149. Carbenoid Reactions of Dimethyl Diazomalonate with Aromatic Thioketones and 1,3-Thiazole-5(4*H*)-thiones

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Dimethyl diazomalonate (**4**) and thiobenzophenone (**2a**) do not react in toluene even after warming to 50°. After addition of catalytic amounts of $Rh_2(OAc)_4$, a smooth reaction under N_2 evolution afforded a mixture of thiiranedicarboxylate **5** and (diphenylmethylidene)malonate **6** (*Scheme 2*). A reaction mechanism *via* an intermediate 'thiocarbonyl ylide' **7**, formed by the addition of the carbenoid species **8** to the S-atom of **2a**, is plausible. Similar reactions were carried out with 9*H*-xanthene-9-thione (**2b**), 9*H*-thioxanthene-9-thione (**2c**, *Scheme 4*), and 1,3-thiazole-5(4*H*)-thione **18** (*Scheme 6*). In the cases of **2b** and **2c**, spirocyclic 1,3-dithiolanetetracarboxylates **14a** and **14b**, respectively, were obtained as the third product. Reaction mechanisms for their formation are proposed in *Scheme 5*: S-transfer from intermediate thiirane **12** to the carbenoid species yielded thioxomalonate **15** which underwent a 1,3-dipolar cycloaddition with 'thiocarbonyl ylide' **16**. An alternative is the formation of 'thiocarbonyl ylide' **17** *via* carbene addition to **15**, followed by 1,3-dipolar cycloaddition with **2b** and **2c**, respectively.

1. Introduction. – Diazoalkanes and their aryl-substituted derivatives react efficiently with thiocarbonyl compounds to give 2,5-dihydro-1,3,4-thiadiazoles as primary products (*cf.* [1–3]). Most of these adducts are unstable at ambient temperature and eliminate N_2 spontaneously or after slight warming to give reactive 'thiocarbonyl ylides' which undergo various reactions such as 1,3-dipolar cycloadditions [4–6], ring closure to thiiranes [7] [8], dimerization to 1,4-dithianes [9–11], and 1,4-H shifts [12]. Recently, we described that α-diazo ketones, -amides, and -esters are less reactive in 1,3-dipolar cycloadditions with thioketones and, therefore, these reactions required higher temperature [13] [14]. Generally, in reactions with carbonyl-substituted diazo compouds, the primary adducts have not been isolated until now, and elimination of N_2 occurred already under the reaction conditions[2]).

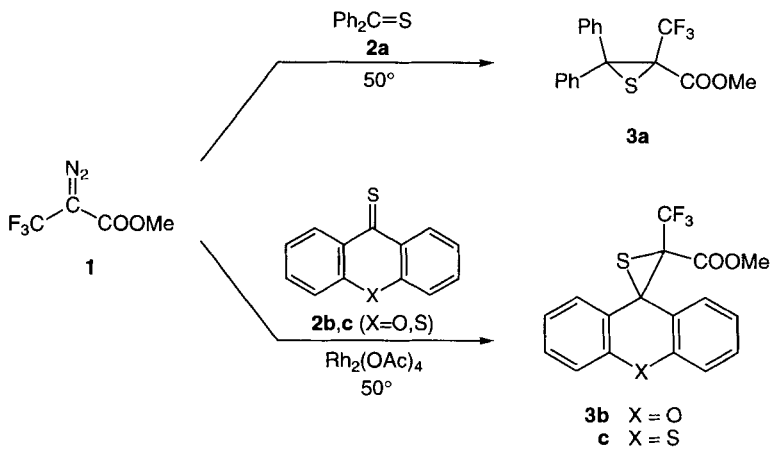
Recently, we described results of reactions of methyl 2-diazo-3,3,3-trifluoropropanoate (**1**) with thiocarbonyl compounds, and we stated that only the most reactive thiobenzophenone (**2a**) reacted under standard conditions with evolution of N_2 to yield thiirane **3a** [16] (*Scheme 1*). Under similar conditions, the less reactive 9*H*-xanthenethione (**2b**) and 9*H*-thioxanthene-9-thione (**2c**) reacted with **1** only the presence of catalytic amounts of rhodium(II) acetate, and the only products detected in the reaction

[1]) Stay at the Institute of Organic Chemistry of the University of Zürich (March–June 1995) as a Swiss Federal Scholar (Bundesstipendiat).

