Heterocyclic Compounds. Part 15.[1] *NN'*-Di-t-Butylthiadiaziridine 1,1-Dioxide: Synthesis and Reactions

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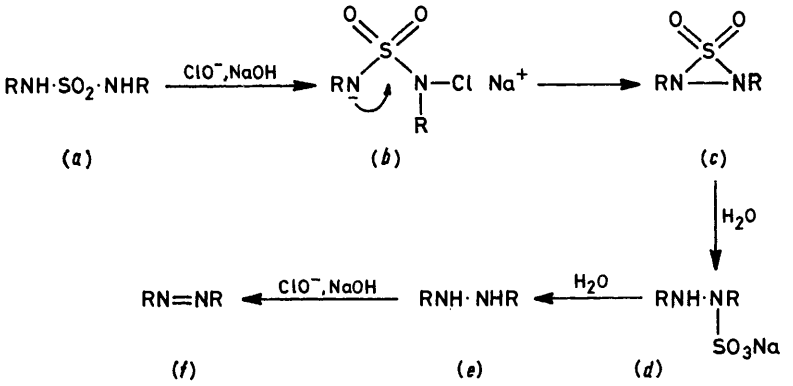
An intermediate involved in the conversion of *NN'*-di-t-butylsulphamide into 2,2'-dimethyl-2,2'-azopropane has been prepared and found to be a thiadiaziridine 1,1-dioxide. Several reactions of this heterocycle are reported, including hydrolysis, methanolysis, and nucleophilic conversions.

TREATMENT of *NN'*-diarylsulphamides with alkaline sodium hypochlorite is known to afford quinone anils.[2] By contrast, *NN'*-dialkylsulphamides under the same conditions yield aliphatic azo-compounds.[3-5] For the latter reaction, a postulated mechanism (Scheme 1) begins with a dialkylsulphamide (*a*) that is converted into an *N*-sodio-*N'*-chloro-intermediate (*b*), which by internal displacement yields a dialkylthiadiaziridine 1,1-dioxide (*c*). This presumably unstable system opens in water to produce a hydrazinesulphonic acid salt (*d*), which, in turn, is hydrolysed to a dialkylhydrazine (*e*). A second equivalent of hypochlorite then serves as an oxidizing agent and so forms the observed azo product (*f*). Support for the last stages of this sequence comes from both iodometric titration evidence and the isolation of several dialkylhydrazines.[4] The precise nature of the (*a*) ⟶ (*b*) conversion is not clear, but it is evident that the simple nitrogen anion (*g*) or the equivalent *N*-chloro-derivative (*h*) must be formed at some early stage.

The suggested presence of the three-membered heterocycle (*c*) is of more interest, since such a compound would be an unusual small ring system. This hetero atomic system possesses the highest oxidation level of the three thiadiaziridines (*i*)—(*k*). Compound (*k*), in turn, is a valence isomer of both the unknown diazene sulphide system (*l*) and the known sulphur-di-imides (*m*).



SCHEME 1 Formation of azoalkanes

In order to study the proposed mechanistic scheme in more detail, we sought to synthesize several possible

[1] Part 14, B. Weinstein and H.-H. Chang, *Tetrahedron Letters*, 1974, 901.

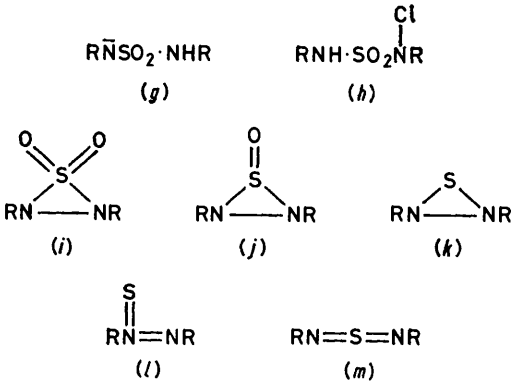
[2] D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc.*, (*C*), 1971, 993.

[3] R. Ohme and E. Schmitz, *Angew. Chem.*, 1965, **77**, 429; *Angew. Chem. Internat. Edn.*, 1965, **4**, 433.

