

## Structure and Transformation of Products of the Reactions of 2,2''-Thiodi-isobutyrophenone with Hydrazine<sup>1</sup>

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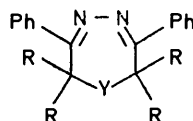
The novel course of the reaction of the title dioxo-sulphide (II) with hydrazine is described. In absence of acid none of the expected dihydrothiadiazepine (Ia) could be detected; the major product, a monohydrazone (IV), being accompanied by other products including 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-3-thia-6,7-diazabicyclo[3.2.1]octane (III) whose structure was elucidated by spectroscopic and X-ray crystallographic methods: compound (III) crystallises in the triclinic space group  $P\bar{1}$  with  $a = 9.911$ ,  $b = 15.297$ ,  $c = 6.257$  Å,  $\alpha = 103.02^\circ$ ,  $\beta = 106.15^\circ$ ,  $\gamma = 81.17^\circ$ ,  $Z = 2$ , and the structure was refined to a final  $R$  value of 7.7% for 2055 independent reflections. The thiadiazepine (Ia) could, however, be obtained by treatment of a crude reaction mixture in pyridine with strong mineral acid, or by dehydration of (III) with acetic acid. The reaction of (III) with molecular oxygen gives, depending on temperature, either the ozonide (VI) or the epoxide (VII) in good yield.

IN connection with a series of conformational studies of seven-membered rings we required the highly hindered 2,7-dihydro-2,2,7,7-tetramethyl-3,6-diphenyl-1,4,5-thiadiazepine (Ia). Closely related systems, for example (IX), are readily prepared<sup>2-4</sup> by the action of hydrazine on the appropriate dioxo-sulphide.

The precursor corresponding to (Ia), 2,2''-thiodi-isobutyrophenone (II), was prepared in high yield by the action of anhydrous sodium sulphide on 2-bromoisobutyrophenone in dimethylformamide. When compound (II) was treated with anhydrous hydrazine in benzene or pyridine for *ca.* 3 weeks, a highly crystalline compound  $C_{20}H_{24}N_2OS$ , m.p. 219–221°, was deposited. This compound was assigned structure (III) on the basis of its molecular weight and the following spectroscopic data:  $\nu_{max}$  (KBr) 3303 and 3275  $cm^{-1}$  (NH) (no OH, C=O, or C=N absorption); n.m.r. signals indicating the presence of two equivalent pairs of diastereotopic geminal methyl groups; † and u.v. absorption typical of a benzenoid chromophore having no further conjugation.

† A diagnostically useful weak coupling between diastereotopic methyl groups appears as a significant broadening of the resonances ( $W_{1/2}$  *ca.* 1.3 Hz), and indicates the geminal non-equivalence. The origin of broadening, also observed for compounds (Ia and b), (V), (VI), and (VII), was confirmed by decoupling in the case of (Ia).

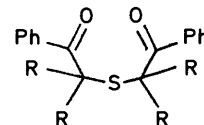
Since compound (III) embodies the first example of the 8-oxa-3-thia-6,7-diazabicyclo[3.2.1]octane ring



(Ia) Y = S, R = Me

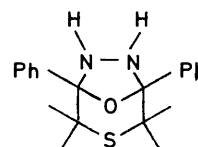
(Ib) Y = SO<sub>2</sub>, R = Me

(IX) Y = S, R = H



(II) R = Me

(X) R = H



(III)

system, we have performed a single crystal X-ray

<sup>1</sup> Preliminary communication, E. Cuthbertson, A. D. U. Hardy, and D. D. MacNicol, *J.C.S. Chem. Comm.*, 1973, 597.

<sup>2</sup> E. Fromm and A. Ehrhardt, *Ber.*, 1921, **54**, 187.

<sup>3</sup> J. D. Loudon and L. B. Young, *J. Chem. Soc.*, 1963, 5496.

<sup>4</sup> I. Sataty, *J. Heterocyclic Chem.*, 1970, **7**, 431.

diffraction analysis on this compound. The course of the analysis is described in the Experimental section, and a general view of the molecular structure of (III) in the crystal is shown in Figure 1, which gives the

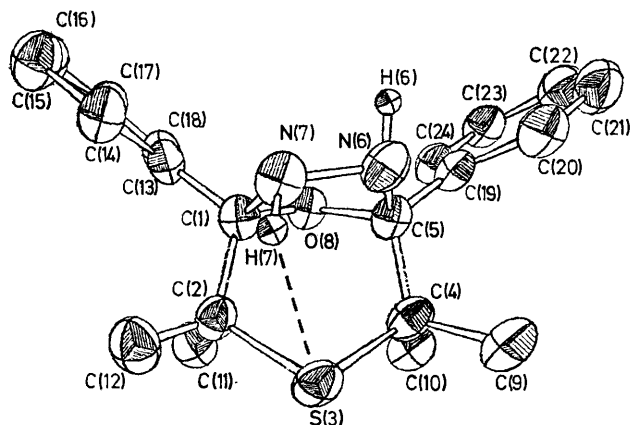
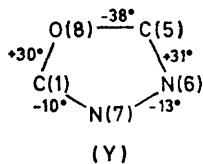


FIGURE 1 An ORTEP drawing showing a general view of the molecular structure of compound (III) (only the hydrogen atoms attached to nitrogen are included, and the intramolecular hydrogen bond involving one of these is denoted by a broken line)

atomic numbering scheme. The bond lengths, listed in Table 2, are normal, with an average non-phenyl carbon-carbon bond length of 1.538 Å, with a range of 1.520–1.554 Å; the carbon-sulphur bond lengths are 1.841(5) and 1.842(5) Å, these values being a little longer than the value of 1.817 Å listed by Sutton,<sup>5</sup> and the C(1)–N(7) distance of 1.495(6) Å is significantly longer than the C(5)–N(6) distance of 1.459(6) Å. The five-membered ring subunit corresponding to C(1), C(5), N(6), N(7), and O(8) has a mean interior ring angle of 105°, and an attempt to describe this unit in terms of a mean-plane through the atoms C(1), C(5), N(6), and N(7) [see Table 6, plane (B)] showed significant deviations from planarity, and the O(8) atom was about 0.5 Å below the best mean plane through these four atoms. The conformation may be described as a slightly distorted half-chair with the torsion angles indicated in (Y).



The six-membered 1,4-oxathian ring adopts a distorted chair conformation with atoms C(1), C(2), C(4), and C(5) closely coplanar [see Table 6, plane (A)]; and atoms S(3) and O(8) displaced by 0.66 and –0.83 Å, respectively, from this plane. The degree of flattening of this six-membered ring system may be appreciated by consideration of the values of the angles marked as

<sup>5</sup> Chem. Soc. Special Publ., No. 18, 1965.

<sup>6</sup> N. de Wolf, C. Romers, and C. Altona, *Acta Cryst.*, 1972, **22**, 715.

$\alpha$  and  $\beta$  in Figure 2. Their values are 36.2° and 74.8° respectively; with the C(2)···C(4) and C(1)···C(5) distances being 2.92 and 2.28 Å, respectively.

Comparison of the above value of  $\alpha$  (36.2°) with the corresponding parameter (46.1°) for a system unconstrained by bridging such as *trans*-2,3-dichloro-1,4-oxathian,<sup>6</sup> indicates the presence of an inverse reflex effect,<sup>7</sup> known to occur in the corresponding carbocycle. Thus, 'pinching' brought about by the *syn*-axial placement of the hydrazo-bridge in (III), results in a displacement of S(3) towards the plane described by the four carbon atoms, with a corresponding decrease in the value of  $\alpha$ .

