Reactions of α-Polyhalo Ketone Tosylhydrazones with Sulfide Ion and Primary Amines. Cyclization to 1,2,3-Thiadiazoles and 1,2,3-Triazoles

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Trichloroacetaldehyde tosylhydrazone acts as an excellent precursor of diazodithioacetate which is generated by treatment of the hydrazone with sulfide ion. This spontaneously cyclizes it to 5-mercapto-1,2,3-thiadiazole. The precursor also gives a 5-amino-1,2,3-triazole on reaction with an amine. α,α-Dichloro ketone tosylhydrazones similarly cyclize to give 1,2,3-thiadiazoles and 1,2,3-triazoles.

Heterocycles, such as 1,2,3-thiadiazoles and 1,2,3-triazoles are useful for various purposes such as modifiers of cephalosporin antibiotoics,[1] or precursors of herbicides[2] or insecticides.[3] For the synthesis of 1,2,3-heterocycles, such as 1,2,3-thiadiazoles and 1,2,3-triazoles, several methods have been developed. Among them, for example, is the preparation of 1,2,3-thiadiazoles by the 1,3-dipolar [2+3] cycloaddition of diazomethane with a thioketone as shown in Fig. 1.[4]

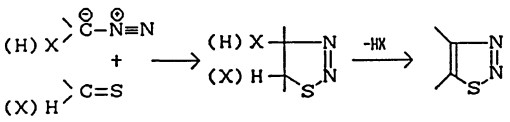
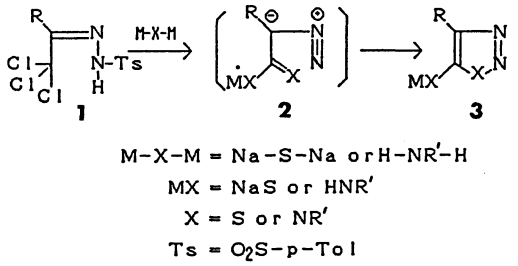


Fig. 1.

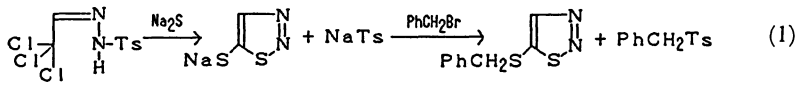
The synthesis of 1,2,3-heterocycles **3** was achieved by the intramolecular cyclization of the intermediate **2** as shown in Scheme 1. For the preparation of 1,2,3-thiadiazole **3** (X=S), diazothioacetate **2** (X=S) is considered as a potential precursor, because **2** (X=S) has the moieties of both the diazo and thiocarbonyl groups in the molecule, which are necessary for the cyclization to the 1,2,3-thiadiazole. However, the diazothioacetate **2** (X=S) is an unknown hypothetical compound, differing from the diazoacetate **2** (X=O). The intermediate **2** (X=S) is thought to be so labile that it will cyclize spontaneously to 1,2,3-thiadiazole **3** (X=S). Here, we chose the α-polyhalo ketone tosylhydrazone **1** as the precursor for the generation of the labile **2** (X=S) and cyclization to **3** (X=S). Similarly diazoacetamidinate **2** (X=NR′) will be generated from the common precursor **1** and **2** (X=NR′) will cyclize to 1,2,3-triazole **3** (X=NR′). Because, the trichloromethyl group in **1** is an equivalent of dithiocaboxylate, C(=S)-SNa, by treatment with Na_2S, and it is also an equivalent of amidine, C(=NR′)-NHR′, by the treatment with H_2NR'. On the other hand, the generation of a diazo group from tosyl hydrazone by treatment with base is well-known as the Bamford-Stevens reaction.[5] Thus, the treatment of **1** with sulfide ion or amine will induce concurrent or stepwise reactions, and will generate labile **2** which will spontaneously cyclize to **3**. Based on the above considerations and analysis, we have developed the intramolecular cyclization method successfully, and we will demonstrate the results of several reactions of α-polyhalo ketone tosylhydrazones with sulfide ion and amines to cyclize to 1,2,3-thiadiazole and 1,2,3-triazole, respectively.



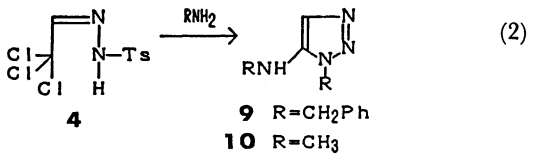
M-X-M = Na-S-Na or H-NR′-H
MX = NaS or HNR′
X = S or NR′
Ts = O_2S-p-Tol

Scheme 1.

