135. 'Three-Component Reaction' with Aromatic Thioketones, Phenyl Azide, and Dimethyl Fumarate

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The reaction of thiobenzophenone (= diphenylmethanethione; **8a**) or 9*H*-fluorene-9-thione (**8b**) and methyl fumarate (**9**) in excess PhN_3 at 80° yields a mixture of diastereoisomeric thiiranes **10** and **11** (*Scheme 1*). A mechanism involving the initial formation of 1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4,5-dicarboxylate **12** by 1,3-dipolar cycloaddition of PhN_3 and **9** is proposed in *Scheme 2*. The diazo compound **13**, which is in equilibrium with **12**, undergoes a further 1,3-dipolar cycloaddition with thioketones **8** to give 2,5-dihydro-1,3,4-thiadiazoles **14**. Elimination of N_2 yields the thiocarbonyl ylide **15** which cyclizes to the corresponding thiirane. Desulfurization of the thiiranes **10** and **11** with hexamethylphosphorous triamide leads to the olefinic compounds **16** (*Scheme 3*). The crystal structures of **10a**, **11a**, and **16b** were determined.

Introduction. – Recently, we published results of our studies on 'three-component reactions' including PhN_3, a C,C-dipolarophile, and a cycloalkanethione such as 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1a**) and adamantanethione (**1b**) [1][2]. With dimethyl fumarate as the dipolarophile, the reaction took an unexpected course, leading to 1-azabuta-1,3-dienes **2** as the major products *via* a cascade of reaction steps. In the discussion of the reaction mechanism, we emphasized the role of an intermediate carbonyl-substituted thiocarbonyl ylide **3**, which, by a 1,5-dipolar electrocyclization, afforded the 1,3-oxathiolane derivative. Following a similar protocol with the cycloalkanethiones **1a,b**, and thiobenzophenone in excess PhN_3, we isolated mixed 1,2,4-trithiolanes **4** as the product of the interception of the intermediate thiocarbonyl *S*-sulfide (thiosulfine) **5** [3] [4].

As demonstrated in [5], the key intermediate in the reactions of PhN_3 with **1a** is the thiocarbonyl *S*-imide **6**. In another experiment, its formation was confirmed by the interception with fumaronitrile; the structure of the [2 + 3] cycloadduct was established by X-ray crystallography [2]. In the reactions with aromatic thioketones, the participation of an analogous species **7** is conceivable, but there is no known example of their interception to form an isolable product.

These results show that the behavior of *S*-centered 1,3-dipoles strongly depends on the substituents; products obtained with sterically crowded cycloalkanethiones differ

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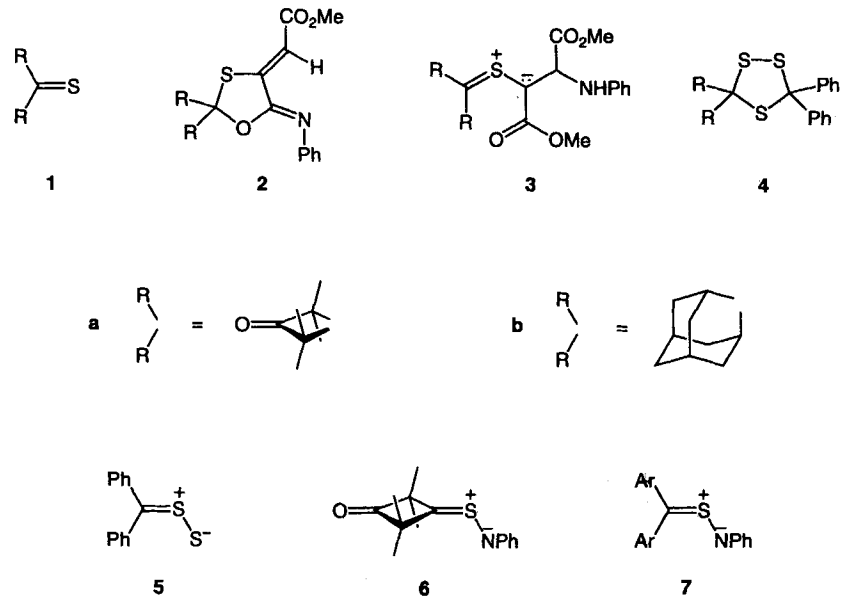


from those with aromatic thioketones. For this reason, we investigated the reactions of aromatic thioketones such as thiobenzophenone (= diphenylmethanethione; **8a**) and 9*H*-fluorene-9-thione (**8b**) in three-component systems with PhN_3 and dimethyl fumarate (**9**) to compare their behavior with those of **1a** and **1b**.