[4] R. Ohme and H. Preuschhoff, *Annalen*, 1968, **713**, 74.

[5] J. W. Timberlake, M. L. Hodges, and K. Betterton, *Synthesis*, 1972, 632.

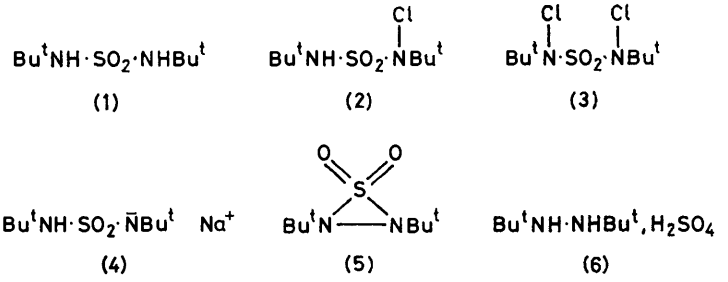
reaction intermediates.[6-8] Addition of t-butyl hypochlorite to di-t-butylsulphamide (1) [9] in methanol at room temperature produced *N*-chloro-*NN'*-di-t-butylsulphamide (2) in high yield. The structure (2) was



based on both spectral [τ 8.62 (s) and 8.50 (s)] and combustion analyses. The use of an excess of hypochlorite did not generate *NN'*-dichloro-*NN'*-di-t-butylsulphamide (3), in agreement with an earlier report.[10]

Although no stereochemical evidence is available at this point, the *trans*-configuration is assigned to the product as a result of steric considerations. The monomeric nature of (5) was confirmed by a cryoscopic molecular weight determination (*M* 216) and indirectly by the mass spectrum. The principal peaks are seen at *m/e* 206 (M^+), 193 ($Bu^tNSO_2\overset{+}{N}HPr^i$), 138 ($Bu^t\overset{+}{N}HSO_2H$), and 57 ($Bu^t$). The complete absence of an *m/e* 142 ion excludes a simple sulphur dioxide elimination from (5) (see later).

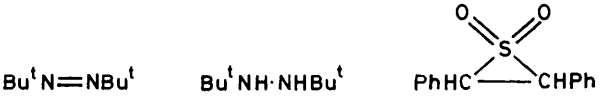
When stored under nitrogen at a low temperature, the heterocycle (5) is fairly stable. By contrast, crystals in an open container slowly change over a week into a new material possessing a sharp taste similar to that of dilute sulphuric acid. A neutralization equivalent and spectral data supported the formulation as *NN'*-di-t-butylhydrazinium sulphate (6). This assignment was verified by a simple synthesis: thus, hydrogenation of *trans*-2,2'-dimethyl-2,2'-azopropane (7a) afforded *NN'*-di-t-butylhydrazine (8),[11] and addition of dilute sulphuric acid gave the authentic salt (6).[12] Alternatively, when solid (5) was kept in a sealed container at room tem-



Treatment of the *N*-chloro-compound (2) with sodium hydride in pentane, potassium t-butoxide in t-butyl alcohol, or aqueous sodium hydroxide afforded in all cases the starting sulphamide (1), and, erratically, a small amount of an unstable semi-solid. The inertness of compound (2) contrasts strongly with the behaviour of *N*-chloro-*NN'*-di-t-butylurea under similar conditions.[11]

If the sulphamide (1) was mixed with 1 equiv. of sodium hydride in pentane at room temperature, the corresponding sodio-derivative (4) was formed quantitatively [τ 8.63 (s) and 8.49 (s)]. The addition of t-butyl hypochlorite at −40 °C to the heterogeneous mixture gave a clear solution within several hours. Work-up in the usual fashion produced a powder, which on sublimation gave crystalline *NN'*-di-t-butylthiadiaziridine 1,1-dioxide (5) in good yield. As expected, this compound possessed a single proton resonance [τ 8.67 (s)] and a supporting i.r. spectrum [$\nu_{max.}$ 1 397 and 1 372 (Bu^t) and 1 337 and 1 180 cm^{-1} (SO_2)].

