1-Arylsulfonylamino-1,2,3-triazole Derivatives from Functionalyzed 1,2-Cyclohexanediones

F. Benedetti, S. Bozzini, M. Forchiassin, G. Nardin, G. Pitacco, C. Russo* and E. Valentin

Dipartimento di Scienze Chimiche, Università degli Studi di Trieste, I-34127 Trieste, Italy

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The heterocyclization reaction of arylsulfonylhydrazones from alkyl substituted 1,2-cyclohexanediones is sensitive to the steric requirements of the alkyl groups. A mechanism for the cyclization in acidic medium is also reported.

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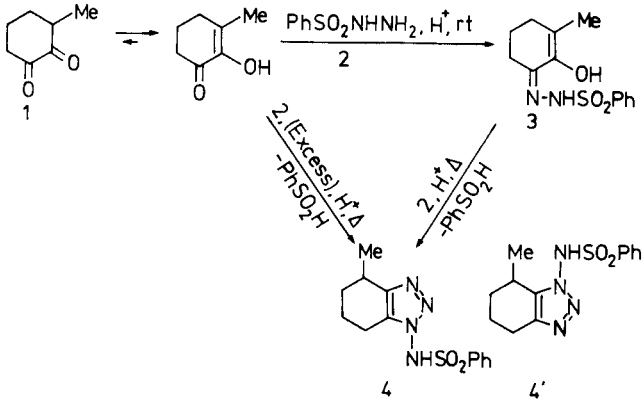
1,2,3-Triazoles containing amino-, amido-, or sulfonylamino substituents have been studied extensively and a broad range of preparations attempted [1]. In particular 1-aminotriazoles and their derivatives are conveniently prepared from *bis*-hydrazones and substituted *bis*-hydrazones of 1,2-diketones, by an intramolecular cyclization of adjacent groups. The cyclization can occur both in the presence of oxidizing agents [2] and in basic [3] or acidic medium [4]. This type of reaction had been applied to acylic and cyclic symmetric substrates and to a small number of derivatives of 1,2-diketones of type R-CO-CO-Ar: in this case the formation of two isomeric triazoles is possible, although not always observed. When the formation of both isomers is reported, the data on the regioselectivity are given in few cases [2a,2c,3b,5].

Within the framework of our researches concerning the functionalization and the reactivity of 1,2-cycloalkanediones [6], we have extended the reaction of formation of 1,2,3-triazoles condensed with carbocyclic rings to asymmetric substrates such at 3- and 4-alkyl-1,2-cyclohexanediones, in which the substituents were the methyl and *t*-butyl groups. The present work was undertaken mainly to study the regioselectivity of the heterocyclization reaction, but also as part of a program designed to prepare bicyclic sulfonylaminotriazole derivatives with potential pharmacological activity [1].

Scheme 1

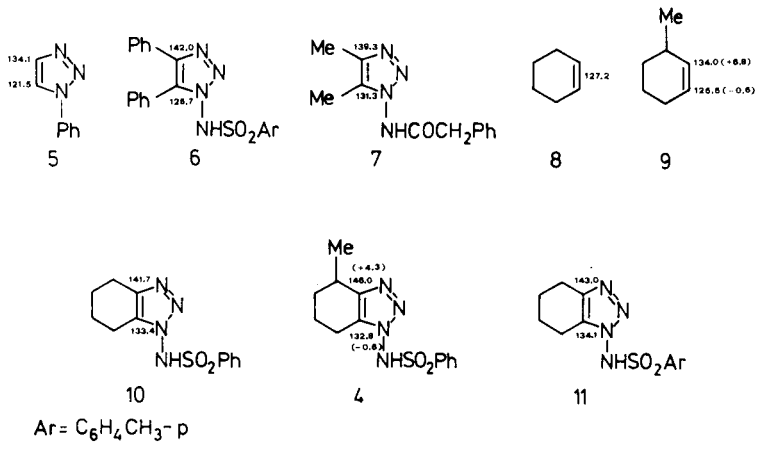


Results and Discussion.

