The Rhodium(II) Acetate-Catalyzed Reaction of Alkenyl and Alkynyl α-Diazoacetates with Thioketene[1)]

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The reaction of allyl α-diazoacetates with di-*t*-butylthioketene catalyzed by $Rh_2(OAc)_4$ gave 4-allyl-2-methylene-1,3-oxathiolan-5-ones through the 1,5-cyclization of a thiocarbonyl ylide intermediate followed by Claisen rearrangement with allene episulfide through the 1,3-cyclization of the intermediate. Other alkenyl and alkynyl diazoacetates also gave similar products through the thiocarbonyl ylide without affording its intramolecular 1,3-dipolar cycloadduct.

Formation of an ylide,[2)] especially a carbonyl ylide[3)] and a thiocarbonyl ylide[4)] through the carbenoid reaction, and its 1,3-dipolar cycloadditions have recently received attention from synthetic and theoretical interests. Intramolecular formation of carbonyl ylides followed by intramolecular 1,3-dipolar cycloaddition has recently been studied extensively by Padwa and others.[5)]

We have reported the formation of 1,3-oxathiole derivatives through the 1,5-cyclization of acyl-substituted thiocarbonyl ylide intermediates generated by the reaction of ketocarbenoid with carbon disulfide[4a,4b)] or isothiocyanates.[4c)] As a continuation of this work, we studied the rhodium(II) acetate-catalyzed reaction of alkenyl and alkynyl diazoacetates with di-*t*-butylthioketene (**2**) expecting a tandem reaction of thiocarbonyl ylide formation and intramolecular 1,3-dipolar cycloaddition. We wish to report here the interesting results of the intramolecular 1,3- and 1,5-cyclizations of the thiocarbonyl ylides without affording the expected intramolecular 1,3-dipolar cycloadduct[2a)] of the thiocarbonyl ylide moiety toward the alkenyl and alkynyl part of the ester group. In the reaction of allyl and 2-propynyl diazoacetates, tandem intramolecular 1,5-cyclization reactions of the thiocarbonyl ylide and Claisen rearrangement were observed.

In this connection, Ando and co-workers[6)] reported the rhodium(II) acetate-catalyzed reaction of dialkyl diazomalonate with di-*t*-butylthioketene to give 5-alkoxy-4-alkoxycarbonyl-2-(di-*t*-butylmethylene)-1,3-oxathiole through the 1,5-cyclization of a thiocarbonyl ylide intermediate.

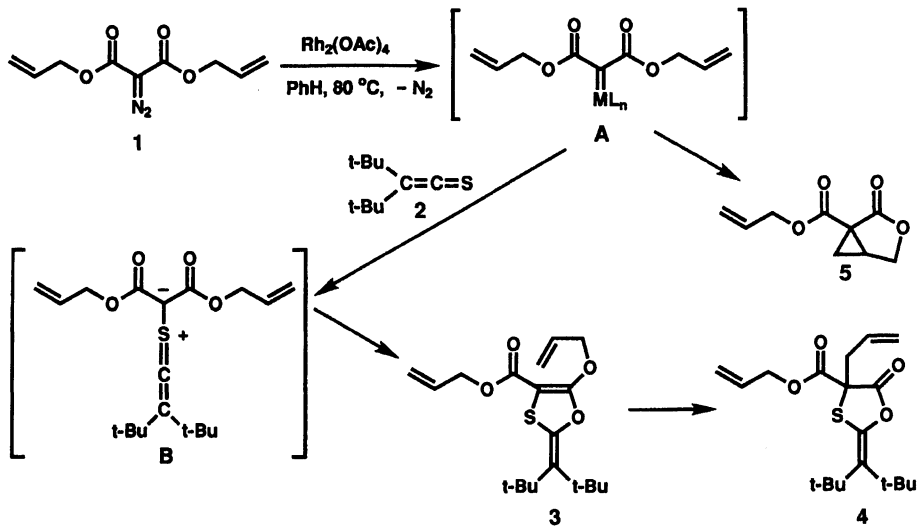
Results and Discussion

The rhodium(II) acetate-catalyzed decomposition of diallyl diazomalonate (**1**) in the presence of an equimolar amount of di-*t*-butylthioketene (**2**) gave allyl 4-allyl-2-(di-*t*-butylmethylene)-5-oxo-1,3-oxathiolane-4-carboxylate (**4**) and a bicyclic cyclopropane derivative (**5**) in 28 and 29% yields, respectively.

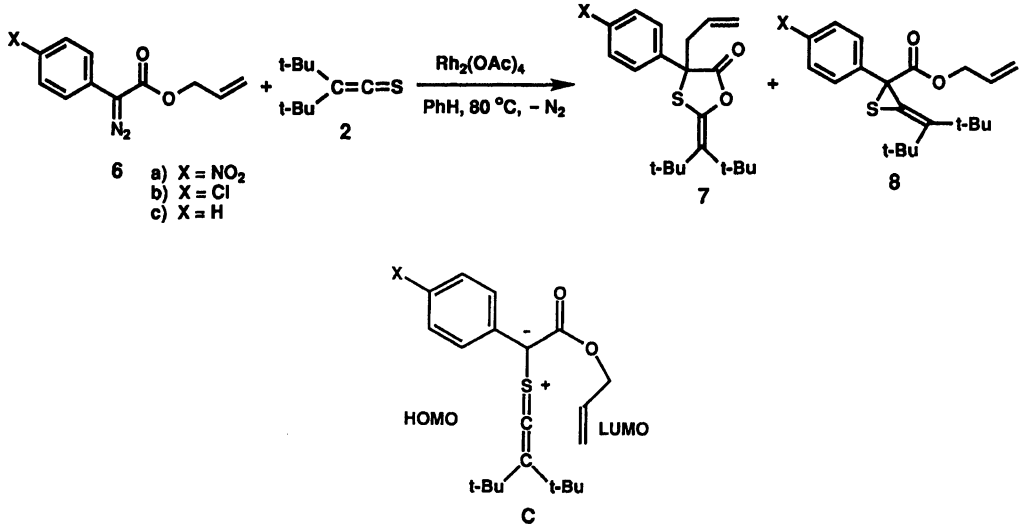
The results of elemental analyses and mass spectrum measurements indicated that **4** was the 1 : 1-product of ketocarbene and di-*t*-butylthioketene. The ^{1}H NMR spectrum of **4** showed methyl signals from two *t*-butyl groups at 1.36 and 1.38 ppm, and signals from an allylic methylene group attached to a carbon atom (C-4) at 2.86 and 2.94 ppm, and that attached to an oxygen atom of an ester group at 4.61 and 4.76 ppm. The ^{13}C NMR signals of **4** at 133.49 (s), 59.44 (s), and 167.56 (s) ppm are assigned to C-2, C-4, and C-5, respectively, of the 1,3-oxathiolan-5-one ring system. The singlet signals at 134.61 and 167.48 ppm were assignable to an *exo*-methylene carbon and an ester carbonyl carbon, respectively. The IR bands at 1781 and 1741 cm^{-1} were assigned to the two carbonyl groups of the lactone and the acyclic ester. The structure of cyclopropane derivative **5** was determined on the basis of the spectral data presented in the Experimental section.