As shown in Figures 1 and 2, there is a hydrogen bond between N(7)H and the sulphur atom. Both the H(7)···S(3) distance (2.50 Å) and the N(7)···S(3) distance (2.95 Å) are less than the sums of the appropriate van der Waals radii (3.05 and 3.35 Å, respectively), and the value of the angle  $\delta$  (50.5°) (see Figure 2) indicates<sup>8</sup> that the N–H···S hydrogen bond is medium-to-weak in strength. The seven-membered ring system

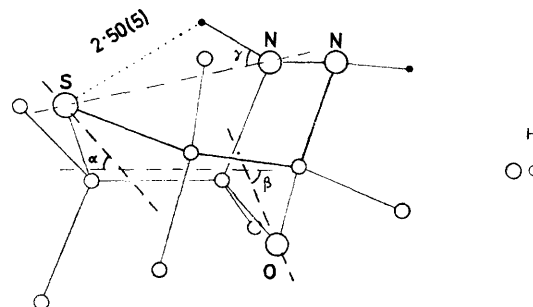


FIGURE 2 A drawing of the molecule (III) showing some important angles ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) and one distance with its associated e.s.d. in parentheses (Å) (the benzene rings are excluded for clarity)

has a slightly flattened boat conformation, as  $\alpha = 36.2^\circ$  and the angle between the two mean planes describing the other end of the boat is  $70.6^\circ$ .

Figure 3 shows the molecular packing projected onto the *ab* plane.

*Other Products from the Reaction of Compound (II) with Hydrazine.*—Evaporation of the benzene solution remaining after isolation of (III) gave, as the major product (60% isolated), an isomer of (III) whose i.r. [ $\nu$ (N–H) and  $\nu$ (C=O)] and <sup>1</sup>H n.m.r. absorptions showed it to be a monohydrazone of (II), the *E*-structure (IV) being indicated by its resistance to cyclisation under a variety of conditions. Carrying out the reaction in the presence of molecular sieves (3A powder) appeared to favour the formation of another compound (V), C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S, isolable with difficulty, the formulated alternative structures (A) and (B) being consistent with the available spectroscopic data. Compound (V) is susceptible to ready thermal or hydrolytic breakdown

<sup>7</sup> C. W. Jefford, A. Baretta, J. Fournier, and B. Waegell, *Helv. Chim. Acta*, 1970, **53**, 1180.

<sup>8</sup> H. O. Dessey, W. A. Jacob, and M. A. Herman, *Spectrochim. Acta*, 1972, **28A**, 1329.

leading to the monohydrazone (IV) and the dioxo-sulphide (II).

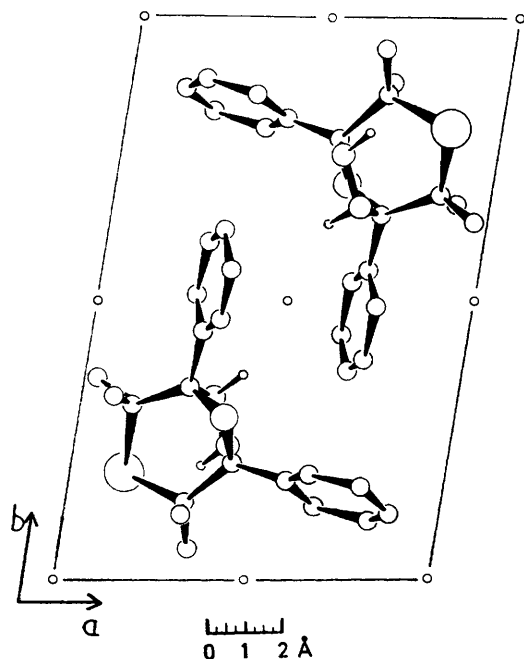
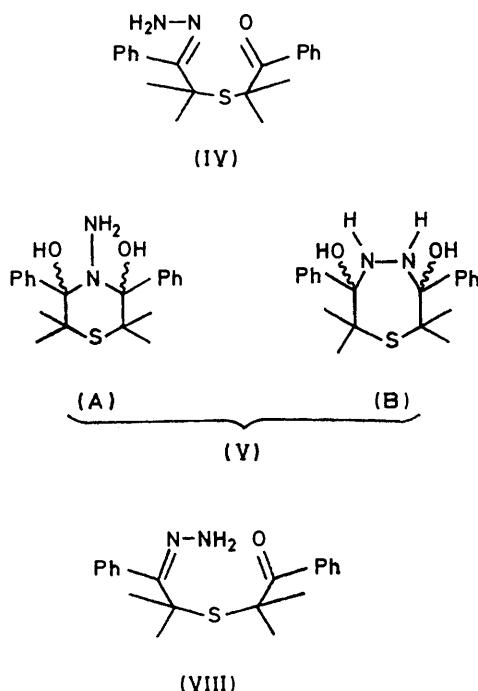


FIGURE 3 A packing diagram for compound (III), showing a unit cell viewed perpendicular to the *ab* plane

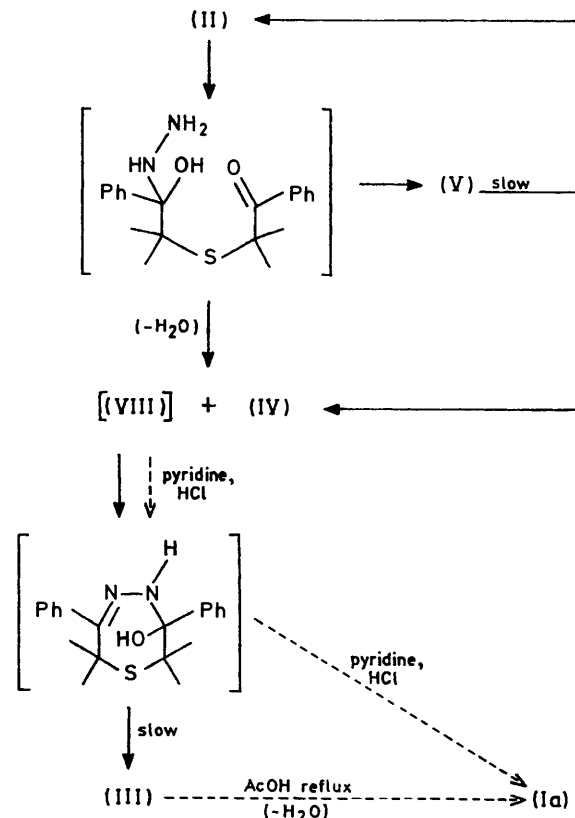
In several runs the course of the reaction was monitored by  $^1\text{H}$  n.m.r. and it was found that compound (III) was only present in appreciable amounts after about 1 week. At times shorter than this, a pair of narrow methyl



resonances ( $W_{\frac{1}{2}}$  ca. 0.8 Hz) was observed close to those of the *E*-hydrazone (IV). The disappearance of these

signals in the presence of traces of acid (in  $\text{CDCl}_3$ ) is accompanied by the appearance of an equivalent amount of (III); and in a separate experiment the addition of acetic acid catalysed the formation of (III), which was isolated in ca. 10% yield. This behaviour is consistent with a tentative assignment of these resonances to the methyl groups of the *Z*-hydrazone (VIII), though a preliminary attempt to isolate this intermediate proved unsuccessful.

In a parallel series of experiments in which the homogeneous pyridine-hydrazine system was used, the course of the reaction was followed by  $^1\text{H}$  n.m.r. for 20 days. The results, given in the Experimental section, show that the concentration of (VIII), the

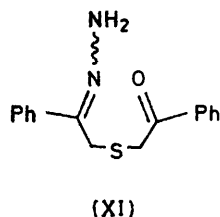


SCHEME 1 Proposed major pathways for products derived from (II); solid arrows indicate reactions occurring at room temperature in hydrazine-benzene or hydrazine-pyridine; dotted arrows indicate treatment with a further reagent

presumed intermediate in the formation of (III), reached a maximum after about 3 days. Treatment of the pyridine solution at this time with an excess of acetic acid gave (III) in 12% (isolated) yield. However, work-up with HCl in aqueous methanol gave instead a 9.5% yield of the originally sought dihydrothiadiazepine (Ia), m.p. 207–208°. The structure (Ia) was confirmed by microanalysis, molecular weight (osmometric), and spectroscopic data [ $\nu(\text{C}=\text{N})$  and no  $\nu(\text{N}-\text{H})$ ;  $m/e$  322 ( $M^+$ );  $^1\text{H}$  n.m.r. data corresponding to slow ring inversion; and u.v. absorption showing some further conjugation of the aromatic rings].

