

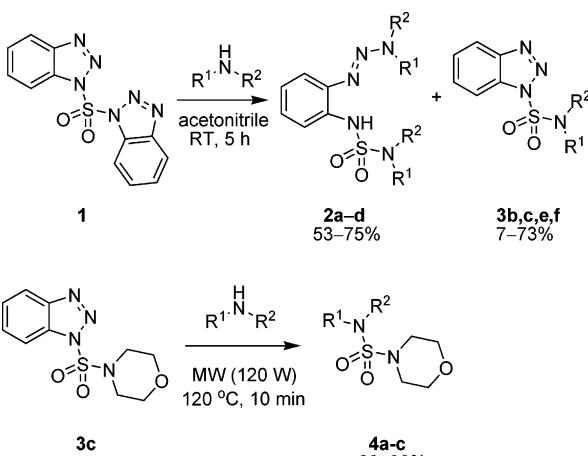
**Synthesis of *o*-Sulfamidotriazobenzenes from 1,1'-Sulfonylbis(benzotriazole)**

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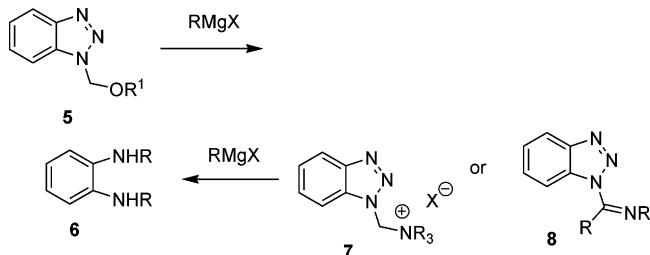


Easily accessible 1,1'-sulfonylbis(benzotriazole) ( $\text{Bt}_2\text{SO}_2$ , **1**) reacts with secondary amines at room temperature to afford (i) the corresponding *o*-sulfamidotriazobenzenes **2a–d** (53–75%) via concurrent substitution of the first and ring opening of the second benzotriazolyl group and (ii) *N*-sulfonylbenzotriazoles **3b,c,e,f** (7–73%). 1-(Morpholine-4-sulfonyl)-1*H*-benzotriazole **3c** reacts with piperidine, pyrrolidine, and *N*-methylpiperazine under microwave irradiation (120 W) at 120 °C for 10 min to give the unsymmetrical sulfamides **4a–c** (80–90%).

Benzotriazole is a useful synthetic auxiliary: it is easily introduced, activates molecules toward numerous transformations, and can be removed readily at the end of the reaction sequence.<sup>1</sup> However, in some reactions cleavage of the triazole ring occurs. The century old classical Graebe–Ullmann synthesis of carbazoles from 1-arylbenzotriazoles occurs at 360 °C via loss of a nitrogen molecule.<sup>2</sup> Pyrolysis of *N*-vinylbenzotriazoles at 500–700 °C gave *N*-phenylketenimines.<sup>3</sup> Recently photodecomposition of tris(benzotriazol-1-yl)methane in benzene gave phenanthridine.<sup>4</sup> Our group encountered benzotriazole ring opening under milder conditions nearly two decades ago;

benzotriazolylmethyl phenethyl ether **5** and benzylmagnesium bromide at 110 °C gave *N*-benzyl-*N'*-phenethyl-*o*-phenylenediamine **6** (Scheme 1) via a single nitrogen atom extrusion in low (10%) yield;<sup>5</sup> *N*-(benzotriazol-1-ylmethyl)-*N*-methylpyrrolidinium iodide **7** and ethylmagnesium iodide gave a mixture of unsymmetrically substituted *o*-phenylenediamines<sup>6</sup> (10–40%) (Scheme 1) and 1-(*N*-phenylacetimidoyl)benzotriazole **8** and its propionimidoyl analogue produced corresponding *o*-phenylenediamines in such reactions.<sup>7</sup>

**SCHEME 1**



Later, ring opening of benzotriazoles with electron-donating substituents and via loss of a nitrogen molecule afforded rearranged heterocycles: quinazolines from 2-(benzotriazol-1-yl)enamines<sup>8</sup> and benzoheterocycles and ortho-substituted anilines from *N*-( $\alpha$ -alkoxyalkyl)benzotriazoles.<sup>9</sup> Ring fragmentation of the diarylbenzotriazolylmethane anion occurred at 20 °C.<sup>10</sup> Acid-catalyzed tandem benzotriazole ring opening/ammonia extrusion of 3-(benzotriazol-1-yl)-1,4-diaryl-1-butene-4-ols gave benzo[*a*]-phenazines.<sup>11</sup> Intramolecular benzotriazole ring opening–ring closure without elimination of nitrogen is preparatively useful for nitrogen-containing fused heterocyclic systems: pyrazolo[5,1-*b*]benzimidazoles,<sup>12</sup> tetrazolo[1,5-*e*][1,2,5]-triazepines,<sup>13</sup> and 1,2,4-triazolo[1,5-*a*]quinoxalines.<sup>14</sup>

