

Reaction of Mesoionic Thiazol-4-ones with Azodicarbonyl Dipolarophiles. Cleavage Modes of the Bi- and Tri-cyclic Adducts

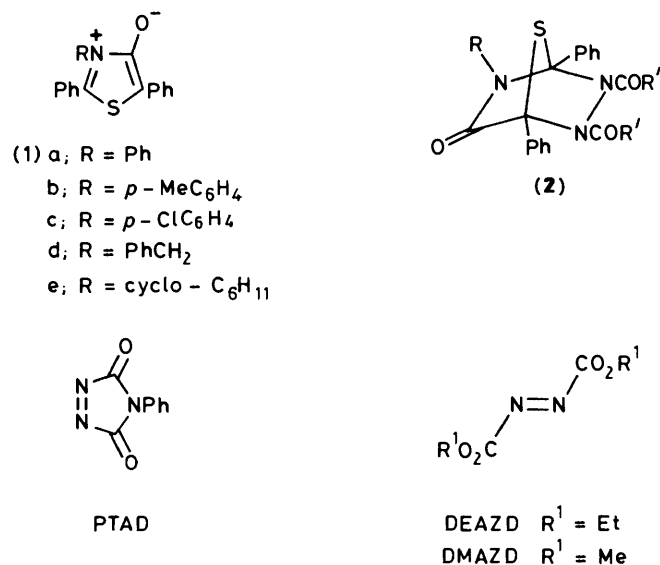
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The thiazolium-4-olates (**1a—e**) were treated with dimethyl and diethyl azodicarboxylate and gave, through 1,3-dipolar cycloaddition, the 3,6-sulphur bridged hexahydro-1,2,4-triazin-5-ones (**2**). When heated in benzene these rearranged to the blue thioxohydrazides (**3**), whilst when heated in methanol or ethanol they reacted with the solvent to give 2-alkoxy-5-hydrazinothiazol-4-ones (**4**). Reaction of the mesoionic compounds (**1**) with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) gave the cycloadducts (**11**) which reacted very readily with water or alcohols to give the thiazol-4-ones (**5**), analogous to (**4**). The structures and stereochemistry of (**2**), (**3**), and (**5**) were established by X-ray analyses. The mechanisms of the ring openings of (**2**) to (**3**) and (**4**), and of (**11**) to (**5**) are discussed.

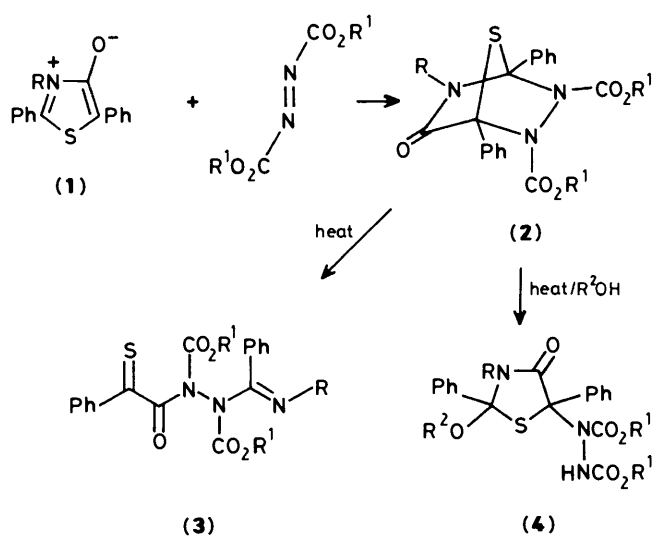
Mesoionic heterocycles are important as masked 1,3-dipoles in cycloadditions.^{1,2} Thus with dipolarophiles they yield bicyclic adducts, which can, in certain cases, be isolated; alternatively the products extrude or eliminate small stable molecules (CO₂, S, RNCO *etc.*) to give monocyclic systems. The additions of mesoionic compounds to azo dipolarophiles have been little reported³⁻⁷ in spite of the fact that such reactions would be expected to provide unusual multi-nitrogen heterocyclic systems with unusual properties and reactivities.

We now describe the reaction of a series of thiazolium-4-olates (**1a—e**) with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) and with dimethyl (DMAZD) and diethyl azodicarboxylate (DEAZD), which should lead to sulphur bridged 1,2,4-triazines of type (**2**).



Results

The reactions of compounds (**1**) with DEAZD in dichloromethane yielded products which contained the elements of both reactants. X-Ray analysis of the product from (**1a**) confirmed the structure as the expected bicyclic system (**2**). Similar reactions in refluxing benzene gave a deep blue colour, and the same colour also appeared on heating compounds (**2**) in benzene. The blue compounds were separated by chromato-



graphy [ca. 50% conversion from (**2**) after 5 h at 80 °C] and were found to be isomeric with (**2**). The colour (λ_{max} , 570 nm, $\epsilon \sim 20$) suggests the presence of a thioxo group⁸ and X-ray analysis of the *N-p*-chloro derivative (Figure 2) established the structure as (**3**). When the reactions were carried out in refluxing methanol or ethanol, a molecule of the alcohol was incorporated into the adducts and the same products were formed on heating the adducts (**2**) in alcohols. The products assigned structure (**4**), were obtained in most cases as mixtures of stereoisomers.

The same set of products was obtained in the reactions of mesoionic compounds (**1**) with DMAZD. The relatively simpler n.m.r. spectra of the methyl esters indicated that products (**4**) were mixtures of stereoisomers rather than of stable conformers which may be formed by a high torsional barrier around the N-N bonds.⁹ The spectrum of (**4a**; R¹ = R² = Me), for example, exhibited six distinct methoxy singlets, and was not changed upon heating.

Within the range of compounds studied, there were two exceptions to the sequences described. The *N*-benzyl cycloadduct (**2d**) did not rearrange to the corresponding thiones (**4d**). The *N*-cyclohexyl derivative (**2e**) on the other hand, could not be isolated, and attempted purification led to water adducts of type (**4**; R = H). The rearranged products (**3e**) and alcohol adducts (**4e**) were, however, obtained directly on carrying out the cycloaddition under the appropriate conditions.