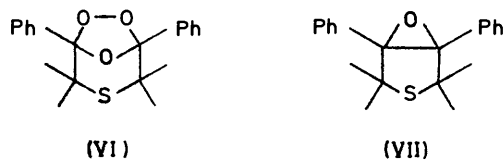
Compound (Ia) was not detected in the product from work-up with hydrogen chloride of the earlier runs in which benzene was used as solvent. Compound (III) in pyridine was precipitated unchanged on treatment with methanolic HCl, implicating another intermediate, possibly (VIII), in the formation of (Ia). However, more prolonged treatment under reflux with glacial acetic acid effected dehydration of (III) to (Ia) in good yield. Compound (Ia) was also converted into its sulphone (Ib). An outline of the above reaction is given in Scheme 1.

In order to determine whether the formation of the novel compound (III) had any parallel in other systems we reinvestigated the action of hydrazine on 2,2'-thiodiacetophenone (X).<sup>2-4</sup> Under a variety of conditions the only products detected were the dihydrothiadiazepine (IX) and a single monohydrazone (XI),



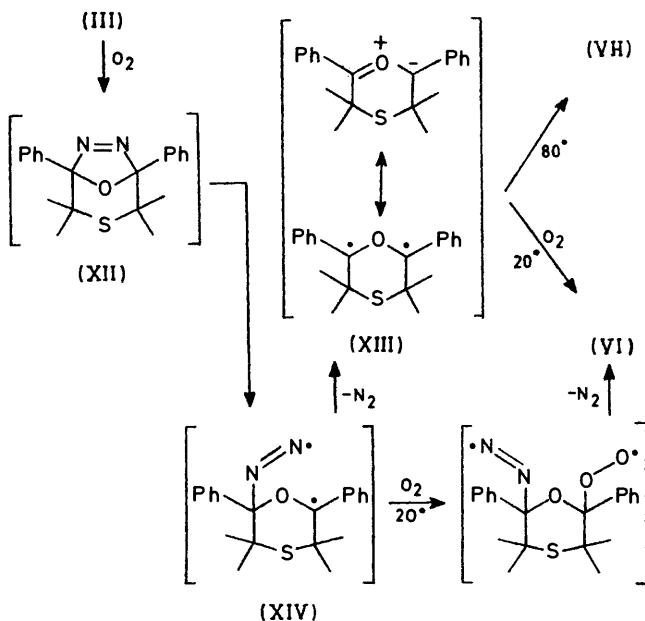
m.p. 131–132°. No evidence was found for an isomeric compound, m.p. 225°, previously reported.<sup>2</sup> This suggests the importance of *gem*-dimethyl substitution in the stabilisation of (III).

**Thermal Stability of Compound (III) and its Reactions with Molecular Oxygen.**—Compound (III) in the crystal state is stable indefinitely in air, and in solution, in the absence of air, shows resistance to thermolysis at 200°. However, in solution in the presence of molecular oxygen the compound undergoes ready oxidation. At room temperature in benzene solution it is transformed cleanly in high yield into the ozonide (VI), m.p. 182–



185° (decomp.), identified on the basis of its molecular weight (osmometric); its i.r. spectrum, which apart from the absence of NH absorption resembles that of (III) and shows no strong absorption attributable to  $\nu(\text{S}=\text{O})$ ; and its <sup>1</sup>H n.m.r. and u.v. data which are similar to those of (III). Further confirmation comes from its reduction by zinc and acetic acid to compound (II). Interestingly, on performing the aerial oxidation of (III) in refluxing benzene a different product can be isolated in good yield. This second product, m.p. 180–181°, C<sub>20</sub>H<sub>22</sub>OS, has *m/e* 310 (*M*<sup>+</sup>) and other spectroscopic properties consistent with the epoxide structure (VII). This duality of oxidation behaviour, summarised in Scheme 2, may arise from differing

concentrations of dissolved molecular oxygen. The initial oxidation step is almost certainly the formation of the azo-compound (XII); this may then undergo further reaction as shown, the nature of the eventual



SCHEME 2 Suggested pathways for oxidation of (III) with molecular oxygen in benzene

product being determined by the availability of molecular oxygen to add to either (XIII) or (XIV) before collapse to the epoxide (VII). In keeping with these suggested pathways, compound (VII) in benzene solution at room temperature does not react with oxygen, nor is any epoxide (VII) observed when the ozonide (VI) is refluxed in benzene. The possible addition of oxygen to the dipolar species (XIII) may have a parallel in the postulated formation of an ozonide, analogous to (VI), as an unisolated intermediate in the oxidation of a previously reported carbonyl ylide.<sup>9</sup>

#### EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. U.v. spectra were measured on a Unicam SP 800A spectrophotometer, i.r. spectra on a Perkin-Elmer 225 or 257 instrument, and <sup>1</sup>H n.m.r. spectra on a Varian T-60 or HA-100 instrument with tetramethylsilane as internal standard. Mass spectra were obtained on an A.E.I.-G.E.C. MS12 spectrometer. Molecular weights were determined on a Mechrolab 301A vapour-pressure osmometer. Light petroleum refers to the fraction of b.p. 60–80° except where stated otherwise.

**X-Ray Crystal Structure Analysis of Compound (III).**—Colourless needles of (III) were obtained by sublimation (110° and 0.02 mmHg).

**Crystal Data.**—C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>OS, *M* = 340.5. Triclinic, *a* = 9.911(6), *b* = 15.297(10), *c* = 6.257(4) Å,  $\alpha$  = 103.02(5)°,  $\beta$  = 106.15(7)°,  $\gamma$  = 81.17(5)°, *U* = 883.7 Å<sup>3</sup>, *D<sub>m</sub>* = 1.24, *D<sub>c</sub>* = 1.27 g cm<sup>-3</sup>, *Z* = 2, *F*(000) = 364, space group *P* $\bar{1}$ . Mo-*K*<sub>α</sub> radiation,  $\lambda$  = 0.7107 Å,  $\mu(\text{Mo-}K_{\alpha})$  = 1.9 cm<sup>-1</sup>.

<sup>9</sup> H. H. Wasserman and D. L. Pavia, *Chem. Comm.*, 1970, 1459.

*Crystallographic Measurements.*—Least-squares best cell dimensions were obtained by a treatment of the  $\theta$ ,  $\chi$ ,  $\phi$  setting angles of twelve reflections measured on a Hilger and Watts Y290 automatic diffractometer controlled by a PDP8 computer. The intensities were measured by the  $\theta$ —2 $\theta$  step scan procedure with Zr-filtered Mo- $K_{\alpha}$  radiation. Background counts were taken at each end of the scan range. The intensities of two standard reflections were monitored after every 40 intensity measurements, and the results used to place the reflections on a common scale; the changes in the standard intensities during data collection were small (<3%). Reflections were surveyed out to  $\theta \leq 28^{\circ}$ . The intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and 2055 reflections with  $I/\sigma(I) > 2.0$  were obtained.

*Structure Analysis.*—The co-ordinates of the sulphur atom were found from a sharpened three-dimensional Patterson map. A three-dimensional electron-density distribution phased on this atom ( $R = 47.2\%$ ) revealed all the remaining oxygen, nitrogen, and carbon atom positions, and confirmed that the space group is  $P\bar{1}$  and not the alternative  $P1$  ( $P\bar{1}$  being previously indicated statistically). The approximate atomic parameters were adjusted by a series of full-matrix least-squares calculations employing the 'X-ray 70' system version of the program ORFLS.<sup>10</sup> The scattering factors employed were those listed in ref. 11. Anomalous dispersion was allowed for in the least-squares calculations, with values of  $\Delta f'$  and  $\Delta f''$  for sulphur taken from ref. 12. Three rounds of refinement on the positional and isotropic thermal parameters of the sulphur, oxygen, nitrogen, and carbon atoms reduced  $R$  to 13.3%. A further two rounds of refinement, with anisotropic temperature factors for all the atoms, reduced  $R$  to 11.0%.

