# *N*-SULFONYLBENZOTRIAZOLES. PART 2. REACTIONS OF 1,1′-SULFONYLDIBENZOTRIAZOLE AND 1-BENZENESULFONYL-1,2,4-TRIAZOLE WITH ALCOHOLS; A NEW APPROACH TO *N*-ALKYLBENZOTRIAZOLES AND *N*-ALKYL-1,2,4-TRIAZOLES[1]

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**Abstract** - 1,1′ Sulfonyldibenzotriazole (**3**) reacts with sodium alkoxides to give *N*-alkylbenzotriazoles. With alkanols, benzotriazolium alkyl sulfates are produced. 1-Benzenesulfonyl-1,2,4-triazole with the sodium salts of alcohols gives 1-alkyl-1,2,4-triazoles. The mechanisms of these reactions are discussed.

*N,N′*-Thionyldiimidazole and *N,N′*-sulfonyldiimidazole are useful sulfinyl and sulfonyl transfer reagents. Thus, *N,N′*-thionyldiimidazole reacts exothermically with alcohols and phenols to form esters of sulfurous acid,[2] and with arylmagnesium halides to afford sulfoxides;[3] with carboxylic acids imidazolides are formed at room temperature in nearly quantitative yield evidently *via* mixed anhydrides.[4] *N,N′*-Sulfonyldiimidazole is less reactive than *N,N′*-thionyldiimidazole; it has been used to prepare the imidazolide of *p*-toluenesulfonic acid from *p*-toluenesulfonic acid.[5] Further applications of these two imidazole derivatives, and of the analogous benzimidazoles, in transfer reactions have been extensively studied.[6-8]

The corresponding chemistry of the thionylated and sulfonylated benzotriazoles is far less known, although interest in them is growing due to the recognition of their biological importance and their increasing

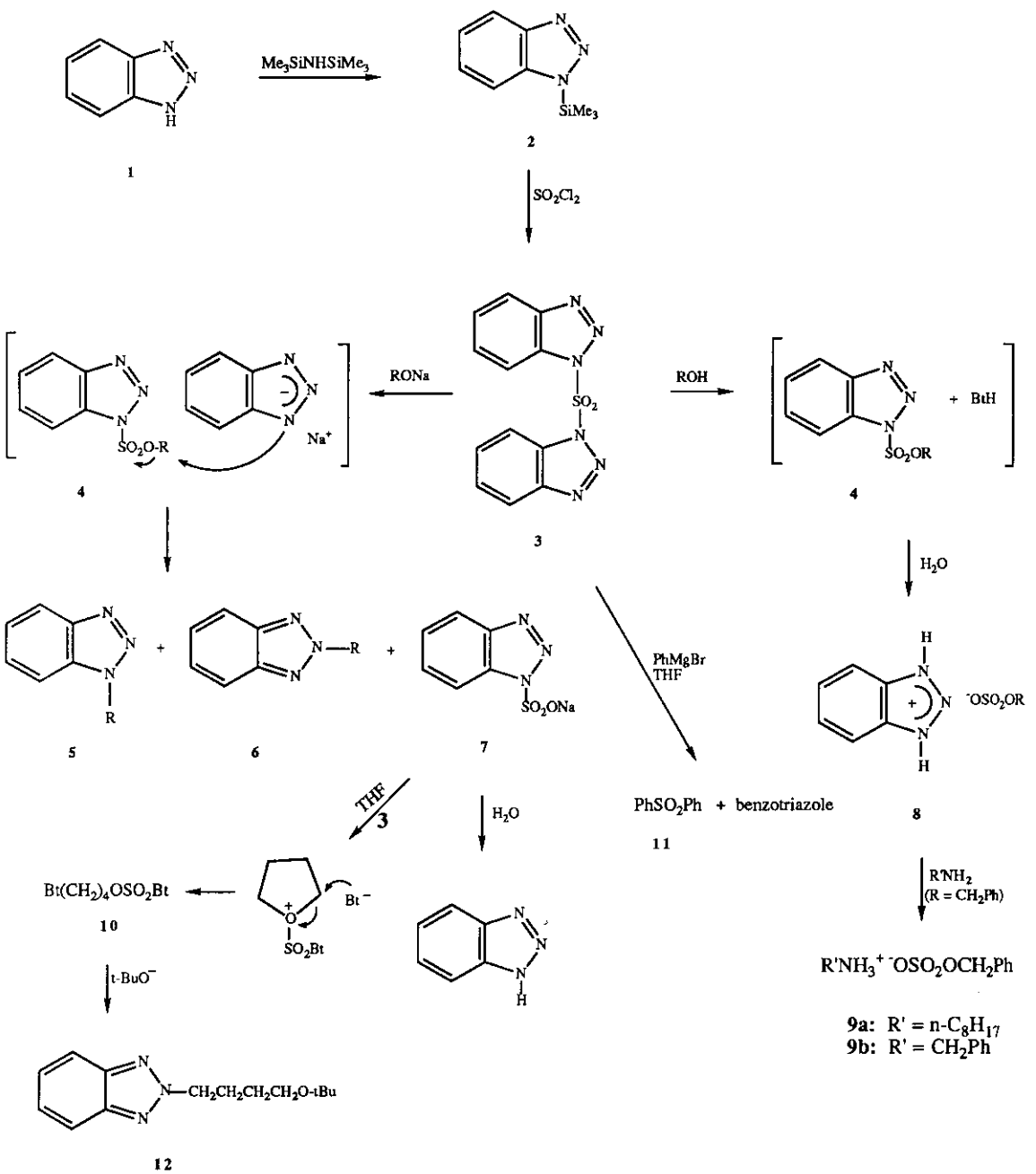
applications in industry. Sulfonyl derivatives of benzotriazole, such as 1,1′-sulfonyldibenzotriazole and *N*-alkylsulfonylbenzotriazoles, are herbicial, insecticial and mutagenic.[9,10] Some have been used as tickisides and fungicides,[10,11] and others as activators for sodium perborate bleaching.[12] So far, the only applications of *N*-sulfonylbenzotriazoles in organic synthesis are those in our preceeding paper[1] on a novel preparation of 1-acylbenzotriazoles from 1-(1-methylsulfonyl)benzotriazole and carboxylic acids. We now report preparations of *N*-alkylbenzotriazoles by the reaction of 1,1′-sulfonyldibenzotriazole (3) with sodium salts of alcohols. 1,1′-Sulfonyldibenzotriazole (3) reacts with a variety of alkanols at room temperature to produce benzotriazolium alkyl sulfates (8). Compound (3) gives diaryl sulfones when treated with arylmagnesium halides. We have also found that the reactions of 1-benzenesulfonyl-1,2,4-triazole with alcohols give the corresponding 1-alkyl-1,2,4-triazoles.

