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# Rice Blast Controlling Activities of Bis (alkoxycarbonyl) ketene dithioacetals and their Related Compounds*

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Many *S, S'*-disubstituted and *S, S'*-cyclic substituted derivatives of bis(alkoxycarbonyl) ketene dithioacetal were prepared and their rice blast controlling activities were investigated. Though some of the *S, S'*-disubstituted derivatives showed good activities, they did not possess systemic fungicidal activity. In the *S, S'*-cyclic substituted derivatives, only 1, 3-dithiolane derivatives showed excellent activities. In the systematic changes of ester moieties in the dithiolane derivatives, diisopropyl 1, 3-dithiolan-2-ylidenemalonate was found as the most desirable compound which showed excellent activities as well as strong systemic action.

## INTRODUCTION

During the course of our studies on the application of organic sulfur compounds to agricultural fungicides, we found that the derivatives of ketene dithioacetal **2** and **43** were very effective to control rice blast which was caused by infection of *Pyricularia oryzae*.[1] Synthetic method of these ketene dithioacetals is well-known as the reaction of active methylene compounds with carbon disulfide.[2] Especially, the reaction of malonic acid ester with carbon disulfide was investigated in detail by K.A. Jensen[3] and L. Dalgaard.[4] The synthetic procedures for **2** and **43** were also reported (Chart-1).[3,8]

In the present study, we have prepared many ketene dithioacetal derivatives and investigated their rice blast controlling activities. On the controlling rice blast, the submerged application into paddy water is thought to be desirable. Since strong systemic fungicidal activity against rice blast is required for this purpose, we also have investigated the systemic fungicidal activity of the derivatives synthesized.

* Studies on Biological Activity of Ketene dithioacetal (Part I)

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## MATERIALS AND METHODS

### 1. *Syntheses*

The compounds used here were synthesized by the method shown in Chart-2.

The syntheses were carried out in the five base-solvent systems showed in Tables 1 and 2. When NaH was used as a base, it was suspended in dried solvent, and malonic ester was added with vigorous stirring. After the evolution of hydrogen ceased, carbon disulfide was added to form the intermediate ene-dithiol. Then, the intermediate was dialkylated or cyclilized with appropriate alkylhalide or dihalide. While, on the case of aqueous NaOH as a base, the base solution was added slowly to the mixture of malonic ester, carbon disulfide and solvent. The formed intermediate was treated similarly as described above.

The typical procedure is given below.

*1) Ethyl 2-carbethoxy-3, 3-bis(ethylmercapto)acrylate* **3**

To a suspension of NaH (4.8 g, 0.2 mole) in 300 ml of dried benzene, diethylmalonate (16 g, 0.1 mole) was slowly added with vigorous stirring. After the addition, stirring was continued for 1.5 hr. Then, carbon disulfide (7.6 g, 0.1 mole) was added to the