Formation of **4** can be explained by the 1,5-cyclization of thiocarbonyl ylide intermediate **B** generated by the attack of carbenoid **A** toward the sulfur atom of thioketene **2** to give 5-allyloxy-1,3-oxathiole derivative **3** followed by Claisen rearrangement (Scheme 1). Cyclopropane derivative **5** is formed by the intramolecular cyclopropanation of carbenoid **A**. In this reaction, the intramolecular 1,3-dipolar cycloaddition of thiocarbonyl ylide **B** was not observed in spite of detailed inspection of the reaction mixture by medium-pressure column chromatography.

The rhodium(II) acetate-catalyzed reaction of allyl *p*-nitrophenyldiazoacetate (**6a**) with di-*t*-butylthioketene (**2**) also gave 4-allyl-4-(*p*-nitrophenyl)-2-(di-*t*-butyl-



Scheme 1.

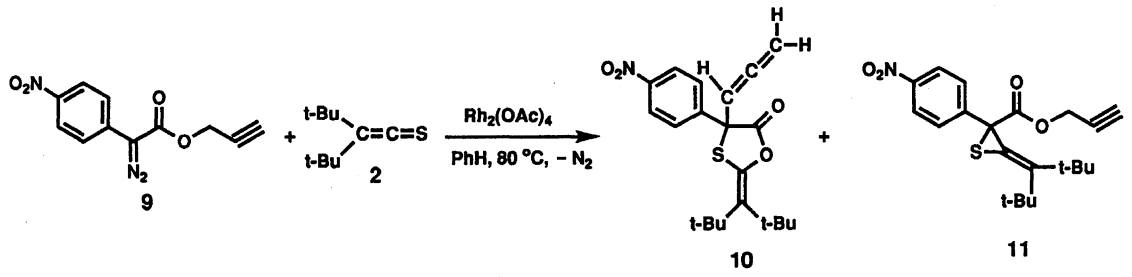


Scheme 2.

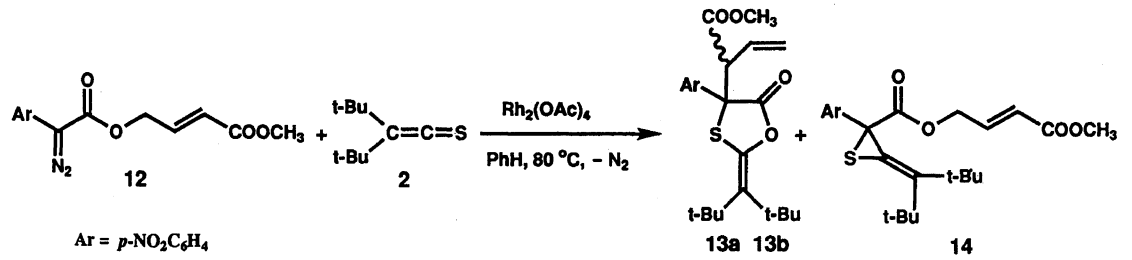
methylene)-1,3-oxathiolan-5-one (**7a**) in a 69% yield through the Claisen rearrangement of a 5-allyloxy-2-methylene-1,3-oxathiole intermediate together with allene episulfide **8a** (21% yield) (Scheme 2). The ^{1}H NMR spectrum of **8a** showed the presence of non-equivalent *t*-butyl groups (at 1.15 and 1.46 ppm) and an *O*-methylene group (at 4.70 ppm). No intramolecular cyclopropanation product was obtained in this reaction which is different from the reaction of diallyl diazomalonate (**1**). This result shows that the formation of a thiocarbonyl ylide by the reaction of a *p*-nitrophenyl substituted ketocarbenoid with a thioketene is much faster than intramolecular cyclopropanation in contrast to the reaction of a carbenoid generated by the decomposition of diallyl diazomalonate, in which thiocarbonyl ylide formation and intramolecular cyclopropanation are competing.

The 1,3-dipolar cycloaddition of a thiocarbonyl ylide with an alkene is usually controlled by the HOMO of the 1,3-dipole and the LUMO of the dipolarophile according to frontier molecular orbital theory.[7] In the intramolecular cycloaddition of thiocarbonyl ylide **C**, substituents (NO_2, Cl, and H) on the benzene ring may affect the rate of cycloaddition by altering the HOMO energy level of the thiocarbonyl ylide. This may also change the ratio of 1,3-oxathiolan-5-one **7** to allene episulfide **8**. The reaction of allyl *p*-chlorophenyldiazoacetate (**6b**) did not give the intramolecular 1,3-dipolar cycloaddition product of thiocarbonyl ylide intermediate **Cb** but gave 1,3-oxathiolan-5-one **7b** and allene episulfide **8b** in a total yield of 93% (**7b** : **8b** =59 : 41). A similar result was obtained in the reaction of allyl phenyldiazoacetate (**6c**) (85% total yield, **7c** : **8c** =63 :37).

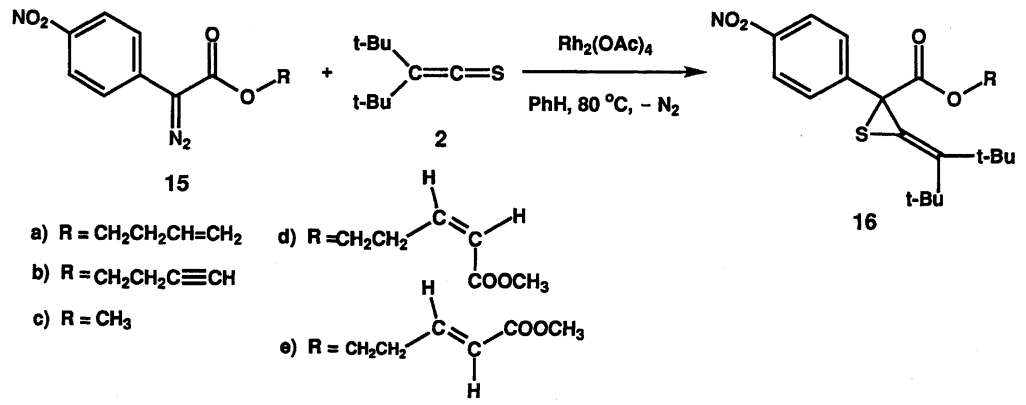
The reaction of 2-propynyl *p*-nitrophenyldiazoacetate (**9**) with **2** gave 4-(1,2-propadienyl)-1,3-oxathiolan-5-one (**10**) together with allene episulfide **11** in 60 and 28% yields, respectively, through a mechanism similar to that for **6** (Scheme 3). The structure of **10** was con-



Scheme 3.