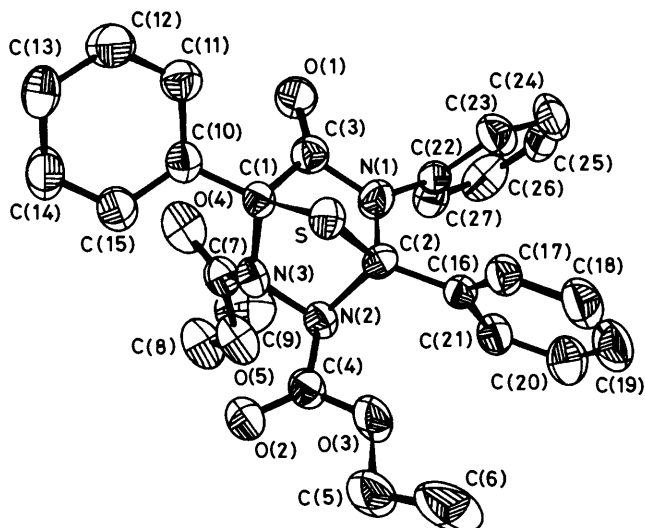


Figure 1. Molecular structure of compound (2a; $R^1 = Et$)

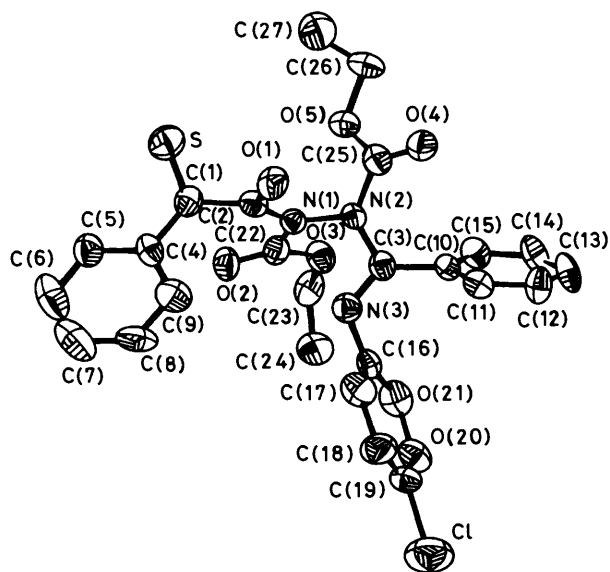


Figure 2. Molecular structure of compound (3c; $R^1 = Et$)

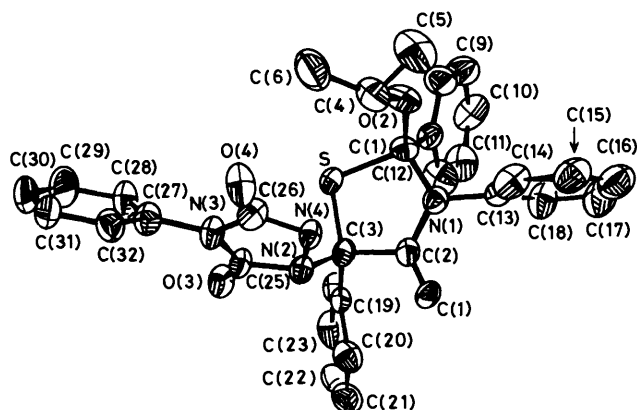
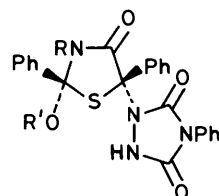


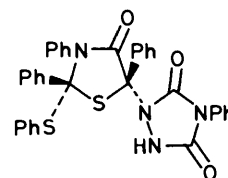
Figure 3. Molecular structure of compound (5a; $R^1 = Pr^1$)

The reaction of the mesoionic compounds (1) with PTAD proceeded faster. In chloroform the products contained the elements of the two reactants plus a molecule of ethanol (present in the chloroform as stabilizer). The reactions were run also in dichloromethane containing 5% of methanol, ethanol, isopropyl alcohol, and water, and in each case a molecule of the alcohol (or water) was incorporated in the products. The reactions in pure dichloromethane yielded in all cases amorphous materials, which upon treatment with alcohols or water gave the same alcohol-containing adducts. Attempts to purify and identify the initial products always resulted in the formation of water adducts. The ethanol and isopropyl alcohol adducts contained, in certain cases, an additional alcohol molecule of crystallization, removable upon drying or recrystallization. Addition of thiophenol to the reaction mixture of (1a) and PTAD also yielded an analogous product, containing the elements of thiophenol.

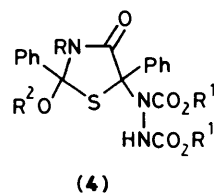
In the PTAD reactions a single product was obtained in each case. The structure of the product of (1a) in the presence of isopropyl alcohol was determined by *X*-ray crystallography as the 5-triazolidinylthiazolidin-4-one (5a; $R^1 = Pr^1$) with the phenyl groups at positions 2 and 5 in a *cis*-relationship (see Figure 3). Accordingly the water and alcohol adducts were assigned as (5) and the thiophenol adduct as (6). A list of all the compounds obtained with their physical and analytical data is given in Tables 1—4.



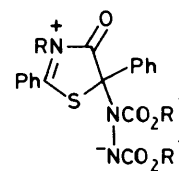
(5) $R^1 = Me, Et, Pr^1$



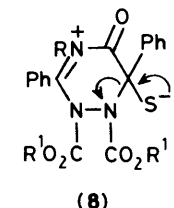
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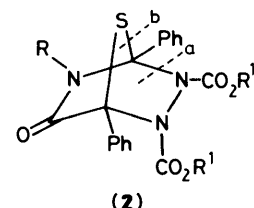
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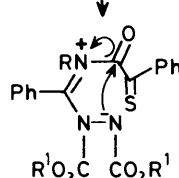
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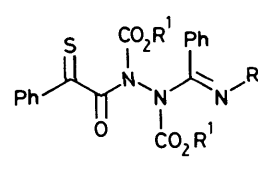
(8)



(2)



(9)



(3)

Table 1. 2,3-Di(alkoxycarbonyl)-1,4-diphenyl-7-thia-2,3,6-triazanorbornan-5-ones (2)

No.	R ¹	Yield (%)	M.p. (°C)	ν _{max./cm⁻¹} (C=O)	Found (%)				Formula	Required (%)			
					C	H	N	S		C	H	N	S
(2a)	Me	76	145	1 740, 1 725	62.8	4.7	8.6	6.8	C ₂₅ H ₂₁ N ₃ O ₅ S	63.2	4.45	8.8	6.7
(2a)	Et	70	148	1 740, 1 720	64.1	5.1	8.1	6.2	C ₂₇ H ₂₅ N ₃ O ₅ S	64.4	5.0	8.35	6.35
(2b)	Me	94	156	1 750, 1 725	63.6	4.8	8.35	6.5	C ₂₆ H ₂₃ N ₃ O ₅ S	63.8	4.7	8.6	6.5
(2b)	Et	82	124	1 750, 1 720	65.0	5.3	8.0	6.6	C ₂₈ H ₂₇ N ₃ O ₅ S	65.0	5.3	8.1	6.2
(2c)	Et	52	137	1 740, 1 720	60.5	4.3	7.8	6.0	C ₂₇ H ₂₄ ClN ₃ O ₅ S	60.3	4.5	7.8	6.0
(2d)	Me	75	132	1 750, 1 730	63.55	4.8	8.6	6.9	C ₂₆ H ₂₃ N ₃ O ₅ S	63.8	4.7	8.6	6.5
(2d)	Et	68	139	1 740, 1 720	65.3	5.3	8.0	6.1	C ₂₈ H ₂₇ N ₃ O ₅ S	65.0	5.3	8.1	6.2

