Asian Journal of Chemistry Vol. 15, No. 1 (2003), 515–518

NOTE

Synthesis of 3-Ethoxy Carbonyl 5-Phenyl-1-*p*-Tolyl 1,2,4-Triazolo [3,4,-c] 1,2,4-Triazole

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Synthesis of 3-ethoxy carbonyl 5-phenyl-1-*p*-tolyl 1,2,4-triazolo [3,4,-c] 1,2,4-triazole (**5a**) by reaction of 5-allylmercapto-5-phenyl 1,2,4-triazole (**3**) with ethyl chloroglyoxalate *p*-tolyl hydrazone (**4**) is described.

Key Words: Synthesis, 3-Ethoxy carbonyl 5-phenyl-1-*p*-tolyl 1,2,4-triazolo [3,4,-c] 1,2,4-triazole

1,2,4-Triazole derivatives have received considerable attention during the recent years due to their useful application in different areas of biological activity and as industrial intermediates. Some derivatives have tuberculo-therapeutic[1], antifungal[2], antinflammatory[3] and antibacterial activity[4] and other derivatives are used in agriculture as herbicide, fungicide and bactericide.

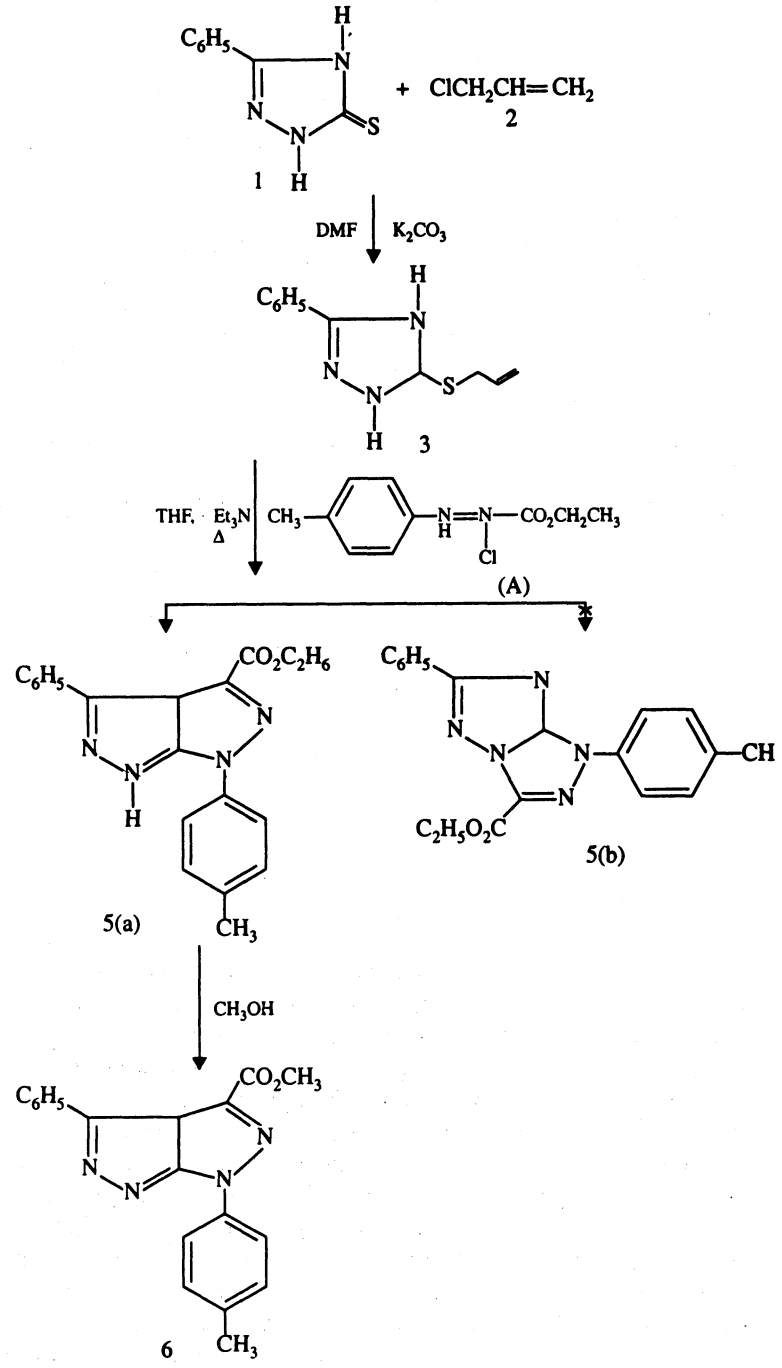
In view of this finding and in continuation of our studies in the same field, we report here in the synthesis of 3-ethoxy-carbonyl-5-phenyl-1-*p*-tolyl-1,2,4-triazolo [3,4,-c] 1,2,4-triazole (**5a**) susceptible to possess various pharmacological activities.

