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SYNTHESIS OF 5-[(4-METHYLPHENYL)SULFINYL]- AND 5-[(4-METHYLPHENYL)SULFONYL]-1-PHENYL-1*H*-TETRAZOLES

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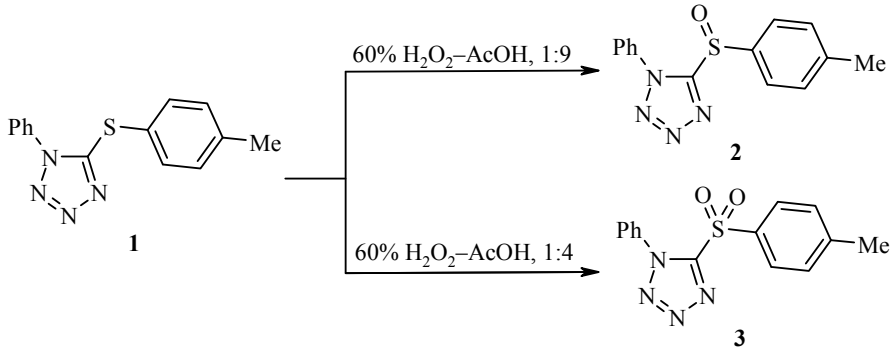
It is known that the reaction of 5-alkylsulfanyltetrazoles with hydrogen peroxide depends on the reaction conditions and can give 5-alkylsulfinyl- or 5-alkylsulfonyltetrazoles [1-3]. However, the oxidation of 5-arylsulfanyltetrazoles has not previously been studied, probably because of the difficulty in obtaining these compounds. We have earlier proposed a method for preparation of 1-substituted 5-arylsulfanyltetrazoles [4]. In this work we have studied the oxidation of 5-[(4-methylphenyl)sulfanyl]-1-phenyl-1*H*-tetrazole (**1**) by hydrogen peroxide in acetic acid.

We have found that reaction of compound **1** with hydrogen peroxide can yield 5-[(4-methylphenyl)sulfinyl]-1-phenyl-1*H*-tetrazole (**2**) and 5-[(4-methylphenyl)sulfonyl]-1-phenyl-1*H*-tetrazole (**3**). The oxidation was carried out under conditions of microwave activation and of convection heating at a temperature of 55ºC.



Oxidation duration on convection heating of compound **1** to compound **2** is 3 h. In the course of the reaction yet before full conversion of compound **1,** the product of full oxidation **3** begins to accumulate in the reaction mixture, that leads to a lowering of the yield and the need to use chromatographic methods for the

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purification of compound **2**. Lowering the temperature and/or the concentration of hydrogen peroxide leads to a marked increase of the process time, but still with the observation of sulfone **3** formation. The said problems were eliminated by the use of microwave activation which resulted in shortening of the reaction time to 1.5 h and in increase in the selectivity of the oxidation reaction.

Increasing the concentration of hydrogen peroxide, the oxidation of derivative **1** using convection heating at 55ºC occurs completely to give compound **3** after 10 h. Under microwave activation conditions the oxidation time can be reduced to 3.5 h and there is an increase in yield to 80% from the 62% yield observed with convection heating.

IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer using KBr pellets. ^{1}H NMR spectra were recorded on a Bruker WM-400 spectrometer (400 MHz) using acetone-d_6. The residual solvent protons at 2.05 ppm were used as standard. Elemental analysis was carried out on an LECO CHNS-932 analyzer. The microwave activity reactions were performed using a Milestone MicroSynth P/N 44072 reactor.

5-[(4-Methylphenyl)sulfanyl]-1-phenyl-1*H*-tetrazole (**1**) was prepared using method [4].

5-[(4-Methylphenyl)sulfinyl]-1-phenyl-1*H*-tetrazole (2). A solution of 5-[(4-methylphenyl)sulfanyl]-1-phenyl-1*H*-tetrazole (**1**) (1.00 g, 3.9 mmol) in a freshly prepared mixture of 60% hydrogen peroxide and acetic acid (1:9) (25 ml) was stirred in the microwave reactor at 55ºC (50 W) for 1.5 h, evaporated *in vacuo* at 35ºC to the beginning of crystallization, and diluted with fourfold amount of water. The precipitate formed was filtered off and dried at 40ºC. Yield 0.71 g (64%); mp 121-122ºC (*n*-BuOH). IR spectrum, ν, cm^{-1}: 601, 665, 674, 763, 818, 1016, 1086, 1108, 1166, 1174, 1296, 1337, 1499, 1592, 2376, 2923, 3035, 3069. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, CH_3); 7.36 (2H, d, *J* = 8.4, H Ar); 7.52 (2H, d, *J* = 8.4, H Ar); 7.63-7.67 (5H, m, H Ph). Found, %: C 58.89; H 4.12; N 19.55; S 11.32. $C_{14}H_{12}N_4OS$. Calculated, %: C 59.14; H 4.25; N 19.70; S 11.28.

The reaction with convection heating was conducted similarly. The reaction time was 3 h. The target compound **2** was separated by column chromatography on silica gel (ethyl acetate–hexane, 1:9). Yield 0.47 g (42%).

5-[(4-Methylphenyl)sulfonyl]-1-phenyl-1*H*-tetrazole (3) was prepared similarly to compound **2** using a freshly prepared mixture of 60% hydrogen peroxide–AcOH (1:4). Reaction time was 3.5 h. Yield 0.94 g (80%); mp 128-130ºC (2-PrOH). IR spectrum, ν, cm^{-1}: 620, 689, 722, 763, 811, 922, 968, 1014, 1042, 1063, 1089, 1101, 1167, 1229, 1269, 1289, 1367, 1393, 1418, 1454, 1490, 1500, 1593, 2924, 3025, 3040, 3061. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49 (3H, s, CH_3); 7.52 (2H, d, *J* = 8.3, H Ar); 7.68-7.72 (5H, m, H Ph); 7.74-7.75 (2H, d, *J* = 8.3, H Ar). Found, %: C 56.22; H 3.95; N 18.88; S 10.41. $C_{14}H_{12}N_4O_2S$. Calculated, %: C 55.99; H 4.03; N 18.65; S 10.68.

The reaction with convection heating was conducted similarly. The reaction time was 10 h. Yield 0.73 g (62%).

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