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Dithiirane or Thiosulfine Intermediates in the Reaction of Acetyl Diaroylchloromethyl Disulfides with Secondary Amines?[#] [1, 2]

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Summary. Since 1979, *Senning*'s acetyl dibenzoylchloromethyl disulfide has been known as one of the first thiosulfine/dithiirane precursors. Its reactions with an excess of morpholine fulfill three advantageous conditions at once: thiosulfine or dithiirane species are intercepted by intermolecular additions, without heating, and without rearrangements. In the present work, reactions between a series of new acetyl diaroylchloromethyl disulfides ((4-*X*-C_6H_4-CO)$_2$-CCl-SSCOCH$_3$; *X* = F, Cl, Br, CH_3, and CH_3O) and an excess of morpholine are studied. As dominating products, 2-(4-morpholinyldithio)-1,3-diaryl-1,3-propanediones are obtained. The reactions are complete within several seconds. In order to obtain high yields of interception products, the mixtures have to be worked up within a few minutes. From the observation of high reaction rates at room temperature, a new reaction mechanism is deduced that involves the initial formation of dithiirane species (alone or before thiosulfine species).

Keywords. Acetyl diaroylchloromethyl disulfides; Dithiiranes; Morpholine; Reactive intermediates; Thiosulfines.

Dithiiran- oder Thiosulfin-Zwischenstufen bei der Reaktion von Acetyl-diaroylchlormethyl-disulfiden mit sekundären Aminen? [1, 2]

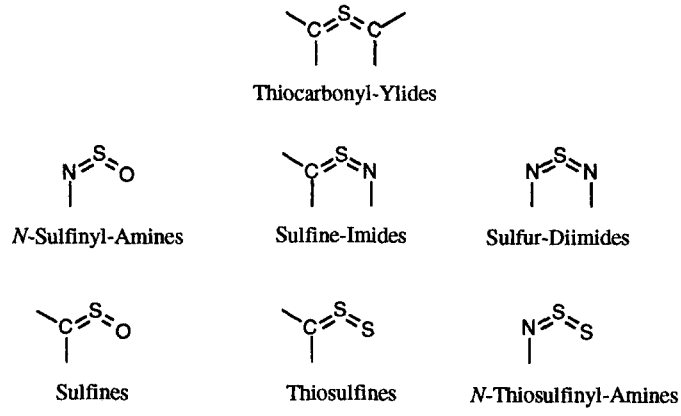
Zusammenfassung. Seit 1979 kennt man *Sennings* Acetyl-dibenzoylchlormethyl-disulfid als eine der ersten Vorläufersubstanzen zur Freisetzung von Thiosulfinen/Dithiiranen. Seine Reaktionen mit einem Überschuß von Morpholin erfüllen drei vorteilhafte Bedingungen auf einmal: Thiosulfin- oder Dithiiran-Spezies werden über intermolekulare Additionen abgefangen, man muß nicht erhitzen, und es finden keine Umlagerungen statt.

In der vorliegenden Arbeit werden Reaktionen zwischen einer Reihe von neuen Acetyl-diaroylchlormethyl-disulfiden ((4-*X*-C_6H_4-CO)$_2$-CCl-SSCOCH$_3$; *X* = F, Cl, Br, CH_3 und CH_3O) und einem Überschuß von Morpholin untersucht. Als dominierende Produkte werden 2-(4-Morpholinyldithio)-1,3-diaryl-1,3-propandione erhalten. Die Reaktionen sind bereits nach wenigen Sekunden abgeschlossen. Um hohe Ausbeuten zu erzielen, müssen die Reaktionsmischungen innerhalb weniger Minuten aufgearbeitet werden. Aus der Beobachtung hoher Reaktionsgeschwindigkeiten bei Raumtemperatur wird ein neuer Reaktionsmechanismus abgeleitet, bei dem zunächst Dithiiran-Spezies auftreten (allein oder vor Thiosulfin-Spezies).

