111. Three-Component Reactions with Sterically Crowded 2,2,4,4-Tetramethyl-3-thioxocyclobutanone, Phenyl Azide, and Electron-Deficient C,C-Dipolarophiles[1]

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Dedicated to Professor *Vladimir Prelog* on the occasion of his 90th birthday

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In order to trap 'thiocarbonyl-aminides' **A**, formed as intermediates in the reaction of thiocarbonyl compounds with phenyl azide, a mixture of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**), phenyl azide, and fumarodinitrile (**8**) was heated to 80° until evolution of N_2 ceased. Two interception products of the 'thiocarbonyl-aminide' A (Ar = Ph) were formed: the known 1,4,2-dithiazolidine **3** (*cf. Scheme 1*) and the new 1,2-thiazolidine **12** (*Scheme 2*). The structure of the latter was established by X-ray crystallography (*Fig. 1*). The analogous 'three-component reaction' with dimethyl fumarate (**9**) yielded, instead of **8**, in addition to the known interception products **3** and **6** (*Scheme 1*), two unexpected products **15** and **16** (*Scheme 3*), of which the structures were elucidated by X-ray crystallography (*Fig. 2*). Their formation is rationalized by a primary [2 + 3] cycloaddition of diazo compound **18** with **1** to give **19**, followed by a cascade of further reactions (*Scheme 4*).

1. Introduction. – In a series of recent papers, we described results of reactions of thiocarbonyl compounds with organic azides. Generally, the primary [2 + 3] cycloadduct easily eliminated N_2 under the reaction conditions (80°, neat) to generate the corresponding 'thiocarbonyl-aminide' (*N*-(alkylidenesulfonio)aminide)[2]. Further transformation is strongly dependent on the substituents attached to the thiocarbonyl C-atom and the aminide N-atom. In general, ring closure of the 'thiocarbonyl-aminide' to give an unstable thiaziridine intermediate, followed by a spontaneous desulfurization resulted in the formation of the imine derivative [1–5] (and refs. cit. therein).

When thioketone **1** was reacted with aryl azides **2** (R = Ar), the intermediate 'thiocarbonyl-aminide' **A** was trapped by unconsumed **1** to afford 1,4,2-dithiazolidines **3** [6] (*Scheme 1*). In the case of benzyl-substituted azides **2** (R = $ArCH_2$), the S-centered 1,3-dipole **A** underwent a rearrangement *via* a 1,4-H shift to give thiooxime *S*-ethers of type **4** [2]. Furthermore, transfer of an S-atom from thiaziridines **B** to **1** gave imines **5** and an intermediate 'thiocarbonyl-thiolate' **C**, which effectively added to C=S bonds to form

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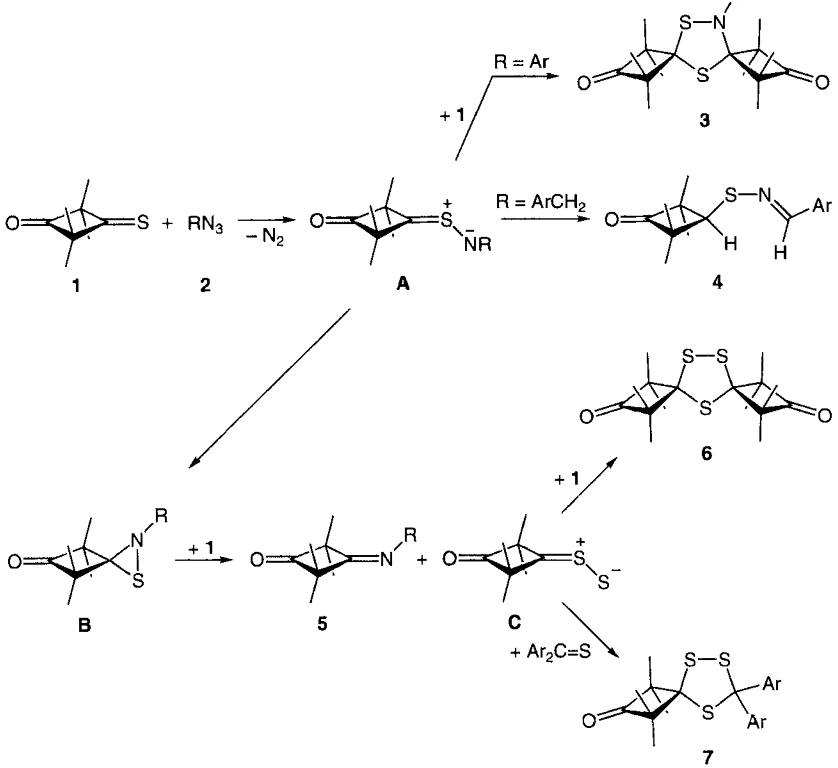
[1] Presented by *G.M.* at the '17th International Symposium on the Organic Chemistry of Sulfur', Tsukuba, Japan, July 1996.