Recently, Ziegler and Subramanian et al. reported the base-catalyzed ring opening of benzotriazoles with electron-withdrawing substituents.<sup>15</sup> 1-[*(*Nonafluorobutane)sulfonyl]-1*H*-benzotriazole ( $\text{BtNf}$ , **9**) with a variety of phenols and naphthols in the presence of a base afforded ortho-substituted azobenzenes

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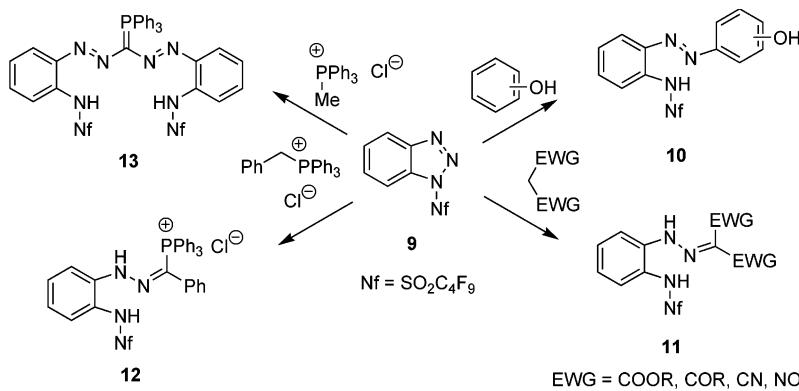
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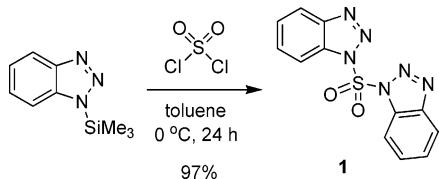
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SCHEME 2



SCHEME 3



**10** (47–94%) (Scheme 2).<sup>15a</sup> This was successfully extended to a mono-triazole-fused phthalocyaninato zinc complex.<sup>15b</sup> Base-catalyzed reactions of BtNf with active methylene compounds afforded  $\alpha$ -functionalized *N*-arylhdyrazones **11** (72–89%) (Scheme 2);<sup>15c</sup> reactions with alkyl triphenylphosphoranylidene and methylenetriphenylphosphorylidene gave phenylazomethylenetriphenylphosphoranes **12** and bis-phenylazomethylenetriphenylphosphorane **13**, respectively.<sup>15d</sup>

Herein, we report that  $\text{Bt}_2\text{SO}_2$  (**1**) with diverse secondary amines involves substitution of one benzotriazolyl group together with ring opening of the second by two molecules of the same amine to give novel *o*-sulfamidotriazobenzenes **2** as the major products along with the expected *N*-sulfonylbenzotriazoles **3** as the minor products.

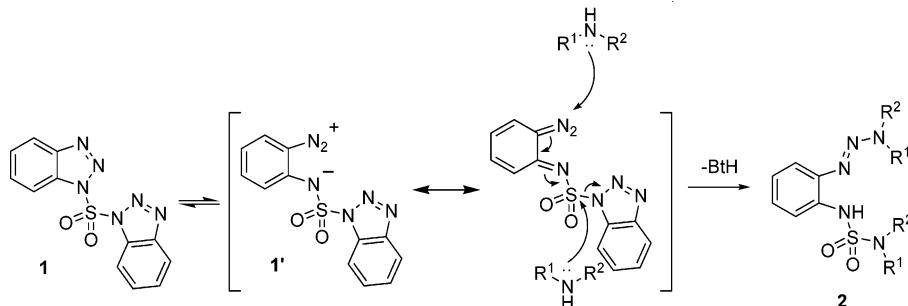
**Synthesis of 1,1'-Sulfonylbis(benzotriazole).** Reaction of 1-trimethylsilanyl-1*H*-benzotriazole (2 mol) with sulfonyl chloride in toluene at 0–25 °C for 24 h affords 1,1'-sulfonylbis(benzotriazole) ( $\text{Bt}_2\text{SO}_2$ , **1**) (97%) (Scheme 3),<sup>16</sup> fully characterized by its NMR and elemental analyses. The detailed molecular structure of **1** was established by X-ray diffraction analysis (see the Supporting Information). The molecule possesses a crystallographic 2-fold rotation axis.

