Topochemical Photopolymerization and Photo-Copolymerization of the Crystals of Unsymmetrically Substituted Diolefin Compounds Having Pyrimidine Ring

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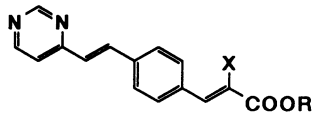
Several new diolefin compounds, methyl and ethyl 4-[2-(4-pyrimidyl)ethenyl]cinnamates (**1a** and **1b**), and methyl, ethyl, and propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamates (**1c**, **1d**, and **1e**) were synthesized, and their photoreactivity in the crystalline state was investigated. The crystals of **1c**, **1d**, and **1e** gave amorphous oligomers having cyclobutane skeletons (average degree of polymerization was approximately 10) through the [2+2] photocycloaddition. The dimers (**2c**, **2d**, and **2e**) were formed in high yields by the exclusive photoexcitation of the monomers. The dimers were isolated by column chromatography. The cyclobutane structure of **2c** and **2d** was β-type homo adduct whereas that of **2e** was β-type hetero adduct. As only one type of adduct was detected for each crystal, photodimerization was interpreted as being of a crystal lattice controlled process. The conversions of these reactions were not as high as that of the reaction in α-type of 2,5-distyrylpyrazine (DSP). The lower conversion was interpreted as being due to alternative reacting sites which inevitably result from the β-type molecular packing and to the drastic displacement of molecules which causes the distortion of crystal lattice. The mixed crystals (**1f**) of **1d** and **1e** (molar ratio 1.3/1), of which the X-ray diffraction pattern is similar to that of **1e**, photopolymerized to give amorphous cooligomers (average degree of polymerization was approximately 5). The reaction went through an intermediate similar to dimer **2e**.

In previous studies we have demonstrated that the topochemical reactivity of various types of diolefin compounds and the configuration of their photoproducts were accurately predictable from the molecular arrangements of these crystals.[1)]

Although the correlation between chemical and crystal structures of organic compounds is very sophisticated, it is obvious that the interaction between electron-donating and -accepting groups in the molecule contributes greatly to determining their crystal structure. From recent results of studies on the photochemical behavior of several unsymmetrically substituted diolefinic crystals, we have revealed that pyridyl, cyano and carbonyl groups were the electron-accepting groups which are potent in affording the photoreactive α-type crystal packing.[2)] In a preceeding report, we have reported that the unsymmetrically substituted diolefin monomer crystals which have a pyrazine ring produce extremely high molecular weight of crystalline linear polymers.[3)]

As the pyrimidine ring is also expected to induce much stronger donor–acceptor interactions with benzene rings, in our present work, we synthesized several new diolefin compounds having pyrimidine rings, as is represented in Scheme 1, and investigated the photochemical behaviors of these crystals. Furthermore, we attempted to prepare several mixed crystals, and investigated these crystals from the point of view of topochemical photo-copolymerization.



comp.	X	R
1a	H	Me
1b	H	Et
1c	CN	Me
1d	CN	Et
1e	CN	n-Pr

Scheme 1.

Results and Discussion

The photoreactivity of **1a,b** (alkyl 4-[2-(4-pyrimidyl)ethenyl]cinnamates) and **1c—e** (alkyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamates) in crystalline state was checked by methods 1 and 2 (see Experimental section).

From the results, it was found that three monomer crystals, **1c—e**, were highly photoreactive and gave the products through [2+2] cycloaddition. On the other hand, the crystal of **1a** was photostable and that of **1b** gave intractable cross-linked photoproducts.

Following the photoreaction of **1c—e**, IR spectra of the products showed the decrease in the absorptions due to olefin bonds and the shift to higher wavenumbers of the absorptions of the carbonyl and cyano groups. ^{1}H NMR spectra of the photoproducts also showed the disappearance of olefin protons in the monomer and the appearance of cyclobutane protons. These spectral evidences indicate that the photoreaction is a [2+2] photocyclopolymerization.

The photoproducts after 24 h irradiation were amorphous white-brown powders. From gel permeation chromatogram (GPC) (eluent: *N,N*-demethylformamide), the photoproducts were found to consist of the dimer (**2**) and the oligomers (**3**) of which the average degree of polymerization was about 10.