perature for 2 days, it was converted into a yellow liquid. Removal of the vial cap produced an immediate decrease in volume, accompanied by a strong odour of sulphur dioxide. The residual liquid, now paler in



colour, was the azoalkane (7a). The alternative *cis*-azo-compound (7b) is reported to be unstable, decomposing at 0 °C into a complex hydrocarbon mixture.[13]

The dramatic difference in decomposition products of the heterocycle (5) must be due in part to both the maintenance of a sulphur dioxide atmosphere and, indirectly, the partial liquification of the gas. which then functions as a solvent. One mechanism to explain the results involves initial attack by water on (5) to

[6] Preliminary communication, H.-H. Chang and B. Weinstein, *J.C.S. Chem. Comm.*, 1973, 397.

[7] For a related synthesis of the thiadiaziridine 1,1-dioxide system (without details), see J. W. Timberlake and M. L. Hodges, *J. Amer. Chem. Soc.*, 1973, **95**, 634; L. M. Trefonas and L. D. Cheung, *ibid.*, p. 636.

[8] For a preparation of the diadamantyl analogue see H. Quast and F. Kees, *Tetrahedron Letters*, 1973, 1655.

[9] J. C. Stowell, *J. Org. Chem.*, 1967, **32**, 2360.

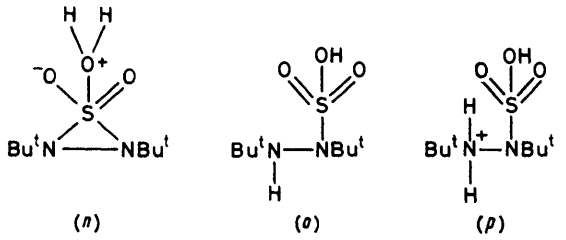
[10] R. Sowada, *J. prakt. Chem.*, 1963, **20**, 310; 1964, **23**, 128.

[11] F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, 1969, **34**, 2254.

[12] K. Hojima and H. I. Chibagase, *Chem. and Pharm. Bull. (Japan)*, 1966, **14**, 961.

[13] T. Mill and R. S. Stringham, *Tetrahedron Letters*, 1969, 1853.

form the charged species (*n*) followed by ring opening to yield the neutral compound (*o*). An *E*2 elimination directly generates the azopropane (7a) and sulphurous acid. At this point, the reaction diverges: in the closed container, sulphurous acid must decompose to

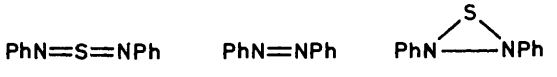


(*n*) (*o*) (*p*)

form sulphur dioxide and water, the former serving as a solvent, whereas the latter goes on to act as a catalyst in a repetition of the initial step; in the open vessel, the sulphurous acid reacts with (*o*) to yield the ion (*p*) and, in time, the salt (6).

The thermal stability of the heterocycle (5) was tested in one more fashion. A freshly sublimed sample was refluxed in dry benzene for 96 h, at which point no change was noted. By contrast, if the reaction was permitted to proceed without attention to control of moisture, then the azopropane (7a) began to appear after 22 h. Thus there is no substantial evidence to support the direct thermal elimination of sulphur dioxide (see earlier discussion of mass spectrum). However, a direct decomposition can be achieved by stirring a solution of (5) in pentane with neutral alumina. The conversion probably proceeds by attack of water, but the rate must be greatly increased owing to a surface effect. These results are different from those in the related *cis*- and *trans*-2,3-diphenylthiirans (9a and b), where thermal loss of sulphur dioxide occurs readily.[14]

The ready conversion of (5) into (7a) by alumina indicated a potential method of synthesis for the parent thiadiaziridine on a solid support. A test of this idea was made in an attempt to generate the unknown thiadiaziridine system (*k*). A solution of diphenylsulphurdi-imide (10) in pentane was passed through an alumina column to give sulphur and azobenzene (11) in