Scheme 4.



Scheme 5.

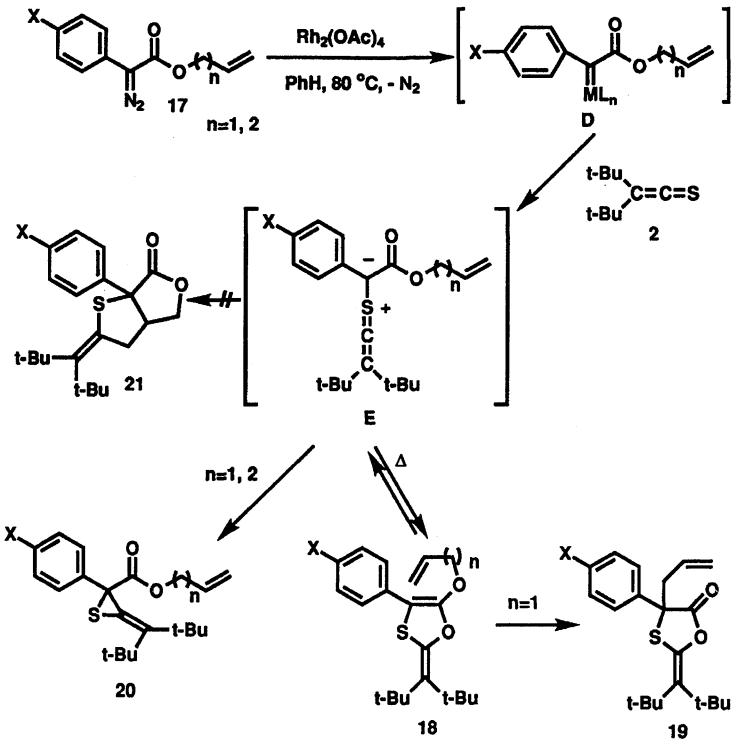
firmed by the characteristic ^{13}C NMR chemical shifts of the allene carbons (at δ=81.37, 93.02, and 208.29) together with the other spectroscopic data. The formation of **10** is explained by the Claisen rearrangement of the 5-(2-propynyloxy)-2-methylene-1,3-oxathiole intermediate.

The lowered LUMO energy level of the dipolarophile by the substitution of an electron-withdrawing group such as a methoxycarbonyl group may accelerate the cycloaddition by the strong interaction between the thiocarbonyl ylide HOMO and the dipolarophile LUMO.[7] However, the reaction of methyl (*E*)-4-(*p*-nitrophenyldiazoacetoxy)-2-butenoate (**12**) with **2** gave only a diastereomeric mixture of 1,3-oxathiolan-5-ones **13a** and **13b** (11 and 41% yields, respectively), and allene episulfide **14** (25% yield) (Scheme 4).

Isolation of 5-alkoxy-2-methylene-1,3-oxathiole, a precursor of 2-methylene-1,3-oxathiolan-5-one, might be expected in the reaction of 3-butenyl or methyl aryldiazoacetates because of suppression of the Claisen rearrangement. The reaction of 3-butenyl *p*-nitrophenyldiazoacetate (**15a**) with **2** gave allene episulfide **16a** in an 82% yield without affording the expected products through the intramolecular cyclopropanation of the corresponding carbene intermediate and through the intramolecular 1,5-cyclization of the thiocarbonyl ylide intermediate, which may give 5-(3-butenyloxy)-2-methylene-1,3-oxathiole, and the intramolecular 1,3-dipolar cycloaddition of the thiocarbonyl ylide intermediate. The ^1H NMR spectrum of **16a** showed the presence of nonequivalent *t*-butyl groups (at δ=1.15 and 1.46) and an *O*-methylene group (at δ=4.27).

The reaction of 3-butynyl *p*-nitrophenyldiazoacetate (**15b**) with **2** also gave allene episulfide **16b** in a 68% yield (Scheme 5). The reaction of methyl *p*-nitrophenyldiazoacetate (**15c**) afforded the corresponding allene episulfide **16c** in a 66% yield. The reactions of methyl (*Z*)- and (*E*)-5-(*p*-nitrophenyldiazoacetoxy)-2-pentenoates (**15d** and **15e**) gave the corresponding allene episulfides **16d** and **16e** in 63 and 52% yields, respectively.

The formation of 1,3-oxathiolan-5-one **19** and/or allene episulfide **20** in the reactions of alkenyl aryldiazoacetates **17** is illustrated in Scheme 6. Ketocarbenoid



Scheme 6.

D formed by the catalytic decomposition of aryldiazoacetates **17** attacks the sulfur atom of di-*t*-butylthioketene to generate thiocarbonyl ylide **E**, which undergoes 1,5-cyclization to give 5-alkenyloxy-2-methylene-1,3-oxathiole **18**. The Claisen rearrangement of **18** to give **19** happens when $n=1$ as shown in Scheme 1. Allene episulfide **20** is formed by the 1,3-cyclization of thiocarbonyl ylide intermediate **E** in both cases of $n=1$ and $n=2$.

The failure of either the isolation of **18a** ($n=1$) or the detection of **18a** by NMR measurements even in the reaction of allyl *p*-nitrophenyldiazoacetate (**6a**) with **2** under mild reaction conditions at 50 °C indicates that the Claisen rearrangement of **18a** ($n=1$) to **19a** is quite fast under these reaction conditions.