Results and Discussion. – When a mixture of equimolar amounts of **8a** and **9** in excess PhN_3 was heated to 80°, the blue color of **8a** disappeared within *ca.* 40 min. Examination of the crude mixture by means of ^{1}H-NMR spectroscopy ($CDCl_3$) revealed the presence of two isomeric thiiranes **10a** and **11a** in a ratio of *ca.* 55:45 (δ(H) of CO_2Me at 3.60 and 3.35 ppm for the major and at 3.69 and 3.30 ppm for the minor isomer) (*Scheme 1*). Product separation by column chromatography (SiO_2) yielded the less polar benzophenone and the more polar mixture **10a**/**11a**. Repeated chromatography followed by recrystallization from EtOH provided **10a** and **11a** in pure form; their crystal structures were established by X-ray crystallography (*Fig. 1*).

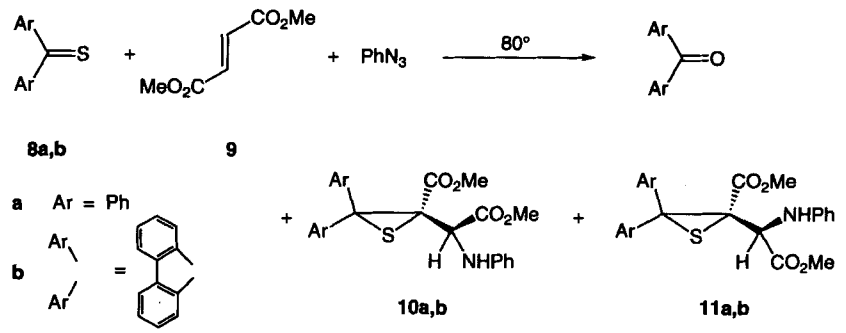
Benzophenone was isolated in up to 33% yield; its formation can be explained by the hydrolysis of *N*-(diphenylmethylidene)aniline during workup. This imine is the product of the 1,3-dipolar cycloaddition of PhN_3 with **8a**, followed by a two-fold extrusion of N_2 and S [3][7][2][3]).

To increase the yield of **10a** and **11a**, we elaborated a two-step procedure in which PhN_3 and **8** were first reacted to give a mixture of the initial cycloadduct **12** and the

[2]) The relatively high yield of benzophenone is in accordance with our previous observation that **8a** reacts rapidly with PhN_3 at 80° [3].

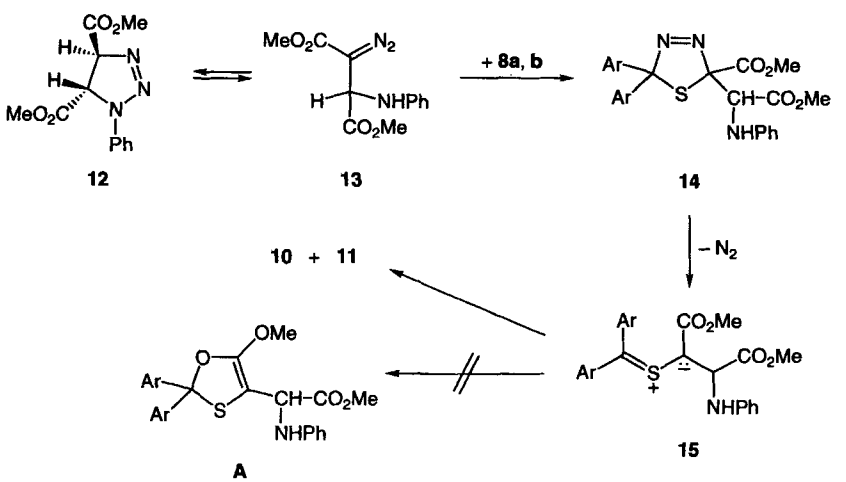
[3]) It is worth mentioning that no trithiolane of type **4** was isolated although **8a** is known as a very efficient dipolarophile [8].

Scheme 1



isomeric diazo compound **13** [9] (*Scheme 2*). It is well-known that diazo compounds react very efficiently with thioketones [10–13]. Therefore, the initial product of the [2 + 3] cycloaddition of **8a** and **13** is most likely the 2,5-dihydro-1,3,4-thiadiazole **14**[4]) which easily extrudes N_2 to give the thiocarbonyl ylide **15** (*Scheme 2*). The formation of **10a** and **11a** results from conrotatory 1,3-dipolar electrocyclizations of **15** (*cf.* [17]). The same two thiiranes can be formed by the conrotatory ring closure of the isomeric (*E*)-configurated thiocarbonyl ylide.

Scheme 2



A similar mixture ot thiiranes **10b** and **11b** was formed in the reaction of **12**/**13** and 9*H*-fluorene-9-thione (**8b**). The ratio of the products was determined in the crude mixture by ^{1}H-NMR (δ(H) of CO_2Me at 3.68 and 3.17 ppm for the major and at 3.78 and 3.74 ppm for the minor isomer).

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[4]) Similar 2,5-dihydro-1,3,4-thiadiazoles with bulky substituents are fairly stable and were isolated in some cases [13–15]. Aryl-substituted derivatives of this type are much less stable and decompose instantaneously, even at –20° [16].