Classical preparations of 1-substituted benzotriazoles are by the reactions of an alkyl or activated aryl halide with benzotriazole under basic conditions. This route can be inconvenient when the corresponding halide is difficult to prepare or unstable. In particular, when the corresponding alcohol is more easily available and/or more stable than the halide the method now described is very convenient.

Benzotriazole (1) and hexamethyldisilazane gave 1-trimethylsilylbenzotriazole (2) which reacted with sulfuryl chloride at 0°C to give *N,N′*-sulfonyldibenzotriazole (3) in 90% yield.[10] The reactions of this derivative (3) with the sodium salts of a variety of alcohols are shown in Scheme 1. *N,N′*-Sulfonyldibenzotriazole (3) was stirred at room temperature with two equivalents of a sodium alkoxide in THF for 24 h. For methanol, *n*-butanol and *sec*-butanol, excess of the alcohol was used as solvent instead of THF. After a simple workup, a mixture of the 1-alkylbenzotriazole (5) and the 2-alkylbenzotriazole (6) was obtained in moderate to good yield except for *t*-butanol (Table 1). Presumably, *N,N′*-sulfonyldibenzotriazole (3) reacts with a sodium alkoxide to form the alkyl (benzotriazol-1-yl)sulfonate (4) and sodium benzotriazolate. Nucleophilic attack by the benzotriazole anion on the alkyl group of the unstable intermediate (4) gave the *N*-alkylbenzotriazoles (5) and (6), and benzotriazol-1-ylsulfonic acid sodium salt (7), which is desulfonylated to benzotriazole during the aqueous workup. Benzotriazole was isolated as the

byproduct from the aqueous residue. The mixtures of 1-alkyl- and 2-alkylbenzotriazoles were separated by column chromatography (Table 1). The alcohols used in this work included methanol, *n*-butanol, *sec*-butanol, 2-(*N*,*N*-dimethylamino)ethanol, 2-furfuryl alcohol, 2-(2-pyridyl)ethanol and 4-(hydroxymethyl)pyridine.

## Scheme 1



The products were readily characterized by their elemental analyses (for solid compounds) or by their high resolution mass spectra (for liquid compounds) and by their $^{1}H$ and $^{13}C$ nmr spectra. The 1- and 2-alkylbenzotriazole isomers are easily distinguished by their nmr spectra because 2-alkylbenzotriazoles have symmetrical patterns for their aromatic proton and carbon signals. The detailed structural assignments of compounds of types (**5**) and (**6**) are listed in the experimental section.

