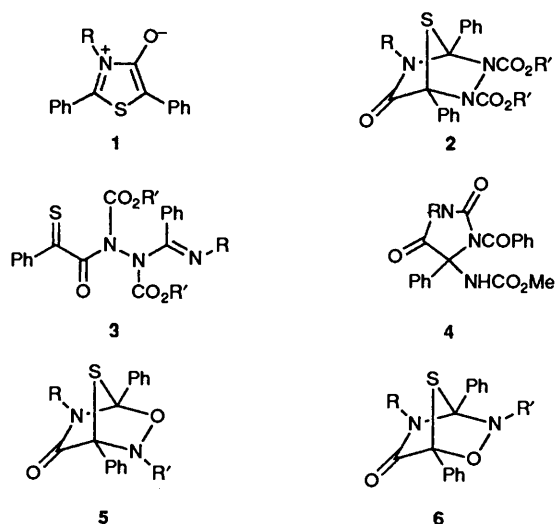# Cycloaddition of Nitroso Dipolarophiles to Thiazolium-4-olates. Part 1. Nitrosobenzene and 1-Chloro-1-nitrosocyclohexane

Tuvia Sheradsky* and Norbert Itzhak
Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Thiazolium-4-olates **1** and nitrosobenzene participated in regiospecific cycloadditions which gave 3-oxa-2,5-diaza-7-thiatrinorbornan-6-ones **5**. On storage, compounds **5** rearranged to the azeto-benzothiazine *S*-oxides **7**, fragmented to the benzil diimides **8**, and a lost sulfur atom to give the iminoimides **9**. The cycloadditions of mesoionic compounds **1** with 1-chloro-1-nitrosocyclohexane exhibited a reversed regiochemistry and formed the trinorbornanes **6**, which were subsequently attacked by nucleophiles at the bridgehead to produce the thiazolones **14**. The mechanisms of formation of all the products are discussed. Structures **7a** and **14d** were confirmed by single-crystal X-ray analyses.

We have previously reported[1] the cycloaddition of azodicarbonyl dipolarophiles to thiazolium-4-olates **1**. These reactions afforded the sulfur-bridged heterocycles **2**, which underwent some very unusual reactions. Examples are the thermal rearrangement of bicycles **2** to linear compounds **3**[1] and the Raney nickel desulfuration of bicycles **2** which gave imidazolidines **4**.[2] We have since studied the analogous cycloaddition of mesoionic compounds **1** to nitroso dipolarophiles, which would lead to systems **5** and **6**, and these can be expected to exhibit even more interesting activities and unusual transformations.

a; R = R¹ = Ph
b; R = R¹ = *p*-MeC₆H₄
c; R = R¹ = *p*-ClC₆H₄
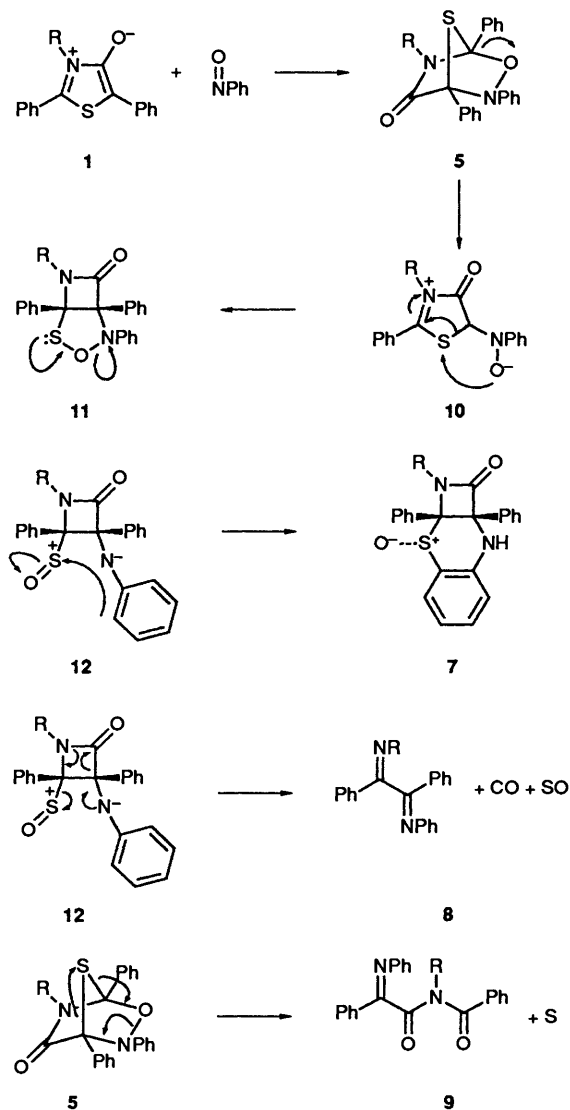d; R = R¹ = PhCH₂
e; R = R¹ = c-C₆H₁₁

