  Bull. Chem. Soc. Jpn., 57, 1505—1509 (1984)

1,3-Dipolar Cycloaddition Reactions of 6-Methylenetricyclo-[3.2.1.$0^{2,7}$]oct-3-en-8-one and Its Related Compounds

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(Received August 18, 1983)

The cycloaddition reactions of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one (**1a**), its corresponding -8-*endo*-ol (**1b**), 1,5,8-trimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-*endo*-ol (**1c**), and 5,8-dimethyl-9-methylenetricyclo[3.3.1.$0^{2,8}$]non-3-en-7-one (**2**) were investigated in order to study the origin of its stereoselectivity or site selectivity. The reaction of 2,4,6-trimethylbenzonitrile oxide (mesitonitrile oxide, MNO) with **1a, b** occurs on the *exo*-mthylene group from the *exo*-side, but on the endocyclic double bond in the case of **1c**. The compound **2** undergoes the addition of MNO on both the exocyclic and endocyclic double bonds to give a corresponding bis-adduct. On the other hand, the reaction of phenyl azide (PA) with **1a—c** occurs on the endocyclic double bond from the endo-side to give a single adduct. The reaction of 6-*exo*-methoxy-1,5,6-trimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one with MNO or PA was also studied to prove the regioselectivity of the cycloadditions of constrained vinylcyclopropane moiety.

Recently the stereoselectivities and/or site selectivities of electrophilic reactions or cycloadditions of molecules containing proximal π-bonds, such as alkylidenenorbornene and alkylidenebenzonorbornadiene have been investigated.[1-5]

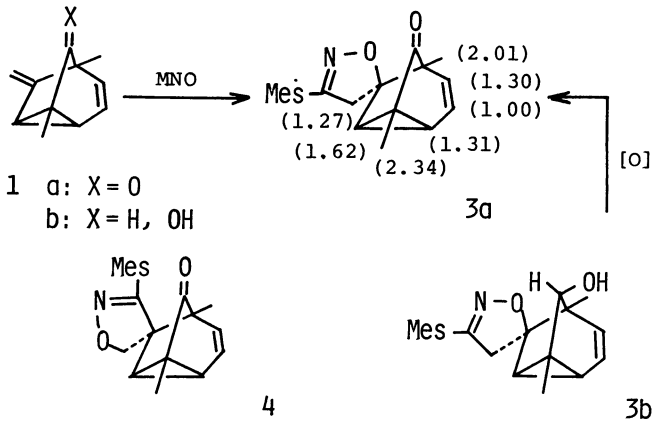
In previous papers, we reported that electrophilic reactions such as solvomercuration, bromination and its related reactions on the exocyclic double bond of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$O^{2,7}$]oct-3-en-8-one (**1a**) and its related compounds of general structure (**A**) exhibit a remarkable stereoselectivity to give

n = 0 or 1 X = O or H, OH Z = Br or HgOAc

(**B**).[6,7] The stereoselectivity was explained by the steric and/or electronic factor of mercurinium or bromonium ion formation and the stereoelectronic control of the endocyclic double bond for the incorporating nucleophiles. In continuation of this study, the 1,3-dipolar cycloadditions of 2,4,6-trimethylbenzonitrile oxide or phenyl azide with **1a**, its corresponding-8-*endo*-ol (**1b**), 1,5,8-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-*endo*-ol (**1c**), 5,8-dimethyl-9-methylenetricyclo[3.3.-1.$0^{2,8}$]non-3-en-7-one (**2**), and 6-*exo*-methoxy-1,5,6-trimethyltricyclo[3.2.1.$0^{2,7}$]-oct-3-en-8-one (**11**) were studied to probe the origin of stereoselectivity or site selectivity. The results are described in this paper.

