Benzotriazoles, Benzotriazines and Quinoxalines with Sulfone Functional Group (I): (Benzotriazol-1-yl)alkyl Arenesulfones

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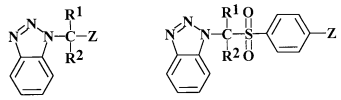
During last decade, many benzotriazol-1-yl derivatives were synthesized by A. Katritzky and others for biological activities,[1] industrial purpose[2] and simply synthetic interest.[3] They reported that benzotriazol-1-yl group (Bt-1-yl) acts as same manner of halogen atoms,[4] although Bt-1-yl group is more stable than halogen atoms. This property makes very easy to synthesize the compounds with electron-releasing groups such as amino,[5] acylamino,[6] alkoxy,[7] acetoxy,[8] alkylthio,[9] phenylthio,[10] γ-aminoalkyl[11] and γ-methoxybenzyl[12] at α-position of (benzotriazol-1-yl)alkyl derivatives.



1 R^1 and R^2 = -H, -Me, -Et; Z = -N-, -O-, -S-Aryl/Alkyl

2 R^1 and R^2 = -H, -Me, -Et; Z = -H, -Me

While many (benzotriazol-1-yl)alkyl derivatives **1** with electron releasing groups at the α-position, including the compounds mentioned above, were reported, the derivatives with arene (or alkane)sulfonyl groups were unknown. In this study, we synthesized arenesulfonyl derivatives of (benzotriazol-1-yl)alkanes **2** for synthetic interest, and we also tested pyrolytic and hydrolytic properties of C-N and C-S bonds in 3-(benzotriazol-1-yl)-3-toluenesulfonyl pentane **8b**.

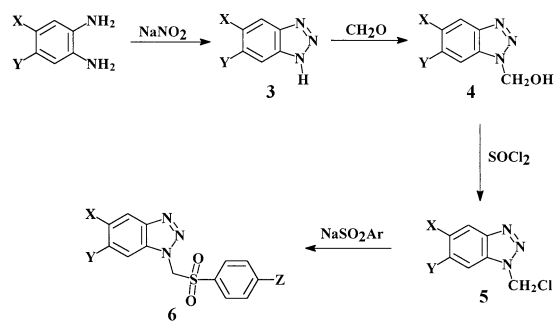
Results and Discussion

1-(Benzotriazol-1-yl)-1-benzenesulfonyl and 1-(Benzotriazol-1-yl)-1-toluenesulfonyl methanes **6a-6l** were synthesized from the substituted benzotriazoles in three steps (Scheme 1). The general information for the synthesis of benzotriazol-1-yl derivatives is shown in Table 1 and 2. The yields of the last steps were in range of 50-90% (Table 1).

Lithiation at α-position of 1-(Benzotriazol-1-yl)-1-toluenesulfonyl methane **6g**, followed by the reaction with ethyl iodide, gave a mixture of mono-ethylated compound **7b** (50% yield) and di-ethylated compound **8b** (28%), which were isolated by column chromatography. The methylation of 1-(Benzotriazol-1-yl)-1-benzenesulfonyl methane **6a** with methyl iodide and the isolation through the same procedure gave the mono-methylated compound **7a** (55%) and the dimethylated compound **8a** (30%) respectively (Scheme 2). The general information for the synthesis of the corresponding compounds is shown in Table 3.

The center carbons of the compounds **7** and **8** have two electron-releasing groups, benzotriazol-1-yl and sulfonyl. We tried qualitatively to test bond strengths of their C-N and C-S bonds by pyrolysis and hydrolysis. For examples, 3-(benzotriazol-1-yl)-3- toluenesulfonylpentane **8b** was pyrolyzed in chlorobenzene under nitrogen stream at 170 °C and hydrolyzed in a closed system at 150 °C, respectively (Scheme 3). The pyrolysis of **8b** gave two compounds, 3-toluenesulfonyl-2-pentene **9** (11.2%) by the C-N bond cleavage and *p*-toluenesulfoxy-*p*-toluenesulfonate **10a** (8.4%) by the C-S bond cleavage, respectively, and the hydrolysis of **8b** gave three compounds, diethylketone **11**, benzotriazole and *p*-toluenesulfonic acid as a result of both C-N and C-S bond cleavages concurrently. The new compound **9**, a mixture of *syn* and *anti*-form, was formed due to the breaking of the C-N bond by heat (see nmr spectrum in Figure 1 and experimental section). We now presume that the compound **10a** was formed by the breaking of the two C-S bonds, followed by the dimerization of two sulfonyl groups. Although di(*p*-toluenesulfonyl) was already reported as a structure **10b**,[13] however, the nmr spectra of the compound **10a** has two different signals of methyl protons and ten carbon-13 signals for two tolyl groups, which supports the structure **10a** instead of **10b**. The general information for synthesis of the corresponding compounds is shown in Table 3.