**Table 1. Preparations of *N*-Alkylbenzotriazoles (5) and (6)**

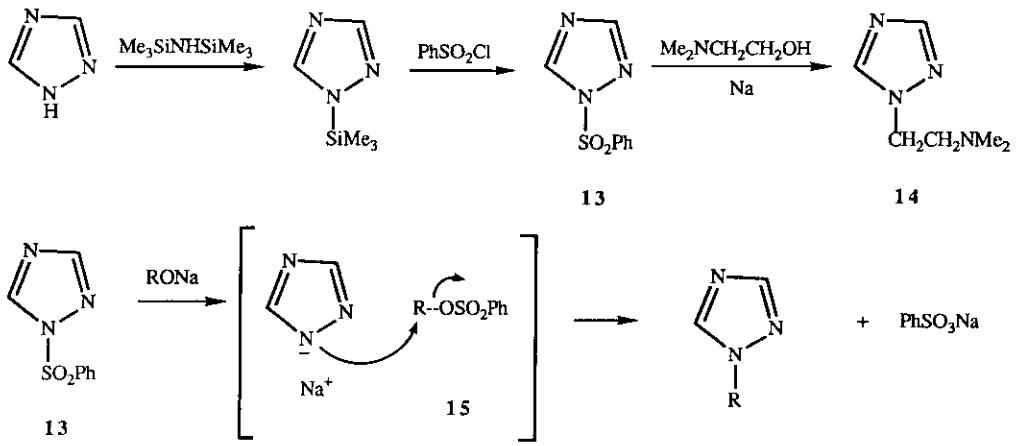
| series | R | total yield 5 + 6 | separated yield[a] 5 | 6 | molecular formula | HRms calcd | found |
|---|---|---|---|---|---|---|---|
| **a** | Me | 71 | --- | --- | $C_7H_7N_3$ | 133.1537 | 133.1541 |
| **b** | Bu | 69 | --- | --- | $C_{10}H_{13}N_3$ | 176.1188 | 176.1190 |
| **c** | $Me_2NCH_2CH_2$ | 74 | 46 | --- | $C_{10}H_{14}N_4$ | 190.1218 | 190.1219 |
| | | | --- | 23 | $C_{10}H_{14}N_4$ | 190.1218 | 190.1219 |
| **d** | 2-$PyCH_2CH_2$ | 45[b] | 26 | --- | $C_{13}H_{12}N_4$ | 224.1062 | 224.1065 |
| | | | --- | 12 | $C_{13}H_{12}N_4$ | 224.1062 | 224.1061 |
| **e** | 2-$FuCH_2$ | 73 | 42 | --- | $C_{11}H_9N_3O$ [c] | --- | --- |
| | | | --- | 21 | $C_{11}H_9N_3O$ | 199.0746 | 199.0744 |
| **f** | sec-Bu | 46 | 22 | --- | $C_{10}H_{13}N_3$ | --- | --- |
| | | | --- | 14 | $C_{10}H_{13}N_3$ | --- | --- |
| **g** | t-Bu | 45[d] | 20 | --- | $C_{10}H_{13}N_3$ | 176.1188 | 176.1195 |
| | | | --- | 15 | $C_{10}H_{13}N_3$ | 176.1188 | 176.1190 |
| **h** | 4-$PyCH_2$ | 10 | --- | 10 | $C_{12}H_{10}N_4$ | 210.0905 | 210.0945 |

a. Isolated yields of **5** and **6** by column chromatography, all compounds are oil except **5e**;
b. The yield was lower because of the simultaneous formation of 4-vinylpyridine; c. mp 76-77°C, Anal. Calcd for C, 66.33; H, 4.52; N, 21.11. Found for C, 66.37; H, 4.55; N, 20.64; d. Compound **10** was also isolated; e. mp 115-116 °C, Anal. Calcd for C, 68.56; H, 4.79; N, 26.65. Found for C, 68.45; H, 4.94; N, 27.00. f.mp 93-94 °C, Anal. Calcd for C, 68.56; H, 4.79; N, 26.65. Found for C, 68.31; H, 4.81; N, 26.88.