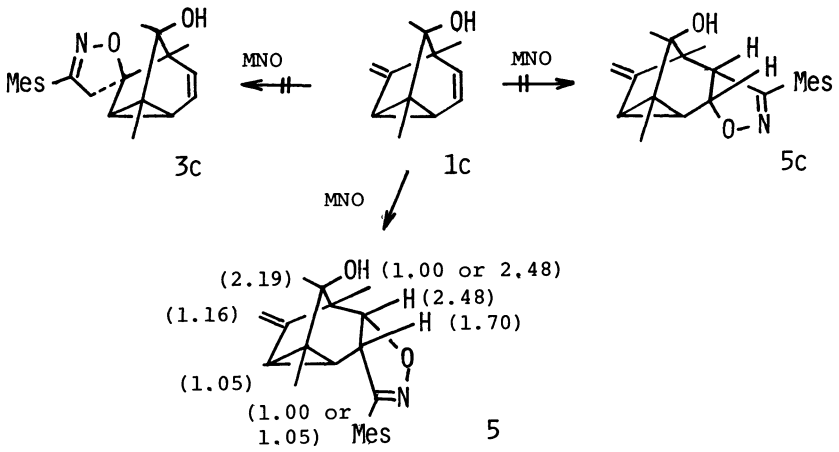
Results and Discussion

The reaction of 2,4,6-trimethylbenzonitrile oxide (mesitonitrile oxide, MNO) with **1a**[8] and **1b**[9] under reflux in benzene for 5 h gave 1:1 adducts **3a** and **3b** in 83 and 82% yields, respectively. The structural proof was based on the elemental analyses and spectroscopic data. The stereochemical arrangement of the MNO moiety of **3a** was deduced from the pseudo-contact NMR spectra obtained by using Eu(fod)$_3$. The relative down field shifts of δ's are given in parentheses in the structural formula.[10] The large values of 2.01 and 2.34 for the methyl groups as compared to the value of 1.27 for the methylene protons of the isoxazoline ring suggest the coordination of Eu(fod)$_3$ occurs on the carbonyl-oxygen and the MNO moiety is *exo* to the carbonyl group. On oxidation with pyridinium chlorochromate, **3b** was converted to **3a** in an 80%



yield, therefore the stereochemistry of **3a** and **3b** were assessed. Regarding the frontier orbital theory, the regioselectivity of the present cycloadditions is explained by LUMO (MNO)-HOMO (**1a, b**) interaction, since the unsubstituted terminus of the exomethylene group (possible large HOMO coefficient) was bound to the carbon terminus of MNO (large LUMO coefficient).[11,12] The regiochemistry of **3a, b** is also favorable for a steric reason. The van der Waals nonbonded interaction energies should be very large in such material as **4** as compared to the adduct **3a, b** (*vide infra*).

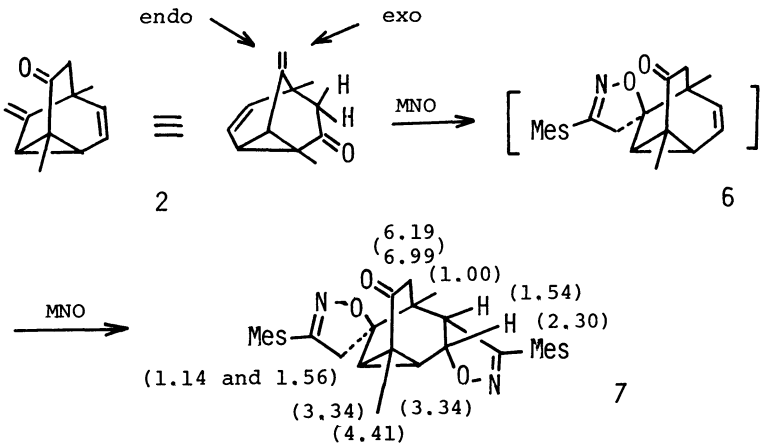
In order to probe the *exo*-selectivity of the present cycloadditions, the reaction of **1c**, which has a bulky methyl group at 8-position, was studied. The reaction of **1c**[13] with MNO under reflux in benzene for 7 h gave 1:1 adduct **5** in a 26% yield, the remainder being recovered starting material **1c** in a 53% yield. The structural proof including the regiochemistry and the stereochemistry of the MNO moiety was assessed on the basis of the spectral data and the pseudo-contact NMR spectra.[10] The relatively large values of 2.48 and 1.70 for the methine protons of the isoxazoline ring clearly indicate the *endo*-orientation of the MNO moiety of **5**. In the adduct **5**, the terminus of the

