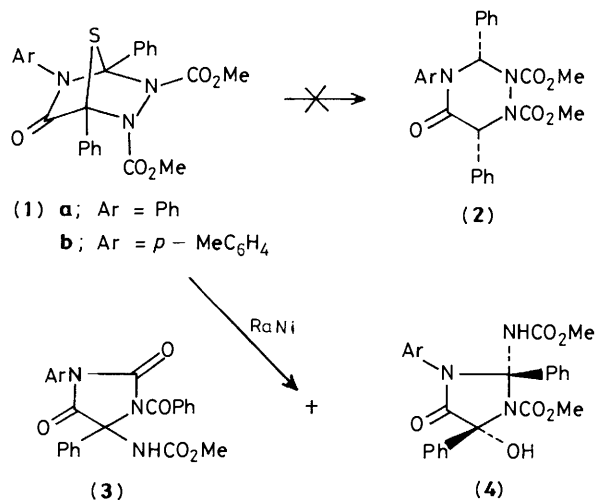# Desulphuration of Sulphur Bridged Hexahydrotriazines: Ring Contraction to Imidazolidines

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Raney nickel desulphuration of 6-aryl-2,3-bis(methoxycarbonyl)-1,4-diphenyl-7-thia-2,3,6-triaza-norbornane-5-ones (1a,b) yielded mainly 3-aryl-1-benzoyl-5-(methoxycarbonylamino)-5-phenyl-imidazolidine-2,4-diones (3a,b). A mechanism which involves six alternating ring-opening and ring-closure steps is suggested. Evidence in favour of this unusual pathway include the following: (*a*) structure of the minor products (4). (*b*) Desulphuration of the 6-benzyl derivative (1c), which allowed isolation of the intermediate (11c). (*c*) Desulphuration of the analogous sulphur bridged pyridone (15), which gave the dihydropyridone (17). Structures (3b), (11c), and (17) were confirmed by X-ray analyses.

In a previous paper[1] we have described the preparation of 3,6-sulphur bridged hexahydro-1,2,4-triazine-5-ones (1) through cycloaddition of thiazolium-4-olates and azodi-carboxylic esters, and reported some ring opening and rearrangement reactions of (1). A possible synthetic use of (1) is removal of the sulphur bridge to give stereospecifically polysubstituted hexahydrotriazines [*e.g.* (2)]. To this end, compounds (1a) and (1b) were treated with Raney nickel[2] [in acetone, owing to the fast reaction of (1) with the customarily used ethanol[1]]. The reaction afforded two unexpected products assigned as (3) and (4) in a 2:1 ratio.

(1) a; Ar = Ph
b; Ar = *p* — MeC6H4

(2)

(3)

(4)

Figure 1. Molecular structure of compound (3b)

The transformation (1)→(3) involves loss of a methylene group (evident from analyses and mass spectra), probably *via* addition of water and elimination of methanol. Indeed compounds (3) showed the presence of only one methyl group in their n.m.r. spectra. The i.r. spectrum of (3b) exhibited peaks at 3 330 cm⁻¹ (NH), 1 800, and 1 715 cm⁻¹ (CO–NR–CO in a 5-membered ring), 1 740 cm⁻¹ (carbamate) and 1 665 cm⁻¹ (non-cyclic amide). The parent peak in the mass spectrum was *m/z* 105 (COPh). All these data indicate structure (3). However, because of its high dissimilarity to the starting material (1), the structure of (3b) was confirmed by a single crystal X-ray analysis (Figure 1). The overall transformation (1)→(3) involves cleavage of five bonds and the formation of four new ones. We suggest a mechanism which consists of six alternating ring openings and ring closures. The key step is analogous to the
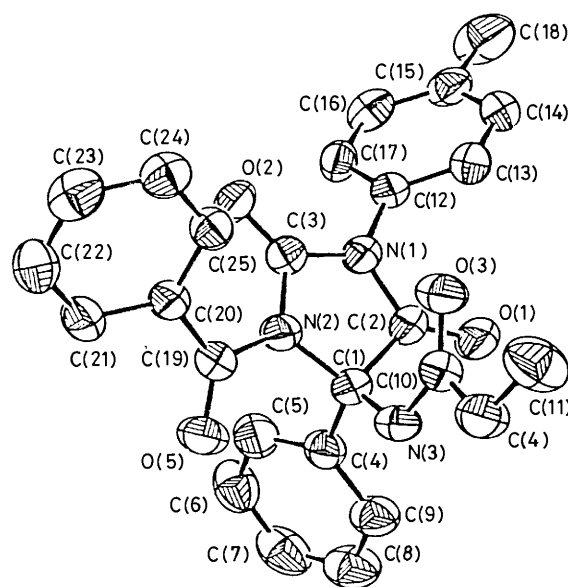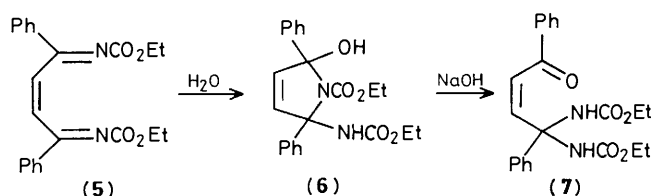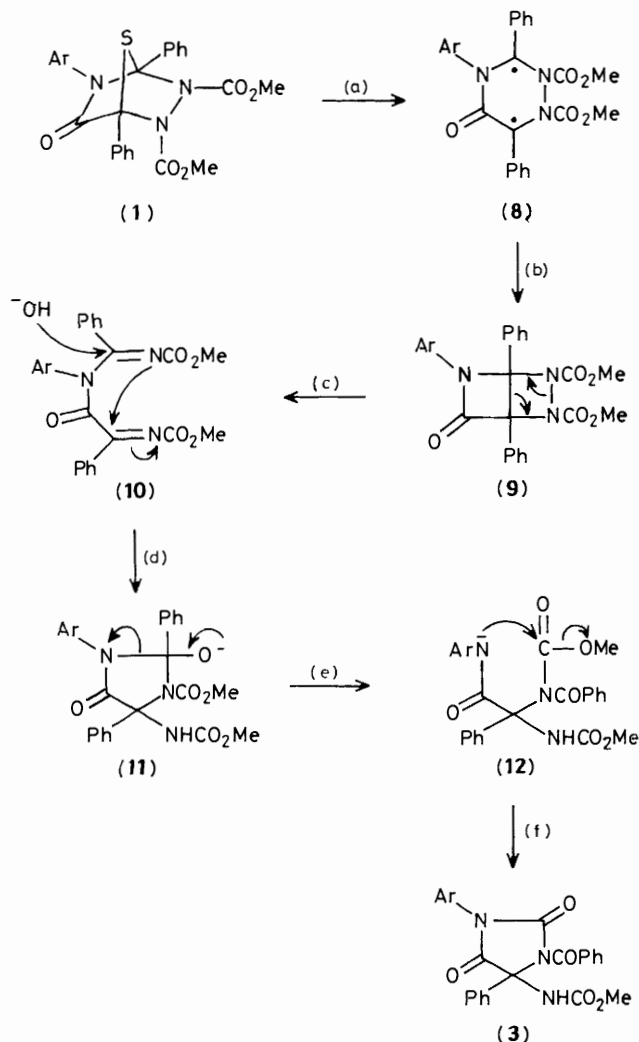
water addition-cyclization described by Rigaudy and Breliers[3] for compound (5) and the subsequent opening (6)→(7). The suggested mechanism is depicted in Scheme 1, followed by a detailed discussion. It should be noted that sodium hydroxide, which always accompanies Raney nickel, was mostly removed and was present in very low concentrations.

