

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

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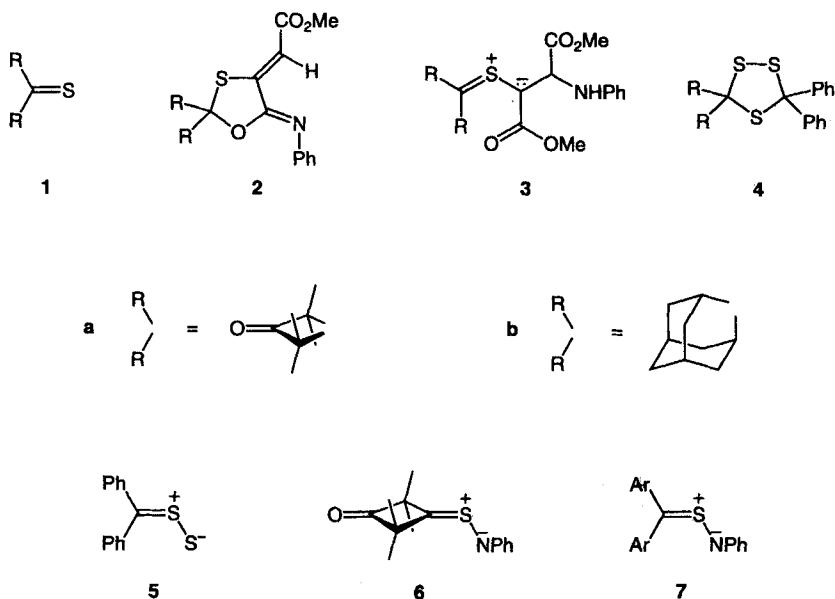
The reaction of thiobenzophenone (= diphenylmethanethione; **8a**) or 9*H*-fluorene-9-thione (**8b**) and methyl fumarate (**9**) in excess PhN₃ at 80° yields a mixture of diastereoisomeric thiiranes **10** and **11** (*Scheme 1*). A mechanism involving the initial formation of 1-phenyl-4,5-dihydro-1*H*-1,2,3-triazole-4,5-dicarboxylate **12** by 1,3-dipolar cycloaddition of PhN₃ 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 N₂ 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 PhN₃, 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 electrocycloization, afforded the 1,3-oxathiolane derivative. Following a similar protocol with the cycloalkanethiones **1a**, **b**, and thiobenzophenone in excess PhN₃, 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 PhN₃ 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**.

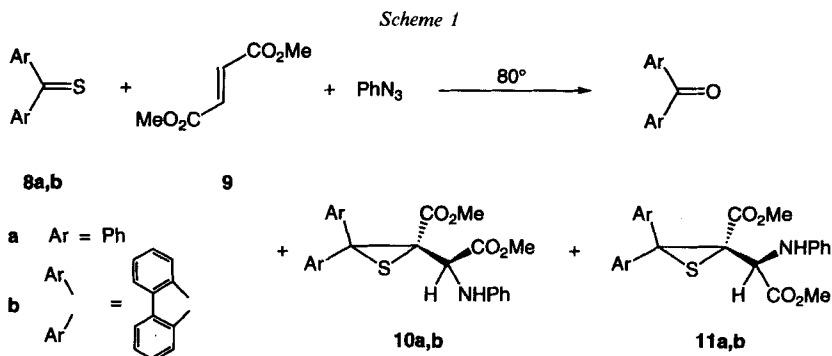
Results and Discussion. – When a mixture of equimolar amounts of **8a** and **9** in excess PhN_3 was heated to 80° , the blue color of **8a** disappeared within *ca.* 40 min. Examination of the crude mixture by means of ^1H -NMR spectroscopy (CDCl_3) revealed the presence of two isomeric thiiranes **10a** and **11a** in a ratio of *ca.* 55:45 ($\delta(\text{H})$ 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*-(diphenylmethyldene)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⁾.

