(*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene and Its Alkylation Reactions

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(*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**) has been synthesized and its alkylation was studied. The results showed that the phenylsulphonyl group is a more powerful α-directing group than the benzotriazolyl group in the corresponding 1,3-dihetero-stabilized allyl anion.

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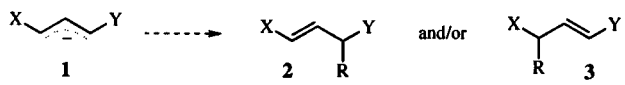
Introduction.

Sulphonyl [1] and benzotriazolyl [2] groups are among the most useful synthetic auxiliaries, and their chemistries have been extensively studied. In the allylic systems, both sulphonyl [3] and benzotriazolyl [4] behave as strong α-alkylation directors (Scheme 1). When other groups, such as alkylthio [5], alkoxy [6], acyl [7], alkoxycarbonyl [7,8] and carbamoyl [9], are present on the γ-position of an allylic sulphone, α-alkylation (to the sulphone) of the ambident anion usually predominates. However, sometimes some γ-alkylation is observed with an acyl [7] or alkoxycarbonyl [8] at the γ-position of an allylic sulphone (Scheme 1), perhaps due to steric effects. When an alkoxy [10] or amino [11] group is present on the γ-position of allylbenzotriazole, only α-alkylation is observed (Scheme 1). Since both the sulphonyl and benzotriazolyl groups are highly useful in organic synthesis, it is of interest to test and compare the effect of a benzotriazolyl group together with a phenylsulphonyl group on alkylation of an allylic anion **1**, as shown in Scheme 1.

Scheme 1



X = alkyl, H, R'S, R'O, or R'NHCO; Y = SO_2Ph, gives **2** as only product
X = R'CO or R'OCO; Y = SO_2Ph, gives **2** as major product
X = alkyl, H, R'O, or R'R"N; Y = Bt, gives **2** as only product
X = Bt, Y = SO_2Ph, unknown

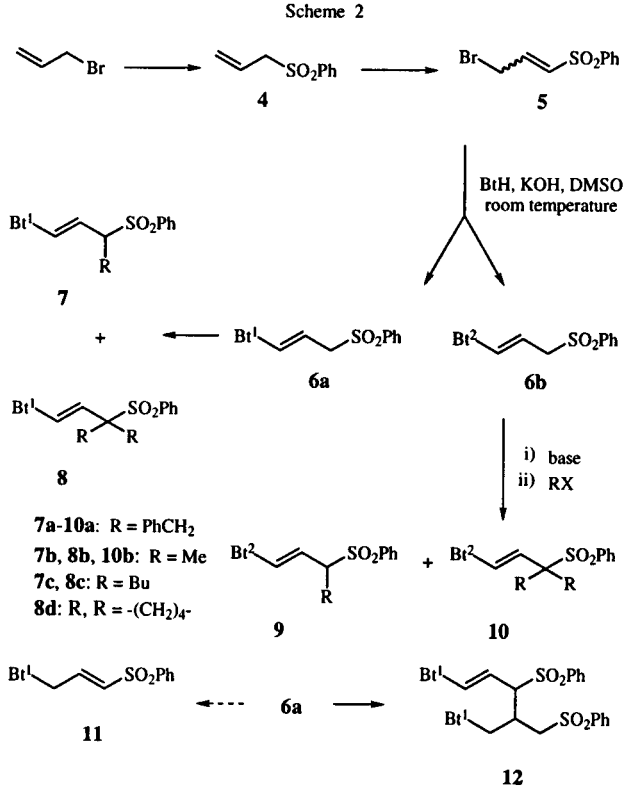
Bt = Benzotriazol-1-yl (Bt^1) and/or benzotriazol-2-yl (Bt^2)

Results and Discussion.

Synthesis of (*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**).