[2]) Recently, the primary, stable cycloadduct of a sterically crowded diazo amide and 2,2,4,4-tetramethyl-3-thioxocyclobutanone could be isolated [15].

mixtures were thiiranes **3b** and **3c**, respectively. In the case of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione, the corresponding thiirane was isolated as a minor product, and olefinic compounds, formed by its desulfurization, were the major components of the reaction mixture. It is likely that the formation of thiiranes **3** proceeds *via* ring closure of intermediate 'thiocarbonyl ylides'. In the noncatalyzed reaction, the precursor of this species is the [2+3] cycloadduct of **1** and **2a**. However, in the catalyzed decomposition of **1**, the formation of a carbenoid must be the first step of the conversion[3]). The electrophilic carbenoid then adds to the S-atom of the thiocarbonyl group to generate the 'thiocarbonyl ylide'.

Scheme 1



Diazomalonates are known as very useful reagents in organic syntheses; especially important are their applications as precursors of carbenes and carbenoids [18–20]. On the other hand, it is well known that diazomalonates are practically unreactive as 1,3-dipoles. Some years ago, *Huisgen* and coworkers found that thioketones are very reactive dipolarophiles ('superdipolarophiles' [3] [21]), and for this reason, we decided to test them as probably the best dipolarophiles in reactions with dimethyl diazomalonate (**4**).

2. Results and Discussion. – According to *Huisgen*, thiobenzophenone (**2a**) is one of the most reactive thiocarbonyl compounds in 1,3-dipolar cycloadditions. In our hands, heating of a solution of equimolar amounts of **2a** and **4** in toluene to 50° did not lead to any change of the mixture. However, addition of a catalytic amount of $Rh_2(OAc)_4$ resulted in a slow evolution of N_2. After 6 h, the reaction was terminated; the initially blue color of the mixture disappeared, and an almost equimolar amount of N_2 was set free. The ^{1}H-NMR spectrum of the mixture showed the presence of two new products in a ratio of *ca.* 7:3 (2*s* at 3.48 and 3.57 ppm, resp. (MeO)). After chromatographic workup, the two products were isolated and identified as thiirane **5** (MeO at 3.50 ppm) and the known alkylidenemalonate **6** [22] (MeO at 3.60 ppm) (*Scheme 2*).

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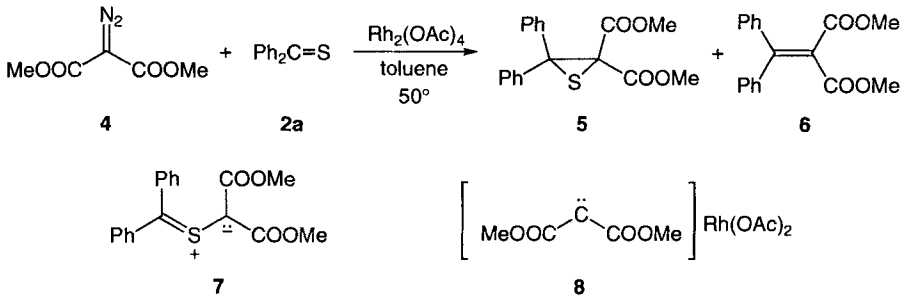
[3]) Unlike reactions of carbenes and carbenoids with other C=X bonds (X = C, N, O), reactions with thiocarbonyl groups are very scarcely described (*cf.* [17]).