[2] The names 'thiocarbonyl-aminide' and 'thiocarbonyl-thiolate' are short forms for '*N*-(alkylidenesulfonio)aminide' and '*S*-(alkylidenesulfonio)thiolate', respectively; commonly these classes of S-centered 1,3-dipoles are named 'thiocarbonyl *S*-imides' and 'thiocarbonyl *S*-sulfides', respectively.

1,2,4-trithiolane **6** [3] (for comparison, see [5]). When a similar reaction was carried out in the presence of an aromatic thioketone (three-component system), mixed 1,2,4-trithiolanes of type **7** were formed in good yields [3].

Scheme 1

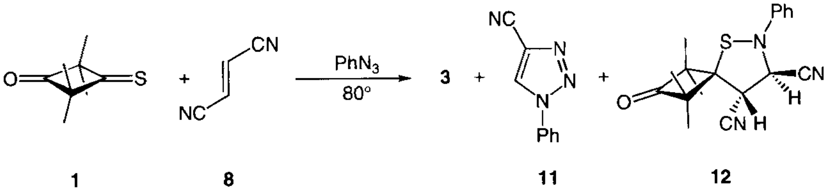


Thioketones are known as 'super-dipolarophiles' [7], and the formation of interception products of type **3**, **6**, and **7** confirmed their high reactivity towards S-centered 1,3-dipoles. From the synthetic point of view, it was desirable to examine whether or not other well known C,C-dipolarophiles can be similarly used to trap the intermediate 'thiocarbonyl *S*-imides' and 'thiocarbonyl *S*-sulfides', respectively. The successful trapping would open a new access to S-heterocycles in a simple one-pot reaction with three components.

2. Results and Discussion. – Several years ago, *Huisgen* and coworkers showed that 'thiocarbonyl *S*-methanides' react very efficiently with electron-deficient C,C-dipolarophiles to give the corresponding [2 + 3] cycloadducts [8] [9]. Based on these results, we expected a similar reactivity of other S-centered 1,3-dipoles. For this reason, and in order to trap 'thiocarbonyl *S*-imides' **A** and/or 'thiocarbonyl *S*-sulfides' **C** derived from thioketone **1**, we chose for our studies well known and easily accessible dipolarophiles, such as fumarodinitrile (**8**), dimethyl fumarate (**9**), and dimethyl acetylenedicarboxylate (**10**). The results obtained with these dipolarophiles differed significantly.

A solution of equimolar amounts of **1** and **8** in an excess of phenyl azide (PhN_3) was heated until the red color of the solution disappeared and N_2 evolution ceased. After removing excess PhN_3, the mixture was analyzed by means of ^1H-NMR spectroscopy: 2 *d*'s at 4.89 and 4.23 ppm with $J = 2.6$ Hz and 4 *s*'s for nonequivalent Me groups at 1.68, 1.63, 1.50, and 1.27 pm revealed the presence of an interception product. In addition to these signals, a characteristic *s* at high field (0.47 ppm) indicated that the previously described **3** [6] was also formed. Chromatographic workup afforded **3**, 1-phenyl-1*H*-1,2,3-triazole-4-carbonitrile (**11**), and the 1,2-thiazolidine derivative **12** (*Scheme 2*). The three products were isolated in almost equal amounts. Their structures were elucidated by means of the spectral data, and in the case of the interception product **12**, the structure was confirmed by X-ray crystallography (*Fig. 1*).