A synthetic pathway to the desired precursor of the allylic anion **1** (X = Bt, Y = $PhSO_2$) was devised through the use of established literature methods, as shown in Scheme 2. The reaction of allyl bromide with the sodium salt of benzenesulfinic acid produced allyl phenyl sulphone (**4**) in 95% yield. Compound **4** was then brominated/dehydrobrominated in one pot to give 3-bromo-1-propenyl phenyl sulphone (**5**) [12]. Crude product **5**, without further purification, was reacted with benzotriazole under basic conditions to give (*E*)-1-benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6a,b**) in 78% yield (**6a**:**6b** = 2:1) after column chromatography. The structures of **6a,b** were determined by comparing their ^1H and ^{13}C nmr with allylbenzotriazole and allyl phenyl sulphone. The chemical shifts of the methylene unit of **6a,b** (δ_H 4.08 and 4.06, δ_C 57.4 and 57.2) are very close to those of the methylene unit of allylic sulphone (δ_H 3.84, δ_C 60.6), but not to allylbenzotriazole (δ_H 5.27 and 5.34, δ_C 50.6 and 58.7). No isomer **11**, with the double bond α,β to the sulphonyl group, was detected.

Scheme 2



The production of **6a,b**, but not **11**, under basic conditions for a long time (24 hours) indicates that compounds **6a,b** are more stable than **11**. Attempts to isomerize the double bond of compound **6a** (**6a** to **11**) failed. When **6a** was treated with 1.0 equivalent of potassium tertiary butoxide in tetrahydrofuran at room temperature for 24 hours, only compound **12** was obtained (quantitative by ^{1}H nmr). When 0.1 equivalents of potassium tertiary butoxide was used, only a small portion of **6a** was converted, and most of that was to compound **12**. These results are expected if one considers that allylsulphones are more thermodynamically stable than the corresponding vinyl isomers [13] whereas allylbenzotriazoles can be isomerized into the corresponding vinylbenzotriazoles [4,14].

Alkylation of (*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**).

The reaction of compound **6a** with 1.0 equivalent of lithium diisopropylamide followed by 1.0 equivalent of benzyl bromide gave only products arising from alkylation α to the sulphonyl moiety, as shown in Scheme 2 and Table 1, in addition to 16% unreacted starting material. It was also shown that if only the benzotriazol-1-yl isomer of **6a** was used as starting material, only benzotriazol-1-yl products **7a** and **8a** were isolated; this was also shown for the benzotriazol-2-yl isomers (Table 1). This allows the use of the mixture **6a,b** in further reactions. The use of methyl iodide as electrophile also gave solely products of α-alkylation to the phenylsulphonyl group, with the ratio, based on ^{1}H nmr of the crude product, of di- (**8b**) to monoalkylation (**7b**) products being 1.33:1 rather than 1:3.45 for benzyl bromide. When butyl bromide was used as the electrophile, the same regioselectivity was observed, with a similar ratio (1.44:1) of dialkylated (**8c**) to monoalkylated (**7c**) products; additionally, compound **12** was produced in 32% yield. When cyclohexanone was used as the electrophile, only compound **12** was produced, in 72% yield. No reaction occurred when chlorotrimethylsilane was used as the electrophile and a complex product slate was produced when benzaldehyde was used.

One further study was performed in which compound **6a** was treated with 1.0 equivalent of lithium diisopropylamide and then butyl bromide at -78°. The reaction was followed by tlc as the temperature was increased. Two hours after the addition of electrophile, and having been kept at -78°, no reaction had occurred. The temperature was then raised to -42° (acetonitrile-dry ice bath), and after an additional two hours, there was still no reaction. After two hours at -15° (ethylene glycol-dry ice bath), small quantities of **8c** and **12** were produced. Two hours at 0° only resulted in an increase in the quantities of products produced. The reaction temperature was then raised to room temperature and the mixture was allowed to stir for 24 hours. The reaction went to completion and formed mostly **8c** and **12**, but a small quantity of **7c** was also produced. The formation of **8c** before **7c** indicates that some of the anion of **7** is generated even when only 1.0 equivalent of base is utilized.