[#] Dedicated to Prof. *Peter K. Claus* on the occasion of his 60[th] birthday

Introduction

Starting from SO_2, there are seven possible classes of reactive organic heterocumulenes, if one or both of its oxygen atoms are replaced by groups like CR_2, NR, or S (Scheme 1). For all but one of them, isolated representatives are known, remarkably even *N*-thiosulfinyl amines [3–5]. With one recent exception (tropanethiosulfine [6]), the exploration of thiosulfines (or thiocarbonyl *S*-sulfides) is still confined to prove their existence as reactive intermediates [7, 8], in particular by rearrangements [9, 10], additions [9, 10], elegant inter- and intramolecular 1,3-dipolar cycloadditions [11–13], and intramolecular [5 + 2] cycloadditions [14]. Transformations between them and dithiiranes have been discussed, too. Recently, the first isolation of sterically protected dithiiranes has been reported [15–17]. Several times thiosulfines and dithiiranes have been postulated to form 1,2,4,5-tetrathianes by dimerization [18, 19]. The state of the art of dithiirane/thiosulfine chemistry has been reviewed recently [20].

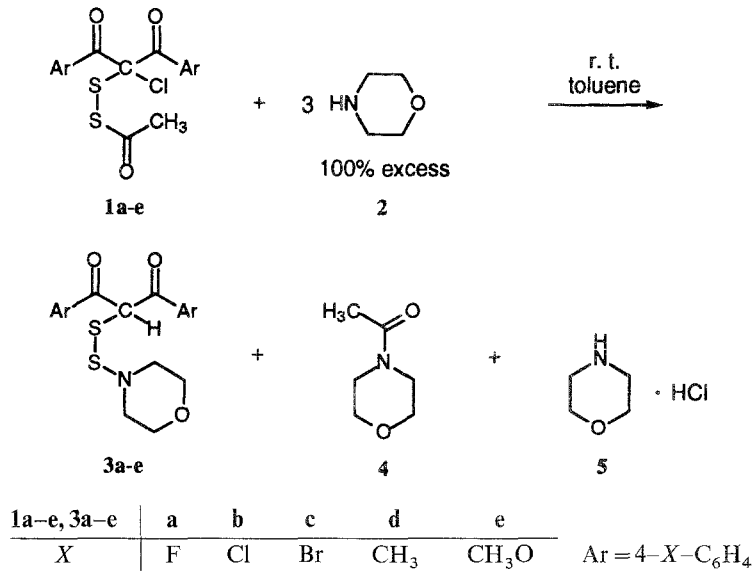


Scheme 1. Sulfur centered organic heterocumulenes

Since 1979, *Senning*'s acetyl-dibenzoylchloromethyl-disulfide is known as one of the first precursor compounds for the liberation of thiosulfines/dithiiranes [9, 10]. Its reaction with an excess of morpholine is unique in this field, as three advantageous conditions are fulfilled at once: thiosulfine or dithiirane species are captured by an *intermolecular* addition; the primary product of the reaction does not rearrange (unlike the primary products from the reactions between most of the other known $R_2CCl\text{-}SSCOCH_3$ and morpholine; for the type of rearrangement, see Scheme 4); and the reaction proceeds already at room temperature.

Results and Discussion

A series of five new acetyl-diaroylchloromethyl-disulfides (**1a–e** [2], *para*-substituted with different electron-withdrawing or electron-donating groups) was reacted with morpholine (molar ratio: 6:1). In all cases, 2-(4-morpholinyldithio)-1,3-diaryl-1,3-propanediones (**3a–e**) were formed as sole or dominating products (Scheme 2).



1a–e, 3a–e	a	b	c	d	e	
X	F	Cl	Br	CH_3	CH_3O	Ar = 4-*X*-C_6H_4

Scheme 2

From the precipitation of morpholinium hydrochloride (**5**) and the yellow colour one can assume that the reaction is finished within a few seconds after the morpholine has been added in one portion. The work-up of the reaction mixture was begun within 1–2 minutes after the start of the reaction. From earlier experiments it is known that decomposition starts within a few minutes; in the course one day, three different decomposition products dominate subsequently.