We now expect that C-N bond breaking of (benzotriazol-



6	X	Y	Z
a	H	H	H
b	Me	H	H
c	NO_2	H	H
d	Cl	H	H
e	Me	Me	H
f	-CH=CH-CH=CH-		H
g	H	H	Me
h	Me	H	Me
i	NO_2	H	Me
j	Cl	H	Me
k	Me	Me	Me
l	-CH=CH-CH=CH-		Me

3, 4, 5 a (X = H, Y = H); b (X = Me, Y = H); c (X = NO_2, Y = H); d (X = Cl, Y = H); e (X = Me, Y = Me); f (X/Y = -CH=CH-CH=CH-)

Scheme 1

Table 1. Yields and general informations for synthesis of benzotriazol-1-yl derivatives

Products[a]	reactants (mol)	solvents & reagents	reaction time (hr)	reaction temp. (°C)	product color	yield, % (rec.sol.)[b]
3a BtH	corresponding	-	-	-	-	-
3b 5-methylBtH	o-phenylene-					99(C_6H_6)
3c 5-nitroBtH	diamine(0.1)	AcOH(2eq.)/			reddish	97(C_6H_6)
3d 5-chloroBtH		$NaNO_2$(2eq.)	3	0/80[c]	brown	91(C_6H_6)
3e 5,6-dimethylBtH						93(C_6H_6)
3f naphth[1,2-*d*]BtH						94(C_6H_6)
4a Bt-CH_2OH	**3a**(0.04)	Ether/CH_2O(1.25eq.)	2	reflux	brown	94(EtOH)
4b 5-methylBt-CH_2OH	**3b**(0.04)					87(EtOH)
4c 5-nitroBt-CH_2OH	**3c**(0.04)					90(EtOH)
4d 5-chloroBt-CH_2OH	**3d**(0.04)					96(EtOH)
4e 5,6-dimethylBt-CH_2OH	**3e**(0.04)					70(EtOH)
4f naphth[1,2-*d*]BtCH_2OH	**3f**(0.04)					92(EtOH)
5a Bt-CH_2Cl	**4a**(0.04)	Bz/$SOCl_2$(2eq.)	2	reflux	brown	81(EtOH)
5b 5-methylBt-CH_2Cl	**4b**(0.04)					86(EtOH)
5c 5-nitroBt-CH_2Cl	**4c**(0.04)					57(EtOH)
5d 5-chloroBt-CH_2Cl	**4d**(0.04)					81(EtOH)
5e 5,6-dimethylBt-CH_2Cl	**4e**(0.04)					82(EtOH)
5f naphth[1,2-*d*]Bt-CH_2Cl	**4f**(0.04)					99(EtOH)
6a Bt-CH_2SO_2Ph	**5a**(0.05)	DMSO/$NaSO_2C_6H_5$	12	40	yellow-	92(EtOH)
6b 5-methylBt-CH_2SO_2Ph	**5b**(0.02)	or $NaSO_2C_6H_4$-CH_3			brown	85(EtOH)
6c 5-nitroBt-CH_2SO_2Ph	**5c**(0.02)	(2eq.)				93(EtOH)
6d 5-chloroBt-CH_2SO_2Ph	**5d**(0.02)					89(EtOH)
6e 5,6-dimethylBt-CH_2SO_2Ph	**5e**(0.02)					73(EtOH)
6f naphth[1,2-*d*]Bt-CH_2SO_2Ph	**5f**(0.02)					64(EtOH)
6g Bt-CH_2SO_2Tol	**5g**(0.02)					59(EtOH)
6h 5-methylBt-CH_2SO_2Tol	**5h**(0.02)					50(EtOH)
6i 5-nitroBt-CH_2SO_2Tol	**5i**(0.02)					71(EtOH)
6j 5-chloroBt-CH_2SO_2Tol	**5j**(0.02)					69(EtOH)
6k 5,6-dimethylBt-CH_2SO_2Tol	**5k**(0.02)					48(EtOH)
6l naphth[1,2-*d*]Bt-CH_2SO_2Tol	**5l**(0.02)					52(EtOH)