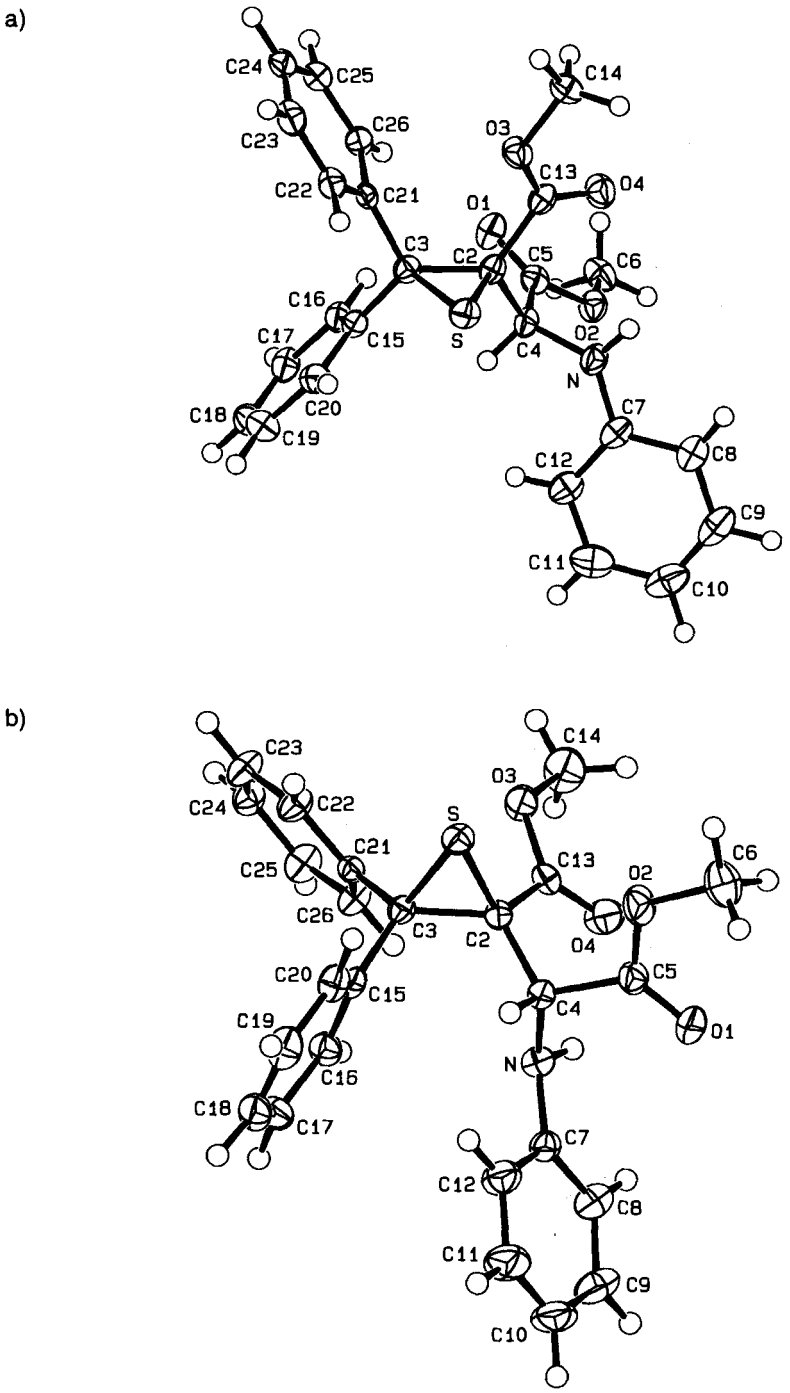


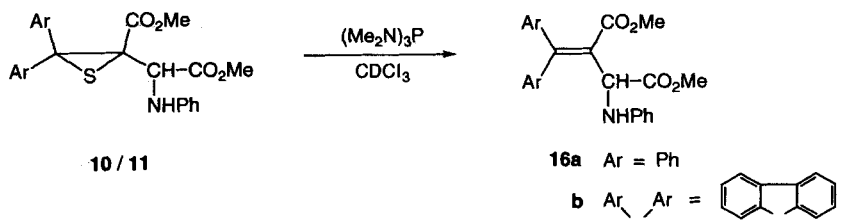
Fig. 1. *ORTEP plots* [6] *of the molecular structure of* a) **10a** *and* b) **11a** (ellipsoids with 50% probability)

Unlike cycloalkanethiones, **8a** and **8b** did not yield 1,3-oxathiolane derivatives of the type **2** in the reaction with **13**. This result indicates that, in the case of aromatic substituted systems, the 1,3-ring closure of thiocarbonyl ylide **15** is favored over the 1,5-dipolar electrocylization to **A**, which is an intermediate in the formation of **2** [1] [2] (*cf.* [18]). This is a further confirmation of the different behavior of *S*-centered 1,3-dipoles with aromatic and aliphatic substituents, respectively (*cf.* [1–5] [15]).

Typical reaction times for the transformations of **12**/**13** and **8** were 2 h, after which the mixtures were separated immediately. In one experiment with **8b**, heating of the mixture was prolonged to 24 h. Chromatographic workup gave the desulfurized product **16b** as the sole product in 56% yield. Obviously, thiiranes of type **10**/**11** are thermally unstable compounds.

