Hetero Diels–Alder Reaction of *N*-Acyl Imines. I. The Reaction of *N'*-Thiobenzoyl-*N*,*N*-dimethylformamidine with Electron-Deficient Dienophiles. Stereochemical and Mechanistic Aspects

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The reaction of *N'*-thiobenzoyl-*N*,*N*-dimethylformamidine (I) with electron-deficient dienophiles was investigated. The reaction of I with *N*-substituted maleimides (II) afforded *exo* and *endo* 1 : 1 cycloadducts (III). The stereochemistry was determined by analysis of ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectral data based on the modified neglect of diatomic overlap (MNDO) optimized structures. An equilibrium was observed between the starting materials (I and II) and 1 : 1 cycloadducts (III). The reaction of I with II in the presence of acetic acid afforded thiazine derivatives (IV), through elimination of dimethylamine from the primary cycloadduct (III). The reactions of I with several electron-deficient dienophiles were also examined. The reaction behavior is discussed in terms of frontier molecular orbital (FMO) theory and kinetic factors.

Keywords hetero Diels–Alder reaction; frontier molecular orbital; *N*-phenylmaleimide; modified neglect of diatomic overlap calculation; stereoselectivity; *N*-thioacyl imine.

The hetero Diels–Alder reaction is one of the most useful reactions for the synthesis of heterocyclic six-membered rings. There have been several reports concerning hetero-azadienes containing a sulfur atom. For example, Quiniou *et al.*[1] investigated the reaction of *N'*-thiobenzoyl-*N*,*N*-dimethylformamidine (I) with electron-deficient olefins and applied this reaction to construct the cephamycin framework.[2] However, the primary cycloadducts are thermally labile, and undergo elimination of dimethylamine to give thiazine derivatives. As far as we know, the mechanistic and stereochemical aspects of the reaction are still obscure because of the lability of the primary cycloadducts. We report here on the reaction behavior of I with electron-deficient dienophiles such as *N*-substituted maleimides (II).

Results

Cycloaddition of *N'*-Thiobenzoyl-*N*,*N*-Dimethylformamidine (I) with *N*-Phenylmaleimide (IIa) A mixture of diene I and IIa in $CHCl_3$ was allowed to stand at room temperature for 2 h to give colorless prisms (IIIa, mp 82.8—84.0 °C). On the other hand, after prolonged standing, another product having a different melting point (III'a, mp 106.8—107.8 °C) was isolated. The infrared (IR) spectra of IIIa and III'a exhibited carbonyl absorption at 1714 and 1710 cm^{-1}, respectively. The mass spectra (MS) of IIIa and III'a showed molecular ion peaks (M^+) at *m/z* 365. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra of IIIa and III'a showed the existence of two methyl groups, two phenyl groups and three methine protons in each case. The spectra closely resembled each other, except for the coupling constant between C_4-H and C_{4a}-H, implying that IIIa and III'a are stereoisomers (*endo*/*exo*) of the 1 : 1 cycloadduct.

The coupling constant between C_4-H and C_{4a}-H was 4.03 Hz for IIIa and 10.30 Hz for III'a, which gave a clue for determination of the stereochemistry of the cycloaddition. The dihedral angles between H-C_4–C_{4a}-H calculated by means of the modified Karplus equation[3] were 51.9° for IIIa and 161.9° for III'a, suggesting that IIIa is the *endo* cycloadduct and III'a is the *exo* cycloadduct. To confirm this presumption, we performed molecular orbital structure optimization on the *endo* and *exo* adducts, using the modified neglect of diatomic overlap (MNDO)[4] approximation. The calculations were started from the geometries obtained from a conventional molecular model, and the structure parameters were fully optimized. The MNDO-

