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Synthesis and herbicidal properties of vinylsulfonylphenyl triketones and their related derivatives

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Abstract : Several vinylsulfonylphenyl triketones and 2-alkoxy- and 2-(*N,N*-diethylamino) ethanesulfonylphenyl triketones have been synthesized, and their herbicidal activities in flooded paddy field were studied. Herbicidal effects of vinylsulfonyl triketones **6a-c** were not satisfactory, whereas 2-alkoxyethanesulfonylphenyl triketones **7a** and **7b** showed good herbicidal activities without meaningful selectivity to rice.

Key words : vinylsulfonyl, triketone, herbicide.

Sulcotrione, triketone type herbicide (Michaely, 1984), have been evaluated to be a prospectable herbicide alternative to triazine-type herbicide by it's highly active to triazine-resisting smooth pigweed and other broad-leaf weeds, and good selectivity to corn (Wilson, 1990). This type herbicides have been known to kill weeds showing bleaching effect, accompanying with accumulation of phytoene and diminishing the content of chlorophyll and to have carotenoid (Soeda, 1987; Mayonado, 1989). It was reported that the molecular basis for the herbicidal activity of these herbicides is in their ability to competitively bind with the active site of 4-hydro- xyphenylpyruvate dioxygenase (Schulz, 1993). Up to now, only two herbicides, sulcotrione and NTBC, of the triketone type compounds have been commercialized.

We were interested in preparing triketone type compounds substituted with vinylsulfonyl group in place of methansulfonyl group of *sulcotrione* for the development of rice herbicide, because we found that phenyl vinylsulfones showed a significant herbicidal effect especially to barnyardgrass, nonetheless safe to rice in flooded paddy conditions (Sung, 1995). The compounds **7a-c** were readily obtained by the Michael-type addition either of alkoxides or amines to the vinylsulfonyl group of vinylsulfonyl triketones, and their herbicidal activities were evaluated in flooded paddy conditions.

Scheme 1 outlines the synthesis of vinylsulfonylphenyl triketones **6** and **7**. Hydroxyethylsulfide **3** was prepared through the nucleophilic substitution of nitro group of **1** with 2-mercaptoethanol followed by hydrolysis of the ester group of **2** with lithium hydroxide at room temperature. Triketones, **5a-c** and **6** were obtained by the coupling reaction of 1,3-dicyclohexanones with acyl chloride **4**, prepared by refluxing **3** with thionyl chloride, and then *in situ* 1,3-migration reaction of benzoyl group was performed using acetonecyanohydrine (Montes, 1996; Ueda, 1992). The sulfides in **5** were oxidized by *m*-CPBA, and then dehydrochlorination by the treatment triethylamine of gave the vinylsulfonyl triketones **6a-c** in good yields. Vinylsulfonyl triketones **6** could be transformed to 2-alkoxy-, or 2-(*N,N*- diethylamino)ethanesulfonylphenyl triketones **7a-c**, respectively, by the Michael-type addition