**Unexpected Reactivity of 1,1'-Sulfonylbis(benzotriazole).** (1). Reaction of 1 equiv of 1,1'-sulfonylbis(benzotriazole) ( $\text{Bt}_2\text{SO}_2$ , **1**) with 3 equiv of pyrrolidine in acetonitrile at rt for 5 h gave (*E*)-*N*-(2-(pyrrolidin-1-ylidazhenyl)phenyl)pyrrolidine-1-sulfonamide **2a** in 55% yield (Table 1). The expected product 1-(pyrrolidine-1-sulfonyl)-1*H*-benzotriazole **3a** was not obtained. The product **2a** was purified by column chromatography, using silica gel and a mixture of hexanes and ethyl acetate as the eluent, and characterized by <sup>1</sup>H and <sup>13</sup>C NMR and satisfactory

TABLE 1. Reaction of  $\text{Bt}_2\text{SO}_2$  **1** with Secondary Amines

entry	amines	product <b>2a–e</b>	yield (%) <sup>a</sup>	product <b>3a–e</b>	yield (%) <sup>a</sup>
1	<chem>C1CCN1</chem>	<b>2a</b>	55	<b>3a</b>	0
2	<chem>C1CCCC1</chem>	<b>2b</b>	53	<b>3b</b>	7
3	<chem>C1CCOC1</chem>	<b>2c</b>	63	<b>3c</b>	11
4	<chem>C1CCN(C1)C</chem>	<b>2d</b>	75	<b>3d</b>	0
5	<chem>Cc1ccccc1</chem>	<b>2e</b>	0	<b>3e</b>	70 <sup>b</sup>
6	<chem>c1ccc(cc1)Nc2ccc(cc2)Nc3ccc(cc3)Nc4ccc(cc4)Nc5ccc(cc5)Nc6ccc(cc6)Nc7ccc(cc7)Nc8ccc(cc8)Nc9ccc(cc9)Nc10ccc(cc10)Nc11ccc(cc11)Nc12ccc(cc12)Nc13ccc(cc13)Nc14ccc(cc14)Nc15ccc(cc15)Nc16ccc(cc16)Nc17ccc(cc17)Nc18ccc(cc18)Nc19ccc(cc19)Nc20ccc(cc20)Nc21ccc(cc21)Nc22ccc(cc22)Nc23ccc(cc23)Nc24ccc(cc24)Nc25ccc(cc25)Nc26ccc(cc26)Nc27ccc(cc27)Nc28ccc(cc28)Nc29ccc(cc29)Nc30ccc(cc30)Nc31ccc(cc31)Nc32ccc(cc32)Nc33ccc(cc33)Nc34ccc(cc34)Nc35ccc(cc35)Nc36ccc(cc36)Nc37ccc(cc37)Nc38ccc(cc38)Nc39ccc(cc39)Nc40ccc(cc40)Nc41ccc(cc41)Nc42ccc(cc42)Nc43ccc(cc43)Nc44ccc(cc44)Nc45ccc(cc45)Nc46ccc(cc46)Nc47ccc(cc47)Nc48ccc(cc48)Nc49ccc(cc49)Nc50ccc(cc50)Nc51ccc(cc51)Nc52ccc(cc52)Nc53ccc(cc53)Nc54ccc(cc54)Nc55ccc(cc55)Nc56ccc(cc56)Nc57ccc(cc57)Nc58ccc(cc58)Nc59ccc(cc59)Nc60ccc(cc60)Nc61ccc(cc61)Nc62ccc(cc62)Nc63ccc(cc63)Nc64ccc(cc64)Nc65ccc(cc65)Nc66ccc(cc66)Nc67ccc(cc67)Nc68ccc(cc68)Nc69ccc(cc69)Nc70ccc(cc70)Nc71ccc(cc71)Nc72ccc(cc72)Nc73ccc(cc73)Nc74ccc(cc74)Nc75ccc(cc75)Nc76ccc(cc76)Nc77ccc(cc77)Nc78ccc(cc78)Nc79ccc(cc79)Nc80ccc(cc80)Nc81ccc(cc81)Nc82ccc(cc82)Nc83ccc(cc83)Nc84ccc(cc84)Nc85ccc(cc85)Nc86ccc(cc86)Nc87ccc(cc87)Nc88ccc(cc88)Nc89ccc(cc89)Nc90ccc(cc90)Nc91ccc(cc91)Nc92ccc(cc92)Nc93ccc(cc93)Nc94ccc(cc94)Nc95ccc(cc95)Nc96ccc(cc96)Nc97ccc(cc97)Nc98ccc(cc98)Nc99ccc(cc99)Nc100ccc(cc100)Nc101ccc(cc101)Nc102ccc(cc102)Nc103ccc(cc103)Nc104ccc(cc104)Nc105ccc(cc105)Nc106ccc(cc106)Nc107ccc(cc107)Nc108ccc(cc108)Nc109ccc(cc109)Nc110ccc(cc110)Nc111ccc(cc111)Nc112ccc(cc112)Nc113ccc(cc113)Nc114ccc(cc114)Nc115ccc(cc115)Nc116ccc(cc116)Nc117ccc(cc117)Nc118ccc(cc118)Nc119ccc(cc119)Nc120ccc(cc120)Nc121ccc(cc121)Nc122ccc(cc122)Nc123ccc(cc123)Nc124ccc(cc124)Nc125ccc(cc125)Nc126ccc(cc126)Nc127ccc(cc127)Nc128ccc(cc128)Nc129ccc(cc129)Nc130ccc(cc130)Nc131ccc(cc131)Nc132ccc(cc132)Nc133ccc(cc133)Nc134ccc(cc134)Nc135ccc(cc135)Nc136ccc(cc136)Nc137ccc(cc137)Nc138ccc(cc138)Nc139ccc(cc139)Nc140ccc(cc140)Nc141ccc(cc141)Nc142ccc(cc142)Nc143ccc(cc143)Nc144ccc(cc144)Nc145ccc(cc145)Nc146ccc(cc146)Nc147ccc(cc147)Nc148ccc(cc148)Nc149ccc(cc149)Nc150ccc(cc150)Nc151ccc(cc151)Nc152ccc(cc152)Nc153ccc(cc153)Nc154ccc(cc154)Nc155ccc(cc155)Nc156ccc(cc156)Nc157ccc(cc157)Nc158ccc(cc158)Nc159ccc(cc159)Nc160ccc(cc160)Nc161ccc(cc161)Nc162ccc(cc162)Nc163ccc(cc163)Nc164ccc(cc164)Nc165ccc(cc165)Nc166ccc(cc166)Nc167ccc(cc167)Nc168ccc(cc168)Nc169ccc(cc169)Nc170ccc(cc170)Nc171ccc(cc171)Nc172ccc(cc172)Nc173ccc(cc173)Nc174ccc(cc174)Nc175ccc(cc175)Nc176ccc(cc176)Nc177ccc(cc177)Nc178ccc(cc178)Nc179ccc(cc179)Nc180ccc(cc180)Nc181ccc(cc181)Nc182ccc(cc182)Nc183ccc(cc183)Nc184ccc(cc184)Nc185ccc(cc185)Nc186ccc(cc186)Nc187ccc(cc187)Nc188ccc(cc188)Nc189ccc(cc189)Nc190ccc(cc190)Nc191ccc(cc191)Nc192ccc(cc192)Nc193ccc(cc193)Nc194ccc(cc194)Nc195ccc(cc195)Nc196ccc(cc196)Nc197ccc(cc197)Nc198ccc(cc198)Nc199ccc(cc199)Nc200ccc(cc200)Nc201ccc(cc201)Nc202ccc(cc202)Nc203ccc(cc203)Nc204ccc(cc204)Nc205ccc(cc205)Nc206ccc(cc206)Nc207ccc(cc207)Nc208ccc(cc208)Nc209ccc(cc209)Nc210ccc(cc210)Nc211ccc(cc211)Nc212ccc(cc212)Nc213ccc(cc213)Nc214ccc(cc214)Nc215ccc(cc215)Nc216ccc(cc216)Nc217ccc(cc217)Nc218ccc(cc218)Nc219ccc(cc219)Nc220ccc(cc220)Nc221ccc(cc221)Nc222ccc(cc222)Nc223ccc(cc223)Nc224ccc(cc224)Nc225ccc(cc225)Nc226ccc(cc226)Nc227ccc(cc227)Nc228ccc(cc228)Nc229ccc(cc229)Nc230ccc(cc230)Nc231ccc(cc231)Nc232ccc(cc232)Nc233ccc(cc233)Nc234ccc(cc234)Nc235ccc(cc235)Nc236ccc(cc236)Nc237ccc(cc237)Nc238ccc(cc238)Nc239ccc(cc239)Nc240ccc(cc240)Nc241ccc(cc241)Nc242ccc(cc242)Nc243ccc(cc243)Nc244ccc(cc244)Nc245ccc(cc245)Nc246ccc(cc246)Nc247ccc(cc247)Nc248ccc(cc248)Nc249ccc(cc249)Nc250ccc(cc250)Nc251ccc(cc251)Nc252ccc(cc252)Nc253ccc(cc253)Nc254ccc(cc254)Nc255ccc(cc255)Nc256ccc(cc256)Nc257ccc(cc257)Nc258ccc(cc258)Nc259ccc(cc259)Nc260ccc(cc260)Nc261ccc(cc261)Nc262ccc(cc262)Nc263ccc(cc263)Nc264ccc(cc264)Nc265ccc(cc265)Nc266ccc(cc266)Nc267ccc(cc267)Nc268ccc(cc268)Nc269ccc(cc269)Nc270ccc(cc270)Nc271ccc(cc271)Nc272ccc(cc272)Nc273ccc(cc273)Nc274ccc(cc274)Nc275ccc(cc275)Nc276ccc(cc276)Nc277ccc(cc277)Nc278ccc(cc278)Nc279ccc(cc279)Nc280ccc(cc280)Nc281ccc(cc281)Nc282ccc(cc282)Nc283ccc(cc283)Nc284ccc(cc284)Nc285ccc(cc285)Nc286ccc(cc286)Nc287ccc(cc287)Nc288ccc(cc288)Nc289ccc(cc289)Nc290ccc(cc290)Nc291ccc(cc291)Nc292ccc(cc292)Nc293ccc(cc293)Nc294ccc(cc294)Nc295ccc(cc295)Nc296ccc(cc296)Nc297ccc(cc297)Nc298ccc(cc298)Nc299ccc(cc299)Nc300ccc(cc300)Nc301ccc(cc301)Nc302ccc(cc302)Nc303ccc(cc303)Nc304ccc(cc304)Nc305ccc(cc305)Nc306ccc(cc306)Nc307ccc(cc307)Nc308ccc(cc308)Nc309ccc(cc309)Nc310ccc(cc310)Nc311ccc(cc311)Nc312ccc(cc312)Nc313ccc(cc313)Nc314ccc(cc314)Nc315ccc(cc315)Nc316ccc(cc316)Nc317ccc(cc317)Nc318ccc(cc318)Nc319ccc(cc319)Nc320ccc(cc320)Nc321ccc(cc321)Nc322ccc(cc322)Nc323ccc(cc323)Nc324ccc(cc324)Nc325ccc(cc325)Nc326ccc(cc326)Nc327ccc(cc327)Nc328ccc(cc328)Nc329ccc(cc329)Nc330ccc(cc330)Nc331ccc(cc331)Nc332ccc(cc332)Nc333ccc(cc333)Nc334ccc(cc334)Nc335ccc(cc335)Nc336ccc(cc336)Nc337ccc(cc337)Nc338ccc(cc338)Nc339ccc(cc339)Nc340ccc(cc340)Nc341ccc(cc341)Nc342ccc(cc342)Nc343ccc(cc343)Nc344ccc(cc344)Nc345ccc(cc345)Nc346ccc(cc346)Nc347ccc(cc347)Nc34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SCHEME 4