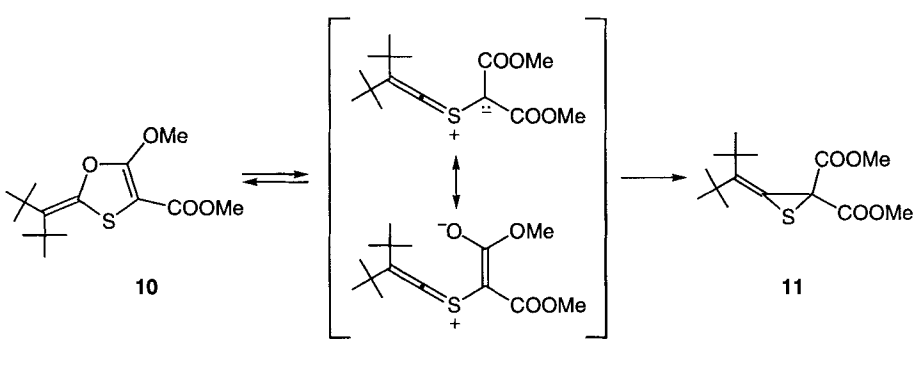
Scheme 2



The formation of **5** results from the cyclization of an intermediate 'thiocarbonyl ylide' **7**, formed by the addition of carbenoid **8** to the S-atom of **2a**. Desulfurization of **5** then yields **6**. The chemistry of 'thiocarbonyl ylides' of type **7** with two electron-withdrawing substituents is almost unknown[4]). In contrast to similar intermediates with alkyl and/or aryl groups, **7** underwent no cycloaddition with the 'superdipolarophile' **2a**. A similar behavior was already found for 'thiocarbonyl ylides' with an ester and a CF_3 group [16]. *Kaufman* and *Weininger* described a photolytical reaction of **2a** with diazomalonate and stated that the major product was diethyl (diphenylmethylidene)malonate [23]. According to the same authors, refluxing of **2a** and diethyl diazomalonate in diglyme gave the same product in good yield. It is likely that, under photolytical conditions and termally at 162°, elimination of the S-atom from primarily formed thiirane occurs rapidly. The advantage of our Rh-catalyzed reaction is that under relatively mild conditions, thiirane **5** can be prepared in fairly good yield.

A similar generation of the 'thiocarbonyl ylide' intermediate **9** has been used by *Tokitoh et al.* [24]: the reaction of di(*tert*-butyl)thioketene and **4** in the presence of $Rh_2(OAc)_4$ at 50° yielded the 2-alkylidene-1,3-oxathiole **10**, which has been shown to be in an equilibrium with **9** (*Scheme 3*). At 70° in CCl_4, **10** rearranged to give allene episulfide **11**.

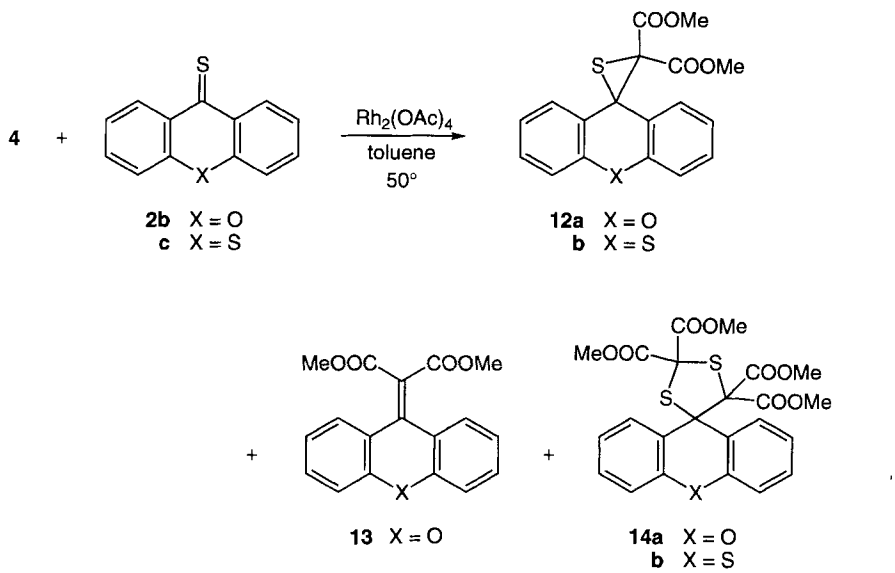
Scheme 3



[4]) Recent experiments concerning the generation of 'thiocarbonyl-*S*-dichloromethanides' will be published elsewhere.