(5)

(6)

(7)

Step (a), *ring opening*. The usual initial step in Raney nickel desulphuration of sulphides[2] leads to the biradical (8).

Step (b), *ring closure*. The crowding around the radical centres does not allow an approach to the catalyst surface and transfer of hydrogen atoms to (8). The biradical therefore undergoes an intramolecular coupling to the bicyclic intermediate (9).

Scheme 1.

Table 1. Crystallographic data

	(3b)	(11c)	(17)
Formula	$C_{24}H_{21}N_3O_5$	$C_{26}H_{25}N_3O_6$	$C_{29}H_{27}NO_5$
M	443.5	475.5	469.5
Space group	$I2_1/C^a$	$P2_1/C$	$P1$
$a/\text{Å}$	19.985(2)	10.421(4)	11.044(3)
$b/\text{Å}$	11.119(2)	22.255(8)	11.700(3)
$c/\text{Å}$	20.435(3)	10.511(4)	9.984(3)
$\alpha/°$	90	90	94.28(7)
$\beta/°$	102.36(2)	93.39(5)	95.37(7)
$\gamma/°$	90	90	79.58(6)
$V/\text{Å}^3$	4 435.7(6)	2 432.0(9)	1 261.0(8)
Z	8	4	2
$D_c/\text{g cm}^{-3}$	1.33	1.30	1.24
μ/cm^{-1}	6.87 (Cu-K_α)	0.36 (Mo-K_α)	0.49 (Mo-K_α)
Total reflections	3 110	3 123	3 226
Unique data	2 703	1 923	2 830
	$[I \geqslant 2\sigma(I)]$	$[I \geqslant 3\sigma(I)]$	$[I \geqslant 2\sigma(I)]$
R	0.046	0.092	0.069
R_w	0.083	0.104	0.079
w	$(\sigma_F^2 + 0.002\ 204\ F^2)^{-1}$	σ_F^{-2}	σ_F^{-2}

^{a} A non-standard aspect of C_2/C (No. 15).

full accord with the assigned structure. Thus compound (**4b**) exhibited in the i.r. region the following absorption: an 3 450 (OH), 3 300 (NH), 1 735 and 1 720 (carbamates CO), and 1 695 cm^{-1} (γ-lactam CO). OH and NH signals were also observed in the n.m.r. spectrum at δ 6.26 (exchangeable with D_2O) and 6.73 respectively.
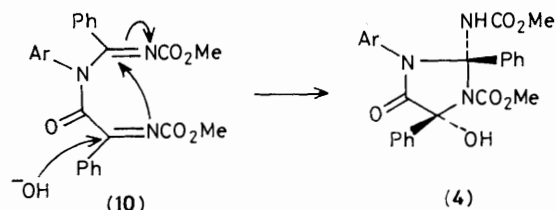
The desulphuration of the *N*-benzyl derivative (**1c**) proceeded *via* the same pathway, but apparently stopped after step (d), and gave a 2:1 mixture of (**11c**) and (**4c**). These two structural isomers, in which the positions of the hydroxy and methoxy-carbonylamino groups are exchanged, have similar spectral properties. The most significant difference was in the non-equivalence of the benzylic protons in the n.m.r. spectra (Δδ = 0.48 and 0.18 p.p.m.). We assumed that the isomer with the small non-equivalence is the one with the smaller OH group adjacent to the benzyl group (**11c**), and this reasoning was confirmed by an *X*-ray analysis of this isomer (Figure 2).