Scheme 2



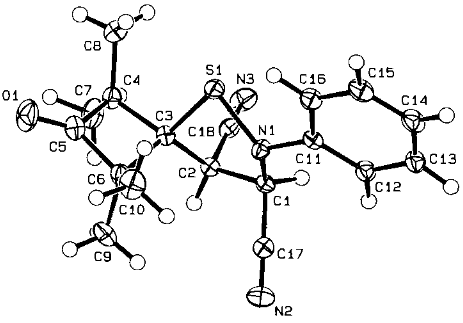


Fig. 1. *ORTEP Plot* [10] *of one of the two independent molecules of 1,2-thiazolidine* **12** *in the asymmetric unit* (with 50% probability ellipsoids)

The route leading to **3** was discussed in detail in one of our previous papers [6] and is depicted in *Scheme 1*. The triazole **11** results from a 1,3-dipolar cycloaddition of PhN_3 with **8**, followed by elimination of HCN from the primary adduct [11]. The third compound **12** is the expected interception product of the three-component reaction. Its formation can be rationalized by a [2 + 3] cycloaddition of intermediate **A** with **8**[3]). The crystal structure shows the *trans* configuration of the CN groups and, therefore, we conclude that the stereospecific cycloaddition occurs in a concerted manner. As the yields of **3** and **12** are almost equal, one may conclude that the dipolarophilic reactivity of **1** and **8** towards **A** must be similar.

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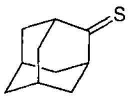
[3]) Recently, *Roesky et al.* described 1,3-dipolar cycloadditions of a stable bis(trifluoromethyl)-substituted 'thiocarbonyl *S*-imide' with some alkenes [12].

In many reactions with S-centered 1,3-dipoles, **1** and adamantanethione (**13**) behaved similarly [13–15]. For this reason, we compared the behavior of **1** and **13** in the three-component reaction with PhN_3 and **8**. At 80°, the reaction with **13** was completed after 4 h, and no interception product of 'adamantanethione *S*-imide' **D** could be detected. Similar to the results described in [5], dispirotrithiolane **14** was found as the major product; **8** was transformed into triazole **11** exclusively. Obviously, **D** undergoes a very rapid cyclization to the corresponding thiaziridine. The subsequent reaction steps, which result in the formation of **14**, correspond with the mechanism presented in detail in [5]. In contrast to **D**, 'thiocarbonyl *S*-imide' **A** seems to be much more stable (*cf.* discussion in [2]) and is sufficiently long lived to be trapped by **8**.



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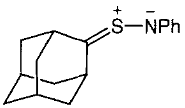
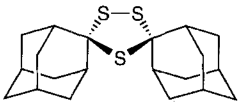


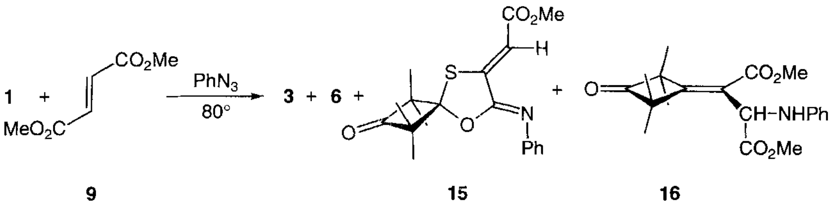
D



14

A similar reaction with dimethyl fumarate (**9**), PhN_3, and **1** resulted in a mixture of the four compounds **3**, **6**, **15**, and **16** (*Scheme 3*), which were separated chromatographically. The formation of **3** and **6** can be rationalized *via* intermediates **A** and **C** (*Scheme 1*). In fact, **15** and **16** are products of a 'three-component reaction'; however, their structures do not correspond with the expected interception product of **A** with **9**. Whereas **15** shows only one ester group in the NMR spectra, compound **16** contains two nonequivalent ester moieties. Furthermore, the different symmetry of **15** and **16** is evidenced by the pattern of Me absorptions (^{1}H-NMR: 2 *s* at 1.50 and 1.27 ppm for **15**, and 3*s* at 1.53, 1.44, and 1.39 ppm in the ratio of 1:2:1 for **16**). The elucidation of both structures was achieved by single-crystal X-ray structure determinations (*Fig. 2*).