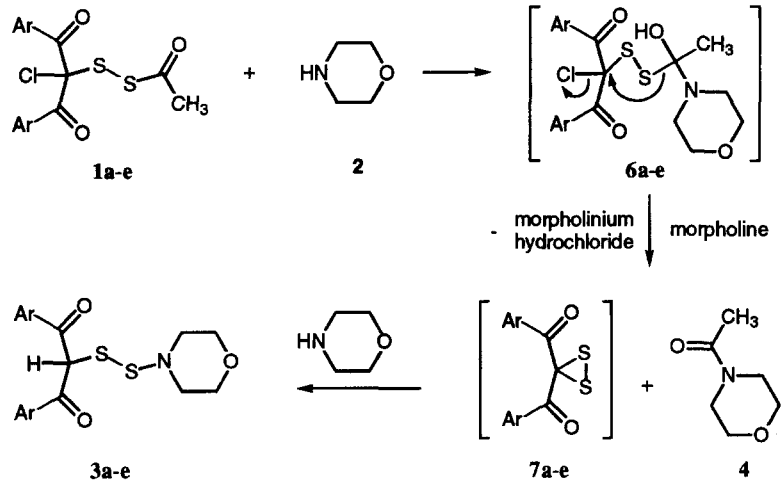
The structures of **3a–e** were confirmed by ^{1}H NMR spectroscopy (central CH at 5.92, 5.91, 5.90, 5.99, and 5.91 ppm), by ^{13}C NMR spectroscopy (central CH at 69.65, 69.27, 68.89, 68.98, and 69.85 ppm), by MS, infrared spectroscopy, and by microanalysis.

When the second part of the work-up, the crystallization, was delayed, a part of the product decomposed, too. After about one day a mixture was found that contained **3a–e** and practically only one type of decomposition product, respectively (in brackets: *X*, ^{1}H NMR, ^{13}C NMR, and percentage of the decomposition product): **3a** (F, 6.75 ppm, 92.47 ppm, 76%), **3b** (Cl, 6.77 ppm, 92.85 ppm, 64%), **3c** (Br, 6.75 ppm, 92.80 ppm, 24%), **3d** (CH_3, 6.80 ppm, 92.41 ppm, low content), **3e** (CH_3O, 6.75 ppm, 91.44 ppm, very low content). So, the stability of **3a–e** in the reaction mixtures is in the order **3a** (F) < **3b** (Cl) < **3c** (Br) < **3d** (CH_3) < **3e** (CH_3O). Fresh solutions of the crude reaction products (crude yields almost quantitative) contain only about 0–5% decomposition products (^{1}H NMR).

In order to test the influence of the secondary amine on the course of the reaction, thiomorpholine and 2,6-dimethylmorpholine were used instead of morpholine. Both amines gave fast reactions (the latter without a precipitate). As there seems to be a stronger tendency to form compounds of the above decomposition type, screening experiments were not continued.

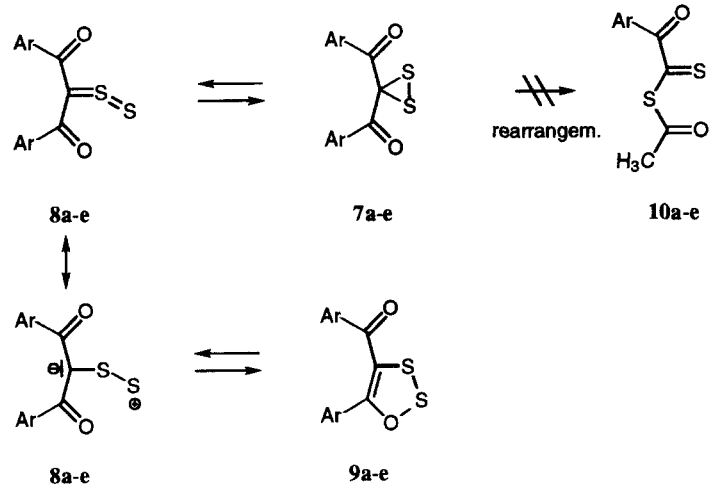
For the transformations **1a–e** to **3a–e**, the following mechanism is proposed (Scheme 3). After the addition of **2**, the reactive intermediates **6a–e** (or the corre-