The 3- and 4-alkyl-1,2-cyclohexanediones needed as starting materials were synthesized following the method of Utaka *et al.* [7]. The reaction of 3-methyl-1,2-cyclohexanedione **1** with phenylsulfonylhydrazine **2** (Scheme 1) carried out at room temperature in acidic medium did not furnish the corresponding *bis*-phenylsulfonylhydrazone, and even operating in large excess of **2** only one monophenylsulfonylhydrazone was isolated, to which the structure **3** was assigned, on the basis of its ir and ^{1}H nmr spectral data.

Gentle heating of the reaction mixture resulted in direct formation of a single product which was identified as 1-phenylsulfonylamino-4-methyl-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**4**). This structural assignment was based on a comparison between the ^{13}C nmr spectra of **4** and those of several 1-substituted 1,2,3-triazoles including the parent bicyclic derivatives **10** and **11** which were prepared in quantitative yield by a slight modification of the method reported in the literature [4]. In 1-substituted 1,2,3-triazoles, as for example compounds **5** [8], **6** [2b] and **7** [9], the resonance of C-5 appears upfield with respect to that of C-4: this appears to be quite general for triazoles, being a consequence of the different hybridization of the nitrogen atoms to which the carbon atoms are attached [9]. On this basis the resonances at δ 133.4 and δ 141.7 in the ^{13}C nmr spectrum of **10** can be assigned to C-7a and C-3a, respectively; similar values are also observed for triazole **11**, thus confirming the assignment. The resonances of C-7a and C-3a are shifted to δ 132.8 ($\Delta\delta$ = -0.6 ppm) and δ 146.0 ($\Delta\delta$ = +4.3 ppm) in the spectrum of **4**. The observed shift is in agreement with the well known shielding effect of a methyl group on the α- and β-sp^2 carbon atoms of an allylic system [10], and is very similar to that observed, for example, in compounds **8** and **9**. On the basis of these considerations the structure **4** and not **4'** was consistent with the ^{13}C nmr spectral data of the compound.

The simplest rationalization of the fact that only one of the two possible isomers **4** and **4'** is formed, is that the