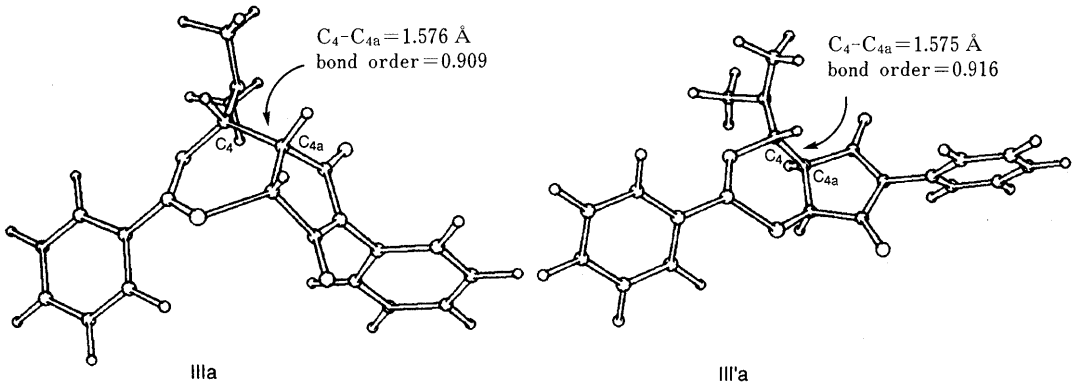

Fig. 1. MNDO-Optimized Structures of Cycloadducts (IIIa and III'a)

IIIa *endo* adduct: $\Delta H_f = 19.19$ kcal/mol, ϕH-C_4–C_{4a}-H = 48.7°.
III'a *exo* adduct: $\Delta H_f = 17.11$ kcal/mol, ϕH-C_4–C_{4a}-H = 163.1°.

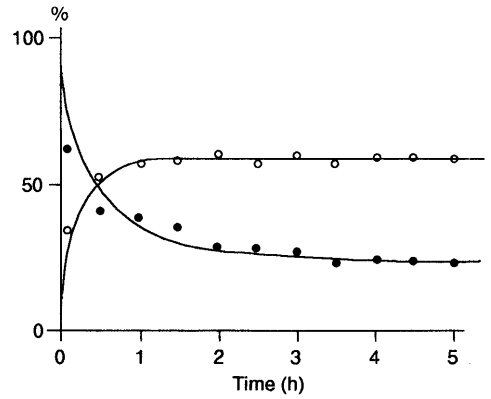

Fig. 2. Time–Course Study of the Reaction of I with IIa
●, I; ○, IIIa + III'a.

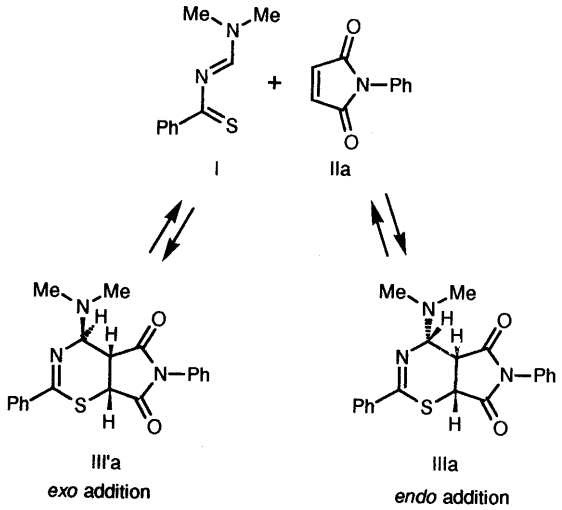

Chart 1

calculated dihedral angles between H-C_4–C_{4a}-H are 48.7° for the *endo* adduct and 163.2° for the *exo* adduct, in good agreement with the experimental data. These results again suggest that IIIa is the *endo* adduct and III'a is the *exo* adduct.

Time Course Study A time course study of the reaction of I with IIa was performed by following the peak area of methyl group signals in the ^{1}H-NMR spectrum of the reaction mixture. As depicted in Fig. 2, the amounts of I and IIIa plus III'a equilibrated within 2 h. Inspection of the ^{1}H-NMR spectra indicated that the ratio of IIIa : III'a was 5.3 : 1 at 2 h and 1 : 2.1 at 5 h.

When the isolated IIIa or III'a was dissolved in $CHCl_3$, I and IIa gradually appeared in the solution, suggesting that retro-Diels–Alder reaction proceeds even at room temperature. In other words, there is an equilibrium between the starting materials (I and IIa) and the products (IIIa and III'a).