The *X*-ray analysis also established the stereochemistry of (**11c**) as shown with the hydroxy and methoxycarbonylamino groups in a *cis* relationship. A probable reason for this stereospecificity is hydrogen bonding in the intermediate anion (**13**) which controls the stereochemistry of the cyclization to (**11**) and keeps the two bonded groups on the same side. By analogy [through the intermediate anion (**14**)], we assigned the stereochemistry of compounds (**4**), and these considerations also apply to compound (**6**). The literature report [3] on (**6**) did not deal with the stereochemical aspects, but the reported data clearly indicate the formation of a single stereoisomer.

Step (c), *ring opening.* The highly strained (**9**) undergoes a retro (2 + 2) cleavage. This occurs at the right hand ring and involves cleavage of the weak N–N bond.

Step (d), *ring closure.* The intermediate (**10**) is similar to compound (**5**). Although the *cis*-ethene linkage in (**5**) is replaced by an amide moiety in (**10**), the distances and the planar shape are very close and water addition with cyclization in the same manner as (**5**)→(**6**) should take place. However, as (**10**) is unsymmetrical, this can proceed in two directions. The pathway to (**3**) involves water attack at the amide nitrogen side.

Step (e), *ring opening.* The elimination can occur either towards the carbamate nitrogen [as in (**6**)→(**7**)] or towards the amide nitrogen [not available in (**6**)], and the latter course is preferred.

Step (f), *ring closure.* The amide anion attacks the carbamate group, with replacement of a methoxide anion and formation of the isolated product (**3**).

This mechanism also accounts for the formation of the minor products. Cyclization of the intermediate (**10**) in the reversed direction, with water attack at the carbon adjacent to the amide carbonyl leads to (**4**). The reaction stops at this stage, as ring opening of (**4**) [like (**6**) ⟶ (**7**)] would require a high concentration of NaOH. Compounds (**4**) were obtained as single stereoisomers and the stereochemical assignment is discussed further below. The spectral properties of (**4**) were in

Table 2. Positional parameters and estimated standard deviations for (3b)

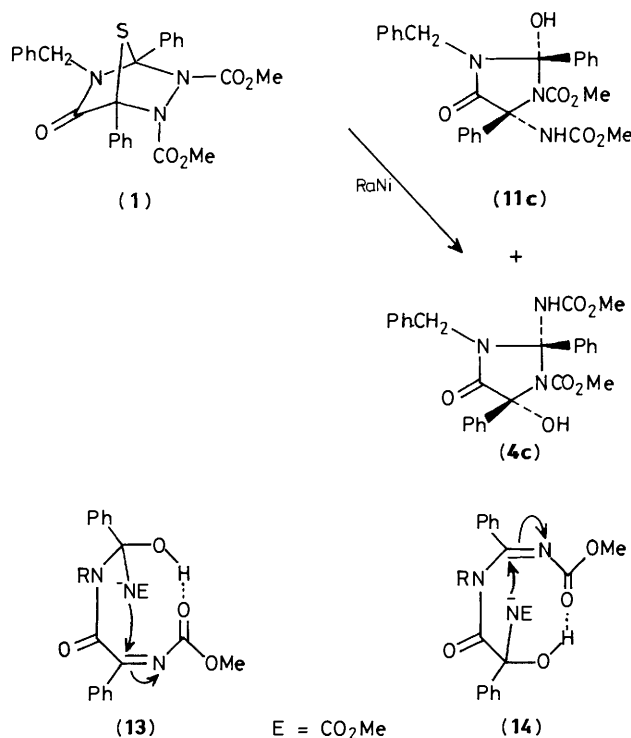| Atom	x	y	z	Atom	x	y	z
O(1)	0.678 28(9)	0.252 8(2)	0.478 78(9)	C(10)	0.547 2(1)	0.249 2(2)	0.550 8(1)
O(2)	0.491 24(8)	0.389 5(2)	0.328 45(7)	C(11)	0.531 3(2)	0.317 0(3)	0.655 0(2)
O(3)	0.550 2(1)	0.351 4(2)	0.531 05(9)	C(12)	0.638 7(1)	0.431 1(2)	0.374 4(1)
O(4)	0.537 91(9)	0.218 1(2)	0.611 09(9)	C(13)	0.683 8(1)	0.494 5(2)	0.422 2(1)
O(5)	0.430 41(9)	0.079 3(1)	0.408 7(1)	C(14)	0.731 5(1)	0.568 8(2)	0.402 7(1)
N(1)	0.596 13(9)	0.341 6(2)	0.395 51(9)	C(15)	0.735 2(1)	0.580 8(2)	0.335 8(1)
N(2)	0.504 91(9)	0.228 8(2)	0.403 47(9)	C(16)	0.686 7(1)	0.522 0(2)	0.289 1(1)
N(3)	0.553 7(1)	0.150 6(2)	0.513 49(9)	C(17)	0.638 4(1)	0.448 9(2)	0.306 9(1)
C(1)	0.563 5(1)	0.167 0(2)	0.446 0(1)	C(18)	0.792 2(2)	0.653 4(4)	0.317 0(2)
C(2)	0.621 0(1)	0.258 3(2)	0.445 3(1)	C(19)	0.438 1(1)	0.185 7(2)	0.397 4(1)
C(3)	0.525 9(1)	0.329 0(2)	0.370 6(1)	C(20)	0.380 0(1)	0.270 3(2)	0.383 1(1)
C(4)	0.563 0(1)	0.050 2(2)	0.415 6(1)	C(21)	0.317 0(1)	0.227 4(2)	0.348 9(1)
C(5)	0.565 5(1)	0.032 3(2)	0.347 0(1)	C(22)	0.259 7(1)	0.299 7(3)	0.339 5(2)
C(6)	0.586 7(1)	−0.068 9(3)	0.317 8(2)	C(23)	0.264 3(1)	0.414 1(3)	0.365 0(1)
C(7)	0.626 2(2)	−0.153 9(3)	0.357 9(2)	C(24)	0.326 8(1)	0.458 4(2)	0.400 4(1)
C(8)	0.644 8(2)	−0.137 0(3)	0.426 0(2)	C(25)	0.384 9(1)	0.386 9(2)	0.409 3(1)
C(9)	0.623 9(1)	−0.034 6(2)	0.455 1(1)				

