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Photolysis of Diisopropyl 1,3-Dithiolan-2-ylidenemalonate, Isoprothiolane Fungicide

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Isoprothiolane (diisopropyl 1,3-dithiolan-2-ylidenemalonate) is a new fungicide effective to control rice blast disease caused by *Pyricularia oryzae*.^{1,2)} It also suppresses the population of planthoppers in the field.²⁾ Showing a systemic property, it can be applied to paddy water as well as to foliage. The photochemical behavior of this unique compound having a dithiolane ring, an exocyclic double bond and ester linkages in the molecule has not been studied well. This paper deals with the photolysis of the fungicide on the thin layer of silica gel and in aqueous solutions exposed to UV light.

After UV irradiation with a 10 W Toshiba germicidal lamp 10 cm above a silica gel thin-layer chromatoplate on which isoprothiolane was placed as a spot, the plate was developed in a solvent system (*n*-hexane : benzene : acetone=9 : 5 : 1, v/v) and visualized by spraying a 1% aqueous potassium permanganate solution. Five spots of degradation products No. 1 (*R_f*=0.00), No. 2 (0.04), No. 3 (0.66), No. 4 (0.75), and No. 5 (0.86) were detected besides that of unreacted isoprothiolane (0.44). For the quantitative analysis a thinchromatograph was used; a chromarod was utilized in the place of the thin-layer plate and submitted to the apparatus equipped with a flame ionization detector.

The half-life of isoprothiolane under the UV irradiation conditions was 3 hours to yield the photolysis products 1.7, 2.8, 22.8, 17.0, and 5.7%, respectively. No. 3 and 4 then decreased gradually, whereas No. 5 increased with a lapse of irradiation time to become the sole major photolysis product after 14 hours.

These five photolysis products were purified

by repeating thin-layer chromatography (*tlc*). The products No. 1 and 2 were identified by comparison with the authentic compounds on *tlc* applying three different solvent systems as the hydrolysis product 1,3-dithiolan-2-ylidenemalononic acid (**1**) and its monodecarboxylation product dithiolanylidenecetic acid (**2**), respectively. The product No. 3 was obtained as yellow needles, mp 130–131°C. The proton NMR spectrum showed that it had isopropyl ester groups [δ 1.32 (6H, doublet), 5.22 (1H, multiplet)] but lacked the ethylene protons of the dithiolane ring at δ 3.41. The mass spectrum suggested that the product No. 3 was the dimer of a degradation product bearing the isopropyl ester groups: *m/e* 460 (M^+), 418 ($M^+-C_3H_6$), 401 ($M^+-C_3H_7O$), 374 ($M^+-C_3H_6CO_2$), 332 ($M^+-C_3H_6-C_3H_6CO_2$), 288 ($M^+-2C_3H_6CO_2$), 202 ($M^+-3C_3H_6CO_2$), 43 ($C_3H_7^+$). The accurate mass measurement of the molecular ion at high resolution, 460.1149, gave the molecular formula $C_{20}H_{28}O_6S_2$ (calculated mass=460.1226). The IR spectrum of the product No. 3 resembled that of isoprothiolane IR ν_{max}^{KBr} cm^{-1} : 1515 (C=C), 1660, 1680 (C=O). The carbonyl stretching was at considerably lower wave number than that normally observed for simple α,β -unsaturated esters. The evidence mentioned above supports the structure **3**, i.e. 2,4-bis[bis(isopropoxycarbonyl)methylene]-1,3-dithietane. The ethyl ester homolog has been synthesized from diethyl sodiomalonate and thiophosgen; IR ν_{max} cm^{-1} 1511, 1672, 1689.³⁾

The product No. 4 obtained as pale yellow cubes, mp 127–128°C, gave almost the same proton NMR spectrum as No. 3; δ 1.32 (6H, doublet, $CH(CH_3)_2$), 5.22 (1H, multiplet, CH