Table 2. 1,2-Di(alkoxycarbonyl)-2-phenylimido-1-(α-thioxophenylacetyl)hydrazines (3)

No.	R ¹	Yield (%)	M.p. (°C)	ν _{max./cm⁻¹} (C=O and C=N)	Found (%)				Formula	Required (%)			
					C	H	N	S		C	H	N	S
(3a)	Me	26	140	1 750, 1 705, 1 650	63.2	4.5	8.9	6.2	C ₂₅ H ₂₁ N ₃ O ₅ S	63.2	4.45	8.8	6.7
(3a)	Et	44	156	1 750, 1 710, 1 650	64.2	5.0	8.2	6.4	C ₂₇ H ₂₅ N ₃ O ₅ S	64.4	5.0	8.35	6.35
(3b)	Et	48	143	1 750, 1 700, 1 645	65.1	5.3	7.8	6.5	C ₂₈ H ₂₇ N ₃ O ₅ S	65.0	5.3	8.1	6.2
(3c)	Et	41	144	1 750, 1 695, 1 640	60.1	4.4	8.0	5.7	C ₂₇ H ₂₄ ClN ₃ O ₅ S	60.3	4.5	7.8	6.0
(3e)	Et	39	120	1 740, 1 705, 1 650	63.6	6.2	8.2	6.6	C ₂₇ H ₃₁ N ₃ O ₅ S	63.6	6.1	8.25	6.3

Table 3. 2-Alkoxy-5-(1,2-dialkoxycarbonyl)hydrazino-2,5-diphenylthiazolidin-4-ones (4)

No.	R ¹	R ²	Yield (%)	M.p. (°C)	ν _{max./cm⁻¹}	Found (%)				Formula	Required (%)			
						C	H	N	S		C	H	N	S
(4a)	Me	Me	86	135	3 270, 1 740, 1 720, 1 700	62.0	5.2	8.1	6.2	C ₂₆ H ₂₅ N ₃ O ₆ S	61.6	5.0	8.3	6.3
(4a)	Et	Et ^a	61	154	3 340, 3 280, 1 755, 1 725, 1 685	63.5	5.8	7.6	5.8	C ₂₉ H ₃₁ N ₃ O ₆ S	63.4	5.7	7.65	5.8
(4b)	Me	Me	82	136	3 300, 1 735, 1 715, 1 695	61.9	5.3	7.8	5.9	C ₂₇ H ₂₇ N ₃ O ₆ S	62.2	5.2	8.1	6.1
(4b)	Me	Et	72	196	3 270, 1 740, 1 710	62.5	5.5	7.9	5.9	C ₂₈ H ₂₉ N ₃ O ₆ S	62.8	5.5	7.85	5.9
(4b)	Et	Me	70	162	3 350, 1 750, 1 720, 1 690	63.2	5.7	7.8	5.5	C ₂₉ H ₃₁ N ₃ O ₆ S	63.4	5.7	7.65	5.8
(4b)	Et	Et	75	176	3 340, 3 280, 1 760, 1 790, 1 715, 1 695	63.7	6.0	7.4	5.5	C ₃₀ H ₃₃ N ₃ O ₆ S	63.9	5.9	7.5	5.7
(4d)	Et	Et	84	160	3 250, 1 760, 1 705, 1 690	64.2	6.0	7.5	5.6	C ₃₀ H ₃₃ N ₃ O ₆ S	63.9	5.9	7.5	5.6
(4e)	Me	Me	74	155	3 310, 1 730, 1 730, 1 695	60.6	6.1	8.2	6.2	C ₂₆ H ₃₁ N ₃ O ₆ S	60.8	6.1	8.2	6.3
(4e)	Et	H	38	90	3 280, 1 740, 1 700, 1 680	61.6	6.6	7.6	6.4	C ₂₇ H ₃₃ N ₃ O ₆ S	61.5	6.3	8.0	6.1
(4e)	Et	Et	62	120	3 295, 1 760, 1 730, 1 680	62.4	6.7	7.7	5.9	C ₂₉ H ₃₇ N ₃ O ₆ S	62.7	6.7	7.6	5.8

^a Purified by chromatography on silica gel.**Table 4.** 2-Alkoxy-2,5-diphenyl-5-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)thiazolidin-4-ones (5)

No.	R ¹	Yield ^a (%)	M.p. (°C)	ν _{max./cm⁻¹}	Found (%)				Formula	Required (%)			
					C	H	N	S		C	H	N	S
(5a)	H	71	138	3 300, 1 765, 1 710, 1 690	66.2	4.6	10.8	6.35	C ₂₉ H ₂₂ N ₄ O ₄ S	66.7	4.2	10.7	6.15
(5a)	Me	79	199	3 100, 1 780, 1 715, 1 670	67.1	4.9	10.4	5.6	C ₃₀ H ₂₄ N ₄ O ₄ S	67.2	4.5	10.4	6.0
(5a)	Et ^b	83	196	3 420, 1 780, 1 718, 1 680	66.2	5.5	9.6	5.2	C ₃₃ H ₃₂ N ₄ O ₅ S	66.4	5.4	9.4	5.4
(5a)	Pr ^{1c}	80	132	3 440, 1 780, 1 710, 1 680	67.3	5.8	8.7	5.0	C ₃₅ H ₃₆ N ₄ O ₅ S	67.3	5.8	9.0	5.1
(5b)	Et	68	188	3 420, 1 785, 1 720, 1 680	67.7	5.4	9.6	6.0	C ₃₂ H ₃₈ N ₄ O ₄ S	68.1	5.0	9.9	5.7
(5c)	Et ^b	76	120	3 440, 1 785, 1 725, 1 690	62.5	4.9	9.2	5.2	C ₃₃ H ₃₁ ClN ₄ O ₅ S	62.8	4.95	8.9	5.1
(5d)	Et	70	182	3 140, 1 780, 1 710, 1 695	68.1	5.1	9.9	5.9	C ₃₂ H ₂₈ N ₄ O ₄ S	68.1	5.0	9.9	5.7
(5e)	Et	80	165	3 160, 1 785, 1 730, 1 670	66.3	6.1	9.75	5.3	C ₃₁ H ₃₂ N ₄ O ₄ S	66.9	5.8	10.1	5.75

^a All yield except (5a; R = H) are according to procedure a. ^b Ethanol solvate. ^c Isopropyl alcohol solvate.