Kinetic Studies As mentioned above, this reaction involves an equilibrium between starting materials (I and II) and cycloadducts (III). The *endo* cycloadduct was formed in the early stage of the reaction, and the *exo* cycloadduct appeared later. Therefore, we assumed that the rate of the *endo* addition can be evaluated at least within the early stage of the reaction. On this assumption, the second-order rate constants in toluene within 0.5 h were obtained by following

Table I. Rate Constants and Activation Parameters for the Reaction of *N'*-Thiobenzoyl-*N*,*N*-Dimethylformamidine (I) with *N*-Phenylmaleimide (IIa)

Temperature (°C)	$k \cdot 10^3$ ($l \cdot mol^{-1} \cdot s^{-1}$)	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
42.2	−1.95		
48.0	−3.33		
58.3	−6.19	16.2[a]	−22
60.6	−9.32		
62.4	−9.91		
64.4	−11.12		

a) Correlation coefficient = 0.995.

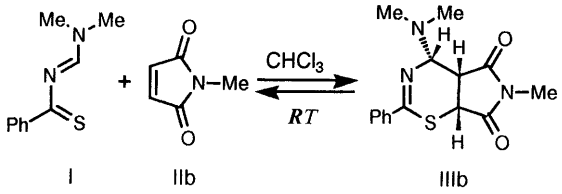

Chart 2

the decrease of the n–π^* absorption at 508 nm of I at various temperatures. The results are summarized in Table I. The activation energy (E_a) is comparable to that observed for the [4+2] cycloaddition of anthracene with maleic anhydride, whereas the entropy of activation ($\Delta S^{\neq}$) is higher than that observed in the same reaction.[5a]

Cycloaddition of I with *N*-Methylmaleimide (IIb) At room temperature, the diene I was allowed to react with equimolar IIb in $CHCl_3$ for 2 h to give colorless prisms (IIIb). The IR spectrum of IIIb exhibited carbonyl absorption at 1710 cm^{-1}. The MS of IIIb showed a molecular peak (M^+) at *m/z* 303. In the ^{1}H-NMR spectrum of IIIb, digital integration showed the existence of three methyl groups, one phenyl group and three methine protons, indicating that IIIb is an 1 : 1 cycloadduct of I and IIb. Considering the MNDO-optimized *endo* and *exo* structures and the observed coupling constants between C_4-H and C_{4a}-H, we can conclude that IIIb is the *endo* adduct.

Cycloaddition of I with *N*-Substituted Maleimides (IIa, b) in the Presence of Acetic Acid The reaction of I with IIa, b in the presence of acetic acid gave the pyrrolo[3,4-*e*]-thiazine derivatives (IVa, b) arising from the 1 : 1 cycloadducts by elimination of dimethylamine. The MS of IVa showed M^+ at *m/z* 320 and the ^{1}H-NMR spectrum showed signals of two phenyl groups in the range of δ 7.40—8.13. The protons at the 4-position (doublet at δ 8.10) and at the 7a-position (doublet at δ 4.79) were also observed. The absorption band at 1710 cm^{-1} was assigned to C=O stretching vibration. A C=N absorption was observed at 1644 cm^{-1}. The spectral data for IVb were similarly assigned. When the isolated IIIa or III'a was dissolved in acetic acid, IVa was immediately formed from both solutions.

Cycloaddition of I with Other Electron-Deficient Dienophiles The reaction behavior of I with some electron-deficient dienophiles was examined. Compound I was allowed to react with dimethyl 2,3-pentadienedioate (V) in CH_2Cl_2 under ice cooling for 50 h to give the thiazine de-

rivative (VI), arising from elimination of dimethylamine from the 1 : 1 cycloadduct of I and V. Spectral data are given in Experimental. The reaction of I with acrolein (VII)