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

Table 3. Selected bond lengths (Å) for compound (3b)

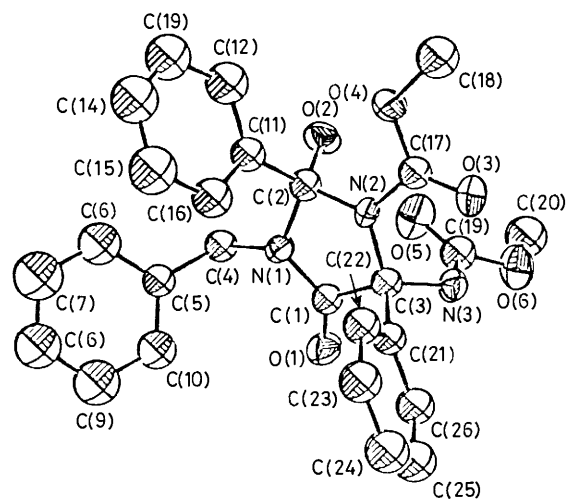|			
O(1)–C(2)	1.202(3)	N(2)–C(1)	1.471(3)
O(2)–C(3)	1.191(2)	N(2)–C(3)	1.410(3)
O(5)–C(19)	1.221(3)	N(2)–C(19)	1.399(3)
N(1)–C(2)	1.387(3)	C(1)–C(2)	1.536(3)
N(1)–C(3)	1.394(3)		

Table 4. Selected angles (°) for compound (3b)

C(2)–N(1)–C(3)	112.1(2)	N(3)–C(1)–C(4)	112.3(2)
C(2)–N(1)–C(12)	122.8(2)	N(1)–C(2)–C(1)	107.2(2)
C(3)–N(1)–C(12)	125.1(2)	O(1)–C(2)–N(1)	126.9(2)
C(1)–N(2)–C(3)	111.7(2)	O(1)–C(2)–C(1)	125.7(2)
C(1)–N(2)–C(19)	127.1(2)	N(1)–C(3)–N(2)	106.5(2)
C(3)–N(2)–C(19)	121.1(2)	O(2)–C(3)–N(1)	126.2(2)
N(2)–C(1)–C(2)	100.9(2)	O(2)–C(3)–N(2)	127.2(2)

(1)

(11c)

RaNi

+

(4c)

(13)   E = CO₂Me   (14)

Figure 2. Molecular structure of compound (11c)

The hydrogen bond between the hydroxy group and the carbamate carbonyl still exists in the products [(11c) and (4)], as revealed by the i.r. spectra and the X-ray picture of (11c). In the n.m.r. spectrum of (4c), change of the solvent from CDCl₃ to (CD₃)₂CO causes a considerable change in the non-equivalence of the benzylic protons, which drops from Δδ 0.48 p.p.m. to Δδ 0.06 p.p.m. This drop is, most probably, due to a change from intra- to inter-molecular hydrogen bonding with the solvent

and, consequently, a complete change in the conformation of the proximate methoxycarbonyl group. In the spectrum of (11c), in which the methoxycarbonyl group lies further away from the benzylic protons, the change of solvent had no effect on the non-equivalence. This phenomenon excludes the possibility that the second product is a stereoisomer of (11c), and confirms structure (4c).

The isolation of (11c) presents evidence for the late stages of the suggested mechanism. In order to gain evidence for the early stages we carried out the desulphuration of compound (15) (prepared from 2,3,5-triphenyl-thiazolium-4-olate and diethyl fumarate). It was expected, owing to the absence of the weak

Table 5. Positional parameters and estimated standard deviations for (11c)