sponding deprotonated forms) are assumed to liberate the dithiiranes **7a–e** by an internal substitution (S_i). Finally, a further molecule of morpholine adds to the highly reactive **7a–e** to give **3a–e** (Scheme 3).



Scheme 3

In a variation of this model, the dithiiranes **7a–e** form thiosulfines **8a–e** (may be influenced by the adjacent carbonyl groups *via* **9a–e** [21, 22]; similarly, the formation of **3a–e** from **9a–e** and morpholine is thinkable) and add **2** (Scheme 4).



Scheme 4

The proposed mechanism *via* dithiirane intermediates including an S_i reaction tries to account for the high observed reaction rates. Experiments to capture possible thiosulfine intermediates by thiofluorenone and to replace the acetyl group in **1a–e** by SiR_3-functions are in preparation.

Experimental

NMR spectra were recorded on Bruker NMR spectrometers: AC 250 F and AM 400 WB (internal standards: *TMS* for ^{1}H NMR, $CDCl_3 = 77.00$ ppm for ^{13}C NMR). $CDCl_3$ was routinely filtered over Al_2O_3. Mass spectra were recorded using electron ionization (EI) on a Varian Mat 311A spectrometer. IR spectra were routinely taken from slurries (paraffin oil) and were recorded on a Perkin Elmer 1600 FTIR spectrometer. Melting points were measured with a Leica melting point microscope (PT100 sensor). Microanalyses were performed at the Institute of Physical Chemistry (Univ. Wien, Mikroanalytisches Laboratorium, Mag. *J. Theiner* and Mr. *S. Frenczko*).

For TLC, silica gel 60 was purchased from Merck. $CHCl_3$ and CH_2Cl_2 were cleaned and dried by distillation from P_4O_{10}. Abbreviations: ar (aromatic), qu (quarternary).

General method for the transformation **1a–e** [2] *to* **3a–e**

This example for a small-scale preparation allows a very fast work-up. Compound **1** (0.15 mmol) is transferred into a 5 ml screw cap vial (diameter 1 cm) and dissolved in 0.5 ml toluene (1 ml for **1c**). Under magnetic stirring (at r.t. in a water bath), 0.90 mmol (79 µl) morpholine (**2**) is added within a few seconds. After 1–2 min, 0.5 ml more toluene are added and the reaction mixture is washed three times with 1.5 ml portions of distilled water (under vigorous shaking, removal of the water phase with a *Pasteur* pipette). After filtration of the organic phase into a second vial (*Pasteur* pipette with cellulose to remove water droplets, rinsing with 0.5 ml toluene), the solution is dried over Na_2SO_4 sicc. After a further filtration (rinsing with 0.5 ml toluene), the solvent and the excess of morpholine are removed under vacuum (r.t., first at 8 torr, later at 0.005 torr) from **3** (oils/crystals). The crude products are suspended in 1 ml dry ethanol and dissolved by the addition of the minimum amount of dry methylene chloride. Upon partial evaporation of the solvents, crystals form (**3e** is difficult to crystallize by this method). Recrystallizations are performed in the same way.