In reactions with diazo compounds, 9*H*-xanthene-9-thione (**2b**) and 9*H*-thioxanthene-9-thione (**2c**) are less reactive dipolarophiles than **2a** [21]. Therefore, reactions of both thioketones with **4** were performed at 60° in the presence of $Rh_2(OAc)_4$ catalyst. After 2–3 days, the equimolar amount of N_2 was produced, and, after chromatographic workup, the products **12–14** were isolated (*Scheme 4*). Similar to the reactions with **2a**, the less polar fractions were identified as thiirane **12** and malonate **13**. The elucidation of the structure of the most polar **14**, a new type of product, based on mass and ^{13}C-NMR spectroscopy.

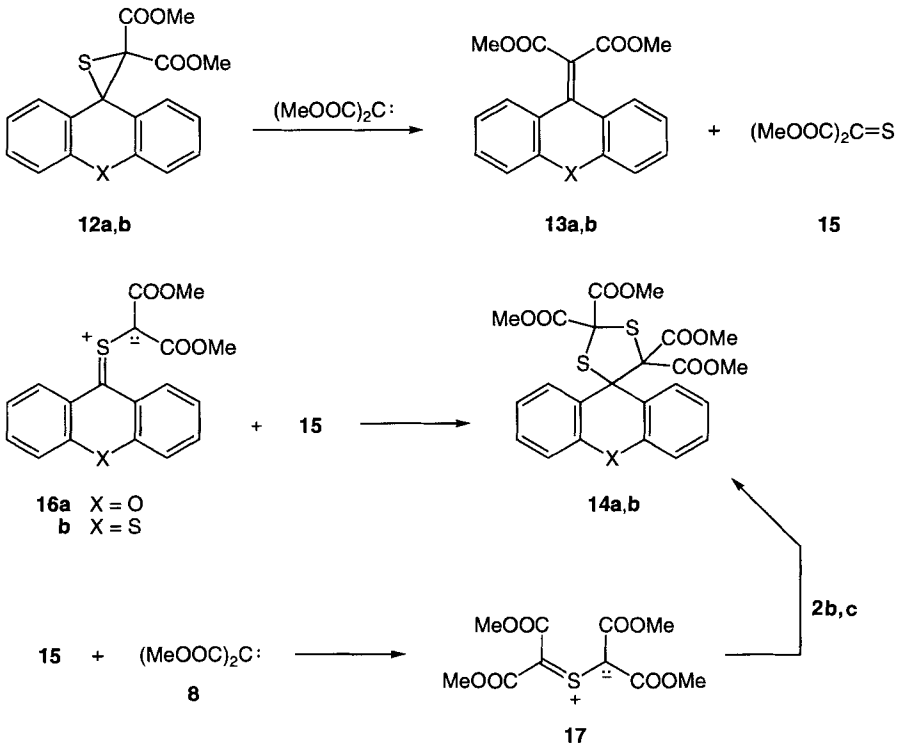
Scheme 4



In the ^{1}H-NMR spectra, **12** and **13** showed only one and **14** two MeO signals. The CI-MS of **14a** and **14b** indicated that both products contain two malonate moieties and two S-atoms in addition to the xanthene and thioxanthene fragment, respectively. The ^{13}C-NMR spectrum of **14a** revealed 3 signals for quaternary C-atoms at 96.1, 69.5, and 67.8 ppm. A similar set of signals was found for **14b**. All these data are in good agreement with the structure of 1,3-dithiolane derivatives.