Only a few 1,3-cycloadditions which involve nitroso dipolarophiles and 1,3-dipoles or mesoions have been reported.[3] In none of them was the primary cycloadduct isolated and characterized. The available data (from both 1,3- and 1,4-cycloadditions)[4] do not allow a reliable prediction of the regiochemistry and of the preferential formation of products **5** or **6** to be made.

Three types of nitroso compounds were used in this study. The results with nitrosobenzene and with 1-chloro-1-nitrosocyclohexane are reported here, and results with acylnitroso dipolarophiles in a forthcoming paper.

Reactions with Nitrosobenzene.—The reaction of substrate **1a** with nitrosobenzene in benzene at room temperature was complete in a few hours, as was evident from the colour change from orange-red to light yellow. From the reaction mixture we isolated four products. The major product (53%, $C_{27}H_{20}N_2O_2S$) contained the elements of both components. Its spectral properties (IR absorption at 1760 cm⁻¹ and lack of NH or OH absorptions) and particularly the fact that upon storage in solution it was transformed into a mixture of the other three products indicate that it is an initial adduct. Based on the structures of its products we have assigned its structure as **5a** (R = R' = Ph). The second product isolated (8%) was an isomer of product **5a** and its IR spectrum showed absorptions of NH (3170 cm⁻¹), C=O (1760 cm⁻¹) and SO (1040 cm⁻¹). An X-ray analysis established the structure as **7a** (see Fig. 1). Analysis of the third product ($C_{26}H_{20}N_2$, 10%) showed the loss of carbonyl, oxygen and sulfur. Comparison with authentic material[5] confirmed the structure **8a**. The fourth product ($C_{27}H_{20}N_2O_2$, 13%) resulted from loss of sulfur from bicycle **5a** and was assigned as **9a**, and this assignment is in accord with the IR spectrum.

Similar results were obtained in the reactions of mesoionic substrates **1b** and **1c** with nitrosobenzene, although the primary adducts **5b** and **5c** were too unstable to be characterized. The reaction of compound **1d** gave only an intractable mixture, from which no defined products could be isolated.

