한국농약과학회지 제4권 제3호(2000)
The Korean Journal of Pesticide Science
Vol. 4, No. 3, pp.89~92(2000)

〈 단 보 〉

Synthesis and Herbicidal Activity of Cyclohexane-1,3-diones: Rice Selective 5-(2-alkyl-2-methylindanyl)cyclohexane-1,3-dione herbicides under paddy submerged conditions

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Abstract : A series of 5-(2-methyl-2-alkylindanyl)cyclohexane-1,3-diones were synthesized and evaluated for herbicidal activities in a green house. Under submerged paddy conditions, those compounds showed high herbicidal activity against barnyardgrass with good tolerance on rice.(Received July 10, 2000; accepted Sep. 15, 2000)

Key words : 5-Phenylcyclohexane-1,3-dione, ACCase inhibitor, herbicide, rice, barnyardgrass.

The oximated 2-acyl-cyclohexane-1,3-diones have been known as acetyl coenzyme A carboxylase (ACCase) inhibiting herbicides (Burton et. al., 1987). These herbicides are of interesting compounds showing selectivity on the control of monocotyledonous weeds in dicotyledonous crops (Iwataki and Hirono, 1979). Recently, it has been found that certain 5-aryl substituted cyclohexane-1, 3-dione derivatives exhibited useful cereal selective herbicidal activity. For example, tralkoxydim, which has 2,4,6-trimethylphenyl moiety on 5 position of cyclohexane-1,3-dione, has been paid attention by their excellent herbicidal selectivity between cereals and grass weeds (sutton et .al., 1987).

Also, in 1990, ICI disclosed a patent covering 5-indanyl and 5-tetrahydronaphthalenyl substituted cyclohexane-1,3-diones without mentioning the selectivity between rice and barnyardgrass in paddy-submerged circumstances (Serban et. al., 1985).

In our program to develop new cyclohexane-1,3-dione herbicide, we have found that 5-(substituted-2,2-dimethylbenzofuran-5-yl)cyclohexane-1,3-diones showed excellent herbicidal activities on barnyardgrass with good tolerance on rice (Ryu et. al., 1997). Those results encouraged us to investigate the herbicidal activity of 5-(2,2-dialkylindanyl)cyclohexane-1,3-diones in which oxygenatom on benzofuranyl moiety is replaced by CH_2.

2-Alkyl-2-methylindan-1,3-diones (**2**) were prepared by treatment of two equivalent of $AlCl_3$ to a mixture of substituted benzene and alkylmethylmalonyl chloride in dry methylene chloride at 10 °C (Woltersdorf et. al., 1984). Reduction of 2-alkyl-2-methylindan-1,3-diones (**2**) to 2-alkyl-2-methylindanes (**3**) was carried out in the presence of zinc-mercury amalgam in 20 % of hydrochloric acid (Clemensen reduction) to afford good yields of desired reduction product **3.** However, the reduction of **2** using hydrazine alcoholic KOH (Wolff-Kishiner's procedure) turned to be unsuccessful (**Scheme 1**).

Adapting those methods and procedures described in the previous report (Ryu et. al., 1998), several types of oximated 2-acyl-5-(2-alkyl-2-methylindanyl)cyclohexane-1,3-dione were prepared (**Scheme 2**).

For the herbicidal evaluation, plant species to be tested were grown to two to three leaf stages. Seeds of pre-germinated *Oryza sativa L.* and dry seeds of various plants were sown in white plastic pots filled with sandy loam soil in the green house. A solution of herbicides was prepared by dissolving test compound in 50 % of acetone containing 0.2 % of Tween-20, and applied in a spray volume of 4,000 L/ha at 8-12 days after seeding. Herbicidal activities were determined fourteen days after treatment and recorded as percent control on a scale 0 to 100, where 0 indicated no visible effect and 100 indicated complete killing of plants. The results of the herbicidal activities were summarized in **Table 1.**