For this purpose 5-allylmercapto-5-phenyl-1,2,4-triazole (**3**) was chosen as suitable starting material. The starting compound 5-allylmercapto-5-phenyl-1,2,4-triazole (**3**) was synthesised by alkylation of 5-phenyl-1H (4H) 1,2,4-trizolo-5-thiones with allyl chloride (**2**) **(Scheme 1).**

IR spectra of (**3**) showed no (C=S) band absorption, but exhibited the (C=C) absorption band at 1630 cm^{-1} characteristic to allyl mercapto group. ^1H NMR spectrum in $CDCl_3$ revealed upfield at 7.9 to 8.55 ppm due to C_3 aromatic protons, whereas the signals corresponding to allylmercapto group were observed at δ 3.70, 5.12 and 5.95 ppm.

Cyclocondensation of allylmercapto-5-phenyl-1,2,4-triazole (**3**) with ethyl chloroglyoxalate *p*-tolyl hydrazone (**4**) in tetrahydrofuran containing triethylamine furnished product with m.f. $C_{19}H_{17}N_5O_2$ **(Scheme-1).**

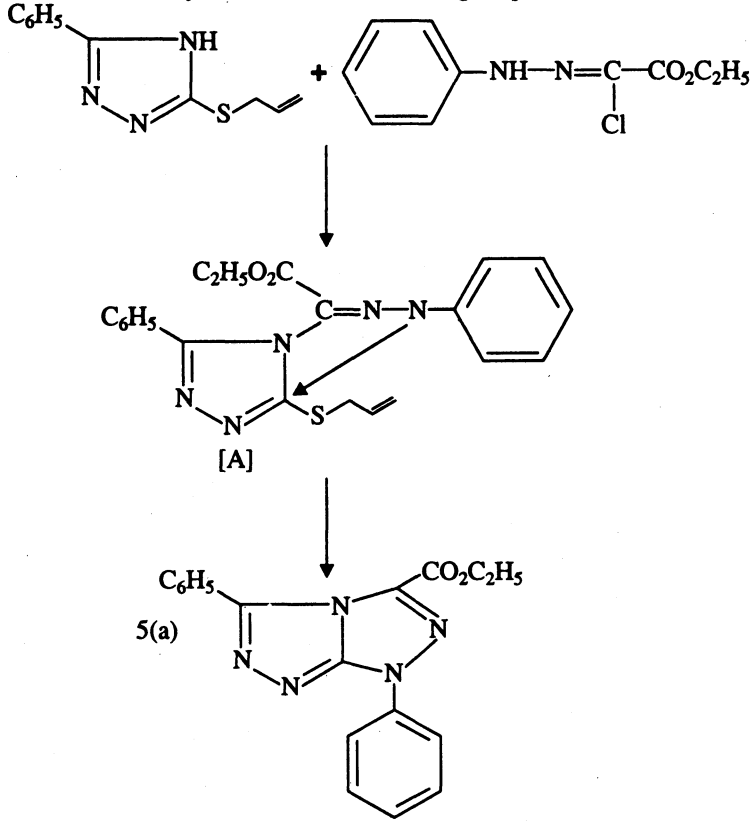
Two possible isomeric structures **5a** and **5b** are considered. Its formulation is assumed to proceed via substitution of the allylmercapto by heteroatom of hydrazidoyl chloride (**4**) followed by subsequent cyclization where the N_1 or N_4 of (**3**) was implicated. IR spectra of this compound revealed the (C=O) band