Two of the final products (**7** and **8**) contain a new bond between the two former bridgehead carbons, and we believe that they were indeed formed through a common intermediate. The suggested pathway is in accord with the usual mode of reactivity we have uncovered previously[1,6] for such strained bicyclic systems which contain several different heteroatoms. Relief of strain is achieved by cleavage of a bridgehead bond to form non-stabilized zwitterions, which find ways to neutralize their charges. These neutralization pathways are often unusual and unexpected. In the present case the cleavage occurs at the C–O bond of **5** to the zwitterion **10**. Neutralization then occurs through attack of the oxygen anion on the sulfur with formation of the C–C bond to give the β-lactam **11**, which is unstable and undergoes cleavage to the zwitterion **12**. Charge neutralization in intermediate **12** occurs in two ways: (a) Attack by the electrophilic sulfur at the *ortho* position of the highly activated N-phenyl ring, to give **7** or (b) a fragmentation process, with loss of CO and SO, which leads to the benzyl diimine **8**. Neutralizations through decarbonylation have been observed by us previously,[7] and eliminations of SO, although rare, have been reported.[8] The formation of imino imides **9** occurs by a completely different route, and probably involves direct loss of sulfur from intermediate **5**.
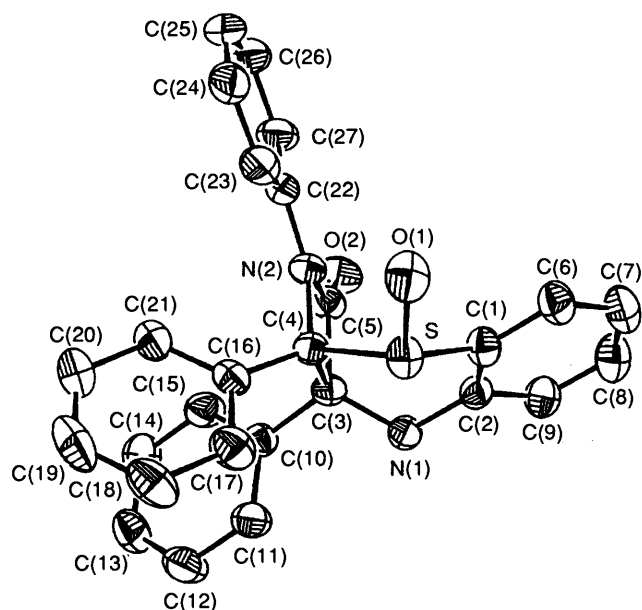
Fig. 1   X-Ray molecular structure of compound 7a
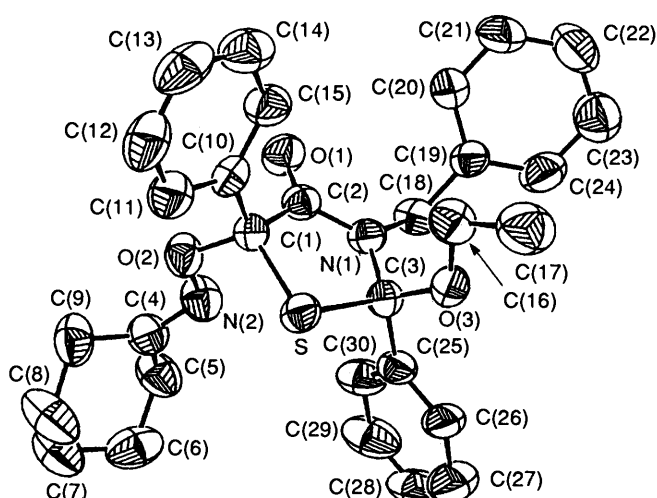
Fig. 2   X-Ray molecular structure of compound 14d

solvent-dependent ratio (3:1 in benzene, 2:1 in dichloro-methane, and 2:3 in methanol). Most significant is the amount of imino imide 9a (~1%) formed in these experiments which is much smaller than that formed directly in the cycloaddition mixture. This supports the possibility that the loss of sulfur from bicycles 5 is a catalytic process.[9]

Reaction with 1-*Chloro-*1-*nitrosocyclohexane.*—This stable and easily prepared nitrosoalkane is very useful as a dienophile. Its Diels–Alder reactions are usually run in a diethyl ether–ethanol mixture, in which the cyclohexyl moiety is cleaved from the cycloadducts to give *N*-unsubstituted cyclic hydroxyl-amines.[10] Accordingly we first tried the reaction of substrate 1d with 1-chloro-1-nitrosocyclohexane in 2:1 diethyl ether–ethanol, and expected to get either compound 5 (R' = H) or its regioisomer 6 (R' = H). From the reaction mixture we isolated only one product, in 37% yield. Analysis showed that it retained the cyclohexyl group and that a molecule of ethanol was also incorporated. An X-ray analysis established the structure as 14d (R'' = Et) (see Fig. 2). The same reaction in dichloromethane (in the absence of ethanol) gave an analogous product with incorporation of water 14d (R'' = H). Similar results were obtained in the reaction of substrate 1c with 1-chloro-1-nitrosocyclohexane. The formation of compounds 14 has to proceed through adducts of type 6, which are transformed into the iminium salts 13. Most significant is the fact that despite the very high electrophility of the iminium carbon, the attack of ethanol didn't occur there but at the bridgehead carbon. The effect of strain thus overcame electronic effects. This mechanism is supported by the stereochemistry of the final product 14, in which the two phenyl groups are in a *trans* relationship, which must result from inversion at a bridgehead.

Regioselectivity.—In the reaction with nitrosobenzene the combined yield of the adduct 5 and products thereof was over 85%. No products resulting from the regioisomeric adduct 6 were observed and the reaction is thus at least highly regio-selective and may be even regiospecific. With 1-chloro-1-nitro-socyclohexane we have obtained only products which result from the adduct 6, but as the maximum yield was only 43%, the regioselectivity remains inconclusive.