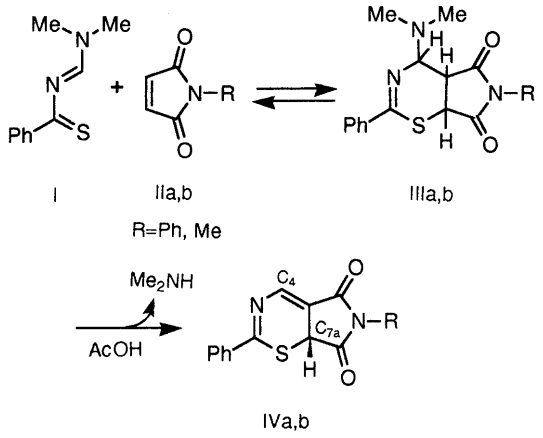

Chart 3

in $CHCl_3$ in the presence of acetic acid gave 2-phenyl-5-formyl-6*H*-thiadine (VIII). Though the reaction of I with crotonaldehyde (IX) was investigated in the same manner, no cycloaddition was observed. However, the reaction of I with IX in the presence of $MeAlCl_2$ afforded 2-phenyl-5-formyl-6-methyl-6*H*-thiadine (X). Methacroline (XI) did not react with I even in the presence of Lewis acids. Further, cyclohexenone (XII) was allowed to react with I in the presence of $AlCl_3$ to give the thiazine derivative (XIII). In these cases, no equilibrium was observed, suggesting that the elimination of dimethylamine proceeds faster than retro-Diels–Alder reaction under the conditions used here.

Discussion

In order to understand the reaction behavior, MNDO calculations of I and dienophiles were performed. The orbital energy levels and coefficients are depicted in Fig. 3. Though the highest occupied molecular orbital (HOMO)