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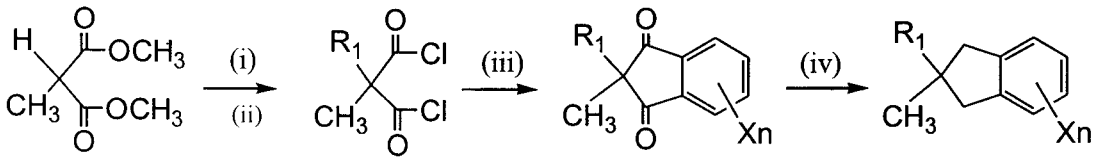


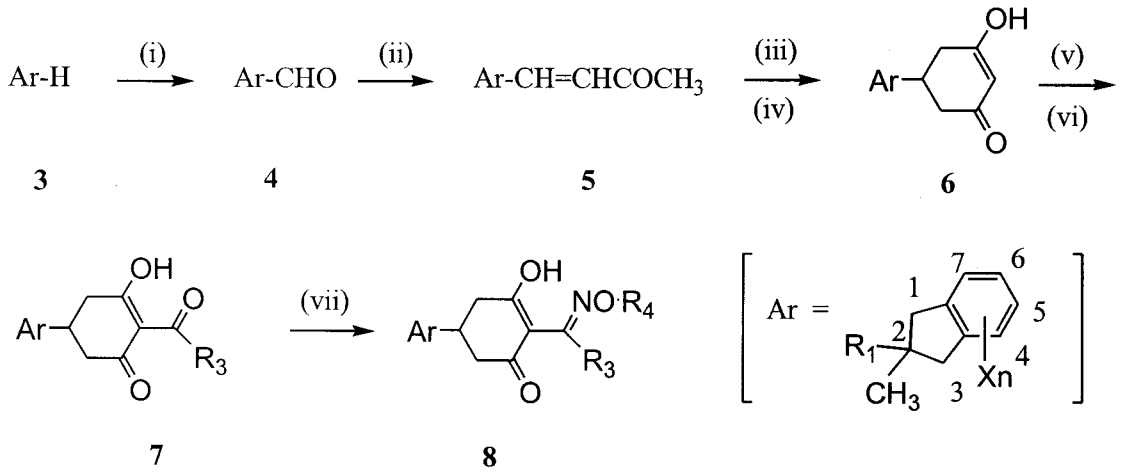
1 2 3

$R_1 = CH_3$,	Xn = 4,5,7-trimethyl	**2a** = 75 %	**3a** = 81 %
$R_1 = CH_3CH_2$,	Xn = 4,5,7-trimethyl	**2b** = 93 %	**3b** = 72 %
$R_1 = CH_3$	Xn = 5-chloro-4,7-dimethyl	**2c** = 96 %	**3c** = 72 %
$R_1 = CH_3CH_2$,	Xn = 5-chloro-4,7-dimethyl	**2d** = 82 %	**3d** =60 %
$R_1 = CH_3$,	Xn = 7-chloro-4,5-dimethyl	**2e** = 83 %	**3e** =52 %
$R_1 = CH_3CH_2$,	Xn = 7-chloro-4,5-dimethyl	**2f** = 75 %	**3f**= 42 %

Conditions: (i) NaOMe, R_1X (ii) 10 % NaOH, H_2O-MeOH (iii) $SOCl_2$ (iii) $AlCl_3$ (2 equiv.), CH_2Cl_2 (iv) Zn/Hg, conc. HCl, ethanol.

Scheme 1. Preparation of 2-alkyl-2-methylindan-1,3-diones **2** and 2-alkyl-2-methylindanes **3**.

When the substituted 2-alkyl-2-methylindanyls (**3**) were introduced into the 5-position on the cyclohexane-1,3-dione skeleton, the interesting herbicidal activity and selectivity were observed. By foliar treatment in green house, the compounds **8a-8l** exhibited typical post-emergent herbicidal activities on monocotyledonous plants such as fall panicum, large crabgrass, barnyardgrass, wheat, common sorgum, barley, and rice at rates of 250 $g.ha^{-1}$ with good tolerance to dicotyledonous plants. Surprisingly, under the submerged paddy conditions, the compounds **8a-8l** showed excellent herbicidal activity against barnyard-



3 4 5 6

7 8

Conditions: (i) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2 (ii) acetone, 5% aqueous NaOH (iii) diethyl malonate, NaOMe (iv) 5% NaOH and then 2 N HCl, heat (v) $(R_3CO)_2O$ (vi) DMAP (cat.), toluene (vii) $R_4ONH_2.HCl$, NaOAc, EtOH

Scheme 2. Preparation of 5-aryl cyclohexane-1, 3-diones.