The twenty-four hydrogen atoms in the molecule were located in a difference electron-density distribution, and were included in subsequent least-squares calculations with isotropic temperature factors. A further two cycles of least-squares adjustment on all atomic and thermal parameters gave a final  $R$  value of 7.7% (wtd.  $R = 6.5\%$ ). The weighting scheme employed in the least-squares calculations was  $w = (A + B|F| + C|F|^2)^{-1}$ , where the parameters  $A$ ,  $B$ , and  $C$  were adjusted during the refinement so that  $\langle w\Delta^2 \rangle$  was approximately constant when calculated over various ranges of  $|F|$  and  $\sin \theta$ . The final values adopted for the parameters were  $A = 0.8470$ ,  $B = -0.0942$ , and  $C = 0.0028$ .

The calculations were carried out on the UNIVAC N.E.L. 1108 computer at East Kilbride. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21204 (10 pp., 1 microfiche).<sup>†</sup> The atomic fractional co-ordinates and temperature factors are listed in Table 1, and various parameters connected with the compound's molecular geometry are listed in Tables 2—6.

*2,2''-Thiodi-isobutyrophenone* (II).—A stirred suspension

<sup>†</sup> For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

<sup>‡</sup> The yield was greatly reduced by the presence of water.

<sup>10</sup> W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, 1962.

<sup>11</sup> H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

<sup>12</sup> 'International Tables for X-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

<sup>13</sup> J. H. Boyer and D. Straw, *J. Amer. Chem. Soc.*, 1953, **75**, 1642.

of anhydrous  $\frac{1}{2}$  sodium sulphide (9.0 g, 0.115 mol) in dry dimethylformamide (150 ml) was treated with 2-bromoiso-butyrophenone<sup>13</sup> (34.0 g, 0.150 mol) in dry dimethylformamide (75 ml). Some heat was evolved, and, after a few minutes, the mixture became deep orange in colour. After being stirred at room temperature for 2 h, the mixture was poured into water (500 ml), precipitating a cream-coloured solid. Recrystallisation from methanol gave colourless plates (19.9 g, 81%), m.p. 103—104° (Found: C, 73.55; H, 6.9.  $C_{20}H_{22}O_2S$  requires C, 73.6; H, 6.8%),  $m/e$  326 ( $M^+$ ),  $\nu_{max}$  (KBr) 1667  $cm^{-1}$  (C=O),  $\tau$  ( $CDCl_3$ ) 1.6—1.9 (4H, m), 2.4—2.8 (6H, m), and 8.43 (12H, s).

*2,2,4,4-Tetramethyl-1,5-diphenyl-8-oxa-3-thia-6,7-diazabicyclo[3.2.1]octane* (III) and *2,2''-Thiodi-isobutyrophenone* (E)-*Monohydrate* (IV) in Benzene without Acid Catalysis. —A solution of the dioxo-sulphide (II) (3.26 g, 10.0 mol) in dry benzene (6 ml) was stirred at room temperature

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses, and thermal parameters; hydrogen atoms are numbered according to the atoms to which they are attached

	X	Y	Z	$U \times 10^3$
C(1)	0.4245(5)	0.2128(3)	0.3560(7)	*
C(2)	0.3167(5)	0.1444(3)	0.3186(8)	*
S(3)	0.1441(1)	0.1947(1)	0.1736(2)	*
C(4)	0.1396(5)	0.3154(3)	0.3041(7)	*
C(5)	0.2889(5)	0.3476(3)	0.3587(7)	*
N(6)	0.3458(4)	0.3333(3)	0.1608(6)	*
N(7)	0.4138(4)	0.2427(3)	0.1397(6)	*
O(8)	0.3867(3)	0.2926(2)	0.5032(4)	*
C(9)	0.0340(5)	0.3626(4)	0.1267(8)	*
C(10)	0.0877(5)	0.3316(4)	0.5184(8)	*
C(11)	0.3102(7)	0.1213(4)	0.5410(9)	*
C(12)	0.3455(6)	0.0579(3)	0.1555(9)	*
C(13)	0.5751(5)	0.1797(3)	0.4600(7)	*
C(14)	0.6627(5)	0.1365(3)	0.3227(8)	*
C(15)	0.8021(6)	0.1093(4)	0.4158(9)	*
C(16)	0.8547(5)	0.1254(4)	0.6463(10)	*
C(17)	0.7688(5)	0.1675(4)	0.7856(9)	*
C(18)	0.6299(5)	0.1943(3)	0.6956(8)	*
C(19)	0.2953(4)	0.4443(3)	0.4795(7)	*
C(20)	0.2644(5)	0.5131(4)	0.3539(9)	*
C(21)	0.2746(6)	0.6020(4)	0.4615(10)	*
C(22)	0.3134(5)	0.6245(3)	0.6945(10)	*
C(23)	0.3427(5)	0.5571(4)	0.8185(9)	*
C(24)	0.3339(5)	0.4683(3)	0.7129(8)	*
H(6)	0.4195(43)	0.3642(27)	0.1941(68)	1.20
H(7)	0.3571(43)	0.2081(27)	0.0466(68)	1.70
H(14)	0.6260(41)	0.1279(25)	0.1673(62)	0.80
H(15)	0.8609(49)	0.0837(30)	0.3139(75)	3.49
H(16)	0.9492(49)	0.1082(30)	0.7061(74)	2.80
H(17)	0.8045(56)	0.1735(34)	0.9379(85)	3.90
H(18)	0.5639(40)	0.2293(25)	0.7949(62)	0.10
H(20)	0.2349(56)	0.4944(33)	0.1902(85)	4.40
H(21)	0.2511(46)	0.6479(28)	0.3668(71)	2.20
H(22)	0.3199(44)	0.6847(28)	0.7714(69)	1.80
H(23)	0.3716(49)	0.5771(31)	0.9727(75)	2.90
H(24)	0.3637(43)	0.4174(27)	0.8031(67)	1.20
H(9a)	0.0706(58)	0.3631(36)	-0.0039(89)	4.30
H(9b)	0.0190(53)	0.4265(32)	0.1901(81)	3.90
H(9c)	-0.0539(49)	0.3391(31)	0.0833(74)	2.59
H(10a)	0.1542(45)	0.3038(29)	0.6376(71)	1.90
H(10b)	0.0725(51)	0.3929(31)	0.5767(79)	3.30
H(10c)	0.0016(51)	0.3011(33)	0.4869(80)	3.00
H(11a)	0.4053(52)	0.0938(29)	0.6221(76)	1.59
H(11b)	0.2994(48)	0.1763(33)	0.6527(84)	2.40
H(11c)	0.2376(49)	0.0790(32)	0.5173(72)	2.40
H(12a)	0.2725(50)	0.0173(31)	0.1396(78)	2.49
H(12b)	0.4315(54)	0.0192(34)	0.2274(85)	4.10
H(12c)	0.3575(42)	0.0684(27)	0.0159(66)	1.10

\* These atoms were assigned anisotropic temperature factors of the form  $T = \exp[-8\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*b^*}U_{12} + 2hla^{*c^*}U_{13} + 2kib^{*c^*}U_{23})]$ .