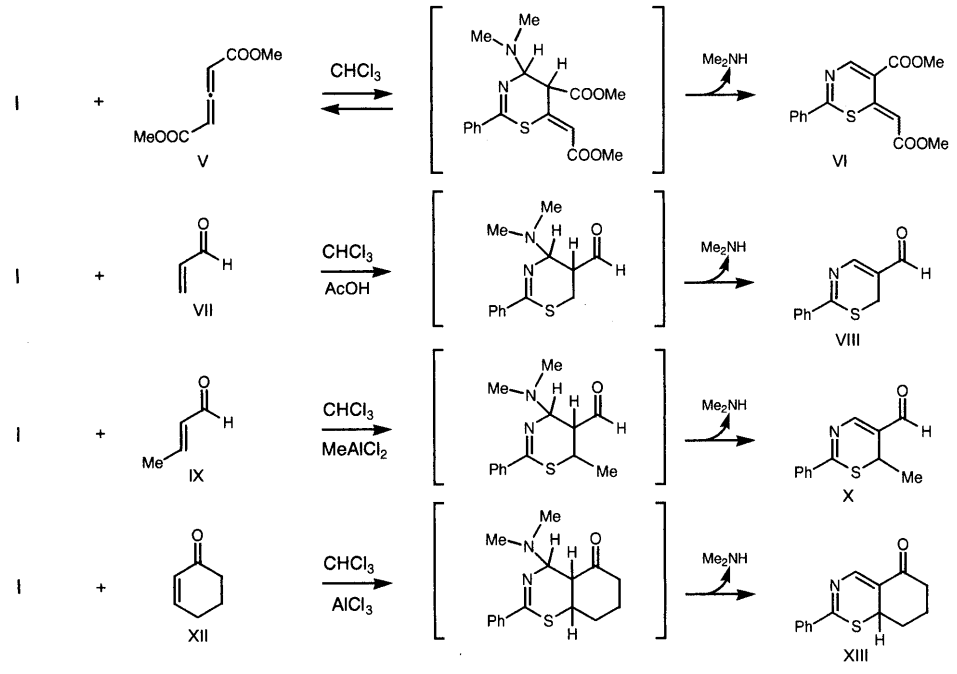

Chart 4

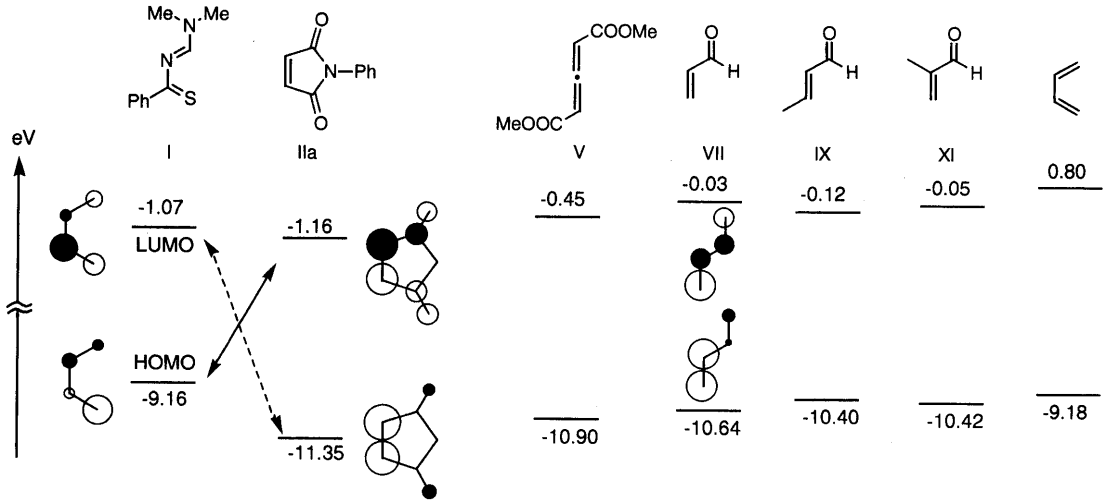

Fig. 3. FMO Energy Levels and Coefficients

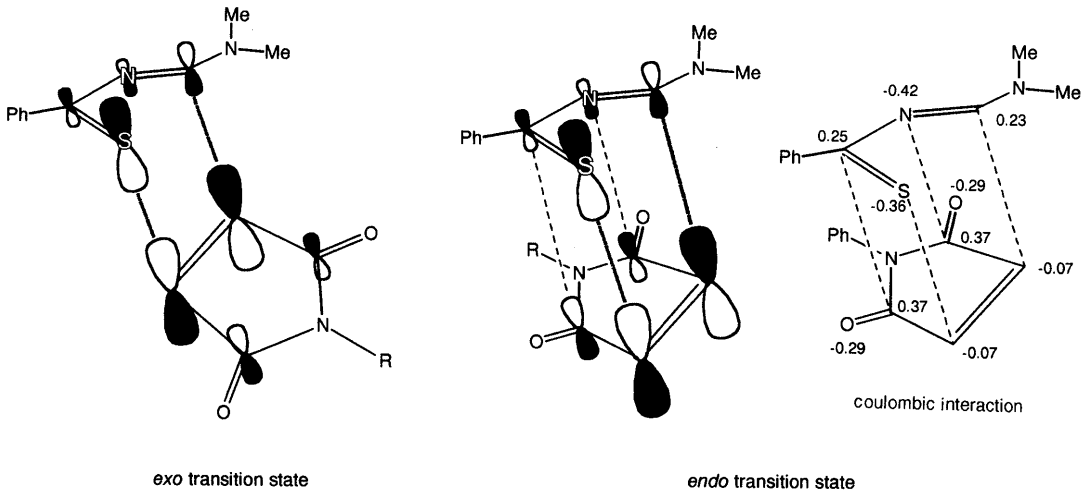

Fig. 4. Secondary Orbital Interaction and Coulombic Interaction in the Transition State

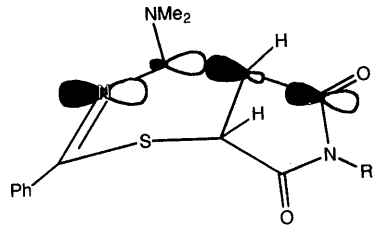

Fig. 5. Through-Bond Interaction in the Cycloadduct (III)

of I lies at nearly the same level as HOMO of butadiene, the lowest unoccupied molecular orbital (LUMO) of I is comparable to that of 2-pyrone, which shows high cycloaddition reactivity toward various olefins.[5b] Since IIa has markedly low frontier molecular orbitals (FMO's), the reaction of I with II falls into the category of "normal-type" reaction in Sustmann's classification,[6] wherein the dominant interaction occurs between HOMO of I and LUMO of II. On the other hand, acrolein derivatives (VII, IX and XI) have nearly equal FMO's, and their reactions with I can be classified as "neutral-type" reactions.[6]