**Table 2. Preparations of Benzotriazolium Alkyl Sulfates**

| Compd | R | Yield (%) | mp(°C) | molecular formula | calcd C | calcd H | calcd N | found C | found H | found N |
|---|---|---|---|---|---|---|---|---|---|---|
| **8a** | Me | 98 | 95-98 | $C_7H_9N_3O_4S$ | 36.36 | 3.92 | 18.17 | 35.96 | 3.77 | 17.76 |
| **8b** | Et | 96 | 96-98 | $C_8H_{11}N_3O_4S$ | 39.18 | 4.52 | 17.13 | 39.05 | 4.73 | 16.73 |
| **8c** | n-Bu | 90 | 75-77 | $C_{10}H_{15}N_3O_4S$ | 43.95 | 5.53 | 15.37 | 43.67 | 5.28 | 15.58 |
| **8d** | i-Bu | 88 | 71-74 | $C_{10}H_{15}N_3O_4S$ | 43.95 | 5.53 | 15.37 | 43.54 | 5.30 | 15.76 |
| **8e** | i-Pr | 96 | 86-89 | $C_9H_{13}N_3O_4S$ | 41.69 | 5.05 | 16.21 | 41.83 | 5.27 | 16.02 |
| **8f** | $PhCH_2$ | 98 | 108-110 | $C_{13}H_{13}N_3O_4S$ | 50.81 | 4.26 | 13.67 | 50.39 | 4.14 | 13.55 |

**Scheme 2**




When sodium *t*-butoxide in THF was used it gave the expected *N*-*t*-butylbenzotriazole (**5g**) which was isolated in low yield, but 1-(2-benzotriazolyl)-4-t-butoxybutane (**10**) was also isolated. It appeared that the ring of the THF solvent was opened by the attack of the benzotriazole anion on the oxonium ion under the reaction conditions to give the intermediate (**10**) as shown in Scheme 1. 1-(2-Benzotriazolyl)-4-*t*-butoxybutane (**12**) was then formed by the replacement of $BtOSO_2$ group by *t*-butoxide. The structure of compound (**12**) was deduced from its high resolution mass spectrum and $^1H$ and $^{13}C$ nmr, especially by the typical X-$CH_2CH_2CH_2CH_2$-Y pattern.

The reaction of benzenesulfonyl-1,2,4-triazole (**13**) with 2-(*N*,*N*-dimethylamino)ethanol in THF under reflux afforded the alkylated triazole (**14**) in 61% yield. The byproduct benzenesulfonic acid was easily removed during the aqueous workup. The two singlets for the triazole protons appeared at 8.11 and 7.84 ppm, and the two triazole carbons were seen at 151.2 and 143.1 ppm. The mechanism of the formation of the *N*-alkyl-1,2,4-triazoles (**14**) is shown in Scheme 2. The nucleophilic attack of an alkoxide on the sulfur atom of **13** led the alkyl benzenesulfonate (**15**), then the nucleophilic substitution of benzenesulfonate by the sodium triazolate gave the final product (**14**).

In conclusion, *N*,*N'* -sulfonyldibenzotriazole (**3**) reacted with a variety of sodium alkoxides to give *N*-alkylbenzotriazoles. The mixture of 1- and 2-alkylbenzotriazoles was readily separated by column chromatography. Similarly, *N*-alkyl-1,2,4-triazoles were prepared from 1-benzenesulfonyl-1,2,4-triazole and sodium alkoxides. Our method is particularly useful for the preparation of *N*-alkylbenzotriazoles and 1-alkyl-1,2,4-triazoles which can not conveniently be synthesized from the corresponding alkyl halides because these halides are not readily available or are unstable.

## EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The $^{1}H$- and $^{13}C$ nmr spectra were recorded with a Varian VXR-300 (FT-mode) spectrometer at 300 MHz and 75 MHz, respectively with tetramethylsilane as an internal standard. Mass spectra were obtained on a AEI mass spectrometer. Elemental analyses were performed at the University of Florida under the supervision of Dr. Powell. Preparation of 1-trimethylsilylbenzotriazole (**2**) has been reported previously.[1]

N-Alkylbenzotriazoles, General Procedure. - *N*,*N'* -Sulfonyldibenzotriazole (3.0 g, 10 mmol) was added to the appropriate sodium alkoxide [from sodium metal (0.46 g, 20 mmol) and the appropriate alcohol (20 mmol)] and dry THF (20 ml) [For methanol, isopropanol and butanol, excess alcohol (20 ml) was used instead of THF]. The mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue dissolved in methylene chloride. The organic layer was washed with NaOH (2M, 20 ml) and water (30 ml), and dried over $MgSO_4$. The solvent was removed under reduced pressure. The mixture of 1- and 2-alkylbenzotriazoles was separated by column chromatoraphy (silica gel, ethyl acetate).

N-Methylbenzotriazoles (**5a** + **6a**). - Isolated as the mixture of 1-methyl- and 2-methylbenzotriazoles (2:1), $^{1}H$ nmr ($CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1-isomer), 7.85 (m, 2-isomer), 7.53 (m) 7.38 (m), 4.52 (s, $CH_3$ of 2-isomer), 4.30 (s, $CH_3$ of 1-isomer); $^{13}C$ nmr: 144.2, 133.1, 127.2, 126.2, 123.8, 119.8, 117.7, 109.6, 42.3, 34.1.