A control experiment to keep allene episulfide **8a** (=**20a**: $n=1$, X=NO_2) at 80 °C for 3 h in a benzene solution indicated that isomerization of episulfide **8a** to give oxathiolan-5-one **7a** (=**19a**) through thiocarbonyl ylide **E** and **18** was confirmed not to occur under the reaction conditions. Different from the reaction of allyl aryldiazoacetates (**6**=**17a**: $n=1$), intermediate 5-methoxy or 5-(3-butenyloxy)-2-methylene-1,3-oxathiole **18b** ($n=2$) obtained by the reaction of methyl of 3-butenyl diazoesters **17b** ($n=2$) can not give the corresponding 1,3-oxathiolan-5-one due to suppression of the Claisen rearrangement. Therefore, regeneration of thiocarbonyl ylide **Eb** by the cleavage of 2-methylene-1,3-oxathiole **18b** may be concluded because of its thermal instability. It is also plausible that 2-methylene-1,3-oxathiole **18a** is in equilibrium with thiocarbonyl ylide **Ea** in the reaction system of allyl diazoesters **17a**. The reaction of 3-butenyl, 3-butynyl, and methyl *p*-nitrophenyldiazoacetates gave allene episulfides in almost the same yields as the total yields of 1,3-oxathiolan-5-one and episulfide in the reaction of allyl aryldiazoacetates. These experimental results also support the equilibrium between 2-methyleneoxathiole **18** and thiocarbonyl ylide **E**.

The intramolecular 1,3-dipolar cycloaddition of thiocarbonyl ylide **E** to give bicyclic lactone **21** was not successful even though an electron-withdrawing methoxycarbonyl group was introduced into the dipolarophile part. The low intramolecular 1,3-dipolar reactivity of **E** may be ascribed to three reasons: (a) the steric hindrance of two bulky *t*-butyl groups to the approach of the dipolarophile part to the thiocarbonyl ylide part of **E**; (b) the 1,5- and 1,3-cyclizations of **E** to give 2-methylene-1,3-oxathiole **18** and allene episulfide **20** are faster than the 1,3-dipolar cycloaddition of **E**; and (c) deactivation of thiocarbonyl ylide **E** by its additional double bond.

The rhodium(II) acetate-catalyzed reaction of allyl *p*-nitrophenyldiazoacetate (**6a**) with thioketene **2** in the presence of 20 molar amounts of a reactive dipolarophile such as *N*-methyl maleimide or dimethyl acetylenedicarboxylate at 80 °C gave **7a** and **8a** without affording the intermolecular 1,3-dipolar cycloadduct of thiocarbonyl ylide **Ca** (X=NO_2). These results indicate that the intramolecular 1,3- and 1,5-cyclizations of thiocarbonyl ylide **Ca** are much faster than the intermolecular 1,3-dipolar cycloaddition. The low intermolecular 1,3-dipolar reactivity of **Ea** may be ascribed to the reasons

discussed above.

Experimental

Melting points were not corrected. IR spectra were recorded on a Perkin–Elmer model 983. ^{1}H NMR (270.05 MHz) and ^{13}C NMR (67.80 MHz) spectra were recorded on a JEOL EX-270 spectrometer in a $CDCl_3$ solution, using TMS as an internal standard. Mass spectra were determined with a JEOL JMS-DX303 mass spectrometer.

Materials. Di-*t*-butylthioketene was prepared by the reported method.[8] Benzene was purified by distillation after reflux on CaH_2 and stored over molecular sieves 4A.

Diallyl Diazomalonate (1) was prepared by the diazo group transfer reaction diallyl malonate as reported by Regitz.[9]

Aryldiazoacetates. Alkenyl and alkynyl aryldiazoacetates were prepared by the method described below using the diazo group transfer reaction.[9] A solution of *p*-tosyl azide (20 mmol) in acetonitrile (10 mL) was added to a solution of an alkenyl or alkynyl arylacetate (20 mmol) and DBU (20 mmol) in acetonitrile (30 mL), and the mixture was stirred at r.t. for 14 h. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in ether. The ether layer was washed with a 5% aqueous solution of potassium hydroxide and water, then dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by alumina column chromatography using ethyl acetate–hexane as an eluent or recrystallization from a suitable solvent.

Allyl *p*-Chlorophenyldiazoacetate (6b): Yield 33%; yellow oil; ^{1}H NMR δ=4.77 (2H, dt, J=5.6 and 1.3 Hz), 5.26—5.39 (2H, m), 5.98 (1H, ddt, J=17.2, 10.6, and 5.6 Hz), and 7.32—7.45 (4H, m); IR (neat, NaCl) 2089 (=N_2) and 1700 (C=O) cm^{-1}.

Allyl Phenyldiazoacetate (6c): Yield 44%; yellow oil; ^{1}H NMR δ=4.77 (2H, d, J=5.6 Hz), 5.25—5.40 (2H, m), 5.91—6.06 (1H, m), and 7.15—7.51 (5H, m); IR (neat, NaCl) 2086 (=N_2) and 1704 (C=O) cm^{-1}.

2-Propynyl *p*-Nitrophenyldiazoacetate (9): Yield 68%; yellow crystals; mp; 109.4—113.3 °C; ^{1}H NMR δ=2.55 (1H, t, J=2.3 Hz), 4.91 (2H, d, J=2.3 Hz), 7.64—7.70 (2H, m), and 8.22—8.27 (2H, m); IR (KBr) 3258 (≡CH), 2097 (=N_2), and 1721 (C=O) cm^{-1}.

3-Butenyl *p*-Nitrophenyldiazoacetate (15a): Yield 31%; yellow crystals; mp 38.1—39.7 °C; ^{1}H NMR δ=2.49 (2H, qt, J=6.6 and 1.3 Hz), 4.37 (2H, t, J=6.6 Hz), 5.10—5.20 (2H, m), 5.82 (1H, ddt, J=17.2, 10.2, and 6.6 Hz), 7.63—7.69 (2H, m), and 8.20—8.25 (2H, m); IR (neat, NaCl) 2097 (=N_2) and 1705 (C=O) cm^{-1}.

3-Butynyl *p*-Nitrophenyldiazoacetate (15b): Yield 51%; yellow crystals; mp 84.5—85.4 °C; ^{1}H NMR δ=2.05 (1H, t, J=2.6 Hz), 2.64 (2H, td, J=6.6 and 2.6 Hz), 4.42 (2H, t, J=6.6 Hz), 7.63—7.69 (2H, m), and 8.21— 8.26 (2H, m); IR (KBr) 3261 (≡CH), 2110 (s, =N_2), and 1702 (s, C=O) cm^{-1}.