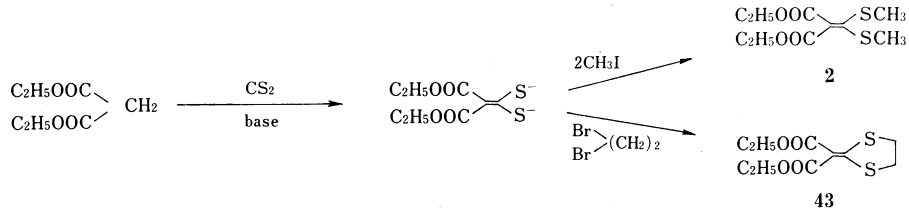


Chart-1

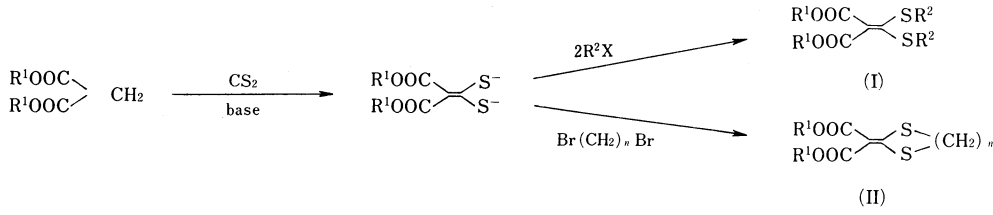


Chart-2

mixture with stirring. Additional stirring was continued for 8 hr and the mixture was allowed to stand overnight. Ethyl bromide (21.8 g, 0.2 mole) was added to the mixture and the mixture was stirred for 1 hr, refluxed for 1 hr, cooled and poured on cold water (100 ml). The organic layer was separated, washed with water, dried ($Na_2SO_4$) and distilled, to yield after removal of the solvent, pale yellow oil (19.8 g, 68% yield), bp 128–134°C/0.5 mmHg.

2) *Diisopropyl 1,3-dithiolan-2-ylidenemalonate* **45**

To a mixture of diisopropyl malonate (18.8 g, 0.1 mole), carbon disulfide (7.6 g, 0.1 mole) and acetone (30 ml), aqueous NaOH solution (8 g of NaOH was dissolved in 20 ml of water, 0.2 mole) was added slowly with stirring and with cooling under 15°C. After the addition, the mixture was stirred for 30 min and dibromoethane (19 g, 0.1 mole) was added. The temperature of the mixture rose slowly to 45°C. The mixture was stirred for 30 min at 50°C, cooled and poured on cracked ice. The resulting solid was collected, washed with water, dried and recrystallized from ether and *n*-hexane to yield white prism (25 g, 85% yield), mp 54.5–55°C.

*2. Biological Tests*

Each test compound was prepared as a 20% wettable powder or a 20% emulsifiable solution and was diluted with water to serial concentrations. The wettable powder was prepared by mixing the active ingredient, clay and surface-active agent (NPE-10) in a ratio of 20 : 75 : 5. The emulsifiable solution was prepared by mixing the active ingredient, xylene, cyclohexanone and surface-active agent (SORPOL-3005) in a ratio of 20 : 45 : 20 : 15.

Evaluation of rice blast controlling activities was carried out with potted rice plant seedlings (designated as "*Jukkoku*") at the 4-leaf stage. After or before the application of test solution diluted to a concentration of 500 ppm with water, the seedlings were inoculated with *Pyricularia oryzae* by the foliar spraying of its spore suspension. Four or five days after inoculation, the number of disease lesions per leaf was counted and the preventive value was caluculated according to the equation (1). Changing the intervals from application to inoculation, the following 4 kinds of activities were evaluated.

1) Inoculation 1 day before application (eradicative effectiveness, abbreviated as −1 in Tables)

2) Inoculation 1 day after application (pro-

tective effectiveness, abbreviated as +1 in Tables)

3) Inoculation 3 days after application (protective and persistent effectiveness, abbreviated as +3 in Tables)

4) Inoculation 6 days after application (protective and persistent effectiveness, abbreviated as +6 in Tables)

Systemic activity was evaluated as the following.

Sixteen seedlings of rice plant (designated as "*Tangin*") were planted on a porcelain pot of 12 cm diameter. A 230 ml of the test solution diluted to a concentration of 25 ppm with water was poured into a pot without direct contact with stem and leaf in seedlings. Five days after application, the seedlings were inoculated with *P. oryzae* similarly

Table 1 *S*, *S'*-Dialkyl derivatives of ethylene-1, 1-dithiols.