In order to clarify the structure of the products, isolation of dimers was attempted.

For the purpose of depressing the photoexcitation of the terminal olefins in the oligomers which reduces the polymerization, the crystalline **1c—e** were irradiated through an optical filter which cuts off the shorter

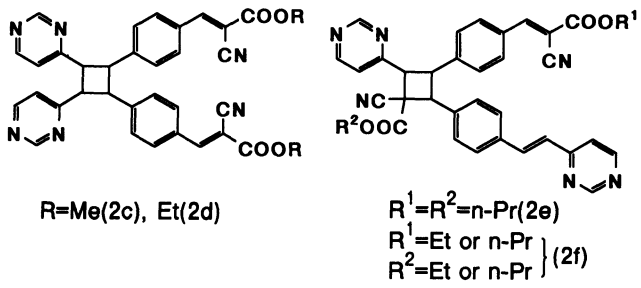
wavelengths.

The irradiation using L38 filter (cut off <350 nm) for **1c** and **1e**, and using L40 filter (cut off <380 nm) for **1d**, respectively, resulted in the accumulation of a great amount (≃90%) of the dimers.

The photoproducts from **1c** and **1d** consisted mostly (≃90%) of the dimer retaining crystallinity whereas the products from **1e** were amorphous. The dimers (**2c—e**) were isolated from the photoproducts and purified by flash column chromatography.

^{1}H NMR and mass analyses revealed that **2c** and **2d** had head-to-head homo adduct type cyclobutane structures, in which two 2-(4-pyrimidyl)ethenyl groups are neighboring, and that **2e** had head-to-head hetero adduct type, in which 2-(4-pyrimidyl)ethenyl and α-cyanocinnamate groups are neighboring to each other, as shown in Scheme 2.

Since only a single structure of the dimers was detected, it was concluded that the photoreaction of **1c—e** crystals proceeded, at least at the photocyclodimerization stage, under the strict control of the monomer crystal lattice.



Scheme 2.

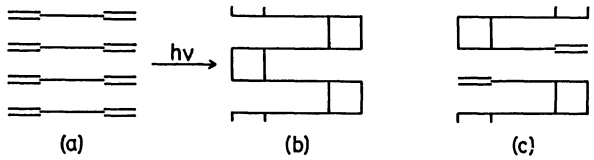


Fig. 1. Schematic illustration of the photopolymerization of (a) β-type crystals of diolefin compounds into (b) zigzag polymers and (c) termination resulting from alternative reactivity of the monomer.

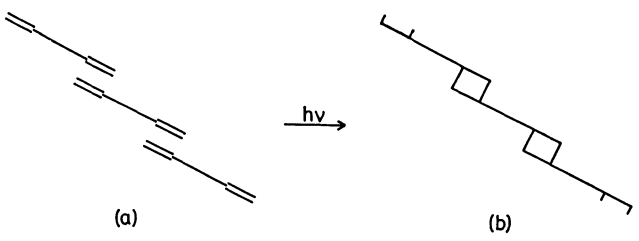


Fig. 2. Schematic illustration of photopolymerization of (a) α-type crystal of diolefin compounds into (b) a linear polymer.

The remarkable change of the dimer skeleton from **1d** to **1e** should doubtlessly correspond to the change of relative orientation of reacting olefins. IR, DSC (differential scanning calorimetry), and PAS (photoacoustic spectra) analyses of the **1d** and **1e** crystals, however, revealed no evident difference between these two crystal structures.

The structures of **2c—e** suggest that the crystals of **1c—e** consist of β-type packing monomers (Fig. 1a), and that the final oligomers are of a zigzag type (Fig. 1b).

In the case of α-type crystals two reacting olefin groups are related with a center of symmetry as is illustrated in the crystals of α-DSP. Therefore, one olefin can react only with one olefin of the neighboring molecule, and the center of gravity of the reacting monomer scarcely moves. These topochemical conditions make possible the α-type crystals to produce linear crystalline polymers of high molecular weight (Fig. 2). On the other hand, such a high crystalline polymer with a high conversion (almost quantitative) has not resulted from the photoreaction of β-type diolefin crystals, not only in the present results but in some of our previous works.[3,4]

The low degree of polymerization with an incomplete conversion (≃85%) and the lack of crystallinity of the photoproducts from β-type crystals can be explained by the following two reasons.