Atom	x	y	z	Atom	x	y	z
O(1)	0.173 3(5)	0.351 8(2)	0.480 6(5)	C(10)	−0.063 7(8)	0.323 3(4)	0.260 0(9)
O(2)	0.436 1(5)	0.313 6(2)	0.208 6(5)	C(11)	0.294 5(7)	0.370 0(3)	0.063 8(7)
O(3)	0.526 6(5)	0.490 0(2)	0.306 4(5)	C(12)	0.354 6(9)	0.341 2(4)	−0.035 3(8)
O(4)	0.533 6(4)	0.431 5(2)	0.132 7(5)	C(13)	0.299 8(9)	0.351 8(4)	−0.161 6(9)
O(5)	0.480 9(5)	0.317 4(2)	0.464 7(5)	C(14)	0.198 8(9)	0.386 1(4)	−0.182(1)
O(6)	0.558 5(5)	0.367 8(3)	0.640 3(5)	C(15)	0.138(1)	0.414 2(5)	−0.090 8(9)
N(1)	0.234 1(5)	0.340 6(3)	0.276 3(5)	C(16)	0.188 9(8)	0.404 9(4)	0.037 3(8)
N(2)	0.386 8(5)	0.412 6(3)	0.272 0(5)	C(17)	0.488 0(7)	0.448 9(4)	0.242 6(7)
N(3)	0.423 5(5)	0.414 3(3)	0.504 9(5)	C(18)	0.637 0(8)	0.468 7(4)	0.091 7(8)
C(1)	0.236 7(7)	0.366 3(3)	0.392 3(7)	C(19)	0.486 5(8)	0.362 9(4)	0.530 5(8)
C(2)	0.343 3(7)	0.358 5(3)	0.201 9(7)	C(20)	0.630 1(9)	0.314 5(4)	0.677 7(9)
C(3)	0.330 9(6)	0.419 4(3)	0.395 4(7)	C(21)	0.255 4(7)	0.477 9(3)	0.406 1(7)
C(4)	0.162 3(6)	0.285 3(3)	0.244 8(7)	C(22)	0.224 3(7)	0.514 8(4)	0.301 3(7)
C(5)	0.028 3(7)	0.297 7(3)	0.189 2(7)	C(23)	0.150 1(7)	0.566 1(4)	0.311 9(8)
C(6)	−0.008 6(9)	0.280 2(4)	0.065 5(9)	C(24)	0.104 7(8)	0.580 2(4)	0.429 1(8)
C(7)	−0.134(1)	0.291 5(5)	0.012(1)	C(25)	0.134 5(8)	0.544 9(4)	0.532 2(9)
C(8)	−0.222(1)	0.318 7(4)	0.083 8(9)	C(26)	0.208 3(7)	0.493 9(4)	0.523 0(8)
C(9)	−0.188(1)	0.333 9(5)	0.207(1)				

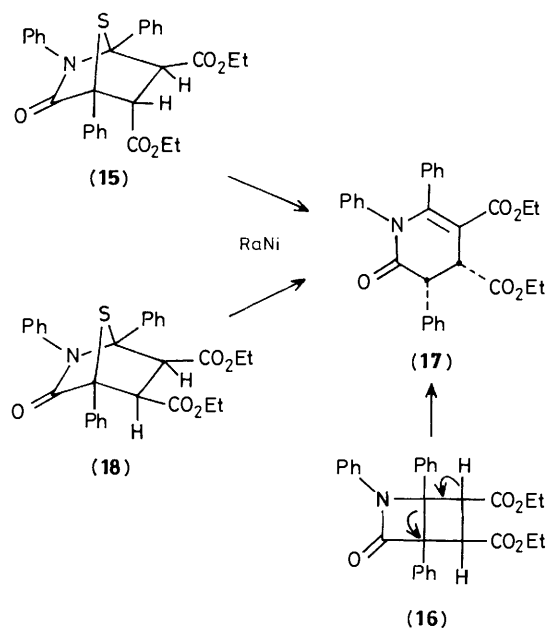Estimated standard deviations in the least significant digits are shown in parentheses.

Table 6. Selected bond lengths (Å) for (11c)

O(1)–C(1)	1.220(9)	N(2)–C(2)	1.468(9)
O(2)–C(2)	1.389(9)	N(2)–C(3)	1.466(9)
N(1)–C(1)	1.345(9)	N(2)–C(17)	1.380(9)
N(1)–C(2)	1.480(9)	N(3)–C(3)	1.455(8)
N(1)–C(4)	1.465(9)		

Table 7. Selected angles (°) for (11c)

C(1)–N(1)–C(2)	113.3(6)	N(1)–C(2)–C(11)	109.3(6)
C(1)–N(1)–C(4)	122.7(6)	O(2)–C(2)–C(11)	110.8(6)
C(2)–N(1)–C(4)	120.4(5)	N(2)–C(3)–C(1)	101.2(5)
C(2)–N(2)–C(3)	113.6(5)	N(2)–C(3)–N(3)	114.2(5)
C(2)–N(2)–C(17)	125.6(6)	N(3)–C(3)–C(21)	108.9(6)
N(1)–C(2)–N(2)	100.2(5)		

N–N bond, that we would be able to isolate (16). The reaction, however, gave an isomer of (16), which was identified through X-ray analysis (see Figure 3) as (17).

(15)

RaNi

(18)

(17)

(16)

Figure 3. Molecular structure of compound (17)

with the phenyl and ethoxycarbonyl groups in a *cis* relationship. The stereoisomer (17) is probably the thermodynamically more stable. Indeed no epimerization was observed on treating (17) with base. Furthermore, the desulphuration of the diethyl maleate adduct (18) in which the two carboxylic groups are *exo*[5] also gave stereospecifically (17).