Scheme 3



A reaction mechanism for the formation of **15** and **16** is proposed in *Scheme 4*. Dimethyl fumarate (**9**) exceeds **1** in reactivity towards PhN_3, and the rapid formation of the triazole derivative **17** is of crucial importance for the course of further conversion. The spontaneous ring opening of **17** to give the diazo compound **18** was studied by *Huisgen* and coworkers many years ago [16]. Furthermore, diazo compounds were shown to be superior reagents for the transformation of thioketones into mostly unstable 2,5-dihydro-1,3,4-thiadiazoles which, by elimination of N_2, generate reactive 'thiocarbonyl ylides' [9] [15] [17] [18]. In an analogous way, **18** reacts with **1** to give the cyclo-

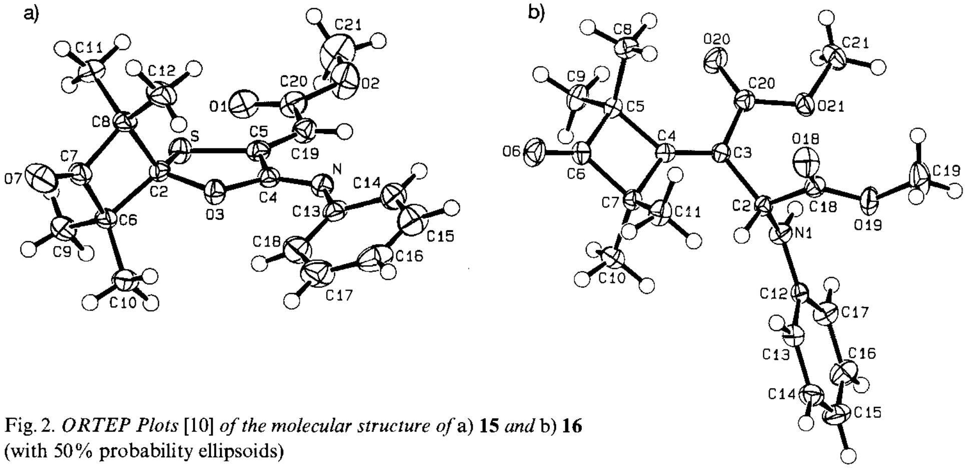
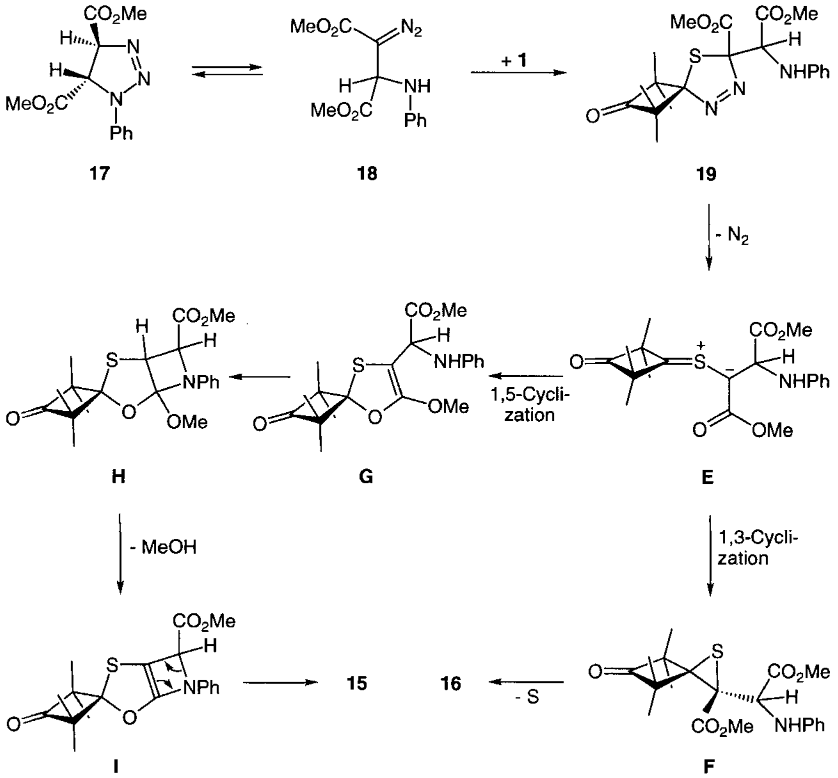


Fig. 2. *ORTEP Plots* [10] *of the molecular structure of* a) **15** *and* b) **16** (with 50% probability ellipsoids)

adduct **19**, and elimination of N_2 yields the 1,3-dipole **E**. This intermediate can undergo two different intramolecular reactions, namely a 1,3- and/or a 1,5-dipolar cyclization (*cf.* [15] [19]). The former results in the formation of thiirane **F** which spontaneously extrudes

