Reaction of Aromatic N-Oxides with Dipolarophiles. XVI.1) Cycloaddition Behavior of Aromatic N-Oxides toward Electron-Deficient Allenes and X-Ray Structure of the 1,4-Dipolar Cycloadduct

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In connection with the pericyclic reaction of pyridine N-oxides with dipolarophiles, the cycloaddition behavior of some aromatic N-oxides toward electron-deficient allenes was investigated. In the reaction of 2-phenylpyridine N-oxide with dimethyl 2,3-pentadienloidoate, the 2,3-dihydropyridine type 1:1 cycloadducts, which resulted from 1,5-sigmatropic rearrangement of the primary cycloadduct, were isolated. The reaction of 3,5-dihaloegenopyridine N-oxides with the allene gave the dehydrohalogenated cycloadducts of the 1,5-sigmatropic rearrangement products. The reaction of 3,5-dimethylpyridine N-oxide with the allene caused deoxygenation to give 3,5-dimethylpyridine, which in turn reacted with two molecules of the allene to give the 1:2 cycloadduct (1,4-dipolar cycloaddition product). The structure of the cycloadduct was determined by single crystal X-ray analysis.

The observed reaction behaviors are discussed in terms of frontier molecular orbital considerations.

Keywords pericyclic reaction; frontier molecular orbital; 1,3-dipolar cycloaddition; 1,4-dipolar cycloaddition; allene; reactivity; X-ray analysis; pyridine N-oxide; 1,5-sigmatropy

During the course of an investigation of the 1,3-dipolar cycloaddition reaction of pyridine N-oxides with N-substituted maleimides, an important question arose concerning the cycloaddition reactivity, i.e., why does only 3,5-dimethylpyridine N-oxide show reactivity toward N-substituted maleimides? We concluded that the inertness of other types of pyridine N-oxides such as unsubstituted pyridine N-oxide or 3-methylpyridine N-oxide might be attributable to their high degree of aromaticity and stabilization of the ground state by charge-transfer (CT) complex formation between the dipoles and dipolarophiles.

It is well known that cyclic planar addends are prone to form the coplanar \( \pi,\pi \)-complex at an early point in the reaction coordinate, leading to the formation of the CT complex, which stabilize the ground state energy of the reaction system prior to cycloaddition. In order to avoid such a ground-state stabilization, we tried to use electron-deficient allenes which do not have a cyclic planar \( \pi \)-electron system, but have an orthogonal \( \pi \)-electron system.

This paper describes the results of cycloaddition of pyridine N-oxides (I) with dimethyl 2,3-pentadienloidoate (II).

Results

Cycloaddition of 2-Phenylpyridine N-Oxide (Ia) with Dimethyl 2,3-Pentadienloidoate (II) Pyridine N-oxide bearing a phenyl substituent at the 2-position (Ia) readily reacted with II to give a mixture of 1:1 cycloadducts assignable to the isomers due to the exo and endo cycloadditions (IIa and IIIa) (Charts 2 and 3). The pericyclic reaction pathways leading to the 1,5-sigmatropic rearrangement products are depicted in Chart 3. The products were separated by chromatography on silica gel. The infrared (IR) spectra of the isolated crystals (IIa and IIIa) showed conjugated and unconjugated carbonyl absorption bands at ca. 1700 and 1740 cm\(^{-1}\), respectively. The carbon nuclear magnetic resonance (\(^{13}\)C-NMR) spectra showed three \( sp^3 \) carbons, suggesting that the products are not the primary adducts (two \( sp^3 \) carbons) but the 1,5-sigmatropically rearranged products, and also showed signals due to an olefinic carbon attached to an oxygen atom (ca. 158 ppm, \(-O-C=\) ) and a carbon ascribable to \( C=CH-\text{COOME} \) (ca. 90 ppm).