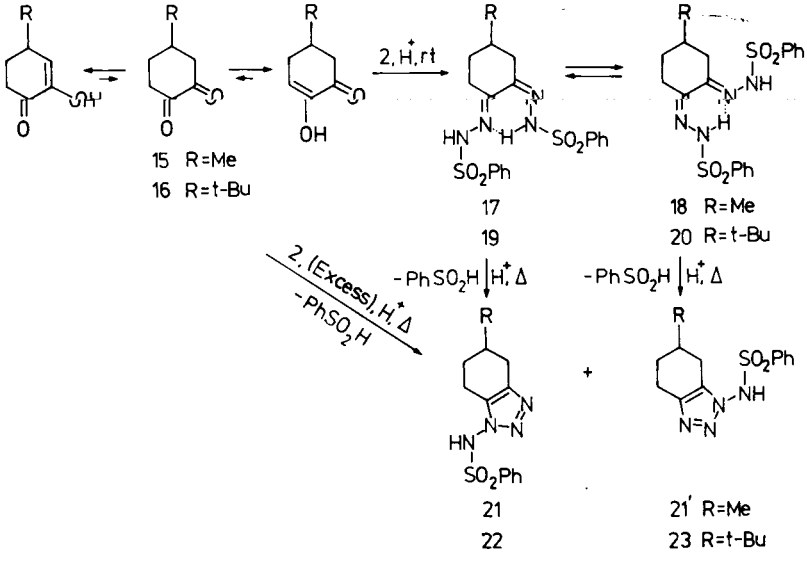
5 6 7 8 9

10 4 11

presence of a substituent, although not very bulky like a methyl group, is determining in directing the heterocyclization reaction through an intermediate with the least interaction between the methyl and the phenylsulfonylamino groups. In other words the cleavage of the sulfonylhydrazone substituent closest to the alkyl group present in the carbocyclic ring is clearly favoured, leading to the formation of the triazole derivative in which the substituents are as far apart as possible. In order to verify whether the triazole system might be formed also in the presence of a very bulky substituent at the 4-carbon atom, we tried to synthesize the analogous of **4** in which the methyl was replaced by a *t*-butyl group. Unfortunately the synthesis of the starting 1,2-diketone failed; in fact the intermediate 2,6-dibromo derivative [11], by treatment with sodium hydroxide, underwent a nucleophilic displacement of the bromine groups instead of the expected elimination reaction, giving the corresponding diol **14**. 4-Methyl- and 4-*t*-butyl-1,2-cyclohexanedione, **15** and **16**, respectively, were also allowed to react with phenylsulfonylhydrazine **2**. Both furnished the corresponding *bis*-phenylsulfonylhydrazones **17**, **18** and **19**, **20**, respectively, as 1:1 mixtures of diastereoisomers, as indicated by ^{1}H nmr spectroscopy. Furthermore, from the chemical shift values of the NH protons, the presence of intramolecular hydrogen bonding was evident. Unfortunately, these mixtures could not be separated into their components which had identical R_f values in both cases. These derivatives, on heating, easily underwent the heterocyclization reaction. (Scheme 2).

The best results were obtained operating in acidic medium, while in the presence of potassium hydroxide the *bis*-sulfonylhydrazones were recovered unchanged after gentle heating in ethanol for 45 minutes; more forcing conditions [3b,3c], *i.e.* heating at 105-150° for 5-15 minutes in 1,2-ethanediol, led to considerable decompo-

Scheme 2



sition and furnished the triazole derivatives in very poor yields ($\leq 10\%$).

As for the reaction of the 4-methyl derivatives **17** and **18**, it came as a surprise that a product was isolated in good yield (70%) which resulted to be a single isomer, as confirmed beyond doubt by ^1H and ^{13}C nmr spectra, besides the tlc analysis carried out under a variety of conditions. The spectral information, however, did not permit a decision on its structure that was definitely determined as **21** by an X-ray analysis.

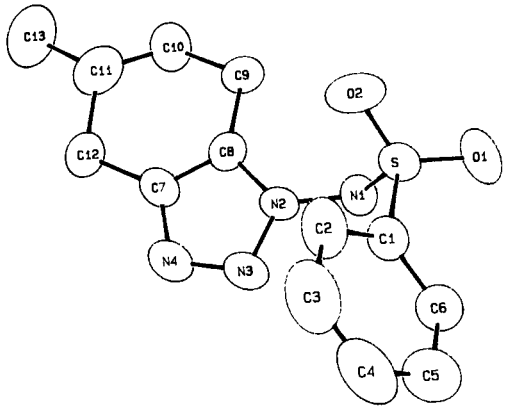
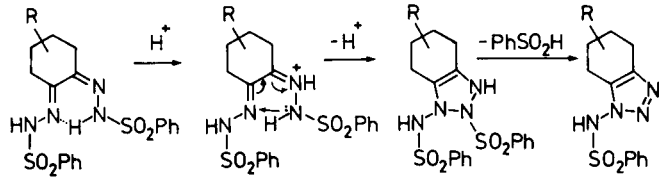


Figure. Ortep plot of **21** showing atom numbering scheme. Atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

On the contrary, a 1:1 mixture of the two isomeric triazoles **22** and **23** was obtained from the 4-*t*-butyl-*bis*-phenylsulfonylhydrazones **19** and **20**. Also in this case the structural assignments for the two isomers could not rest unequivocally on the interpretation of spectral evidences, so that a preliminary single crystal X-ray analysis was undertaken on one of the two products which was shown to be **23** [12].

In the light of these results it is felt that the course of the reaction depends on the geometry of the *bis*-hydrazone intermediates. The mechanism we propose for the formation of triazoles in acidic medium is that depicted in Scheme 3. It involves protonation of the imine nitrogen atom free from intramolecular hydrogen bonding, followed by nucleophilic attack of the adjacent nitrogen atom onto the other imine group, followed by heteroaromatization with loss of sulfinic acid.