A smooth and nearly quantitative desulfurization of the isomeric thiiranes **10a**/**11a** and **10b**/**11b**, was achieved by treatment of their $CDCl_3$ solutions with hexamethyl-

Scheme 3



10 / 11

16a Ar = Ph

b Ar, Ar =

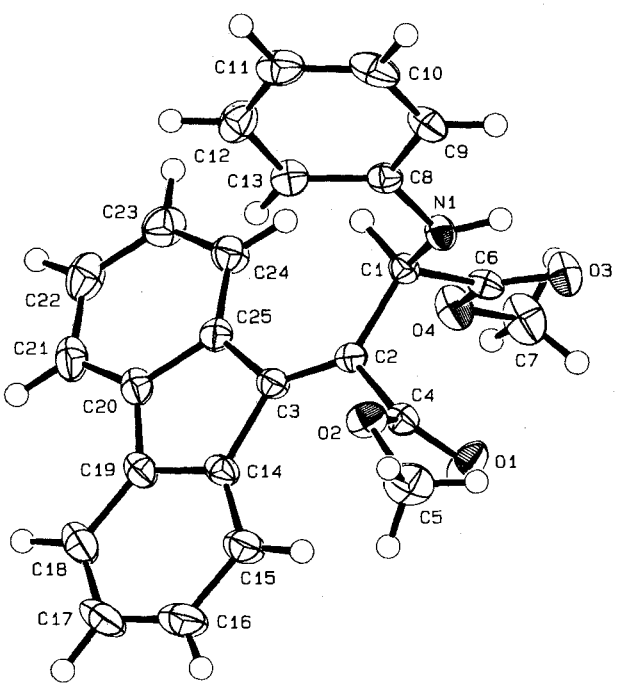


Fig. 2. *ORTEP plot* [6] *of the molecular structure of* **16b** (ellipsoids with 50% probability)

phosphorous triamide at room temperature. In each case, only one product **16a** and **16b**, respectively, was formed. The structure of **16b** was confirmed by an X-ray analysis (*Fig. 2*).

We thank the analytical services of our institutes for spectra and elemental analyses. Financial support by the *Polish State Committee for Scientific Research* (grant No. 3 TO9A 15710), the *Swiss National Science Foundation*, and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

Experimental Part

General. See [5]. PhN_3 was prepared from phenylhydrazine by diazotization at 0° [19], *diphenylmethanethione* (**8a**) from benzophenone by thionation with *Lawesson* reagent [20], and *9H-fluorene-9-thione* (**8b**) from *9H*-fluoren-9-one by treatment with H_2S/HCl in EtOH soln. in the presence of an equimolar amount of trimethyl orthoformate [21]. M.p.s: capillary, *Büchi-SMP-20* apparatus; uncorrected. For recording of spectra, the following instruments were used: NMR ($CDCl_3$): *Varian-Gemini 200 BB* (^1H, 200 MHz; ^{13}C, 50.4 MHz) and *Bruker B-ACS-60* (^1H, 300 MHz; ^{13}C, 75.6 MHz). IR (KBr): *Specord 71 IR*. MS: *Varian MAT-112 S*.

1. *Reaction of* **8a** with PhN_3 *and Dimethyl Fumarate* **9**: *One-Step Reaction.* A stirred mixture of **8a** (397 mg, *ca.* 2 mmol) and **9** (288 g, 2 mmol) in excess PhN_3 (1 ml, *ca.* 9.2 mmol) was heated to 80° (oil bath). After 40 min, the evolution of N_2 ceased and 34 ml of N_2 (*ca.* 70% of the theor. amount) were collected in a gas burette. Excess PhN_3 was removed by bulb-to-bulb distillation at 60°/0.1 Torr, and the remaining viscous oil was separated by column chromatography (SiO_2, petroleum ether with increasing amount of CH_2Cl_2), yielding 120 mg (33%) of benzophenone (with CH_2Cl_2/petroleum ether 3:7) and 435 mg (*ca.* 50%) of **10a**/**11a** 55:45 as a colorless, viscous oil (with CH_2Cl_2/petroleum ether 6:4).

2. *Two-Step Procedure for the Reaction of* **8a** *and* **8b** *with* PhN_3 *and* **9**. 2.1. *General Procedure.* A soln. of **9** (432 mg, 3 mmol) in PhN_3 (1 ml, *ca.* 9.2 mmol) was heated to 80° for 1.5 h. Excess of PhN_3 was removed by bulb-to-bulb distillation at 60°/0.1 Torr, and the residue was stored in a closed flask for 7 days ar r.t. After this time, the ratio **13**/**12** was 3:1 (^1H-NMR). To the crude **12**/**13** in toluene (1 ml), freshly purified **8a** or **8b** (2 mmol) was added. The coloured solns. were stirred at r.t. until the evolution of N_2 ceased (*ca.* 1 h for **8a** and 2 h for **8b**). After evaporation, the residue was separated chromatographically (SiO_2, petroleum ether with increasing amount of CH_2Cl_2). Fractions containing incompletely separated **10** and **11** were isolated with petroleum ether/CH_2Cl_2 2:3. Repeated prep. TLC (SiO_2, Et_2O/pentane 1:4, 4 × developed) afforded fairly well separated products which were recrystallized from MeOH to give anal. pure products.