The heterodiene I showed remarkably high cycloadditivity toward *N*-substituted maleimides (II). This reactivity can not be accounted for by simple FMO consideration involving secondary orbital effects.[7] Inspection of the MNDO calculation data indicates that Coulomb interactions play an important role in determination of the reactivity and regioselectivity. For example, the net charges of the N atom of the diene and the carbonyl carbon of maleimide are -0.42 and $+0.37$, respectively, providing additional stabilization energy arising from the second term of the perturbation equation.[8] As depicted in Fig. 4, besides the secondary orbital interaction, electronic force is also operative, wherein the position of the FMO attractions between the addends are identical with those of the Coulombic attractions.

In the case of IX and XI, steric interference between the methyl groups of the reaction site is responsible for the low reactivity toward I.

The regioselectivity can be also explained by considering the magnitude of the FMO coefficients and net charges.

Next, mention should be made of the facile retro-Diels–Alder reaction of the cycloadducts. Inspection of the MNDO optimized structures of the adducts (IIIa, b and III'a, b) indicates that the newly created bond (C_4–C_{4a}, 1.573 to 1.580 Å) is considerably elongated as compared with normal C–C single bonds. This can be explained in terms of "through-bond interaction."[9] The *p*-orbital of the imide carbonyl carbon interacts with that of the imino nitrogen atom through the C_4–C_{4a} bond according to the symmetry rule.[7] In this situation, the *anti*-bonding σ-orbital is occupied by electrons, resulting in a decrease of bond order, and distortion of the dihydrothiazine ring of the adducts derived from the presence of long C–S bonds in the six-membered ring enhances the elongation. In fact, the MNDO bond orders of C_4–C_{4a} in IIIa and III'a are both small (0.909 and 0.916), substantiating this view.

In conclusion, taking into consideration that the *endo* transition state is stabilized by secondary interactions, the formation of the *endo* adducts is kinetically controlled and the *exo* adducts are produced under thermodynamic control. The MNDO heat of formation of the *exo* adduct (III'a) is 2.08 kcal/mol smaller than that of the *endo* adduct (IIIa) (Fig. 1).

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were taken with Hitachi R-600 (60 MHz) and JEOL GX-400 (400 MHz) spectrometers for *ca.* 10% (w/v) solution, with tetramethylsilane as an internal standard; chemical shifts are expressed in δ values. IR spectra were recorded on a Hitachi 270-30 infrared spectrophotometer equipped with a double-blade grating. UV spectra were recorded on a Hitachi 150-20 spectrophotometer. MS were taken with a JEOL JMS-DX303HF double-focussing spectrometer operating at an ionization potential of 75 eV. Molecular orbital calculations were performed on a FACOM M-780 computer at the Computer Center of Kumamoto University and on a Fujitsu S4/2 engineering work station (EWS). Graphic analysis of the MO calculation was performed on a Fujitsu S4/2 EWS and a FM R-60HD personal computer.

Materials *N'*-Thiobenzoyl-*N*,*N*-dimethylformamidine (I) was prepared according to the established method.[10] *N*-Substituted maleimides (II) were prepared according to Cava *et al.*[11] Other chemicals were commercial products.

Cycloaddition of *N'*-Thiobenzoyl-*N*,*N*-dimethylformamidine (I) with *N*-Substituted Maleimides (II). General Procedure for Isolation of *endo* Cycloadducts A solution of I (200 mg, 1.0 mmol) and II (1.0 mmol) in 15 ml of $CHCl_3$ was stirred for 2 h at room temperature. After the reaction, the reaction mixture was concentrated *in vacuo*. The residue was treated with cold Et_2O. The precipitated crystals were collected by suction filtration and washed with a small amount of cold Et_2O to give III.

IIIa: mp 82.8—84.0 °C (66%, colorless prisms).[12] IR (KBr): 1714, 1598 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 2.63 (6H, s, NMe_2), 3.78 (1H, d, J=4.03 Hz, C_4-H), 4.08 (1H, dd, J=4.03, 9.89 Hz, C_{4a}-H), 4.42 (1H, d, J=9.89 Hz, C_{7a}-H), 7.31—8.00 (10H, m, aromatic CH). MS m/z: 365 (M^+).