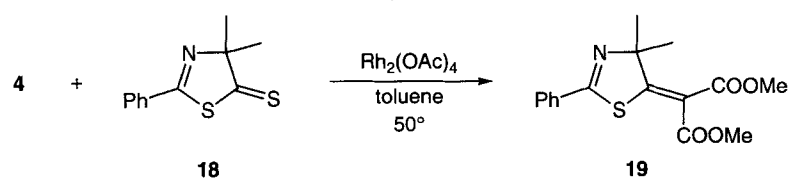
The formation of the unexpected products **14a,b** may be formulated as shown in *Scheme 5*. The crucial step is the formation of the new thiocarbonyl compounds **15**. We propose that **15** is formed by S-transfer from thiirane **12** to the carbene species. Subsequent interception of 'thiocarbonyl ylide' **16** by **15** results in the formation of **14**. However, a second route to **14** should also be taken into account: reaction of the carbene species **8** with *in situ* generated **15** could give 'thiocarbonyl ylide' **17** which, *via* cycloaddition with **2**, can also lead to **14**. The trapping of 'thiocarbonyl ylides' by thiones is a characteristic reaction of these S-centered 1,3-dipoles and known as *Schönberg* reaction [25]. A desulfurization of a thiirane by carbenoid **8**, similar to **12** → **13**, has been postulated by *Takano et al.*, but in their experiments, all attempts to isolate or to trap the resulting thiocarbonyl compound were unsuccessful [26].

Scheme 5



From our previous studies it is known that 1,3-thiazole-5(4*H*)-thiones of type **18** are much less reactive as dipolarophiles compared with aromatic thioketones [16]. The $Rh_2(OAc)_4$-catalyzed reaction of **4** and **18** at 60° yielded (1,3-thiazol-5-ylidene)malonate **19** in almost quantitative yield as the sole product (*Scheme 6*).

Scheme 6



It is worth noting that in the IR spectrum (KBr) of **19** two ester-CO absorptions at 1725 and 1705 cm^{-1} were observed. The nonequivalent ester groups also show remarkable differences in the ^{13}C-NMR spectrum: the low-field signal appears at 172.3 and the high-field one at 166.4 ppm. These differences can be explained by the assumption that the ester group *cis* to the S-atom is coplanar with the C=C bond (*i.e.*, an α,β-unsaturated ester) whereas the *trans*-oriented ester group, because of steric hindrance with the geminal dimethyl groups, is twisted out of the C=C plane (*cf.* [16]).

The formation of **19** corresponds very well with results obtained from reactions of **4** and analogous diazo compounds with tetrahydrofuran-2-thiones in refluxing benzene

[26] [27]. In this case, despite of the lower temperature in our experiments, the desulfurization of primarily formed thiirane was complete. This simple methodology for the formation of methylidene derivatives of heterocyclic thiones, which is closely related to *Eschenmoser*'s 'sulfide contraction *via* alkylative coupling' [28], has already been used in natural-product syntheses [27]. Our present studies show that this rather general strategy can be performed as a 'one-pot reaction' under relatively mild conditions.

In contrast to [24], using the 'carbenoid procedure', we could not detect products of 1,5-electrocyclization of ester-substituted 'thiocarbonyl-ylide' intermediates, neither in reactions with aromatic thioketones nor with 1,3-thiazole-5(4*H*)-thione **18**.

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Experimental Part

1. *General.* See [5]. Thioketones **2a–c** were prepared from the corresponding ketones by treatment with *Lawesson* reagent [29]; 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**18**) was synthesized according to [30]. Dimethyl diazomalonate (**4**) was prepared from dimethyl malonate by treatment with tosyl azide in benzene as described in [31].

2. *Reactions of Thiocarbonyl Compounds with Dimethyl Diazomalonate* (**4**). 2.1. *General Procedure.* At r.t., **4** (177.0 mg, 1.1 mmol) was added to a soln. of the thiocarbonyl compound (1.0 mmol) in toluene (0.5 ml). No N_2 evolution was observed, neither at r.t. nor at 50°. After addition of a catal. amount (*ca.* 0.1 mmol) of $Rh_2(OAc)_4 \cdot H_2O$ at 50°, N_2 evolution started and was followed volumetrically. After 6–42 h, the evolution of N_2 ceased. The mixtures were filtered through a short SiO_2 column (*ca.* 3 cm) to remove the catalyst and dark decomposition products. After evaporation, the residues were analyzed by ^{1}H-NMR (1,1,2,2-tetrachloroethane as a standard) to establish yields of the products. Prep. TLC (SiO_2) and crystallization yielded pure products.