Experimental
M.p.s were taken with a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 157 spectrometer (Nujol mulls), and NMR spectra (CDCl₃ solutions) on a Bruker WH-200 spectrometer. *J*-Values are

Upon storage in solution, intermediate 5a was converted within two days to a mixture of products 7a and 8a, in a

Table 1 Positional parameters and estimated standard deviations for compound **7a**

Atom	x/a	y/b	z/b	Atom	x/a	y/b	z/b
S	0.235 23(4)	0.306 03(5)	0.247 68(7)	C(12)	0.194 8(2)	0.041 9(3)	0.748 0(3)
O(1)	0.1973 (1)	0.385 2(1)	0.158 5(2)	C(13)	0.132 6(2)	−0.015 1(2)	0.760 6(3)
O(2)	0.119 1(1)	0.020 1(1)	0.134 0(2)	C(14)	0.089 7(2)	−0.034 6(2)	0.636 1(3)
N(1)	0.268 2(1)	0.093 1(2)	0.304 1(2)	C(15)	0.108 9(2)	0.003 5(2)	0.496 7(3)
N(2)	0.110 3(1)	0.188 1(1)	0.208 4(2)	C(16)	0.132 6(1)	0.270 1(2)	0.464 0(3)
C(1)	0.276 7(1)	0.223 5(2)	0.119 4(3)	C(17)	0.178 2(2)	0.319 5(2)	0.565 5(3)
C(2)	0.294 5(1)	0.128 1(2)	0.167 3(3)	C(18)	0.151 0(2)	0.352 9(2)	0.701 8(3)
C(3)	0.191 4(1)	0.110 6(2)	0.337 3(3)	C(19)	0.078 3(2)	0.337 8(3)	0.736 0(3)
C(4)	0.163 0(1)	0.223 3(2)	0.323 9(3)	C(20)	0.032 0(2)	0.289 9(3)	0.635 7(4)
C(5)	0.135 4(1)	0.091 5(2)	0.207 3(3)	C(21)	0.058 7(2)	0.256 6(2)	0.499 5(3)
C(6)	0.301 7(2)	0.261 9(2)	−0.014 7(3)	C(22)	0.048 9(1)	0.232 8(2)	0.133 9(3)
C(7)	0.347 6(2)	0.204 9(2)	−0.102 7(3)	C(23)	0.032 3(2)	0.332 2(2)	0.154 9(3)
C(8)	0.367 8(2)	0.110 8(2)	−0.053 5(4)	C(24)	−0.030 5(2)	0.373 0(3)	0.086 9(3)
C(9)	0.341 6(2)	0.071 9(2)	0.079 0(3)	C(25)	−0.075 3(2)	0.314 2(3)	−0.003 1(3)
C(10)	0.171 7(1)	0.061 9(2)	0.483 4(3)	C(26)	−0.059 1(2)	0.216 2(3)	−0.025 0(4)
C(11)	0.215 0(2)	0.078 9(2)	0.610 7(3)	C(27)	0.004 0(2)	0.174 2(2)	0.042 2(3)

Table 2 Selected bond lengths (Å) and angles (°) for compound **7a**

|			
S=O(1)	1.493(2)	O(1)–S–C(1)	107.5(1)
S–C(1)	1.775(3)	O(1)–S–C(4)	107.6(1)
O(2)–C(5)	1.199(3)	C(1)–S–C(4)	99.8(1)
N(1)–C(2)	1.401(3)	C(2–N(1)–C(3)	117.9(2)
N(1)–C(3)	1.453(3)	N(1)–C(3)–C(4)	116.5(2)
N(2)–C(4)	1.473(3)	N(1)–C(3)–C(5)	116.1(2)
N(2)–C(5)	1.381(3)	C(4)–C(3)–C(5)	84.1(2)
C(3)–C(4)	1.609(3)	S–C(4)–N(2)	113.1(2)
C(3)–C(5)	1.551(3)	S–C(4)–C(3)	111.5(2)
		N(2)–C(4)–C(3)	87.2(2)
		N(2)–C(5)–C(3)	92.9(2)

given in Hz. Column chromatography was done on E. Merck silica gel 60 (70–230 mesh). HPLC analyses were carried out on a Merck-Hitachi system, using a 100RP-18 column. Light petroleum refers to the fraction with boiling range 40–60 °C.