The stereochernistries of IIa and IIIa were determined by careful inspection of their proton nuclear magnetic resonance (\(^{1}H\)-NMR) spectral data. The proton on the exocyclic double bond [\(-O-C(R)=CH(\text{COOME})\)] of IIa and IIIa resonated at 5.36 and 5.31 ppm, respectively. The configuration of the proton is considered to be \( trans \) with

![Chart 1](chart1.png)

![Chart 2](chart2.png)

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respect to the ether group in each case on the basis of the chemical shifts of structurally similar compounds. This observation rules out the possibility that the ether group and the olefinic proton of the double bond are cis-oriented (see structure A in Fig. 1).

Next, the configuration of the methoxy carbonyl group on C5, which reflects the stereochemistry of the cycloaddition (endo-exo nature of IIIa and III’a) was determined on the basis of the coupling constant between the C2' and C3'-protons. The 1H-NMR spectral data are shown in Fig. 1. The C3'-proton of IIIa appeared as a weakly split doublet, whereas the proton of III’a appeared as a singlet. Molecular models, which satisfy the above spectral behaviors, suggest that the tetrahydrofuran rings take a puckered conformation as depicted in Fig. 1.

Inspection of the correlation between the angle between the plane of the exocyclic double bond and the adjacent σ-bond (C2'-H) and the allylic coupling constant \( J_{23} \) also supports the assignments. In IIIa, the C3 proton resonance occurs as a doublet of doublet \( (J_{23}=1.46 \text{ Hz}) \), indicating that the C3 proton appears as a singlet, since the allylic coupling to the exocyclic proton is very small \( (J_{23}<0.2 \text{ Hz}) \), indicating that the C3 proton lies nearly in the plane of the double bond.

In the endo adduct (IIIa), there appears to be a sizable amount of van der Waals compression between the methoxycarbonyl group and its environment, whereas, in the case of exo adduct (III’a), such an interaction must not be serious. This would be consistent with the fact that compound IIIa exhibited the unconjugated ester carbonyl absorption at 1748 cm\(^{-1}\), which is 10 cm\(^{-1}\) higher than that of III’a.

It should be noted that the exocyclic double bonds of IIIa and III’a did not isomerize to the endocyclic form (III’a) under the reaction conditions used (see Chart 2).

**Chart 3**

**Cycloaddition of 3,5-Dichloropyridine N-Oxide (Ib) and 3,5-Dibromopyridine N-Oxide (Ic) with II**

The 1,3-dipole (Ib) showed high reactivity toward the allene (II), giving the cycloadduct IIIb as a sole product. The mass spectrum (MS) of IIIb showed an M+ peak suggesting the formation of the furopyridine-type compound through elimination of HCl from the 1,5-sigmatropically rearranged product. The IR spectrum of IIIb exhibited two carbonyl absorption bands at 1740 and 1712 cm\(^{-1}\). The adduct IIIb showed a simple 1H-NMR spectral pattern consisting of a singlet peak due to Ar-CH2-N-O- and two aromatic protons having a meta coupling. The alternative structure of IIIb can be excluded based on the chemical shift of the z-carbon of the furan ring and the other examples of the cycloaddition studied in this work. The presence of triethylamine as a trapping agent for HCl gave a higher yield as compared with the reaction carried out without the base.

In the case of the reaction of 3,5-dibromopyridine N-oxide (Ic) with II, a similar result was obtained to give IIIc.

**Cycloaddition of Quinoline N-Oxide (Id) with II**

The reaction of Id with II gave pale yellow crystals (IIId). The MS suggested formation of the 1:1 adduct. The 1H-NMR spectrum exhibited a broad signal at 17.28 ppm due to a hydrogen-bonded proton. These results indicate that the primary adduct underwent ring cleavage to give the 2-methylene-type compound, which transformed into the 2-vinyl-type compound (see Chart 5). In this reaction, the 1,5-sigmatropic rearrangement could not be observed.