Scheme 4

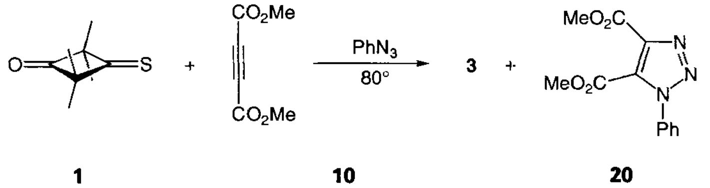


sulfur to give olefin **16**. As discussed in our recent paper on trithiolane formation [3], **1** can intercept atomic sulfur to generate 'thiocarbonyl *S*-sulfide' **C**, which reacts with a second molecule of **1** to yield trithiolane **6** (*Scheme 1*). The 1,5-dipolar cyclization of **E** to give 1,3-oxathiolane **G** initiates a cascade of reactions. We propose that the formation of **15** involves a ring closure of **G** to the spirobicyclic azetidine derivative **H**, elimination of MeOH, and electrocyclic ring opening of **I**.

With the aim of avoiding formation of **3** and **6**, as well as to improve the yield of **15** and **16**, we elaborated a two-step procedure including a preliminary formation of **17**/**18** from PhN_3 and **9**. After five days at room temperature, **18** was the major component in the equilibrium, and the mixture was treated with an equimolar amount of **1**. Under these conditions, **15** and **16** were formed in 42% yield each. Similarly, the formation of a 1-azabuta-1,3-diene derivative of type **15** was also found in a three-component reaction with adamantanethione (**13**), **9**, and PhN_3 [20].

As a third dipolarophile, we tested dimethyl acetylenedicarboxylate (**10**) in the reaction with **1** and PhN_3 (*Scheme 5*). The ^1H-NMR analysis of the reaction mixture revealed the presence of only one product, besides **3**, which contains ester functions. After treatment of the mixture with MeOH, the known crystalline dimethyl 1-phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate (**20**) was obtained in good yield. This result indicates that **10** reacts much faster with PhN_3 than with thioketone **1**[4]).

Scheme 5



In conclusion, the presented results show that the course of 'three-component reactions' with **1**, PhN_3, and a C,C-dipolarophile depends strongly on the type of the dipolarophile. As **8** is an efficient trapping reagent for 'thiocarbonyl *S*-imides' of type **A**, the interception product **12** was obtained in good yield. Dimethyl fumarate (**9**) combines faster with PhN_3 than with **1**. The transformation of the primary cycloadduct **17** into **18** generated a new 1,3-dipole (diazo compound), which exceeded PhN_3 in reactivity towards **1**.

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 157 10), the *Swiss National Science Foundation*, and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *G. M.* thanks Mrs. *M. Celeda* for technical assistance.

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[4]) In a separate experiment, it was shown that **10**, dissolved in PhN_3 and heated to 80°, disappeared completely after *ca.* 10 min; the only product in the mixture was **20**.

Experimental Part

1. *General.* See [6]. 2,2,4,4-Tetramethyl-3-thioxocyclobutanone (**1**) was prepared from the corresponding dione by treatment with P_2S_5 in boiling pyridine [6]; adamantanethione (**13**) was synthesized in the same way according to [21]. PhN_3 was prepared by diazotation of phenylhydrazine [22]. M.p.'s: in capillaries; uncorrected.

2. *Reactions of* **1** *with Phenyl Azide in the Presence of a C,C-Dipolarophile.* 2.1. *General Procedure.* In freshly distilled PhN_3 (1 ml, 1.1 g, *ca.* 9.2 mmol), **1** (316.5 mg, 2 mmol) and the respective dipolarophile (2 mmol) were dissolved. The red mixture was heated with an external oil bath (80°) under stirring. Evolution of N_2 was followed volumetrically using a gas burette attached to the reaction flask. Reactions were interrupted when the evolution of N_2 ceased (corresponding times and amount of N_2 in parentheses). Excess PhN_3 was removed at 80–90°/0.6 Torr ('Kugelrohr'), and the residues were separated chromatographically or treated with small amounts of MeOH to afford crystallization.