The first reason is that if we assume all olefins are in the same topochemical environment there are four possible reactive sites of the [2+2] photodimerization for each photoexcited molecule in a typical β-type packing crystal. This may cause the termination of further chain growth of the polymer by some probabilities as schemed in Fig. 1c. The second is that with the formation of cyclobutane a large displacement of the reacting molecules may occur to result in serious distortion of crystal lattice. Such a large displacement may make the reacting crystal to be amorphous at latter stages of the photoreaction. In contrast to β-type crystals, the extremely clean-cut photoreaction of the α-type crystals has been interpreted in terms of "seesaw" mechanism,[5] in which the reacting monomer rotates around its center of gravity, that scarcely moves.

In view of the molecular arrangements, the β-type packing is not explicable by electrostatic interactions which seem to be effective in α-type packing. The π–π orbital interaction of facing pyrimidine and benzene rings and/or N–N interaction may contribute to the formation of β-type packings.

It is of great interest to extend the study of a topochemical [2+2] photopolymerization into that of the photocopolymerization. Although there have been a few preliminary reports on the formation of mixed diolefin crystals,[6,7] none of them described [2+2] topochemical copolymerization. In our present work

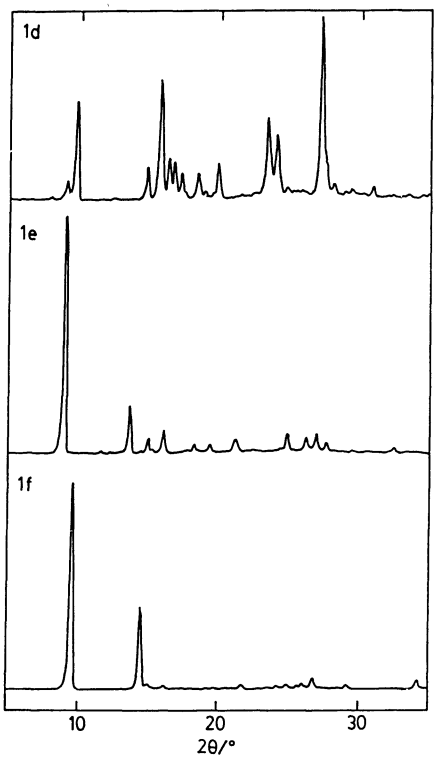


Fig. 3. X-Ray diffraction patterns of the crystals of **1d** (upper), **1e** (middle), and **1f** (lower).

after several attempts a well-defined mixed crystal consisting of two derivatives **1d** and **1e** was successfuly prepared, as was expected from their similar chemical structures. However, no other mixed crystals were obtained from any other combination of the monomers.

A mixed crystal of **1d** and **1e** (molar ratio 1.3:1, **1f**) was obtained by recrystallization from a 1-propanol solution containing an equimolar amount of the two monomers. **1f** had a melting point (160.0—165.0 °C) which is intermediate between those of **1d** (mp 184.0—185.0 °C) and **1e** (mp 149.5—151.0 °C), and showed almost the same X-ray diffraction pattern as that of **1e**, suggesting nearly the same crystal structure (Fig. 3).

The photoirradiation of **1f** for 24 h with a 100 W high-pressure mercury lamp gave amorphous co-oligomers, which had an average polymerization degree of about 5. Structure of the dimer isolated (**2f**) was proved to be head-to-head hetero adduct by mass analysis (Scheme 2), which is the same as that of **2e**, as was expected from the X-ray diffraction pattern of **1f**.

These results indicate that **1d** is included in the crystal lattice of **1e** as isomorphous and that the mixed crystal behaved analogously to **1e**, to afford the head-to-head hetero zigzag type co-oligomers on photoirradiation.