Trichloroacetaldehyde tosylhydrazone (**4**), a precursor of the reactive intermediate **2** (X=S, MX=NaS), is a known compound and was prepared as described in the literature.[6] The cyclization reaction was carried out as follows: Into a solution of 3 equivalents of sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) in 50% aqueous ethanol, hydrazone **4** was added. The solution was concentrated and the deposited crystals collected. Treatment of the crystals with benzyl bromide gave 5-benzylthio-1,2,3-thiadiazole (**7**) in 67% yield and benzyl *p*-tolyl sulfone (**8**) in 41% yield, as shown in Eq. 3. The result suggested that the deposited crystals were composed of sodium 1,2,3-thiadiazol-5-yl sulfide (**5**) and sodium *p*-toluenesulfinate (**6**). In practice, an attempt to separate them by fractional recrystallization from ethanol gave **5** and **6** in 60 and 84% yields. The reaction yielded the 1,2,3-thiadiazole **5** via intramolecular cyclization of the reactive intermediate **2** generated from the precursor **4**. This result encouraged us to extend the reaction using other bases, such as amines and hydroxide ion.

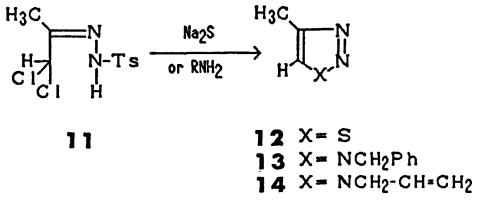


Accordingly, amines were allowed to react with **4**. Although treatment with aqueous ammonia provided no identified materials, a treatment with excess benzylamine in methanol gave 1-benzyl-5-benzylamino-1,2,3-triazole (**9**) in 30% yield, along with large amounts of mixed salts of benzylamine. With methylamine, 1-methyl-5-methylamino-1,2,3-triazole (**10**) was also afforded in 25% yield (Eq. 2).

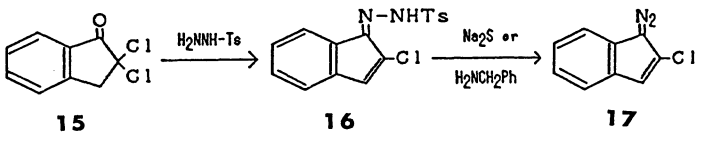


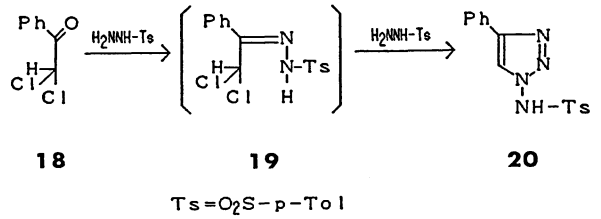
In the case of hydroxide ion, the expected reaction product of the precursor **4**, 1,2,3-oxadiazole, is known to be unstable, except for the case of sydnone.[7] In practice, treatment of **4** with sodium hydroxide solution gave no identified products.

We were next interested in the reaction of thioacetaldehyde **2** (X=S, MX=H) as the reactive intermediate. The precursor for the generation of **2** (X=S, MX=H) should be a dichloride, such as **11**. A precursor, α,α-dichloroacetone tosylhydrazone (**11**), was prepared by the same method as above for **4**.[6] By treatment of **11** with sodium sulfide, only a trace amount of 4-methyl-1,2,3-thiadiazole (**12**) was detected by NMR spectroscopy. This will be related to the volatility of the product **12**. On the other hand, reaction of **11** with excess benzylamine gave 1-benzyl-4-methyl-1,2,3-triazole (**13**), in a high yield of 84% as shown in Eq. 3. Allylamine likewise gave 1-allyl-4-methyl-1,2,3-triazole (**14**) in 83% yield. The precursor **11** also cyclized successfully.

