Synthesis, plant growth regulating activity and herbicide antidote activity of new pyrano[2,3-d]pyrimidines

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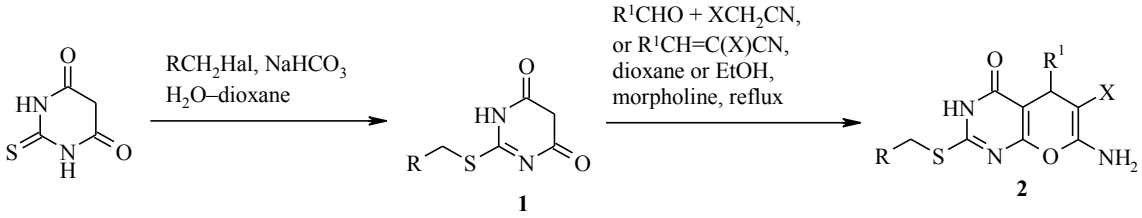
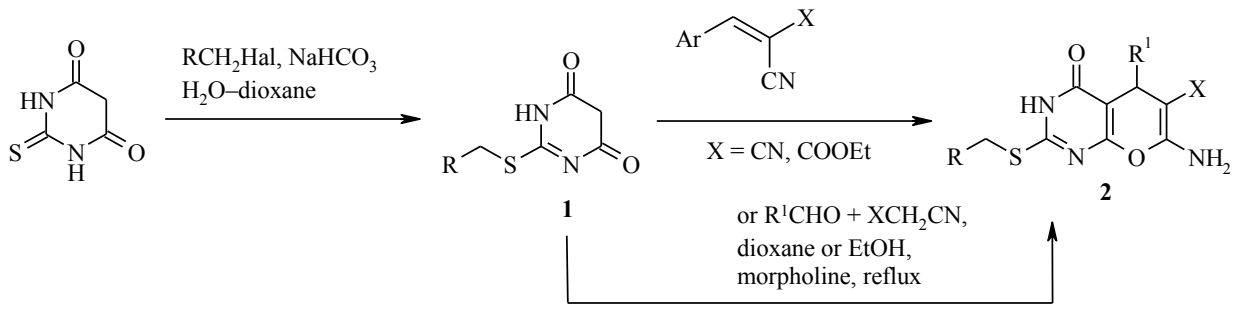
Abstract: The reaction of S-alkyl thiobarbiturates with aromatic aldehydes and malononitrile (or arylmethylidenemalononitrile) leads to hitherto unknown 4H-pyrano[2,3-d]pyrimidines. Plant growth regulating activity and herbicide antidote activity were studied in the series of the obtained compounds. We found that ethyl {[7-amino-6-cyano-5-(4-methoxyphenyl)-4-oxo-3,5-dihydro-4H-pyrano[2,3-d]pyrimidin-2-yl)thio}acetic acid revealed moderate activity as 2,4-D antidote.

Keywords: S-alkyl thiobarbiturates, 4H-pyrano[2,3-d]pyrimidines, NMR studies, plant growth regulating activity, herbicide antidote activity.



1 **2**

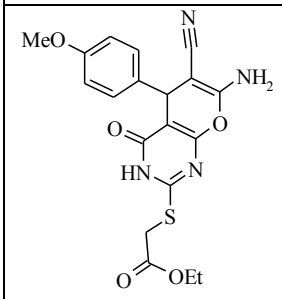
Barbituric acids belong to the practically important group of pyrimidine compounds. Several barbituric acids showed antiviral, fungicidal and bactericidal activity due to antagonism with the pyrimidine bases. The chemistry of barbituric acids and their structural analogs, thiobarbituric acids, have been reviewed in details [1-5]. However, the survey of literature reveals a little information about the reactions of S-alkyl thiobarbituric acids as methylene compounds. Meanwhile, S-alkyl thiobarbituric acids are easily available, and their structural features make them very promising candidates for the use in the synthesis of biologically active compounds. S-alkyl thiobarbituric acids **1** could be readily prepared by treatment of thiobarbituric acid with alkyl halides in aqueous dioxane or aqueous-EtOH solution in the presence of a base ($NaHCO_3$, NaOH) (Scheme 1).



R = CO_2Et, Ph, $CH=CH_2$, $(CH_2)_nCH_3$; R^1 = Ar, 3-Py, i-Pr; X = CN, CO_2Et.

We found that the products of S-alkylation **1** reacted as typical active methylene compounds. Thus, three-component condensation with active methylene nitriles (malononitrile or ethyl cyanoacetate) and aldehydes leads to the formation of pyrano[2,3-d]pyrimidines **2** (Scheme 1). Somewhat bigger yields were obtained when 3-arylacrylonitriles were reacted with pyrimidines **1**. We have studied the action of a number of the compounds **2** as sunflower growth regulators, as well as antidotes for 2,4-D. The results obtained for compound **2a** (R = CO_2Et, R^1 = 4-$CH_3OC_6H_4$, X = CN) (as a typical representative compound) are presented in Tables 1 and 2.

Table 1. Test results for **2a** as growth regulators on sunflower seedlings

Compound	Estimated	Control	Concentration, %							
			10^{-2}		10^{-3}		10^{-4}		10^{-5}	
		A	A	B	A	B	A	B	A	B
 **2a**	By hypocotyl length	84	53	63	76	90	79	94	81	96
	By root length	158	53	35	102	65	121	77	131	83

A – hypocotyl length in mm

B – hypocotyl length in % with respect to A.

Table 2. Test results of **2a** as antidotes for 2,4-D

Compound	Estimated	Control	Herbicide (reference)		Concentration, %							
					10^{-2}		10^{-3}		10^{-4}		10^{-5}	
		A	A	C	A	B	A	B	A	B	A	B
2a	By hypocotyl length	85	48	44	44	92	51	106	48	100	62	103
	By root length	157	60	62	59	98	69	115	63	105	80	134

A – hypocotyl length in mm

B – hypocotyl length in % with respect to A.

It can be seen that compound **2a** reveals no plant growth regulating activity, but acts as 2,4-D antidote in low concentrations.

References

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