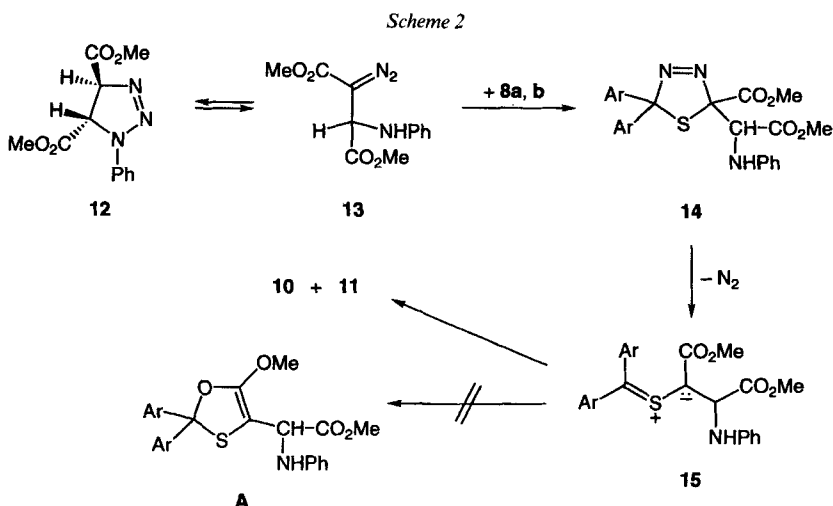
To increase the yield of **10a** and **11a**, we elaborated a two-step procedure in which PhN_3 and **8** were first reacted to give a mixture of the initial cycloadduct **12** and the

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].



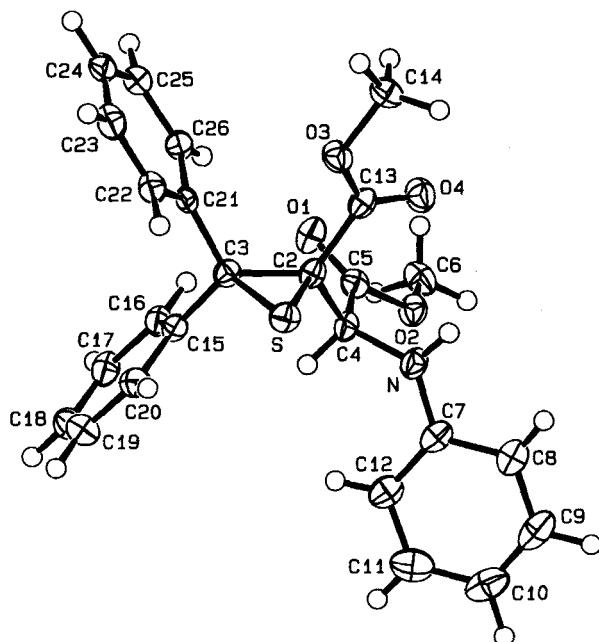
isomeric diazo compound **13** [9] (Scheme 2). It is well-known that diazo compounds react very efficiently with thioketones [10–13]. Therefore, the initial product of the [2 + 3] cycloaddition of **8a** and **13** is most likely the 2,5-dihydro-1,3,4-thiadiazole **14**⁴ which easily extrudes N₂ to give 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*)-configured thiocarbonyl ylide.



A similar mixture of thiiranes **10b** and **11b** was formed in the reaction of **12/13** and 9H-fluorene-9-thione (**8b**). The ratio of the products was determined in the crude mixture by ¹H-NMR (δ(H) of CO₂Me at 3.68 and 3.17 ppm for the major and at 3.78 and 3.74 ppm for the minor isomer).

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].

a)



b)

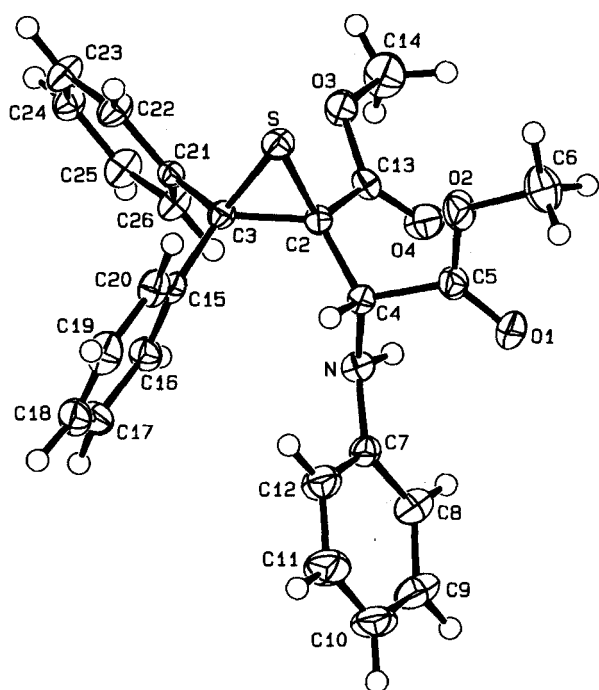


Fig. 1. ORTEP plots [6] of the molecular structure of a) 10a and b) 11a (ellipsoids with 50% probability)