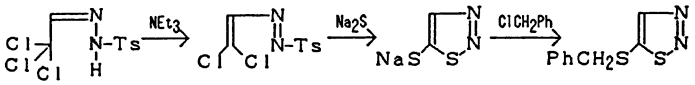


The preparation of two other α,α-dichloroketones, **15** and **18** was attempted by the cyclization reaction. By treatment with tosylhydrazine, 2,2-dichloro-1-indanone (**15**) gave 2-chloro-1-indenone tosylhydrazone (**16**) with simultaneous removal of hydrogen chloride (Eq. 4). The hydrazone **16** provided 2-chloro-1-diazoindene (**17**) as a common product, by reaction both with sodium sulfide and with benzylamine. The difficult substitution of sulfur or amine nucleophiles for a chlorine atom in **16** or **17** and stabilization of the diazo group by a benzene ring will lead to the isolation of the diazo compound **17**. On the other hand, when α,α-dichloroacetophenone (**18**) was treated with tosylhydrazine (Eq. 5), the compound isolated was unexpectedly cyclized 4-phenyl-1-(*p*-toluenesulfonamido)-1,2,3-triazole (**20**). This indicates that tosylhydrazone **19** was so labile that tosylhydrazine reacted with **19** to give **20**.



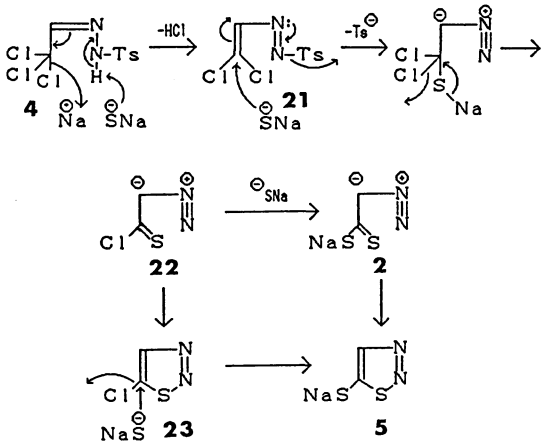


As a final example, 1,1-dichloro-2-(*p*-tolylsulfonylazo)ethene (**21**) was obtained from **4** by gentle treatment with triethylamine as reported by Bott[6] (Eq. 6). The 1,1-dichloroethenyl derivative **21** similarly cyclized to **5** by reaction with sodium sulfide; it was identified as the benzyl derivative **7**.



4 21 5 7 (6)

From the mechanistic view point, the production of 5-mercapto-1,2,3-thiadiazole (**5**) from **21** suggests that the reaction may proceed via the intermediate **21**. We can speculate that the course of the cyclization reaction is as shown in Scheme 2. According to



Scheme 2.

which, the reaction with Na_2S initiates a removal of hydrogen chloride from **4** to give a stable intermediate **21**. The addition of second sulfide ion for the substitution for chlorine atom in **21** by addition-elimination manner induces the simultaneous removal of toluenesulfinate ion to generate a diazomethane moiety to afford intermediate **22**. From **22** to the final product **5**, two routes are possible. One is that the reaction proceeds by the attack of a third sulfide ion to generate diazodithiocarboxylate **2** (X=S); alternatively cyclization may occur first, to give stable 5-chloro-1,2,3-thiadiazole (**23**). This is already known to easily substitute a sulfide ion for a chlorine atom,[8] although we could not detect it in the reaction mixture. The reaction of **4** with amines can take place by the same mechanism as shown above. However, generation of the diazo intermediate, **2** or **22**, in the course of the reaction still remains an uncertainty, because in the Bamford-Stevens reaction, the reaction conditions are generally *more drastic.*[5] *But in a particular case, such as a* monotosylhydrazone of α-diketone, it is known that the hydrazone easily gave an α-diazoketone by treatment with 0.1 M† sodium hydroxide solution at room temperature.[9] In this case the contribution of the α-carbonyl group is important for the genaration of diazo group under such mild conditions. Similarly the thiocarbonyl group may act a significant role for the smooth generation of the diazo moiety in **2** or **22**.

† 1 M=1 mol dm^{-3}.

Further detailed studies to clarify the intermediate role of the diazodithioacetate **2** are in progress.

Experimental

Measurements: All the melting points are uncorrected. NMR spectra were taken with Varian EM-390 and XL-100 instruments. Mass spectra were obtained with a Hitachi RMU-6MG instrument. IR were measured with a JASCO A-202 instrument.