In spite of the electrostatic interaction between electron donating groups of the molecule (benzene ring) and one of the accepting groups (pyrimidine ring, carbonyl, and cyano groups in present crystals), the π–π orbital interaction of facing benzene and pyrimidine rings and/or N–N interaction is considered to contribute to the formation of the β-type stacking.

Experimental

Measurements. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL PMX-60SI spectrophotometer or a JEOL GX-400 spectrometer. X-Ray diffraction pattern was recorded on a Rigaku Rotaflex RU-200 spectrometer (λ=1.54184 Å). Melting points were determined by a Laboratory Devices MEL-TEMP and are uncorrected. Gel permeation chromatography (GPC) of the photoproducts was performed at 40 °C on a Shodex (GPC AD 800/P+AD 805/S+AD 803/S+AD 802/S) column (DMF solution).

Preparation of Monomers. 4-[2-(4-Pyrimidyl)ethenyl]-benzaldehyde. Terephthalaldehyde (9.2 g, 69 mmol) was dissolved in a mixed solvent of acetic anhydride (24 ml) and acetic acid (16 ml) at 70 °C. 4-Methylpyrimidine (5.0 g) was added to the solution and refluxed for 4 h. After cooling to room temperature, 50 ml of benzene was added and extracted with 100 ml of 1 mol l^{-1} hydrochloric acid three times, followed by neutralization by 2 mol l^{-1} sodium hydroxide. The precipitates were collected by filtration and dried under reduced pressure. The solid mass was purified by flash column chromatography (Wako gel C-300, eluent: dichloromethane:methanol=99.5:0.5 (v/v)), followed by recrystallization from benzene–hexane. 3.6 g of 4-[2-(4-Pyrimidyl)-ethenyl]benzaldehyde was obtained. Yield 33%; mp 162.0—163.5 (benzene–hexane); IR (KBr) 2850, 1700, 1600, 1390, 1310, 1210, 970, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=10.04 (1H, s, formyl), 9.21 (1H, d, J=1.5 Hz, pyrimidyl), 8.74 (1H, d, J=5.2 Hz, pyrimidyl), 7.96 (1H, d, J=15.6 Hz, olefin), 7.93 (2H, d, J=8.2 Hz, phenylene), 7.76 (2H, d, J=8.2 Hz, phenylene), 7.35 (1H, dd, J=1.5 and 5.2 Hz, pyrimidyl), 7.19 (1H, d, J=15.6 Hz); UV (99.5% CH_2Cl_2): 325 (ε=35000). Found: C, 74.12; H, 4.79; N, 13.31%. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.32%.

4-[2-(4-Pyrimidyl)ethenyl]cinnamic Acid. To a solution of 4-[2-(4-pyrimidyl)ethenyl]benzaldehyde (1.00 g, 4.8 mmol) in 25 ml of pyridine were added malonic acid (1.98 g, 19.0 mmol) and piperidine (0.1 ml), and the solution was stirred for 13 h at 90 °C. After cooling to room temperature, 50 ml of 2 mol l^{-1} hydrochloric acid was added. The precipitates were collected and dried under reduced pressure, and recrystallized from *N*,*N*-dimethylformamide. 4-[2-(4-Pyrimidyl)ethenyl]cinnamic acid (0.63 g) was obtained as the complex with DMF. The final crystals, containing about 10% molar ratio of DMF, were supplied to the following esterification procedure.

Alkyl 4-[2-(4-Pyrimidyl)ethenyl]cinnamates (1a and 1b). To a suspension of the complex of 4-[2-(4-pyrimidyl)-ethenyl]cinnamic acid with DMF (0.180 g) in methanol (40 ml) was added concentrated sulfuric acid (1.0 ml), and the mixture was refluxed for 3 h to give a homogeneous solution. After cooling to room temperature, the solution was filtered to remove unreacted acid, and the filtrate was neutralized by 1 mol l^{-1} aqueous sodium hydroxide and extracted with dichloromethane. After evaporation of the