2.2. *Reaction with Fumarodinitrile* (**8**; 10 h, 35 ml of N_2, *i.e. ca.* 70% of calc. amount). Prep. TLC (SiO_2, CH_2Cl_2/petroleum ether 7:3) afforded **3** (160 mg, 43% rel. to **1**), **11** (100 mg, 29% rel. to **8**), and **12** (160 mg, 25%).

1,1,3,3,7,7,9,9-Octamethyl-11-phenyl-5,10-dithia-11-azadispiro[3.1.3.2]undecane-2,8-dione (**3**): $R_f \approx 0.7$. M.p. 139–141° ([6]: 140–142°).

*1-Phenyl-1*H*-1,2,3-triazole-4-carbonitrile* (**11**): $R_f \approx 0.5$. Recrystallization from MeOH gave pale yellow crystals. M.p. 120–122° ([11]: 123°).

trans-*1,1,3,3-Tetramethyl-6-phenyl-2-oxo-5-thia-6-azaspiro[3.4]octane-7,8-dicarbonitrile* (**12**): $R_f \approx 0.2$. Thick oil which, after recrystallization from MeOH, gave colorless prisms. M.p. 142–144°. IR (KBr): 2980*m* (br.), 2250*w* (C≡N), 1791v*s* (C=O), 1596v*s*, 1498v*s*, 1465*s*, 1386*m*, 1369*m*, 1286*s* (br.), 1177*m*, 1030*m*, 982*m*, 690*s*, 688*s*. ^{1}H-NMR ($CDCl_3$): 7.35–7.25, 7.05–7.0 (2*m*, 5 arom. H); 4.89 (*d*, *J* = 2.6, H–C(7)); 4.24 (*d*, *J* = 2.6, H–C(8)); 1.68, 1.63, 1.50, 1.27 (4*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 214.8 (*s*, C=O); 144.0 (*s*, 1 arom. C); 129.8, 122.0, 116.6 (3*d*, 5 arom. CH); 116.9, 115.6 (2*s*, 2 CN); 68.7, 61.9, 57.4 (3*s*, C(1), C(3), C(4)); 44.0 (*d*, C(8)); 22.5, 22.1, 22.0, 20.4 (4*s*, 4 Me). CI-MS (NH_3): 343 (100, $[M + NH_4]^+$), 326 (54, $[M + 1]^+$), 325 (22, $M^{+\cdot}$), 309 (5), 299 (30). Anal. calc. for $C_{18}H_{19}N_3OS$ (325.43): C 66.43, H 5.88, N 12.91, S 9.85; found: C 66.46, H 5.99, N 12.92, S 10.10.

2.3. *Reaction with Dimethyl Fumarate* (**9**; 5 h, 40 ml of N_2, *i.e. ca.* 80% of calc. amount). After evaporation of unconsumed PhN_3, the residue was triturated with 2 ml MeOH and the mixture cooled in the refrigerator: 171 mg (46%) of crystalline **3**. M.p. 141–143° [6]. The mother liquor was chromatographed (SiO_2, column, petroleum ether with increasing amount of CH_2Cl_2), yielding with petroleum ether/CH_2Cl_2 8:2, 83 mg (24%) of *1,1,3,3,7,7,9,9-octamethyl-5,10,11-trithiadispiro[3.1.3.2]undecane-2,8-dione* (**6**; m.p. 100–102° ([3]: 101–103°)), and with petroleum ether/CH_2Cl_2 6:4, 288 mg (40%) of **15** and traces (*ca.* 1–2%) of **16**.

A soln. of **9** (288 mg, 2 mmol) in PhN_3 (1 ml, 1.1 g, *ca.* 9.2 mmol) was heated for 1 h with an external oil bath (80°). The excess PhN_3 was removed by bulb-to-bulb distillation at 60°/0.1 Torr, and the residue was left to stand for 5 d at r.t. After this period, the oily mixture contained **17** and **18** in a ratio of 15:85 (^{1}H-NMR). This mixture was treated with **1** (316.5 mg, 2 mmol), and the red mixture was heated for 2 h to 80° (45 ml of N_2, *ca.* 90% of calc. amount). After cooling to r.t., MeOH (3 ml) was added and the soln. cooled in the refrigerator. After *ca.* 15 h, **15** (302 mg, 42%) was collected. Column chromatography of the mother liquor (SiO_2, petroleum ether/CH_2Cl_2 6:4) afforded **16** (302 mg, 42%).