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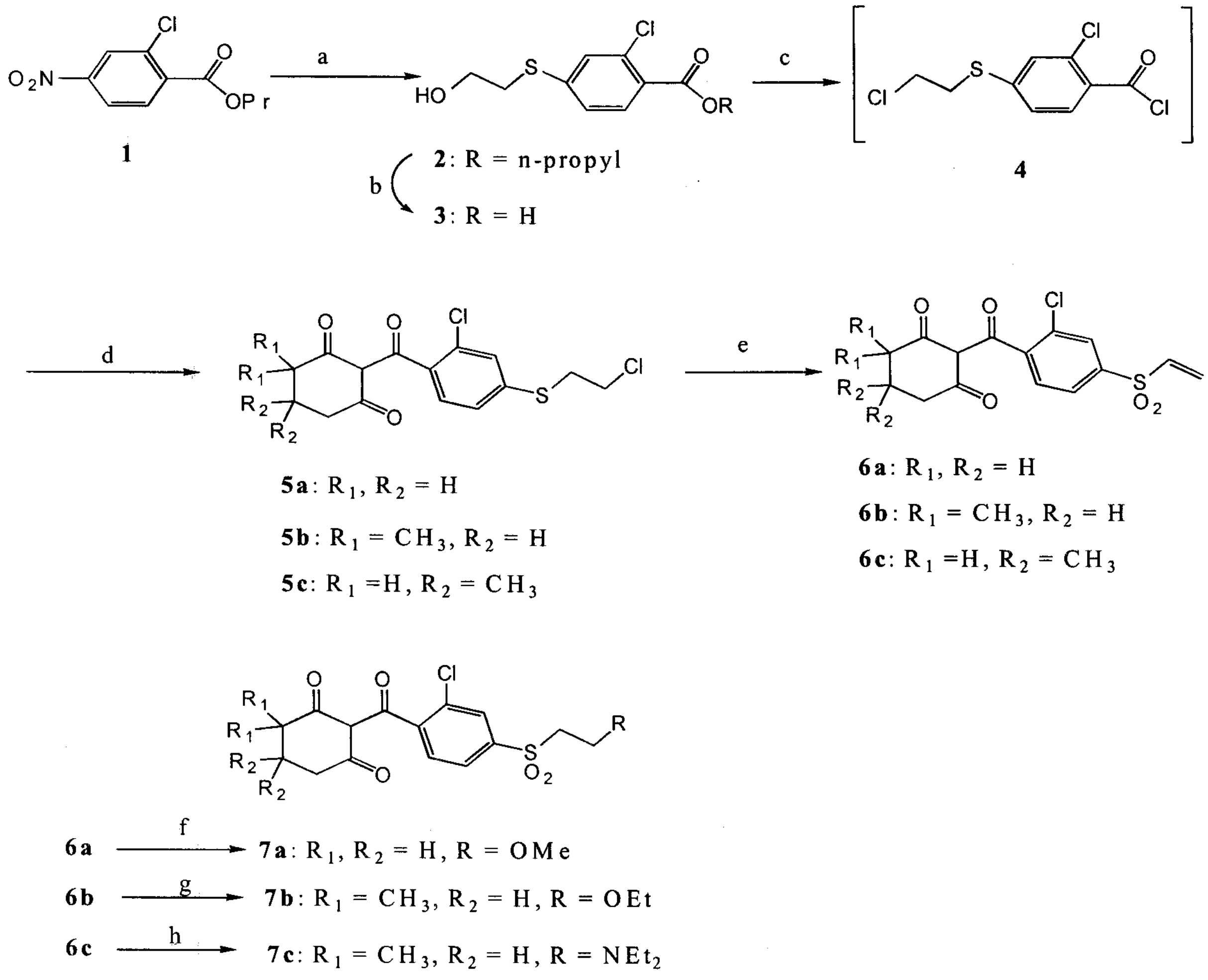

(a) 2-mercaptoethanol, K_2CO_3, acetone, reflux (b) LiOH, MeOH/H_2O = 3/1, rt (c) $SOCl_2$, reflux (d) 1,3-cyclohexandione, triethylamine, CH_2Cl_2, then, acetonecyanohydrine (e) MCPBA , CH_2Cl_2, then, triethylamine (f) LiOH, MeOH/H_2O = 3/1, rt (g) NaOEt, EtOH, rt (h) diethylamine, CH_2Cl_2.

Scheme 1

either of alkoxides or amine to vinylsulfonyl group. Treatment of vinylsulfones **6a** with lithium hydroxide in aqueous methanol at room temperature readily afforded the methoxyethanesulfonylphenyl triketones **7a**, however, more basic condition (sodium ethoxide) was required for the transformation of **6b** to 2-(*N*, *N*-diethylamino) ethanesulfonylphenyl triketone **7b**. 2-(*N,N*-Diethylamino)ethanesulfonylphenyl triketone **7c** was readily obtained by treatment of vinylsulfone **6c** with diethylamine in methylene chloride in good yields.