(CH₃)₂). However, the ester carbonyl stretching differed from that of No. 3 to give two bands at 1660 and 1715 cm⁻¹, indicating two different kinds of ester groups were in the molecule. The mass of the molecular ion, 492, was bigger than that of No. 3 by 32, suggesting No. 4 might be either the dioxygenated derivative or the trithio analog of No. 3. The accurate mass of the molecular ion measured at high resolution, 492.0903, did not correspond with the elemental composition of the oxygenated product C₂₀H₂₈O₁₀S₂ (calculated mass=492.1124), but did with the trithio analog C₂₀H₂₈O₈S₃ (calculated mass=492.0946). Thus, the structure **4**, that is 3,5-bis[bis(isopropoxy-carbonyl)methylene]-1,2,4-trithiolane, is the most probable structure for the product No. 4. The mass fragmentation pattern also supported this structure: *m/e* 492 (M⁺), 460 (M⁺-S), 432 (M⁺-C₃H₇OH), 406 (M⁺-C₃H₆-CO₂), 401 (M⁺-S-C₃H₆CO₂), 364 (M⁺-C₃H₆-CO₂-C₃H₆), 43 (C₃H₇⁺).

The product No. 5 was obtained as yellow crystals, mp 117-118°C. Its molecular ion peak at *m/e* 256 accompanied by the peaks of P+2 (38.2%) and P+4 (5.8%) indicated the molecular formula of S₈ whose calculated isotope contribution to the P+2 and P+4 peaks are 35.2 and 5.6%, respectively. The fragmentation pattern also supported this formula: *m/e* 224 (M⁺-S), 192 (M⁺-2S), 160 (M⁺-3S), 128 (M⁺-4S), 96 (M⁺-5S), 64 (M⁺-6S).

By UV irradiation, the product No. 1 gave No. 2 and No. 5, whereas No. 2 yielded only No. 5. On the other hand, No. 3 and No. 4 were interconvertible besides producing No. 5 by the irradiation. The transformation of a trithiolane into a dithietane by the action of alkali has been reported.⁴⁾ Thus, the photolytic pathway of isoprothiolane is proposed as shown in Fig. 1.

In aqueous solutions, isoprothiolane gave the hydrolysis product **1** and insoluble polymer by irradiation with an immersed high pressure mercury lamp (Riko UVL 100 H) which emitted mainly the UV light of longer wavelength than 300 nm. In deionized water the half-life of isoprothiolane was 73.6 hours. However, paddy water greatly accelerated the photolysis rate, shortening the half-life to

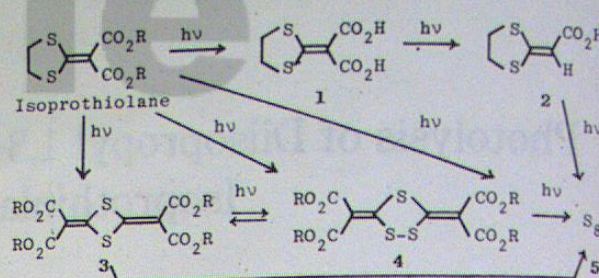


Fig. 1 Photolysis of isoprothiolane (R=i-C₃H₇) with UV on silica gel.

6.3 hours. Similar phenomenon has been observed in the photolysis of the herbicide molinate (S-ethyl hexahydro-1H-azepine-1-carbothioate).⁵⁾

No mutagenic action was found in the dithietane (**3**) and trithiolane (**4**) products on the reverse mutation system of Ames' *Salmonella* strains.⁶⁾ Since the wavelength of sunlight at the earth's surface is usually longer than 295 nm, these heterocyclic photolysis products are not always produced under the environmental conditions. More details including the effects of sunlight, oxygen, solid surface, and photosensitizers on the photolysis of isoprothiolane will be reported elsewhere.

REFERENCES

- 1) T. Tsumura: *Jap. Pestic. Inform.* 27, 20 (1976)
- 2) T. Sugimoto, F. Araki & K. Taninaka: *J. Pestic. Sci.* 2 (Sp. Iss.), 505 (1977)
- 3) M. S. Raasch: *J. Org. Chem.* 35, 3470 (1970)
- 4) P. Yates & T. R. Lynch: *Can. J. Chem.* 49, 1477 (1971)
- 5) C. J. Soderquist, J. B. Bowers & D. G. Crosby: *J. Agric. Food Chem.* 25, 940 (1977)
- 6) S. Funayama: personal communications (1978)

要 約

殺菌剤イソプロチオラン (ジイソプロピル 1,3-ジチオラン-2-イリデンマロネート) の光分解

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シリカゲル薄層上, 紫外線照射によりイソプロチオランは速やかに分解し, 5種の分解物がtlcによって検出された。それらはtlc, 機器分析等によりエステル加水分解物(1), そのモノ脱炭酸生成物(2), ジチエタン誘