Methyl (*E*)-4-(*p*-Nitrophenylacetoxy)-2-butenoate. 4-(1-Pyrrolidinyl)pyridine (336 mg, 2.26 mmol) was added to a solution of *p*-nitrophenylacetic acid (3.62 g, 20.0 mmol), methyl (*E*)-4-hydroxy-2-butenoate[10] (2.12 g, 20.0 mmol), and dicyclohexylcarbodiimide (DCC; 4.56 g, 22.1 mmol) in dichloromethane (50 mL), and the resulting mixture was stirred for 4 h at r.t. The solid precipitate was removed by filtration and washed with dichloromethane. The organic solution was washed with an aqueous solution of sodium hydrogencarbonate and water, then dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was separated by silica gel column chromatography using ethyl acetate–hexane as an eluent. The crude product was recrystallized from ethanol to give pure methyl (*E*)-4-(*p*-nitrophenylacetoxy)-2-butenoate (3.47 g): Yield 70%; colorless needles; mp 62.5—63.4 °C; ^{1}H NMR δ=3.74 (3H, s), 3.83 (2H, s), 4.80 (2H, dd, J=4.8 and 2.0 Hz), 5.96 (1H, dt, J=15.8 and 2.0 Hz), 6.93 (1H, dt, J=15.8 and 4.8 Hz), 7.45—7.52 (2H, m), and 8.14—8.22 (2H, m); IR (KBr) 1722 (C=O) cm^{-1}.

Methyl (*E*)- 4- (*p*- Nitrophenyldiazoacetoxy)- 2-butenoate (12). A solution of *p*-tosyl azide (0.499 g, 2.53 mmol) in acetonitrile (3 mL) was added to a solution of methyl (*E*)-4-(*p*-nitrophenylacetoxy)-2-butenoate (0.616 g, 2.48 mmol) and DABCO (0.561 g, 5.00 mmol) in acetonitrile (10 mL), and the mixture was stirred at r.t. for 2 h. A treatment similar to that described above gave **12** (361 mg): Yield 54%; yellow crystals; mp 125.1—134.9 °C (decomp); ^{1}H NMR δ=3.77 (3H, s), 4.98 (2H, dd, J=4.8 and 1.8 Hz), 6.06 (1H, dt, J=15.8 and 1.8 Hz), 7.01 (1H, dt, J=15.8 and 4.8 Hz), 7.64—7.70 (2H, m), and 8.22—8.28 (2H, m); IR (KBr) 2102 (=N_2), 1724 (C=O), and 1697 (C=O) cm^{-1}.

Methyl, (*Z*)- and (*E*)-5-(*p*-Nitrophenylacetoxy)-2-pentenoates. 4-(1-Pyrrolidinyl)pyridine (0.11 g, 0.74 mmol) was added to a solution of *p*-nitrophenylacetic acid (1.31 g, 7.23 mmol), methyl 5-hydroxy-2-pentenoate[11] (1.14 g, 8.76 mmol), and DCC (1.84 g, 8.92 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred for 15 h at r.t. Separation of the residue by silica gel column chromatography using ethyl acetate-hexane gave methyl (*Z*)- and (*E*)-5-(*p*-nitrophenylacetoxy)-2-pentenoates.

Methyl (*Z*)- 5- (*p*- Nitrophenylacetoxy)- 2- pentenoate (721 mg): Yield 34%; colorless needles; mp 52.5—53.8 °C; ^{1}H NMR δ=3.01 (2H, q, J=6.3 Hz), 3.71 (3H, s), 3.73 (2H, s), 4.24 (2H, t, J=6.3 Hz), 5.87 (1H, d, J=11.5 Hz), 6.19 (1H, dt, J=11.5 and 6.3 Hz), 7.45—7.47 (2H, m), and 8.17—8.20 (2H, m); IR (KBr) 1734 (C=O) and 1710 (C=O) cm^{-1}. Found: C, 57.47; H, 5.18; N, 4.85%. Calcd for $C_{14}H_{15}NO_6S$: C, 57.34; H, 5.16; N, 4.78%.

Methyl (*E*)- 5- (*p*- Nitrophenylacetoxy)- 2- pentenoate (306 mg): Yield 44%; colorless oil; ^{1}H NMR δ=2.53 (2H, qd, J=6.8 and 1.7 Hz), 3.74 (5H, s, OCH_3+ CH_2COO), 4.24 (2H, t, J=6.8 Hz), 5.81 (1H, dt, J=15.7 and 1.7 Hz), 6.86 (1H, dt, J=15.7 and 6.8 Hz), 7.42—7.47 (2H, m), and 8.16—8.23 (2H, m); IR (KBr) 1735 (C=O) and 1725 (C=O) cm^{-1}. Found: C, 57.44; H, 5.10; N, 4.85%. Calcd for $C_{14}H_{15}NO_6S$: C, 57.34; H, 5.16; N, 4.78%.

Methyl (*Z*)-5-(*p*-Nitrophenyldiazoacetoxy)-2-pentenoate (15d): Yield 77%; yellow needles; mp 102.5—105.2 °C; ^{1}H NMR δ=3.12 (2H, qd, J=6.7 and 1.6 Hz), 3.73 (3H, s), 4.43 (2H, t, J=6.7 Hz), 5.94 (1H, dt, J=11.6 and 1.6 Hz), 6.27 (1H, dt, J=11.6 and 6.7 Hz), 7.63—7.68 (2H, m), and 8.19—8.25 (2H, m); IR (KBr) 2095 (=N_2), 1711 (C=O), and 1697 (C=O) cm^{-1}.

Methyl (*E*)-5-(*p*-Nitrophenyldiazoacetoxy)-2-pentenoate (15e): Yield 66%; yellow needles; mp 63.3—64.5 °C; ^{1}H NMR δ=2.65 (2H, qd, J=6.7 and 1.5 Hz), 3.75 (3H, s), 4.43 (2H, t, J=6.7 Hz), 5.95 (1H, dt, J=15.8 and 1.5 Hz), 6.95 (1H, dt, J=15.8 and 6.7 Hz), 7.62—7.67 (2H, m),

and 8.21—8.26 (2H, m); IR (KBr) 2101 (=N_2), 1717 (C=O), and 1700 (C=O) cm^{-1}. Found: C, 52.78; H, 4.19; N, 13.44%. Calcd for $C_{14}H_{13}NO_3S$: C, 52.67; H, 4.10; N, 13.16%.

General Procedure for the Rhodium(II) Acetate-Catalyzed Decomposition of α-Diazo Esters in the Presence of Di-*t*-butylthioketene. A solution of a diazo ester (1.00 mmol) in dry benzene (10 mL) was added dropwise over a period of ca. 4 h to a refluxing benzene solution (20 mL) of di-*t*-butylthioketene (1.00 mmol) in the presence of suspended rhodium(II) acetate (13.3 mg, 3×10^{-2} mmol) under nitrogen atmosphere. The solution was heated at 80 °C until no more diazo compound was detected by TLC or IR spectra. The resulting reaction mixture was concentrated under reduced pressure. The residue was separated by medium-pressure liquid chromatography (silica gel, eluted with ethyl acetate–hexane).

The reaction of diallyl diazomalonate (**1**) with di-*t*-butylthioketene gave allyl 5-oxo-1,3-oxathiolane-4-carboxylate **4** and cyclopropane derivative **5** in 28 and 29% yields, respectively.

