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SYNTHESIS OF SOME 2-ARYL-SPIRO- [3'-ARYL-THIAZOLIDIN-2'THIONE 4' 5-1, 3,4-OXADIAZOLE [3,2, C] -THIAZOLINES AS FUNGICIDES

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ABSTRACT

Some 2-Aryl-spiro-3'-aryl-thiazolidin-2'-thione 4'5-[1, 3, 4] oxadiazole [3, 2-c] thiazolines have been synthesized by cyclisation of 3-Arylamido-spiro-[3'arylthiazolidin-2'-thione-4'2-thiazolidin -4-ones with conc. H_2SO_4. The compounds have been evaluated for their fungicidal activities against A. niger and H. oryzae.

Keywords: *1, 3, 4- oxadiazole, thiazoline, thiazolidin and spiro.*

Certain compounds having 1,3,4-oxadiazole nucleus have been reported as fungicidal[1,2] and bactericidal[3] and thiazolidines for their varied biological activities[4]. Therefore, it was planned to investigate a system which combines these two biolabile components in a ring together to give compact and planner structure such as I & II for screening their fungicidal activities against A. niger and H. oryzae.

EXPERIMENTAL

All melting points are uncorrected. I R spectra were recorded on a Perkin-Elmer, spectrophotometer (model 557) in KBr pellets and PMR spectra on Perkin-Elmer R-32 spectrometer in DMSO-d_6 using TMS as internal reference. Elemental analysis (C, H, N) were satisfactory. Procedure for one typical case for each step has been described [scheme-1].

3-Arylamido-spiro [3'-aryl-thiazolidin-2'-thione-4'2-thiazolidin-4-ones. I_a

3-Aryl-4 substituted aryl hydrazino-thiazolidin-2-thione (0.01M) and mercapto acetic acid (0.15 M) were refluxed in dioxane (20.0 ml) for 4h. the reaction mixture after cooling poured into water and finally neutralized by $NaHCO_3$. The resulting solid was filtered, washed and recrystallized from ethanol to give I_a.

IR (KBr): 3500(-OH), 3250 (-NH), 1720, 1640 (> C=0 gps), 1120 (>C=S), 1590, 1490, 1400 cm^{-1} (aromatics).

PMR (DMSO-d_6) **δ**: 3.2 (s, 4H-S-CH_2), 6.0-6.7 (m, 8H, ArH), 9.2 (b, 2H, NH).

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2-Aryl-spiro-[3'-aryl thiazolidine-2'-thiones 4', 5 – [1,3,4] -oxadiazole-(3,2-c) thiazolines] II_a

The requisite 3-arylamido spiro-[3'-aryl-thiazolidin-2'-thione-4', 2- thiazolidine]-4-one (I) (.01M) was added slowly to the cone. H_2SO_4 (0.015M) in cold. It was kept for an hour at room temperature. Then in the resulting mass water was added and neutralized by liquid ammonia. The solid product thus obtained was filtered and recrystallized with ethanol to give II_a.