$R^1OOC$, $SR^2$ / $R^1OOC$, $SR^2$

| No. | $R^1$ | $R^2$ | Base-solvent* | Yield (%) | bp/mm., $n_D^t$, (mp) (°C) (°C) |
|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | A | 45 | (75-77)[3,6,7] |
| 2 | $C_2H_5$ | $CH_3$ | A | 73 | 148-149/1.5[3,8] |
| 3 | $C_2H_5$ | $C_2H_5$ | A | 68 | 128-134/0.5 |
| 4 | $C_2H_5$ | *n*-$C_3H_7$ | A | 78 | 151/0.8 |
| 5 | $C_2H_5$ | *n*-$C_4H_9$ | A | 80 | 156-161/0.7 |
| 6 | $C_2H_5$ | *n*-$C_{12}H_{25}$ | A | 79 | >250/0.2 |
| 7 | $C_2H_5$ | $CH_3SCH_2$ | A | 68 | 158-167/0.8-1.0 |
| 8 | $C_2H_5$ |  | B | 77 | >200/0.2[3,9] |
| 9 | $C_2H_5$ |  | B | 82 | >200/0.2 |
| 10 | $C_2H_5$ | $Cl_2C{=}CHCH_2$ | A | 42 | 193-196/0.7 |
| 11 | *iso*-$C_3H_7$ | $CH_3$ | C | 76 | 152-153/1.5 |
| 12 | *iso*-$C_3H_7$ | $C_2H_5$ | A | 19 | 143-149/1-2 |
| 13 | *iso*-$C_3H_7$ | *n*-$C_3H_7$ | A | 58 | 156-162/0.2 |
| 14 | *iso*-$C_3H_7$ | *n*-$C_4H_9$ | A | 69 | $1.4948^{28}$ |
| 15 | *iso*-$C_3H_7$ |  | A | 63 | >180/0.5 |
| 16 | *iso*-$C_3H_7$ |  | A | 64 | >170/0.7 |
| 17 | $CH_2{=}CHCH_2$ | $CH_3$ | C | 40 | 143-146/0.8 |
| 18 | $CH_2{=}CHCH_2$ | $C_2H_5$ | C | 35 | 136-139/0.8 |
| 19 | *n*-$C_4H_9$ | $C_2H_5$ | C | 95 | $1.5078^{28}$ |
| 20 | *iso*-$C_4H_9$ | $C_2H_5$ | C | 87 | $1.5056^{28}$ |
| 21 | *sec*-$C_4H_9$ | $CH_3$ | C | 84 | $1.5040^{28}$ |
| 22 | *sec*-$C_4H_9$ | $C_2H_5$ | C | 92 | $1.5049^{28}$ |
| 23 | *tert*-$C_4H_9$ | $CH_3$ | C | 88 | $1.5050^{28}$ |
| 24 | *tert*-$C_4H_9$ | $C_2H_5$ | C | 65 | $1.5039^{28}$ |
| 25 | *n*-$C_5H_{11}$ | $C_2H_5$ | C | 86 | $1.5042^{28}$ |
| 26 | *iso*-$C_5H_{11}$ | $C_2H_5$ | C | 92 | $1.5031^{28}$ |
| 27 | *cyclo*-$C_6H_{11}$ | $CH_3$ | C | 91 | $1.5326^{28}$ |
| 28 | *cyclo*-$C_6H_{11}$ | $C_2H_5$ | C | 64 | $1.5280^{28}$ |
| 29 | *n*-$C_7H_{15}$ | $C_2H_5$ | C | 93 | $1.4990^{28}$ |
| 30 | *n*-$C_8H_{17}$ | $C_2H_5$ | C | 88 | $1.4963^{28}$ |
| 31 |  | $CH_3$ | C | 82 | $1.5799^{28}$ |
| 32 |  | $C_2H_5$ | C | 94 | $1.5810^{28}$ |
| 33 | $CH_3OC_2H_4$ | $C_2H_5$ | C | 92 | $1.5179^{28}$ |
| 34 | $C_2H_5OC_2H_4$ | $C_2H_5$ | C | 74 | $1.5030^{28}$ |
| 35 | *n*-$C_4H_9OC_2H_4$ | $C_2H_5$ | C | 83 | $1.4932^{28}$ |
| 36 | $CH_3OC_4H_8$ | $C_2H_5$ | C | 85 | $1.5031^{28}$ |

* Base-solvent: A: NaH-benzene, B: *tert*-AmONa-benzene, C: NaH-THF, D: 30% aq-NaOH-DMSO, E: 30% aq-NaOH-acetone.