The formation of (17) requires a 1,3-hydrogen migration. The fact that the migration was completely regiospecific and no product of a migration of the other hydrogen was detected, indicates that (16) was an intermediate in this process, since a reversed polarization of the central bond in (16) is highly unlikely. Noteworthy is the stereospecific formation of (17),

Experimental

M.p.s were taken with a Thomas-Hoover apparatus. I.r. spectra (Nujol mulls) were recorded with a Perkin-Elmer 157 spectrophotometer. N.m.r. spectra (CDCl₃ solutions) were taken on a Bruker WH-300 instrument, and mass spectra (70 eV) on a Varian MAT 311 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. Raney

Table 8. Positional parameters and estimated standard deviations for (**17**)

Atom	x	y	z	Atom	x	y	z
O(1)	0.924 7(3)	0.148 8(3)	0.146 1(4)	C(13)	0.606 6(4)	−0.130 4(4)	0.120 5(5)
O(2)	0.382 5(3)	0.279 7(3)	0.289 8(4)	C(14)	0.577 3(5)	−0.238 0(5)	0.134 7(6)
O(3)	0.384 3(3)	0.092 1(3)	0.233 2(3)	C(15)	0.555 4(5)	−0.271 4(5)	0.256 9(8)
O(4)	0.750 4(4)	0.261 3(3)	0.421 9(4)	C(16)	0.560 4(6)	−0.195 1(5)	0.368 5(6)
O(5)	0.630 4(3)	0.431 6(3)	0.383 2(4)	C(17)	0.587 0(5)	−0.085 5(4)	0.357 6(5)
N	0.771 4(3)	0.057 4(3)	0.195 9(4)	C(18)	0.437 5(4)	0.185 3(4)	0.254 3(4)
C(1)	0.815 1(5)	0.151 8(4)	0.151 9(5)	C(19)	0.255 2(4)	0.105 0(4)	0.259 8(5)
C(2)	0.646 7(4)	0.062 7(4)	0.221 1(4)	C(20)	0.222 5(5)	−0.011 7(5)	0.243 0(7)
C(3)	0.570 0(4)	0.167 5(4)	0.230 1(4)	C(21)	0.673 5(5)	0.320 2(4)	0.352 6(5)
C(4)	0.619 3(4)	0.277 9(4)	0.216 9(4)	C(22)	0.676 6(5)	0.481 0(5)	0.512 5(6)
C(5)	0.715 5(4)	0.252 0(4)	0.110 6(5)	C(23)	0.790 2(5)	0.528 5(6)	0.505 1(7)
C(6)	0.862 4(4)	−0.042 8(4)	0.236 0(5)	C(24)	0.760 5(4)	0.358 9(4)	0.073 7(5)
C(7)	0.921 0(4)	−0.116 0(4)	0.136 0(5)	C(25)	0.710 5(5)	0.409 7(4)	−0.044 0(5)
C(8)	1.008 2(5)	−0.210 9(4)	0.176 6(7)	C(26)	0.743 8(6)	0.512 0(5)	−0.080 4(7)
C(9)	1.034 9(5)	−0.232 3(5)	0.311 3(7)	C(27)	0.829 3(7)	0.581 7(5)	0.003 6(8)
C(10)	0.976 7(5)	−0.157 4(5)	0.407 7(6)	C(28)	0.879 4(5)	0.512 6(5)	0.120 0(7)
C(11)	0.890 5(5)	−0.061 4(4)	0.368 7(5)	C(29)	0.845 8(5)	0.410 8(5)	0.155 9(6)
C(12)	0.611 8(4)	−0.052 5(4)	0.234 1(5)				

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

Table 9. Selected bond lengths (Å) for compound (**17**)

O(1)–C(1)	1.211(6)	C(2)–C(3)	1.361(6)
N–C(1)	1.397(6)	C(3)–C(4)	1.509(7)
N–C(2)	1.413(6)	C(4)–C(5)	1.548(6)
C(1)–C(5)	1.508(6)		

Table 10. Selected angles (°) for compound (**17**)

C(1)–N–C(2)	122.6(4)	C(2)–C(3)–C(4)	119.8(4)
N–C(1)–C(5)	114.5(4)	C(2)–C(3)–C(18)	125.5(4)
O(1)–C(1)–N	120.7(5)	C(3)–C(4)–C(5)	107.8(4)
O(1)–C(1)–C(5)	124.7(5)	C(5)–C(4)–C(21)	112.5(4)
N–C(2)–C(3)	119.9(4)	C(1)–C(5)–C(4)	109.6(4)
C(3)–C(2)–C(12)	125.8(4)	C(4)–C(5)–C(24)	113.5(4)

nickel was of W-2 activity,[6] the water in its slurry was replaced by acetone before use.

Desulphuration of (**1a**).—To a solution of (**1a**) (0.95 g, 2 mmol) in acetone (60 ml), Raney nickel (*ca.* 10 g, slurry in acetone) was added. The mixture was stirred at room temperature for 4 h after which the nickel was allowed to settle at the bottom of the flask when the solution was removed by decantation. After three washings of the catalyst with acetone, the combined acetone solution was filtered and evaporated to give a quantitative yield of thick oil. T.l.c. showed the presence of two products and the mixture was chromatographed on silica gel (50 g), eluant chloroform–light petroleum (5:1) to afford the following.

1-*Benzoyl*-5-(*methoxycarbonylamino*)-3,5-*diphenylimidazolidine*-2,4-*dione* (**3a**), eluted first, was crystallized from dichloromethane–light petroleum (0.27 g, 32%), m.p. 162 °C (Found: C, 67.4; H, 4.6; N, 9.75. $C_{24}H_{19}N_3O_5$ requires C, 67.1; H, 4.5; N, 9.8%); $\nu_{max.}$ 3 320 (NH), 1 795, and 1 740 and 1 710 cm^{-1} (CO); δ 7.72—7.32 (15 H, m), 6.36 (1 H, s), and 3.75 (3 H, s); m/z 429 (M^+, 55%), 282 (45), 205 (96), 197 (72), 119 (45), 118 (42), 105 (100), 104 (65), 91 (23), and 77 (96).