Thiazolium-4-olates **1**.—Their preparation has been described previously.[11]

Reaction of 2,3,5-Triphenylthiazolium-4-olate **1a** *with Nitrosobenzene.*—A solution of compound **1a** (0.66 g, 2 mmol) and nitrosobenzene (0.21 g, 2 mmol) in benzene (20 cm³) was left at room temperature overnight. The colour changed from orange-red to light yellow. The mixture was evaporated under reduced pressure and the residue was dissolved in ethanol (10 cm³). After 30 min the precipitate of 1,2,4,5-*tetraphenyl-7-thia-3-oxa-2,5-diazatrinorbornan-6-one* **5a** (0.46 g, 53%) was collected, m.p. 137 °C (Found: C, 74.6; H, 4.8; N, 6.4; S, 7.0. $C_{27}H_{20}N_2O_2S$ requires C, 74.3; H, 4.6; N, 6.5; S, 7.3%); *m/z* 404 (M⁺ − S, 1%), 360 (17), 181 (18), 180 (100), 105 (4) and 77 (49).

Evaporation of the filtrate and addition of diethyl ether (10 cm³) caused precipitation of a solid, which was crystallized from chloroform–light petroleum to give 1,2a,3,8a-*tetrahydro-*1,2a,8a-*triphenyl-2H-azeto*[2,3-b][1,4]*benzothiazin-2-one* 8-*oxide* **7a** (70 mg, 8%), m.p. 198 °C (Found: C, 74.5; H, 4.8; N, 6.6; S, 7.3%); ν_{max}/cm⁻¹ 3170 (NH), 1760 (C=O) and 1040 (S=O); *m/z* 408 (M⁺ − CO, 26%), 228 (8), 212 (50), 181 (31), 180 (100), 105 (21) and 77 (96).

The residue from the filtrate was dissolved in ethanol (10 cm³) and left overnight. The yellow precipitate thus formed was recrystallized from ethanol to give N-(N-*phenylbenzimidoyl-carbonyl*)*benzanilide* **9a** (70 mg, 13%), m.p. 174 °C (Found: C, 80.6; H, 5.0; N, 6.7. $C_{27}H_{20}N_2O_2$ requires C, 80.2; H, 5.0; N, 7.0%); ν_{max}/cm⁻¹ 1700, 1685 (C=O), 1620 (C=N), 1595 and
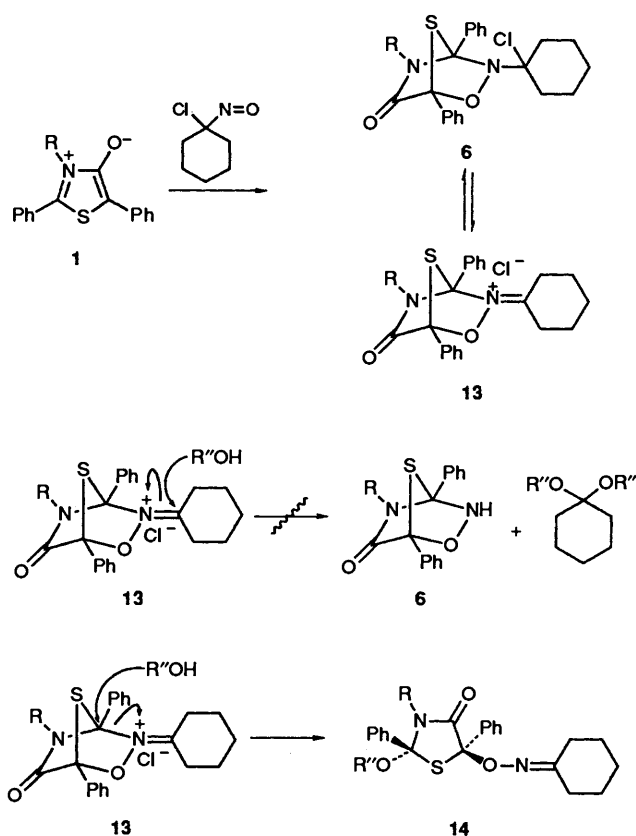
1585; *m/z* 404 (M⁺, 12), 301 (7), 181 (63), 180 (100), 119 (3), 105 (88) and 77 (95).

Evaporation of the mother liquor and chromatography on silica gel (eluent chloroform) yielded N,N′-diphenylbenzil di-imine **8a** (70 mg, 9.5%), m.p. 140 °C (lit.,[5] 140 °C).

