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Synthesis of Thiadiazole Zineb

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Abstract

Abstract: In this paper, a series of 2-amino-5-alkyl-1, 3, 4-thiadiazole zineb were prepared by reacting 2-amino-5-alkyl-1, 3, 4-thiadiazole, CS_2 and $ZnCl_2$. Its synthesis conditions was discussed. The optimal conditions were obtained as follows: reaction time 120 min, reaction temperature 30℃, molar ratio n (thiadiazole): n (zinc chloride): n (CS_2): n (NaOH) = 1:1:1.05:1.05, the products was synthesized in water. All compounds were characterized by elemental analysis, Infrared (IR)analysis to determine their structure.

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Key words: 2-amino-5-alkyl-1,3,4-thiadiazole zineb; carbon disulfide; sodium hydroxide; synthetic

1. Introduction

According to the analysis of experts in German Federal Institute of Biology (OBBA) and the National Research Council (NRC), in this century, chemical pesticides are still the theme of global plant protection. Currently, new methods and new concepts about pest control continue to emerge, Pesticides containing heterocyclic will be the main direction[1].

1,3,4-thiadiazole is a kind of five-membered heterocyclic compounds containing S,N heteroatom, the 2,5 position on 1,3,4-thiadiazole and its derivatives substituted can participate in many Chemical reactions, they are often introduced into the pesticide molecule as the active groups, which is a hot topic in academic research of modern agriculture[2-3].

Dyson zinc is a broad-spectrum protection of organic sulfur fungicides used for spraying with foliar, the chemical properties of those active ingredients are more active, easily oxidized into cyanogen isothiocyanate compounds in the water, Which has a strong base Inhibition on the enzyme containing-SH in the pathogen body, and can directly kill the bacteria spores and inhibit germination of spores and

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prevent bacteria invading plants, However, it has a small killing effect on pathogen filaments that have invaded the body of plant[4-5].

This article is to integrate the thiadiazole structure and on behalf of the Forest Science zinc structured together with reasonable scientific, combine four kinds of synthetic of Dyson thiadiazole zinc, shown in Figure 1. To get the best plant fungicides, thus greatly enhance the efficacy and delay the production of drug-resistant bacteria.

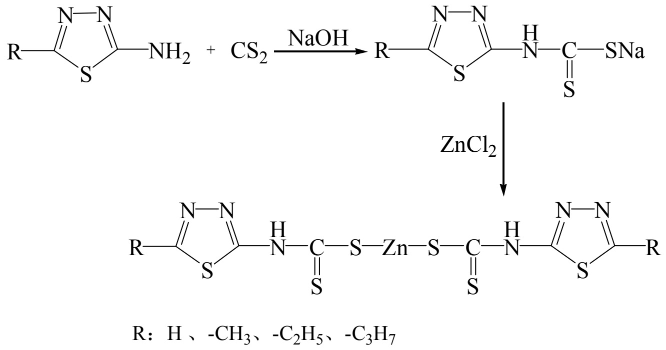

Fig1 the synthesis procedure of 2-Amino-5-aryl-1, 3, 4-thiadiazole zineb

2 Discussion

2.1 The choice of solvent

The compounds like 2-amino-5-alkyl-1,3,4-thiadiazole soluble in alcohols, water and pyridine, using ethanol as solvent, the product is always mixed with a small amount of orange-red solid, whose nature t is very similar with the product and its difficult to separate them. it may be the reaction processit of the reaction of carbon disulfide and ethanol by-product of the reaction system.

Use pyridine as solvent, 2-amino-5-alkyl-1, 3, 4-thiadiazole compounds solubility in pyridine, is too small, and the excess pyridine the reaction system, easily separated.

According to the results, of 2-amino-5-alkyl-1, 3, 4-thiadiazole has a better solubility in the aqueous solution in 30℃. Therefore, this experiment choose water as a solvent. it is easily separated, economical and environmentally friendly.

2.2 Effect of CS2

In this study, using water as solvent, n (thiadiazole): n (zinc chloride): n (Na0H) = 1:1:1.05 (mol ratio), adding CS_2 for 45min, reaction time is 180min, and the reaction temperature is 30℃. With the molar ratio increase of CS_2 and thiadiazole indicates the raw materials ratio on the yield of one-way. The results are in Table 1.

Tab.1 Effect of reactant mole ratio method on productive rate

$n(CS_2)$:n(thiadiazole)	1.0	1.05	1.10	1.15	1.20
yield/%	89	92	91	89	82

Seen from Table 1, the molar ratio of CS_2 and thiadiazole on the reaction yield is not affected too much. With the molar ratio increases, the yield increased, when the ratio increased to 1.05 , the yield is highest ,so the most appropriate response Molar ratio is 1.05.

2.3 Effect of NaOH

In this study, using water as solvent, n (thiadiazole): n (zinc chloride): n (CS_2) = 1:1:1.05 (mol ratio), adding CS_2 time for 45min, reaction time is 180min, and the reaction temperature is 30℃ .With the changes of molar ratio of NaOH thiadiazole, research materials ratio on the yield of one-way. The results are in Table 2.

Tab.2 Effect of reactant mole ratio method on productive rate

n(NaOH):n(thiadiazole)	1.0	1.05	1.10	1.15	1.20
yield/%	87	90	90	87	75

Seen from Table 2, with the molar ratio increases, the yield increase, but to a certain molar ratio the yield will not increase. The excess of NaOH will lead to high alkali content in products, with the situation; there are by-products, $Zn(OH)_2$ precipitation in the subsequent reaction. So the most suitable mole ratio is 1.05.