Methyl [(Z,Z)-1,1,3,3-Tetramethyl-2-oxo-6-(phenylimino)-5-oxa-8-thiaspiro[3.4]octan-7-yliden]acetate (**15**): Pale yellow crystals. M.p. 124–125° (MeOH): IR (KBr): 1780v*s* (ketone C=O), 1700*s* (ester C=O), 1665*s* (C=N), 1600*s* (C=C), 1435*m*, 1315v*s*, 1250*s*, 1200*s*, 1168*s*, 1070*s*, 1025*s*, 838*m*, 760*m*, 690*m*. ^{1}H-NMR ($CDCl_3$): 7.35–7.15 (*m*, 5 arom. H); 7.00 (*s*, =CH); 3.85 (*s*, MeO); 1.38, 1.14 (2*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 216.7 (*s*, C=O); 167.5 (*s*, *C*O$_2$Me); 152.9, 146.8 (2*s*, C(4), C(5)); 144.7 (*s*, 1 arom. C); 128.8, 125.5, 123.4 (3*d*, 5 arom. CH); 111.4 (*d*, =CH); 98.3 (*s*, C(2)); 66.6 (*s*, C(2′), C(4′)); 52.1 (*q*, MeO); 23.1, 18.1 (2*s*, 4 Me). CI-MS (NH_3): 360 (100, $[M + 1]^+$), 289 (6). Anal. calc. for $C_{19}H_{21}NO_4S$ (359.43): C 63.49, H 5.89, N 3.90, S 8.92; found: C 63.57, H 5.84, N 3.79, S 9.13.

Dimethyl 2-(Phenylamino)-3-(2,2,4,4-tetramethyl-3-oxocyclobutylidene)butanedioate (**16**): Colorless crystals. M.p. 97–99° (EtOH). IR (KBr): 3400–3350*m* (NH), 1790*s* (ketone C=O), 1730*s*, 1710*s* (2 ester C=O), 1660*m*, 1600*m* (C=C), 1515*m*, 1430*m*, 1320*m*, 1310*m*, 1295*s*, 1270*s*, 1250*s*, 1200*m*, 1140*m*, 1000*m*, 760*m*. ^{1}H-NMR ($CDCl_3$): 6.8–6.65, 7.25–7.15 (2*m*, 5 arom. H); 4.85 (br. *s*, NH); 3.80, 3.72 (2*s*, 2 MeO); 1.44 (*s*, 2 Me); 1.52, 1.39 (2*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 218.8 (*s*, C=O); 171.8, 166.7, 165.7 (3*s*, 2 *C*O$_2$Me, C(3)); 146.6 (*s*, 1 arom. C); 124.6 (*s*, C(3′)); 129.3, 118.9, 114.0 (3*d*, 5 arom. CH); 64.4, 63.4 (2*s*, C(2′), C(4′)); 56.9 (*d*, C(2)); 52.7, 51.8 (2*q*, 2 MeO); 22.7, 22.3, 21.2, 20.9 (4*q*, 4 Me). EI-MS: 359 (11, $M^{+\cdot}$), 301 (17), 300 (100, $[M - CO_2Me]^+$), 272 (18), 240 (16), 212 (22), 104 (11), 91 (6), 77 (7). Anal. calc. for $C_{20}H_{25}NO_5$ (359.40): C 66.83, H 7.01, N 3.89; found: C 67.01, H 6.79, N 3.95.

2.4. *Reaction with Dimethyl Acetylenedicarboxylate* (**10**, 4 h; *ca.* 30 ml of N_2, *i.e. ca.* 60% of calc. amount). After evaporation of excess PhN_3 under vacuum, the crystalline residue was triturated with EtOH (2 ml): 450 mg (86%) of *dimethyl 1-phenyl-1*H*-1,2,3-triazole-4,5-dicarboxylate* (**20**). Colorless crystals. M.p. 125–127° ([23]: 126–127°).

The mother liquor was evaporated and the residue analyzed by ^{1}H-NMR. A characteristic set of *s*'s at 2.0–0.5 ppm revealed the presence of **3**, and no product with MeO groups could be detected.