*N*-Butylbenzotriazoles (**5b + 6b**). - Isolated as the mixture of 1-butyl- and 2-butylbenzotriazoles (5:4), $^1$H nmr ($CDCl_3$): δ 8.06 (d, J = 8.3 Hz, 1-isomer), 7.86 (m, 2-isomer), 7.50 (m), 7.38 (m), 4.73 (t, J = 7.1 Hz, $CH_2$ of 2-isomer), 4.64 (t, J = 7.0 Hz, $CH_2$ of 1-isomer), 2.10 (m, $CH_2$ of 2-isomer), 1.99 (m, $CH_2$ of 1-isomer), 1.41 (m, 2H), 0.96 (m, $CH_3$); $^{13}$C nmr: 144.2, 133.0, 127.0, 126.0, 123.6, 119.9, 117.8, 109.2, 56.2, 47.8, 31.9, 31.6, 19.9, 19.7, 13.4.

1-[2-(*N*,*N*-Dimethylamino)ethyl]benzotriazole **5c**. - $^1$H Nmr ($CDCl_3$): δ 8.05 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 8.2 Hz, 1H), 7.36 (t, J = 8.1 Hz, 1H), 4.73 (t, J = 7.0 Hz, 2H), 2.90 (t, J = 7.0 Hz, 2H, $CH_2$), 2.31 (s, 6H, 2 x $CH_3$); $^{13}$C nmr: δ 145.9, 133.1, 127.2, 123.7, 119.9, 109.4, 58.3, 46.4, 45.5, 29.6.

2-[2-(*N*,*N*-Dimethylamino)ethyl]benzotriazole **6c**. - $^1$H Nmr ($CDCl_3$): 7.85 (dd, J = 6.5 and 3.1 Hz, 2H), 7.37 (dd, J = 6.6 and 3.1 Hz, 2H), 4.85 (t, J = 6.8 Hz, 2H, $CH_2$), 3.06 (t, J = 6.8 Hz, 2H, $CH_2$), 2.33 (s, 6H, 2 x $CH_3$); $^{13}$C nmr: 144.3, 126.2, 117.9, 58.6, 54.4, 45.4.

1-[2-(2-Pyridyl)ethyl]benzotriazole **5d**. - $^1$H Nmr ($CDCl_3$): δ 8.55 (d, J = 4.8 Hz, 1H, PyH), 7.98 (d, J = 8.3 Hz, 1H, BtH), 7.43 - 7.30 (m, 4H), 7.09 (dd, J = 7.5 and 4.9 Hz, 1H, PyH), 6.91 (d, J = 7.6 Hz, 1H, PyH), 5.07 (t, J = 6.9 Hz, 2H, $CH_2$), 3.47 (t, J = 7.0 Hz, 2H, $CH_2$); $^{13}$C nmr: 157.0, 149.3, 145.4, 136.3, 132.9, 126.8, 123.5, 123.4, 121.7, 119.4, 109.2, 47.2, 37.9.

2-[2-(2-Pyridyl)ethyl]benzotriazole **6d**. - $^1$H Nmr ($CDCl_3$): δ 8.57 (d, J = 4.4 Hz, 1H, PyH), 7.83 (m, 2H, BtH), 7.53 - 7.04 (m, 5H), 5.19 (t, J = 7.3 Hz, 2H, $CH_2$), 3.36 (t, J = 7.4 Hz, 2H, $CH_2$); $^{13}$C nmr: 158.7, 149.5, 144.2, 136.7, 126.2, 123.3, 121.9, 117.9, 55.7, 38.0.

1-[(2-Furyl)methyl]benzotriazole **5e**. - $^1$H Nmr ($CDCl_3$): δ 8.05 (d, J = 8.2 Hz, 1H, BtH), 7.56 (d, J = 8.3 Hz, 1H), 7.48 (t, J = 8.2 Hz, 1H), 7.38 (m, 2H), 6.44 (d, J = 3.3 Hz, 1H), 6.35 (d, J = 5.1 Hz, 1H), 5.83 (s, 2H, $CH_2$); $^{13}$C nmr: 147.7, 143.2, 127.5, 123.9, 119.9, 110.7, 109.9, 109.7, 109.6, 107.6, 45.0 ($CH_2$).

2-[(2-Furyl)methylbenzotriazole **6e**. - $^1$H Nmr ($CDCl_3$): δ 7.86 (dd, J = 6.7, 3.4 Hz, 2H), 7.42 (d, J = 2.7 Hz, 1H), 7.36 (dd, J = 6.8, 3.1 Hz, 2H), 6.54 (d, J = 3.3 Hz, 1H), 6.36 (d, J = 3.2 Hz, 1H); $^{13}$C nmr: 143.4, 126.4, 118.1, 110.5, 110.4, 107.5, 102.1, 52.7.