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 electrocyclicization 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-

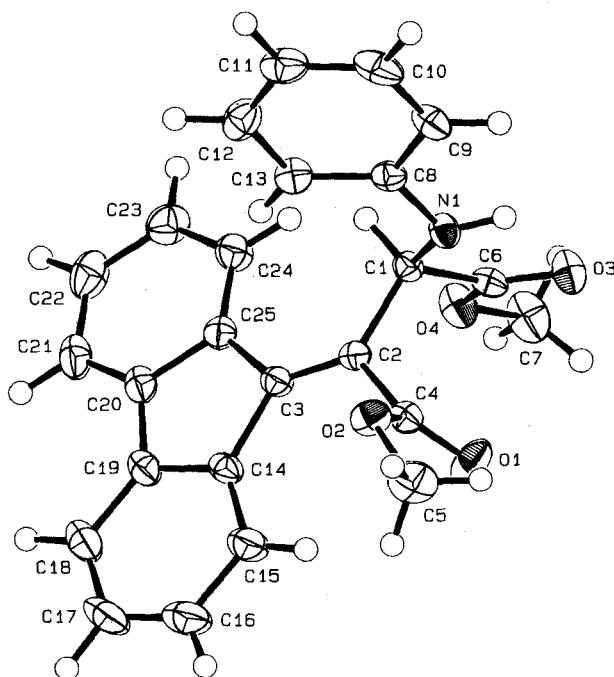
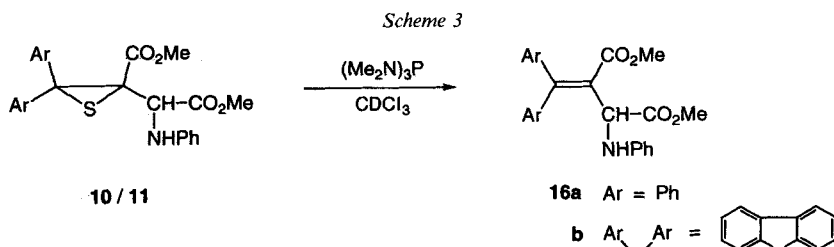


Fig. 2. ORTEP plot [6] of the molecular structure of **16b** (ellipsoids with 50% probability)

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).