2-(4-Morpholinyldithio)-1,3-bis-(4-fluorophenyl)-1,3-propanedione (**3a**; $C_{19}H_{17}F_2NO_3S_2$)

Preparation from 60.1 mg (0.15 mmol) recrystallized **1a** and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 58.8 mg (95.8%); m.p.: 97–99.5 °C; IR (paraffin): $\nu = 3073.1$[a], 2959.9[a], 2921.0[a], 2855.1[a], 1682.0 ($\nu_{C=O}$), 1666.5, 1594.5 (ν_{arC-C}), 1507.3[a], 1449.3[a], 1409.5[a], 1303.2, 1284.8, 1254.2, 1236.3, 1188.1, 1157.7, 1109.9, 1055.9, 1008.0, 932.7 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.87$ (dd, 4H, H_2C–N), 3.65 (dd, 4H, H_2C–O), 5.92 (s, 1H, O=C–CH–C=O), 7.14 (m, 4H, ar *meta*), 8.06 (m, 4H, ar *ortho*) ppm; ^{13}C NMR (62.9 MHz): $\delta = 55.42$ (t, H_2C–N), 66.83 (t, H_2C–O), 69.65 (d, O=C–CH–C=O), 116.13 (*meta*-C, $^3J_{CF} = 22.0$ Hz), 131.27 (*ipso*-C), 132.17 (*ortho*-C, $^4J_{CF} = 9.7$ Hz), 166.20 (C–F, $^2J_{CF} = 257.4$ Hz), 190.04 (C=O) ppm; MS (100 °C): $m/z = 409$ (2, M^+), 345 (0.15, M–S_2), 260 (14), 259 (11, M–$C_4H_8NOS_2$), 165 (11, F–C_6H_4–CO–CH_2–CO^+), 150 (11), 149 (14), 123 (100, F–C_6H_4–CO^+), 95 (46, F–$C_6H_4^+$), 87 (27), 86 (28), 75 (15), 69 (22), 57 (44); $C_{19}H_{17}F_2NO_3S_2$ (409.47); calc.: C 55.73, H 4.18, N 3.42, S 15.66; found: C 55.78, H 4.23, N 3.38, S 15.55.

2-(4-Morpholinyldithio)-1,3-bis-(4-chlorophenyl)-1,3-propanedione (**3b**; $C_{19}H_{17}Cl_2NO_3S_2$)

Preparation from 65.1 mg (0.15 mmol) recrystallized **1b** and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 63.0 mg (94.9%); m.p.: 119.5–121.5 °C; IR (paraffin): $\nu = 1693.2$ ($\nu_{C=O}$), 1662.1, 1589.7 (ν_{arC-C}), 1284.1, 1257.5, 1112.1, 1092.3, 1012.3, 934.4 cm^{-1}; ^{1}H NMR (250 MHz): $\delta = 2.38$ (s, 6H, CH_3), 2.86 (dd, 4H, H_2C–N), 3.65 (dd, 4H, H_2C–O), 5.91 (s, 1H, O=C–CH–C=O), 7.42 (d, 4H, ar *meta*, $^3J_{AB} = 8.6$ Hz), 7.95 (d, 4H, ar *ortho*, $^3J_{AB} = 8.6$ Hz) ppm; ^{13}C NMR (62.9 MHz): $\delta = 55.42$ (t, H_2C–N), 66.82 (t, H_2C–O), 69.27 (d, O=C–CH–C=O), 129.26 (ar C–H), 130.69 (ar C–H), 133.15 (ar qu C), 140.77 (ar qu C), 190.33

[a] Thin crystal film on silicon

(C=O) ppm; MS (200 °C): m/z = 436 (5, M−5H), 351 (2), 292 (7), 291 (7), 224 (4), 181 (9, Cl−C_6H_4−CO−CH_2−CO^+), 141 (35), 139 (100, Cl−C_6H_4−CO^+), 130 (22), 113 (16), 111 (51, Cl−$C_6H_4^+$), 86 (37), 75 (31), 69 (30), 64 (27), 56 (20), 44 (18); $C_{19}H_{17}Cl_2NO_3S_2$ (442.38); calc.: C 51.59, H 3.87, N 3.17, S 14.49; found: C 51.11, H 3.65, N 3.08, S 15.33.