Discussion

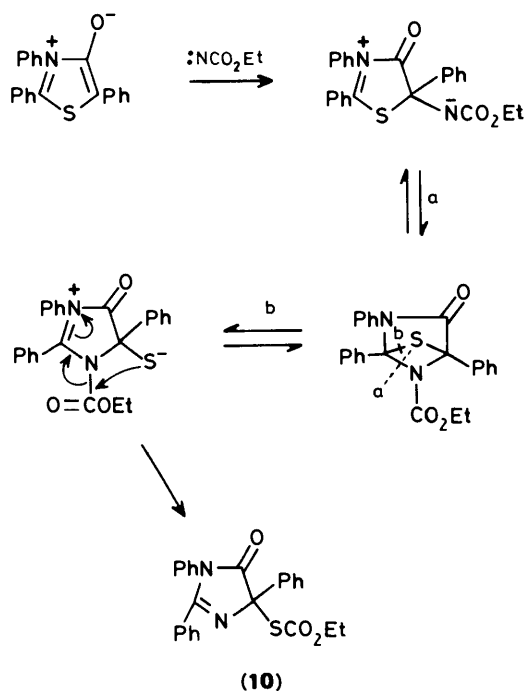
Undoubtedly the initial reaction of the mesoionic compounds (1) with azodicarbonyl compounds is the expected cycloaddition, as was evident from the successful isolation of several compounds of type (2). The strained systems (2) can undergo thermal cleavage at either a C–N bond (path a) to the zwitterion (7) or at a C–S bond (path b) to the zwitterion (8).

Both zwitterions (7) and (8) can achieve charge neutralization

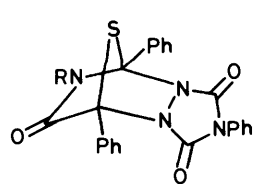
by cyclization to (2) and thus at elevated temperatures an equilibrium system (7) ⇌ (2) ⇌ (8) is reached. The zwitterion (7) can be trapped by alcohols or water and thus in their presence the equilibrium shifts to the left to give (4). In the absence of nucleophiles the equilibrium shifts to the right as (8) can rearrange to (9), in which the charges are neutralized by an irreversible transformation to the blue products (3). The stereochemistry on the C=N bond in (3) with the N–R and C–Ph

groups in a *cis* relationship supports this mechanism. We have previously¹⁰ reported a case involving a similar situation in which a bicyclic system is in equilibrium with two monocyclic zwitterions formed by cleavage of C–N and C–S bonds. This was observed on treating ethoxycarbonylnitrene with (1a) to give (10). Charge neutralization was achieved in this case by N→S acyl migration.

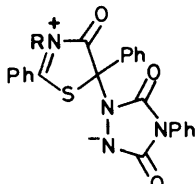
The X-ray analysis of (2) reveals that the *N*-ethoxycarbonyl group which is β to the ring carbonyl is *endo* while the one β to the *N*-aryl (or alkyl) group is *exo*,¹¹ with a torsional angle of 109.5° around the N–N bond. Clearly such geometry would be impossible for the adducts of (1) with PTAD, in which the two *N*-carbonyl groups have to be in nearly eclipsed conformation. It is, therefore, to be expected that the initial PTAD adducts of type (11) would be much more strained and reactive than (2). Indeed, compounds (11) are highly sensitive towards moisture and alcohols, undergoing a facile opening to (5) even at low temperatures.



In contrast to the analogous cleavages of (2), the ring openings of (11) are stereospecific. It is unlikely that the *cis* relationship of the two phenyl groups in (5) originates in a stereospecific attack of alcohols on the zwitterion (12), as the bulk size of the phenyl and triazolyl groups do not differ considerably. The stereospecific formation of (8) most certainly results from retention of the stereochemistry of (11) in the transformation (11) → (5). We suggest that compounds (5) are formed by a fast direct reaction of the tricyclic adducts (11) with the protic reagents without a prior opening to (12). This



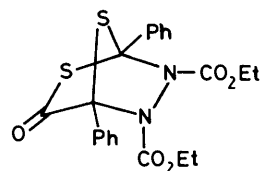
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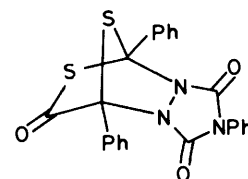
(12)

mechanism is also supported by the lack of formation of any products analogous to (3) in all the reactions of (1) with PTAD.

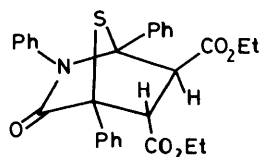
The high reactivity of the adducts (2) and (11) is surprising since the related compounds (13)–(16) reported in the literature^{6,12} are perfectly stable, and do not undergo any of the cleavage reactions described here. Another interesting unclarified point is the reversed effect of the *N*-benzyl and *N*-cyclohexyl groups on the stability of (2).



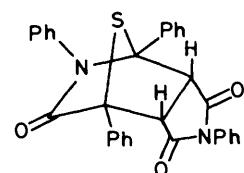
(13)



(14)



(15)



(16)

Experimental

M.p.s were taken with a Thomas-Hoover apparatus. U.v. spectra (in ethanol) were recorded on a Contron-Uvicon 860 spectrophotometer and i.r. spectra (Nujol mulls) on a Perkin-Elmer 157 spectrophotometer. N.m.r. spectra (CDCl₃ solutions) were taken on a Bruker WH-300 instrument. Light petroleum refers to the fraction with a boiling range of 40–60 °C. E. Merck silica gel 60 (70–230 mesh) was used for chromatography.