Since it has been reported that the use of 2.0 equivalents of base is sometimes necessary for alkylation of similar systems to occur [15], and these conditions usually give high yields of dialkylated products, such conditions were used on our system. Chlorotrimethylsilane was still unreactive and the benzaldehyde reaction again gave complex results. However, benzyl bromide and methyl iodide gave dialkylated products in 82% (**8a**) and 84% (**8b/10b**) yields, respectively. The anion can also react with α,ω-dibromoalkanes to form the cyclized product. For example, the reaction of the preformed dianion (from **6a**) reacted with 1,4-dibromobutane to give product **8d** in 64% yield.

In summary, (*E*)-1-benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**) was easily prepared from allyl bromide in a three step sequence in 74% overall yield. The temperature study shows that products formally derived from the dianion of (*E*)-1-benzotriazolyl-3-phenylsulphonylpropene are formed even when only 1.0 equivalent of base is utilized. It was also shown that the use of 2.0 equivalents of base and electrophile gives high yields of

Table 1

Alkylation of (*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**)

6	RX	Method [a]	Products **7-10** [b]			
			7/9	Yield (%)	**8/10**	Yield (%)
6a	$PhCH_2Br$	A	**7a**	38	**8a**	6
6b	$PhCH_2Br$	A	**9a**	38	**10a**	0
6a	MeI	A	**7b**	[c]	**8b**	[c]
6a	*n*-BuBr [d]	A	**7c/9c**	18	**8c/10c**	26
6a	$PhCH_2Br$	B	-	-	**8a**	82
6a,b	MeI	B	-	-	**8b/10b**	84
6a	$(CH_2CH_2Br)_2$	B [e]	-	-	**8d**	64

[a] For details of Method A, B. see experimental; [b] Isolated yields; [c] A mixture of **7b** and **8b** was isolated in 75% yield (ratio **7b/8b** = 2:3); [d] Compound **12** was also isolated in 32% yield; [e] Only one equivalent of electrophile was used.

α,α-dialkylated products. The easy generation of the first carbanion and the carbanion of the mono alkylated compound and also the regioselectivity in the alkylation of **6** can be attributed to the greater capability of a sulphonyl group to stabilize an adjacent carbanion than a benzotriazole group. However, the low reactivity of the anions toward electrophiles other than alkyl halides will limit the application of this method.

EXPERIMENTAL

All melting points were measured on a hot-stage microscope given in degrees Celsius and are uncorrected. The ^1H and ^{13}C nmr data were collected from a deuterium chloroform solution on a VXR-300 spectrometer (300 MHz and 75 MHz respectively), with tetramethylsilane and deuteriochloroform as internal references, respectively. Column chromatography was carried out using 230-400 mesh silica gel. Allyl phenyl sulphone (**4**) and 3-bromo-1-propenyl phenyl sulphone (**5**) were prepared by literature methods [12].

(*E*)-1-(Benzotriazol-1-yl)-3-(phenylsulphonyl)-1-propene (**6a**) and (*E*)-1-(Benzotriazol-2-yl)-3-(phenylsulphonyl)-1-propene (**6b**).

A mixture of benzotriazole (6.3 mmoles), 3-bromo-1-propenyl phenyl sulphone **5** (6 mmoles) and potassium hydroxide (6.5 mmoles) were stirred in dimethylsulfoxide (15 ml) at room temperature for one day. The reaction was quenched with 1 *N* hydrochloric acid and extracted with ethyl acetate (20 ml). The organics were washed with 0.5 *N* hydrochloric acid (3 x 5 ml) and then with water (5 ml). The aqueous solution was extracted with ethyl acetate (3 x 5 ml). The combined organics were washed with brine (5 ml), dried over sodium sulfate and evaporated to give an oil. The products (**6a**:**6b** = 2:1) were isolated independently by column chromatography in 78% total yield using methylene chloride as eluent.

(*E*)-1-(Benzotriazol-1-yl)-3-(phenylsulphonyl)-1-propene (**6a**).