2-(4-Morpholinyldithio)-1,3-bis-(4-bromophenyl)-1,3-propanedione (**3c**; $C_{19}H_{17}Br_2NO_3S_2$)

Preparation from 78.4 mg (0.15 mmol) recrystallized **1c** and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 55.6 mg (92.5%); m.p.: 126.5–128.5 °C; IR (thin crystal film on silicon): ν = 2959.0, 2922.3, 2855.0, 1690.8 ($\nu_{C=O}$), 1664.4, 1583.8 (ν_{arC-C}), 1396.5, 1283.7, 1255.8, 1070.9, 998.9, 934.0 cm^{-1}; ^1H NMR (250 MHz): δ = 2.86 (dd, 4H, H_2C–N), 3.65 (dd, 4H, H_2C–O), 5.90 (s, 1H, O=C–CH–C=O), 7.59 (d, 4H, ar *meta*, $^3J_{AB}$ = 8.6 Hz), 7.87 (d, 4H, ar *ortho*, $^3J_{AB}$ = 8.6 Hz) ppm; ^{13}C NMR (100.6 MHz): δ = 55.35 (t, H_2C–N), 66.74 (t, H_2C–O), 68.89 (d, O=C–CH–C=O), 129.54 (ar qu C), 130.65 (ar C–H), 132.19 (ar qu C), 133.50 (ar C–H), 190.45 (C=O) ppm; MS (240 °C): m/z = 526 (2), 524 (1, M−5H), 472 (2), 441 (9), 381 (9), 313 (2), 270 (5), 268 (5), 185 (90), 183 (100, Br−C_6H_4−CO^+), 157 (33), 155 (37, Br−$C_6H_4^+$), 130 (32), 86 (42), 76 (31), 69 (24), 57 (14); $C_{19}H_{17}Br_2NO_3S_2$ (531.28); calc.: C 42.95, H 3.23, N 2.64, S 12.07; found: C 42.63, H 3.09, N 2.64, S 12.51.

2-(4-Morpholinyldithio)-1,3-di-(4-tolyl)-1,3-propanedione (**3d**; $C_{21}H_{23}NO_3S_2$)

Preparation from 58.9 mg (0.15 mmol) recrystallized **1d** and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 55.7 mg (92.5%); m.p.: 106.5–108.5 °C; IR (paraffin): ν = 1681.6 ($\nu_{C=O}$), 1660.6, 1605.2 ($\nu_{arC=C}$), 1285.4, 1255.9, 1183.2, 1110.2, 932.2 cm^{-1}; ^1H NMR (250 MHz): δ = 2.38 (s, 6H, CH_3), 2.86 (dd, 4H, H_2C–N), 3.63 (dd, 4H, H_2C–O), 5.99 (s, 1H, O=C–CH–C=O), 7.23 (d, 4H, ar *meta*, $^3J_{AB}$ = 8.3 Hz), 7.91 (d, 4H, ar *ortho*, $^3J_{AB}$ = 8.3 Hz) ppm; ^{13}C NMR (62.9 MHz): δ = 21.65 (q, CH_3), 55.29 (t, H_2C–N), 66.82 (t, H_2C–O), 68.98 (d, O=C–CH–C=O), 129.34 (ar C–H), 129.48 (ar C–H), 132.56 (*ipso*-C), 144.93 (*para*-C), 191.12 (C=O) ppm; MS (200 °C): m/z = 337 (1, M−S_2), 252 (75), 251 (76), 237 (11), 218 (24), 161 (34), 150 (22), 128 (13), 119 (100, H_3C–C_6H_4–CO^+), 91 (77, $C_7H_7^+$), 69 (58), 64 (31), 56 (17); $C_{21}H_{23}NO_3S_2$ (401.54); calc.: C 62.82, H 5.77, N 3.49, S 15.97; found: C 62.39, H 5.88, N 3.42, S 16.18.