TABLE 1 (Continued)

The final values of these parameters ( $U_{ij} \times 10^4$ ) are (with standard deviations in parentheses):

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	458(28)	380(27)	279(24)	-58(22)	121(20)	33(20)
C(2)	389(26)	453(29)	405(27)	2(22)	70(21)	62(23)
S(3)	412(8)	572(9)	435(8)	-117(6)	-3(6)	15(6)
C(4)	376(27)	560(31)	386(27)	-44(22)	92(21)	76(23)
C(5)	398(27)	412(28)	298(24)	3(21)	85(20)	93(21)
N(6)	386(23)	528(26)	372(22)	22(19)	131(18)	144(19)
N(7)	494(24)	510(26)	276(21)	-38(20)	103(17)	29(18)
O(8)	405(18)	414(19)	269(16)	-19(14)	73(13)	72(14)
C(9)	401(30)	691(38)	527(32)	14(26)	46(24)	135(28)
C(10)	522(31)	686(38)	513(32)	-91(28)	261(25)	57(27)
C(11)	646(39)	580(39)	504(35)	-184(33)	58(29)	204(31)
C(12)	669(36)	515(33)	535(34)	-106(27)	128(27)	49(27)
C(13)	458(27)	326(27)	395(27)	-16(21)	49(21)	111(21)
C(14)	490(31)	542(33)	394(29)	24(25)	78(23)	36(24)
C(15)	509(35)	682(38)	560(36)	60(28)	128(28)	44(29)
C(16)	410(31)	627(37)	694(39)	13(27)	-24(28)	177(30)
C(17)	488(34)	594(35)	492(32)	-50(27)	-57(25)	142(27)
C(18)	510(30)	435(28)	370(26)	-63(22)	59(22)	58(21)
C(19)	309(25)	482(31)	440(28)	27(21)	107(21)	174(24)
C(20)	522(31)	664(35)	509(30)	25(26)	218(25)	133(26)
C(21)	568(34)	596(35)	746(41)	76(27)	233(29)	248(31)
C(22)	500(32)	428(33)	752(40)	-44(25)	225(28)	17(30)
C(23)	478(30)	501(34)	521(32)	-73(25)	111(25)	-34(28)
C(24)	405(28)	501(32)	400(27)	-27(23)	77(22)	79(24)

TABLE 2

Interatomic distances (Å) and valency angles (deg.) with standard deviations in parentheses

## (a) Bond lengths

S(3)-C(2)	1.841(5)	C(13)-C(1)	1.511(6)
S(3)-C(4)	1.842(5)	C(13)-C(14)	1.382(7)
O(8)-C(1)	1.422(5)	C(13)-C(18)	1.400(6)
O(8)-C(5)	1.438(5)	C(14)-C(15)	1.381(7)
N(6)-N(7)	1.439(5)	C(15)-C(16)	1.369(8)
N(6)-C(5)	1.459(6)	C(16)-C(17)	1.375(8)
N(6)-H(6)	0.882(44)	C(17)-C(18)	1.371(7)
N(7)-C(1)	1.495(6)	C(19)-C(5)	1.504(6)
N(7)-H(7)	0.840(38)	C(19)-C(20)	1.399(8)
C(2)-C(1)	1.545(7)	C(19)-C(24)	1.380(6)
C(2)-C(11)	1.531(9)	C(20)-C(21)	1.380(7)
C(2)-C(12)	1.520(7)	C(21)-C(22)	1.376(8)
C(4)-C(5)	1.554(7)	C(22)-C(23)	1.376(9)
C(4)-C(9)	1.527(7)	C(23)-C(24)	1.374(7)
C(4)-C(10)	1.522(8)		

Average C(sp<sup>3</sup>)-H is 0.980 Å

Average C(sp<sup>2</sup>)-H is 0.959 Å

## (b) Valency angles

C(2)-S(3)-C(4)	105.0(2)	N(6)-C(5)-C(4)	113.6(3)
C(1)-O(8)-C(5)	105.7(3)	C(19)-C(5)-C(4)	112.8(4)
C(1)-N(7)-N(6)	106.6(3)	S(3)-C(4)-C(5)	109.9(3)
C(1)-N(7)-H(7)	101.3(3.3)	S(3)-C(4)-C(9)	104.9(3)
H(7)-N(7)-N(6)	108.7(2.7)	S(3)-C(4)-C(10)	110.0(4)
C(5)-N(6)-N(7)	105.6(4)	C(5)-C(4)-C(9)	111.3(5)
C(5)-N(6)-H(6)	109.4(2.8)	C(5)-C(4)-C(10)	110.7(4)
H(6)-N(6)-N(7)	100.5(2.5)	C(9)-C(4)-C(10)	109.9(4)
S(3)-C(2)-C(1)	107.0(3)	C(1)-C(13)-C(14)	120.2(4)
S(3)-C(2)-C(11)	110.9(4)	C(1)-C(13)-C(18)	121.0(4)
S(3)-C(2)-C(12)	104.6(3)	C(14)-C(13)-C(18)	118.8(4)
C(11)-C(2)-C(12)	109.3(5)	C(13)-C(14)-C(15)	120.7(4)
C(11)-C(2)-C(1)	112.4(4)	C(14)-C(15)-C(16)	119.9(5)
C(12)-C(2)-C(1)	112.4(5)	C(15)-C(16)-C(17)	120.3(5)
C(13)-C(1)-C(2)	114.2(4)	C(16)-C(17)-C(18)	120.5(5)
C(13)-C(1)-O(8)	107.8(3)	C(17)-C(18)-C(13)	119.9(5)
C(13)-C(1)-N(7)	110.7(4)	C(5)-C(19)-C(20)	119.8(4)
C(2)-C(1)-O(8)	108.6(4)	C(5)-C(19)-C(24)	122.2(4)
C(2)-C(1)-N(7)	110.5(3)	C(20)-C(19)-C(24)	118.0(4)
N(7)-C(1)-O(8)	104.5(3)	C(19)-C(20)-C(21)	120.7(5)
O(8)-C(5)-N(6)	103.6(3)	C(20)-C(21)-C(22)	120.4(6)
O(8)-C(5)-C(19)	107.9(3)	C(21)-C(22)-C(23)	119.1(5)
O(8)-C(5)-C(4)	108.5(4)	C(22)-C(23)-C(24)	120.9(5)
N(6)-C(5)-C(19)	109.8(4)	C(23)-C(24)-C(19)	120.9(5)

Average H-C(sp<sup>3</sup>)-H angle is 107.6°

Average C(sp<sup>3</sup>)-C(sp<sup>3</sup>)-H angle is 111.2°

Average C(sp<sup>2</sup>)-C(sp<sup>2</sup>)-H angle is 119.8°

TABLE 3

Some short intramolecular separations (<3.2 Å)

S(3)···H(7)	2.50	O(8)···N(7)	2.31
S(3)···N(7)	2.95	N(6)···H(20)	2.53
S(3)···N(6)	3.16	N(7)···H(14)	2.52
S(3)···O(8)	3.04	C(2)···H(7)	2.29
C(1)···C(5)	2.28	C(19)···H(6)	2.45
O(8)···H(24)	2.39	H(7)···H(12c)	2.10
O(8)···H(18)	2.42	H(10a)···H(11b)	2.24
O(8)···N(6)	2.28	C(2)···C(4)	2.92

TABLE 4

Some intermolecular separations (<3.8 Å)

C(21)···C(10 <sup>IV</sup> )	3.61	H(6)···H(22 <sup>III</sup> )	2.54
C(14)···C(12 <sup>III</sup> )	3.71	C(13)···C(21 <sup>III</sup> )	3.74
N(6)···C(23 <sup>III</sup> )	3.69	C(24)···C(23 <sup>IV</sup> )	3.73
N(6)···C(22 <sup>III</sup> )	3.37	C(23)···C(23 <sup>IV</sup> )	3.76
N(7)···C(22 <sup>III</sup> )	3.42	C(11)···N(7 <sup>V</sup> )	3.72
C(13)···C(22 <sup>III</sup> )	3.75	H(7)···H(11b <sup>V</sup> )	2.32
C(14)···C(22 <sup>III</sup> )	3.73	S(3)···C(16 <sup>VI</sup> )	3.79
C(18)···C(21 <sup>III</sup> )	3.79		
H(6)···C(22 <sup>III</sup> )	2.57		

The superscripts refer to the following transformations of the atomic co-ordinates:

I	-x, 1-y, 1-z	IV	1-x, 1-y, 2-z
II	1-x, -y, -z	V	x, y, 1+x
III	1-x, 1-y, 1-z	VI	1+x, y, 1+z

TABLE 5

Some torsion angles (deg.)