5-*Hydroxy*-1-(*methoxycarbonyl*)-2-(*methoxycarbonylamino*)-2,3,5-*triphenylimidazolidin*-2-*one* (**4a**), eluted next, was also crystallized from dichloromethane–light petroleum (0.37 g, 40%), m.p. 207 °C (Found: C, 64.8; H, 5.0; N, 8.8. $C_{25}H_{23}N_3O_6$ requires C, 65.1; H, 5.0; N, 9.1%); $\nu_{max.}$ 3 400 (OH), 3 280 (NH), and 1 730 and 1 690 cm^{-1} (CO); δ 7.88—7.14 (15 H, m), 6.44 (1 H, s), 6.33 (1 H, s), 3.80 (3 H, s), and 3.53 (3 H, s); m/z 461 (M^+, 2%), 341 (100), 282 (89), 254 (48), 237 (70), 223 (35), 205 (100), 180 (22), 162 (23), 151 (23), 118 (97), 105 (100), 104 (68), and 77 (62).

Desulphuration of (**1b**).—The procedure described above for (**1a**) was followed for (**1b**) (0.98 g, 2 mmol). An n.m.r. spectrum

of the crude product showed the presence of (**3b**) and (**4b**) in a 2:1 ratio. Chromatography on silica gel with chloroform–light petroleum (9:1) as eluant afforded the pure components.

1-*Benzoyl*-5-(*methoxycarbonylamino*)-5-*phenyl*-3-(p-*tolyl*)-*imidazolidine*-2,4-*dione* (**4a**), eluted first, was crystallized from dichloromethane–light petroleum (0.48 g, 54%), m.p. 185 °C (Found: C, 67.3; H, 4.7; N, 9.2. $C_{25}H_{21}N_3O_5$ requires C, 67.7; H, 4.8; N, 9.5%); $\nu_{max.}$ 3 330 (NH), and 1 800, 1 740, 1 715, and 1 665 cm^{-1} (CO); δ 7.71—7.20 (14 H, m), 6.30 (1 H, s), 3.76 (3 H, s), and 2.35 (3 H, s); m/z 443 (M^+, 83%), 283 (67), 211 (84), 205 (85), 165 (16), 133 (83), 105 (100), 104 (83), 91 (23), and 77 (86).

5-*Hydroxy*-1-(*methoxycarbonyl*)-2-(*methoxycarbonylamino*)-2,3-*diphenyl*-3-(p-*tolyl*)*imidazolidin*-2-*one* (**4b**), eluted next, was crystallized from dichloromethane–light petroleum (0.25 g, 26%), m.p. 195 °C (Found: C, 65.7; H, 5.3; N, 8.5. $C_{26}H_{25}N_3O_6$ requires C, 65.7; H, 5.3; N, 8.8%); $\nu_{max.}$ 3 450 (OH), 3 300 (NH), and 1 735, 1 720, and 1 695 cm^{-1} (CO); δ 7.76—6.97 (14 H, m), 6.73 (1 H, s), 6.26 (1 H, s), 3.80 (3 H, s), 3.53 (3 H, s), and 2.21 (3 H, s); m/z 475 (M^+, 6%), 341 (35), 296 (96), 268 (38), 237 (62), 205 (67), 165 (25), 162 (22), 133 (23), 118 (94), 105 (100), 104 (79), and 77 (72).

Desulphuration of (**1c**).—Reaction of (**1c**) (1.96 g, 4 mmol) with Raney nickel, as described above, gave a colourless oil (1.6 g, 85%) which was shown to contain the presence of two products (t.l.c.). The mixture was dissolved in ether (30 ml) and when set aside (2 h) precipitated crystals (homogeneous by t.l.c.). These were filtered off and crystallized from dichloromethane–light petroleum to give 3-*benzyl*-5-*hydroxy*-1-(*methoxycarbonyl*)-2-(*methoxycarbonylamino*)-2,5-*diphenylimidazolidin*-2-*one* (**4c**) (0.7 g, 41%), m.p. 175 °C (Found: C, 65.7; H, 5.6; N, 8.65. $C_{26}H_{25}N_3O_6$ requires C, 65.7; H, 5.3; N, 8.8%); $\nu_{max.}$ 3 410 (OH), 3 240 (NH), and 1 740, 1 730, and 1 680 cm^{-1} (C=O); δ 7.89—6.98 (15 H, m), 5.87 (1 H, s), 5.01 (1 H, s), 4.58 (1 H, d), 4.12 (1 H, d, J 15.5 Hz), 3.81 (3 H, s), and 3.51 (3 H, s);

m/z 475 (M^+, 5%), 458 (87), 295 (47), 267 (48), 237 (99), 210 (53), 205 (92), 118 (92), 105 (100), 104 (45), 91 (983), and 77 (54).