Table 5. Crystallographic data

	(2a; R ¹ = Et)	(3c; R ¹ = Et)	(5a; R ¹ = Pr ¹)
Formula	C ₂₇ H ₂₅ N ₃ O ₅ S	C ₂₇ H ₂₄ ClN ₃ O ₅ S	C ₃₂ H ₂ N ₄ O ₄ S
<i>M</i>	503.57	538.02	564.7
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	9.820(2)	11.938(3)	20.098(3)
<i>b</i> /Å	21.616(4)	11.948(3)	11.923(2)
<i>c</i> /Å	11.935(3)	19.419(4)	27.285(4)
β /°	95.42(4)	104.11(4)	107.88(2)
<i>V</i> /Å ³	2 522.36(7)	2 686.3(7)	6 223(1)
<i>Z</i>	4	4	8
$\rho_{\text{calc.}}$ /g cm ⁻³	1.326	1.330	1.21
μ (Mo- <i>K</i> _α)/cm ⁻¹	1.30	2.17	1.08
No. of unique reflections	4 356	4 470	3 723
Reflections with <i>I</i> ≥ 2σ(<i>I</i>)	3 361	2 649	3 095
<i>R</i>	0.053	0.072	0.098
<i>R</i> _w	0.063	0.079	0.155 ^a
<i>w</i>	σ_F^{-2}	$(\sigma_F + 0.000\ 204)^{-2}$	$(\sigma_F^2 + 0.040\ 59 \cdot F^2)^{-1}$

^a This high value is due to traces of isopropyl alcohol incorporated in the crystal.

Table 6. Positional parameters and estimated standard deviations for compound (**2a**; R¹ = Et)

Atom	x	y	z	Atom	x	y	z
Cl	0.957 2(2)	0.118 6(2)	0.431 7(1)	C(10)	0.426 6(5)	0.282 5(5)	0.274 5(3)
S	0.108 0(1)	0.398 5(2)	0.524 01(9)	C(11)	0.516 1(5)	0.342 8(5)	0.258 3(3)
O(1)	0.303 4(4)	0.477 7(3)	0.438 7(2)	C(12)	0.536 3(6)	0.333 6(7)	0.191 7(4)
O(2)	0.256 6(4)	0.163 9(3)	0.500 7(2)	C(13)	0.470 5(8)	0.264 9(7)	0.141 1(4)
O(3)	0.243 0(3)	0.113 0(3)	0.386 7(2)	C(14)	0.382 5(7)	0.205 9(6)	0.156 9(3)
O(4)	0.231 5(3)	0.424 2(4)	0.253 0(2)	C(15)	0.358 7(5)	0.213 8(5)	0.223 5(3)
O(5)	0.107 0(3)	0.366 3(3)	0.316 3(2)	C(16)	0.592 2(5)	0.238 3(5)	0.407 8(3)
N(1)	0.268 7(4)	0.294 1(4)	0.417 0(2)	C(17)	0.684 4(5)	0.306 3(5)	0.439 1(3)
N(2)	0.290 7(4)	0.310 2(4)	0.350 4(2)	C(18)	0.798 3(5)	0.268 7(6)	0.445 4(3)
N(3)	0.479 3(4)	0.276 0(4)	0.405 6(2)	C(19)	0.815 7(5)	0.164 5(6)	0.422 3(3)
C(1)	0.243 9(5)	0.379 6(5)	0.529 1(3)	C(20)	0.725 0(6)	0.094 4(5)	0.392 8(3)
C(2)	0.278 5(4)	0.388 7(5)	0.459 9(3)	C(21)	0.614 1(5)	0.133 2(5)	0.385 5(3)
C(3)	0.406 0(5)	0.291 5(4)	0.346 8(3)	C(22)	0.256 0(5)	0.183 2(5)	0.440 0(3)
C(4)	0.336 9(5)	0.371 8(5)	0.594 5(3)	C(23)	0.234 2(5)	-0.006 2(5)	0.404 2(3)
C(5)	0.311 8(6)	0.364 7(5)	0.660 6(3)	C(24)	0.350 1(6)	-0.056 4(6)	0.426 5(4)
C(6)	0.399 3(8)	0.359 8(6)	0.721 4(4)	C(25)	0.208 9(5)	0.373 5(5)	0.300 6(3)
C(7)	0.513 8(8)	0.368 3(6)	0.717 5(4)	C(26)	0.014 5(5)	0.425 7(5)	0.267 3(3)
C(8)	0.538 6(6)	0.376 5(6)	0.653 3(4)	C(27)	-0.086 3(6)	0.426 2(7)	0.301 2(4)
C(9)	0.452 2(5)	0.377 2(5)	0.590 9(3)				

Estimated standard deviations in the least significant digits are shown in parentheses.

Table 7. Selected bond lengths (Å) for compound (**2a**; R¹ = Et)

S-C(1)	1.834(2)	N(1)-C(3)	1.382(3)
S-C(2)	1.858(3)	N(1)-C(22)	1.438(3)
O(1)-C(3)	1.204(3)	N(2)-N(3)	1.439(3)
O(2)-C(4)	1.191(3)	N(2)-C(2)	1.495(3)
O(3)-C(4)	1.307(3)	N(2)-C(4)	1.431(3)
O(3)-C(5)	1.448(3)	N(3)-C(1)	1.494(3)
O(4)-C(7)	1.202(4)	N(3)-C(7)	1.392(3)
O(5)-C(7)	1.325(3)	C(1)-C(3)	1.538(4)
O(5)-C(8)	1.474(4)	C(1)-C(10)	1.499(4)
N(1)-C(2)	1.466(3)	C(2)-C(16)	1.506(3)

Table 8. Selected angles (°) for compound (**2a**; R¹ = Et)

C(1)-S-C(2)	78.7(1)	S-C(2)-N(1)	102.7(2)
C(4)-O(3)-C(5)	118.4(2)	S-C(2)-N(2)	100.2(2)
C(7)-O(5)-C(8)	115.2(3)	S-C(2)-C(16)	117.0(2)
C(2)-N(1)-C(3)	112.2(2)	N(1)-C(2)-N(2)	106.4(2)
C(2)-N(1)-C(22)	124.8(2)	N(1)-C(2)-C(16)	113.1(2)
C(3)-N(1)-C(22)	122.0(2)	N(2)-C(2)-C(16)	115.7(2)
N(3)-N(2)-C(2)	104.3(2)	O(1)-C(3)-N(1)	126.7(3)
N(3)-N(2)-C(4)	109.0(2)	O(1)-C(3)-C(1)	128.7(3)
C(2)-N(2)-C(4)	119.9(2)	N(1)-C(3)-C(1)	104.6(2)
N(2)-N(3)-C(1)	109.9(2)	O(2)-C(4)-O(3)	125.9(3)
N(2)-N(3)-C(7)	116.2(2)	O(2)-C(4)-N(2)	123.8(3)
C(1)-N(3)-C(7)	116.6(2)	O(3)-C(4)-N(2)	110.1(2)
S-C(1)-N(3)	103.5(2)	O(3)-C(5)-C(6)	109.6(3)
S-C(1)-C(3)	100.2(2)	O(4)-C(7)-O(5)	126.7(3)
S-C(1)-C(10)	111.5(2)	O(4)-C(7)-N(3)	121.9(3)
N(3)-C(1)-C(3)	103.5(2)	O(5)-C(7)-N(3)	111.3(3)
N(3)-C(1)-C(10)	115.8(2)	O(5)-C(8)-C(9)	110.6(3)
C(3)-C(1)-C(10)	120.0(2)		