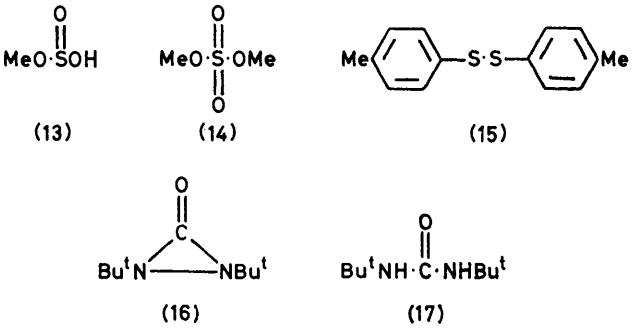


(10) (11) (12)

almost quantative yield. These products suggest that diphenylthiadiaziridine (12) might have been formed in the reaction. Further investigations related to this observation are under way.

Hydrogenation of the thiadiaziridine dioxide (5) in methanol over 10% palladium–charcoal at atmospheric pressure appeared to be complete within a short period, so the solution was filtered and the solvent removed by distillation. The first fraction was low-boiling, smelled of sulphur dioxide, and was pale yellow; the remaining portions were clear and possessed the correct b.p. for methanol. The solid residue was the sulphamide (1) in low yield. The coloured solution was then shown to contain the azoalkane (7a), which accounted for the apparent discrepancy in material balance. No di-t-butylhydrazine (8) was noted, probably owing to its ready oxidation during work-up. On the basis of this observation, it was concluded that the heterocycle (5) was undergoing solvolysis during the hydrogenation.

This idea was verified by proton resonance monitoring of a solution of (5) in methanol at room temperature. Within a few minutes a low-field singlet began to appear and after 20 min only (7a) was present. For a similar reaction in [$^2H_4$]methanol, the final time approached 70 min, strongly indicative of a kinetic isotope effect (*ca.* 3.5). An alternative mechanism employing methanol rather than water in the (*n*) ⟶ (*p*) scheme



(13) (14) (15)

(16) (17)

can thus be proposed. The accompanying product is methyl hydrogen sulphite (13), rather than sulphurous acid. [Some evidence exists for the formation of the sulphite (13) when thionyl chloride or sulphur dioxide is added to methanol.[15]] The reaction was repeated on a larger scale and methanol was removed by distillation. This time, a new low-field signal was seen [τ 5.87 (s)] in the clear methanol fractions. Addition of diazomethane produced a proton resonance [τ 6.03 (s)] whose position was identical with that given by authentic dimethyl sulphate (14). Confirmation of identity was also established by g.l.c. Thus, if (13) is formed it must be changed rapidly by traces of water into methanol and sulphurous acid or, more slowly, by oxidation to methyl hydrogen sulphate.

When compound (5) was stirred with *p*-thiocresol in ether at room temperature, a reaction occurred that was complete after 4 days. On evaporation and the usual work-up, *NN'*-di-t-butylsulphamide (1) was isolated in high yield, as well as a second product identified as di-*p*-tolyl disulphide (15).[16] A radical-transfer scheme can explain this result.

So far, the chemistry of the thiadiaziridine 1,1-dioxide system [17] appears to parallel that of the known di-

[14] F. G. Bordwell, J. M. Williams, E. B. Hoyt, and B. B. Jarvis, *J. Amer. Chem. Soc.*, 1968, **90**, 429.
[15] A. Simon and R. Paetzold, *Z. anorg. Chem.*, 1960, **303**, 53.
[16] C. N. Yiannios and J. V. Karabinose, *J. Org. Chem.*, 1963, **28**, 3246.
[17] A preliminary communication on this subject reports somewhat different results: J. W. Timberlake, M. L. Hodges, and A. W. Garner, *Tetrahedron Letters*, 1973, 3843.

aziridinones.[10,18] For example, di-t-butyldiaziridinone (16) undergoes catalytic hydrogenation to produce *NN'*-di-t-butylurea (17). Again, when compound (16) reacts with ethanethiol at room temperature for 20 days, or with phenylmethanethiol in refluxing benzene for 72 h, the urea (17) and the corresponding disulphide are obtained. Other conversions have been reported for (16), such as electrochemical reduction [19] or reaction with 2,4,6-tri-t-butylphenol to generate a stable free radical.[10] Similar tests will be undertaken with the thiadiaziridine 1,1-dioxide system.