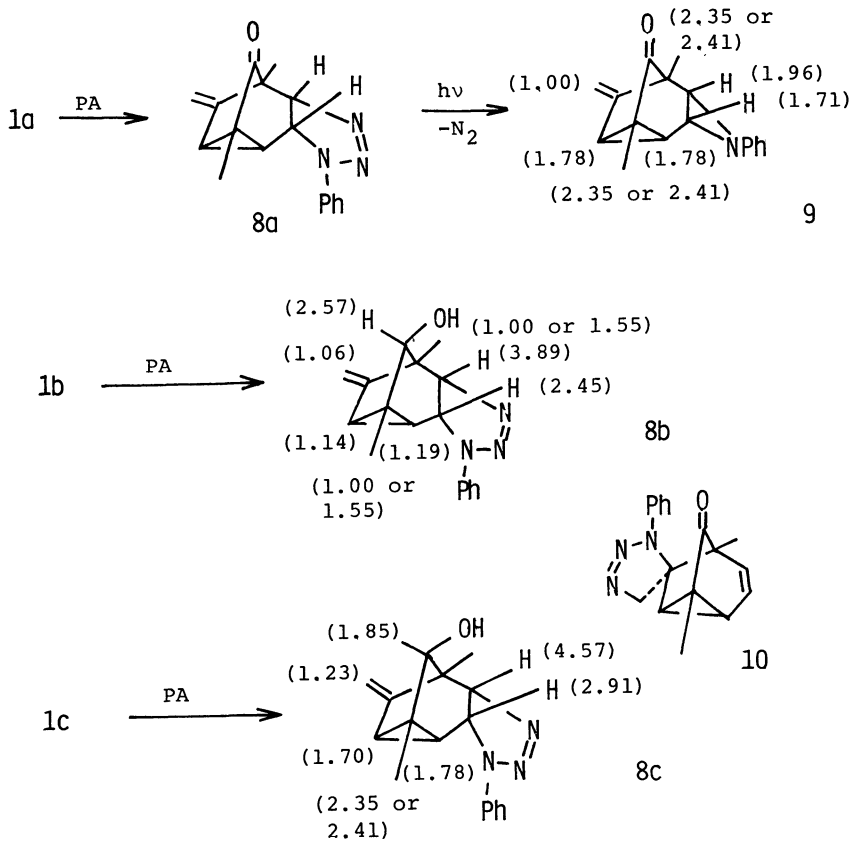


divinylcyclopropane moiety (possible large LUMO coefficient) was bound to the oxygen of MNO (large HOMO coefficient).[11,12] The bulky methyl group at 8-position of **1c** seems to prevent the *exo*-attack to give **3c**, which is expected from LUMO (MNO)–HOMO (**1c**) interaction as in the case of **1a**, **b**. The *endo*-arrangement of the MNO moiety of **5** is suggestive of the steric effect between the bulky mesityl group and two methyl groups at 1-and 5-positions. The blocked LUMO (MNO)–HOMO (**1c**) interaction to give **5c** stands in contrast to the cycloaddition of MNO with the vinylcyclopropane moiety of **11** (*vide infra*). The *endo*-attack of MNO on the *exo*-methylene group of **1c**, as well as **1a**, **b**, was prevented completely. This feature suggests a stereoelectronic effect of the endocyclic double bond[6] rather than a steric effect.

In order to probe this point, the reaction of **2**,[14] in which the *exo*-methylene group is located symmetrically with respect to the carbon skeleton, was investigated. The reaction of MNO with **2** under reflux in benzene for 20 h gave the bis-adduct **7** in a 48% yield, leaving 27% of **2**. Unfortunately the mono-adduct **6** was not isolated even in the presence of an excess amount of **2**. The structural proof and the stereochemical arrangement of the isoxazoline moiety were deduced from the spectral data.[10] The reaction of MNO with the *exo*-methylene gorup of **1a** or **1b** seemed to be faster than that with the endocyclic double bond of **1c** (*vide supra*), therefore it is suggested that the mono-adduct **6** might be the primary cycloadduct leading to **7**. An electrophilic reaction of sulfenyl chloride with **1a** could give a 1:1 adduct on the *exo*-methylene group, while that of **2** could give a 1:1 adduct on the *exo*-methylene group and a bis-adduct which can be derived from the former mono-adduct. Thus the endocyclic double bond of **2** seems to be more reactive than that of **1a**.[15] This fact may also suggest the intermediacy of **6** in the present cycloaddition. Regarding the steric hindrance of the hydrogen at the α-position of the carbonyl group, the *exo*-attack of MNO on the *exo*-methylene group of **2** seems unfavorable as compared to the endo-attack. However, MNO appeared to attack the *exo*-methylene group of **2** from the *exo*-side. Thus the *endo*-attack of **1a**—**c** or **2** may be prevented by the repulsive orbital interaction, which would be experienced with the endocyclic double bond.