2.2. *With* **8a**. *Methyl (*RS,RS*)-2-(Methoxycarbonyl)-3,3-diphenyl-α-(phenylamino)thiiraneacetate* (**10a**): 259 mg (30%), isolated as the slightly more polar fraction. Colorless crystals. M.p. 110–111° (MeOH). IR: 3320*m* (br., NH), 1740*vs* (C=O), 1700*vs* (C=O), 1600*s*, 1520*s*, 1490*m*, 1440*m*, 1320*m*, 1310*s*, 1280*s*, 1260*m*, 1240*m*, 1010*m*, 780*s*, 720*s*. ^1H-NMR: 7.71 (*d*-like, 2 arom. H); 7.51 (*d*-like, 2 arom. H); 7.3–7.05 (*m*, 8 arom. H); 6.71 (*t*-like, 1 arom. H); 6.58 (*d*-like, 2 arom. H); 4.54 (br. *s*, NH); 3.91 (*s*, CH); 3.69, 3.30 (2*s*, 2 MeO). ^{13}C-NMR: 171.2, 170.4 (2*s*, 2 C=O); 147.3, 141.4, 138.1 (3*s*, 3 arom. C); 129.8, 129.0, 127.9, 127.7, 127.3, 118.9, 114.0 (7*d*, 15 arom. CH); 66.6, 60.1 (2*s*, C(2), C(3)); 61.3 (*d*, C(α)); 52.6, 52.3 (2*q*, MeO). EI-MS: 433 (10, $M^{+\cdot}$) 401 (4, $[M - S]^+$), 374 (20), 342 (55), 310 (20), 270 (10), 210 (30), 207 (32), 197 (37), 178 (17), 164 (100), 104 (66), 77 (39). Anal. calc. for $C_{25}H_{23}NO_4S$ (433.51): C 69.26, H 5.35, N 3.23, S 7.40; found: C 69.18, H 5.26, N 3.49, S 7.11.

*Methyl (*RS,SR*)-2-(Methoxycarbonyl)-3,3-diphenyl-α-(phenylamino)thiiraneacetate* (**11a**): 294 mg (34%), isolated as the less polar fraction. Colorless crystals. M.p. 99–101° (MeOH). IR: 3380*m* (NH), 1740*s* (C=O), 1710*s* (C=O), 1602*s*, 1505*s*, 1430*s*, 1350–1200*s* (br.), 1150*m*, 955*s*, 755*s*, 715*s*, 680*s*. ^1H-NMR: 7.58 (*d*-like, 2 arom. H); 7.47 (*d*-like, 2 arom. H); 7.3–7.15 (*m*, 3 arom. H); 7.05–6.9 (*m*, 5 arom. H); 6.62 (*t*-like, 1 arom. H); 6.07 (*d*-like, 2 arom. H); 5.88 (*d*, J = 9.0, NH; disappears after treatment with D_2O); 3.68 (*d*, J = 9.0, CH), 3.60, 3.35 (2*s*, 2 MeO). ^{13}C-NMR: 171.9, 170.8 (2*s*, 2 C=O); 146.1, 140.7, 137.7 (3*s*, 3 arom. C); 129.8, 128.7, 128.1, 128.0, 127.7, 127.5, 118.3, 113.6 (8*d*, 15 arom. CH); 62.5 (*d*, C(α)); 65.1, 55.3 (2*s*, C(2), C(3)); 52.8, 52.4 (2*q*, 2 MeO). CI-MS (NH_3): 434 (100, $[M + 1]^+$), 402 (24, $[M - S + 1]^+$), 341 (20), 277 (14). Anal. calc. for $C_{25}H_{23}NO_4S$ (433.51): C 69.26, H 5.35, N 3.23; found: C 69.29, H 5.16, N 3.28.

2.3. *With* **8b**. *Methyl (*RS,RS*)-3'-(Methoxycarbonyl)-α-(phenylamino)spiro[9H-fluorene-9,2'-thiirane]-3'-acetate* (**10b**): 380 mg (44%), isolated as the more polar fraction (petroleum ether/CH_2Cl_2 45:55). Colorless crystals. M.p. 177–170° (MeOH). IR: 3390*m* (NH), 1730*vs* (br., C=O), 1605*vs* (C=O), 1520*s*, 1505*s*, 1450*s*, 1435*s*, 1310*vs* (br.), 1230*vs*, 1250*vs*, 1150*s*, 1075*s*, 745*s*, 730*vs*, 690*s*. ^1H-NMR: 7.78 (*d*-like, 1 arom. H); 7.74 (*d*-like, 1 arom. H); 7.49 (*d*-like, 1 arom. H); 7.45–7.2 (*m*, 7 arom. H); 7.02 (*d*-like, 2 arom. H); 6.86 (*t*-like, 1 arom. H);