[a]BtH = benzotriazole, Bt- = benzotriazol-1-yl, Ph = phenyl, Tol = *p*-tolyl. [b]recrystalizing solvent, [c]0/80 = first step 0 °C & next step 80 °C.

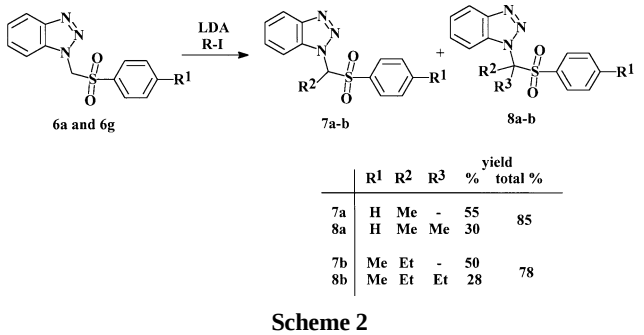
Table 2. Important spectral data of benzotriazol-1-yl derivatives prepared

Products	m/z (rel. intensity) /base peak[a]	^{1}H NMR δ ($CDCl_3$)	IR (KBr, cm^{-1})
3a	-	-	-
3b	133(69)/104	7.89(d, 1H), 7.63(s, 1H), 7.36(d, 1H), 2.47(s, 3H)	3303, 2773, 1200, 797
3c	164(76)/63	9.23(s, 1H), 8.85(d, 0.67H), 8.30(dd, 0.33H), 7.93(d, 1H)[d]	3312, 1514, 1346, 827
3d	153(100)	7.93(s, 1H), 7.84(s, 1H), 7.48(d, 1H)[d]	3323, 1480, 814
3e	147(70)/118	7.64(s, 2H), 2.41(s, 6H)[d]	3306, 2886, 1446, 1210,
3f	169(67)/141	8.44(s, 2H), 8.12-8.06(m, 2H), 7.53-7.43(m, 2H)[d]	3158, 2819, 1231, 768
4a[b]	-	8.08(d, 1H), 7.93(d, 1H), 7.59(t, 1H), 7.44(t, 1H), 7.24(br, 1H), 6.05(s, 2H)	-
4b	104(100)	7.92-7.71(m, 1H), 7.34-7.11(m, 2H), 6.11(d, 2H), 2.57(s, 3H)	3319, 2946, 1595, 1512
4c	164(100)	8.99-7.95(m, 3H), 7.16(d, 2H)	3206, 2896, 1524, 1348, 1093
4d	153(100)	8.00-7.14(m, 3H), 6.03(d, 2H)	3457, 2949, 1097, 841
4e	118(100)	7.69(s, 0.5H), 7.54(s, 1H), 7.41(s, 0.5H), 6.01(s, 2H), 2.33(s, 3H), 2.10(s, 3H)	3193, 2953, 1074, 842
4f	141(100)	8.53-7.38(m, 6H), 7.04(br, 1H), 6.10(s, 2H)	3211, 2953, 1069, 847
5a[b]	-	8.06(d, 1H), 7.89(d, 1H), 7.62(t, 1H), 7.46(t, 1H), 6.68(s, 2H)	-
5b	181(30)/91	7.90-7.19(m, 3H), 6.30(s, 2H), 2.50(d, 3H)	3035, 1221, 807
5c	212(10)/177	9.06-7.82(m, 3H), 6.47(d, 2H)	2949, 1543, 1390, 1097
5d	201(31)/138	7.99-7.30(m, 3H), 6.26(dd, 2H)	2949, 1097, 841
5e	195(41)/132	7.76(s, 1H), 7.35(s, 1H), 6.28(s, 2H), 2.37(d, 3H), 2.10(s, 3H)	2976, 1085, 852
5f	217(28)/140	8.61-7.40(m, 6H), 6.09(s, 2H)	3039, 1399, 1066, 855
6a	-	8.04(d, 1H), 7.73-7.28(m, 8H), 5.98(d, 1H)	-
6b	287(tr[c])/91	7.85-7.19(m, 8H), 5.80(d, 2H), 2.47(d, 3H)	3001, 1152, 807
6c	132(100)	8.95-7.52(m, 8H), 6.54(s, 2H)	2949, 1565, 1390, 1183