2-(4-Morpholinyldithio)-1,3-bis-(4-methoxyphenyl)-1,3-propanedione (**3e**; $C_{21}H_{23}NO_5S_2$)

Preparation from 63.7 mg (0.15 mmol) recrystallized **1e** and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 62.7 mg (96.5%); oil; IR (neat): ν = 3075.1, 2961.6, 2840.7, 1681.7 ($\nu_{C=O}$), 1667.5, 1660.0, 1651.5, 1599.7 (ν_{arC-C}), 1573.9, 1513.9, 1505.4, 1455.1, 1422.1, 1166.5, 1113.1, 1029.7, 939.0 cm^{-1}; ^1H NMR (400 MHz): δ = 2.86 (dd, 4H, H_2C–N), 3.63 (dd, 4H, H_2C–O), 3.63 (s, 6H, OCH_3), 5.91 (s, 1H, O=C–CH–C=O), 6.89 (d, 4H, ar *meta*, $^3J_{AB}$ = 8.9 Hz), 8.01 (d, 4H, ar *ortho*, $^3J_{AB}$ = 8.9 Hz) ppm; ^{13}C NMR (100.6 MHz): δ = 55.33 (t, H_2C–N), 55.47 (q, OCH_3), 66.85 (t, H_2C–O), 69.85 (d, O=C–CH–C=O), 113.98 (*meta*-C), 128.02 (*ipso*-C), 131.77 (*ortho*-C), 164.08 (*para*-C), 190.20 (C=O) ppm; MS (200 °C): m/z = 347 (1), 284 (71), 177 (14), 160 (14), 135 (100, H_3CO–C_6H_4–CO^+) 108 (58), 92 (18), 77 (31), 64 (32), 57 (22), $C_{21}H_{23}NO_5S_2$ (433.54); calc.: C 58.18, H 5.35, N 3.23, S 14.79; found: C 57.52, H 5.60, N 3.09, S 14.79.

2-(4-Morpholinyldihio)-1,3-diphenyl-1,3-propanedione (**3f**; $C_{19}H_{19}NO_3S_2$)

The known compound **3f** [9, 10] was prepared for a comparison of its spectra with Refs. [9, 10] and with the new compounds **3a–e.** Preparation from 54.7 mg (0.15 mmol) recrystallized **1f** (Ar = 4–C_6H_5) and 79 µl **2** (0.90 mmol, 78.4 mg); crude yield: 51.2 mg (91.4% (Refs. [9, 10]: 25% after recrystallization)); m.p.: 116–118 °C (Refs. [9, 10]: 120–121 °C); IR (paraffin): ν = 1687.1 ($\nu_{C=O}$), 1667.7, 1593.9, 1578.2, 1281.3, 1114.7, 939.5 cm^{-1} (Ref. [10]: 1680, 1660 cm^{-1} (KBr)), ^1H NMR (250 MHz): δ = 2.87 (dd, 4H, H_2C–N), 3.63 (dd, 4H, H_2C–O), 6.06 (s, 1H, O=C–CH–C=O), 7.44 (dd, 4H, ar *meta*), 7.57 (t, 2H, ar *para*, ^3J = 7.3 Hz), 8.00 (d, 4H, ar *ortho*, ^3J = 7.1 Hz) ppm; ^{13}C NMR (62.9 MHz): δ = 55.32 (t, H_2C–N),

66.83 (t, H_2C–O), 68.67 (d, O=C–CH–C=O), 128.83 (ar C–H), 129.20 (ar C–H), 133.93 (*para*-C), 135.01 (*ipso*-C), 191.45 (C=O) ppm; MS (90 °C): $m/z = 373$ (1, M^+), 286 (1, $C_{15}H_{10}O_2S_2^+$), 256 (4, $C_{15}H_{12}O_2S^+$), 254 (3), 224 (24, $C_{15}H_{12}O_2^+$), 223 (26, $C_{15}H_{11}O_2^+$), 204 (9), 147 (14, C_6H_5–CO–CH_2–CO^+), 130 (10), 122 (23), 105 (100, C_6H_5–CO^+), 87 (59), 86 (41), 77 (81, $C_6H_5^+$), 57 (67), 51 (21).

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