Reaction of Compound **1b** *with Nitrosobenzene.*—As described above, using 2 mmol of each component. No precipitation of intermediate **5b** from ethanol occurred. The solution was evaporated and the oily residue was dissolved in diethyl ether (15 cm³). After storage overnight *compound* **7b** had precipitated out (200 mg, 30%) and was crystallized twice from dichloromethane–light petroleum, m.p. 205 °C (Found: C, 74.4; H, 4.8; N, 6.2; S, 7.3. $C_{28}H_{22}N_2O_2S$ requires C, 74.65; H, 4.9; N, 6.2; S, 7.1%); δ_H 7.78–6.66 (18 H, m), 4.70 (1 H, s) and 2.26 (3 H, s);

Table 3 Positional parameters and estimated standard deviations for compound **14d**

Atom	x/a	y/b	z/b	Atom	x/a	y/b	z/b
S	0.220 20(6)	0.161 96(9)	0.084 58(9)	C(13)	0.109 1(4)	0.456 4(4)	−0.168 6(4)
O(1)	0.341 1(2)	0.167 2(2)	−0.161 3(2)	C(14)	0.193 6(4)	0.448 1(4)	−0.162 4(4)
O(2)	0.181 9(2)	0.097 9(2)	−0.115 3(2)	C(15)	0.231 9(3)	0.358 6(3)	−0.127 7(4)
O(3)	0.360 7(2)	0.234 4(2)	0.187 6(2)	C(16)	0.346 6(3)	0.337 6(3)	0.151 4(4)
N(1)	0.366 4(2)	0.158 9(2)	0.019 0(3)	C(17)	0.365 2(4)	0.407 5(4)	0.244 8(4)
N(2)	0.221 6(2)	0.002 2(3)	−0.090 7(3)	C(18)	0.455 0(2)	0.143 1(3)	0.016 5(4)
C(1)	0.226 4(2)	0.176 8(3)	−0.057 9(3)	C(19)	0.505 5(2)	0.240 1(3)	0.019 2(3)
C(2)	0.316 7(3)	0.167 1(3)	−0.074 1(3)	C(20)	0.498 5(3)	0.308 6(4)	−0.062 9(4)
C(3)	0.331 8(2)	0.155 5(3)	0.120 0(3)	C(21)	0.545 6(4)	0.392 5(4)	−0.061 8(5)
C(4)	0.175 1(3)	−0.072 4(4)	−0.115 0(4)	C(22)	0.603 1(3)	0.411 0(4)	0.022 0(5)
C(5)	0.211 4(3)	−0.175 9(4)	−0.097 0(4)	C(23)	0.611 3(3)	0.345 9(5)	0.106 1(5)
C(6)	0.159 4(4)	−0.245 9(4)	−0.038 9(4)	C(24)	0.562 3(3)	0.259 9(4)	0.104 0(4)
C(7)	0.073 5(4)	−0.247 1(4)	−0.095 4(5)	C(25)	0.350 0(2)	0.056 3(4)	0.181 2(4)
C(8)	0.037 8(4)	−0.138 9(5)	−0.100 0(6)	C(26)	0.352 8(3)	0.056 9(4)	0.290 2(4)
C(9)	0.087 3(3)	−0.069 4(4)	−0.158 7(4)	C(27)	0.368 5(4)	−0.033 0(6)	0.346 7(5)
C(10)	0.187 3(3)	0.275 8(3)	−0.097 9(3)	C(28)	0.378 3(4)	−0.122 1(6)	0.293 8(7)
C(11)	0.102 9(3)	0.284 8(4)	−0.103 1(4)	C(29)	0.373 3(3)	−0.124 5(4)	0.184 0(6)
C(12)	0.064 8(3)	0.376 0(4)	−0.137 7(4)	C(30)	0.358 9(3)	−0.034 3(4)	0.129 0(4)

Table 4 Selected bond lengths (Å) and angles (°) for compound **14d**

S–C(1)	1.829(4)	C(1)–S–C(3)	95.3(2)
S–C(3)	1.851(4)	N(2)–O(2)–C(1)	108.9(3)
O(1)–C(2)	1.214(5)	C(2)–N(1)–C(3)	120.4(3)
O(2)–N(2)	1.435(4)	S–C(1)–O(2)	110.5(3)
O(2)–C(1)	1.426(5)	S–C(1)–C(2)	106.0(3)
N(1)–C(2)	1.372(5)	S–C(1)–C(10)	111.0(3)
N(1)–C(3)	1.454(5)	N(1)–C(2)–C(1)	113.4(3)
N(2)–C(4)	1.261(6)	S–C(3)–N(1)	104.7(3)
C(1)–C(2)	1.529(6)	S–C(3)–C(25)	107.6(3)