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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-fluorene-9-one by treatment with $\text{H}_2\text{S}/\text{HCl}$ 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 $60^\circ/0.1$ 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 $60^\circ/0.1$ Torr, and the residue was stored in a closed flask for 7 days at 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 , Et₂O/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. $110\text{--}111^\circ$ (MeOH). IR: 3320m (br, NH), 1740vs (C=O), 1700vs (C=O), 1600s, 1520s, 1490m, 1440m, 1320m, 1310s, 1280s, 1260m, 1240m, 1010m, 780s, 720s. ^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 (2s, 2 MeO). ^{13}C -NMR: 171.2, 170.4 (2s, 2 C=O); 147.3, 141.4, 138.1 (3s, 3 arom. C); 129.8, 129.0, 127.9, 127.7, 127.3, 118.9, 114.0 (7d, 15 arom. CH); 66.6, 60.1 (2s, C(2), C(3)); 61.3 (d, C(x)); 52.6, 52.3 (2q, MeO). EI-MS: 433 (10, M^+) 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 $\text{C}_{25}\text{H}_{23}\text{NO}_4\text{S}$ (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. $99\text{--}101^\circ$ (MeOH). IR: 3380m (NH), 1740s (C=O), 1710s (C=O), 1602s, 1505s, 1430s, 1350–1200s (br.), 1150m, 955s, 755s, 715s, 680s. ^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 (2s, 2 MeO). ^{13}C -NMR: 171.9, 170.8 (2s, 2 C=O); 146.1, 140.7, 137.7 (3s, 3 arom. C); 129.8, 128.7, 128.1, 128.0, 127.7, 127.5, 118.3, 113.6 (8d, 15 arom. CH); 62.5 (d, C(x)); 65.1, 55.3 (2s, C(2), C(3)); 52.8, 52.4 (2q, 2 MeO). CI-MS (NH_3): 434 (100, $[M + 1]^+$), 402 (24, $[M - S + 1]^+$), 341 (20), 277 (14). Anal. calc. for $\text{C}_{25}\text{H}_{23}\text{NO}_4\text{S}$ (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. $177\text{--}170^\circ$ (MeOH). IR: 3390m (NH), 1730vs (br., C=O), 1605vs (C=O), 1520s, 1505s, 1450s, 1435s, 1310vs (br.), 1230vs, 1250vs, 1150s, 1075s, 745s, 730vs, 690s. ^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 (2s, 2 MeO). ^{13}C -NMR: 170.2, 168.0 (2s, 2 C=O); 147.3, 143.3, 142.3, 141.4, 141.1 (5s, 5 arom. C); 129.4, 129.0, 128.6, 127.2, 127.0, 123.9, 122.4, 120.1, 119.7, 114.9 (10d, 13 arom. CH); 63.1 (d, CH); 59.2, 56.2 (2s, C(2'), C(3')); 53.1, 52.5 (2q, 2 MeO). CI-MS (NH_3): 432 (61, $[M + 1]^+$), 400 (100, $[M - S + 1]^+$), 307 (11). Anal. calc. for $\text{C}_{25}\text{H}_{21}\text{NO}_4\text{S}$ (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[9H-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: 3380m (NH), 1746vs (C=O), 1720vs (C=O), 1600s, 1515s, 1510s, 1450s, 1435s, 1330m, 1305s, 1260s (br.), 750s, 730vs. ^1H -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 (2s, 2 MeO). ^{13}C -NMR: 171.8, 168.1 (2s, 2 C=O); 145.8, 142.2, 141.2, 140.9, 140.3 (5s, 5 arom. C); 129.1, 128.8, 127.2, 127.1, 123.4, 122.1, 120.3, 118.5, 113.4 (9d, 13 arom. CH); 63.2 (d, CH); 55.2, 54.5 (2s, C(2'), C(3')); 53.3, 52.8 (2q, MeO). EI-MS: 432 (100, $[M + 1]^+$), 400 (64, $[M - S + 1]^+$), 340 (27), 339 (28), 307 (95). Anal. calc. for $\text{C}_{25}\text{H}_{21}\text{NO}_4\text{S}$ (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 ^1H -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. ^1H -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: 3405m (NH), 1730vs (C=O), 1600s, 1502s, 1492m, 1446m, 1433m, 1325w, 1262s, 1238s, 1190m, 1140s, 1115m, 1070w, 1006m, 982w, 770m, 748s, 706s, 690s. ^1H -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 (2s, 2 MeO). ^{13}C -NMR: 171.9, 169.0 (2s, 2 C=O); 152.7, 145.9, 141.7, 140.0, 128.1 (5s, 3 arom. C, 2 olef. C); 129.6, 129.0, 128.8, 128.6, 128.4, 128.2, 128.0, 118.7, 114.7 (9d, 15 arom. CH); 58.4 (d, CH); 52.8, 51.7 (2q, 2 MeO). CI-MS (NH_3): 402 (100, $[M + 1]^+$), 342 (16), 277 (69). Anal. calc. for $\text{C}_{25}\text{H}_{23}\text{NO}_4$ (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-(9H-fluoren-9-ylidene)-3-(phenylamino)butanedioate (16b)*: 112 mg (56%). Yellow crystals. M.p. 214–215° (MeOH). IR: 3370m (NH), 1745vs (C=O), 1715vs (C=O), 1605s, 1505s, 1450s, 1430s, 1310s, 1280s, 1260s, 1205s, 1165s, 1140s, 1110s, 780m, 755s, 730s. ^1H -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 (2s, 2 MeO). ^{13}C -NMR: 170.3, 168.1 (2s, 2 C=O); 146.2, 141.7, 140.4, 137.8, 136.9, 136.4, 131.1 (7s, 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 (10d, 13 arom. CH); 56.8 (d, CH); 53.4, 52.2 (2q, 2 MeO). CI-MS (NH_3): 400 (100, $[M + 1]^+$), 368 (11, $[M - S + 1]^+$), 309 (19), 293 (47). Anal. calc. for $\text{C}_{25}\text{H}_{21}\text{NO}_4$ (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].