solvent, the residue was recrystallized from methanol. 0.091 g of **1a** was obtained. Mp 159.0—160.5 °C (methanol); IR (KBr) 1710, 1580, 1310, 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.19 (1H, d, J=1.5 Hz, pyrimidyl), 8.70 (1H, d, J=5.5 Hz, pyrimidyl), 7.89 (1H, d, J=15.9 Hz, olefin), 7.70 (1H, d, J=16.2 Hz, olefin), 7.62 (2H, d, J=8.2 Hz, phenylene), 7.56 (2H, d, J=8.2 Hz, phenylene), 7.32 (1H, dd, J=1.5 and 5.5 Hz, pyrimidyl), 7.10 (1H, d, J=15.9 Hz, olefin), 6.48 (1H, d, J=16.2 Hz, olefin), 3.82 (3H, s, methyl); UV (99.5% CH_2Cl_2) 343 (ε=46700). Found: C, 71.88; H, 5.24; N, 10.52%. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.15; H, 5.31; N, 10.52%.

In a similar manner, 0.150 g of the same complex was esterified with ethanol to give 0.064 g of **1b**. Mp 106.0—108.0 °C (ethanol); IR (KBr) 1720, 1640 ,1210, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.18 (1H, d, J=1.2 Hz, pyrimidyl), 8.70 (1H, d, J=5.2 Hz, pyrimidyl), 7.89 (1H, d, J=16.2 Hz, olefin), 7.68 (1H, d, J=15.9 Hz, olefin), 7.62 (2H, d, J=8.5 Hz, phenylene), 7.56 (2H, d, J=8.5 Hz, phenylene), 7.32 (1H, dd, J=1.2 and 5.2 Hz, pyrimidyl), 7.10 (1H, d, J=16.2 Hz, olefin), 6.48 (1H, d, J=15.9 Hz, olefin), 4.28 (2H, q, J=7.0 Hz, methylene), 1.35 (3H, t, J=7.0 Hz, methyl); UV (99.5% CH_2Cl_2) 343 (ε=34400). Found: C, 72.54; H, 5.77; N, 10.04%. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.76; N, 9.99%.

Alkyl α-Cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamates) (1c, 1d, and 1e). To a solution of 4-[2-(4-pyrimidyl)ethenyl]-benzaldehyde (1.99 g, 9.4 mmol) in 200 ml of methanol were addedmethyl cyanoacetate (1.21 g, 12.2 mmol) and piperidine (0.1 ml), and the mixture was refluxed for 7 h. The yellow precipitates appeared during the reaction. After cooling, the precipitates were collected by filtration, and recrystallized from methanol to give 1.23 g of **1c**. Yield 72%; mp 223.0—225.0 °C; IR (KBr) 2210, 1740, 1600, 1290, 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.21 (1H, d, J=1.5 Hz, pyrimidyl), 8.74 (1H, d, J=5.5 Hz, pyrimidyl), 8.26 (1H, s, olefin), 8.05 (2H, d, J=15.9 Hz, phenylene), 7.93 (1H, d, J=15.9 Hz, olefin), 7.72 (2H, d, J=8.6 Hz, phenylene), 7.36 (1H, dd, J=1.5 and 5.5 Hz, pyrimidyl), 7.19 (1H, d, J=15.9 Hz, olefin), 3.95 (3H, s, methyl); UV (99.5% CH_2Cl_2) 360 (ε=65900). Found: C, 70.24; H, 4.46; N, 14.33%. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.10; H, 4.47; N, 14.43%.

Similar condensations of 4-[2-(4-pyrimidyl)ethenyl]benzaldehyde with ethyl and propyl cyanoacetate gave **1d** and **1e** in 83% and 71% yield, respectively.

1d. Mp 184.0—185.0 °C (ethanol); IR (KBr) 2220, 1710, 1590, 1270, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.21 (1H, d, J=1.2 Hz, pyrimidyl), 8.74 (1H, d, J=5.2 Hz), 8.24 (1H, s, olefin), 8.05 (2H, d, J=8.5 Hz, phenylene), 7.93 (1H, d, J=16.0 Hz, olefin), 7.72 (2H, d, J=8.5 Hz, phenylene), 7.36 (1H, dd, J=1.2 and 5.2 Hz, pyrimidyl), 7.19 (1H, d, J=16.0 Hz, olefin), 4.40 (2H, q, J=7.3 Hz, methylene), 1.41 (3H, t, J=7.3 Hz, methyl); UV (99.5% CH_2Cl_2) 359 (ε=43200). Found: C, 70.55; H, 4.84; N, 13.75%. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.82; H, 4.92; N, 13.77%.