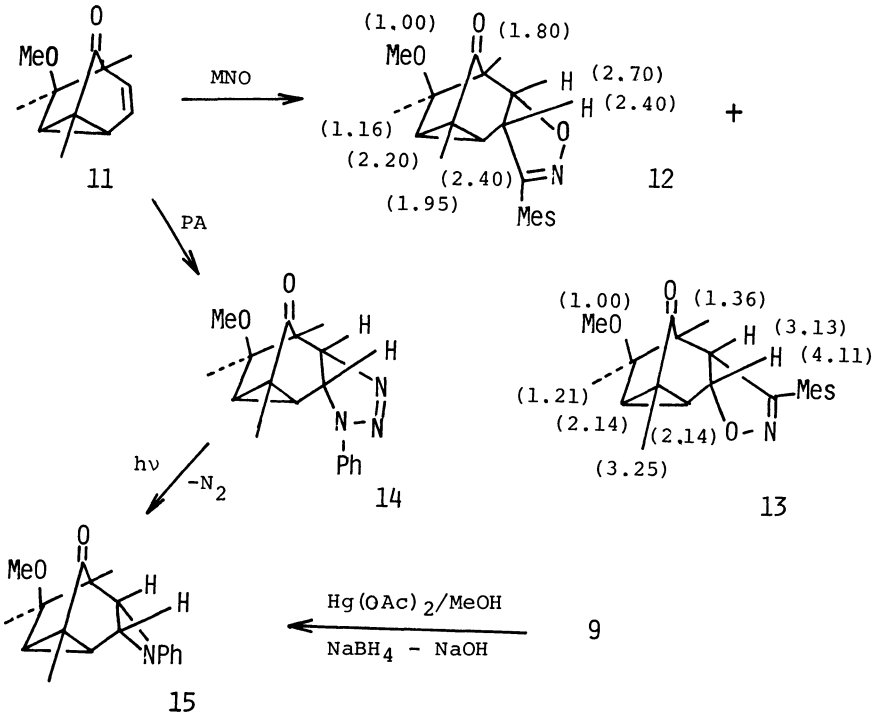
The cycloaddition of phenyl azide (PA) to the compounds **1a**—**c** was carried out under reflux in cyclohexane for 1 week to give 1:1 adducts **8a**—**c**. No adduct on the *exo*-methylene group was obtained. The structural proof including the stereochemistry and regiochemistry was based on the spectral data.[10] Photoirradiation of **8a** could undergo a clean elimination of a nitrogen molecule to give aziridine **9**, the structure of which including stereochemistry was also confirmed by the spectral data. Since the terminus of the divinylcyclopropane moiety (possibly with a large HOMO coefficient) was bound to the nitrogen bearing no phenyl group (large LUMO coefficient),[12] the regiochemistry of the adducts **8a**—**c** appears to be controlled by the LUMO (PA)–HOMO (**1a**, **b**, **c**) inter-





actions. The attack of PA on another terminus of the divinylcyclopropane moiety (*exo*-methylene group) to give **10** would be impossible because of the large steric hindrance. The attack of PA on the *exo*-methylene group from the *endo*-side would also be prevented because of the large steric effect and the stereoelectronic effect (*vide supra*).

The HOMO of MNO[16] and PA[12] are −8.3 and −9.5 eV, and LUMO have been estimated at +0.11 and −0.22 eV. Thus the low lying LUMO (PA), as compared to the high lying LUMO (MNO), appeared to control the regioselectivity of **8a—c**. On the other hand, the regiochemistry of **3c** or the second isoxazoline moiety of **7** seemed to be controled by HOMO



(MNO)-LUMO (**1c**) or LUMO (MNO)-HOMO (**6**) interactions, respectively.

Furthermore the cycloaddition of MNO or PA with constrained vinylcyclopropane was studied. The reaction of **11** with MNO under similar conditions gave the 1:1 adducts **12** and **13** in 13 and 10% yields, along with unreacted **11** in 70% yield. The structural proof is based on the spectroscopic data. On the other hand, the reaction of **11** with PA in cyclohexane under similar conditions described above gave single adduct **14** in 40% yield along with the unreacted **11** in 23% yield. The photoirradiation of **14** afforded 89% of aziridine **15**, which was also obtained by the methoxymercuration-demercuration of **9**. Thus the structure of **14** was established. Therefore both the high lying LUMO and HOMO of MNO, as compared to that of PA, can intervene in the cycloaddition of a constraiened vinylcyclopropane system such as **11**, while only low lying LUMO in the case of PA. In the adduct **12**, **13**, and **14**, 1,3-dipoles were incorporated from the *endo*-side to the carbonyl group. Regarding the steric effect of methyl groups at 1-and 5-positions, *endo*-orientation seems to be favorable.