**Cycloaddition of 3,5-Dimethylpyridine N-Oxide (Ie) with II**

When II was added to a solution of Ie in CHCl3, the reaction mixture showed a red color. Purification of the product by silica gel chromatography gave unstable orange crystals. When a solution of the crystals in benzene was
allowed to stand overnight at room temperature, several spots were recognized on a thin layer chromatogram. The MS of the product suggested that the cycloaddition of Ie with II gave a 1:2 cycloadduct (IV). However, the high resolution MS (HRMS) did not give definitive evidence for the 1:2 adduct because the product contained a small amount of impurities. The IR spectrum of IV showed three carbonyl absorption bands at 1760, 1741 and 1708 cm⁻¹. From these observations, we considered the product to be the [4+2]π cycloadduct (B) of the 1,5-sigmatropically rearranged product and II. However, the visible absorption spectrum of IV exhibited an absorption maximum at 480 nm due to a highly conjugated structure and a ¹H-NMR study of IV was in apparent disagreement with the structure B. Therefore, we performed a single crystal X-ray analysis. Fortunately, single crystals of the adduct could be obtained by slow evaporation of a solution in benzene. The structure was solved by the direct method using the
MULTAN78 program and refined by the block-diagonal least-square method. The final R value obtained was 0.05. The ORTEP drawing shown in Fig. 2 reveals the product to have a 9H-quinolizine-type structure, presumably derived from deoxygenation of 3,5-dimethylpyridine N-oxide (Ie) followed by cycloaddition with two molecules of II. The sum of the angles around the N₄ nitrogen atom is about 360°, indicating that the N₄ is an sp² nitrogen. The atoms of C₃, C₈, C₉, C₁₀, N₁, C₂, and C₃ make a planar structure with which the τ-plane defined by the C₃ and C₂₂ atoms makes an angle of 25°. The bond lengths indicate that the 14π-electrons form a resonance structure consistent with the visible absorption spectrum observed at 480 nm. The stereochemistry of the two hydrogen atoms on C₃ and C₆ is revealed to be cis.

1,4-Dipolar Reactions of 3,5-Dimethylpyridine and 3,5-Dibromopyridine with II In order to clarify the formation mechanism of IV, the reaction of 3,5-dimethylpyridine with II was carried out. When 3,5-dimethylpyridine was mixed with II at room temperature, an exothermic reaction took place to afford IV in 63% yield. In the case of 3,5-dibromopyridine, a similar reaction occurred to afford the 1:2 adduct (V).

The structure of V was determined by comparison of the IR and ¹H-NMR spectral data with those of IV. Reactions of Other Pyridine N-Oxides with II The alene (II) showed moderate cycloaddition reactivity toward both unsubstituted and electron-deficient pyridine N-oxides even at room temperature.

In the reaction of 3-methoxycarbonylpyridine N-oxide
(If) with II, the reaction solution turned red, indicating that the 1,4-dipolar cycloaddition took place. However, the corresponding 1,4-dipolar cycloadduct could not be isolated. The thin-layer chromatogram of the reaction mixture showed the presence of several products. The product isolated was colorless crystals (III), and was determined to be an addition compound of the 1,5-sigmatropic rearrangement product and ethanol. The stereochemistry was confirmed by comparison of the $^1$H-NMR spectral data with those of IIIa and III' a (Chart 7).

The reaction of pyridine N-oxide (Ig) with II gave not only the 1,5-sigmatropic rearrangement product but also the 1,4-dipolar cycloaddition product, though their structures have not yet been determined by spectroscopic methods. A coherent interpretation of the spectral data and suitable single crystals for X-ray analysis have not yet been obtained. 3-Methylpyridine N-oxide showed similar reaction behavior.