C(4)-S(3)-C(2)-C(1)	-39	H(7)-N(7)-C(1)-C(2)	-7
C(2)-S(3)-C(4)-C(5)	36	C(10)-C(4)-C(5)-N(6)	179
C(1)-O(8)-C(5)-N(6)	-38	C(10)-C(4)-C(5)-C(19)	-55
C(5)-O(8)-C(1)-N(7)	30	S(3)-C(2)-C(1)-O(8)	64
C(5)-O(8)-C(1)-C(2)	-88	S(3)-C(2)-C(1)-N(7)	-51
C(5)-N(6)-N(7)-C(1)	-13	S(3)-C(2)-C(1)-C(13)	-176
C(5)-N(6)-N(7)-H(7)	96	C(12)-C(2)-C(1)-O(8)	178
H(6)-N(6)-N(7)-C(1)	101	C(12)-C(2)-C(1)-N(7)	64
H(6)-N(6)-N(7)-H(7)	-151	C(12)-C(2)-C(1)-C(13)	-62
N(7)-N(6)-C(5)-O(8)	31	C(11)-C(2)-C(1)-O(8)	-58
N(7)-N(6)-C(5)-C(4)	-86	C(11)-C(2)-C(1)-N(7)	-173
H(6)-N(6)-C(5)-O(8)	39	C(11)-C(2)-C(1)-C(13)	62
H(6)-N(6)-C(5)-C(19)	166	S(3)-C(4)-C(5)-O(8)	-57
N(6)-N(7)-C(1)-O(8)	-10	S(3)-C(4)-C(5)-N(6)	58
N(6)-N(7)-C(1)-C(2)	106	S(3)-C(4)-C(5)-C(19)	-176
H(7)-N(7)-C(1)-O(8)	-124	C(9)-C(4)-C(5)-O(8)	-173
H(7)-N(7)-C(1)-C(13)	120	C(9)-C(4)-C(5)-N(6)	-58
		C(9)-C(4)-C(5)-C(19)	68
		C(10)-C(4)-C(5)-O(8)	65

TABLE 6

Displacements (Å) of atoms from planes through various sets of atoms; atoms not included in the derivation of the plane are indicated in italics

Plane (A)	Plane (B)		
C(1)	0.025	C(1)	-0.045
C(2)	-0.020	C(5)	0.046
C(4)	0.019	N(6)	-0.072
C(5)	-0.025	N(7)	0.071
S(3)	0.661	O(8)	-0.490
O(8)	-0.833	C(2)	1.338
N(6)	1.270	C(4)	1.512
N(7)	1.384	C(13)	-1.107
C(13)	-0.415	C(19)	-0.840
C(19)	-0.622	H(6)	-0.912
H(7)	1.816	H(7)	0.872
H(6)	1.231		

Angles between plane normals are: A/B 70.6°, C/D 70.0°.

Plane (C)	Plane (D)		
C(19)	0.004	C(13)	0.006
C(20)	-0.006	C(14)	-0.001
C(21)	0.003	C(15)	-0.005
C(22)	0.001	C(16)	0.005
C(23)	-0.002	C(17)	0.000
C(24)	0.000	C(18)	-0.006
C(5)	0.048	C(1)	0.071

with anhydrous hydrazine<sup>14</sup> (1.5 ml). After 3 weeks, crystals of (III) had been deposited. These were filtered off, dried under vacuum, and recrystallised from benzene-light petroleum giving colourless needles (0.32 g), m.p. 219–221° (evacuated sealed tube) [Found: C, 70.3; H, 7.25; N, 8.79%; *M* (osmometric in toluene), 338. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O.S requires C, 70.55; H, 7.1; N, 8.25%; *M*, 340], *m/e* 340 (15 eV; weak, *M*<sup>+</sup>);  $\nu_{\max}$  (KBr) 3303 (N–H), 3275 (N–H), 1107, 1053, and 892,  $\nu_{\max}$  (CCl<sub>4</sub>) 3301, 1049, and 888 cm<sup>-1</sup>;  $\tau$  (CDCl<sub>3</sub>) 2.3–2.8 (10H, m), 5.05br (2H), 8.45 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz), and 8.77 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz); no intense u.v. absorption at  $\lambda > 230$  nm.

The filtrate was washed with water (3 × 10 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated *in vacuo*. Fractional crystallisation from light petroleum gave more (III) (total 0.44 g, 13%), and the monohydrazone (IV) (2.05 g, 60%) as colourless tablets (from light petroleum), m.p. 86–87° (Found: C, 70.45; H, 7.25; N, 7.95. C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O.S requires C, 70.55; H, 7.1; N, 8.25%), *m/e* 340 (*M*<sup>+</sup>),  $\nu_{\max}$  (KBr) 3430 (N–H) and 1662 (C=O),  $\nu_{\max}$  (CCl<sub>4</sub>) 3430 and 1672 cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 1.6–1.8 (2H, m), 2.4–2.8 (8H, m), 5.0br (2H), 8.32 (6H, s,  $W_{\frac{1}{2}}$  ca. 0.8 Hz), and 8.55 (6H, s,  $W_{\frac{1}{2}}$  ca. 0.8 Hz);  $\lambda_{\max}$  (EtOH) 242 ( $\epsilon$  16,000) and 280sh nm ( $\epsilon$  3500).

*Further Studies of the Reaction of Compound (II) with Hydrazine in Benzene.*—A series of reactions was carried out by stirring mixtures of compound (II) (3.26 g) and anhydrous hydrazine (1.5 ml) in dry benzene (8 ml) (a) without molecular sieves, (b) with Union Carbide molecular sieve of different types (3A pellets or powder, or 5A pellets or powder). The reactions were monitored at various stages by evaporation *in vacuo* of the benzene from a small sample followed by <sup>1</sup>H n.m.r. analysis (in CDCl<sub>3</sub>). For reaction times of 2–6 days, the methyl region indicated, along with unchanged (II), the presence of compounds (IV) and (V). Additional methyl signals ( $W_{\frac{1}{2}}$  ca. 0.8 Hz) at  $\tau$  8.27 and 8.51 were tentatively assigned to the *Z*-monohydrazone (VIII) (see Discussion section). The results of the various runs were variable; in general the only consistent effect attributable to the presence of molecular sieves was a slight increase in the formation of (V) in the presence of type 3A powder.

*Isolation of Compound (V).*—Compound (II) (3.26 g) was treated with hydrazine in the presence of 3A sieve powder (as above). After 6 days, the mixture was filtered, and the filtrate concentrated *in vacuo*. The resulting oil (3.2 g) slowly deposited crystals. This material was triturated with light petroleum and filtered with suction. The <sup>1</sup>H n.m.r. spectrum of the resulting white solid showed it to be a mixture of (V) and (IV) (ca. 3 : 1). Boiling this material with light petroleum resulted in complete decomposition of (V), as did attempted sublimation (at 70° and 0.05 mmHg), giving a mixture (ca. 3 : 1) of (IV) and (II). Compound (V) was purified, with considerable loss, by rapid crystallisation from light petroleum (b.p. 40–60°), followed by low-temperature (ca. –10°) crystallisation from anhydrous ether. Colourless needles of (V) (ca. 100 mg) were obtained, m.p. 110–115° (decomp.) (Found: C, 67.2; H, 7.55; N, 8.0. Calc. for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S: C, 67.0; H, 7.3; N, 7.8%), *m/e* 340 (no *M*<sup>+</sup>),  $\nu_{\max}$  (KBr) 3440 (O–H), 3350 (N–H), 3285 (N–H), 1139, 1056, and 991 cm<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 2.2–2.8 (10H, m), 7.0br (4H), 8.52 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz), and 8.77 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz); no intense u.v. absorption at  $\lambda > 230$  nm.

*Preparation of Compound (III) by using Acid Catalysis.*—Compound (II) (3.26 g) was treated with hydrazine in the

presence of type 3A sieve pellets (as above). After 4 days, the mixture was filtered, the sieve washed with ether, and the combined filtrate washed with water (4 × 25 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation gave an oil (3.2 g), whose <sup>1</sup>H n.m.r. spectrum showed the presence of (II), (IV) (major component), and (VIII), but not (V), owing to the aqueous work-up.