The herbicidal activity of **5**, **6**, and **7** were evaluated under paddy submerged conditions according to the following methods. The sterilized paddy soil was filled in a test pot having a surface area of 140 cm^2 and test species were planted. The test compounds were added on the surface as an acetone solutions by proper rate. The pots were placed in a greenhouse and watered for 3 weeks. The herbicidal activity data were taken visually by percent control, wherein 0 signifies no herbicidal effect and 100 signifies complete kill. The results are summarized in Table 1 and Table 2. As listed in Table 1, compounds **5a-c** showed herbicidal effects at a rate of 0.25 kg/ha without selectivity. Herbicidal effects of vinylsulfonyl triketones **6a-c** were comparably weak with non selectivity to rice, differently from our expectation. **6a** and **6b** showed moderate herbicidal activities at a rate of 4 kg/ha, while **6c** and **7c** showed weak herbicidal activity at a rate of 0.25 kg/ha. Herbicidal effects of 2-alkoxyethanesulfonylphenyl triketones **7a** and **7b** were kept up well to the dosage of 63 g/ha, no meaningful selectivity to rice.

Spectral Data :

2-Chloro-4-(2-hydroxy)thioethoxybenzoic acid propyl ester (**2**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.79 - 7.19 (3H, m, Ar), 4.28 (2H, t, J = 6.6 Hz, COO-CH_2-), 3.83 (2H, q, J = 5.9 Hz, O-CH_2-), 3.18 (2H, t, J = 6.0 Hz, S-CH_2-), 2.35 (1H, t, J = 5.5 Hz, -OH), 1.78 (2H, m, -CH_2-), 1.02 (3H, t, J = 7.3 Hz, -CH_3).

2-Chloro-4-(2-hydroxy)thioethoxybenzoic acid (**3**): ^{1}H NMR (acetone-d_6, 200 MHz) δ 7.89 - 7.31 (3H, m, Ar), 3.79 (2H, m, O-CH_2-), 3.22 (2H, t, J = 6.0 Hz, S-CH_2-).

2-[2-Chloro-4-(2-chlorothioethoxy)benzoyl]cyclohexane-1,3-dione (**5a**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 - 7.12 (3H, m, Ar), 3.65 (2H, t, J = 7.5 Hz, Cl-CH_2-), 3.26 (2H, t, J = 7.5 Hz, S-CH_2-), 2.61 - 2.19 (4H, m, -CH_2-CH_2-), 2.80 - 1.89 (6H, m).

2-[2-Chloro-4-(2-chlorothioethoxy)benzoyl]-4,4-dimethylcyclohexane-1,3-dione (**5b**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.21 - 7.00 (3H, m, Ar), 3.55 (2H, m, Cl-CH_2-), 3.16 (2H, m, S-CH_2-), 2.75 - 1.76 (4H, m, -CH_2-CH_2-), 1.01 (6H, s, -CH_3).

2-[2-Chloro-4-(2-chlorothioethoxy)benzoyl]-5,5-dimethyl cyclohexane-1,3-dione (**5c**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.38 - 7.14 (3H, m, Ar), 3.55 (2H, t, J = 7 Hz, Cl-CH_2-), 3.18 (2H, t, J = 7 Hz, S-CH2-), 2.61 - 2.19 (4H, m, -CH_2-CH_2-), 1.02 (6H, s, -CH_3).

2-(2-Chloro-4-vinylsulfonylbenzoyl)cyclohexane-1,3-dione (**6a**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.90 - 7.34 (3H, m, Ar), 6.76 - 6.11 (3H, m, vinyl), 2.82 - 2.01 (6H, m, -CH_2-CH_2-CH_2-).