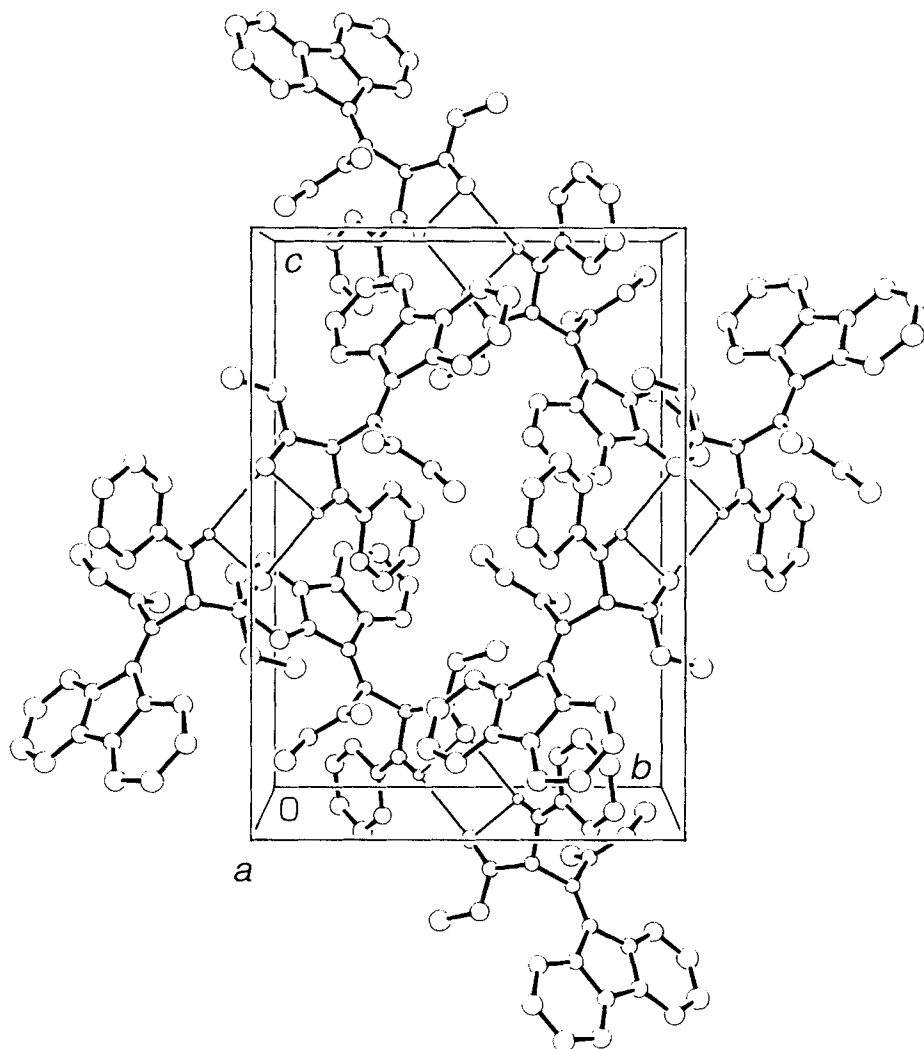
⁵⁾ Slow warming caused a partial melting below 170° and complete melting at 205–208°.

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 ₄ S	C ₂₅ H ₂₃ NO ₄ S	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	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>Z</i>	8	4	4
Reflections for cell determination	25	25	25
2 θ Range for cell determination [°]	36–40	38–40	37–40
Unit cell parameters			
<i>a</i> [Å]	16.368(3)	6.431(2)	10.367(4)
<i>b</i> [Å]	19.286(5)	20.966(2)	11.660(3)
<i>c</i> [Å]	13.711(7)	16.352(3)	16.650(3)
β [°]	90	91.62(3)	93.21(2)
<i>V</i> [Å ³]	4328(2)	2204.1(8)	2009.5(9)
<i>F</i> (000)	1824	912	840
<i>D_x</i> [g cm ^{−3}]	1.331	1.306	1.320
μ (MoK α) [mm ^{−1}]	0.182	0.178	0.0895
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2 $\theta_{\text{(max)}}$ [°]	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>I</i> > 2 σ (<i>I</i>)]	3261	3824	3451
Parameters refined	373	373	355
Final <i>R</i>	0.0608	0.0428	0.0530
<i>wR</i>	0.0563	0.0409	0.0423
Weights: <i>p</i> in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.005	0.005
Goodness of fit	2.215	1.671	1.788
Secondary extinction coefficient	1.9(3) · 10 ^{−7}	1.99(7) · 10 ^{−6}	–
Final $\Delta_{\text{max}}/\sigma$	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 σ (<i>d</i> (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: R₂²(10); Fig. 3), and the two interactions can be described by the binary graph set R₂²(4).

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

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