Chinese Chemical Letters Vol. 15, No. 10, pp 1167-1169, 2004
http://www.imm.ac.cn/journal/ccl.html

Simple, Mild and Convenient Synthesis of Two Novel N-Dichloroacetyl Oxazolidines and their Biological Activities

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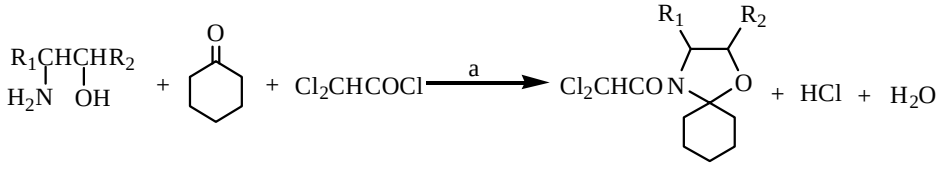
Abstract: Two N-dichloroacetyl oxazolidines were synthesized with a simple, mild and convenient method. All the compounds were characterized by IR, ^{1}HNMR and elemental analysis. The preliminary biological test showed that the compounds protected maize against injury by some herbicides to some extent.

Keywords: Herbicide safener, oxazolidines, synthesis.

Herbicide safeners selectively protect crop plants from herbicide damage without reducing activity in target weed species. These compounds have been considerable interested since their discovery 50 years ago. N-Dichloroacetyl oxazolidines, being a novel kind of herbicide safeners, can protect crop plants against injury by thiocarbamate and chloroacetanilide herbicides and some of these compounds also showed potential in protecting crops from toxicity due to sulfonylurea or imidazolinone herbicides[1,2].

A series of N-dichloroacetyl oxazolidines have been synthesized in order to investigate the relationship between their chemical structures and biological activity[3]. The title compounds are novel N-dichloroacetyl oxazolidines. The synthetic route of compounds **1a~b** is shown in **Scheme 1**[4].

Scheme 1



a)NaOH

1a~b

1a, R_1=C_2H_5, R_2=H
1b, R_1=H, R_2=$CH_2CH_2CH_3$

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The preparation of compounds **1a~b**: 0.034 mol of amino alcohols and 3.5 mL (0.034 mol) of cyclohexanone were mixed with 20 mL of benzene and stirred for 1 hr at 33~35°C. The reaction mixture was chilled at 0°C and 3.8 mL of 33% NaOH aq. solution was added. 3.9 mL of dichloroacetyl chloride was dropped slowly, maintaining the temperature at 0°C. Stirring was continued for 1 hr. The organic phase was washed with water until pH=7. Benzene and water were distilled off. White crystal was obtained.

The preliminary test of biological activity: Maize (Dongnong 248) seeds, untreated and treated with compound **1a~b**, were planted 1.5 cm deep in plastic trays, in which soil was treated with herbicide of different concentration. Trays were incubated at 28°C for 6 days. The plant height and content of GSH were evaluated according to the method of Gronwald [5].

The preliminary test of biological activity indicated that the plant height of maize could be elevated by these compounds (**Table 1**). 50 mg/kg of compound **1a** increased the height of maize by 9.2%, while 50 mg/kg of compound **1b** elevated that of maize by 9.8%, when the concentratiom of acetochlor was 3.000 kg/hm^2. Initial studies on the mechanism of the protective effect of these compounds as herbicide safener indicated that the title compounds could elevate GSH **(Table 2)**. The level of GSH was increased by 7% and 11% with 50 mg/kg of compound **1a** and 30 mg/kg of compound **1b**, respectively, when the concentratiom of acetochlor was 3.000 kg/hm^2. The biological activities of these compounds are being further studied.

Table 1 The influence of the herbicide safeners upon the height of maize

Herbicide safener (mg/kg)		acetochlor (kg/hm^2)			
		2.250	2.625	3.000	3.375
		Height of maize(cm)			
	0	9.75	9.45	8.65	7.89
1a	15	9.75	9.58	8.90	8.09
	30	9.65	9.70	9.10	7.80
	50	9.85	9.82	9.45	8.23
1b	15	9.90	9.76	9.05	8.86
	30	9.70	9.76	9.30	9.15
	50	9.90	9.60	9.50	8.85

Table 2 The influence of the herbicide safeners upon GSH in maize*

Herbicide safener (mg/kg)		acetochlor (kg/hm^2)			
		2.250	2.625	3.000	3.375
		Glutathione content(nmol/g,%contrast)			
	0	103.30	93.40	84.91	75.00
1a	15	99.06	91.98	84.91	80.19
	30	96.70	94.81	89.15	82.55
	50	104.25	95.75	91.04	77.83
1b	15	108.49	103.30	103.30	94.34
	30	103.30	98.58	94.34	88.68
	50	91.98	89.15	83.02	81.60

*GSH: glutathione

Ackowledgment

We are grateful to the National Natural Science Foundation of China (No. 30171069) and Innovative Plan from Backbone of General Universities' Teachers in Heilongjiang Province for financial support for this work.

References and Notes

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6. **1a:** Yield 55.08%; mp: 100-102°C; IR(KBr,cm^{-1}): 2938(m, C-H), 1663(s, C=O), 1134(m, C-N); ^{1}HNMR($CDCl_3$,400MHz, δ ppm): 6.07(s, 1H, Cl_2CH-), 3.78 (m, 1H, N-CH-), 3.907 (d, 2H, J=3.9Hz, -CH_2-O-), 1.238-1.842 (m, 12H, 6CH_2-), 0.967 (t,3H,J=6.0Hz,CH_3-); Anal. Calcd. for $C_{12}H_{19}Cl_2NO_2$: C, 51.44; H, 4.999; N, 6.835. Found: C, 51.55; H,5.074; N, 6.590. **1b:** Yield 63.38%; mp: 102~104°C; IR(KBr,cm^{-1}): 2934(m, C-H)，1674(s, C=O)，1190(m, C-N). ^{1}HNMR($CDCl_3$,400MHz, δ ppm): 6.04 (s, 1H, Cl_2CH-), 3.89 (d, 2H, J=3.9Hz, N-CH_2-), 3.25 (m, 1H, -CH-O-), 1.47-2.62 (m, 14H, 7CH_2-), 0.975(t, 3H, J=6.0Hz,CH_3-). Anal. Calcd. for $C_{13}H_{21}Cl_2NO_2$: C, 53.07; H, 7.194; N,4.761. Found: C, 53.19; H, 7.250; N, 4.779.

Received 8 September, 2003