Thiazolium-4-olates (**1**).—These were prepared as described previously.¹³

3-Cyclohexyl-2,5-diphenylthiazolium-4-olate is a new compound and was prepared in 45% yield in the same manner by reaction of *N*-cyclohexylthiobenzamide¹⁴ with α -bromophenylacetic acid and triethylamine and subsequently with acetic anhydride; it had m.p. 174 °C (Found: C, 75.35; H, 6.5; N, 4.1; S, 9.9. C₂₁H₂₁NOS requires C, 75.2; H, 6.3; N, 4.2; S, 9.5%); λ_{\max} 418 nm (ϵ 12 800) and 266 (12 000); ν_{\max} 1 615 cm⁻¹.

2,3-Di(alkoxycarbonyl)-1,4-diphenyl-7-thia-2,3,6-triazano-*norbornane-5-ones* (**2**): *General Procedure*.—A solution containing the mesoionic thiazolone (**1**) (5 mmol) and the dialkyl azodicarboxylate (DEAZD or DMAZD) (5 mmol) in dichloromethane (30 ml) was stirred at room temperature overnight, during which time the colour changed from red to light yellow. The solvent was evaporated and the oily residue crystallized from CH₂Cl₂-light petroleum to give pure compound (**2**). A list of compounds (**2**) obtained with physical and analytical data is presented in Table 1. The reaction of (**1e**) yielded (**4e**; R = H) (see Table 3).

1,2-Di(alkoxycarbonyl)-2-phenylimidoyl-1-(α -thioxophenylacetyl)hydrazines (**3**): *General Procedure*.—A solution containing the mesoionic thiazolone (**1**) (2 mmol) and the dialkyl azodicarboxylate (DEAZD or DMAZD) (2 mmol) in benzene (15 ml) was refluxed for 5 h, during which time the red colour changed to dark blue. The solution was evaporated and the oily residue chromatographed on silica gel (30 g). Chloroform-light petroleum (1:1) eluted a blue band. The resulting blue oil solidified with time and on crystallization from CH₂Cl₂-light petroleum gave compound (**3**) as blue crystals, λ_{\max} 570 (ϵ 20) and 324 nm (11 000—18 000). A list of compounds obtained and their data are presented in Table 3. Further elution with chloroform gave compounds (**2**). The reaction with (**1d**) gave (**2d**) only.

2-Alkoxy-5-(1,2-dialkoxycarbonyl)hydrazino-2,5-diphenylthiazolidin-4-ones (**4**): *General Procedure*.—A solution containing the mesoionic thiazolone (**1**) (2 mmol) and the dialkyl azodicarboxylate (DEAZD or DMAZD) (2 mmol) in methanol or ethanol (20 ml) was refluxed for 1 h. After evaporation, the oily residue was crystallized from CH₂Cl₂-light petroleum to give (**4**). A list of compounds (**4**) and their data are presented in Table 3. The n.m.r. spectra usually showed complex multiplets, however when R¹ = R² = Me they exhibited six 1.5 H singlets; for (**4a**) at δ 3.86, 3.79, 3.77, 3.69, 3.64, and 3.61; for (**4e**) at 3.80, 3.74, 3.71, 3.67, 3.61, and 3.59.

2-Alkoxy-cis-2,5-diphenyl-5-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)thiazolidin-4-ones (**5**): *General Procedure*.—(a). A solution of PTAD (0.88 g, 5 mmol) in dichloromethane (15

Table 9. Positional parameters and estimated standard deviations for compound (**3c**; R¹ = Et)

Atom	x	y	z	Atom	x	y	z
Cl	0.957 2(2)	0.118 6(2)	0.431 7(1)	C(10)	0.426 6(5)	0.282 5(5)	0.274 5(3)
S	0.108 0(1)	0.398 5(2)	0.524 01(9)	C(11)	0.516 1(5)	0.342 8(5)	0.258 3(3)
O(1)	0.303 4(4)	0.477 7(3)	0.438 7(2)	C(12)	0.536 3(6)	0.333 6(7)	0.191 7(4)
O(2)	0.256 6(4)	0.163 9(3)	0.500 7(2)	C(13)	0.470 5(8)	0.264 9(7)	0.141 1(4)
O(3)	0.243 0(3)	0.113 0(3)	0.386 7(2)	C(14)	0.382 5(7)	0.205 9(6)	0.156 9(3)
O(4)	0.231 5(3)	0.424 2(4)	0.253 0(2)	C(15)	0.358 7(5)	0.213 8(5)	0.223 5(3)
O(5)	0.107 0(3)	0.366 3(3)	0.316 3(2)	C(16)	0.592 2(5)	0.238 3(5)	0.407 8(3)
N(1)	0.268 7(4)	0.294 1(4)	0.417 0(2)	C(17)	0.684 4(5)	0.306 3(5)	0.439 1(3)
N(2)	0.290 7(4)	0.310 2(4)	0.350 4(2)	C(18)	0.798 3(5)	0.268 7(6)	0.445 4(3)
N(3)	0.479 3(4)	0.276 0(4)	0.405 6(2)	C(19)	0.815 7(5)	0.164 5(6)	0.422 3(3)
C(1)	0.243 9(5)	0.379 6(5)	0.529 1(3)	C(20)	0.725 0(6)	0.094 4(5)	0.392 8(3)
C(2)	0.278 5(4)	0.388 7(5)	0.459 9(3)	C(21)	0.614 1(5)	0.133 2(5)	0.385 5(3)
C(3)	0.406 0(5)	0.291 5(4)	0.346 8(3)	C(22)	0.256 0(5)	0.183 2(5)	0.440 0(3)
C(4)	0.336 9(5)	0.371 8(5)	0.594 5(3)	C(23)	0.234 2(5)	-0.006 2(5)	0.404 2(3)
C(5)	0.311 8(6)	0.364 7(5)	0.660 6(3)	C(24)	0.350 1(6)	-0.056 4(6)	0.426 5(4)
C(6)	0.399 3(8)	0.359 8(6)	0.721 4(4)	C(25)	0.208 9(5)	0.373 5(5)	0.300 6(3)
C(7)	0.513 8(8)	0.368 3(6)	0.717 5(4)	C(26)	0.014 5(5)	0.425 7(5)	0.267 3(3)
C(8)	0.538 6(6)	0.376 5(6)	0.653 3(4)	C(27)	-0.086 3(6)	0.426 2(7)	0.301 2(4)
C(9)	0.452 2(5)	0.377 2(5)	0.590 9(3)				

Estimated standard deviations in the least significant digits are shown in parentheses.