**Discussion**

As mentioned above, the dimethyl pentadienedioate (II) showed high reactivity toward aromatic N-oxides bearing both electron-donating and accepting substituents and the reactions proceeded at room temperature to give the cycloadducts. This is in sharp contrast to the reaction conditions (100—130°C) required in the 1,3-dipolar cycloaddition reaction with dipolarophiles such as phenyl isocyanate, $^7$ N-substituted maleimides$^{29}$ or epoxynaphthalene.$^{30}$

As far as we know, there has been no report concerned with the cycloadducts formed by the 1,3-dipolar cycloaddition of aromatic N-oxides with allenes.$^{8}$ In order to understand the reaction behavior, modified neglect of diatomic overlap (MNDO)$^{9}$ calculations were performed. The calculated orbital energy levels and coefficients are listed in Table IV.

As can be seen in Fig. 3, the reaction of pyridine N-oxides with II falls into the category of a "normal-type" reaction in Sustmann's classification$^{10}$ for cycloadditions, wherein the dominant interaction is the one between the highest occupied molecular orbital (HOMO) of the 1,3-dipole and the lowest unoccupied molecular orbital (LUMO) of the dipolarophile. In the case of 3,5-dichloropyridine N-oxide (Ib), the frontier molecular orbital (FMO) energy levels lie between the FMO energy levels of the allene (II), indicating that the "inverse-type" interaction also plays an important role in determining the cycloaddition reactivity. A similar argument may be applied to the reaction behavior of 2-phenylpyridine N-oxide (Ia) because phenyl groups compress the FMO energy levels.$^{11}$

The LUMO energy level ($-1.16$ eV) of maleimide is considerably lower than that of II ($-0.45$ eV) implying that maleimides would show higher cycloaddition reactivity toward I than the allene (II) if only FMO separation was considered. Contrary to expectation, the experimental results are inconsistent with the FMO prediction. This indicates that the primary FMO interaction energy between I and II is perhaps not the sole factor responsible for the high reactivity. Inspection of the MNDO calculation data of pyridine N-oxides (I) and II suggests that the huge lobe of the p$_z$ orbital (in the molecular plane) exists on the oxygen atom of I in the next HOMO (NHOMO), which can strongly interact with the p$_z$ orbital of the central carbon atom of II, stabilizing the transition state (Fig. 4). This interaction may contribute to the formation of the $\equiv C=\cdots O-\equiv N_2$ bond, building up the resonance structure.
of the enol ether moiety in the primary cycloadduct.\textsuperscript{12)}

As regards the regiochemistry of the 1,3-dipolar reaction, the observed regiochemistry of the reaction of I with the allene (II) follows the principle of maximum overlap of the FMO theory\textsuperscript{11}) as exemplified in Fig. 4. Bonding occurs between the central carbon of II and the oxygen atom of I where the largest coefficients of the interacting frontier orbitals are found. The net charges of II are very small, indicating that the coulombic interaction may be unimportant as a controlling factor in the early stage of the reaction.

The endo-selectivity could not be observed, as exemplified in the 1,3-dipolar reaction of 2-phenylpyridine N-oxide (Ia) with II, in which a 1:1 mixture of the endo and exo cycloadducts was obtained. In the reaction, the secondary orbital overlap\textsuperscript{23)} between the nitrogen of Ia and the carbonyl carbon of II is considered to be poor.

The configuration of the exocyclic double bonds of IIIa and III' also reflected the stereoechemistry of the primary cycloaddition, in which the coulombic attraction of the oxygen atom of Ia and the carbonyl carbon of II may be operative (see Chart 3).

Though the deoxygenation mechanism is still obscure, the formation reaction of 9\textit{H}-quinolinizine-type compounds is formally considered to be a so-called "1,4-dipolar cycloaddition"\textsuperscript{14)} wherein 1,4-dipoles formed from pyridines plus allene react with an additional allene to give [2\(\pi\) + 2\(\pi\) + 2\(\pi\)] cycloadducts. Taking into consideration that the reactions readily took place in a nonpolar solvent such as benzene, and the central allene carbon (C\textsubscript{p}) has a small negative net charge (C\textsubscript{p} = -0.026, C\textsubscript{g} = -0.034), the reaction should proceed via a nonionic concerted transition state (Fig. 5) rather than via an ionic intermediate (see Chart 8). The formation of 9\textit{H}-quinolinizine-type compounds can be account for in terms of the three system interaction,\textsuperscript{15)} in which pyridines act as HOMO\textsuperscript{16)} and two molecules of allenes act as LUMO's. The structures of the cycloadducts follow the principle that the larger lobe should unite with the larger one (large-large/small-small interaction) according to the perturbation theory.\textsuperscript{11b)}