IIIb: mp 103—106 °C (45%, colorless prisms).[12] IR (KBr): 1710, 1594 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 2.63 (6H, s, NMe_2), 2.89 (3H, s, Me), 3.66 (1H, d, J=4.40 Hz, C_4-H), 3.97 (1H, dd, J=4.40, 9.89 Hz, C_{4a}-H), 4.28 (1H, d, J=9.89 Hz, C_{7a}-H), 7.36—8.76 (5H, m, aromatic CH). MS m/z: 303 (M^+).

Cycloaddition of I with *N*-Phenylmaleimide (IIa). Procedure for Isolation of *exo* Cycloadduct (III'a) A solution of I (200 mg, 1.0 mmol) and IIa (360 mg, 2.1 mmol) in 10 ml of C_6H_6 was stirred for 24 h at room temperature. After the reaction, the reaction mixture was concentrated *in vacuo*. The residue was treated with cold Et_2O. The precipitated crystals were collected by suction filtration and washed with a small amount of cold Et_2O to give III'a, mp 106.8—107.8 °C (20%, colorless prisms).[12] IR (KBr): 1714, 1598 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 2.59 (6H, s, NMe_2), 3.04 (1H, dd, J=8.07, 10.3 Hz, C_{4a}-H), 4.01 (1H, d, J=10.3 Hz, C_4-H), 4.50 (1H, d, J=8.07 Hz, C_{7a}-H), 7.46—8.13 (10H, m, aromatic CH). ^{13}C-NMR ($CDCl_3$) δ: 40.56 (Me), 42.84 (Me), 43.78 (C_{4a}), 43.90 (C_{7a}), 81.79 (C_4), 161.35 (C_2), 172.37 (C=O), 173.19 (C=O). MS m/z: 365 (M^+).

Time Course Study A solution of I (19 mg, 0.1 mmol) and IIa (17 mg, 0.1 mmol) in $CDCl_3$ (0.4 ml) was used for measurement at 25 °C. The result are shown in Fig. 2.

Kinetics A toluene solution (3.0 ml) containing I (5.0 mmol) and IIa (5.0 mmol) was placed in a ground glass-stoppered glass cell controlled to ±0.05 °C. The rates were followed at a given temperature by measuring the decrease of the absorption at 508 nm at regular time intervals.

Cycloaddition of I with IIa in the Presence of Acetic Acid A solution of I (200 mg, 1.0 mmol), IIa (180 mg, 1.0 mmol) and 5 ml of acetic acid in 15 ml of $CHCl_3$ was stirred for 1 h at room temperature. After the reaction, the precipitated yellow crystalline mass was collected and washed with water and a small amount of Et_2O to give IVa, mp 212—214 °C (56%, yellow prisms from *n*-hexane–Me_2CO). IR (KBr): 1710, 1644, 1504 cm^{-1}: ^{1}H-NMR (in $CDCl_3$) δ: 4.79 (1H, d, J=2.20 Hz, C_{7a}-H), 8.10 (1H, d, J=2.20 Hz, C_4-H), 7.40—8.13 (10H, m, aromatic CH). MS m/z: 320 (M^+). *Anal.* Calcd for $C_{18}H_{12}N_2O_2S$: C, 67.48; H, 3.78; N, 8.74. Found: C, 67.18; H, 3.77; N, 8.76.

Cycloaddition of I with *N*-Methylmaleimide (IIb) in the Presence of Acetic Acid A solution of I (200 mg, 1.0 mmol), IIb (115 mg, 1.0 mmol) and 5 ml of acetic acid in 15 ml of $CHCl_3$ was stirred for 2 h at room temperature. After the reaction, the mixture was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using *n*-hexane–AcOEt (1 : 1) as an eluent to give IVb, mp 178—181 °C (47%, yellow prisms from *n*-hexane–Me_2CO). IR (KBr): 1702, 1644, 1506 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 3.15 (3H, s, Me), 4.59 (1H, d, J=2.20 Hz, C_{7a}-H), 7.97 (1H, d, J=2.20 Hz, C_4-H), 7.48—8.09 (5H, m, aromatic CH). MS m/z: 258 (M^+). HRMS: M^+ for $C_{13}H_{10}N_2O_2S$ m/z: 258.0456. Found: 258.0463.