This compound was obtained as a white solid (ethyl acetate), mp 157-158°; ^1H nmr: δ 8.09 (d, J = 8.3 Hz, 1H), 7.96-7.93 (m, 2H), 7.71-7.55 (m, 5H), 7.47-7.38 (m, 2H), 6.42 (dt, J = 7.7, 14.3 Hz, 1H), 4.08 (dd, J = 0.9, 8.0 Hz, 2H); ^{13}C nmr: δ 146.0, 133.9, 132.2, 130.8, 129.4, 129.0, 128.4, 128.2, 124.5, 120.2, 109.5, 106.2, 57.4.

Anal. Calcd. for $C_{15}H_{13}N_3O_2S$: C, 60.19; H, 4.38; N, 14.04. Found: C, 60.36; H, 4.36; N, 13.55.

(*E*)-1-(Benzotriazol-2-yl)-3-(phenylsulphonyl)-1-propene (**6b**).

This compound was obtained as a white solid (ethyl acetate), mp 168-169°; ^1H nmr: δ 7.93 (d, J = 7.7 Hz, 2H), 7.84-7.81 (m, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.42-7.35 (m, 3H), 6.83 (dt, J = 8.2, 14.0 Hz, 1H), 4.06 (d, J = 8.0 Hz, 2H); ^{13}C nmr: δ 144.8, 137.6, 134.5, 134.1, 129.3, 128.4, 127.7, 118.2, 111.0, 57.2.

Anal. Calcd. for $C_{15}H_{13}N_3O_2S$: C, 60.19; H, 4.38; N, 14.04. Found: C, 60.46; H, 4.37; N, 13.85.

General Procedure for the Alkylation of (*E*)-1-Benzotriazolyl-3-(phenylsulphonyl)-1-propene (**6**).

Method A.

To a solution of compound **6** (1 or 2 mmoles) in tetrahydrofuran (20 ml) at -78° was added 1.05 equivalents of lithium diisopropylamide under an inert atmosphere. After 30 minutes of stirring, one equivalent of electrophile was added and the solution allowed to warm to room temperature overnight. The reaction was quenched by water (10 ml) and the layers separated. The aqueous layer was extracted with ether (3 x 10 ml). The combined organics were washed with brine (5 ml), dried over sodium sulfate and evaporated to give a residue, which was then purified by column chromatography.

Method B.

The same as Method A, except that 2.1 equivalents of lithium diisopropylamide and 2.0 equivalents of electrophile were used instead.

(*E*)-1-(Benzotriazol-1-yl)-3-phenylsulphonyl-4-phenyl-1-butene (**7a**).

This compound was obtained from the reaction of **6a** with benzyl bromide as electrophile by Method A, as a white solid (ethyl acetate) in 38% yield, mp 187-189°; ^1H nmr: δ 8.04 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.57-7.37 (m, 5H), 7.27-7.14 (m, 5H), 7.01 (d, J = 14.3 Hz, 1H), 6.29 (dd, J = 10.0, 14.3 Hz, 1H), 4.02 (dt, J = 3.0, 10.7 Hz, 1H), 3.70 (dd, J = 3.0, 13.7 Hz, 1H), 3.03 (dd, J = 11.5, 13.5 Hz, 1H); ^{13}C nmr: δ 146.1, 136.9, 135.9, 134.2, 131.1, 129.2, 129.1, 128.8, 128.6, 127.1, 124.8, 120.4, 111.9, 109.7, 68.7, 34.2.

Anal. Calcd. for $C_{22}H_{19}N_3O_2S$: C, 67.85; H, 4.92; N, 10.79. Found: C, 67.59; H, 4.96; N, 10.82.

(*E*)-1-(Benzotriazol-1-yl)-3-phenylsulphonyl-1-butene (**7b**).

This compound was made by the reaction of **6a** with methyl iodide as electrophile by Method A. It could not be separated from **8b** by chromatography.

(*E*)-1-(Benzotriazol-1-yl)-3-phenylsulphonyl-1-heptene (**7c**).