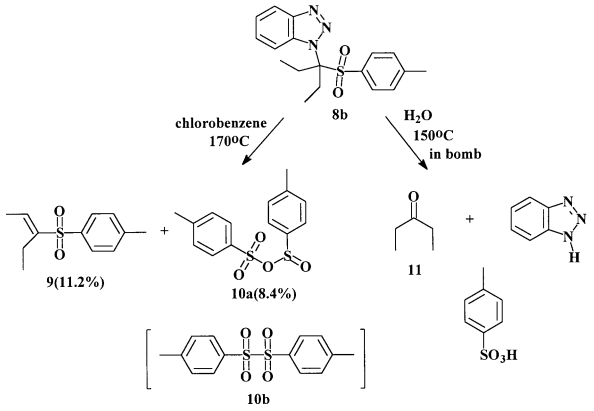
Table 2. Continued

Products	m/z (rel. intensity) /base peak[a]	^{1}H NMR δ ($CDCl_3$)	IR (KBr, cm^{-1})
6d	-	7.97-7.28(m, 8H), 6.29(dd, 2H)	2943, 1387
6e	301(tr[c])/91	7.92-7.31(m, 7H), 6.28(s, 2H), 2.39(s, 3H)	2949, 1183, 841
6f	-	8.60(s, 1H), 8.09-7.47(m, 10H), 6.40(s, 2H)	2999, 2933, 1305, 1150
6g[b]	-	8.03(d, 1H), 7.75(d, 1H), 7.60(t, 1H), 7.46(t, 1H), 7.40(d, 2H), 7.24(d, 2H), 5.59(s, 2H), 2.42(s, 3H)	-
6h	-	7.86-7.15(m, 7H), 5.77(d, 2H), 2.48(d, 3H), 2.34(s, 3H)	3004, 2907, 1322, 1152
6i	-	8.95(s, 1H), 8.41-7.30(m, 6H), 6.43(s, 2H), 2.45(s, 3H)	2949, 1565, 1183
6j	-	7.84-7.16(m, 7H), 5.80(d, 2H), 2.46(s, 3H)	3080, 2978, 1451, 1152
6k	118(100)	7.69(s, 1H), 7.37-7.16(m, 5H), 5.75(s, 2H), 2.37(s, 3H), 2.35(s, 3H), 2.34(s, 3H)	2950, 1188, 848
6l	-	8.09-7.23(m, 10H), 6.21(s, 2H), 2.38(s,3 H)	2996, 2899, 1320, 1152

[a]GC/mass spectra (70 eV), [b] ^{13}C NMR data; **4a**: 145.53, 132.30, 127.38, 124.12, 119.08, 110.96, 70.24, **5a**: 145.52, 131.64, 128.03, 124.39, 119,37, 109.87, 53.35, **6g**: 130.18, 128.76, 128.71, 124.75, 120.16, 110.34, 77.40, 76.98, 76.56, 67.42. [c]tr = trace. [d]solv. = acetone-d_6.



Scheme 2



Scheme 3

1-yl)alkyl arylsulfones **12** by the attacking of nucleophiles may occure easily to give many corresponding alkyl arylsulfones, because benzotriazol-1-yl group has very similar property to halogen atoms as mentioned in the introduction above, and may be substituted by versatile nucleophiles. Scheme 4 shows several expected reactions of (benzotriazol-1-yl)arenesulfonyl alkanes **12**: Grignard reaction (**13**),[14] the reactions with alkoxide and thioalkoxide (**14** and **17**),[15] the reduction (**15**)[16] by $NaBH_4$, the reaction with amines (**16**),[16] and the Friedel-Craft reaction (**18**),[17] etc. (Scheme 4). We are going to deal with them in the next studies.