as described above. Four days after inoculation, the number of disease lesions per leaf was counted and the preventive value was caluculated according to the equation (1).

$$\% \text{ disease control} = (A-B)/A \times 100 \quad (1)$$

$A$; Number of disease lesions of untreated leaf

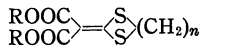
$B$; Number of disease lesions of treated leaf

## RESULTS AND DISCUSSION

Results of the syntheses are shown in Tables 1 and 2. The choice of the base-solvent system seemed to be the most important factor to give high yields. The rice blast controlling activities of the test compounds are summerized according to structure resemblance in Tables 3, 4, 5, 6 and 7.

Tables 3 and 4 show the result of anti-blast activities of $S, S'$-disubstituted derivatives in which the ester radicals were fixed as ethyl (Table 3) and as isopropyl (Table 4). In contrast, Table 5 shows the result of various ester homologues in which the sub-

Table 2 1, 3-Dithia-cyclic-2-ylidene malonate.



| No. | R | $n$ | Base-solvent | Yield (%) | bp/mm., $n_D^t$, (mp) (°C) (°C) | Recrystd. from |
|---|---|---|---|---|---|---|
| 37 | $CH_3$ | 1 | D | 78 | (158-9) | AcOEt-ether |
| 38 | $C_2H_5$ | 1 | D | 58 | (104-5) | EtOH-ether |
| 39 | *n*-$C_3H_7$ | 1 | D | 67 | (77.5-8) | Ether-*n*-hexane |
| 40 | *iso*-$C_3H_7$ | 1 | E | 72 | (104-5) | Ether-*n*-hexane |
| 41 | *n*-$C_4H_9$ | 1 | D | 69 | (33.5-4) | *n*-Hexane |
| 42 | $CH_3$ | 2 | A | 65 | (69.5-70.5)[3] | Ether-*n*-hexane |
| 43 | $C_2H_5$ | 2 | B | 86 | (58)[3,8] | Ether-*n*-hexane |
| 44 | *n*-$C_3H_7$ | 2 | A | 51 | (50.5-51) | Ether-*n*-hexane |
| 45 | *iso*-$C_3H_7$ | 2 | E | 85 | (54.5-55) | Ether-*n*-hexane |
| 46 | $CH_2$=$CHCH_2$ | 2 | A | 82 | 171-174/0.2 | |
| 47 | *n*-$C_4H_9$ | 2 | A | 75 | 177-183/0.25 | |
| 48 | *iso*-$C_4H_9$ | 2 | C | 63 | 171-173/0.09 | |
| 49 | *sec*-$C_4H_9$ | 2 | C | 95 | 175-180/0.5 | |
| 50 | *tert*-$C_4H_9$ | 2 | C | 76 | (88-90) | *n*-Hexane |
| 51 | *n*-$C_5H_{11}$ | 2 | C | 58 | 192-194/0.07 | |
| 52 | *iso*-$C_5H_{11}$ | 2 | C | 67 | 185-186/0.08 | |
| 53 | *cyclo*-$C_6H_{11}$ | 2 | C | 87 | (121-2) | *n*-Hexane |
| 54 | *n*-$C_7H_{15}$ | 2 | C | 64 | $1.5233^{28}$ | |
| 55 | *n*-$C_8H_{17}$ | 2 | C | 50 | (32-3) | Ether-*n*-hexane |
| 56 |  | 2 | C | 52 | (68-9) | *n*-Hexane |
| 57 | $CH_3OC_2H_4$ | 2 | C | 55 | 204-205/0.09 | |
| 53 | $C_2H_5OC_2H_4$ | 2 | C | 52 | 196-197/0.06 | |
| 59 | *n*-$C_4H_9OC_2H_4$ | 2 | C | 74 | $1.5261^{28}$ | |
| 60 | $CH_3OC_4H_8$ | 2 | C | 96 | $1.5358^{28}$ | |
| 61 | $CH_3$ | 3 | D | 31 | (51-51.5) | Ether-*n*-hexane |
| 62 | $C_2H_5$ | 3 | D | 53 | (60-60.5)[3] | Ether-*n*-hexane |
| 63 | *n*-$C_3H_7$ | 3 | D | 55 | (42.5-43) | Ether-*n*-hexane |
| 64 | *iso*-$C_3H_7$ | 3 | C | 35 | (95-6) | Ether-*n*-hexane |
| 65 | *n*-$C_4H_9$ | 3 | D | 78 | $1.5460^{28}$ | |
| 66 | $CH_3$ | 4 | D | 13 | 146-149/0.15 | |
| 67 | $C_2H_5$ | 4 | D | 16 | 134-136/0.15 | |
| 68 | *n*-$C_3H_7$ | 4 | D | 20 | 146-148/0.2 | |
| 69 | *iso*-$C_3H_7$ | 4 | E | 32 | (71-3) | Ether-*n*-hexane |
| 70 | *n*-$C_4H_9$ | 4 | D | 21 | 158-161/0.15 | |