Table 10. Selected bond lengths (Å) for compounds (**3c**; R¹ = Et)

Cl-C(19)	1.743(6)	N(1)-C(2)	1.392(7)
S-C(1)	1.618(5)	N(1)-C(22)	1.418(7)
O(1)-C(2)	1.203(7)	N(2)-C(3)	1.413(7)
O(2)-C(22)	1.198(7)	N(2)-C(25)	1.414(6)
O(3)-C(22)	1.313(6)	N(3)-C(3)	1.272(6)
O(3)-C(23)	1.474(7)	N(3)-C(16)	1.412(7)
O(4)-C(25)	1.191(7)	C(1)-C(2)	1.502(8)
O(5)-C(25)	1.327(7)	C(1)-C(4)	1.473(6)
O(5)-C(26)	1.454(6)	C(3)-C(10)	1.486(8)
N(1)-N(2)	1.395(6)		

Table 11. Selected angles (°) for compounds (**3c**; R¹ = Et)

C(22)-O(3)-C(23)	115.9(4)	O(1)-C(2)-C(1)	118.3(5)
C(25)-O(5)-C(26)	114.2(4)	N(2)-C(3)-N(3)	116.3(5)
N(2)-N(1)-C(2)	115.8(4)	N(2)-C(3)-C(10)	116.5(5)
N(2)-N(1)-C(22)	118.7(4)	N(3)-C(3)-C(10)	126.9(5)
C(2)-N(1)-C(22)	124.8(5)	O(2)-C(22)-O(3)	128.6(5)
N(1)-N(2)-C(3)	115.0(5)	O(2)-C(22)-N(1)	120.9(5)
N(1)-N(2)-C(25)	117.0(4)	O(3)-C(22)-N(1)	110.5(5)
C(3)-N(2)-C(25)	124.6(4)	O(3)-C(23)-C(24)	110.3(5)
C(3)-N(3)-C(16)	121.1(5)	O(4)-C(25)-O(5)	127.2(6)
S-C(1)-C(2)	115.2(5)	O(4)-C(25)-N(2)	123.7(5)
S-C(1)-C(4)	126.5(4)	O(5)-C(25)-N(2)	109.1(5)
C(2)-C(1)-C(4)	117.6(5)	O(5)-C(26)-C(27)	106.0(5)
O(1)-C(2)-N(1)	120.3(5)		

ml) was added dropwise to a stirred solution of a mesoionic thiazolone (**1**) (5 mmol) and an alcohol (1 ml; methanol, ethanol, or isopropyl alcohol) in dichloromethane (25 ml). The dark red colour turned light yellow immediately at the end of the addition. The solution was then evaporated and the residue crystallized from the reaction alcohol or from CH₂Cl₂-light petroleum to give compound (**4**).

(b) The cycloaddition of PTAD to (**1**) was carried out as above in pure dichloromethane. After evaporation the solid residue was immediately dissolved in an alcohol. The alcohol was evaporated off and the residue crystallized as above. For the preparation of (**5a**; R = H) the crude product was first dissolved in acetone and the solution was diluted with water. A list of compounds (**5**) and their data is presented in Table 4.

2-Phenylthio-2,3,5-triphenyl-5-(3,5-dioxo-4-phenyl-1,2,4-triazolin-1-yl)thiazolidin-4-one (6).—To a solution of (**1a**) (0.83 g, 2.5 mmol) in dichloromethane (20 ml) a solution of PTAD (0.44 g, 2.5 mmol) was added dropwise. Thiophenol (0.82 g, 7.5 mmol) was then added and the solution was stirred for 1 h at room temperature. Evaporation and crystallization from ether gave the title compound (**6**) (1.1 g, 72%), m.p. 198 °C (Found: C, 68.0; H, 4.3; N, 9.15; S, 10.0. C₃₅H₂₆N₄O₃S₂ requires C, 68.4; H, 4.3; N, 9.1; S, 10.5%); ν_{\max} . 1 780, 1 720, and 1 680 cm⁻¹.

Crystal Structure of Compound (2a; R¹ = Et).—Data were measured on a PW 1100/20 Philips four-circle computer-controlled diffractometer; Mo-K α (λ = 0.710 69 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained at a least-squares fit of 24 centred reflections in the range of $13 \leq \theta \leq 15^\circ$. Intensity data were collected using the ω - 2θ technique to a maximum of 2θ or 50° . The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan\theta^\circ$ with a scan speed of 3° min^{-1} . Background measurements were made for 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. The position of the S atom was found in a Patterson map. Refinement of the structure proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$.¹⁵ The discrepancy indices $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 5.

Crystal Structure of Compound (3c; R¹ = Et).—The determination procedure was the same as for (**2a**) above. The unit cell dimensions were however obtained by a least-squares fit of 25 centred reflections in the range of $10 \leq 2\theta \leq 14^\circ$ and both S and Cl atoms were found in a Patterson map.

Crystal Structure of Compound (5; R' = Prⁱ).—Data were measured on an ENRAF-NONIUS CAD-4 Automatic Diffractometer. Mo-K α (λ = 0.710 69 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 24 centred reflections in the range of $10 \leq \theta \leq 13^\circ$.

Intensity data were collected using the ω - 2θ technique to a maximum 2θ of 45° . The scan width, $\Delta\omega$, for each reflection was

Table 12. Positional parameters and estimated standard deviations for compound (5a; R' = Prⁱ)