2.2. *With Thiobenzophenone* (**2a**). For 6 h; prep. TLC with pentane/CH_2Cl_2 6:4: two fractions.

Dimethyl 3,3-Diphenylthiirane-2,2-dicarboxylate (**5**): 46% (NMR); isolated 130 mg (40%). Colorless crystals. M.p. 92–93° (pentane/CH_2Cl_2). IR (KBr): 1745*vs* (C=O), 1490*m*, 1447*m*, 1432*s*, 1275*m* (br.), 1250–1200*s* (br.), 1125*vs*, 1052*vs*, 975*m*, 952*m*, 765*s* (br.), 732*m*, 708*s*, 695*s*. ^{1}H-NMR: 7.45–7.4 (*m*, 4 arom. H); 7.3–7.25 (*m*, 6 arom. H); 3.50 (*s*, 2 MeO). ^{13}C-NMR: 166.0 (*s*, 2 C=O); 138.9 (*s*, 2 arom. C); 129.1, 128.0, 127.9 (3*d*, 10 arom. CH); 62.7 (*s*, C(2)); 57.3 (*s*, C(3)); 53.2 (*q*, 2 MeO). CI-MS: 329 (25, $[M + 1]^+$), 297 (100, $[M - S]^+$), 282 (95, $[M - MeS]^+$), 265 (31). Anal. calc. for $C_{18}H_{16}O_4S$ (328.37): C 65.84, H 4.91, S 9.76; found: C 65.55, H 5.35, S 10.05.

Dimethyl (Diphenylmethylidene)malonate (**6**): 18% (NMR); isolated 40 mg (13%). Colorless crystals. M.p. 119–121° (EtOH at −10°; [21]: 122–123°). IR (KBr): 1730*vs* (C=O), 1700*vs* (C=O), 1600*s* (C=C), 1440*s*, 1425*s*, 1330*vs*, 1300*s*, 1245*vs* (br.), 1165*s*, 1080*vs*, 770*s*, 695*s*. ^{1}H-NMR: 7.35–7.3 (*m*, 6 arom. H); 7.25–7.15 (*m*, 4 arom. H); 3.60 (*s*, 2 MeO). ^{13}C-NMR: 166.3 (*s*, 2 C=O); 156.4 (*s*, Ph_2C); 139.8 (*s*, 2 arom. C); 129.2, 129.0, 128.1 (3*d*, 10 arom. CH); 125.4 (*s*, $C(CO_2Me)_2$); 52.1 (*q*, 2 MeO). EI-MS: 296 (92, $M^{+\cdot}$), 265 (73, $[M - MeO]^+$), 236 (100, $[M - CO_2Me]^+$), 205 (18), 197 (30), 178 (42), 165 (19), 105 (31).

2.3. *With 9H-Xanthene-9-thione* (**2b**). For 40 h; prep. TLC with hexane/CH_2Cl_2 1:1: three fractions.

Dimethyl Spiro[thiirane-2,9′-[9H]xanthene]-3,3-dicarboxylate (**12a**): 31% (NMR); isolated 80 mg (22%). Colorless crystals. M.p. 150–152° (hexane/CH_2Cl_2). IR (KBr): 1740*vs* (br., C=O), 1725*vs* (br., C=O), 1475*s*, 1450*vs*, 1435*s*, 1312*s*, 1265*vs* (br.), 1235*vs*, 1055*m*, 767*s*, 760*s*. ^{1}H-NMR: 7.5–7.05 (*m*, 8 arom. H); 3.39 (*s*, 2 MeO). ^{13}C-NMR: 164.6 (*s*, 2 C=O); 154.7, 119.3 (2*s*, 4 arom. C); 129.5, 127.3, 123.0, 116.4 (4*d*, 8 arom. CH); 59.9 (*s*, C(3)); 53.2 (*q*, 2 MeO); 51.1 (*s*, C(2)). EI-MS: 342 (5, $M^{+\cdot}$), 310 (69, $([M - S]^+$), 283 (35, $[M - CO_2Me]^+$), 282 (100), 279 (44), 268 (15), 251 (32), 224 (29), 211 (19), 194 (13), 180 (17), 163 (13). Anal. calc. for $C_{18}H_{14}O_5S$ (342.35): C 63.15, H 4.12, S 9.36; found: C 62.95, H 3.98, S 9.11.