2-(2-Chloro-4-vinylsulfonylbenzoyl)-4,4-dimethylcyclohexane-1,3-dione (**6b**): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.90 - 7.41 (3H, m, Ar), 6.80 - 6.11

Table 1. Herbicidal activity of trikrtones 5a~6c in flooded paddy condition

Comp.	rate (kg/ha)	ORYSA[a] (3leaf)	ORSYA (seed)	ECHOR[b]	SCPJU[c]	MOOVA[d]	CYPSE[e]	SAGPY[f]
5a	4.000	80	100	100	100	100	-	100
	1.000	40	70	95	90	100	-	100
	0.250	0	20	30	30	40	-	30
5b	4.000	100	100	100	100	100	100	100
	1.000	80	100	100	90	80	100	90
	0.250	30	60	70	60	60	-	60
	0.063	20	30	70	40	40	0	60
5c	4.000	100	100	100	100	100	100	100
	1.000	80	100	80	70	100	-	90
	0.250	40	50	30	30	50	-	50
	0.063	20	0	0	0	0	-	0
6a	4.000	50	40	50	90	100	50	100
6b	4.000	100	100	100	60	90	-	60
	1.000	30	50	80	60	70	-	50
	0.250	0	30	10	40	10	-	40
6c	4.000	10	0	70	80	80	100	70

[a]Rice, [b]Barnyardgrass, [c]Bulrush, [d]Monochoria, [e]Flat-sedge, [f]Arrow head.

(3H, m, vinyl), 2.90 - 1.38 (4H, m, $-CH_2-CH_2-$), 1.14 (6H, s, $-CH_3$).

2-(2-Chloro-4-vinylsulfonylbenzoyl)-5,5-dimethylcyclohexane-1,3-dione (**6c**): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.93 - 7.34 (3H, m, Ar), 6.75 - 6.09 (3H, m, vinyl), 2.68 (2H, s, $-CH_2-$), 2.32 (2H, s, $-CH_2-$), 1.12 (6H, s, $-CH_3$).

2-[2-Chloro-4-(2-methoxyethylsulfonyl)benzoyl]cyclohexane-1,3-dione (**7a**): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.93 - 7.34 (3H, m, Ar), 3.37 (2H, m, $O-CH_2-$), 3.43 (3H, m, SO_2-CH_2-), 3.26 (3H, s, $O-CH_3$), 3.20 - 2.04 (6H, m, $-CH_2-CH_2-CH_2-$).

2-[2-Chloro-4-(2-ethoxyethylsulfonyl)benzoyl]-4,4-dimethylcyclohexane-1,3-dione (**7b**): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.91 - 7.27 (3H, m, Ar), 3.82 - 3.28 (6H, m), 2.60 - 1.40 (4H, m), 1.07 (6H, brs, $-CH_3$), 1.25 - 1.04 (3H, m, $-CH_3$).

2-[2-Chloro-4-(2-diethylaminoethylsulfonyl)benzoyl]-4,4-dimethylcyclohexane-1,3-dione (**7c**): ^1H NMR ($CDCl_3$, 200 MHz) δ 7.91 - 7.27 (3H, m, Ar), 3.82 - 3.28 (6H, m), 2.60 - 1.40 (4H, m), 1.07 (6H, brs, $-CH_3$), 1.25 - 1.04 (3H, m, $-CH_3$).

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Table 2. Herbicidal activity of trikrtones 7a~d in flooded paddy condition

Comp.	rate (kg/ha)	ORYSA[a)] (3leaf)	ORSYA (seed)	ECHOR[b)]	SCPJU[c)]	MOOVA[d)]	CYPSE[e)]	SAGPY[f)]
7a	4.000	100	100	100	100	100	100	100
	1.000	90	100	90	90	100	100	100
	0.250	30	50	60	90	100	100	100
7b	4.000	100	100	100	100	100	×	100
	1.000	100	100	100	100	100	×	100
	0.250	70	100	100	90	90	×	100
	0.063	30	30	100	80	90	×	60
7d	4.000	60	70	100	100	95	100	90
	1.000	30	40	90	100	×	95	40
	0.250	0	20	20	40	40	×	50

[a)]Rice, [b)]Barnyardgrass, [c)]Bulrush, [d)]Monochoria, [e)]Flat-sedge, [f)]Arrow head.