Atom	x	y	z	Atom	x	y	z
S	0.647 28(8)	0.570 5(1)	0.159 02(5)	C(13)	0.497 5(3)	0.335 8(5)	0.101 0(2)
O(1)	0.559 8(2)	0.417 6(3)	0.031 5(2)	C(14)	0.432 8(3)	0.369 3(6)	0.075 0(3)
O(2)	0.524 2(2)	0.521 3(4)	0.177 6(2)	C(15)	0.376 9(3)	0.296 5(6)	0.061 5(3)
O(3)	0.727 4(2)	0.726 5(3)	0.086 3(2)	C(16)	0.388 3(4)	0.189 4(7)	0.075 2(3)
O(4)	0.500 6(2)	0.844 5(4)	0.045 9(2)	C(17)	0.456 8(5)	0.148 8(7)	0.102 0(4)
N(1)	0.555 0(2)	0.416 6(4)	0.113 8(2)	C(18)	0.510 1(3)	0.226 2(5)	0.115 2(3)
N(2)	0.621 0(2)	0.632 2(3)	0.057 5(2)	C(19)	0.708 0(3)	0.482 9(4)	0.086 8(2)
N(3)	0.621 5(2)	0.819 4(4)	0.068 1(2)	C(20)	0.707 7(3)	0.455 8(5)	0.036 4(3)
N(4)	0.551 7(2)	0.669 3(4)	0.050 9(2)	C(21)	0.766 1(4)	0.406 1(6)	0.027 5(3)
C(1)	0.579 0(3)	0.470 0(5)	0.165 1(2)	C(22)	0.824 6(4)	0.385 5(7)	0.070 1(3)
C(2)	0.579 9(3)	0.449 2(4)	0.074 9(2)	C(23)	0.824 5(3)	0.410 3(6)	0.118 2(3)
C(3)	0.642 0(3)	0.535 4(4)	0.093 5(2)	C(24)	0.765 4(3)	0.457 8(5)	0.127 1(3)
C(4)	0.486 0(4)	0.614 5(5)	0.148 6(3)	C(25)	0.665 7(3)	0.727 8(4)	0.073 3(2)
C(5)	0.409 6(4)	0.597 8(8)	0.148 3(4)	C(26)	0.551 4(3)	0.785 3(5)	0.053 7(2)
C(6)	0.512 2(5)	0.724 1(7)	0.171 7(5)	C(27)	0.644 8(3)	0.933 7(4)	0.078 6(2)
C(7)	0.612 3(3)	0.389 3(5)	0.207 3(2)	C(28)	0.701 7(4)	0.955 5(5)	0.120 6(3)
C(8)	0.595 0(4)	0.386 8(6)	0.253 3(2)	C(29)	0.726 0(4)	1.064 6(6)	0.130 5(3)
C(9)	0.628 4(4)	0.314 1(6)	0.292 1(3)	C(30)	0.691 9(4)	1.149 8(6)	0.096 4(3)
C(10)	0.679 4(4)	0.243 3(7)	0.286 9(3)	C(31)	0.634 4(4)	1.125 4(5)	0.055 4(3)
C(11)	0.696 0(4)	0.243 9(6)	0.242 5(3)	C(32)	0.612 0(3)	1.018 2(5)	0.046 5(3)
C(12)	0.664 7(4)	0.316 5(6)	0.203 6(3)				

Estimated standard deviations in the least significant digits are shown in parentheses.

Table 13. Bond lengths (Å) for compound (5a; R' = Prⁱ)

S-C(1)	1.867(6)	N(2)-C(3)	1.490(6)
S-C(3)	1.807(5)	N(2)-C(25)	1.433(6)
O(1)-C(2)	1.190(6)	N(3)-C(25)	1.387(6)
O(2)-C(1)	1.392(7)	N(3)-C(26)	1.402(7)
O(2)-C(4)	1.442(7)	N(3)-C(27)	1.441(6)
O(3)-C(25)	1.182(6)	N(4)-C(26)	1.385(7)
O(4)-C(26)	1.205(7)	C(1)-C(7)	1.492(7)
N(1)-C(1)	1.477(6)	C(2)-C(3)	1.575(7)
N(1)-C(2)	1.362(8)	C(3)-C(19)	1.529(7)
N(1)-C(13)	1.462(7)	C(4)-C(5)	1.55(1)
N(2)-N(4)	1.418(6)	C(4)-C(6)	1.48(1)

Table 14. Selected angles (°) for compound (5a; R' = Prⁱ)

C(1)-S-C(3)	96.7(3)	O(1)-C(2)-N(1)	126.4(5)
C(1)-O(2)-C(4)	122.1(5)	O(1)-C(2)-C(3)	121.4(5)
C(1)-N(1)-C(2)	121.6(5)	N(1)-C(2)-C(3)	112.2(5)
C(1)-N(1)-C(13)	121.0(4)	S-C(3)-N(2)	113.1(3)
C(2)-N(1)-C(13)	117.0(5)	S-C(3)-C(2)	105.7(3)
N(4)-N(2)-C(3)	113.1(4)	S-C(3)-C(19)	115.1(4)
N(4)-N(2)-C(25)	106.9(4)	N(2)-C(3)-C(2)	104.9(5)
C(3)-N(2)-C(25)	113.2(5)	N(2)-C(3)-C(19)	108.5(4)
C(25)-N(3)-C(26)	110.9(4)	C(2)-C(3)-C(19)	109.0(4)
C(25)-N(3)-C(27)	124.4(5)	O(2)-C(4)-C(5)	105.4(6)
C(26)-N(3)-C(27)	124.6(5)	O(2)-C(4)-C(6)	112.8(8)
N(2)-N(4)-C(26)	109.0(4)	C(5)-C(4)-C(6)	109.9(7)
S-C(1)-O(2)	113.5(4)	O(3)-C(25)-N(2)	125.7(5)
S-C(1)-N(1)	103.2(3)	O(3)-C(25)-N(3)	128.4(5)
S-C(1)-C(7)	108.3(4)	N(2)-C(25)-N(3)	105.9(5)
O(2)-C(1)-N(1)	111.7(5)	O(4)-C(26)-N(3)	127.1(5)
O(2)-C(1)-C(7)	107.1(4)	O(4)-C(26)-N(4)	126.4(6)
N(1)-C(1)-C(7)	113.1(5)	N(3)-C(26)-N(4)	106.5(5)

0.80 + 0.35 tan θ . An aperture with a height of 4 mm and a variable width, calculated as (2 + tan θ) mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 5.49° min⁻¹. The rate for the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 40 and the maximum scan time would not exceed 60 s. If in a preliminary scan $I/\sigma(I) < 2$, this measurement was used as the datum. Scan rates varied from 1.26 to 5.49° min⁻¹. Of the 96

steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were checked after 100 reflections to check the effects of crystal movement. If the standard deviation of the h , k , and l values of any orientation reflection exceeded 0.06, a new orientation matrix was calculated on the basis of the recentring of the 24 reference reflections.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN direct method analysis.¹⁶ After several cycles of refinements¹⁵ the positions of the hydrogen atoms were found in the difference map, and added with a constant isotropic temperature factor of 0.5 Å² to the refinement process. A final difference Fourier synthesis map showed several peaks less than 3e Å³ which might correspond to some traces of PrⁱOH.

The discrepancy indices, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 5.

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