Scheme 3



Table

Positional Parameters and their Estimated Standard Deviations

Atom	x	y	z	B(Å²)
S	0.19037(7)	0.17727(6)	0.9733(2)	3.93(3)
O1	0.2341(2)	0.1989(2)	1.0528(5)	5.8(1)
O2	0.1447(2)	0.2105(2)	0.9358(5)	5.8(1)
N1	0.2226(2)	0.1585(2)	0.8315(5)	3.5(1)
N2	0.1875(2)	0.1370(2)	0.7329(5)	3.18(9)
N3	0.1778(2)	0.0825(2)	0.7248(5)	4.2(1)
N4	0.1456(2)	0.0753(2)	0.6178(5)	4.5(1)
C1	0.1647(2)	0.1169(2)	1.0491(6)	3.5(1)
C2	0.1094(3)	0.1050(3)	1.0390(7)	5.1(2)
C3	0.0900(3)	0.0573(4)	1.0992(8)	6.9(2)
C4	0.1256(4)	0.0232(3)	1.1658(8)	7.1(2)
C5	0.1805(4)	0.0358(3)	1.1747(7)	6.2(2)
C6	0.2009(3)	0.0823(3)	1.1161(6)	4.5(1)
C7	0.1355(2)	0.1259(2)	0.5612(6)	3.7(1)
C8	0.1622(2)	0.1652(2)	0.6325(6)	3.2(1)
C9	0.1630(3)	0.2252(3)	0.6050(7)	5.0(2)
C10	0.1366(4)	0.2355(3)	0.4696(8)	7.7(2)
C11	0.0952(4)	0.1988(4)	0.4215(9)	8.5(2)
C12	0.1035(3)	0.1374(3)	0.4347(6)	4.6(2)
C13	0.0680(4)	0.2151(4)	0.291(1)	9.6(3)

Since the *bis*-sulfonylhydrazones are pairs of diastereoisomers, one would have expected the formation of two isomeric triazoles in each case. While this was actually found for the 4-*t*-butyl derivatives **19** and **20**, only one triazole was formed in the case of **17** and **18**. A tentative explanation could be that under the acidic conditions an equilibration between the *bis*-hydrazones occurred. Owing to the different mobility of the two rings, such an equilibration might be fast for the 4-methyl derivatives **17** and **18** and slow for the 4-*t*-butyl derivatives **19** and **20**. Therefore only one triazole was eventually formed in the former case and two in the latter.

EXPERIMENTAL

Melting points are uncorrected and were determined on a Büchi apparatus. Ir spectra were recorded with a Perkin-Elmer 1320 double beam spectrophotometer. The ^1H nmr spectra were run on a FT Bruker WP spectrometer operating at 80 MHz; chemical shifts are reported downfield from TMS (deuteriochloroform solution) or DSS (dimethyl sulfoxide-d_6 solution); exchangeable protons were detected by deuterium oxide-d_2 addition. The ^{13}C nmr spectra were recorded in dimethyl sulfoxide-d_6 [approximately 10% (w/v) solutions] on a FT Bruker WP spectrometer operating at 20.1 MHz. The mass spectra (ei, positive ions) were obtained using a VG 70 70 mass spectrometer operating at 70 eV; samples were introduced *via* a direct inlet probe, with a source temperature ranging from 200 to 230°. Microanalyses were carried out on a Hewlett-Packard 185 Instrument. The tlc analyses were performed on Stratocrom SIF 254 W60 plates (Whatman Inc., for C. Erba), developed with 8.5:1.5 benzene-anhydrous ethanol; the spots were located both by filtered uv light (λ max 254 and 366 nm) and by spraying with 0.2*M* potassium permanganate in concentrated sulfuric acid. Flash chromatography was performed on silica gel 60 (C. Erba, 230-400 mesh ASTM) using 9:1 hexane-anhydrous ethanol as eluant. Gas chromatographic analyses of 1,2-cyclohexanediones were performed with a GC 6000 Vega series C. Erba apparatus equipped with a FID (SE 30 Column, 190°).