1-sec-Butylbenzotriazole **5f**. - $^1$H Nmr ($CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.37 (t, J=6.8Hz, 1H), 7.27 (t, J=7.7Hz, 1H), 4.76 (m, 1H, CH), 2.20-1.96 (m, 2H), 1.83 (d, J = 6.9 Hz, 3H), 0.75 (t, J=7.3Hz, 3H, $CH_3$); $^{13}$C nmr: 146.0, 132.4, 126.8, 123.6, 119.9, 109.6, 57.5 (CH), 29.3 20.3, 10.7.

2-sec-Butylbenzotriazole **6f**. - $^1$H Nmr ($CDCl_3$): δ 7.88 (dd, J = 6.8, 3.2 Hz, 2H), 7.36 (dd, J = 6.4, 3.2 Hz, 2H), 4.91 (m, 1H, CH), 2.22 (m, 1H), 2.00 (m, 1H), 1.70 (d, J = 6.8 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H); $^{13}$C nmr: 143.9, 125.9, 118.0, 64.9 (CH), 30.2 ($CH_2$), 20.8, 10.5 ($CH_3$).

1-tert-Butylbenzotriazole **5g**. - $^1$H Nmr ($CDCl_3$): δ 8.09 (d, J=8.3 Hz, 1H), 7.40 (d, J=7.4 Hz, 1H), 7.44 (t, J=7.1 Hz, 1H), 7.36 (t, J=8.2 Hz, 1H), 1.88 (s, 9H, 3 x $CH_3$); $^{13}$C nmr: δ 146.5, 131.8, 126.4, 123.3, 120.2, 111.9, 60.3, 29.4.

2-tert-Butylbenzotriazole **6g**. - $^1$H Nmr ($CDCl_3$): δ 7.88 (dd, J = 6.2, 3.1 Hz, 2H), 7.36 (dd, J = 6.2, 3.1 Hz, 2H), 1.83 (s, 9H, 3 x $CH_3$), $^{13}$C nmr: 143.8, 125.8, 118.0, 64.2, 29.9.

1-[(4-Pyridyl)methyl]benzotriazole **5h**. - $^1$H Nmr ($CDCl_3$): δ 8.55 (d, J = 5.9 Hz, 2H, PyH), 8.10 (d, J = 8.3 Hz, 1H, BtH), 7.85 (d, J = 8.3 Hz, 1H, BtH), 7.57 (t, J = 8.1 Hz, 1H, BtH), 7.46 (t, J = 8.1 Hz, 1H, BtH), 7.21 (d, J = 5.9 Hz, 2H, PyH), 6.09 (s, 2H, $CH_2$); $^{13}$C nmr: 150.1, 145.3, 144.7, 132.9, 127.7, 124.2, 122.2, 119.3, 110.5, 49.6.

1-[(3-Pyridyl)methyl]benzotriazole **5i**. - $^1$H Nmr ($CDCl_3$): δ 8.68 (s, 1H), 8.56 (dd, J = 4.8, 1.5 Hz, 1H), 8.06 (d, J = 7.3 Hz, 1H), 7.56 (m, 1H), 7.33 (m, 4H), 5.87 (s, 2H); $^{13}$C nmr: 149.7, 148.6, 145.9, 135.1, 132.4, 130.4, 127.5, 123.9, 123.6, 119.9, 109.1, 49.2.

2-[(4-Butoxy)butyl]benzotriazole **12**. - Oil, $^1$H nmr ($CDCl_3$): δ 7.85 (dd, J=4.5 and 1.6 Hz, 2H, BtH), 7.37 (dd, J=4.6 and 1.6Hz, 2H, BtH), 4.76 (t, J=7.3Hz, 2H, $OCH_2$), 3.38 (t, J=6.3 Hz, 2H, $NCH_2$), 2.21 (m, 2H), 1.60 (m, 2H), 1.47 (s, 9H, 3 x $CH_3$); $^{13}$C nmr: 144.1, 126.1, 117.9, 72.2 (C), 60.6 ($OCH_2$), 56.2 ($NCH_2$), 27.5, 27.2. Hrms Calcd for $C_{14}H_{21}N_3O$: 248.1750; Found: 248.1752.

Benzotriazolium Alkyl Sulfate, General Procedure. - A mixture of *N,N'*-sulfonyldibenzotriazole (3.0 g, 10 mmol) and the appropriate alcohol (15 ml) was stirred at room temperature until all the solid dissolved. The excess alcohol was evaporated under reduced pressure and the residue washed with ether to give the benzotriazolium alkyl sulfate as a colorless solid.