Table 3. Analytical and spectral data of compound **7-10** (see Scheme 2 and 3 for their structures)

product	Found (%)	Calcd (%)	^{1}H NMR δ ($CDCl_3$)	^{13}C NMR δ ($CDCl_3$)
7a	C, 58.72 H, 4.53 N, 14.70	C, 58.52 H, 4.56 N, 14.63	8.03(d, 2H), 7.76(d, 1H), 7.58(m, 2H), 7.38(m, 5H), 6.03(q, 1H), 2.25(d, 3H)	146.13, 134.81, 132.56, 129.24, 129.15, 128.76, 128.36, 124.64, 120.17, 111.07, 74.51, 12.99
7b	C, 60.58 H, 5.33 N, 13.24	C, 60.93 H, 5.44 N, 13.33	8.05(d, 1H), 7.56(t, 1H), 7.42(t, 1H), 7.29(d, 2H), 7.15(d, 2H), 5.80(t, 1H), 2.78(qi, 2H)[a], 2.37(s, 3H), 0.93(t, 3H)	146.18, 132.67, 131.61, 129.86, 128.99, 128.35, 124.61, 120.16, 111.14, 80.35, 71.69, 21.64, 19.81
8a	C, 59.69 H, 5.00 N, 14.00	C, 59.78 H, 5.02 N, 13.95	8.06(d, 2H), 7.56(m, 2H), 7.44(t, 1H), 7.31(t, 1H), 7.15(d, 2H), 2.35(s, 6H)	134.61, 132.86, 129.57, 129.24, 128.93, 128.33, 128.08, 124.37, 120.14, 113.90, 81.73, 22.24
8b	C, 62.18 H, 6.17 N, 12.20	C, 62.95 H, 6.17 N, 12.24	8.06(d, 1H), 8.01(d, 1H), 7.56(t, 1H), 7.41(t, 1H), 7.07(d, 2H), 6.82(d, 2H), 2.98(si, 2H)[b], 2.83(si, 2H), 2.33(s, 3H), 1.19(t, 6H)	146.52, 145.60, 133.26, 130.42, 129.50, 129.32, 128.05, 124.23, 120.05, 114.14, 87.64, 23.30, 21.61, 8.08
9	C, 56.75 H, 6.34	C, 56.23 H, 6.29	7.67(d, 2H), 7.36(d, 2H), 4.17(q, 1H), 3.01(q, 0.4H), 2.94(q, 0.6H), 2.67(q, 0.6H), 2.60(q, 0.4H), 2.47(s, 3H), 1.40(d, 3H), 1.08(t, 3H)	203.02, 180.11, 145.37, 129.70, 129.33, 69.88, 37.16, 21.67, 11.99, 7.48
10	C, 60.66 H, 5.10	C, 60.42 H, 5.07	7.47(d, 2H), 7.25(d, 2H), 7.21(d, 2H), 7.13(d, 2H), 2.42(s, 3H), 2.38(s, 3H)	144.04, 142.02, 140.46, 140.44, 136.47, 130.18, 129.34, 127.59, 21.64, 21.46

[a]qi = quintet. [b]si = sixtet.