Trichloroacetaldehyde Tosylhydrazone (4): This was prepared according to the method described in the literature from trichloroacetaldehyde and tosylhydrazine.[6]

Sodium 1,2,3-Thiadiazol-5-yl Sulfide (5) and Sodium *p*-Toluenesulfinate (6): To a solution of sodium sulfide ($Na_2S \cdot 9H_2O$) (18.0 g, 74.9 mmol) in 50% aqueous ethanol (40 ml) under ice-cooling, trichloroacetaldehyde tosylhydrazone (**4**) (6.31 g, 20.0 mmol) was added as powder portion wise over a period of 5 min. The stirring was continued at that temperature for 10 min and at room temperature for 1 h. The solution was then concentrated under reduced pressure at 50 °C to one third of the volume. The deposited precipitates of a mixture of **5** and **6** were collected by filtration after cooling with ice. The crystals, dried under reduced pressure in desiccator, were dissolved in ethanol (100 ml) and treated with active charcoal. Ethanol was distilled off by heating until the volume of the solution reduced to ca. 50 ml. On cooling with ice, precipitates of **6** were deposited and filtered off. The filtrate was concentrated again to a half. From the solution, **6** was crystallized again on cooling and filtered off. By complete removal of the solvent, 1.68 g of **5** was obtained (60% yield). All filtered **6** fractions were combined and totally 3.00 g of **6** was collected (84% yield).

5: IR (KBr disc); 3350, 1665, 1640, 1400, 1200, 1120, 1040, 870, 820 cm^{-1}; ^{1}H-NMR (D_2O, TSP deuterated) δ=8.2 (singlet).

5-Benzylthio-1,2,3-thiadiazole (7) and Benzyl *p*-Tolyl Sulfone (8): The dried crystalline mixture of **5** and **6** (1.00 g) obtained as above was dissolved in 50% aqueous ethanol (6 ml) and to this was added benzyl bromide (806 mg, 4.71 mmol) at room temperature. The solution was extracted with dichloromethane, after 1 h. The organic layer was washed with brine, dried over anhydrous sodium sulfate, and the solvent removed to leave *1.13* g of residue. Column chromatographic separation (silica gel, CH_2Cl_2) of the residue gave **7** (449 mg, 67% yield) and **8** (315 mg, 41% yield), respectively.

7: Mp 49—51 °C; ^{1}H-NMR ($CDCl_3$) δ=4.14 (2H, s), 7.30 (5H, s); MS (70 eV) *m/z* 208 (M^+, 2.3%), 180 (1.5%), 179 (5.3%), 147 (7.8%), 122 (15.1%), 91 (100%).

8: ^{1}H-NMR ($CDCl_3$) δ=2.39 (3H, s), 4.25 (2H, s), 6.95—7.55 (9H, m).

1-Benzyl-5-benzylamino-1,2,3-triazole (9): To a solution of trichloroacetaldehyde tosylhydrazone (**4**) (3.2 g, 10 mmol) in methanol (10 ml) under ice-cooling, was added a

solution of benzylamine (6.4 g, 60 mmol) in methanol (5 ml) dropwise. Stirring was continued at ice-water temperature for 2.5 h. Methanol was removed below 30 °C under reduced pressure. Benzene was added to the residue and the solid was crushed to a fine powder. Insoluble crystals of benzylamine salts (2.7 g) were removed by filtration and the benzene layer was washed with 1 M sodium hydroxide aqueous solution and brine. Removal of solvent after drying over anhydrous magnesium sulfate left a dark residue which was purified by column chromatography (silica gel, hexane: AcOEt=1:2) to afford **9** (0.77 g, 30% yield).

9: Mp 102—108 °C: ^{1}H-NMR (d_6-DMSO) δ=4.25 (2H, bt), 5.41 (2H, s), 6.50 (1H, bt), 6.81 (1H, s), 7.10—7.43 (10H, m): IR (KBr disc) 3050, 1670, 1600, 1500, 1450, 1290, 1240 cm^{-1}: MS (70 eV) m/z 264 (M^+, 83%), 236 (4.1%), 104 (26.0%), 91 (100%).

1-Methyl-5-methylamino-1,2,3-triazole (10): To a solution of 40% aqueous methylamine (4.7 g, 60 mmol) in water (15 ml) and methanol (10 ml) under ice-cooling, powdered trichloroacetaldehyde tosylhydrazone (**4**) (3.2 g, 10 mmol) was added portion wise. Stirring was continued at room temperature for 19 h and the product was extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The residue (1.02 g) on removal of the solvent under reduced pressure was purified by column chromatography (silica gel, AcOEt) to give **10** (0.27 g, 25% yield).

10: Mp 61—63 °C: ^{1}H-NMR ($CDCl_3$) δ=2.83 (3H, s), 3.77 (3H, s), 4.91(1H, bs), 6.87 (1H, s): IR (KBr disc) 3050, 2810, 1440, 1310, 1280 cm^{-1}: MS (70 eV) m/z 112 (M^+, 44.6%), 83 (15.5%), 69 (41.0%), 55 (44.7%), 42 (100%).