Dimethyl (9H-Xanthene-9-ylidene)malonate (**13a**): 32% (NMR); isolated 80 mg (26%). Pale yellow crystals. M.p. 95–97° (EtOH). IR (KBr): 1750*s* (C=O), 1710*vs* (br., C=O), 1610*m* (br., C=C), 1450*s*, 1340*m*, 1250*vs* (br.), 1210*m* (br.), 1173*m*, 1155*m*, 1075*s*, 775*m*. ^{1}H-NMR: 7.7–7.1 (*m*, 8 arom. H); 3.75 (*s*, 2 MeO). ^{13}C-NMR: 166.2 (*s*, 2 C=O); 152.6, 120.9 (2*s*, 4 arom. C); 137.8 (*s*, Ar_2C); 130.9, 127.0, 123.2, 116.9 (4*d*, 8 arom. CH); 120.0 (*s*,

$C(CO_2Me)_2$); 52.6 (*q*, 2 MeO). EI-MS: 310 (100, M^+), 279 (72, $[M - MeO]^+$), 251 (25), 221 (23), 220 (22), 211 (28), 194 (22), 180 (16), 163 (20). Anal. calc. for $C_{18}H_{14}O_5$ (310.31): C 69.67, H 4.54; found: C 69.56, H 4.21.

Tetramethyl Spiro[1,3-dithiolane-4,9'-[9H]xanthene]-2,2,5,5-tetracarboxylate (**14a**): 17% (NMR); isolated 70 mg (14%, 25% rel. to **4**). Colorless viscous oil. IR ($CHCl_3$): 1745*vs* (br., C=O), 1475*m*, 1440*m*, 1320*m*, 1285*m*, 1240*s* (br.). ^{1}H-NMR: 8.32 (*d*, J = 1.3, 2 arom. H); 7.35–7.3 (*m*, 2 arom. H); 7.15–7.05 (*m*, 4 arom. H); 3.95 (*s*, 2 MeO); 3.44 (*s*, 2 MeO). ^{13}C-NMR: 167.3, 165.9 (2*s*, 4 C=O); 151.6, 119.7 (2*s*, 4 arom. C); 131.8, 130.2, 122.6, 116.2 (4*d*, 8 arom. CH); 96.1, 69.5, 67.8 (3*s*, C(2), C(4), C(5)); 54.6, 53.4 (2*q*, 4 MeO). CI-MS: 522 (100, $[M + NH_4]^+$), 505 (18, $[M + 1]^+$), 473 (45, $[M - MeO]^+$), 343 (90), 311 (19), 310 (34), 282 (14), 213 (44). Anal. calc. for $C_{23}H_{20}O_9S_2$ (504.51): C 54.75, H 3.99, S 12.71; found: C 54.29, H 3.53, S 12.51.

2.4. *With 9H-Thioxanthene-9-thione* (**2c**). For 72 h (from time to time, new portions of catalyst were added); prep. TLC with hexane/CH_2Cl_2 1:1: two fractions.