Symbols are the same as in Table 1.

Table 3 Anti-blast activities of $\begin{matrix}C_2H_5OOC\\C_2H_5OOC\end{matrix}\!\!>\!\!=\!\!<\begin{matrix}SR\\SR\end{matrix}$

| No. | R | Evaluation of controlling activities on rice blast* | | | | |
|---|---|---|---|---|---|---|
| | | −1 | +1 | +3 | +6 | Systemic |
| 2 | $CH_3$ | C** | D | | | D |
| 3 | $C_2H_5$ | B | D | | | D |
| 4 | $n$-$C_3H_7$ | B | D | | | D |
| 5 | $n$-$C_4H_9$ | D | C | D | | D |
| 6 | $n$-$C_{12}H_{25}$ | D | D | | | |
| 8 |  | D | D | | | |
| 9 |  | D | D | | | |
| 7 | $CH_3SCH_2$ | D | C | D | | D |
| 10 | $Cl_2C{=}CHCH_2$ | D | A | C | D | D |

* −1: Inoculation 1 day before application
+1: Inoculation 1 day after application
+3: Inoculation 3 days after application
+6: Inoculation 6 days after application
Systemic: Systemic anti-blast activity on submerged application

** A: value above 90% B: value 90-80%
C: value 80-60% D: Noneffect
These evaluation methods were described in Materials and Methods.

Table 4 Anti-blast activities of $\begin{matrix}iso\text{-}C_3H_7OOC\\iso\text{-}C_3H_7OOC\end{matrix}\!\!>\!\!=\!\!<\begin{matrix}SR\\SR\end{matrix}$

| No. | R | Evaluation of controlling activities on rice blast | | | | |
|---|---|---|---|---|---|---|
| | | −1 | +1 | +3 | +6 | Systemic |
| 11 | $CH_3$ | A | D | | | D |
| 12 | $C_2H_5$ | A | D | | | D |
| 13 | $n$-$C_3H_7$ | D | D | | | |
| 14 | $n$-$C_4H_9$ | D | D | | | |
| 15 |  | D | D | | | |
| 16 |  | D | D | | | |

Symbols are the same as in Table 3.

stitutent attached to sulfur atom is ethyl. As shown in these Tables, when the radicals linked to sulfur are simple and lower alkyl, they show moderate eradicative (−1) activity (**2**, **3** and **4**). Compound **10** showed excellent protective (+1) activity, but this activity did not persist. Among diisopropyl esters, *S*, *S'*-dipropyl homologue **13** showed the activity no longer. Thus relationship is shown in Fig. 1. Figure 1 shows that the peak of activitiy is shifted according to the ester groups. From the result of Table 5, definitive role of ester group against activities is not obvious, however, the compounds having

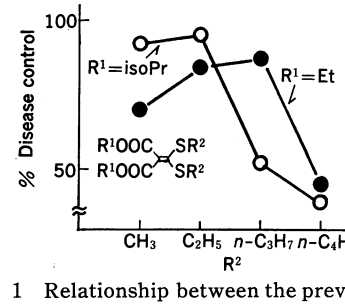



Fig. 1 Relationship between the preventive value of rice blast and the substituent $R^2$ on sulfur in $\begin{matrix}R^1OOC\\R^1OOC\end{matrix}\!\!>\!\!=\!\!<\begin{matrix}SR^2\\SR^2\end{matrix}$.