Table 1. Herbicidal activity of 5-(2-alkyl-2-methyl-indanyl) cyclohexane- 1,3-diones 8 under submerged paddy conditions[a)]

Comp.	Ar	R3	R4	Rate (g · ha-1)	ORYSA[b)] (3-leaves)	ORYSA (seed)	ECHOR[c)]	Others[d)]
8a	3a	ethyl	methyl	125	900	100	100	0
				31	0	100	100	0
				8	0	70	95	0
				2	0	0	95	0
8b	3a	propyl	methyl	125	20	100	100	0
				31	0	100	100	0
				8	0	20	95	0
				2	0	0	95	0
8c	3b	ethyl	allyl	125	0	100	100	0
				31	0	50	100	0
				8	0	30	50	0
8d	3b	propyl	allyl	125	0	100	100	0
				31	0	20	95	0
8e	3c	ethyl	ethyl	125	20	100	100	0
				31	0	100	100	0
				8	0	0	95	0
8f	3c	propyl	rthyl	125	0	100	100	0
				31	0	20	100	0
8g	3d	ethyl	methyl	126	0	100	100	0
				31	0	30	60	0
h8	3d	propyl	ethyl	125	0	60	100	0
8i	3e	ethyl	ethyl	125	0	100	100	0
				31	0	100	100	0
				8	0	0	80	0
8j	3e	propyl	ethyl	125	0	100	100	0
				31	0	0	95	0
8k	3f	ethyl	ethyl	125	0	100	100	0
				31	0	30	70	0
8l	3f	propyl	ethyl	125	0	40	100	0

[a)]0 indicated no visible effect and 100 indicated complete killing of plants. [b)]ORYSA : *Oryza sativa* L. [c)]ECHOR : *Echinochloa crus-galli*. [d)]*Scipus jincoides* ROXB., *Monchoris vaginalis* PRESL., *Cyperus serotinus* ROTTB., and *Sagittaria pygmaea* MTQ.

grass with good tolerance to rice. Among them, the compound 8b showed excellent herbicidal activity against barnyardgrass with good tolerance on transplanted rice at a rate of 2-125 g.ha^{-1}. However, the herbicidal spectrum was limited to show no herbicidal activity on *Scirpus jincoides* ROXB., *Monochoris vaginalis* PRESL., *Cyperus serotinus* ROTTB., and *Sagittaria pygmaea* MTQ. at a rate of 500 g.ha^{-1}.

The effect of substituents on 2-position of indanyl moieties was studied. The introduction of 2,2,4,5,7-pentamethylindanyl moiety to the 5 positions of cyclohexane-1,3-dione exhibited the excellent herbicidal activities on barnyardgrass (compounds **8a** and **8b** in **Table 1**).

However, the introduction of 2-ethyl-2-methyl groups to indanyl moiety diminished herbicidal activity. Also, introduction of chlorine atom to the indanyl moiety did not increase herbicidal activity. Evaluation of herbicidal activity in a green house indicated that the compound **8b** showed most control of barnyardgrass in 5-15 days after transplantation at rate of 8-125 g/ha.

In conclusion, 5-(2-alkyl-2-methylindan-6-yl)cy-clohexane-1,3-diones showed a high herbicidal activity and selectivity between rice and barnyardgrass under submerged paddy conditions. Among them, **8b** gave the most excellent activity against barnyardgrass with good tolerance on transplanted rice.

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담수조건에서 벼에 선택적인 5-(2-alkyl-2-methylindanyl)cyclohexane-1,3-dione 유도체의 합성과 제초활성

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요약 : 제초제 후보물질로서 5-(2-methyl-2-alkylindanyl)cyclohexane-1,3-dione 유도체를 합성하여 제초활성을 온실조건에서 평가하였다. 담수 조건에서 이 화합물들은 3 엽기의 이앙벼에 대해 안전하면서 논피에 대해 높은 제초활성을 보였다.

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