1) Synthesis of Alkyl-1,2-cyclohexanediones.

The title compounds were prepared by the method of Wallach [13] as described by Utaka *et al.* [7].

3-Methyl-1,2-cyclohexanedione (**1**).

The ketone had mp 58-60° (lit [14] 62°); ir (neat): 3400, 3320 sh, 1650 br cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.27 (m, 6H, OH), 1.97 (s, 3H, Me).

4-Methyl-1,2-cyclohexanedione (**15**).

The ketone had mp 35-36°, bp 85°/12 torr (lit [14] 35°; 90-95°/16 torr); ir (neat): 3440 br, 1670 cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.1 (m, 2H, C=CH and OH), 1.17 and 1.07 (two d, 6H, Me).

4-*t*-Butyl-1,2-cyclohexanedione (**16**).

The ketone had bp 94-95°/10 torr (lit [15] 74-5°/1.2 torr); ir (neat): 3420 br, 1670 br cm^{-1}; ^1H nmr (deuteriochloroform): δ 6.2 (m, 2H, C=CH and OH), 0.93 and 0.87 (two s, 9H, CMe_3).

2-*t*-Butyl-2,6-dihydroxycyclohexanone (**14**).

The compound had mp 98-99° (triturated with light petroleum); ir (nujol): 3470, 3410, 1720 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.80 (m, 1H, C*H*-OH), 3.7 (d, 1H, C(6)-OH), 2.7 (s, 1H, C(2)-OH), 1.07 (s, 9H, CMe_3).

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.7; H, 9.76.

2) Synthesis of Arylsulfonylhydrazones.

The title compounds were prepared by treating the corresponding 1,2-cyclohexanediones (13 mmoles) with the arylsulfonylhydrazines (26 mmoles) in methanol (15 ml) in the presence of catalytic amounts of sulfuric acid, at room temperature for 24 hours. The precipitate was filtered off and repeatedly washed with water before crystallization.

1,2-Cyclohexanedione *bis*-Phenylsulfonylhydrazone (**12**) [4].

The compound had mp 119-120° (from methanol), yield 70%; ir (nujol): 3210 cm^{-1}; ^1H nmr (deuteriochloroform): δ 12.6 (s, 1H, NH), 8.9 (m, 1H, NH).

1,2-Cyclohexanedione *bis*-*p*-Tolylsulfonylhydrazone (**13**).

The compound had mp 133-134° (from ethanol), yield 55%; ir (nujol): 3200, 3120 cm^{-1}; ^1H nmr (deuteriochloroform): δ 12.47 (s, 1H, NH), 8.67 (s, 1H, NH), 1.83 (s, 3H, Me).

Anal. Calcd. for $C_{20}H_{24}N_4O_4S_2$: C, 53.57; H, 5.39; N, 12.49; S, 15.40. Found: C, 53.51; H, 5.33; N, 12.41; S, 15.35.

3-Methyl-1,2-cyclohexanedione 1-Phenylsulfonylhydrazone (**3**).

The compound had mp 144-145° (from ethanol), yield 78%; ir (nujol): 3440, 3220 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.23-7.30 (m, 6H, aromatic protons and NH), 6.0 (s, 1H, OH), 1.83 (s, 3H, Me).

Anal. Calcd. for $C_{13}H_{16}N_2O_3S$: C, 55.69; H, 5.75; N, 9.99; S, 11.44. Found: C, 55.62; H, 5.77; N, 9.91; S, 11.37.

4-Methyl-1,2-cyclohexanedione *bis*-Phenylsulfonylhydrazones (**17**) and (**18**).

The mixture had mp 125-127° (from methanol), yield 80%; ir (nujol): 3200 cm^{-1}; ^1H nmr (deuteriochloroform): δ 12.57 (s, 1H, NH), 8.73 (s, 1H, NH), 1.0 and 0.93 (2d, 3H, Me).