Table 5 Crystallographic data

	7a	14d
Formula	$C_{27}H_{20}N_2O_2S$	$C_{30}H_{32}N_2O_3S$
M	436.5	500.7
Space group	$P2_1/n$	$P2_1/n$
a/Å	18.174(4)	16.486(4)
b/Å	13.491(4)	13.115(3)
c/Å	8.926(3)	12.674(3)
$\beta/°$	91.05(3)	97.75(4)
$V/Å^3$	2188.2(7)	2726.5(8)
Z	4	4
D_c/g cm^{-3}	1.33	1.22
μ/cm^{-1} (Mo-Kα)	1.34	1.14
Total reflections	4922	6080
Unique data [$I \geq 3\sigma(I)$]	3478	3407
R	0.051	0.072
R_w	0.080	0.092
w	$\sigma^2 + 0.002\ 477\ F^2$	σ_F^2

v_{max}/cm^{-1} 3320 and 1750; m/z 422 (M⁺ − CO, 51%), 302 (22), 284 (7), 228 (9), 212 (87), 211 (52), 195 (84), 194 (100), 165 (13), 104 (49), 91 (95) and 77 (54).

An ethanolic solution of the residue obtained upon evaporation of the filtrate deposited, after storage overnight, crystals of *compound* **9b** (230 mg, 27%), m.p. 148 °C (Found: C, 80.65; H, 5.4; N, 6.8. $C_{28}H_{22}N_2O_2$ requires C, 80.4; H, 5.3; N, 6.8%); v_{max}/cm^{-1} 1690, 1680 (C=O) and 1620.

Chromatography of the residue obtained from the mother liquor afforded *compound* **8b** (130 mg, 17%), m.p. 112 °C (Found: C, 86.9; H, 6.1; N, 7.4. $C_{27}H_{22}N_2$ requires C, 86.6; H, 5.9; N, 7.5%).

Reaction of Compound **1c** *with Nitrosobenzene.*—Carried out as above. The β-*lactam* **7c** was obtained in 7.5% yield, m.p. 214 °C (Found: C, 68.55; H, 3.9; N, 5.85; S, 6.9; Cl, 7.1. $C_{27}H_{19}ClN_2O_2S$ requires C, 68.9; H, 4.1; N, 5.9; S, 6.8; Cl, 7.5%); v_{max}/cm^{-1} 3320 and 1755; m/z 443 (M⁺ − CO, 24%), 301 (40), 228 (31), 216 (73), 215 (68), 214 (100), 212 (99), 150 (15), 105 (29) and 77 (28).

Reaction of Compound **1c** *with* 1-*Chloro*-1-*nitrosocyclohexane.*—A solution of compound **1c** (0.73 g, 2 mmol) and 1-chloro-1-nitrosocyclohexane (0.3 g, 2 mmol) in benzene (30 cm³) was stirred overnight at room temperature. Ethanol (10 cm³) was added and after 1 h the solution was evaporated and the residue was crystallized from ethanol to give the *thiazolone* **14c** (R″ = Et) (0.45 g, 43%), m.p. 128 °C (Found: C, 66.8; H, 5.8; N, 5.4; S, 5.6. $C_{29}H_{29}ClN_2O_3S$ requires C, 66.85; H, 5.6; N, 5.4; S, 6.15%); δ_H 7.95–7.05 (14 H, m), 3.80 and 3.51 (1 H each, dq, J_1 7, J_2 2), 2.60–2.36 (4 H, m), 1.83–1.55 (6 H, m) and 1.30 (3 H, t); v_{max}/cm^{-1} 1700 (C=O), 1645 (C=N) and 940 (N–O).

Reaction of Compound **1d** *with* 1-*Chloro*-1-*nitrosocyclo-*

hexane.—(a) *In diethyl ether–ethanol.* A mixture of compound **1d** (1.03 g, 3 mmol) and 1-chloro-1-nitrosocyclohexane (0.44 g, 3 mmol) in diethyl ether–ethanol (3:1, 30 cm³) was stirred overnight at room temperature. The light yellow solution was evaporated and the oily residue was chromatographed on silica gel. Elution with chloroform–hexane (8:2) gave the *thiazolone* **14d** (R″ = Et), which was crystallized from dichloromethane–light petroleum, m.p. 135 °C (0.55 g, 37%) (Found: C, 72.3; H, 6.6; N, 5.6; S, 5.95. $C_{30}H_{32}N_2O_3S$ requires C, 72.0; H, 6.4; N, 5.6; S, 6.4%); δ_H 7.97–7.15 (15 H, m), 4.58 and 4.16 (1 H, each, d, *J* 15), 3.52 and 2.71 (1 H each, dq, J_1 7, J_2 2), 2.73–2.51 (2 H, m), 2.33 (2 H, m), 1.72–1.58 (6 H, m) and 0.93 (3 H, t); v_{max}/cm^{-1} 1695 (C=O), 1650 (C=N) and 950 (N–O).