EXPERIMENTAL

M.p.s were determined with a Reichert Thermopan apparatus. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer (potassium bromide discs for solids). ^{1}H N.m.r. spectra were obtained on a Varian A-60 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS-9 spectrometer at 70 eV. Silica gel GF-254 (Merck) was employed as the t.l.c. support and spots were detected by u.v. light or iodine vapour. Microanalyses were provided by Chemalytics, Inc. (Tempe, Arizona), and by PCR, Inc. (Gainsville, Florida). Molecular weight (osmotic) determinations were performed by Galbraith Laboratories, Inc. (Knoxville, Tennessee). All solvents were reagent grade and the light petroleum had a boiling range of 30—60 °C. Anhydrous magnesium sulphate was used for drying.

N-*Chloro*-NN'-*di-t-butylsulphamide* (2).—To a stirred solution of *NN'*-di-t-butylsulphamide (1) (2.08 g, 10.0 mmol) [9] in methanol (25 ml), t-butyl hypochlorite (1.14 ml, 10.0 mmol) was added dropwise. The mixture was stirred for an additional 0.5 h, then evaporated to yield a white solid. Crystallization from chloroform gave white needles of the N-*chloro-derivative* (2.12 g, 87%), m.p. 98—100° (Found: C, 39.3; H, 7.75; Cl, 14.3; N, 11.1; S, 12.9. $C_8H_{19}ClN_2O_2S$ requires C, 39.6; H, 7.9; Cl, 14.6; N, 11.6; S, 13.2%); $\nu_{max.}$ 3 287 (N–H), 1 398, 1 394, 1 369 (Bu^t), 1 336 (SO_2 asym.), 1 150 (SO_2 sym.), and 932 and 878 cm^{-1} (N–SO_2); τ 8.62 (9 H, s), 8.50 (9 H, s), and 5.22br (1 H).

Reactions of the N-*Chlorosulphamide* (2) *with Base.*—(a) *Sodium hydride.* To a slurry of pre-washed sodium hydride (50% oil dispersion; 110 mg, 2.29 mmol) in *NN*-dimethylformamide (100 ml), the *N*-chlorosulphamide (2) (500 mg, 2.06 mmol) was added, and the mixture was stirred for 4 h. Water (150 ml) was added and the mixture was extracted with ether (2 × 100 ml). The organic layer was dried and evaporated; the residue was the sulphamide (1) (211 mg, 49%).

(b) *Potassium t-butoxide.* A mixture of compound (2) and potassium t-butoxide (1.12 g, 10 mmol) was dissolved in t-butyl alcohol (100 ml) and stirred overnight. T.l.c. indicated no change, so an additional equivalent of potassium t-butoxide was then added and the solution was stirred for 10 h. After partitioning between water and benzene, the organic layer was dried and evaporated to yield, after crystallization from benzene, the sulphamide (1) (0.91 g, 44%). A small amount of unidentified oily material was isolated from the mother liquor after evaporation; τ 8.65 (s).

(c) *Sodium hydroxide.* A mixture of compound (2) (2.10 g, 8.70 mmol), N-sodium hydroxide (25 ml), and pentane (50 ml) was stirred overnight. Benzene (80 ml) was added to dissolve the solid and the organic layer was removed, dried, and evaporated to yield the sulphamide (1) (0.80 g, 38%).