α,α-Dichloroacetone Tosylhydrazone (11): To a solution of p-tosylhydrazine (6.7 g, 36 mmol) in propionic acid (30 ml), was added α,α-dichloroacetone (5.0 g, 39 mmol) and the reaction mixture was stirred at room temperature for 4 h. To this was added cyclohexane (30 ml) and the reaction mixture was cooled in ice bath. The white crystals which deposited were collected by filtration to give **11** (10 g, 94% yield).

11: Mp 137—138 °C (decomp): ^{1}H-NMR (d_6-DMSO) δ=1.85 (3H, s), 2.37 (3H, s), 7.40 (2H, m), 9.17 (1H, s), and 2.03 (3H, s), 2.37 (3H, s), 6.70 (1H, s), 7.40 (2H, m), 7.77 (2H, m): IR (KBr disc) 3230, 1600, 1340, 1170 cm^{-1}: MS (70 eV) m/z 294 (M^+, 2.3%), 155 (14.5%), 91 (100%).

Detection of 4-Methyl-1,2,3-thiadiazole (12): A solution of sodium sulfide ($Na_2S \cdot 9H_2O$)(3.00 g, 12.5 mmol) in water (7 ml) was covered with a layer of ether (12 ml), under ice-cooling, α,α-dichloroacetone tosylhydrazone (**11**) (1.48 g, 5.00 mmol) was added portion wise and stirring was continued for 19 h at that temperature. The ether layer was separated, washed with brine, and dried over anhydrous sodium sulfate. Ether was removed at atmospheric pressure at 55 °C to leave a trace of colorless residue. The ^{1}H-NMR of the residue revealed the signals due to 4-methyl-1,2,3-thiadiazole (**12**) at 2.85(s) and 8.20(s).

1-Benzyl-4-methyl-1,2,3-triazole (13): To a solution of α,α-dichloroacetone tosylhydrazone (**11**) (3.0 g, 10 mmol) in methanol (10 ml) under ice-cooling, was added a solution of benzylamine (5.3 g, 50 mmol) in methanol (5 ml) dropwise, followed by stirring at that temperature for 2 h. To the residue after removal of methanol under reduced pressure, benzene (10 ml) was added. The precipitates were crushed under ice-cooling, and removed by filtration. The benzene layer was washed with 1 M sodium hydroxide and brine, dried over anhydrous magnesium sulfate and the solvent removed leaving a dark residue. The residue was purified by column chromatography (silica gel, hexane: AcOEt=1:1) to afford **13** (1.46 g, 84% yield).

13: Mp 61—62 °C: ^{1}H-NMR ($CDCl_3$) δ=2.30 (3H, s), 5.43 (2H, s), 7.17 (1H, s), 7.21—7.37 (5H, m): IR (KBr disc) 3070, 2950, 1500, 1440, cm^{-1}: MS (70 eV) m/z 173 (M^+, 31.8%), 91 (100%), 65 (74.9%).

1-Allyl-4-methyl-1,2,3-triazole (14): To a solution of allylamine (2.9 g, 50 mmol) in methanol (15 ml), under ice-cooling, powdered dichloroacetone tosylhydrazone (**11**) was added portion wise. The mixture was stirred at that temperature for 4.5 h and at room temperature for 1.5 h. The solvent was removed under reduced pressure and replaced with dichloromethane. The solution was washed with 1 M sodium hydroxide and brine and dried over anhydrous magnesium sulfate. The residual oil on removal of solvent was purified by distillation (15 mmHg,† 100—160 °C) to give **14** (125 mg, 83%) as an oil.

14: ^{1}H-NMR ($CDCl_3$) δ=2.33 (3H, s), 4.90 (2H, dd), 5.25 (2H, m), 6.00 (1H, m), 7.30 (1H, d): IR (KBr plate) 3100, 2950, 1650, 1440, 1210, 1050, cm^{-1}: MS (70 eV) m/z 123 (M^+, 15.2%), 54 (36.1%), 41 (100%).

2,2-Dichloro-1-indanone (15): This was prepared according to the literature[10] from 1-indanone and copper(II) chloride.

2-Chloro-1-indenone Tosylhydrazone (16): 2,2-Dichloro-1-indanone (**15**) (0.54 g, 2.7 mmol) in ethanol (10 ml) was added to a solution of tosylhydrazine (0.50 g, 2.7 mmol) and 12 M hydrochloric acid (0.25 ml) and the mixture was stirred at room temperature for 20 h. The yellow crystals which deposited were collected by filtration. The filtrate was concentrated to half the volume and the crystals collected by filtration. Totally, 0.70 g of 2-chloro-1-indenone tosylhydrazone (**16**) was obtained (78% yield).