In conclusion, the selective *exo*-attack on the *exo*-methylene group of **1a**, **b** and **2** giving **3a**, **b** and **6**, respectively, seems to be controlled by the stereoelectronic effect, which would prevent the *endo*-attack. The site selectivity giving **5** or **8a—c** would be caused by the sterically hindered *exo*-attack of 1,3-dipoles on the *exo*-methylene group and the stereoelectronically hindered *endo*-attack on the *exo*-methylene group. The stereochemistry and the regiochemistry of 1,3-dipolar cycloaddition of endocyclic double bond of **1a—c**, **6**, and **11** seemed to be controlled by the steric effect of the methyl groups at the ring junction and frontier orbital interaction, respectively.

Experimental

IR spectra were recorded on a Shimadzu IR-400 spectrometer. The mass spectral studies were conducted using a Hitachi RMU-60 spectrometer. All NMR spectra were recorded on a JEOL PS-100 high resolution spectrometer using tetramethylsilane as the internal standard. The shift data were obtained by adding small increments of $Eu(fod)_3$ to the sample and noting the extent to which each peak was shifted. The relative shift-slopes were obtained by dividing each of the slopes by the slope of the least shifted signal. The analyses were performed by the Science and Engineering Research Laboratory, Waseda University.

*Cycloaddition of **1a** with 2,4,6-Trimethylbenzonitrile Oxide (Mesitonitrile Oxide, MNO).* A solution of **1a** (160 mg, 1 mmol) and MNO (161 mg, 1 mmol) in 3 cm^3 of anhydrous benzene was refluxed for 5 h. After the solvent removal *in vacuo*, the residue was separated by TLC on silica gel using dichloromethane as the eluent. The first band from the TLC plates contained 20 mg (13%) of **1a**. The second band from the TLC plates gave 267 mg (83%) of the adduct **3a**: mp 150—151 °C (from hexane); IR ($CHCl_3$), 1607, 1336 cm^{-1}; NMR ($CDCl_3$), δ=1.21 (3H, s), 1.38 (3H, s), 2.12—2.33 (1H, m), 2.32 (6H, s), 2.35 (3H, s), 2.43 (1H, d, J=8.1 Hz), 3.02 (1H, d, J=18.6 Hz), 5.68 (1H, dXd, J=8.4, 3.0 Hz), 6.27 (1H, dXd, J=8.4, 5.1 Hz), 7.05—7.16 (2H, broad s); MS, m/z (rel intensity), 321 (M^+, 50), 159 (100). Found: C, 78.75; H, 7.21; N, 4.22%. Calcd for $C_{21}H_{23}O_2N$: C, 78.47; H, 7.21; N, 4.36%.

*Cycloaddition of **1b** with MNO.* A solution of **1b** (162 mg, 1 mmol) and MNO (161 mg, 1 mmol) in 3 cm^3 of anhydrous benzene was refluxed for 5 h. After the solvent removal *in vacuo*, the residue was separated by TLC on silica gel using dichloromethane as the eluent. The first band from the TLC plates contained 13 mg (8%) of **1b**. The second band from the TLC plates gave 265 mg (82%) of the adduct **3b**: mp 97—98 °C (from hexane); IR (CCl_4), 3561—3251, 1610, 1053 cm^{-1}; NMR (CCl_4), δ=1.41 (3H, s), 1.56—1.72 (2H, m), 2.22 (6H, s), 2.30 (3H, s), 2.57 (1H, d, J=18.6 Hz), 2.91 (1H, d, J=18.6 Hz), 3.79—3.93 (1H, broad s), 5.37 (1H, dXd, J=8.4, 1.2 Hz), 6.41 (1H, dXd, J=8.4, 5.4 Hz), 6.93—7.02 (2H, broad s). Found: C, 77.70; H, 7.47; N, 4.11%. Calcd for $C_{21}H_{25}O_2N$: C, 77.98; H, 7.79; N, 4.35%.