The ethereal filtrate was evaporated and the residue redissolved in ether (20 ml). An insoluble fraction (0.5 g) which was a mixture of (**4c**) and (**11c**) was filtered off and the filtrate evaporated. Crystallization of the residue from dichloromethane–light petroleum yielded 3-*benzyl-2-hydroxy-1-(methoxycarbonyl)-5-(methoxycarbonylamino)-2,5-diphenylimidazolidin-2-one* (**11c**), m.p. 192 °C (Found: C, 65.7; H, 5.45; N, 8.65. $C_{26}H_{25}N_3O_6$ requires C, 65.7; H, 5.3; N, 8.8%); $v_{max.}$ 3 320, 3 250, 1 720, 1 710, and 1 690 cm^{-1}; δ 7.66—6.83 (15 H, m), 6.37 (1 H, s), 6.26 (1 H, s), 4.39 (1 H, d), 4.21 (1 H, d, J 14.8 Hz), 3.74 (3 H, s), and 3.49 (3 H, s); m/z 475 (M^+, 2%), 458 (100), 457 (68), 381 (24), 267 (89), 237 (100), 205 (97), 118 (97), 105 (98), 104 (55), 91 (84), and 77 (61).

2-exo,3-endo-*Bis(ethoxycarbonyl)-1,4,6-triphenyl-6-aza-7-thianorbornan-5-one* (**15**).—This was prepared from 2,3,5-triphenylthiazolium-4-olate and diethyl fumarate according to the procedure described in the literature[4,5] for the reaction with dimethyl fumarate (75% yield); it had m.p. 116 °C (Found: C, 69.2; H, 5.5; N, 3.1; S, 6.15. $C_{29}H_{27}NO_5S$ requires C, 69.45; H, 5.4; N, 2.8; S, 6.35%); $v_{max.}$ 1 735, 1 710, and 1 700 cm^{-1}.

2,3-exo-*Bis(ethoxycarbonyl-1,4,6-triphenyl-6-aza-7-thianorbornane-5-one* (**18**).—This was prepared from 2,3,5-triphenylthiazolium-4-olate and diethyl maleate in 80% yield, m.p. 177 °C (Found: C, 69.15; H, 5.4; N, 2.8; S, 6.8. $C_{29}H_{27}NO_5S$ requires C, 69.45; H, 5.4; N, 2.8; S, 6.35%); $v_{max.}$ 1 755, 1 740, and 1 705 cm^{-1}.

4,5-*Bis(ethoxycarbonyl)-1,3,6-triphenyl-3,4-dihydropyridin-2(1H)-one* (**17**).—Reaction of compound (**15**) (0.01 g, 2 mmol) with Raney nickel in acetone as described above yielded a thick oil which was chromatographed on silica gel with chloroform–light petroleum (5:1) as eluant. The product obtained and crystallized from dichloromethane–light petroleum (0.77 g, 82%) had m.p. 123 °C (Found: C, 74.1; H, 5.8; N, 3.0. $C_{29}H_{27}NO_5$ requires C, 74.2; H, 5.8; N, 3.0%); $v_{max.}$ 1 725, 1 710, and 1 675 (C=O), and 1 620 cm^{-1} (C=C); δ 7.33—7.08 (15 H, m), 4.44 (1 H, d), 4.14 (2 H, q), 4.06 (1 H, d, J 6.2 Hz), 3.93—3.88 (2 H, m), 1.16 (3 H, t, J 7.1 Hz), and 0.88 (3 H, t, J 7.1 Hz); m/z 469 (M^+, 51%), 396 (100), 368 (17), 351 (34), 350 (41), 323 (16), 278 (12), 180 (50), and 77 (28).

Compound (**17**) was also obtained in the same manner from (**18**).

X-*Ray Crystal Structure Analysis of* (**3b**).—Data were measured on an Enraf–Nonius CAD-4 Automatic Diffractometer. Cu-$K_α$ (λ = 1.541 78 Å) radiation with a graphite crystal monochromator in the incident beam was used. The standard CAD-4 centring, indexing, and data collection programs were used. The unit-cell dimensions were obtained by a least-squares fit of 18 centred reflections in the range of 28 ≤ θ ≤ 34°.

Intensity data were collected using the ω—2θ technique to a maximum 2θ of 120°. The scan width, Δω, for each reflection was 0.80 + 0.15 tanθ. An aperture with a height of 4 mm and a variable width, calculated as 12.0 + $\frac{1}{2}$ tanθ) mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 8.24°/min the rate for the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 25 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 1.27 to 8.24°/min. 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 0.08, a new orientation matrix was calculated on the basis of the recentring of the 18 reference reflections.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the direct method analysis.[7] After several cycles of refinements* the positions of the hydrogen atoms were found, and added with a constant isotropic temperature factor of 0.05 A^2 to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.15 e Å^{-3} scattered about the unit cell without a significant feature.

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 1.

X-*Ray Crystal Structure Analysis of* (**11c**) *and* (**17**).—Data were measured on a PW1100/20 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 by a least-squares fit of 18 centred reflections in the range of 10 ≤ θ ≤ 14°. Intensity data were collected using the ω—2θ technique to a maximum 2θ of 45°. The scan width, Δw, for each reflection was 1.00 + 0.35 tanθ with a scan speed of 0.05 °/min. Background measurements were made for a total 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. All non-hydrogen atoms were found by using the results of the SHELX86[7] direct method analysis. After several cycles of refinements[8] the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0.05 Å^2 to the refinement process. Refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. A final difference peaks less than 0.5 [0.3 for (**17**)] e/Å^{-3} scattered about the unit cell without a significant feature.

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 1. Complete listings of the bond lengths and bond angles together with the thermal parameters are available on request from the Cambridge Crystallographic Data Centre.†

* See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1989, Issue 1.
† All crystallographic computing was done on a Cyber 74 computer.

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