(b) *In dichloromethane.* Quantities as above in dichloromethane (30 cm³) containing water (0.5 cm³). After the mixture had been stirred overnight and evaporated the residue was repeatedly washed with diethyl ether (3 × 20 cm³). The combined washings were concentrated to 10 cm³, and upon storage deposited crystals of the *thiazolone* **14d** (R″ = H) (0.35 g, 25%), m.p. 128 °C (Found: C, 71.55; H, 6.1; N, 6.0; S, 6.95. $C_{28}H_{28}N_2O_3S$ requires C, 71.2; H, 6.0; N, 5.9; S, 6.8%); δ_H 7.73–7.12 (15 H, m), 4.48 and 4.24 (1 H each, d, *J* 15), 2.65 (2 H, m), 2.12 (2 H, m) and 1.72–1.62 (6 H, m); v_{max}/cm^{-1} 3250 (OH), 1695 (C=O), 1650 (C=N) and 950 (N–O).

X-Ray Crystal Structure Analyses.—Data were measured on

a PW1100/20 Philips Four-Circle Computer-Controlled Diffractometer; Mo-Kα (λ = 0.071 069 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 18 centred reflections in the range $11 \leqslant \theta \leqslant 15°$. Intensity data were collected using the $\omega-2\theta$ technique to a maximum 2θ of 45°. The scan width, Δw, for each reflection was $1.00 + 0.35 \tan\theta$ with a scan speed of 0.05°/min. Background measurements were made for a total of 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 Lorenz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELK86[12] direct methods analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated, and added with a constant isotopic temperature factor of 0.05 Å[2] to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma_w(|F_o| - |F_c|)^2$. Residual electron density was less than 0.3 e Å^{-3}. Atomic coordinates and selected bond lengths and angles for compound 7a are given in Tables 1 and 2; those data for compound 14d are in Tables 3 and 4.

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

---

* Tables of positional and thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. For details of the scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, issue 1, 1992.

References

1 T. Sheradsky and N. Itzhak, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1979.
2 T. Sheradsky and N. Itzhak, *J. Chem. Soc., Perkin Trans. 1*, 1989, 33.
3 *Nitrile oxides*: F. Minisci, R. Galli and A. Quilico, *Tetrahedron Lett.*, 1963, 785; *Nitrile ylides*: K. Bunge, R. Huisgen, R. Raab and H. J. Sturm, *Chem. Ber.*, 1972, **105**, 1307; K. Burger, K. Einhellig, W. D. Roth and E. Daltrozzo, *Chem. Ber.*, 1977, **110**, 605; *Azomethine ylides*: J. W. Lown and J. P. Moser, *Can. J. Chem.*, 1970, **48**, 2227; J. W. Lown and M. H. Akhtar, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1459; *Diazoalkanes*: H. Staudinger and K. Mieschler, *Helv. Chim. Acta*, 1919, **2**, 554.
4 D. L. Boger and S. M. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic, San-Diego, 1987, pp. 72.
5 M. Siegfeld, *Ber. Dtsch. Chem. Ges.*, 1892, **25**, 2600.
6 T. Sheradsky and D. Zbaida, *Tetrahedron Lett.*, 1981, **22**, 1639.
7 T. Sheradsky and D. Zbaida, *J. Org. Chem.*, 1980, **45**, 4850.
8 J. Barluenga, J. F. Lopez-Ortiz, M. Tomas and V. Gotor, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1891.
9 R. Huisgen, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1989, **43**, 63.
10 For example: B. Belleau and Y. K. Au-Young, *J. Am. Chem. Soc.*, 1963, **85**, 64.
11 T. Sheradsky and D. Zbaida, *J. Org. Chem.*, 1980, **45**, 2165.
12 G. Sheldrick, SHELK86. A FORTRAN-77 Program for the Solution of Crystal Structures from Diffraction Data. Institut für Anorganische Chemie der Universität Göttingen.