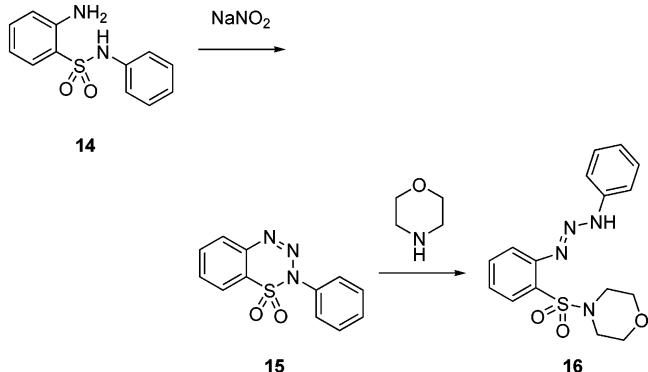
The NH group of **2a** appears downfield at  $\delta$  7.81 ppm (singlet) as a result of H-bonding to the neighboring N atom. The <sup>13</sup>C NMR spectrum of **2a** showed eight signals corresponding to the product. Further the detailed molecular structure of (*E*)-*N*-(2-(pyrrolidin-1-ylidaz恒基)phenyl)pyrrolidine-1-sulfonamide **2a** was established unambiguously by X-ray diffraction analysis (see the Supporting Information). In view of the novelty of the *o*-sulfamidotriazobenzene structure and the mechanism of its formation, we reacted 1 equiv of Bt<sub>2</sub>SO<sub>2</sub> (**1**) with 3 equiv of piperidine, morpholine, and diethylamine in acetonitrile at rt for 5 h to give (*E*)-*N*-(2-(piperidin-1-ylidaz恒基)phenyl)piperidine-1-sulfonamide (**2b**), (*E*)-*N*-(2-(morpholinodiaz恒基)phenyl)morpholine-4-sulfonamide (**2c**), and (*E*)-*N*-(2-(diethylamino-1-ylidaz恒基)phenyl)diethylamine-1-sulfonamide (**2d**) (53%, 63%, and 75%, respectively) along with 1-(piperidine-1-sulfonyl)-1*H*-benzotriazole (**3b**), 1-(morpholine-4-sulfonyl)1*H*-benzotriazole (**3c**), and 1-(diethylamine-1-sulfonyl)-1*H*-benzotriazole (**3d**) (7%, 11%, and 0%, respectively) (Table 1). The structure of **2c** was confirmed by X-ray crystallography but the crystals were all highly twinned and hence the data did not refine to a level suitable for publication. We tried the experiments with a larger excess of secondary amines, but the yields of products **2a-d** and **3b,c** were not increased. However, the yield of **3c** was increased to 45% when the reaction was heated at 80 °C for 24 h.