4.70 (br. *s*, NH, CH); 3.68, 3.17 (2*s*, 2 MeO). ^{13}C-NMR: 170.2, 168.0 (2*s*, 2 C=O); 147.3, 143.3, 142.3, 141.4, 141.1 (5*s*, 5 arom. C); 129.4, 129.0, 128.6, 127.2, 127.0, 123.9, 122.4, 120.1, 119.7, 114.9 (10*d*, 13 arom. CH); 63.1 (*d*, CH); 59.2, 56.2 (2*s*, C(2'), C(3')); 53.1, 52.5 (2*q*, 2 MeO). CI-MS (NH_3): 432 (61, $[M+1]^+$), 400 (100, $[M-S+1]^+$), 307 (11). Anal. calc. for $C_{25}H_{21}NO_4S$ (431.51): C 69.59, H 4.91, N 3.25; found: C 69.58, H 4.89, N 3.11.

*Methyl (*RS,SR*)-3'-(Methoxycarbonyl)-α-(phenylamino)spiro[9*H*-fluorene-9,2'-thiirane]-3'-acetate* (**11b**): 293 mg (34%), isolated as the less polar fraction (petroleum ether/CH_2Cl_2 60:40). Colorless crystals. M.p. 170–172° (MeOH)[5]). IR: 3380*m* (NH), 1746v*s* (C=O), 1720v*s* (C=O), 1600*s*, 1515*s*, 1510*s*, 1450*s*, 1435*s*, 1330*m*, 1305*s*, 1260*s* (br.), 750*s*, 730v*s*. ^{1}H-NMR: 7.69 (*d*-like, 1 arom. H); 7.63 (*d*-like, 1 arom. H); 7.4–7.35 (*m*, 2 arom. H); 7.25–7.1 (*m*, 3 arom. H); 7.05–6.95 (*m*, 3 arom. H); 6.62 (*t*-like, 1 arom. H); 6.34 (*d*-like, 2 arom. H); 4.87 (*d*, *J* = 9.0, NH); 4.69 (*d*, *J* = 9.0, CH); 3.78, 3.74 (2*s*, 2 MeO). ^{13}C-NMR: 171.8, 168.1 (2*s*, 2 C=O); 145.8, 142.2, 141.2, 140.9, 140.3 (5*s*, 5 arom. C); 129.1, 128.8, 127.2, 127.1, 123.4, 122.1, 120.3, 118.5, 113.4 (9*d*, 13 arom. CH); 63.2 (*d*, CH); 55.2, 54.5 (2*s*, C(2'), C(3')); 53.3, 52.8 (2*q*, MeO). EI-MS: 432 (100, $[M+1]^+$), 400 (64, $[M-S+1]^+$), 340 (27), 339 (28), 307 (95). Anal. calc. for $C_{25}H_{21}NO_4S$ (431.51): C 69.59, H 4.91, N 3.25; found: C 70.07, H 4.76, N 3.16.

3. *Desulfurization of* **10** *and* **11**. To a soln. of **10a** or **11a** (108 mg, 0.25 mmol) in $CDCl_3$ (1 ml), hexamethylphosphorous triamide (60 mg, 0.37 mmol) was added dropwise at r.t. The colourless solns. turned yellow immediately, and complete conversion of **10a** and **11a**, resp., into **16a** was shown by ^{1}H-NMR. Both solns. were combined and evaporated, and the residual pale-yellow oil was dissolved in hexane (3 ml). After storage overnight at −20°, the clear soln. was decanted and then evaporated. ^{1}H-NMR revealed nearly pure **16a**, contaminated with traces of hexamethylphosphorothioic triamide. Further treatment with pentane afforded anal. pure *dimethyl 2-(diphenylmethylidene)-3-(phenylamino)butanedioate* (**16a**): 140 mg (70%). Pale-yellow crystals. M.p. 86–87° (hexane). IR: 3405*m* (NH), 1730v*s* (C=O), 1600*s*, 1502*s*, 1492*m*, 1446*m*, 1433*m*, 1325*w*, 1262*s*, 1238*s*, 1190*m*, 1140*s*, 1115*m*, 1070*w*, 1006*m*, 982*w*, 770*m*, 748*s*, 706*s*, 690*s*. ^{1}H-NMR: 7.4–7.35 (*m*, 3 arom. H); 7.3–7.25 (*m*, 5 arom. H); 7.1–7.0 (*m*, 4 arom. H); 6.69 (*t*-like, 1 arom. H); 6.38 (*d*-like, 2 arom. H); 5.16 (*s*, CH); 4.85 (br. *s*, NH); 3.82, 3.43 (2*s*, 2 MeO). ^{13}C-NMR: 171.9, 169.0 (2*s*, 2 C=O); 152.7, 145.9, 141.7, 140.0, 128.1 (5*s*, 3 arom. C, 2 olef. C); 129.6, 129.0, 128.8, 128.6, 128.4, 128.2, 128.0, 118.7, 114.7 (9*d*, 15 arom. CH); 58.4 (*d*, CH); 52.8, 51.7 (2*q*, 2 MeO). CI-MS (NH_3): 402 (100, $[M+1]^+$), 342 (16), 277 (69). Anal. calc. for $C_{25}H_{23}NO_4$ (401.46): C 74.79, H 5.77, N 3.49; found: C 74.18, H 5.69, N 3.35.