When a small sample of this mixture, dissolved in CDCl<sub>3</sub>, was left for 1 day, the n.m.r. spectrum indicated complete disappearance of (VIII) and appearance of an equivalent amount of (III) as estimated from the peak areas.

The remainder of the crude product mixture was dissolved in methanol (25 ml). Addition of a crystal of (III) resulted in precipitation of only ca. 1 mg of (III). Acetic acid (3 drops) was added, causing colourless needles (0.33 g, 10%) to separate, identical (by i.r. and <sup>1</sup>H n.m.r.) with (III).

*Reaction of Compound (II) with Hydrazine in Benzene: Work-up with Hydrogen Chloride.*—Compound (II) (3.26 g) was treated with anhydrous hydrazine without sieve (as above). After 4 days, the benzene solution was divided into two equal portions which were treated as follows. (a) The benzene solution was diluted with chloroform (40 ml), and the solution treated with an excess of dry hydrogen chloride. (b) The benzene solution was diluted with methanol (40 ml) and the solution treated with an excess of dry hydrogen chloride. For both (a) and (b), work-up and crystallisation from methanol gave (III). The dihydrothiadiazepine (Ia) could not be detected in either case by <sup>1</sup>H n.m.r.

Methyl chemical shifts of (II)–(V) and (VIII) in pyridine-hydrazine (ca. 9 : 1) were: (II)  $\tau$  8.43; (III)  $\tau$  8.45 and 8.77; (IV) 8.27 and 8.45; (V)  $\tau$  8.42 and 8.67; (VIII) 8.26 and 8.44.

*Reaction of Compound (II) with Hydrazine in Pyridine.*—(a) A solution of compound (II) (0.163 g, 0.50 mmol) and anhydrous hydrazine (0.016 ml, 0.5 mmol) in dry pyridine (0.4 ml) was left at room temperature and its <sup>1</sup>H n.m.r. spectrum (in pyridine) observed at intervals. After 7 days, a large amount of unchanged (II) remained.

(b) The experiment was repeated, with hydrazine in excess (0.045 ml, 1.4 mmol). The reaction was followed to completion (20 days), and the variation in the concentrations of the components is represented qualitatively as follows: Compound (II): concentration decreased steadily, being undetectable after 5 days. Compound (III): a trace present after 3 days; increased slowly to limit (ca. 15%) at 15–20 days. Compound (IV): formed rapidly in early stages; increased steadily to limit (ca. 70%) at 15–20 days. Compound (V): formed in early stages, reaching maximum (ca. 20%) after 2–3 days; then decreased slowly, reaching ca. zero after 15–20 days. Compound (VIII): formed in early stages, reaching maximum (ca. 20%) after 3 days; then decreasing slowly, reaching ca. zero after 15–20 days.

After 20 days, crystals had formed in the solution. Addition of a little water and filtration gave (III) (24 mg, 14%).

A solution of (II) (3.26 g, 10 mmol) and hydrazine (0.90 ml) in dry pyridine (8 ml) was left at room temperature for 3 days. Work-up was carried out in one of ways [(a)–(c)] detailed below.

(a) *Attempted isolation of (VIII).* The pyridine solution was diluted with ether (25 ml), washed with water (6 × 25 ml), dried (K<sub>2</sub>CO<sub>3</sub>), and concentrated *in vacuo*. An

<sup>14</sup> A. C. Day and M. C. Whiting, *Org. Synth.*, 1970, 50, 3.

attempted fractional crystallisation from ether-light petroleum gave only the *E*-hydrazone (IV) (total yield from 3 crops, 2.2 g, 65%). The <sup>1</sup>H n.m.r. spectrum of the oil obtained after concentration of the mother liquors indicated the presence of (VIII) along with residue (IV), some unchanged (II), and other unidentified material. Crystals were not obtained from this mixture.

(b) *Preparation of (III) in pyridine.* The pyridine solution (see above) was poured into methanol (20 ml), and, with stirring, the solution was made slightly acidic by addition of an excess of glacial acetic acid. Needles of (III) slowly separated. Precipitation of (III) was completed by addition of a little water, and the crystals were filtered off and washed with aqueous methanol. Recrystallisation from ethanol gave pure (III) (0.660 g, 12%).

(c) *Preparation of 2,7-dihydro-2,2,7,7-tetramethyl-3,6-diphenyl-1,4,5-thiadiazepine (Ia).* The pyridine solution (see above) was added dropwise with stirring, during 20 min, to 10M-hydrochloric acid (22 ml) in methanol (25 ml), with cooling to 5–10°. The precipitate, which was filtered off and washed with methanol and then with water to neutrality, was almost pure (Ia) (0.305 g, 9.5%). Recrystallisation from benzene-light petroleum gave colourless needles, m.p. 207–208° [Found: C, 74.85; H, 7.05; N, 8.26%; *M* (osmometric in toluene), 316. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>S requires C, 74.5; H, 6.9; N, 8.7%; *M*, 322], *m/e* 322 (*M*<sup>+</sup>); λ<sub>max</sub> (EtOH) 232 (ε 12,000) and 275 (4800) nm, ν<sub>max</sub> (KBr) 1576 (C=N), 1570 (C=N), 1286, 1109, 1007, and 985 cm<sup>-1</sup>; τ (CDCl<sub>3</sub>) 2.4–2.8 (10H, m), 8.02 (6H, s, *W*<sub>1/2</sub> ca. 1.4 Hz), and 8.90 (6H, s, *W*<sub>1/2</sub> ca. 1.7 Hz; with decoupling at τ 8.02, *W*<sub>1/2</sub> becomes ca. 1.2 Hz).

*Treatment of Compound (III) with Pyridine and Methanolic Hydrogen Chloride.*—A solution of compound (III) (200 mg) in pyridine (15 ml) was subjected to the methanolic hydrogen chloride work-up conditions described above. Recovery of the precipitated white solid and <sup>1</sup>H n.m.r. analysis showed it to be unchanged (III).

*Conversion of Compound (III) into the Thiadiazepine (Ia).*—A solution of compound (III) (0.068 g, 0.20 mmol) in nitrogen-purged glacial acetic acid (2 ml) was refluxed for 16 h in a static nitrogen atmosphere. The solution was then cooled, diluted with chloroform (5 ml), washed with saturated sodium hydrogen carbonate solution (3 × 10 ml) and water (2 × 5 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The residual solid was recrystallised from benzene-light petroleum, giving colourless needles (0.036 g, 56%), m.p. 206–207°, identical (i.r.) with (Ia).

*Effect of Heat and Acids on the E-Monohydrazone (IV).*—(a) A solution of (IV) (50 mg) in dry benzene (10 ml) was refluxed for 16 h. (b) A solution of (IV) (57 mg) in benzene (100 ml) containing glacial acetic acid (3 drops) was refluxed for 2 h. (c) A solution of (IV) in CDCl<sub>3</sub> (0.4 ml) containing a trace of toluene-*p*-sulphonic acid was left at room temperature for 3 days. In all cases, <sup>1</sup>H n.m.r. showed that (IV) remained substantially unchanged. No cyclised products [(Ia) or (III)] nor *Z*-hydrazone (VIII) were detected.

*2,7-Dihydro-2,2,7,7-tetramethyl-3,6-diphenyl-1,4,5-thiadiazepine 1,1-Dioxide (Ib).*—To a stirred solution of compound (Ia) (0.208 g, 0.646 mmol) in methylene chloride (3 ml) at 0° a solution of 76% *m*-chloroperbenzoic acid (0.294 g, 1.29 mmol) in methylene chloride (5 ml) was added dropwise during 10 min. Stirring was continued for a further 30 min, after which the mixture was filtered. The filtrate was

washed with sodium hydrogen sulphite solution (5 ml), saturated sodium hydrogen carbonate solution (10 ml), and water (2 × 5 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. Recrystallisation of the resulting solid (244 mg) from benzene gave the sulphone (Ib) as colourless plates, m.p. 197–199° (decomp.) (Found: C, 67.8; H, 6.3; N, 8.15. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 67.8; H, 6.25; N, 7.9%), λ<sub>max</sub> (EtOH) 247 (ε 10,200) and 275 nm (6900); ν<sub>max</sub> (KBr) 1560 (C=N), 1298 (S=O), 1285 (S=O), 1154 (S=O), 1105, and 1011 cm<sup>-1</sup>; τ (CDCl<sub>3</sub>) 2.3–2.7 (10H, m), 8.13 (6H, s, *W*<sub>1/2</sub> ca. 1.4 Hz), and 8.46 (6H, s, *W*<sub>1/2</sub> ca. 1.6 Hz).