An important factor which must be taken into consideration in the interpretation of the cycloaddition behavior of I toward dipolarophiles is the stability of the reactants, e.g., the high degree of aromaticity of I.\textsuperscript{17)} It is worth mentioning that in the reaction of I with II, the orbital interaction energy overcomes the aromaticity of I.

**Experimental**

All melting points are uncorrected. \(^1\text{H}\)NMR spectra were taken with Hitachi R-600 and JEOL GX-400 spectrometers for ca. 10% (w/v) solutions, with trimethylsilylamine (TMS) as an internal standard; chemical shifts are expressed in \(\delta\) values. IR spectra were recorded on a Hitachi 270-30 infrared spectrophotometer. Visible absorption spectra were taken with a Hitachi 150-20 spectrometer. MS were taken with a JEOL JMS-DX303HF double-focusing spectrometer operating at an ionization potential of 70 eV.
potential of 75 eV. Flash chromatography was carried out with Merck Silica Gel 60.

MO calculations (orbital (MO) calculations were performed on a FACOM M-360 computer at the Information Processing Center of Kumamoto University. Graphic analysis of the MO calculation and X-ray data were performed on a FACOM G-150 work station and a Fujitsu FM-60HD personal computer.

Materials: Dimethyl 2,3-pentadienedioic (II), 17) 2-phenylpropiophenone N-oxide (I), 3) 3-phenylpropionic acid N-oxide (Ib), 18) 3,5-dimethylpyridine N-oxide (Ic), 18) quinoline N-oxide (Id), 18) 3,5-dimethylpyridine N-oxide (Ie), 18) 3-methoxycarbonylpyridine N-oxide (II) 18) and pyridine N-oxide (Ig) 18) were prepared according to the established methods.

Cycloaddition of 2-Phenylpyridine N-Oxide (Ia) with Dimethyl 2,3-Pentadienedioic (II) Compound II (13 mmol) was added to a solution containing la (10 mmol) in CH2Cl2. After the addition was complete, the mixture was stirred at room temperature for 12 h. The solvent was evaporated off. The residue was submitted to silica gel chromatography using a hexane:ethyl acetate (4:1) mixture as the eluent to give IIIa (yield 86%) and IIIa (yield 8%).

exo Adduct (Iia): mp 144—146°C (colorless prisms from benzene). IR (KBr): 1738, 1700 (C=O) cm⁻¹. 1HNMR (in CDCl3): 1.35 (8H, s, COOME), 3.78 (3H, s, COOME), 4.72 (1H, d, J = 6.6 Hz, C6H3—CH2), 4.97 (1H, s, C6H3—CH2), 5.00 (1H, dd, J = 6.6, 5.8 Hz, C6H3—CH2), 5.31 (1H, s, C6H3—CH2), 6.65 (1H, dd, J = 5.8, 3.1 Hz, C6H3—CH2), 7.06 (1H, d, J = 10.2 Hz, C6H3—CH2), 7.49—7.79 (9H, m, Ar). 13C NMR (in Acetone-d6): 128.6 (3Q), 128.0 (2Q), 127.4 (2C), 123.7 (2C, C6H3—CH2), 117.4 (2C), 116.1 (2C), 108.2 (2C), 104.9 (2C), 102.4 (2C), 101.4 (2C). MS m/z: 327 (M⁺). HRMS, M⁺ for C15H11N2O2: m/z 327.1107. Found: 327.1102.