Allyl 4-Allyl-2-(di-*t*-butylmethylene)-5-oxo-1,3-oxathiolane-4-carboxylate (4): Colorless oil; ^{1}H NMR δ=1.36 (9H, s), 1.38 (9H, s), 2.86 (1H, dd, J=14.5 and 7.3 Hz), 2.94 (1H, dd, J=14.5, 7.3 and 1.3 Hz), 4.61 (1H, ddt, J=13.2, 5.6, and 1.3 Hz), 4.76 (1H, ddt, J=13.2, 5.6 and 1.3 Hz), 5.22—5.40 (4H, m), and 5.80—5.96 (4H, m); ^{13}C NMR δ=32.42 (q), 32.76 (q), 36.95 (s), 37.53 (t), 39.84 (s), 59.44 (s), 66.87 (t), 119.12 (t), 121.19 (t), 130.66 (d), 130.85 (d), 133.49 (s), 134.61 (s), 167.48 (s), and 167.56 (s); IR (neat, NaCl) 1781 (C=O) and 1745 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 352 (M^+, 22), 154 (59), and 139 (100). Found: C, 64.74; H, 8.01%. Calcd for $C_{19}H_{28}O_4S$: C, 64.79; H, 8.06%.

Cyclopropane Derivative 5: Colorless oil; ^{1}H NMR δ=1.41 (1H, t, J=5.1 Hz), 2.11 (1H, dd, J=8.1 and 5.1 Hz), 2.78 (1H, dt, J=8.1 and 4.9 Hz), 4.20 (1H, d, J=9.5 Hz), 4.38 (1H, dd, J=9.5 and 4.6 Hz), 4.69 (2H, dt, J=5.6 and 1.3 Hz), 5.25—5.43 (2H, m), and 5.93 (1H, ddt, J=17.2, 10.6, and 5.6 Hz); ^{13}C NMR δ=20.71 (t), 27.91 (d), 29.24 (s), 66.21 (t), 66.91 (t), 118.81 (t), 131.18 (d), 166.30 (s), and 170.25 (s); IR (neat, NaCl) 1778 (C=O) and 1725 (C=O) cm^{-1}.

The reaction of allyl *p*-nitrophenyldiazoacetate (**6a**) with **2** gave allyl 1,3-oxathiolan-5-one **7a** and allene episulfide **8a** in 69 and 21% yields, respectively.

4-Allyl-2-(di-*t*-butylmethylene)-4-(*p*-nitrophenyl)-1,3-oxathiolan-5-one (7a): Yellow oil; ^{1}H NMR δ=1.32 (9H, s), 1.40 (9H, s), 3.04 (2H, d, J=6.9 Hz), 5.17—5.23 (2H, m), 5.68 (1H, ddt, J=17.0, 10.1, and 6.9 Hz), 7.80—7.85 (2H, m), and 8.21—8.27 (2H, m); ^{13}C NMR δ=32.46 (q), 32.71 (q), 37.00 (s), 39.78 (s), 44.38 (t), 60.44 (s), 121.27 (t), 123.75 (d), 127.89 (d), 130.71 (d), 133.00 (s), 135.20 (s), 145.20 (s), 147.61 (s), and 170.18 (s); IR (neat, NaCl) 1771 (C=O), 1523 (N=O), 1348 (N=O), and 1204 cm^{-1}; MS (EI, assignment, rel intensity %) 389 (M^+, 17), 203 (30), 154 (43), and 139 (100). Found: C, 64.90; H, 6.87; N, 3.66%. Calcd for $C_{21}H_{27}NO_4S$: C, 64.76; H, 6.99; N, 3.60%.

Allyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)-thiirane-2-carboxylate (8a): Yellow oil; ^{1}H NMR δ=1.15 (9H, s,), 1.46 (9H, s), 4.70 (2H, dt, J=5.6 and 1.3 Hz), 5.23—5.41 (2H, m), 5.91 (1H, ddt, J=17.2, 10.6, and 5.6 Hz), 7.73—7.79 (2H, m), and 8.12—8.17 (2H, m).

The reaction of allyl *p*-chlorophenyldiazoacetate (**6b**) with **2** gave a mixture of 1,3-oxathiolan-5-one **7b** and allene episulfide **8b** in 55 and 38% yields, respectively. The molar ratio was determined by integration of the ^{1}H NMR spectrum of the mixture.

4-Allyl-2-(di-*t*-butylmethylene)-4-(*p*-chlorophenyl)-1,3-oxathiolan-5-one (7b): Colorless oil; ^{1}H NMR δ=1.31 (9H, s), 1.39 (9H, s), 2.92—3.06 (2H, m), 5.13—5.22 (2H, m), 5.68 (1H, ddt, J=17.2, 9.9, and 7.1 Hz), 7.32—7.37 (2H, m), and 7.53—7.58 (2H, m); ^{13}C NMR δ=32.51 (q), 32.76 (q), 36.96 (s), 39.69 (s), 44.24 (t), 60.17 (s), 120.64 (d), 128.15 (d), 128.76 (d), 131.35 (d), 133.64 (s), 134.27 (s), 134.38 (s), 136.72 (m), and 170.88 (s); IR (neat; NaCl) 1771 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 378 (M^+), 192 (43), 154 (43), and 139 (100). Found: C, 66.80; H, 7.19%. Calcd for $C_{21}H_{27}O_2SCl$: C, 66.56; H, 7.18%.

Allyl 2-(*p*-Chlorophenyl)-3-(di-*t*-butylmethylene)-thiirane-2-carboxylate (8b): ^{1}H NMR (mixture with oxathiolan-5-one **7b**) δ=1.15 (9H, s), 1.45 (9H, s), 4.68 (2H, dt, J=5.6 and 1.3 Hz), 5.22—5.39 (2H, m), 5.91 (1H, ddt, J=17.2, 10.2, and 5.6 Hz), 7.23—7.28 (2H, m), and 7.47—7.53 (2H, m).

The reaction of allyl phenyldiazoacetate (**6c**) with **2** gave a mixture of 1,3-oxathiolan-5-one **7c** and allene episulfide **8c** in 54% and 32% yields, respectively. The molar ratio was determined by integration of the ^{1}H NMR spectrum of the mixture.

4-Allyl-2-(di-*t*-butylmethylene)-4-phenyl-1,3-oxathiolan-5-one (7c): Colorless oil; ^{1}H NMR (mixture with allene episulfide **8c**) δ=1.32 (9H, s), 1.39 (9H, s), 2.95—3.10 (2H, m), 5.11—5.22 (2H, m), 5.72 (1H, ddt, J=17.0, 9.4 and 7.4 Hz), 7.19—7.40 (3H, m), and 7.58—7.63 (2H, m).