Analogous desulfurizations of **10b** and **11b**, resp., yielded *dimethyl 2-(9*H*-fluoren-9-ylidene)-3-(phenylamino)butanedioate* (**16b**): 112 mg (56%). Yellow crystals. M.p. 214–215° (MeOH). IR: 3370*m* (NH), 1745v*s* (C=O), 1715v*s* (C=O), 1605*s*, 1505*s*, 1450*s*, 1430*s*, 1310*s*, 1280*s*, 1260*s*, 1205*s*, 1165*s*, 1140*s*, 1110*s*, 780*m*, 755*s*, 730*s*. ^{1}H-NMR: 7.96 (*d*-like, 1 arom. H); 7.75 (*d*-like, 1 arom. H); 7.68 (*d*-like, 1 arom. H); 7.45–7.15 (*m*, 5 arom. H); 7.1–7.05 (*m*, 2 arom. H); 6.70 (*t*-like, 1 arom. H); 6.58 (*d*-like, 2 arom. H); 5.92 (br. *s*, CH); 5.08 (very br. *s*, NH); 3.82, 3.80 (2*s*, 2 MeO). ^{13}C-NMR: 170.3, 168.1 (2*s*, 2 C=O); 146.2, 141.7, 140.4, 137.8, 136.9, 136.4, 131.1 (7*s*, 5 arom. C, 2 olef. C); 129.7, 129.3, 127.5, 127.3, 126.3, 123.9, 120.0, 119.5, 118.7, 113.5 (10*d*, 13 arom. CH); 56.8 (*d*, CH); 53.4, 52.2 (2*q*, 2 MeO). CI-MS (NH_3): 400 (100, $[M+1]^+$), 368 (11, $[M-S+1]^+$), 309 (19), 293 (47). Anal. calc. for $C_{25}H_{21}NO_4$ (399.46): C 75.17, H 5.30, N 3.51; found: C 75.09, H 5.41, N 3.54.

4. *Crystal-Structure Determination of* **10a**, **11a**, *and* **16b** (see *Table* and *Figs. 1–3*[6]). The intensities were collected on a *Rigaku AFC5R* diffractometer in the $\omega/2\theta$-scan mode using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction was applied for **10a** [22]. Data collection and refinement parameters are listed in the *Table*, views of the molecules are shown in *Figs. 1* and *2*. The structures were solved by direct methods using SHELXS86 [23], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference electron density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All refinements were carried out on *F* using full-matrix least-squares procedures. A correction for secondary extinction was applied for **10a** and **11a**. Neutral atom scattering factors for non-H-atoms were taken from [24a] and the scattering factors for H-atoms from [25]. Anomalous dispersion effects were included in F_{calc} [26]; the values for *f'* and *f''* were those of [24b]. All calculations were performed using the TEXSAN crystallographic software package [27].

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[5]) Slow warming caused a partial melting below 170° and complete melting at 205–208°.

[6]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/56. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: + 44-(0)1223-336033 or e-mail: teched@ccdc.cam.ac.uk).

Table. *Crystallographic Data for Compounds* **10a**, **11a**, *and* **16b**

	10a	**11a**	**16b**
Crystallized from	methanol	methanol	methanol
Empirical formula	$C_{25}H_{23}NO_4S$	$C_{25}H_{23}NO_4S$	$C_{25}H_{21}NO_4$
Formula weight	433.52	433.52	399.44
Crystal colour, habit	colourless, prism	colourless, prism	yellow, prism
Crystal dimensions [mm]	0.20 × 0.25 × 0.50	0.20 × 0.30 × 0.43	0.28 × 0.28 × 0.43
Temperature [K]	173(1)	173(1)	173(1)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/n$
Z	8	4	4
Reflections for cell determination	25	25	25
2θ Range for cell determination [°]	36–40	38–40	37–40
Unit cell parameters a [Å]	16.368(3)	6.431(2)	10.367(4)
b [Å]	19.286(5)	20.966(2)	11.660(3)
c [Å]	13.711(7)	16.352(3)	16.650(3)
β [°]	90	91.62(3)	93.21(2)
V [Å^3]	4328(2)	2204.1(8)	2009.5(9)
$F(000)$	1824	912	840
D_x [g cm^{-3}]	1.331	1.306	1.320
$\mu(MoK_\alpha)$ [mm^{-1}]	0.182	0.178	0.0895
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	55	60
Absorption correction (min; max)	0.770; 1.121	–	–
Total reflections measured	6285	5669	6445
Symmetry-independent reflections	4968	5068	5870
Reflections used [$I > 2\sigma(I)$]	3261	3824	3451
Parameters refined	373	373	355
Final R	0.0608	0.0428	0.0530
wR	0.0563	0.0409	0.0423
Weights: p in $w = [\sigma^2(F_0) + (pF_0)^2]^{-1}$	0.005	0.005	0.005
Goodness of fit	2.215	1.671	1.788
Secondary extinction coefficient	$1.9(3) \cdot 10^{-7}$	$1.99(7) \cdot 10^{-6}$	–
Final Δ_{max}/σ	0.0002	0.0006	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]	0.53; −0.43	0.27; −0.28	0.36; −0.28
Range of $\sigma(d(C-C))$ [Å]	0.004–0.006	0.002–0.004	0.003–0.004