C6H5
H
N
N
N
S
1
H
+ ClCH2CH=CH2
2
DMF
K2CO3
C6H5
H
N
N
N
S
H
3
THF, Et3N
Δ
CH3
N=N
H
CO2CH2CH3
Cl
(A)
C6H5
CO2C2H6
N
N
N
H
5(a)
CH3
C6H5
N
N
N
N
CH
C2H5O2C
5(b)
CH3OH
C6H5
CO2CH3
N
N
N
6
CH3

Scheme-1

absorption of ester group at 1720 cm^{-1}. ^1H NMR spectrum showed in addition to signals of methyl phenyl group at δ 2.4 ppm, signals corresponding to C_3 phenyl protons at 7.9 to 8.55 ppm and those relative to ester group at δ 1.5 and 4.5 ppm.

The formation of compound **5a** is assumed to proceed *via* alkylation of triazole amino at position 4 by hydrazidoyl bromide giving rise to an intermediate [A], which undergoes an intramolecular cyclization by attack of arylamino on carbon at position 3 of triazole ring, followed by the loss of allyl-merkapto group **(Scheme-2).** It has been noticed that *trans*-esterification occurred when the compound **5a** was recrystallised in methanol to give product **(6) (Scheme-1).**



Scheme-2

In conclusion we have described a new way for synthesis of 3-ethoxy carbonyl 5-phenyl *p*-tolyl 1,2,4-triazolo [3,4,-c] 1,2,4-triazole **(5a)** from easily accessible starting material 5-phenyl-1H (4H) 1,2,4-triazole **(5)** thione **(1).**

IR spectra were recorded on Perkin-Elmer 577 spectrometer (KBr disks); ^1H NMR or Bruker AC 250 (250 MHz) spectrometer (chemical shifts are given in δ ppm downfield TMS internal standard).

Synthesis of 5-allylmercapto-5-phenyl-1,2,4 triazole (3)

To a solution of **1** (0.0017 mole) in 60 mL of NN-dimethyl formamide (DMF) was added an equimolar amount of K_2CO_3, allyl chloride and 0.0017 mole of

benzyl triethyl ammonium chloride. The mixture was stirred at room temperature for 24 h. The solution was filtered by suction filtration, the filtrate was evaporated off to afford a colourless product which after trituration in ether give an analytical pure sample yield 65%, ^{1}H NMR ($CDCl_3$): 3.5 (2H, d), 5.05 (1H, d), 5.2 (1H, d), 5.95 (1H, m); aromatic proton C_3 proton 7.95 to 8.55.

Synthesis of 3-ethoxy carbonyl-5-phenyl-1-*p*-tolyl 1,2,4-triazolo [3,4-c] triazole (5a)

A suspension of equal-molar amount (0.001 mole) of (3) and ethyl chloroglyoxalate *p*-tolylhyrazone (4) in THF 30 mL was treated with triethylamine (0.0012 mole) and the reaction mixture was refluxed for 24 h. The precipitated solid was filtered by suction filtration; the filtrate was evaporated off and the crude material was chromatographed over silica gel using a mixture of (ethyl acetate/hexane 40/60) as eluent to give product **5a**, yield 80%.

^{1}H NMR ($CDCl_3$) 7.29–8.55 (4H, m) 2.40 (3H, s) 1.50 (3H, t) 4.54 (2H, q) and C_3-phenyl proton (7.29–8.45 ppm, m).

ACKNOWLEDGEMENT

The authors are thankful to Prof. C.S. Panda, Head, Department of Chemistry, Berhampur University, Orissa and Roland Institute of Pharmaceutical Sciences for providing research facilities.

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(*Received*: 3 May 2002; *Accepted:* 28 September 2002) AJC-2876