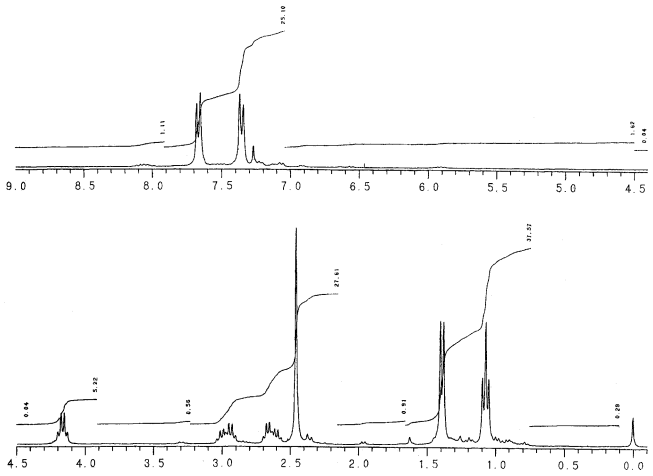
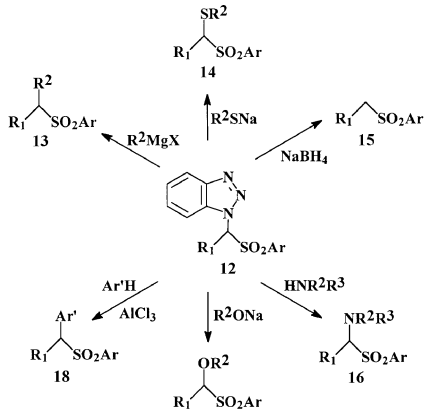


Figure 1. ^{1}H NMR spectrum of 3-toluensulfonyl-2-pentene (**9**) (solv. $CDCl_3$)



Scheme 4

Experimental Section

Apparatus for identification of compounds. ^{1}H and ^{13}C nmr spectra were taken on the Varian XR 300 (Bruker AVANCE 400), and chemical shifts given in ppm downfield from TMS as the internal standard. IR specta were taken on the Mattson Research II Model. And we also used GC/mass spectrometer (Hewlett Packard 5971A), Elementary Analyzer (Carbo Erbo EA 1108) and Melting Point Apparatus (Jencons 9200).

Synthesis of 1-(benzotriazol-1-yl)-1-arenesulfonyl methanes 6.

5-Methylbenzotriazole 3b (5-methylBtH): To a cold solution of 3,4-diaminotoluene (0.1 mol) dissolved in 2 eq. of glacial acetic acid and 30 mL of water, $NaNO_2$ solution (2 eq.) in 25 mL of water was once poured, and followed by temperature rising at 75-80 °C for one hour. Oily substance was formed when stirred for 3 hours in an ice bath. The reaction mixture was extracted with 100 mL of chloroform and washed with distilled water twice. After dried on $MgSO_4$, the solvent was removed, the crystal was washed with *n*-hexane and was recrystallized in benzene. Reddish brown crystal of 5-methyl derivatives **3b** of benzotriazole(H-Bt) was obtained in 99% yield. mp 79-80 °C. The compounds **3c** (5-nitroBtH), **3d** (5-chloroBtH), **3e** (5,6-dimethylBtH) and **3f** (naphth [1,2-*d*]BtH) were prepared by the similar procedure. The general information for the reaction products, solvents, reaction times and yields is shown in table 1 and nmr, ir spectra and GC/mass data in Table 2.

1-(Benzotriazol-1-yl)-1-hydroxymethanes: To an ether (100 mL) solution of **3b** (40 mmol), was added formaldehyde (50 mmol), and the resulting solution was refluxed for 2 hours. After the solvent was removed and water (30 mL) was added, the solid was filtered under reduced pressure. Brown crystal of 1-(5-methylbenzotriazol-1-yl)-1-hydroxy-methane **4b** (5-methylBt-CH_2OH) was recrystallized in ethanol: yield 87%, mp 118-119 °C. The compounds **4c** (5-nitroBt-CH_2OH), **4d** (5-chloroBt-CH_2OH), **4e** (5,6-dimethyl-Bt-CH_2OH) and **4f** (naphth[1,2-*d*]Bt-CH_2OH) were prepared by the similar procedure. The information of the reactions and the products is shown in Table 1 and 2.

1-(Benzotriazol-1-yl)-1-chloromethanes: To a benzene (80 mL) solution of **4b** (33.4 mmol), was dropwise added $SOCl_2$ (67 mmol, 5 mL), and the solution was refluxed for 2 hours. After the solid was washed with water (50 mL) and dried with anhydrous $MgSO_4$. Brown crystal of 1-(5-methylbenzotriazol-1-yl)-1-chloromethane **5b** (5-methylBt-CH_2Cl) was recrystallized in ethanol. Yield 86%, mp 85-86 °C. The compounds **5c** (5-nitroBt-CH_2Cl), **5d** (5-chloroBt-CH_2Cl), **5e** (5,6-dimethylBt-CH_2Cl) and **5f** (naphth[1,2-*d*]Bt-CH_2Cl) were prepared by the similar procedure. The information of the reactions and the products is shown in Table 1 and 2.