3. *Attempted Interception of Adamantanethione* S-*Imide and* S-*Sulfide with* **8**. In analogy to *Exper. 2.1*, adamantanethione (**13**; 332 mg, 2 mmol) and an equimolar amount of **8** in PhN_3 (1 ml, 1.1 g, *ca.* 9.2 mmol) were heated to 80°. After removing excess PhN_3, the solid residue was treated wit MeOH (2 ml): 280 mg (77%) of *dispiro[tricyclo[3.3.1.1^{3,7}]decane-2,3'-[1,2,4]trithiolane-5',2''-tricyclo[3.3.1.1^{3,7}]decane]* (**14**). Colorless crystals. M.p. 186–188° ([5]: 187–189°).

The mother liquor was concentrated and the residue separated by prep. TLC (SiO_2, petroleum ether/CH_2Cl_2 1:1): 40 mg (14%) of adamantanone (m.p. 253–255°; [24]: 256–258°), 20 mg (5%) of **14**, and 100 mg (29%) of **11**.

Table. *Crystallographic Data for Compounds* **12**, **15**, *and* **16**

	12	**15**	**16**
Crystallized from	MeOH	MeOH/CH_2Cl_2	EtOH
Empirical formula	$C_{18}H_{19}N_3OS$	$C_{19}H_{21}NO_4S$	$C_{20}H_{25}NO_5$
Formula weight	325.43	359.44	359.42
Crystal color, habit	colorless, prism	colorless, irregular prism	colorless, prism
Crystal dimensions [mm]	0.23 × 0.23 × 0.50	0.30 × 0.35 × 0.40	0.23 × 0.25 × 0.45
Crystal temp. [K]	173(1)	173(1)	173(1)
Crystal system	monoclinic	triclinic	triclinic
Lattice parameters			
Reflections for cell determination	22	25	25
2θ range [°]	$30 < 2\theta < 38$	$39 < 2\theta < 40$	$38 < 2\theta < 40$
a [Å]	8.356(2)	11.359(3)	12.610(1)
b [Å]	17.172(2)	11.996(2)	13.607(1)
c [Å]	23.902(1)	8.117(2)	15.965(1)
α [°]	90	109.69(1)	98.67(1)
β [°]	97.103(9)	105.65(2)	95.41(1)
γ [°]	90	102.90(2)	105.718(9)
V [Å^3]	3403.0(8)	947.6(4)	964.1(3)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	8	2	2
D_x [g cm^{-3}]	1.270	1.260	1.238
Absorption coefficient μ (MoK_α) [mm^{-1}]	0.1880	0.193	0.0886
2θ (max) [°]	60	60	55
Absorption correction min, max	0.868, 1.187	0.735, 1.315	–
Total reflections measured	10860	5770	4635
Symmetry independent reflections	9912	5509	4437
Reflections observed	6550	4465	3397
Criterion	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Variables	567	310	335
Final R	0.0406	0.0513	0.0393
R_w[a])	0.0399	0.0596	0.0390
Goodness of fit s	1.740	2.703	1.889
p for $1/w = \sigma^2(F_o) + (pF_o)^2$	0.005	0.0075	0.0075
Final Δ_{max}/σ	0.0008	0.0004	0.0004
$\Delta\rho$ (max, min) [e Å^{-3}]	0.34, −0.26	0.50, −0.36	0.32, −0.19

[a]) Function minimized $\Sigma w(|F_o| - |F_c|)^2$.

4. *Crystal-Structure Determination of* **12**, **15**, *and* **16** (see *Table* and *Figs. 1* and *2*)[5]. The intensities were collected on a *Rigaku-AFC5R* diffractometer in the $\omega/2\theta$-scan mode using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction was applied for **12** and **15** [25]. The crystal of **15** was of rather poor quality and had a very irregular shape. 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 [26], 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 temperature factors. All refinements were carried out on F using full-matrix least-squares procedures. Neutral atom scattering factors for non-H-atoms were taken from [27a] (for **12**) and [28a] (for **15** and **16**) and the scattering factors for H-atoms from [29]. Anomalous dispersion effects were included in F_{calc} [30]; the values for f' and f'' were those of [27b] (for **12**) and [28b] (for **15** and **16**). All calculations were performed using the TEXSAN crystallographic software package [31].

In **12**, there are two independent molecules in the asymmetric unit which have very similar conformations. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher-symmetry space group using the MISSYM routine [32] of the program PLATON [33], but none could be found.

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[5] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/3. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033, or email: teched@chemcrys.cam.ac.uk).

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