This compound was obtained by the reaction of **6a** with *n*-butyl bromide as the electrophile by Method A in 18% yield as a yellow oil; ^1H nmr: δ 8.10 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.6 Hz, 2H), 7.67-7.42 (m, 6H), 7.28 (d, J = 14.3 Hz, 1H), 6.24 (dd, J = 9.9, 14.3 Hz, 1H), 3.76 (dt, J = 2.9, 10.5 Hz, 1H), 2.26-2.22 (m, 1H), 1.83-1.72 (m, 1H), 1.47-1.30 (m, 4H), 0.86-0.91 (m, 3H); ^{13}C nmr: δ 146.3, 137.1, 134.0, 131.2, 129.2, 129.1, 128.9, 128.7, 124.9, 120.5, 112.7, 109.9, 67.5, 28.9, 27.4, 22.2, 13.7; hrms: (FAB) Calcd. for $C_{19}H_{21}N_3O_2S$ + H, 356.1433. Found: 356.1448.

(*E*)-1-(Benzotriazol-1-yl)-4-phenyl-3-(phenylmethyl)-3-phenylsulphonyl-1-butene (**8a**).

This compound was obtained from the reaction of **6a** with benzyl bromide as the electrophile by Method A (6% yield) or Method B (82% yield) as a white solid (acetone), mp 113-116°; ^1H nmr: δ 7.97 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.7 Hz, 1H), 7.45-7.25 (m, 6H), 7.18-7.02 (m, 10H), 6.43 (d, J = 14.8 Hz, 1H), 3.40 (s, 4H); ^{13}C nmr: δ 146.2, 135.8, 134.8, 133.9, 131.1, 130.9, 129.1, 128.7, 128.5, 128.2, 127.2, 124.8, 120.3, 116.0, 109.9, 70.6, 38.2; hrms: (FAB) Calcd. for $C_{29}H_{25}N_3O_2S$ + H, 480.1746. Found: 480.1762.

(*E*)-1-(Benzotriazol-1-yl)-3-methyl-3-phenylsulphonyl-1-butene (**8b**).

This compound was crystallized from the crude reaction mixture of the reaction of **6a** with methyl iodide as electrophile by Method A (34% yield) or from **6a,b** by Method B (total 84% yield for **8b** and **10b**); the benzotriazol-1-yl isomer is white needles (acetone), mp 167-170°; ^{1}H nmr: δ 8.10 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.4 Hz, 2H), 7.71-7.43 (m, 6H), 7.33 (d, J = 14.6 Hz, 1H), 6.64 (d, J = 14.6 Hz, 1H), 1.66 (s, 6H); ^{13}C nmr: δ 146.3, 134.8, 134.0, 131.2, 130.5, 128.7, 128.6, 126.7, 124.9, 120.4, 119.1, 110.0, 63.6, 21.3.

Anal. Calcd. for $C_{17}H_{17}N_3O_2S$: C, 62.37; H, 5.23; N, 12.83. Found: C, 62.55; H, 5.20; N, 12.89.

(*E*)-1-(Benzotriazol-1-yl)-3-phenylsulphonyl-1-heptene (**8c**).

This compound was obtained from the reaction of **6a** with *n*-butyl bromide by Method A in 26% yield as a white solid (ethyl acetate), 117-118°; ^{1}H nmr: δ 8.10 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.69-7.56 (m, 3H), 7.49-7.43 (m, 3H), 7.21 (d, J = 14.8 Hz, 1H), 6.40 (d, J = 14.8 Hz, 1H), 2.21-2.13 (m, 2H), 1.89 (dt, J = 13.5, 2.7 Hz, 2H), 1.67-1.60 (m, 2H), 1.41-1.40 (m, 6H), 0.96 (t, J = 6.8 Hz, 6H); ^{13}C nmr: δ 146.4, 135.7, 133.9, 131.2, 130.4, 128.7, 128.6, 127.3, 124.9, 120.6, 119.7, 110.0, 69.8, 30.1, 25.7, 23.3, 13.9.

Anal. Calcd. for $C_{23}H_{29}N_3O_2S$: C, 67.12; H, 7.10; N, 10.21. Found: C, 67.15; H, 7.34; N, 10.23.