Cycloaddition of I with Dimethyl 2,3-Pentadienedioate (V) A solution of I (480 mg, 2.5 mmol) and V (500 mg, 3.2 mmol) in 10 ml of CH_2Cl_2 was stirred under ice-cooling for 50 h. After the reaction, the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel using *n*-hexane–AcOEt (1 : 1) as an eluent to give VI. mp 138—140 °C (20%, red prisms from *n*-hexane). IR (KBr): 1714, 1682, 1480 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 3.77 (3H, s, COOMe), 3.89 (3H, s, COOMe), 6.79 (1H, s, =CH–), 8.22 (1H, s, C_4-H), 7.46—8.06 (5H, m, aromatic CH). ^{13}C-NMR ($CDCl_3$) δ: 51.43 (Me), 52.64 (Me), 108.38 (=CH–), 111.48 (C_5), 141.41 (C_4), 148.48 (C_6), 171.68 (C_2). MS m/z: 303. HRMS: M^+ for $C_{15}H_{13}NO_4S$ m/z: 303.0565. Found: 303.0547.

Cycloaddition of I with Acrolein (VII) in the Presence of Acetic Acid A solution of I (1.0 g, 5.1 mmol), VI (0.35 g, 6.3 mmol) and 5 ml of acetic acid in 50 ml of $CHCl_3$ was stirred for 3 h at room temperature. After the reaction, the mixture was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using *n*-hexane–AcOEt (1 : 1) as an eluent to give VIII, mp 66—69 °C (Lit.,[13] mp 67—69 °C) (73%, orange prisms from Me_2CO–hexane). IR (KBr): 1688, 1600 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 3.69 (2H, narrow d, J=0.6 Hz, C_6-H), 7.80 (1H, narrow d, J=0.6 Hz, C_4-H), 7.46–7.62 (3H, m, aromatic CH), 8.01—8.07 (2H, m, aromatic CH). MS m/z: 203 (M^+).

Cycloaddition of I with Crotonaldehyde (IX) A solution of I (200 mg, 1.0 mmol), IX (73 mg, 1.0 mmol) and a 1.0 M solution of $MeAlCl_2$ in hexane (1.0 ml, 1.0 mmol) in 20 ml of $CHCl_3$ was refluxed for 2.5 h. After the reaction, the mixture was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using *n*-hexane–AcOEt (1 : 1) as an eluent to give X. (52%, yellow oil). IR (KBr): 1672, 1594 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 1.25 (3H, d, J=6.96 Hz, C_6-Me), 4.26 (1H, d, J=6.96 Hz, C_6-H), 7.78 (1H, s, C_4-H), 7.27—8.09 (5H, m, aromatic CH), 9.64 (1H, s, CHO). MS m/z: 217 (M^+). HRMS, M^+ for $C_{12}H_{11}NOS$ m/z: 217.0561. Found: 217.0536.

Cycloaddition of I with Cyclohexenone (XII) A solution of I (200 mg, 1.0 mmol), IX (300 mg, 1.5 mmol) and $AlCl_3$ (140 mg, 1.0 mmol) in 20 ml of $CHCl_3$ was refluxed for 1.5 h. After the reaction, the mixture was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by chromatography on silica gel using *n*-hexane–AcOEt (1 : 1) as an eluent to give XIII, mp 133—136 °C (77%, yellow prisms from *n*-hexane–Me_2CO). IR (KBr): 1660, 1568 cm^{-1}. ^{1}H-NMR (in $CDCl_3$) δ: 1.80—2.72 (6H, m, $-CH_2-CH_2-CH_2-$), 3.94 (1H, m, C_{4a}-H), 7.45—8.10 (5H, m, aromatic CH). MS m/z: 243 (M^+). HRMS, M^+ for $C_{14}H_{13}NOS$ m/z: 243.0718. Found: 243.0719.

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