Synthesis of 5-(4-nitrophenoxy)-1H-tetrazole

Fatemeh Sarikhani1, Hafezeh Nabipour2,3,*, Nader Noroozi Pesyan1, Shahriar Ghammamy4
1Department of Chemistry, Faculty of Science, University of Urmia, (IRAN)
2Islamic Azad University, Takestan Branch, Department of Chemistry, Takestan, (IRAN)
3Member of Young Researchers Club, Islamic Azad University, Takestan, (IRAN)
4Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, (IRAN)
E-mail: ha.nabipour@gmail.com
Received: 11th November, 2010 ; Accepted: 21st November, 2010

INTRODUCTION

The tetrazole moiety exhibits a wide and growing number of applications. This nitrogen-rich ring system is used in propellants[1], explosives[2], and pharmaceuticals[3]. Practicing medicinal chemists who may be interested in an evaluation of more comprehensive tabular surveys may also consult some of the review materials listed in this bibliography[4-8]. Synthesis of tetrazoles has been reported since the mid-century, there is still a dearth of efficient processes. Tetrazoles are an increasing popular functionality[9]. With wide-ranging applications. Structural elucidation of tetrazoles involved is helpful in understanding how and why they own these functions. For tetrazole and its 5-substituted derivatives, tautomeric and ring-chain isomerisms are known (Scheme 1)[10].

To date, reports on mass spectrometric investigations of 5-substituted tetrazoles are scarce[11-15]. In those case, loss of N2 is only of minor importance. In continuation of our studies on organic reactions, we report here an efficient method for the synthesis of tetrazole via reaction of 5- (phenoxy)-1H-tetrazole with acid nitric in the presence of solvent. Tetrazole derivative were synthesized and characterized by using elemental analyses, FT-IR, NMR.

EXPERIMENTAL

Materials and general methods

The reagents and solvents were of analytical grade. Sodium azide, phenol, and other material were purchased from Merck Company. 1H and 13C NMR spectra of deuterated chloroform (CDCl3) and solutions of the compounds were registered on a Bruker WM-300 spectrometer (300 MHz) using trimethylsilane as internal standard. The infrared spectra of the compounds as KBr-disks were recorded in the range of 400–
Synthesis of phenyl cyanate

17.6 g of the crude phenol were dissolved in 70 ml of acetone. The solution was cooled to -30°C and 19.8 g of liquefied cyanogen bromide were added under stirring. Within a period of 60 min a solution of 26 ml of triethyl amine in 20 ml of acetone was added dropwise. During the addition the temperature of the reaction solution was maintained between -30°C and -20°C. The solution was then stirred for further 60 min at room temperature to complete the reaction. These operations were carried out under appropriate safety precautions in a well-ventilated hood. After filtration the reaction solution was concentrated in vacuo. The oily residue was chromatographed over a silica gel column using n-hexane/ethyl acetate (vol. ratio 10:3) as eluent (Scheme 2). IR (KBr, cm⁻¹): 2974, 2277, 2239, 1602, 1501, 1459, 1167, 1086, 1012, 687 cm⁻¹. ¹H NMR (DMSO-d₆, 300MHz): δ (ppm) 6.73-7.28.

Synthesis of 5-(phenoxy)-1H-tetrazole

A three-necked 50 ml flask was equipped with a distillation head, a dropping funnel. 1.4 g sodium azide in 10 ml water placed in the flask. After loading the dropping funnel with 2.4 g of the phenyl cyanate, the distillation apparatus was heated in an oil bath thermostatted at 150°C. The contents of the dropping funnel were dropped into the heated flask over a period of 30 min. The solution was cooled to -30°C and 0.5 g of HCl was added under stirring. The precipitate were combined and washed with water and then dried over polyphosphoric anhydride (Scheme 3). Compound recrystallized from methanol. IR (KBr, cm⁻¹): 3060, 2901-2281, 1621, 1577, 1488, 1276, 1189, 1055, 977, 853, 781, 687, 611, 482. ¹H NMR (DMSO-d₆, 300MHz): δ (ppm) 7.743 (m, 2H), 7.252 (m, 3H). ¹³C NMR (DMSO-d₆, 75MHz): 166.80, 154.50, 130.52, 126.09, 119.38.

Synthesis of 5-(4-nitrophenoxy)-1H-tetrazole

In a 50 ml beaker, 14 g of 5-(phenoxy)-1H-tetrazole is dissolved in 60-50 ml acid nitric. The beaker is placed in an ice-salt bath and cooled to 0-5°C whilst stirring vigorously. Then ice-salt bath was removed and temperature of the solution is allowed to rise above 40°C. The precipitate are combined and washed with water and then dried over polyphosphoric anhydride (Scheme 4). Compound recrystallized from chloroform. IR (KBr, cm⁻¹): 3113, 2892-2476, 1928, 1584, 1543, 1487, 1351, 1201, 1165, 1061, 864.62, 738, 687, 649. ¹H NMR (DMSO-d₆, 300MHz): δ (ppm) 8.3 (d, J=9Hz, 2H) 7.53 (d, J=9.3 Hz, 2H). ¹³C NMR (DMSO-d₆, 75MHz): δ (ppm) 166.79, 159.17, 144.70, 126.44, 119.70.

RESULTS AND DISCUSSION

Phenyl cyanate was readily converted to 5-(phenoxy)-1H-tetrazole by treating them with sodium azide and hydrochloric acid in water. Infrared spectrum of compound 5-(phenoxy)-1H-tetrazole showed a sharp absorption and at 3060 cm⁻¹ which is attributed to secondary amino group. The synthesized compound 5-(4-nitrophenoxy)-1H-tetrazole showed absorption bands 3113, 2892-2476 cm⁻¹ which are attributed to proton tetrazole ring. Characteristic absorption bands were observed for nitro group and aromatic region of the synthesized compound. ¹H-NMR spectra of the synthesized 5-(4-nitrophenoxy)-1H-tetrazole showed doublet at 7.53 ppm two protons ortho and doublet at 8.28 ppm two protons meta. 1-H (NH) proton of the tetrazole is undetectable in NMR spectra.
The method described in this paper, allows the preparation of unique substituted tetrazoles from commercial and available phenol and easy to prepare from sodium azides and various nitration agents. The important aspects of this protocol, are mild reaction conditions, availability of the purity of the obtained products with no further crystalization.

REFERENCES