2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5).—To a slurry of pre-washed sodium hydride dispersion (1.00 g, 41.6 mmol) in pentane (200 ml), *NN'*-di-t-butylsulphamide (1) (8.32 g, 40 mmol) was added and the mixture was stirred for 4 h. A portion of the white, insoluble product was collected and dried; m.p. >250°; τ 8.63 (s) and 8.49 (s). t-Butyl hypochlorite (4.54 ml, 40 mmol) in pentane (20 ml) was added dropwise while the mixture was cooled below −30 °C (solid CO_2–acetone bath). Stirring and cooling were continued for 5 h. The mixture was then filtered and the solid washed with more pentane. The combined organic phases were evaporated at below 35 °C to yield a colourless oil, which solidified upon refrigeration. Sublimation at room temperature *in vacuo* with cold water cooling afforded 2,3-*di-t-butylthiadiaziridine* 1,1-*dioxide* (5) (5.12 g, 62%), m.p. 35—36° (Found: C, 46.45; H, 8.8; N, 13.2; S, 15.05. $C_8H_{18}N_2SO_2$ requires C, 46.6; H, 8.8; N, 13.6; S, 15.5%); $\nu_{max.}$ 1 395 and 1 372 (Bu^t), 1 337 (SO_2 asym.), and 1 180 cm^{-1} (SO_2 sym.); τ 8.67 (s); *m/e* 206 (M^+), 193 (M^+ − CH), 191 (M^+ − CH_3), 137 (M^+ − C_4H_7N), 71 ($C_4H_9N^+$), 70 ($C_4H_8N^+$), 64 (SO_2^+), and 57 ($C_4H_9^+$); *M* (vapour pressure osmometry; acetone as solvent) 219 (calc. 206).

Decomposition of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5) *in an Open System.*—The thiadiaziridine (500 mg, 2.42 mmol) was left in a small vial exposed to the atmosphere. The sample softened, but no appreciable change in m.p. was detected after 24 h. Four days later, the sample had changed into fine particles, m.p. 150—160°. Recrystallization from chloroform–ethanol gave NN'-*di-t-butylhydrazinium sulphate* (6) as a white solid (276 mg, 49%), m.p. 168° (decomp.) (Found: C, 39.2; H, 9.2; N, 11.7; S, 13.1. $C_8H_{22}N_2SO_4$ requires C, 39.6; H, 9.2; N, 11.6; S, 13.2%); $\nu_{max.}$ 582 and 610 cm^{-1} (HSO_4); τ (D_2O) 8.72 (s). This compound has a sulphuric acid-like taste and an equivalent weight of 132.8 (calc. 121.0). The end point (phenolphthalein) was not sharp.

NN'-*Di-t-butylhydrazine* (8).—*trans*-2,2'-Dimethyl-2,2'-azopropane (7a) [11] (14.2 g, 0.1 mol) in acetic acid (80 ml) with 10% palladium–carbon (0.4 g) was hydrogenated in a Parr apparatus (50 lb in^{-2}). After 24 h the catalyst was removed and the acetic acid evaporated off. The residue (acetate salt) solidified upon cooling and was then shaken with saturated aqueous potassium hydroxide (50 ml). The organic layer was separated and dried (NaOH) to afford *NN'*-di-t-butylhydrazine (8) (12.3 g, 86%). This compound is easily oxidized in air back to compound (7a). A sample of the air-stable hydrochloride, prepared by passing hydrogen chloride gas through a solution of (8) in ether, was recrystallized from carbon tetrachloride–chloroform to afford white needles, m.p. 210—211° (lit.,[18] 211—213°). The sulphate salt was obtained by adding dilute sulphuric acid, evaporating to dryness, and recrystallizing from chloroform–ethanol; m.p. 168° (decomp.).

Decomposition of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5) *in a Closed System.*—The thiadiaziridine (500 mg, 2.42 mmol) was placed in a tightly capped small vial. The white solid was transformed over 24 h into a bright yellow

[18] F. D. Greene, J. C. Stowell, and J. G. Pacifici, *J. Org. Chem.*, 1969, **34**, 2263.

[19] A. J. Fry, W. E. Britton, R. Silson, F. E. Greene, and J. G. Pacifici, *J. Org. Chem.*, 1973, **38**, 2620.

liquid with some suspended particles. On opening the cap, a blast of gas (sulphur dioxide) escaped and there was a noticeable shrinkage of the liquid volume. The now pale yellow liquid was filtered and identified as *trans*-2,2′-dimethyl-2,2′-azopropane (7a) (311 mg, 90.5%).