Anal. Calcd. for $C_{19}H_{22}N_4O_4S_2$: C, 52.52; H, 5.10; N, 12.89; S, 14.75. Found: C, 52.40; H, 5.06; N, 12.8; S, 14.8.

4-*t*-Butyl-1,2-cyclohexanedione *bis*-Phenylsulfonylhydrazones (**19**) and (**20**).

The mixture had mp 124-125° (from methanol), yield 42%; ir (nujol): 3220 cm^{-1}; ^1H nmr (deuteriochloroform): δ 12.67 (s, 1H, NH), 8.96 (s, 0.5H, NH), 8.76 (s, 0.5H, NH), 0.87 (s, 9H, CMe_3).

Anal. Calcd. for $C_{22}H_{28}N_4O_4S_2$: C, 55.46; H, 5.88; N, 11.76; S, 13.40. Found: C, 55.36; H, 5.83; N, 11.70; S, 13.37.

Synthesis of 1-Arylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazoles.

1) In Acidic Medium.

a) The *bis*-arylsulfonylhydrazone (10 mmoles) was dissolved in methanol (20 ml) containing few drops of concentrated hydrochloric acid, and the solution was refluxed for 1.5 hours. The precipitate was filtered off and purified by crystallization.

b) Equimolar amounts of monoarylsulfonylhydrazone and arylsulfonylhydrazine dissolved in methanol containing few drops of concentrated hydrochloric acid were treated as described under a). The product was purified by column chromatography.

c) Alkyl 1,2-cyclohexanedione (10 mmoles) and arylsulfonylhydrazine (20 mmoles) dissolved in methanol containing few drops of hydrochloric acid were heated as reported under a). After removal of the solvent at reduced pressure the oily residue was washed with light petroleum and chromatographed.

2) In Basic Medium.

Equimolar amounts of 1,2-cyclohexanedione *bis*-arylsulfonylhydrazones and potassium hydroxide were dissolved in ethanol and heated under reflux for 45 minutes. After removal of the solvent at reduced pressure, water was added to the residue until a precipitate was formed. Physical properties, methods of synthesis and corresponding yields, analytical and the significant spectral data are reported under the single headings.

1-Phenylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**10**).

The product had mp 176-177° (from methanol) (lit [4] 175°; method 1a, 67% yield), method 2, 100% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): [16] δ 8.0 (m, 5H, aromatic protons), 2.63 and 1.47 (two m, 8H, carbocyclic protons); ^{13}C nmr: δ 19.1, 21.3, 21.5, 22.1, 128.1, 129.6, 133.4, 134.3, 137.9, 141.7; ms: m/z 278 (M^+, 4), 109 (M -$ArSO_2$ -N_2, 88), 81 (100).

1-*p*-Tolylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**11**).

The product had mp 179-180° (from methanol), method 2, 100% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.67 (m, 4H, aromatic protons), 2.45 (s, 3H, Me); ^{13}C nmr: δ 19.9, 21.9, 22.0, 22.1, 22.6, 128.9, 130.2, 134.1, 134.5, 143.0, 145.8; ms: m/z 292 (M^+, 5), 109 (M -$ArSO_2$ -N_2, 100).

Anal. Calcd. for $C_{13}H_{16}N_4O_2S$: C, 53.4; H, 5.52; N, 19.16; S, 10.97. Found: C, 53.2; H, 5.58; N, 19.13; S, 10.95.

4-Methyl-1-phenylsulfonylamino-4,5,6,7-tatrahydrobenzo-1,2,3-triazole (**4**).

The product had mp 164-165° (from methanol), method 1b, 60% yield, method 1c, 45% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethylsulfoxide-d_6): δ 7.87 (m, 5H, aromatic protons), 1.27 (d, 3H, Me); ^{13}C nmr: δ 19.3, 20.2, 27.3, 31.2, 128.0, 129.6, 132.8, 134.3, 137.8, 146.0; ms: m/z 292 (M^+, 0.2), 123 (M -$ArSO_2$ -N_2, 100).