1e. Mp 149.5—151.0 °C (1-propanol); IR (KBr) 2230, 1730, 1600, 1280, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.21 (1H, d, J=1.2 Hz, pyrimidyl), 8.74 (1H, d, J=5.2 Hz, pyrimidyl), 8.24 (1H, s, olefin), 8.05 (2H, d, J=8.6 Hz, phenylene), 7.93 (1H, d, J=16.2 Hz, olefin), 7.72 (2H, d, J=8.6 Hz, phenylene), 7.35 (1H, dd, J=1.2 and 5.2 Hz, pyrimidyl), 7.19 (1H, d, J=16.2 Hz, olefin), 4.30 (2H, t, J=6.7 Hz, methylene), 1.81 (2H, m, methylene), 1.00 (3H, t, J=1.2 Hz, methyl); UV (99.5% CH_2Cl_2) 360 (ε=69800). Found: C, 71.41; H, 5.47; N, 12.89%. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.47; H, 5.33; N, 13.17%.

Mixed Crystal (1f). Recrystallization of an equimolar mixture of **1d** (300 mg, 0.98 mmol) and **1e** (313 mg, 0.98 mmol) from 180 ml of propanol gave 350 mg of 1.3:1 mixed crystal (**1f**). The ratio was determined by 400 MHz ^1H NMR. Mp 160.0—165.0 °C (1-propanol).

Isolation of Dimers. The crystals of **1c—f** were photoirradiated by method 3. The dimers **2c, d** (1,2-bis[4-[2-cyano-2-(alkoxycarbonyl)ethenyl]phenyl]-3,4-di(4-pyrimidyl)cyclobutane) and **2e,f** (alkyl 1-cyano-3-[4-[2-cyano-2-(alkoxycarbonyl)-ethenyl]phenyl]-2-[4-[2-(4-pyrimidyl)ethenyl]phenyl]-4-(4-pyrimidyl)-1-cyclobutanecarboxylate) were isolated from the products by flash column chromatography (eluent: dichloromethane with 1—5% methanol). IR, ^1H NMR, and mass spectra analyses of **2c—f** were performed without further purification.

2c. IR (KBr) 2220, 1740, 1600, 1580, 1470, 1440, 1390, 1270, 1215, 1190, 1090, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.01 (2H, d, J=1.2 Hz, pyrimidyl), 8.52 (2H, d, J=5.2 Hz, pyrimidyl), 8.14 (2H, s, olefin), 7.83 (4H, d, J=8.4 Hz, phenylene), 7.26 (4H, d, J=8.4 Hz, phenylene), 7.14 (2H, dd, J=5.2 and 1.2 Hz, pyrimidyl), 4.99 (2H, m, cyclobutane), 4.63 (2H, m, cyclobutane), 3.90 (6H, s, methyl); MS m/z 582 (M^+), 398, 290 ($M^+/2-1$), 276, 258, 230.

2d. IR (KBr) 2230, 1730, 1600, 1580, 1550, 1470, 1390, 1270, 1220, 1195, 1090, 1020, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.01 (2H, d, J=1.1 Hz, pyrimidyl), 8.52 (2H, d, J=5.2 Hz, pyrimidyl), 8.12 (2H, s, olefin), 7.83 (4H, d, J=8.4 Hz, phenylene), 7.24 (4H, d, J=8.4 Hz, phenylene), 7.12 (2H, dd, J=5.2 and 1.1 Hz, pyrimidyl), 4.97 (2H, m, cyclobutane), 4.61 (2H, m, cyclobutane), 4.36 (4H, q, J=7.0 Hz, methylene), 1.38 (6H, t, J=7.0 Hz, methyl); MS m/z 610 (M^+), 426, 304 ($M^+/2-1$), 276, 232.