Bt<sub>2</sub>SO<sub>2</sub> (**1**) did not react with methylphenyl amine or di-p-tolylamine at rt; however, refluxing in acetonitrile for 12 h produced 1-(methylphenylamine-1-sulfonyl)-1*H*-benzotriazole (**3e**) and 1-(di-p-tolylamine-4-sulfonyl)-1*H*-benzotriazole (**3f**) (70% and 73%, respectively) (Table 1). These results suggest that alkylaryl amines or diaryl amines do not give benzotriazole ring-opened products whereas dialkyl amines easily give *o*-sulfamidotriazobenzenes at rt. This difference in reactivity may be due to a large difference in nucleophilicity between the alkyl and aryl amines.

A possible mechanism for the formation of *o*-sulfamidotriazobenzenes **2** is outlined in Scheme 4: Bt<sub>2</sub>SO<sub>2</sub> (**1**) exists in equilibrium with the diazonium betaine structure **1'**.<sup>17</sup> Two molecules of amine attack a single molecule of **1** at different positions—at the diazo group of **1'** assisted by the electron-withdrawing sulfone group, and at the sulfur atom with elimination of a benzotriazole (BtH) moiety. This leads to product **2** after a proton shift (Scheme 4). A similar mechanism of ring opening was proposed for the reactions of BtNf (**9**).<sup>15</sup>

*o*-Sulfamidotriazobenzenes of type **2** were unknown; however, closely related *o*-sulfonamidotriazobenzenes have been used as color formers.<sup>18</sup> *o*-Sulfonamidotriazobenzenes **16** have been prepared by ring cleavage of cyclic triazosulfones **15**,<sup>19</sup> diazotization of **14** gave the intermediate **15** (Scheme 5).<sup>20</sup>

SCHEME 5



*o*-Sulfamidotriazobenzenes **2** combine the features of both a triazine and a sulfamide group. Many triazines are known to display potent antitumor activity.<sup>21</sup> Sulfamides on the other hand are of interest as (i) components stable to enzymatic hydrolysis in peptidomimetics,<sup>22</sup> (ii) active components in epinephrine analogues,<sup>23</sup> (iii) agonists of the 5-HT<sub>1D</sub> receptor (regulating serotonin levels),<sup>24</sup> and (iv) HIV protease inhibitors.<sup>25</sup>

We utilized the byproduct *N*-sulfonylbenzotriazoles **3** for the synthesis of unsymmetrical sulfamides. Thus reaction of 1-(morpholine-4-sulfonyl)-1*H*-benzotriazole (**3c**) with pyrrolidine, piperidine, and *N*-methylpiperazine under microwave irradiation (120 W) at 120 °C for 10 min gave novel 4-(pyrrolidin-1-sulfonyl)morpholine (**4a**) and known 4-(piperidin-1-sulfonyl)morpholine<sup>26</sup> (**4b**) and 4-(4-methylpiperazine-1-sulfonyl)morpholine<sup>27</sup> (**4c**) in 90%, 88%, and 80% yields, respectively

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**TABLE 2.** Reaction of **3c** with Secondary Amines

entry	amines	Product <b>4a–b</b>	Yield (%) <sup>a</sup>
1			90
2			88
3			80

<sup>a</sup> Isolated yields of pure products.