Table 5 Anti-blast activities of $\begin{matrix}ROOC\\ROOC\end{matrix}\!\!>\!\!=\!\!<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$

| No. | R | Evaluation of controlling activities on rice blast | | | | |
|---|---|---|---|---|---|---|
| | | −1 | +1 | +3 | +6 | Systemic |
| 3 | $C_2H_5$ | C | D | | | D |
| 12 | *iso*-$C_3H_7$ | A | D | | | D |
| 18 | $CH_2$=$CHCH_2$ | D | D | | | |
| 19 | *n*-$C_4H_9$ | A | A | A | D | D |
| 20 | *iso*-$C_4H_9$ | D | B | C | D | D |
| 22 | *sec*-$C_4H_9$ | A | B | C | D | D |
| 24 | *tert*-$C_4H_9$ | D | D | | | |
| 25 | *n*-$C_5H_{11}$ | D | D | | | |
| 26 | *iso*-$C_5H_{11}$ | D | C | D | | D |
| 29 | *n*-$C_7H_{15}$ | D | D | | | D |
| 30 | *n*-$C_8H_{17}$ | D | D | | | |
| 28 | *cyclo*-$C_6H_{11}$ | D | D | | | |
| 32 |  $CH_2$ | D | D | | | |
| 33 | $CH_3OC_2H_4$ | A | D | | | D |
| 34 | $C_2H_5OC_2H_4$ | D | C | D | | D |
| 35 | *n*-$C_4H_9OC_2H_4$ | D | C | D | | D |
| 36 | $CH_3OC_4H_8$ | D | C | D | D | D |

Symbols are the same as in Table 3.

Table 6 Anti-blast activities of $\begin{matrix}ROOC\\ROOC\end{matrix}\!\!>\!\!=\!\!<\begin{matrix}S\\S\end{matrix}\!\!>(CH_2)_n$

| No. | R | *n* | Evaluation of controlling activities on rice blast | | | | |
|---|---|---|---|---|---|---|---|
| | | | −1 | +1 | +3 | +6 | Systemic |
| 38 | $C_2H_5$ | 1 | D | D | | | |
| 43 | $C_2H_5$ | 2 | A | C | C | D | A |
| 62 | $C_2H_5$ | 3 | D | D | | | |
| 67 | $C_2H_5$ | 4 | D | D | | | |
| 40 | *iso*-$C_3H_7$ | 1 | D | D | | | |
| 45 | *iso*-$C_3H_7$ | 2 | B | A | A | B | A |
| 64 | *iso*-$C_3H_7$ | 3 | D | D | | | |
| 69 | *iso*-$C_3H_7$ | 4 | D | D | | | |

Symbols are the same as in Table 3.

longer alkyl group of ester shows no longer the activity. Dibutyl ester homologue **19** showed very excellent both eradicative and protective activities and had moderate persistent effect (+3 and +6), but the compound did not show a systemic fungicidal action on submerged application.

Generally speaking, some of the compounds in Tables 3, 4 and 5 showed excellent controlling effect against rice blast, however, the effectiveness did not persist and the systemic fungicidal activity on submerged application was not shown.