*Reactions of 2,2''-Thiodiacetophenone (X) with Hydrazine.*<sup>2</sup>—(a) A solution of dioxo-sulphide (X) (0.540 g, 2.0 mmol) [prepared similarly to (II)] and hydrazine hydrate (0.10 ml, 2.0 mmol) in ethanol (3 ml) was refluxed for 4 h. On cooling, the solution deposited crystals of the dihydrothiadiazepine (IX) (0.25 g), m.p. 176–178° (lit.,<sup>2</sup> 175°), ν<sub>max</sub> (KBr) 1565 and 1017 cm<sup>-1</sup>; τ (CDCl<sub>3</sub>) 1.9–2.3 (4H, m), 2.3–2.8 (6H, m), 6.35 (2H, d, *J* 12 Hz), and 6.67 (2H, d, *J* 12 Hz).

(b) Hydrazine hydrate (0.28 ml, 5.6 mmol) was added to a boiling solution of (X) (1.53 g, 5.67 mmol) in ethanol (10 ml). The mixture was refluxed for 10 min and cooled quickly in ice, and the precipitated crystals (0.53 g) were filtered off. Recrystallisation from ethanol gave colourless plates (0.355 g) of a pure hydrazone (XI), m.p. 131–132° (lit.,<sup>2</sup> 128°), ν<sub>max</sub> (KBr) 3365 (N–H), 3300 (N–H), 3205 (N–H), 1687 (C=O), 1682 (C=O), and 1198, ν<sub>max</sub> (CCl<sub>4</sub>) 3420, 3305, 3220, 1693, and 1678 cm<sup>-1</sup>; τ (CDCl<sub>3</sub>) 1.9–2.8 (10H, m), 3.9br (2H), 6.10 (2H, s), and 6.19 (2H, s).

(c) A solution of (X) (1.35 g, 5.0 mmol) and anhydrous hydrazine (0.5 ml, 15 mmol) in dry pyridine (5 ml) was left at room temperature for 3 h. Work-up with acetic acid [as for preparation of (III) in pyridine] gave, as the only detectable product, the dihydrothiadiazepine (IX) (ca. 1.0 g), identical (i.r. and <sup>1</sup>H n.m.r.) with authentic material.

*Reaction of the Hydrazone (XI) with Acetic Acid.*<sup>2</sup>—(a) Compound (XI) (10 mg) was dissolved in hot (100°) glacial acetic acid. Fine colourless needles began to separate immediately. The mixture was rapidly cooled and diluted with water. The solid obtained was identical (i.r.) with the dihydrothiadiazepine (IX). No NH absorption was detected.

(b) To a solution of (XI) (40 mg) in CDCl<sub>3</sub> in an n.m.r. tube was added glacial acetic acid (2 drops), and the <sup>1</sup>H spectrum was run immediately. New signals (corresponding to ca. 10% of the mixture) had appeared at positions identical with those for the methylene protons of (IX). The spectrum was scanned repeatedly, and the concentration of (IX) was seen to increase until, after 30 min, no hydrazone (XI) was detected and the spectrum was identical with that of pure (X). No intermediates were detected.

*Attempted Hydrolysis<sup>2</sup> of the Dihydrothiadiazepine (IX).*—Samples of compound (IX) (0.270 g, 1.0 mmol) were treated as follows: (a) refluxed for 3 days with water (0.2 ml) in ethanol (5 ml); (b) refluxed for 1 day with water (0.2 ml) and glacial acetic acid (1 drop) in ethanol (5 ml); (c) refluxed for 1 day with water (0.2 ml) and a trace of sodium hydroxide in ethanol (5 ml). In all cases, (IX) was unchanged.

*Thermal Stability of Compound (III).*—A degassed solution of compound (III) (100 mg) in dry, peroxide-free tetrahydropyran (2 ml) in a sealed tube was heated for 20 min at 200°. The material obtained after removal of solvent was (<sup>1</sup>H n.m.r. and i.r.) unchanged (III).



**2,2,4,4-Tetramethyl-1,5-diphenyl-6,7,8-trioxa-3-thiabicyclo-[3.2.1]octane (VI).**—A solution of compound (III) (0.170 g, 0.50 mmol) in benzene (10 ml) was stirred vigorously for 1 day at room temperature, with free access of air. Removal of the benzene under reduced pressure gave almost pure ozonide (VI), uncontaminated with (VII). Recrystallisation from ethanol gave pure (VI) (0.137 g, 80%), as colourless *needles*, m.p. 182—185° (decomp.) [Found: C, 69.8; H, 6.7; N, 0.0%; *M* (osmometric in toluene), 347.  $C_{20}H_{22}O_3S$  requires C, 70.15; H, 6.5%; *M*, 342], *m/e* 252 (no  $M^+$ );  $\nu_{max}$  (KBr) 1132, 1074, and 1043  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.4—2.8 (10H, m), 8.41 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz), and 8.73 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz); no intense u.v. absorption at  $\lambda > 230$  nm.

Identical results were obtained by carrying out the reaction in an atmosphere of pure oxygen, whether or not light was excluded.

**Reduction of the Ozonide (VI) by Zinc in Acetic Acid.**—A solution of compound (VI) (14.3 mg) in acetic acid (1 ml) was stirred with an excess of zinc dust at room temperature for 2 days, then centrifuged. The solution diluted with water and the precipitated solid recrystallised from methanol giving colourless plates (10 mg), m.p. 102—104°, identical (i.r. and  $^1H$  n.m.r.) with those of dioxo-sulphide (II).

**2,2,4,4-Tetramethyl-1,5-diphenyl-6-oxa-3-thiabicyclo[3.1.0]-hexane (VII).**—A solution of compound (III) (0.450 g, 1.32 mmol) in benzene (10 ml) was stirred and refluxed for 1 day with free access of air. The yellow solution obtained was concentrated *in vacuo* and the crude epoxide (VII) was obtained, the  $^1H$  n.m.r. spectrum showing the presence of

only a trace of ozonide (VI). Minor impurities were removed by a short silicic acid column (Mallinckrodt; methylene chloride as eluant), and recrystallisation from ethanol gave colourless *needles* of (VII) (0.180 g, 44%), m.p. 180—181° [Found: C, 77.55; H, 7.25; N, 0.0%; *M* (osmometric in chloroform), 317.  $C_{20}H_{22}OS$  requires C, 77.4; H, 7.15; *M*, 310], *m/e* 310 ( $M^+$ );  $\nu_{max}$  (KBr) 1129 and 950  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.4—3.0 (10H, m), 8.35 (6H, s,  $W_{\frac{1}{2}}$  1.3 Hz), and 8.63 (6H, s,  $W_{\frac{1}{2}}$  ca. 1.3 Hz); no intense u.v. absorption at  $\lambda > 230$  nm.

**Treatment of the Epoxide (VII) with Molecular Oxygen.**—Compound (VII) (150 mg) was stirred in benzene solution in air at room temperature, under conditions identical with those used for preparing the ozonide (VI). Recovery of the material after 1 day and  $^1H$  n.m.r. analysis showed it to be completely unchanged (VII).

**Effect of Heat on the Ozonide (VI).**—The ozonide (VI) (150 mg) was heated under reflux in benzene for 1 day. The  $^1H$  n.m.r. spectrum of the solid obtained after evaporation showed it to be mainly unchanged (VI), though some decomposition to unidentified products had occurred; no trace of the epoxide (VII) was detected.

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