endo Adduct (Iia): mp 119—122°C (colorless needles from benzene). IR (KBr): 1748, 1704 (C=O) cm⁻¹. 1HNMR (in CDCl3): 1.37 (8H, s, COOME), 3.66 (3H, s, COOME), 4.90 (1H, d, J = 8.8 Hz, C6H3—CH2), 4.99 (1H, dd, J = 7.3, 8.8 Hz, C6H3—CH2), 5.05 (1H, dd, J = 5.1, 10.2 Hz, C6H3—CH2), 3.56 (1H, d, J = 1.4 Hz, C6H3—CH2), 6.75 (1H, dd, J = 5.1, 10.2 Hz, C6H3—CH2), 7.03 (1H, d, J = 10.2 Hz, C6H3—CH2), 7.49—7.92 (5H, m, Ar). 13C NMR (in Acetone-d6): 128.4 (2Q), 126.8 (3Q), 125.5 (3C), 124.2 (3C), 117.6 (2C), 116.1 (2C), 108.2 (2C), 104.9 (2C), 102.4 (2C), 101.4 (2C). MS m/z: 327 (M⁺). HRMS, M⁺ for C15H11N2O2: m/z 327.1107. Found: 327.1095.

Cycloadditions of 3,5-Dichloropyridine N-Oxide (Ib) or 3,5-Dibromopyridine N-Oxide (Ic) with II Compound II (6 mmol) was added to a solution containing Ib or Ic (3 mmol) in tetrahydrofuran (THF) (10 mL). After the addition was complete, the mixture was stirred at room temperature for 24 h. The solvent was evaporated off. The residue was submitted to silica gel chromatography using a hexane:ethyl acetate (1:1) mixture as the eluent to give IIIb (yield 38%) or IIIc (yield 17%). The reaction of Ib with II in the presence of triethylamine gave IIb in 69% yield.

Adduct (Iib): mp 111—112°C (colorless needles from benzene). IR (KBr): 1738, 1712 (C=O) cm⁻¹. 1HNMR (in CDCl3): 1.27 (3H, s, CH3), 3.73 (3H, s, COOME), 4.02 (3H, s, COOME), 4.32 (2H, s, CH2—N), 7.82 (1H, d, J = 2.0 Hz, Ar), 8.86 (1H, J = 2.0 Hz, Ar). MS m/z: 283, 285 (M⁺, relative intensity 3:1). HRMS, M⁺ for C12H8Cl2N2O2: m/z 283.2647. Found: 283.2524. M⁺ for C12H8Br2N2O2: m/z 283.0225. Found: 283.0243.

Adduct (Iic): mp 109—111°C (colorless prisms from benzene). IR (KBr): 1738, 1710 (C=O) cm⁻¹. 1HNMR (in CDCl3): 1.27 (3H, s, CH3), 4.02 (3H, s, COOME), 4.32 (2H, s, CH2—N), 7.96 (1H, d, J = 2.0 Hz, Ar), 8.76 (1H, J = 2.0 Hz, Ar). MS m/z: 327, 330 (M⁺, relative intensity 1:088). HRMS, M⁺ for C12H8Br2N2O2: m/z 327.9720. Found: 327.9723.

Reaction of Quinoline N-Oxide (Id) with II A solution of II (10 mmol) in CH2Cl2 was added to a solution containing Id (10 mmol) in absolute benzene was added. After the addition was complete, the mixture was stirred at room temperature for 2 h. The solvent was evaporated off. The solid was recrystallized from benzene-MeOH to give IIId in 37% yield. mp 116—118°C (yellow prisms from benzene-MeOH). IR (KBr): 1738, 1712, 1654 (C=O) cm⁻¹. 1HNMR (in CDCl3): 1.37 (12H, s, COOME), 3.82 (3H, s, COOME), 3.86 (2H, s, CH2—CH3), 7.39—8.13 (8H, m Ar), 17.28 (1H, br, NH). MS m/z: 301 (M⁺). HRMS, M⁺ for C14H10N2O2: m/z 301.0950. Found: 301.0937.