As shown in Table 6, only 1, 3-dithiolane derivatives in 1, 3-dithiacyclic-2-ylidenemalonates showed excellent activities. Dithiethane ($n$=1), dithiane ($n$=3) and dithiepane ($n$=4) derivatives did not show any activities against rice blast. Figure 2 shows the relationship between ring size (number of methylene)

Table 7 Anti-blast activities of 

| No. | R | Evaluation of controlling activities on rice blast | | | | |
|---|---|---|---|---|---|---|
| | | −1 | +1 | +3 | +6 | Systemic |
| 42 | $CH_3$ | D | D | | | C |
| 43 | $C_2H_5$ | A | C | C | D | A |
| 44 | *n*-$C_3H_7$ | B | A | C | D | C |
| 45 | *iso*-$C_3H_7$ | B | A | A | B | A |
| 46 | $CH_2CH{=}CH_2$ | D | B | D | | D |
| 47 | *n*-$C_4H_9$ | D | D | | | |
| 48 | *iso*-$C_4H_9$ | B | C | C | D | D |
| 49 | *sec*-$C_4H_9$ | B | B | B | B | D |
| 50 | *tert*-$C_4H_9$ | D | B | A | A | B |
| 51 | *n*-$C_5H_{11}$ | D | D | | | D |
| 52 | *iso*-$C_5H_{11}$ | A | D | | | D |
| 53 | *cyclo*-$C_6H_{11}$ | D | B | D | D | D |
| 54 | *n*-$C_7H_{15}$ | D | D | | | D |
| 55 | *n*-$C_8H_{17}$ | D | D | | | D |
| 56 |  | D | D | | | D |
| 57 | $CH_3OC_2H_4$ | C | D | | | D |
| 58 | $C_2H_5OC_2H_4$ | C | D | | | D |
| 59 | *n*-$C_4H_9OC_2H_4$ | B | D | | | D |
| 60 | $CH_3OC_4H_8$ | D | D | | | |

Symbols are the same as in Table 3.

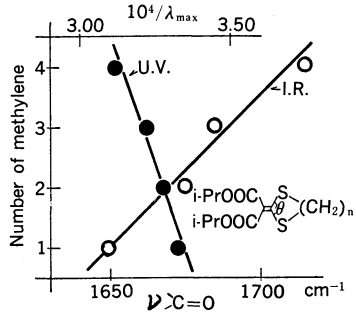



Fig. 2 Relationship between the number of methylene in diisopropyl 1, 3-dithiacyclic-2-ylidene malonate and $1/\lambda_{max}$. (●) and carbonyl stretching vibration (○).

and their reciprocal of $\lambda_{max}$ in UV absorption spectrum and >C=O stretching vibration in IR absorption spectrum. In both spectra, the linear relationship was obtained according to the ring size. It was reported that 1, 3-overlap of sulfur atoms in these structures strongly affects to the spectra.[5] Therefore, these linear relationship would be due to the S–C–S angle $\theta$. On the fact that only 1, 3-dithiolane shows excellent activities, it may be assumed that the ring size and the angle $\theta$ are very important factors for the anti-blast activity.

Table 7 shows the results of anti-blast activities of 1,3-dithiolan-2-ylidene malonates. Compound **45** showed very excellent effectiveness both foliar and submerged application. Moreover, the persistent effect of this compound was very good. Generally speaking, the appropriate alkyl size of ester group is necessary to show excellent activity. The alkyl substituent in the structure would contribute to the hydrophobicity of compound. From the results in Table 7, it was suggested that the compound having 4 to 8 carbon numbers in the ester moiety showed high activity.

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## 要 約

マロン酸エステルと二硫化炭素を塩基の存在下で反応させ，得られる置換エチレンジチオールをアルキル化，あるいは環化させて多数の誘導体を合成し，それらのイネいもち病防除活性をポット植の稲を用いて評価した．イネいもち病に対し，治療的，予防的，持続的効果の判定のほかに水面施用的な活性を検討し，化合物の浸透移行性を評価した．

*S*, *S'*-ジ置換体のなかには茎葉散布的には優れた活性を示すものも見られたが，浸透移行性に欠けた．*S*, *S'*-閉環誘導体のうちでは，1,3-ジチオラン型の化合物にのみ優れた活性が発現した．多数の 1,3-ジチオラン誘導体のなかで，diisopropyl 1, 3-dithiolan-2-ylidenmalonate が効果の持続性，浸透移行性の点から最も優れていた．


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