Allyl 3-(Di-*t*-butylmethylene)-2-phenylthiirane-2-carboxylate (8c): ^{1}H NMR (mixture with oxathiolan-5-one **7c**) δ=1.16 (9H, s), 1.46 (9H, s), 4.69 (2H, dt, J=5.6 and 1.4 Hz), 5.25—5.40 (2H, m), 5.92 (1H, ddt, J=17.2, 10.6, and 5.6 Hz), 7.19—7.40 (3H, m), and 7.51—7.56 (2H, m).

The reaction of 2-propynyl *p*-nitrophenyldiazoacetate (**9**) with **2** gave 1,3-oxathiolan-5-one **10** and allene episulfide **11** in 60 and 28% yields, respectively.

2-(Di-*t*-butylmethylene)-4-(*p*-nitrophenyl)-4-(1,2-propadienyl)-1,3-oxathiolan-5-one (10): Yellow oil; ^{1}H NMR δ=1.37 (9H, s), 1.38 (9H, s), 5.09 (2H, d, J=6.6 Hz), 5.74 (1H, t, J=6.6 Hz), 7.75—7.79 (2H, m), and 8.21—8.25 (2H, m); ^{13}C NMR δ=32.36 (q), 32.65 (q), 37.01 (s), 39.76 (s), 59.23 (s), 81.37 (t), 93.02 (d), 123.60 (dd), 128.54 (d), 132.88 (s), 136.05 (s), 144.38 (s), 147.65 (s), 168.64 (s), and 208.29 (s); IR (KBr) 1952 (=C=) and 1762 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 387 (M^+, 12), 201 (65), 154 (34), and 139 (100). Found: C, 64.82; H, 6.51; N, 3.83%. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61%.

2-Propynyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (11): Yellow oil; ^{1}H NMR δ=1.16 (9H, s), 1.47 (9H, s), 2.52 (1H, t, J=2.5 Hz), 4.74 (1H, dd, J=15.5 and 2.5 Hz), 4.87 (1H, dd, J=15.5 and 2.5 Hz), 7.74—7.78 (2H, m), and 8.13—8.17 (2H, m); IR (KBr) 3292 (≡CH), 2126 (C≡C), and 1729 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 387 (M^+, 51) and 292 (100). Found: C, 65.29; H, 6.57; N, 3.67%. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61%.

The reaction of methyl 4-(*p*-nitrophenyldiazoacetoxy)-

2-butenoate (**12**) with **2** gave a pair of diastereomers of 1,3-oxathiolan-5-ones (**13a** and **13b**), the stereochemistry of which was not determined, together with allene episulfide **14** in 11, 41, and 25% yields, respectively.

Methyl 2-[2-(Di-*t*-butylmethylene)-4-(*p*-nitrophenyl)-5-oxo-1,3-oxathiolan-4-yl]-3-butenoate (13a): Colorless crystals; mp 111.6—113.6 °C; ^{1}H NMR δ=1.33 (9H, s), 1.44 (9H, s), 3.53 (3H, s), 4.23 (1H, d), 5.42 (1H, d, J=10.0 Hz), 5.42 (1H, d, J=17.2 Hz), 6.04 (1H, ddd, J=17.2, 10.0, and 8.3 Hz), 7.95—8.00 (2H, m), and 8.21—8.25 (2H, m); ^{13}C NMR δ=32.56 (q), 32.73 (q), 36.98 (s), 39.76 (s), 52.51 (q), 58.46 (d), 62.88 (s), 123.36 (t), 123.67 (d), 128.31 (d), 130.20 (d), 133.85 (s), 134.86 (s), 143.75 (s), 147.85 (s), 168.72 (s), and 170.19 (s); IR (KBr) 1769 (C=O) and 1736 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 447 (M$^+$, 10), 261 (60), 233 (21), 154 (46), and 139 (100). Found: C, 61.45; H, 6.51; N, 3.21%. Calcd for $C_{23}H_{29}NO_6S$: C, 61.73; H, 6.53; N, 3.13%.

Methyl 2-[2-(Di-*t*-butylmethylene)-4-(*p*-nitrophenyl)-5-oxo-1,3-oxathiolan-4-yl]-3-butenoate (13b); Colorless crystals; mp 138.0—138.7 °C (from ethyl acetate–hexane); ^{1}H NMR δ=1.35 (9H, s), 1.43 (9H, s), 3.78 (3H, s), 4.17 (1H, d, J=9.6 Hz), 4.89 (1H, d, J=16.8 Hz), 5.13 (1H, d, J=10.6 Hz), 5.56 (1H, ddd, J=16.8, 10.6, and 9.6 Hz), 7.95—8.00 (2H, m), and 8.20—8.25 (2H, m); ^{13}C NMR δ=32.47 (q), 32.72 (q), 36.88 (s), 39.84 (s), 52.74 (q), 58.60 (d), 62.04 (s), 122.98 (t), 123.41 (d), 128.90 (d), 129.61 (d), 132.66 (s), 133.87 (s), 143.54 (s), 147.70 (s), 169.68 (s), and 169.89 (s); IR (KBr) 1764 (C=O) and 1725 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 447 (M$^+$, 9), 261 (37), and 139 (100). Found: C, 61.62; H, 6.49; N, 3.04%. Calcd for $C_{23}H_{29}NO_6S$: C, 61.73; H, 6.53; N, 3.13%.

(*E*)-3-Methoxycarbonyl-2-propenyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (14): Yellow oil; ^{1}H NMR δ=1.16 (9H, s), 1.49 (9H, s), 3.76 (3H, s), 4.82 (1H, ddd, J=16.2, 4.3, and 2.0 Hz), 4.93 (1H, ddd, J=16.2, 4.3, and 2.0 Hz), 6.09 (1H, dt, J=15.8 and 2.0 Hz), 6.95 (1H, dt, J=15.8 and 4.3 Hz), 7.75—7.80 (2H, m), and 8.14—8.19 (2H, m); ^{13}C NMR δ=31.31 (q), 31.35 (q), 38.18 (s), 39.77 (s), 40.10 (st), 51.70 (q), 63.79 (t), 121.59 (s), 122.06 (d), 123.31 (d), 129.05 (d), 140.08 (d), 140.67 (s), 145.57 (s), 146.92 (s), 165.97 (s), and 168.56 (s); IR (KBr) 1724 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 447 (M$^+$, 41) and 292 (100). Found: C, 59.14; H, 6.32; N, 3.01%. Calcd for $C_{23}H_{29}NO_6S$: C, 61.73; H, 6.53; N, 3.13%.