2e. IR (KBr) 2220, 1730, 1580, 1460, 1390, 1270, 1210, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.25 (1H, d, J=1.2 Hz, pyrimidyl), 9.15 (1H, d, J=1.0 Hz, pyrimidyl), 8.80 (1H, d, J=5.2 Hz, pyrimidyl), 8.67 (1H, d, J=5.2 Hz, pyrimidyl), 8.11 (1H, s, olefin), 7,82 (2H, d, J=8.2 Hz, phenylene), 7.78 (1H, d, J=15.9 Hz, olefin), 7.47 (2H, d, J=8.2 Hz, phenylene), 7.41 (1H, dd, J=5.2 and 1.2 Hz, pyrimidyl), 7.28 (1H, dd, J=5.2 and 1.0 Hz, pyrimidyl), 7.20 (2H, d, J=8.2 Hz, phenylene), 7.06 (2H, d, J=8.2 Hz, phenylene), 6.99 (1H, d, J=15.9 Hz, olefin), 5.19 (1H, t, J=11.3 and 10.4 Hz, cyclobutane), 4.93 (1H, d, J=11.3 Hz, cyclobutane), 4.72 (1H, d, J=10.4 Hz, cyclobutane), 4.24 (2H, t, J=6.6 Hz, methylene), 3.99 (2H, m, methylene), 1.75 (2H, m, methylene), 1.48 (2H, m, methylene), 0.99 (3H, t, J=7.5 Hz, methyl), 0.84 (3H, t, J=7.5 Hz, methyl); MS m/z 638 (M^+), 551, 463, 421, 318 ($M^+/2-1$), 276, 232.

2f. IR (KBr) 2220, 1725, 1600, 1580, 1470, 1390, 1270, 1210, 1190, 1090, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=9.25 (1H, d, J=1.2 Hz, pyrimidyl), 9.14 (1H, s, pyrimidyl), 8.80 (1H, m, pyrimidyl), 8.66 (1H, d, J=5.2 Hz, pyrimidyl), 8.11 (1H, s, olefin), 7.82 (2H, d, J=8.2 Hz, phenylene), 7.78 (1H, d, J=16.0 Hz, olefin), 7.47 (2H, d, J=8.2 Hz, phenylene), 7.41 (1H, m, pyrimidyl), 7.28 (1H, m, pyrimidyl), 7.20 (2H, d, J=8.2 Hz, phenylene), 7.06 (2H, d, J=8.2 Hz, phenylene), 6.99 (1H, d, J=16.0 Hz, olefin), 5.19 (1H, m, cyclobutane), 4.94 (1H, d, J=11.3 Hz, cyclobutane), 4.72 (1H, d, J=10.4 Hz, cyclobutane), 4.37—3.89 (4.5H, m, methylene), 1.82—0.82 (number of H is unknown for impurities, m, methylene and methyl); MS m/z 638 (M^+, R^1=Pr, R^2=Pr), 624 (M^+, R^1=Et,

R^2=Pr or R^1=Pr, R^2=Et), 610 (M^+, R^1=Et, R^2=Et), 531, 421, 407, 396, 318 ($M^+/2-1$, R=Pr), 304 ($M^+/2-1$, R=Et), 276, 260, 232.

Photoreaction. Photoreaction was carried out as follows. Method 1) KBr pellets containing a small amount of monomer crystals were irradiated with a 500 W super high-pressure mercury lamp under nitrogen atomosphere. Method 2) Finely powdered crystals of **1c—f** (200—500 mg) were dispersed in 300 ml of water containing a few drops of surfactant (NIKKOL TL-10FF), and irradiated with a 100 W high-pressure mercury lamp (Eikosha EHBWF-100) through a uranium glass filter with rigorous stirring under nitrogen atomosphere. Method 3) Finely powdered crystals of **1c—f** (100—200 mg) were dispersed in 90 ml of water containing a few drops of surfactant (NIKKOL TL-10FF) and irradiated with a 500 W super high-pressure mercury lamp (Ushio USH-500D) through a L38 filter (cut off <350 nm) for **1c**, **1e**, and **1f**, or a L40 filter (cut off <380 nm) for **1d** with stirring under nitrogen atomosphere.

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