Dimethyl Spiro[thiirane-2,9'-[9H]thioxanthene]-3,3-dicarboxylate (**12b**): 42% (NMR); isolated 110 mg (31%). Colorless crystals. M.p. 124–126° (EtOH/CH_2Cl_2). IR (KBr): 1740*vs* (C=O), 1435*s*, 1270*vs* (br.), 1220*vs* (br.), 1115 *m*, 1050*s*, 760*s*, 740*s*. ^{1}H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.5–7.45 (*m*, 2 arom. H); 7.3–7.2 (*m*, 4 arom. H); 3.38 (*s*, 2 MeO). ^{13}C-NMR: 165.0 (*s*, 2 C=O); 136.8, 132.8 (2*s*, 4 arom. C); 128.9, 127.8, 126.5, 126.2 (4*d*, 8 arom. CH); 59.2, 56.3 (2*s*, C(2), C(3)); 53.1 (*q*, 2 MeO). EI-MS: 358 (5, M^+), 326 (100, $[M - S]^+$), 298 (51), 295 (52), 284 (14), 267 (41), 240 (18), 236 (20), 227 (16), 208 (29), 196 (20), 163 (16), 152 (21). Anal. calc. for $C_{18}H_{14}O_4S_2$ (358.41): C 60.32, H 3.94, S 17.89; found: C 60.08, H 3.66, S 17.98.

Tetramethyl Spiro[1,3-dithiolane-4,9'-[9H]thioxanthene]-2,2,5,5-tetracarboxylate (**14b**): 24% (NMR); isolated 105 mg (20%, 36% rel. to **4**). Colorless viscous oil[5]. IR ($CHCl_3$): 1745*vs* (br., C=O), 1460 *m*, 1435*s*, 1230*vs* (br.), 1180*m*. ^{1}H-NMR: 8.47 (*d*, J = 1.3, 2 arom. H); 7.3–7.15 (*m*, 6 arom. H); 3.89 (*s*, 2 MeO); 3.50 (*s*, 2 MeO). ^{13}C-NMR: 167.0, 165.9 (2*s*, 4 C=O); 133.5, 130.7 (2*s*, 4 arom. C); 133.0, 128.0, 125.7, 125.3 (4*d*, 8 arom. CH); 96.0, 76.2, 67.0 (3*s*, C(2), C(4), C(5)); 54.4, 53.3 (2*q*, 4 MeO). CI-MS: 538 (20, $[M + NH_4]^+$), 537 (37, $[M + NH_3]^+$), 521 (44, $[M + 1]^+$), 507 (100), 489 (13), 358 (34), 298 (22).

2.5. *With 4,4-Dimethyl-2-phenyl-1,3-thiazole-5(4H)-thione* (**18**). For 9 h; prep. TLC with hexane/CH_2Cl_2 1:1: *Dimethyl (4,5-Dihydro-4,4-dimethyl-2-phenyl-1,3-thiazol-5-ylidene)malonate* (**19**) in 87% (NMR) yield; isolated 250 mg (78%). Colorless plates. M.p. 137–138° (EtOH). IR (KBr): 1725*vs* (C=O), 1705*vs* (C=O), 1620*m* (C=C), 1550*s*, 1450*s*, 1440*s*, 1280*s*, 1235*vs* (br.), 1190*vs*, 1010*s*, 990*m*, 955*s*, 940*m*, 770*s*, 750*m*, 690*s*. ^{1}H-NMR: 7.9–7.85 (*m*, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 3.88, 3.82 (2*s*, 2 MeO); 1.62 (*s*, 2 Me). ^{13}C-NMR: 172.3, 166.4 (2*s*, 2 C=O); 164.8 (*s*, C=N); 160.8 (*s*, C(5')); 132.4 (*s*, 1 arom. C); 131.6, 128.8, 128.1 (3*d*, 5 arom. CH); 115.1 (*s*, $C(CO_2Me)_2$); 85.0 (*s*, C(4')); 52.7, 52.6 (2*q*, 2 MeO); 26.9 (*q*, 2 Me). EI-MS: 319 (60 M^+), 304 (100), 288 (17), 272 (60), 260 (60), 216 (22), 184 (53), 169 (15), 154 (45), 152 (85), 145 (36), 104 (32), 73 (42). Anal. calc. for $C_{16}H_{17}NO_4S$ (319.17): C 60.17, H 5.37, N 4.39, S 10.04; found: C 59.97, H 5.46, N 4.21, S 10.21.

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