In **10a**, as well as in the diastereoisomer **11a**, there is an intramolecular H-bond between NH and the C=O group of the more distant ester group (graph set: S(6) [28]; distance N···O(4) 2.980(4) and 2.824(2) Å; angle N–H···O(4) 119(3) and 123(2)°, resp.). The NH group of **16b** forms bifurcated H-bonds. One interaction is an intramolecular one with the carbonyl O-atom of the immediately adjacent ester group (graph set: S(5) [28]; distance N···O(3) 2.695(2)Å, angle N–H···O(3) 108(2)°). The other very weak interaction is an intermolecular H-bond with the same carbonyl O-atom from a neighboring molecule (distance N(1)···O(3′) 3.397(3) Å, angle N(1)–H···O(3′) 160(2)°). This latter interaction links the molecules into centrosymmetric dimers (graph set: $R_2^2(10)$; *Fig. 3*), and the two interactions can be described by the binary graph set $R_2^2(4)$.

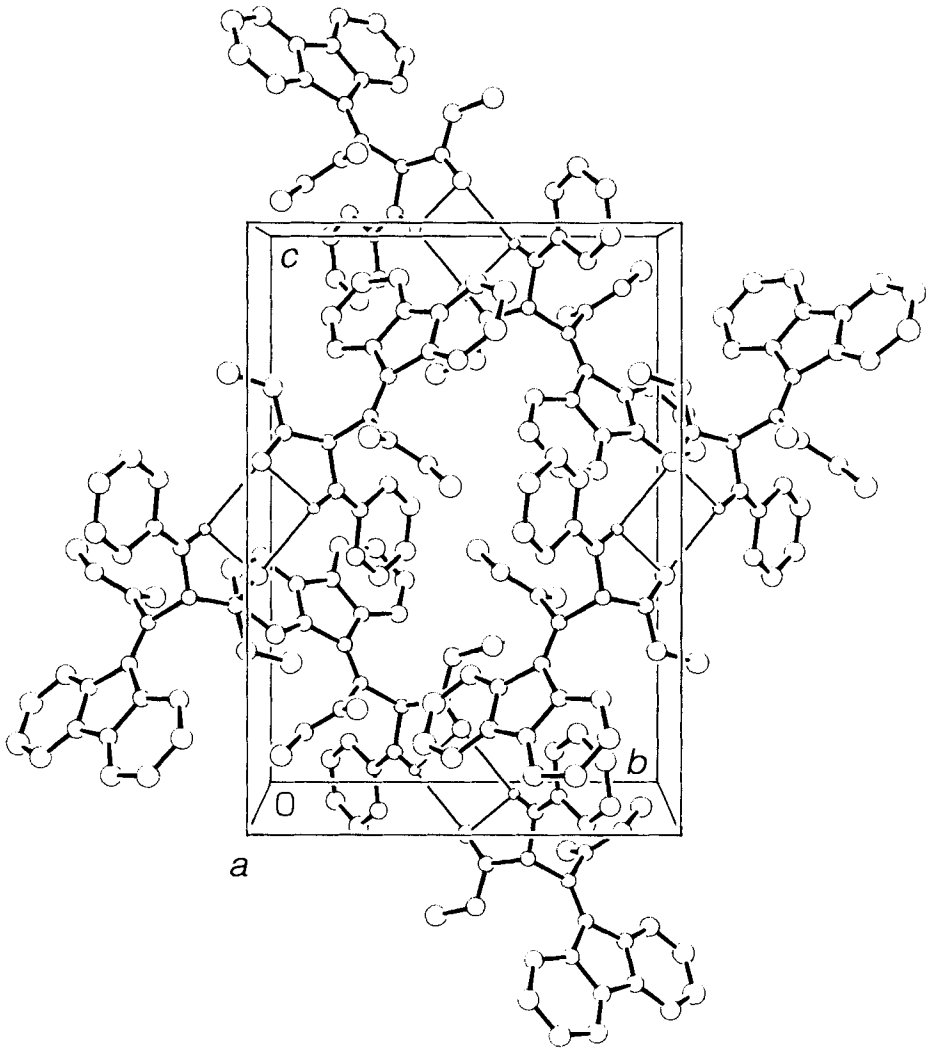

Fig. 3. *Crystal packing of* **16b**

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