2.4 Effect of reaction time

In this study, using water as solvent, n (thiadiazole): n (zinc chloride): n (CS_2): n (Na0H) = 1:1:1.05: 1.05 (molar ratio), the addition time of CS_2 is 45min; the reaction temperature is 30℃. By changing the heat of reaction time, study the effect of react time on productive rate. The results are in Table 4.

Tab.3 Effect of react time on productive rate

react time /min	90	120	150	180	210
yield/%	79	84	88	92	92

As can be seen from Table 3, with the reaction time increases, the yield increased. After the reaction time increases more than 120min, the increase yield is not obvious. So the best reaction time is 120min

2.5 Effect of reaction temperature

In this study, using water as solvent, n (thiadiazole): n (zinc chloride): n (CS_2): n (Na0H) = 1:1:1.05: 1.05 (molar ratio), the addition time of CS_2 is 45min, reaction Time is180min. Changing the reaction temperature, study the eeffect of react temperature on productive rate on the yield of one-way. The results are in Table 5.

Tab.4Effect of react temperature on productive rate

reaction temperature /℃	15	20	25	30	35
yield/%	77	82	88	90	89

As can be seen from Table 4, with the reaction temperature increased, the yield increase, but the yield will decline to a certain percentage. It is because that the temperature of the reaction will rise when carbon disulfide is being dropped, the reaction temperature should not exceed 40℃, the heat reaction time can not exceed 40℃ in the reaction system. The product is unstable at high temperature; the temperature is too high as to cause product decomposition. Therefore, the optimum reaction temperature is 30℃.

3 Experimental

In a flask with a reflux condenser (pick a drying tube), dropping funnel, dropped by the quantitative increase of 2-amino-5-alkyl-1, 3, 4-thiadiazole, Na0H solution successively, heating, stirring dissolved. When the temperature turn to 30℃, dropping CS_2 slowly, when dropping, controlling the speed, the reaction temperature is maintained at a certain range. When the dropping of CS_2 is finished, stirring constantly, detecting the reaction by thin layer chromatography (ethyl acetate). After the completion of the reaction, stirring cooled to room temperature, adding quantitative $ZnCl_2$ solution, 30min reaction is completed, filtration, drying the products.

A: $C_6H_4N_6S_6Zn$

Pale yellow solid, Yield: 95.4%; IR (KBr, cm^{-1}): 3308($\upsilon_{N\text{-}H}$); 1609($\upsilon_{C=N}$); 1045($\upsilon_{C\text{-}S\text{-}C}$); 1425($\upsilon_{N\text{-}C}$); 1217($\upsilon_{C=S}$); 916($\upsilon_{C\text{-}S}$); 522($\upsilon_{S\text{-}Zn}$); Anal.Calcd .for $C_6H_4N_6S_6Zn$:C,17.24%; H,0.96%; N,20.11%; Found:C,17.26%; H,1.02%; N,20.02%.

B: $C_8H_8N_6S_6Zn$

Pale yellow solid, Yield: 94.1%; IR (KBr, cm^{-1}): 3413($\upsilon_{N\text{-}H}$); 1616($\upsilon_{C=N}$); 1081($\upsilon_{C\text{-}S\text{-}C}$); 1429($\upsilon_{N\text{-}C}$); 1199($\upsilon_{C=S}$); 981($\upsilon_{C\text{-}S}$); 524($\upsilon_{S\text{-}Zn}$); Anal.Calcd .for $C_8H_8N_6S_6Zn$:C,21.55%; H,1.81%; N,18.84%; Found:C,21.63%; H,1.73%; N,18.89%.

C: $C_{10}H_{12}N_6S_6Zn$

Pale yellow solid, Yield: 90.1%; IR (KBr, cm^{-1}): 3287($\upsilon_{N\text{-}H}$); 1610($\upsilon_{C=N}$); 1034($\upsilon_{C\text{-}S\text{-}C}$); 1430($\upsilon_{N\text{-}C}$); 1180($\upsilon_{C=S}$); 921($\upsilon_{C\text{-}S}$); 525($\upsilon_{S\text{-}Zn}$); Anal.Calcd .for $C_{10}H_{12}N_6S_6Zn$:C,25.34%; H,2.55%; N,17.73%; Found:C,25.46%; H,2.53%; N,17.85%.

D: $C_{12}H_{16}N_6S_6Zn$

Pale yellow solid, Yield: 90.3%; IR (KBr, cm^{-1}): 3376($\upsilon_{N\text{-}H}$); 1610($\upsilon_{C=N}$); 1047($\upsilon_{C\text{-}S\text{-}C}$); 1459($\upsilon_{N\text{-}C}$); 1177($\upsilon_{C=S}$); 973($\upsilon_{C\text{-}S}$); 525($\upsilon_{S\text{-}Zn}$); Anal.Calcd .for $C_{12}H_{16}N_6S_6Zn$:C,28.71%; H,3.21%; N,16.74%; Found:C,28.75%; H,3.29%; N,16.68%.

4 Results

This article includes four products that were prepared: when the products are the 2-amino-5-alkyl-1,3,4-thiadiazole as H for the alkyl, used A for the representation; when the products are the 2-amino-5-alkyl-1,3,4-thiadiazole as CH_3- for alkyl ,expressed with B; when the products are 2-amino-5-alkyl-1,3,4-thiadiazole as C_2H_5- for alkyl ,Indicated by C; when the products are the 2-amino-5-alkyl-1,3,4 -thiadiazole as C_3H_7- for the alkyl, expressed with D. All the products were characterized by IR and elemental analyses.

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