Benzotriazolium Methyl Sulfate **8a**. - $^1$H Nmr (DMSO-$d_6$): δ 7.96 (m, 2H), 7.49 (m, 2H), 3.49 (s, 3H, $CH_3$); $^{13}$C nmr: 138.2, 125.7, 115.1, 53.2.

Benzotriazolium Ethyl Sulfate **8b**. - $^1$H Nmr (DMSO-$d_6$): δ 7.94 (m, 2H), 7.46 (m, 2H), 3.81 (q, J = 7.1 Hz, 2H, $CH_2$), 1.15 (t, J = 7.1 Hz, 3H, $CH_3$); $^{13}$C nmr: 138.7, 125.5, 115.0, 51.5, 15.2.

Benzotriazolium n-Butyl Sulfate **8c**. - $^1$H Nmr (DMSO-$d_6$): δ 8.18 (m, 2H), 7.68 (m, 2H), 4.28 (t, J = 5.9 Hz, 2H, $CH_2$), 1.72 (m, 2H), 1.42 (m, 2H), 0.90 (t, J = 6.8 Hz, 3H); $^{13}$C nmr: 135.1, 129.5, 114.3, 68.9, 31.1, 18.8, 13.5.

Benzotriazolium i-Butyl Sulfate **8d**. - $^1$H Nmr (DMSO-$d_6$): δ 12.61 (br, 2H), 7.94 (m, 2H), 7.47 (m, 2H), 4.14 (m, 1H, CH), 1.47 (m, 2H, $CH_2$), 1.16 (d, J = 6.3 Hz, 3H, $CH_3$), 0.84 (t, J = 7.3 Hz, 3H, $CH_3$): $^{13}$C nmr: 138.7, 125.5, 115.0, 73.9 (CH), 29.4, 20.3, 9.66.

Benzotriazolium i-Propyl Sulfate **8e**. - $^1$H Nmr (DMSO-$d_6$): δ 8.12 (m, 2H), 7.63 (m, 2H), 4.92 (m, 1H, CH), 1.41 (d, J = 6.2 Hz, 6H, 2 x $CH_3$); $^{13}$C nmr: 135.4, 129.1, 114.3, 74.3 (CH), 22.9 ($CH_3$).

Benzotriazolium Benzyl Sulfate **8f**. - $^1$H Nmr (DMSO-$d_6$): δ 7.96 (m, 2H), 7.48 (m, 2H), 7.40-7.30 (m, 5H), 4.87 (s, 2H, $CH_2$); $^{13}$C nmr: δ 138.8, 137.9, 128.3, 128.0, 127.6, 125.6, 115.1, 67.8 ($CH_2$).

n-Octylammonium Benzyl Sulfate **9a**. - Benzotriazolium benzyl sulfate (1.54 g, 5 mmol) and octylamine (0.65 g, 5 mmol) were stirred at room temperature in dry methylene chloride (30 ml) for 10 min. The solvent was evaporated and the residue was washed with ether to give compound (**9a**) in 1.58g (100% yield), mp 71-74°C. $^1$H Nmr ($CDCl_3$): δ 7.43-7.25 (m, 5H, ArH), 7.14 (br, $NH_2$), 5.05 (s, 2H, $CH_2$), 2.75 (m, 2H, $CH_2$), 1.52 (m, 2H, $CH_2$), 1.16 (m, 10H), 0.85 (t, J = 6.7 Hz, 3H, $CH_3$); $^{13}$C nmr: δ 135.7, 128.4, 128.3, 128.0, 70.2, 40.3, 31.7, 29.1, 29.0, 27.4, 26.3, 22.5, 14.0. Anal. Calcd for $C_{15}H_{27}NO_4S$: C, 56.76; H, 8.57; N, 4.41. Found: 57.03; H, 8.79; N, 4.38.

Anilinium Benzyl Sulfate **9b**. - This compound is prepared by the same procedure as **9a** in 100% yield, mp 170-172°C. $^1$H Nmr (DMSO-$d_6$): δ 7.51 (t, J = 7.0 Hz, 2H), 7.44-7.30 (m, 8H), 4.81 (s, 2H, $CH_2$); $^{13}$C nmr: δ 137.7, 131.9, 129.9, 128.2, 128.1, 127.6, 127.4, 123.0, 67.7 ($CH_2$). Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.07; H, 5.27; N, 4.53.

Diphenyl sulfone **11**. - $^1$H Nmr ($CDCl_3$): 7.25 (t, J = 7.5 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H); $^{13}$C nmr: 143.0, 129.3, 121.0, 117.8.