(Table 2). Products **4a–c** were purified by flash column chromatography, using silica gel and a mixture of hexanes and ethyl acetate as the eluent, and characterized by their spectral properties.

In summary, the reaction of  $\text{Bt}_2\text{SO}_2$  (**1**) with secondary amines at room temperature provides the first entry to novel *o*-sulfamidotriazobenzenes **2** in good yields by a convenient straightforward one-step method. Byproduct *N*-sulfonylbenzotriazoles **3** enable the preparation of unsymmetrical sulfamides **4** in high yields.

## Experimental Section

1,1'-Sulfonylbis(benzotriazole) (**1**) was prepared by a slight modification of a previously published procedure.<sup>16</sup>

**General Procedure for the Preparation of 2a–d and 3b,c,e,f.** To 1,1'-sulfonylbenzotriazole (1 g, 3.3 mmol) in anhydrous acetonitrile (15 mL) was added dropwise amine (9.9 mmol, 3 equiv) with stirring at rt for 5 h. The mixture after removal of the solvent was subjected to column chromatography (5–20% ethyl acetate in hexanes) to give pure products **2a–d** and **3b,c,e,f**.

**(E)-N-(2-(Pyrrolidin-1-yl)phenyl)pyrrolidine-1-sulfonamide (2a):** white crystals (55%); mp 109–111 °C (hexanes/dichloromethane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.81 (s, 1H), 7.57 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.43 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.08 (td,  $J$  = 7.4, 1.5 Hz, 1H), 7.01 (td,  $J$  = 7.8, 1.5 Hz, 1H), 3.95 (br s, 2H), 3.63 (br s, 2H), 3.29 (t,  $J$  = 6.9 Hz, 4H), 2.06 (br s, 4H), 1.75–1.69 (m, 4H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  139.1, 131.8, 125.6, 123.8, 119.1, 115.8, 48.3, 25.6. Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ : C, 51.99; H, 6.54; N, 21.65. Found: C, 52.16; H, 6.58; N, 21.44.

**Crystal data for 2a:**  $\text{C}_{14}\text{H}_{21}\text{N}_5\text{O}_2\text{S}$ , MW 323.42, monoclinic, space group  $P2_1/c$ ,  $a$  = 10.1479(3) Å,  $b$  = 10.2295(3) Å,  $c$  = 14.7132(4) Å,  $\beta$  = 99.468(1)°,  $V$  = 1506.54(7) Å<sup>3</sup>,  $F(000)$  = 688,

$Z$  = 4,  $T$  = –180 °C,  $\mu(\text{Mo K}\alpha)$  = 0.231 mm<sup>–1</sup>,  $D_{\text{calcd}}$  = 1.426 g·cm<sup>–3</sup>,  $\theta_{\text{max}}$  55° (CCD area detector, Mo K $\alpha$  radiation), GOF = 0.96,  $wR(F^2)$  = 0.087 (all 1044 data),  $R$  = 0.030 (936 data with  $I > 2\sigma I$ ).

**(E)-N-(2-(Piperidin-1-yl)phenyl)piperidine-1-sulfonamide (2b):** white crystal (53%); mp 74–76 °C (hexanes/dichloromethane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.73 (br s, 1H), 7.54 (d,  $J$  = 8.0 Hz, 1H), 7.46 (d,  $J$  = 7.8 Hz, 1H), 7.10 (t,  $J$  = 7.3 Hz, 1H), 7.02 (t,  $J$  = 7.4 Hz, 1H), 3.80 (br s, 4H), 3.26–3.10 (m, 4H), 1.73 (br s, 6H), 1.58–1.34 (m, 6H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  138.4, 132.1, 126.1, 123.7, 119.1, 116.2, 47.0, 25.2, 24.1, 23.5. Anal. Calcd for  $\text{C}_{16}\text{H}_{25}\text{N}_5\text{O}_2\text{S}$ : C, 54.68; H, 7.17; N, 19.93. Found: C, 54.64; H, 7.26; N, 19.75.

**(E)-N-(2-(Morpholinodiazaryl)phenyl)morpholine-4-sulfonamide (2c):** white crystal (63%); mp 123–125 °C (hexanes/dichloromethane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.70 (br s, 1H), 7.57 (d,  $J$  = 8.2 Hz, 1H), 7.49 (d,  $J$  = 8.1 Hz, 1H), 7.17 (t,  $J$  = 7.4 Hz, 1H), 7.07 (t,  $J$  = 7.7 Hz, 1H), 3.88 (d,  $J$  = 4.8 Hz, 4H), 3.82 (d,  $J$  = 4.7 Hz, 4H), 3.62 (t,  $J$  = 4.0 Hz, 4H), 3.21 (t,  $J$  = 4.3 Hz, 4H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  137.9, 132.0, 127.1, 124.2, 119.4, 116.9, 66.1, 46.3. Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{N}_5\text{O}_4\text{S}$ : C, 47.31; H, 5.96; N, 19.70. Found: C, 47.57; H, 5.99; N, 19.67.