The reaction of 3-butenyl *p*-nitrophenyldiazoacetate (**15a**) with **2** gave allene episulfide **16a** in an 82% yield.

3-Butenyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (16a): Yellow oil; ^{1}H NMR δ=1.15 (9H, s), 1.46 (9H, s), 2.43 (2H, qt, J=6.6 and 1.2 Hz), 4.27 (2H, t, J=6.6 Hz), 5.08—5.17 (2H, m), 5.79 (1H, ddt, J=17.2, 10.6, and 6.6 Hz), 7.73—7.77 (2H, m), and 8.11—8.16 (2H, m); ^{13}C NMR δ=31.36 (q), 31.40 (q), 32.69 (t), 38.16 (s), 39.78 (s), 40.55 (s), 65.38 (t), 117.63 (t), 121.98 (s), 123.24 (d), 129.14 (d), 133.52 (d), 140.30 (s), 146.09 (s), 146.86 (s), and 169.12 (s); IR (neat, NaCl) 1726 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 404 (M$^+$+1, 15), 403 (M$^+$, 39), 347 (31), and 55 (100). Found: C, 65.35; H, 7.12; N, 3.89%. Calcd for $C_{22}H_{29}NO_4S$: C, 65.48; H, 7.24; N, 3.47%.

The reaction of 3-butynyl *p*-nitrophenyldiazoacetate (**15b**) with **2** gave allene episulfide **16b** in a 68% yield.

3-Butynyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (16b): Yellow oil; ^{1}H NMR δ=1.16 (9H, s), 1.47 (9H, s), 2.01 (1H, t, J=2.6 Hz), 2.57 (2H, qt, J=6.6 and 2.6 Hz), 4.30 (1H, dt, J=10.6 and 6.6 Hz), 4.35 (1H, dt, J=10.6 and 6.6 Hz), 7.74—7.79 (2H, m), and 8.12—8.17 (2H, m); ^{13}C NMR δ=18.72 (t), 31.37 (q), 31.39 (q), 38.18 (s), 39.81 (s), 40.46 (s), 63.94 (t), 70.31 (d), 79.67 (s), 121.79 (s), 123.28 (d), 129.13 (d), 140.58 (s), 145.86 (s), 146.90 (s), and 168.94 (s); IR (neat, NaCl) 3294 (≡CH) and 1728 (C=O) cm^{-1}; MS (EI, assignment, rel intensity %) 401 (M$^+$, 62), 345 (58), 331 (57), and 57 (100). Found: C, 65.93; H, 6.73; N, 3.70%. Calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49%.

The reaction of methyl *p*-nitrophenyldiazoacetate (**15c**) with **2** gave allene episulfide **16c** in a 66% yield.

Methyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (16c): Yellow crystals; mp 67.8—69.2 °C (from ether–pentane); ^{1}H NMR δ=1.15 (9H, s), 1.46 (9H, s), 3.83 (3H, s), 7.73—7.76 (2H, m), and 8.13—8.16 (2H, m); ^{13}C NMR δ=31.25 (q), 31.30 (q), 38.08 (s), 39.68 (s), 40.34 (s), 53.09 (q), 121.68 (s), 123.17 (d), 128.97 (d), 140.31 (s), 145.99 (s), 146.76 (s), and 169.52 (s); IR (KBr) 1731 (C=O) cm^{-1}. Found: C, 62.64; H, 6.86; N, 3.86%. Calcd for $C_{19}H_{25}NO_4S$: C, 62.78; H, 6.93; N, 3.85%.

The reaction of methyl (*Z*)-5-(*p*-nitrophenyldiazoacetoxy)-2-pentenoate (**15d**) (0.5 mmol) with **2** (0.5 mmol) gave allene episulfide **16d** in a 63% yield.

(*Z*)-4-Methoxycarbonyl-3-butenyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (16d): Yellow oil; ^{1}H NMR δ=1.14 (9H, s), 1.45 (9H, s), 3.07 (2H, dt, J=7.0 and 6.3 Hz), 3.71 (3H, s), 4.34 (3H, t, J=6.3 Hz), 5.89 (1H, dt, J=11.6 and 1.7 Hz), 6.24 (1H, dt, J=11.6 and 7.0 Hz), 7.73—7.79 (2H, m), and 8.12—8.17 (2H, m); ^{13}C NMR δ=28.08 (t), 31.25 (q), 31.28 (q), 38.05 (s), 39.67 (s), 40.33 (s), 51.07 (q), 65.00 (t), 121.61 (d), 121.82 (s), 123.17 (d), 129.05 (d), 140.25 (s), 144.88 (d), 145.84 (s), 146.78 (s), 166.19 (s), and 168.97 (s); IR (KBr) 1724 (C=O) cm^{-1}. Found: C, 62.60; H, 6.71; N, 3.22%. Calcd for $C_{24}H_{31}NO_6S$: C, 62.45; H, 6.77; N, 3.03%.

The reaction of methyl (*E*)-5-(*p*-nitrophenyldiazoacetoxy)-2-pentenoate (**15e**) (0.25 mmol) with **2** (0.25 mmol) gave allene episulfide **16e** in a 52% yield.

(*E*)-4-Methoxycarbonyl-3-butenyl 3-(Di-*t*-butylmethylene)-2-(*p*-nitrophenyl)thiirane-2-carboxylate (16e): Yellow oil; ^{1}H NMR δ=1.13 (9H, s), 1.45 (9H, s), 2.57 (2H, qd, J=6.6 and 1.4 Hz), 3.74 (3H, s), 4.31 (1H, dt, J=12.2 and 6.6 Hz), 4.36 (1H, dt, J=12.2 and 6.6 Hz), 5.91 (1H, dt, J=15.8 and 1.4 Hz), 6.91 (1H, dt, J=15.8 and 6.6 Hz), 7.71—7.76 (2H, m), and 8.12—8.17 (2H, m); ^{13}C NMR δ=31.07 (t), 31.32 (q), 31.34 (q), 38.13 (s), 39.75 (s), 40.37 (s), 51.50 (q), 64.06 (t), 121.77 (s), 123.27 (d), 123.60 (d), 129.09 (d), 140.47 (s), 143.71 (d), 145.79 (s), 146.86 (s), 166.30 (s), and 169.04 (s); IR (KBr) 1724 (C=O) cm^{-1}. Found: C, 62.34; H, 6.67; N, 3.03%. Calcd for $C_{24}H_{31}NO_6S$: C, 62.45; H, 6.77; N, 3.03%,

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