1-Benzenesulfonyl-1,2,4-triazole **13**. - A mixture of 1,2,4-triazole (3.45 g), freshly distilled hexamethyldisilazane (8.1 g, 0.05 mol) and a few crystals of ammonium sulfate (ca. 50 mg, 0.05 mol) was refluxed (125°C) under anhydrous conditions with stirring. The solid 1,2,4-triazole dissolved within 20 min and the heating was continued for an additional 15hr. The reaction mixture was fractionated in vacuo to obtain 1-trimethylsilyl-1,2,4-triazole as a colorless liquid, bp 36°C/1 mm Hg, 6.4 g(yield 91%); $^1$H nmr ($CDCl_3$): 7.73 (s, 1H), 7.61 (s, 1H), 0.05 (s, 9H); $^{13}$C nmr: 153.8, 147.9, 1.49 ($CH_3$). Benzenesulfonyl chloride (8.8 g, 0.05 mol) was added dropwise to 1-trimethylsilyl-1,2,4-triazole (7.05 g, 0.05 mol) at 0°C. A white precipitate formed within 20 min, methylene chloride (20 ml) was added to the mixture and stirring continued for 10 h at room temperature. The solvent was evaporated and the residue recrystallized from benzene, mp 107-108°C, 9.0g(yield 86%); $^1$H nmr ($CDCl_3$): δ 8.77 (s, 1H), 8.10 (dd, J = 6.4 and 3.4 Hz, 2H), 8.04 (s, 1H), 7. 73 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 6.6 Hz, 2H); $^{13}$C nmr: 154.3, 144.6, 144.5, 135.6, 129.7, 128.6. Anal. Calcd for $C_8H_7N_3O_2S$: C, 45.93; H, 3.37; N, 20.08. Found: C, 45.84; H, 3.30; N, 20.34.

1-[2-(*N,N*,-Dimethylamino)ethyl)-1,2,4-triazole **14**. - A mixture of 1-benzenesulfonyl-1,2,4-triazole (2.09 g, 10 mmol), sodium metal (12 mmol), and 2-(*N,N*-dimethylamino)ethanol (12 mmol) in THF (20 ml) was refluxed for 3 days with stirring. The solvent was evaporated and methylene chloride (30 ml) added to the residue. The organic layer was washed with KOH (2M, 20 ml) and water, and dried over $MgSO_4$. The solvent was removed and the crude product purified by column chromatography (silica gel, ethyl acetate/ethanol 1:1) as an oil. $^1$H Nmr ($CDCl_3$): δ 8.11 (s, 1H), 7.84 (s, 1H), 4.18 (t, J = 6.4 Hz, 2H, $CH_2$), 2.66 (t, J = 6.4 Hz, 2H, $CH_2$), 2.18 (s, 6H, 2 x $CH_3$); $^{13}$C nmr: 151.2, 143.1, 57.9, 47.4, 45.0. Hrms calcd for $C_6H_{13}N_4$: 141.1140; found: 141.1149.

## REFERENCES


1. A.R. Katritzky, N. Shobana, J. Pernak, A.S. Afridi, and W.Q. Fan, *Tetrahedron*, **1992**, 48, 7817.
2. H.A. Staab, *Angew. Chem., Int. Ed. Eng.*, **1962**, 1, 351.
3. S. Bast and K.K. Andersen, *J. Org. Chem.*, **1968**, 33, 846.
4. H.A. Staab and K. Wendel, *Angew. Chem.*, **1961**, 73, 26.
5. H.A. Staab and K. Wendel, *Liebigs Ann. Chem.*, **1966**, 694, 86.
6. M. Ogata, H. Matsumoto, and S. Shimizu, *Heterocycles*, **1980**, 14, 955.
7. M. Ogata, H. Matsumoto, S. Kida, and S. Shimizu, *Tetrahedron Lett.*, **1979**, 5011.
8. M. Ogata and H. Matsumoto, *Synthetic Commun.* , **1980**, 10, 559.
9. R. Soundararajan and T.R. Balasubramanian, *Chem. & Ind. (London)*, **1985**, 3, 92.
10. P.P. Purygin, I.P. Ivanov, Z.P. Laletiva, and E.S. Selezneva, *Khim. Farm. Zh.*, **1983**, 17, 1319 (*Chem. Abstr.*, **1984**, 100, 120976c).
11. K. Sasse, R. Wegler, and F. Grewe, *Brit. Pat.* **1961**, 885,843 (*Chem. Abstr.*,**1962**, 57, 4676).
12. J.H. Finley, G.R. Brubaker, and B.M. Baum, *Eur. Pat. Appl.* **1980** 9,998 ( *Chem. Abstr.*, **1980**, 93, 116350p).
13. R. Gassend, J.C. Maire, and J.-C. Pommier, *J. Organomet. Chem.*, **1977**, 133, 169.
14. J.P. Henichart, R. Houssin, C. Lespagnol, J.C. Cazin, and M. Cazin, *Chim. Ther.*, **1973**, 8, 358.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