1-(Benzotriazole-1-yl)-1-arenesulfonylalkanes: A mixture of **5b** (13.4 mmol) and sodium benzenesulfinate in DMSO (30 mL) was warmed at 40 °C and stirred for 12 hours. After the product was extracted with chloroform (150 mL), the solution was washed with water (150 mL) 3-4 times and the organic layer was dried with anhydrous $MgSO_4$. And after the solvent was removed, yellowish brown crystal of 1-(5-methylbenzotriazol-1-yl)-1-benzenesulfonylmethane **6b** (5-methylBt-CH_2SO_2Ph) was recrystallized in ethanol: The compounds **6c** (5-nitroBt-CH_2SO_2Ph), **6d** (5-chloroBt-CH_2SO_2Ph), **6e** (5,6-dimethylBt-CH_2SO_2Ph), **6f** (naphth-[1,2-*d*]Bt-CH_2SO_2Ph), **6g** (Bt-CH_2SO_2Tol), **6h** (5-methylBt-CH_2SO_2Tol), **6i** (5-nitroBt-CH_2SO_2Tol), **6j** (5-chloroBt-CH_2SO_2Tol), **6k** (5,6-dimethylBt-CH_2SO_2Tol) and **6l** (naphth[1,2-*d*]Bt-CH_2SO_2Tol) were prepared by the similar procedure. The information of the reactions and the products is shown in Table 1 and 2.

(Benzotriazol-1-yl)alkyl arylsulfone 7 and 8.

Alkylation of 6a and 6g: To **6a** (10.5 mmol) in THF (80 mL), LDA solution (12 mmol, *n*-hexane) was dropwise added for 10 min at -20 °C under nitrogen stream, and then was dropewise added the solution of methyl iodide (12 mmol) at an ambient temperature. The reaction mixture was stirred for 5 hrs at room temperature, and the solution was poured into ice water (150 g), neutralized with 2% HCl and extracted with chloroform (3×50 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed. From the residue 1-(benzotriazol-1-yl)-1-benzenesulfonylethane **7a** and 2-(benzotriazol-1-yl)-2-benzenesulfonylpropane **8a**

were isolated by column chromatography (Merck silica gel 60/230-400 mesh and toluene : AcOEt = 20 : 1, 1st part **8a**, 2nd part **7a**). Ethylation of **6g** gave 1-(benzotriazol-1-yl)-1-toluenesulfonylpropane **7b** and 3-(benzotriazol-1-yl)-3-toluenesulfonylpentane **8b** through the similar procedure. The information of products and the reactions is shown in Table 3.

Pyrolysis of 8b: **8b** (1.72 g, 5 mmol) dissolved in chlorobenzene was heated at 165-170 °C for 20 min under nitrogen stream. The solvent of the reaction mixture was removed by distillation under reduced pressure, and from the residue three compounds, di(*p*-toluenesulfonyl) **10a**, the starting material **8b** and 3-toluenesulfonyl-2-pentene **9** which appears as a mixture of *syn* and *anti*-isomers (not isolated, see Figure 1), were obtained by column chromatography (toluene : AcOEt = 20 : 1). The information of the products is shown in Table 3.

Hydrolysis of 8b: The water solution (1 mL) of **8b** (1.14 g, 3.3 mmol) and phenylhydrazine (0.76 g, 7 mmol) was heated at 150 °C for 1 hr in a small steel bomb which was tightly closed. After the reaction mixture was neutralized with 5% NaOH solution and 10 mL of water was added, the solution was extracted with CH_2Cl_2, and the solvent was removed. From the water solution *p*-toluenesulfonic acid was recovered and from the residue two compounds were isolated by column chromatography (toluene : AcOEt = 20 : 1), which are diethylketone phenylhydrazone (formed from diethyketone **11**), benzotriazole. The information of the products is shown in Table 3.

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