Cycloaddition of 3,5-Dimethylpyridine N-Oxide (Ie) with II Compound II (4 mmol) was added to a solution containing le (4 mmol) in CHCl3. After the addition was complete, the mixture was stirred at room temperature for 0.5 h. The solvent was evaporated off. The residue was submitted to silica gel chromatography using a hexane:ethyl acetate (1:1) mixture as the eluent to give IV. The crude product was dissolved in ether (20 mL). The ether solution was chilled in a refrigerator for 6 h to give red needles (yield 21%). MS m/z: 355 (M⁺, relative intensity 1:066) (aq. Ki), D₉ = 1.315 g cm⁻³. Z = 2, MoKα radiation (40 kV-20 mA), λ = 0.7107 Å.

The cell constants were determined by a least-squares procedure using the values of the Bragg angles of 17 reflections measured on a Rigaku AFC6 four-circle autobrilograph equipped with a graphite monochromated MoKα source. The apparatus was interfaced to a PANAFACOM U-1200 microcomputer.

The space group Pt (No. 2) was selected from the number of molecules per unit cell (Z = 2) and was later confirmed in the course of the structure refinement. Intensity data were collected in the range of 2θ = 55° using the 0θθθ scanning technique. Two reflections were monitored after measurement of every 100 reflections. Of the 2272 independent reflections, 1672 were treated as observed (Fo>3σ F). The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption.

Structure solution and Refinement An overall temperature factor obtained from a Wilson plot did not give the correct solution. The residual, the value of 0.50 Å² was used to calculate the normalized structure factor. The structure was solved by the direct method using the MULTAN78
series of programs. An E map calculated with 390 signed E's (E > 1.2), which gave a combined figure of merit of 2.255, revealed the positions of all the expected nonhydrogen atoms. Refinements were carried out by the block-diagonal least-squares method. Six cycles of isotropic refinement and 6 cycles of anisotropic refinement led to an R index of 0.094. All the hydrogens were located at calculated positions. After adding the hydrogens but keeping their thermal parameters fixed (B(H) = B(C) + 1.0), we obtained a final R of 0.0501. Thermal parameters of the hydrogens attached to the methy1 and methoxy groups were fixed for their anisotropic vibration. In final refinements, the following weights were used for the observed reflections: w = 1.0 for F_U < 20.0, w = 400/F_U^2 for F_U > 20.0.

All structure-solving programs were from the Information Processing Center of Kumamoto University with the Universal Crystallographic Computation Program System (UNICS III).

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References and Notes
4) a) The olefinic proton of trans (MeO)2Pt = O)OC(Me) = CH2(COO)Me resonated at 5.47 ppm, upfield by about 0.3 ppm from the position of the cis-isomer; L. M. Jackmann and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., London, 1969, pp. 184—192 and references cited therein; b) A referee pointed out that the geometric assignment of IIa should be made by comparison of the 1H-NMR spectra of the two isomers. However, we could not recognize any signals due to the geometric isomer (A). Suitable single crystals of IIa (or IIIa) for X-ray analysis have not yet been obtained.; c) A. P. Marchand, "Stereocchemical Applications of NMR Studies in Rigid Bicyclic Systems," Verlag Chemie International Inc., Florida, 1982, pp. 108—110.
12) The release of the strain involved in the allene system is also an important driving force for the cycloaddition. The MNDO calculations and experimental data for heat of formation of simple unsaturated compounds indicate that ΔΗ_allene of the allene-to-propene conversion is about 10 kcal larger than that of the propene to propane conversion.13)
16) The HOMO of 3,5-dimethylpyridine has a node close to the N atom. The NHOMO (—10.35 eV) is considered to play an important role in the cycloaddition. The NHOMO coefficients of N and C1 and C2 are —0.461 and —0.144, respectively.