(*E*)-1-(Phenylsulphonyl)-1-[2-benzotriazol-1-yl)vinyl]cyclopentane (**8d**).

This compound was obtained by the reaction of **6a** with 1,4-dibromobutane by Method B (only one equivalent of electrophile) in 64% yield; white needles (ethyl acetate), mp 176-177°; ^{1}H nmr: δ 8.12 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.68-7.57 (m, 3H), 7.51-7.43 (m, 3H), 7.30 (d, J = 14.8 Hz, 1H), 6.53 (d, J = 14.6 Hz, 1H), 2.65-2.59 (m, 2H), 2.02-2.00 (m, 4H), 1.81-1.77 (m, 2H); ^{13}C nmr: δ 146.4, 136.5, 133.8, 131.2, 130.1, 128.8, 128.7, 127.2, 124.9, 120.5, 119.0, 110.0, 73.6, 33.3, 24.4.

Anal. Calcd. for $C_{19}H_{19}N_3O_2S$: C, 64.57; H, 5.42; N, 11.89. Found: C, 64.25; H, 5.52; N, 11.81.

(*E*)-1-(Benzotriazol-2-yl)-3-phenylsulphonyl-4-phenyl-1-butene (**9a**).

This compound was obtained from the reaction of **6b** with benzyl bromide as the elctrophile using Method A, as a white solid (ethyl acetate) in 38% yield, mp 189-191°; ^{1}H nmr: δ 7.93 (d, J = 7.7 Hz, 2H), 7.81-7.77 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.58-7.50 (m, 2H), 7.39-7.35 (m, 2H), 7.26-7.15 (m, 5H), 6.92 (d, J = 14.0 Hz, 1H), 6.74 (dd, J = 10.1, 14.0 Hz, 1H), 3.98 (dt, J = 11.3, 2.8 Hz, 1H), 3.72 (dd, J = 2.8, 13.7 Hz, 1H), 3.04 (dd, J = 11.6, 13.5 Hz, 1H); ^{13}C nmr: δ 144.8, 136.9, 135.9, 134.1, 134.0, 129.2, 129.1, 128.8, 127.7, 127.6, 127.1, 118.2, 116.2, 68.4, 34.1.

Anal. Calcd. for $C_{22}H_{19}N_3O_2S$: C, 67.85; H, 4.92; N, 10.79. Found: C, 67.52; H, 4.53; N, 10.81.

(*E*)-1,5-Di(benzotriazol-1-yl)-3-(phenylsulphonyl)-4-[(phenylsulphonyl)methyl]-1-pentene (**12**).

This compound was obtained as a white solid (ethyl acetate) from the reaction of **6a** with *n*-butyl bromide by Method A (32% yield), with cyclohexanone by Method A (72% yield) and without electrophile by Method B using potassium tertiary butoxide as base instead of lithium diisopropylamide (quantitative by ^{1}H nmr), mp 129-132°; ^{1}H nmr: δ 8.12-8.03 (m, 4H), 7.78-7.58 (m, 7H), 7.53-7.33 (m, 6H), 7.26-7.19 (m, 2H), 6.49 (dd, J = 11.0, 14.0 Hz, 1H), 5.39 (dd, J = 2.5, 14.8 Hz, 1H), 4.85-4.77 (m, 1H), 4.28 (d, J = 12.4 Hz, 1H), 3.94 (d, J = 10.7 Hz, 1H), 3.32-3.28 (m, 2H); ^{13}C nmr: δ 146.1, 145.9, 138.8, 136.0, 134.5, 134.1, 132.7, 131.6, 131.5, 129.7, 129.1, 129.0, 128.4, 128.2, 125.1, 124.5, 120.5, 120.0, 109.6, 109.5, 105.1, 64.9, 53.3, 47.9, 34.0.

Anal. Calcd. for $C_{30}H_{26}N_6O_4S_2$: C, 60.19; H, 4.38; N, 14.04. Found: C, 60.33; H, 4.41; N, 13.72.

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