16: Mp 162—165 °C: ^{1}H-NMR (d_6-DMSO) δ=2.40 (3H, s), 6.87 (1H, s), 7.00—7.40 (5H, m): IR (KBr disc) 3450, 3250, 1600, 1345, 1170 cm^{-1}: MS (70 eV) m/z 332 (M^+, 2.1%), 176 (46.7%), 148 (93.8%), 113 (100%).

2-Chloro-1-diazoindene (17); Reaction of 16 with Benzylamine: A mixture of 2-chloro-1-indenone tosylhydrazone (**16**) (0.49 g, 1.5 mmol) and benzylamine (0.66 g, 5.9 mmol) in methanol (10 ml) was stirred under ice cooling for 1 h, at room temperature for 4 h, and finally at reflux temperature for 1 h. The solvent was removed under reduced pressure and to the residue was added a mixture of benzene and ether (v/v=1/1, 20 ml). The organic layer was washed with saturated sodium hydrogencarbonate solution and brine, and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave a residue which was separated by column chromatography (silica gel, hexane:AcOEt=1:1) to afford **16** (0.08 g, 16%) and 2-chloro-1-diazoindene (**17**) (0.07 g, 27% yield).

17: ^{1}H-NMR ($CDCl_3$) δ=6.30 (1H, s), 7.03—7.47 (4H, m): IR (KBr disc): 2100, 1505, 1430 cm^{-1}: MS (70 eV) m/z 176 (M^+, 41.7%), 148 (81.8%), 113 (100%).

2-Chloro-1-diazoindene (17); Reaction of 16 with Sodium

† 1 mmHg=133.322 Pa.

Sulfide: To a solution of sodium sulfide ($Na_2S \cdot 9H_2O$) (2.2 g, 9.0 mmol) in methanol (8 ml) was added 2-chloro-1-indenone tosylhydrazone (**16**) (1.0 g, 3.0 mmol) in methanol (10 ml) under ice-cooling and stirring was continued for 46 h at room temperature. The reaction mixture was filtered and the filtrate was concentrated until the precipitates began to deposit. The precipitates were collected by filtration. ^{1}H-NMR and IR spectra of the crystals showed that **17** was produced.

4-Phenyl-1-(*p*-toluenesulfonamido)-1,2,3-triazole (20): A mixture of α,α-dichloroacetophenone (**18**) (purchased from Aldrich Chemical Co.) (10.4 g, 60 mmol) and *p*-tosylhydrazine (5.6 g, 30 mmol) in ethanol (50 ml) was refluxed for 1 h. The crystals formed by concentration of the solution were collected by filtration after cooling with ice. The crystals of **20** were produced (1.94 g, 20% yield).

20: Mp 202—203 °C (decomp): Elemental analysis, Found: C, 57.43; H, 4.41; N, 17.58; S, 10.10%: Calcd for $C_{15}H_{14}N_4O_2S$: C, 57.31; H, 4.49; N, 17.82; S, 10.20%: ^{1}H-NMR (d_6-DMSO) δ=2.40 (3H, s), 7.17—7.87 (9H, m), 8.07 (1H, s): IR (KBr disc) 3050, 1600, 1480, 1370, 1170, 1090 cm^{-1}: MS (70 eV) *m/z* 314 (M^+, 3.8%), 171 (44.7%), 155 (52.5%), 145 (100%).

5-Benzylthio-1,2,3-thiadiazole (7) from 1,1-Dichloro-2-(*p*-tolylsulfonylazo)ethene (21): To a solution of sodium sulfide ($Na_2S \cdot 9H_2O$) (600 mg, 2.50 mmol) in water (1.0 ml) and ethanol (0.5 ml), was added 1,1-dichloro-2-(*p*-tolylsulfonylazo)ethene (**21**) (280 mg, 1.00 mmol) prepared by the method reported by Bott[6] from trichloroacetaldehyde tosylhydrazone (**4**) and triethylamine in dichloromethane at 0 °C in ethanol (0.5 ml) slowly at room temperature, and the reaction mixture was stirred for 1 h. The solution was cooled with ice and benzyl chloride was added (0.5 ml). After 1 h, ether was added and the organic layer was washed with brine, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. Removal of excess benzyl chloride in vacuo at 60 °C gave **7** as orange crystals (94 mg, 45%).

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