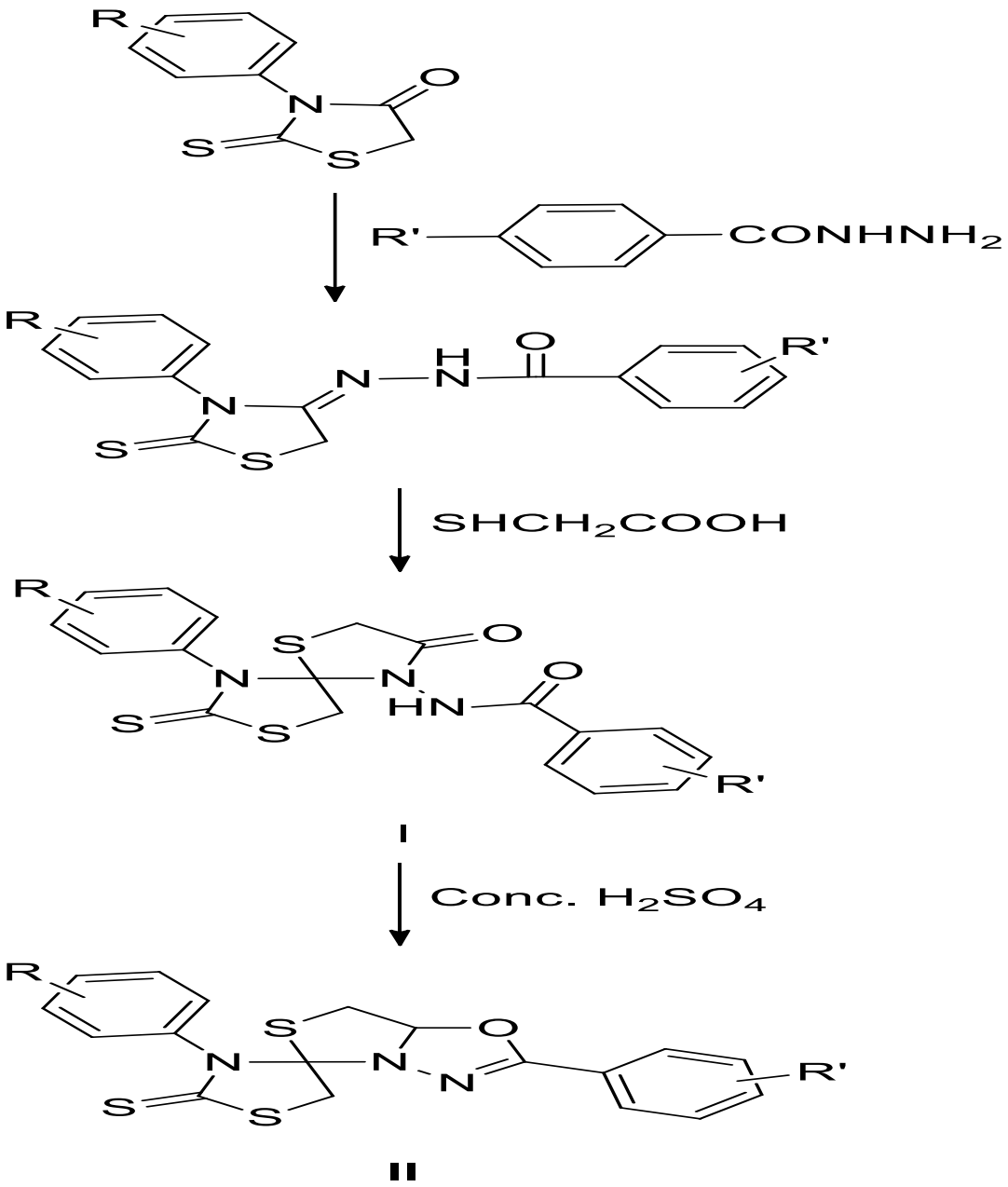
IR (KBr): 3520 (-OH), 1120 (>C=S), 1600, 1490, 1400 cm^{-1} (aromatic)

PMR- (DMSO-d_6) **δ**: 3.4 (s,1H -CH_2), 4.2 (s, 1H-CH), 6.2-7.8 (m, 8H, Ar-H)

FUNGICIDAL ACTIVITY

The fungicidal activity of I a-e and II a-e was evaluated by Agar growth technique[5] at 500, 100 and 10 ppm concentrations against the fungi. A. niger and H. orygae using Dithane M-45 a commercial fungicidal, as standard. The results are recorded in Table 1.

All the compounds exhibited moderate fungitoxicity which decreased on dilution. Compound II_d showed the highest activity (86% at 500 ppm and 66% at 10 ppm) which was quite comparable to that of commercial fungicide. Dithane M-45 (95% of 500 ppm and 72% at 10 ppm) tested under similar condition. Further investigation of this compound on wider range of fungi as well as at more dilution is desirable.



I

II

Scheme 1

a: R = H, R' = 2-OH
b: R = 4-CH_3, R' = 4-OCH_3
c: R = 4-CH_3, R' = 4-CH_3
d: R = H, R' = 2,4-Cl_2
e: R = H, R' = 2-Cl

Table-1: Fungicidal activity of compound II

Compound	Percentage Inhibition after 96 h. Organisms : A. niger H. oryzae Cove used					
	500 ppm	100 ppm	10 ppm	500 ppm	100 ppm	10 Ppm
II_a	62	55	45	65	54	42
II_b	64	58	55	60	50	40
IIc	75	70	65	72	68	55
II_d	86	79	68	85	80	70
II_e	80	65	60	82	69	58

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