**(E)-N-(2-(Diethylamino-1-yl)phenyl)diethylamine-1-sulfonamide (2d):** white crystal (75%); mp 54–56 °C (hexanes/dichloromethane); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.82 (br s, 1H), 7.46 (t,  $J$  = 8.0 Hz, 2H), 7.08 (t,  $J$  = 7.2 Hz, 1H), 7.00 (t,  $J$  = 7.2 Hz, 1H), 3.78 (q,  $J$  = 6.3 Hz, 4H), 3.26 (q,  $J$  = 7.0 Hz, 4H), 1.28 (br s, 6H), 1.05 (t,  $J$  = 7.0 Hz, 6H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  138.8, 131.8, 125.6, 123.5, 118.6, 116.2, 42.0, 13.5. Anal. Calcd for  $\text{C}_{14}\text{H}_{25}\text{N}_5\text{O}_2\text{S}$ : C, 51.35; H, 7.70; N, 21.39. Found: C, 51.51; H, 7.78; N, 21.30.

**1-(Piperidine-1-sulfonyl)-1*H*-benzotriazole (3b):** white crystal (10%); mp 50–52 °C (hexanes); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J$  = 8.3 Hz, 1H), 8.79 (d,  $J$  = 8.3 Hz, 1H), 7.63 (t,  $J$  = 8.1 Hz, 1H), 7.48 (t,  $J$  = 8.1 Hz, 1H), 3.43 (t,  $J$  = 5.4 Hz, 4H), 1.55 (m, 6H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  144.8, 132.5, 129.7, 125.4, 120.2, 112.2, 48.1, 24.8, 23.0. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$ : C, 49.61; H, 5.30; N, 21.04. Found: C, 49.66; H, 5.27; N, 21.02.

**1-(Morpholine-4-sulfonyl)-1*H*-benzotriazole (3c):** white crystal (14%); mp 135–137 °C (hexanes); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J$  = 8.4 Hz, 1H), 7.97 (d,  $J$  = 8.4 Hz, 1H), 7.65 (t,  $J$  = 8.1 Hz, 1H), 7.51 (t,  $J$  = 8.1 Hz, 1H), 3.77 (t,  $J$  = 4.8 Hz, 4H), 3.44 (t,  $J$  = 4.8 Hz, 4H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  144.7, 132.5, 130.1, 125.6, 120.4, 111.9, 65.7, 46.9. Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$ : C, 44.77; H, 4.51; N, 20.88. Found: C, 45.14; H, 4.44; N, 20.81.

**Benzotriazole-1-sulfonic acid *N*-methyl *N*-phenylamide (3e):** pink crystal (70%); mp 74–76 °C (hexanes); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J$  = 8.3 Hz, 1H), 7.53 (d,  $J$  = 8.3 Hz, 1H), 7.41–7.44 (m, 2H), 7.25–7.28 (m, 3H), 7.11–7.08 (m, 2H), 3.59 (s, 3H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  144.6, 139.3, 132.8, 129.7, 129.5, 128.9, 127.0, 125.4, 120.1, 112.1, 40.8. Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$ : C, 54.15; H, 4.19; N, 19.43. Found: C, 54.07; H, 4.06; N, 19.81.

**Benzotriazole-1-sulfonic acid *N,N*-di-*p*-tolylamide (3f):** white needles (73%); mp 125–127 °C (hexanes); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.02 (dd,  $J$  = 7.4, 1.6 Hz, 1H), 7.53 (dd,  $J$  = 7.4, 1.5 Hz, 1H), 7.39 (td,  $J$  = 7.0, 1.2 Hz, 2H), 7.34 (td,  $J$  = 7.0, 1.2 Hz, 2H), 7.22 (d,  $J$  = 8.4 Hz, 4H), 7.02 (d,  $J$  = 8.4 Hz, 4H), 2.20 (s, 6H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  144.7, 138.8, 137.4, 132.7, 130.2, 129.6, 127.9, 125.3, 120.0, 112.4, 21.0; HRMS-FAB  $m/z$  [M + Na]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2\text{SNa}$  401.1043, found 401.1053.

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**Supporting Information Available:** Characterization data and details for the crystal structure of **1** and **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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