Thermal Stability of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5) *in Refluxing Benzene*.—A solution of freshly sublimed thiadiaziridine (5) (0.50 g) in benzene (10 ml) was heated to reflux and the reaction was monitored by n.m.r. spectroscopy. Samples (0.5 ml) taken at intervals of 4—10 h showed that compound (5) remained unchanged for periods of 2, 7, and 10 days. This experiment was repeated three times with the same results. In another run, when the solution was not protected from moisture, the solute was changed quantitatively into *trans*-2,2′-dimethyl-2,2′-azopropane (7a). Care should be exercised during the evaporation so as not to lose the product (b.p. 109—110°). Alternatively, a solution of compound (5) in pentane was passed through a neutral alumina column. The only compound found after evaporation of the solvent was the azoalkane (7a) (302 mg, 88.5%). Caution is advised as the sulphur dioxide gas generated during the reaction may sometimes disrupt the packing of the column.

Reaction of Diphenylsulphurdi-imide (10) *with Silica Gel*.—Diphenylsulphurdi-imide (10) (1.00 g, 4.66 mmol) [20,21] was slowly eluted through a silica gel column (2.5 × 50 cm) with pentane. Mild decomposition occurred, but no disruption was observed in the flow of eluant. Sulphur (95 mg, 64%) was obtained by evaporation of the first fraction. The next fraction contained azobenzene (11) (792 mg, 93%), identical with an authentic sample.

Hydrogenation of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5).—Methanol (40 ml) and the thiadiaziridine (5) (500 mg, 2.42 mmol) were placed in a flask which was then flushed with dry nitrogen. 10% Palladium–charcoal (10%; 80 mg) was added and hydrogen was bubbled through for 90 min with stirring. The catalyst was removed and the solution evaporated to leave *NN*′-di-t-butylsulphamide (1) (113 mg, 23%).

Reaction of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5) *with Methanol*.—(*a*) The thiadiaziridine (5) (1.50 g, 7.26 mmol) dissolved in methanol (20 ml) was stirred at room temperature for 2 h. The solution was fractionally distilled to produce the *trans*-azoalkane (7a) (0.61 ml). The n.m.r. spectrum showed that some methanol was still present as an impurity in the distilled material. Methyl hydrogen sulphite was detected in the liquid residue by a similar procedure.

(*b*) In an n.m.r. tube, the thiadiaziridine (5) (30 mg) was dissolved in methanol (0.5 ml) and tetramethylsilane was added as internal reference. The n.m.r. spectrum was taken every 5 min in order to observe the decrease in the signal at τ 8.67 [Bu^t of (5)] and the increase in that at τ 8.87 [Bu^t of (7)]. No reaction was observed in the first 10 min, but then a rapid change proceeded to within 80% of completion at 15 min, and was over at 20 min. When the same procedure was repeated with [$^2H_4$]methanol in place of methanol, the reaction did not start until after 40 min; 80% completion appeared at 60 min, and 100% at 70 min. The induction period was erratic and not seen in all samples.

Reaction of 2,3-*Di-t-butylthiadiaziridine* 1,1-*Dioxide* (5) *with* p-*Thiocresol*.—*p*-Thiocresol (744 mg, 6.00 mmol) and the thiadiaziridine (5) (618 mg, 3.00 mmol) were dissolved in ether (30 ml) and the solution was stirred at room temperature. After 2 days, the reaction was almost complete, but was allowed to continue for another 2 days. The solution was evaporated and light petroleum (30 ml) was added to the oily residue. The insoluble solid was *NN*′-di-t-butylsulphamide (1) (566 mg, 91%). The filtrate was evaporated and the residue was crystallized to yield di-*p*-tolyl disulphide (15) (631 mg, 86%), m.p. 44—45°, identical (i.r. and n.m.r. spectra) with an authentic specimen.[16]

We thank Professor J. W. Timberlake, University of New Orleans, for a comparison of samples and a discussion of his data.

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[20] G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smaller, and A. Trede, *Angew. Chem. Internat. Edn.*, 1962, **1**, 89.
[21] R. Cramer, *J. Org. Chem.*, 1961, **26**, 3476.