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LETTERS TO THE EDITOR

Synthesis of Azole-Containing Allylamines

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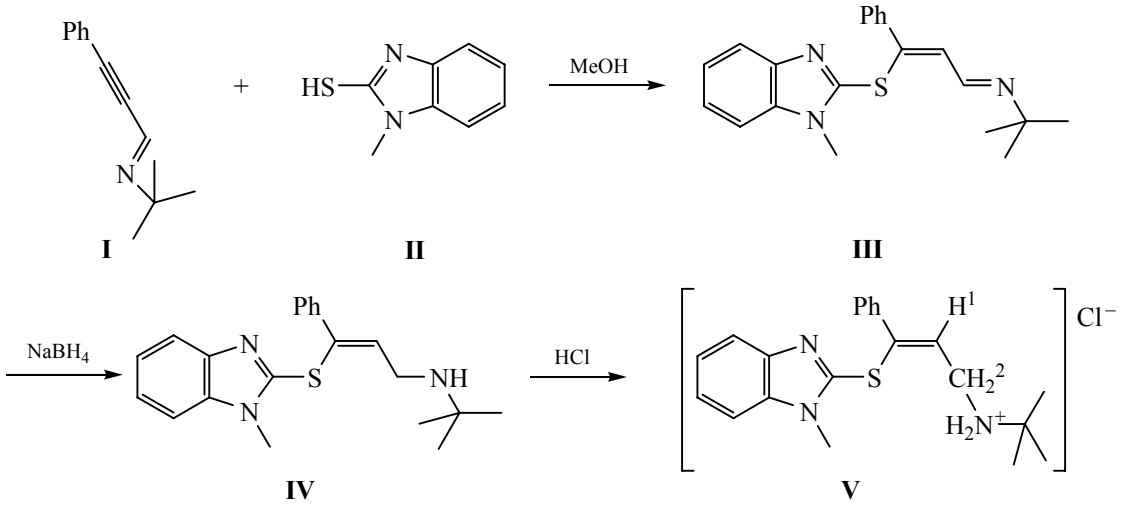
Allylamine derivatives like terbinafine and naftifine are known to be effective modern fungicidal drugs [1, 2]. There are no data on the use of α,β-acetylene aldimines [3, 4] in the synthesis of allylamines. 3-Heteroaryl-substituted allylamines were found to be obtained via the sequential double nucleophilic addition [3] of 1-methyl-2-mercaptoimidazole and sodium borohydride to α,β-acetylene aldimine.



The reaction proceeds in methanol. Initially, thiol **II** reacts with α,β-acetylene aldimine **I** to form azadiene **III**, which is then reduced with sodium borohydride to allylamine **IV**. The allylamine was isolated as a crystalline hydrochloride **V**, which is stable in air and has a distinct melting point. The ^{1}H NMR spectrum of compound **V** contains the proton signals characteristic of the protonated allylamine groups: a triplet of methylidene proton (H^1) at δ 6.87 ppm ($^3J_{HH}$ 7.1 Hz) and a multiplet of two methylene protons at δ 4.09 ppm. A signal of two protons of the ammonium group (NH_2^+) appears as a broadened singlet at δ 10.02 ppm.

The one-pot method of synthesis allows the preparation of previously unknown and inavailable azole-containing allylamines and isolating them as crystalline hydrochlorides.

***tert*-Butyl-[3-(1-methyl-1*H*-benzimidazol-2-ylsulfanyl)-3-phenylallyl]amine (V).** To a solution of 0.01 mol of acetylene aldimine in 50 ml of methanol was added with stirring a solution of 0.01 mol of 1-methyl-2-mercapto-1*H*-benzimidazole. After 30 min to the reaction mixture was added in small portions a 3-fold molar excess of sodium borohydride. The mixture was

refluxed for 15 min, then cooled and diluted with 10-fold excess of water. The resulting emulsion was twice extracted with diethyl ether. The combined extracts were dried over anhydrous sodium sulfate. The solvent was evaporated in a vacuum on a rotary evaporator, and the residue was dissolved in acetone. Since allylamines obtained are thick viscous oils, which are difficult to crystallize, they were isolated as hydrochlorides by adding dropwise concentrated hydrochloric acid to pH 5. The precipitated crystals were filtered off and dried in air. The resulting compound is colorless crystals, readily soluble in ethanol and methanol. Yield 75%, mp 242°C. ^{1}H NMR spectrum, δ, ppm (400.13 MHz, DMSO-d_6): 1.44 s (9H), 3.97 s (3H), 4.09 m (2H), 6.87 t (1H, $^{3}J_{HH}$ 7.1 Hz), 7.15–7.34 m (3H), 7.35–7.48 m (2H), 7.63–7.64 m (2H), 7.74 d (1H, $^{3}J_{HH}$ 7.1 Hz), 10.02 s (2H). ^{13}C NMR spectrum, δ_C, ppm (101 MHz, DMSO-d_6): 147.22, 138.07, 134.22, 133.61, 129.78, 129.14, 127.86, 125.82, 125.58, 115.22, 112.62, 56.80, 41.53, 32.45, 25.61.

REFERNCES

1. Shivakumar, H.N., Vaka, S.R., Madhav, N.V., Chandra, H., and Murthy, S.N., *J. Pharm. Sci*., 2010, vol. 99, no. 10, p. 4267.
2. Marks, S., Cantrell, W., Varma, R., and Elewski, B., *J. Drugs Dermatol*., 2010, vol. 9, no. 7, p. 750.
3. Shimizu, M., Hachiya, I., and Mizota, I., *Chem. Commun*., 2009, vol. 1, no. 3, p. 874.
4. Stadnichuk, M.D., Khramchikhin, A.V., Piterskaya, Yu.L., and Suvorova, I.V., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 4, p. 616.