7.28 (2H, d/d, J = 7.9/2.6 Hz, phenyl), 7.40 (3H, m, phenyl); ^{13}C NMR (67.8 MHz, $CDCl_3$) J = 12.2 (q), 13.2 (q), 46.0 (t), 61.9 (t), 120.8 (d), 123.9 (s), 128.1 (d), 128.4 (d), 129.8 (s), 134.6 (s), 152.8 (s), 159.2 (s), 165.9 (s), 193.2 (s); IR (KBr) 1718 (C=O), 1558, 1468, 1270, 1254, 1012, 968 cm^{-1}; MS (EI, 70 eV) *m/z* 347 (M^+). Found: C, 62.04; H, 6.19; N, 3.90%. Calcd for $C_{18}H_{21}NO_2S_2$: C, 62.22; H, 6.09; N, 4.03%.

5-Acetyl-4-diethylamino-6-phenyl-2*H*-thiopyran-2-thione (5f). A mixture of 4-phenyl-3-butyn-2-one (291 µl, 2 mmol) and 246 mg (0.5 mmol) of **1** in 30 ml of 1,4-dioxane was refluxed under nitrogen for 8 h. A workup as described above gave 183 mg (58%) of **5f**: Orange plates (ether); mp 134.5—135.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.21 (t, 6H, J = 7.0 Hz, $\underline{CH_3}CH_2$), 2.05 (s, 3H, CH_3CO), 3.35 (q, 4H, J = 7.0 Hz, $CH_3\underline{CH_2}$), 7.24 (s, 1H, vinyl H), 7.3—7.5 (m, 5H, phenyl); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.2 (q), 31.7 (q), 46.7 (t), 122.9 (d), 128.6 (d), 129.4 (d), 130.3 (s), 133.3 (s), 133.5 (s), 154.0 (s), 156.3 (s), 196.6 (s), 199.8 (s); IR (KBr) 1694 (C=O), 1560, 1466, 1456, 1260, 972 cm^{-1}; MS (EI, 70 eV) *m/z* 317 (M^+). Found: C, 64.52; H, 5.96; N, 4.53%. Calcd for $C_{17}H_{19}NOS_2$: C, 64.32; H, 6.03; N, 4.41%.

Ethyl 4-Diethylamino-6-methyl-2-thioxo-2*H*-thiopyran-5-carboxylate (5g). Ethyl 2-butynoate (232 µl, 2 mmol) was added with a syringe to a boiling solution of 246 mg (0.5 mmol) of **1** in 30 ml of dibutyl ether. The mixture was refluxed for 2 h. A workup as described above gave 92 mg (32%) of **5g**: Dark brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.23 (t, 6H, J = 7.3 Hz, $\underline{CH_3}CH_2$), 1.41 (t, 3H, J = 7.3 Hz, $\underline{CH_3}CH_2OCO$), 2.31 (s, 3H, CH_3), 3.40 (q, 4H, J = 7.3 Hz, $CH_3\underline{CH_2}$), 4.35 (q, 2H, J = 7.3 Hz, $CH_3\underline{CH_2}OCO$), 7.15 (s, 1H, vinyl H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 12.3 (q), 13.9 (q), 20.7 (q), 45.7 (t), 62.0 (t), 120.3 (d), 122.8 (s), 153.4 (s), 156.6 (s), 166.1 (s), 192.1 (s); IR (KBr) 1726 (C=O), 1566, 1472, 1428, 1250, 962 cm^{-1}. Found: C, 54.77; H, 6.78; N, 4.89%. Calcd for $C_{13}H_{19}NO_2S_2$: C, 54.71; H, 6.71; N, 4.91%.

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