Anal. Calcd. for $C_{13}H_{16}N_4O_2S$: C, 53.40; H, 5.52; N, 19.16; S, 10.97. Found: C, 53.65; H, 5.50; N, 19.20; S, 10.92.

5-Methyl-1-phenylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**21**).

The product had mp 214-215° (from methanol), method 1a, 75% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.95 (m, 5H, aromatic protons), 1.07 (d, 3H, Me); ^{13}C nmr: δ 18.3, 20.7, 28.7, 29.5, 29.6, 128.1, 129.6, 133.2, 134.3, 137.9, 141.9; ms: m/z 292 (M^+, 0.4), 123 (M -$ArSO_2$ -N_2, 44), 81 (100).

Anal. Calcd. for $C_{13}H_{16}N_4O_2S$: C, 53.4; H, 5.52; N, 19.16; S, 10.97. Found: C, 53.5; H, 5.56; N, 19.1; S, 10.95.

5-*t*-Butyl-1-phenylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**22**).

The product had mp 140° (from methanol), method 1a, 30% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.77 (m, 5H, aromatic protons), 0.98 (s, 9H, CMe_3); ^{13}C nmr: δ 19.5, 23.0, 23.4, 27.2,

32.2, 44.6, 128.1, 129.6, 133.5, 134.3, 137.9, 142.6; ms: m/z 334 (M^+, 0.4), 165 (M -$ArSO_2$, -N_2, 25), 77 (100).

Anal. Calcd. for $C_{16}H_{22}N_4O_2S$: C, 57.4; H, 6.50; N, 16.7; S, 9.58. Found: C, 57.1; H, 6.48; N, 16.6; S, 9.57.

6-*t*-Butyl-1-phenylsulfonylamino-4,5,6,7-tetrahydrobenzo-1,2,3-triazole (**23**).

The product had mp 191-192° (from methanol), method 1a, 30% yield; ir (chloroform): 3320 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.83 (m, 5H, aromatic protons), 0.93 (s, 9H, CMe_3); ^{13}C nmr: δ 20.4, 21.9, 24.1, 27.1, 32.2, 44.1, 128.2, 129.7, 133.9, 134.4, 138.2, 141.9; ms: m/z 334 (M^+, 1), 165 (M -$ArSO_2$ -N_2, 74), 57 (100).

Anal. Calcd. for $C_{16}H_{22}N_4O_2S$: C, 57.4; H, 6.5; N, 16.7; S, 9.58. Found: C, 57.5; H, 6.48; N, 16.8; S, 9.53.

Crystal Data for **21**.

The following data were collected: $C_{13}H_{16}N_4O_2S$, M = 291.4, Tetragonal, a = b = 24.210(4), c = 9.940(2) Å, V = 5826(2) $Å^3$, Z = 16, space group $I4_1/a$, MoKα radiation λ = 0.71069 Å. Preliminary cell parameters and space group were determined from Weissenberg and Precession photographs and then refined on an Enraf-Nonius CAD4 fully automated diffractometer using setting angles of 25 reflections in the range $12° < \theta < 18°$. Intensity data were collected in the range $3° \leq \theta \leq 28°$ using $\omega/2\theta$ scan technique. The structure was solved by conventional Patterson and Fourier methods. Hydrogen atoms were located at calculated positions and held fixed (B = 5.0 $Å^2$) during refinement. Full-matrix least-squares refinement with anisotropic thermal parameters for all the refined atoms converged to the final R factors of 0.062 for 1457 independent reflections. All data processing was performed on a PDP 11/44 computer with use of the Enraf-Nonium SDP program library. Neutral atom scattering factors were taken from the literature [17]. Final atomic parameters are listed in Table.

Calculated coordinates of hydrogen atoms, observed and calculated structure factors, and anisotropic temperature factors are available from the authors.

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