*Oxidation of **3b**.* To a stirred suspension of pyridinium chlorochromate (100 mg, 0.46 mmol) and anhydrous sodium acetate (20 mg, 0.24 mmol) in 0.5 cm^3 of dichloromethane, was added **3b** (100 mg, 0.31 mmol) in 0.5 cm^3 of dichloromethane under a nitrogen stream. After the reaction mixture was stirred for 5 h, it was chromatographed on Florisil using dichloromethane as the eluent to give 78 mg (80%) of the ketone **3a**, which was identified by mixed mp.

*Cycloaddition of **1c** with MNO.* A solution of **1c** (176 mg, 1 mmol) and MNO (161 mg, 1 mmol) in 3 cm^3 of benzene was refluxed for 7 h. After the solvent removal *in vacuo*, the residue was separated by TLC on silica gel using dichloromethane as the eluent. The first band from the TLC plates contained 93 mg (53%) of **1c**. The second band from the TLC plates gave 88 mg (26%) of the adduct **5**: mp 203—204 °C (from EtOH); IR ($CHCl_3$), 3694, 1608, 1070 cm^{-1}; NMR ($CDCl_3$), δ=1.08 (3H, s), 1.12 (6H, s), 1.55—1.80 (1H, m), 1.64 (1H, d, J=6.0 Hz), 2.24 (9H, s), 4.13 (1H, dXd, J=11.4, 2.4 Hz), 4.72 (1H, d, J=11.4 Hz), 4.77 (1H, s), 4.89 (1H, s), 6.81 (2H, broad s); MS, m/z (rel intensity), 337 (M^+, 100), 338 (100). Found: C, 77.95; H, 8.34; N, 3.92%. Calcd for $C_{22}H_{27}O_2N$: C, 78.30; H, 8.07; N, 4.15%.

*Cycloaddition of **2** with MNO.* A solution of **2** (140 mg, 0.8 mmol) and MNO (161 mg, 1 mmol) in 1.5 cm^3 of benzene was refluxed for 20 h. After the solvent removal *in vacuo*, the residue was separated by TLC on silica gel using benzene-ether (1/1) as the eluent. The first band from the TLC plates afforded 38 mg (27%) of **2**. The second band from the TLC plates contained 193 mg (48%) of the adduct **7**; mp above 250 °C (from EtOH); IR ($CHCl_3$), 2941, 1684, 1456, 1381, 1325, 891 cm^{-1}; NMR ($CDCl_3$), δ=1.22 (3H, s), 1.37 (3H, s), 1.40 (1H, d, J=7.5 Hz), 2.01 (1H, d, J=7.5 Hz), 2.23 (1H, d, J=18.3 Hz), 2.81 (18H, s), 2.84 (1H, d, J=18.3 Hz), 3.11 (1H, d, J=18.2 Hz), 3.83 (1H, d, J=10.2 Hz), 3.99 (1H, d, J=18.2 Hz), 4.54 (1H, d, J=10.2 Hz), 6.92 (4H, s); MS, m/z (rel intensity), 497 (M+1, 41), 496 (M^+, 100). Found: C, 77.45; H, 7.47; N, 5.33%. Calcd for $C_{32}H_{36}O_3N_2$: C, 77.39; H, 7.31; N, 5.64%.

*Cycloaddition of **1a** with Phenyl Azide (PA).* A solution of **1a** (100 mg, 0.63 mmol) and PA (150 mg, 1.27 mml) in 5 cm^3 of cyclohexane was refluxed for 7 d. After the removal of the solvent, the residue was recrystallized from carbon tetrachloride to give 104 mg (60%) of the adduct **8a**. The filtrate contained 8 mg (8 %) of **1a**. For **8a**: mp 143—145 °C (dec); IR ($CHCl_3$), 1738, 1667, 1600, 1493, 1108, 1091, 1067, 965 cm^{-1}; NMR (CCl_4), δ=1.10 (3H, s), 1.44 (3H, s), 2.45 (1H, dXd, J=7.5, 1.9 Hz), 2.67 (1H, d, J=7.5 Hz), 4.46 (1H, dXd, J=11.7, 1.9 Hz), 4.62 (1H, d, J=11.7 Hz), 4.87 (1H, s) 4.97 (1H, s), 6.86—7.47 (5H, m), MS, m/z (rel intensity), 279 (M^+, absent), 251 (25), 118 (100). Found: C, 72.54; H, 6.09; N, 14.15%. Calcd for $C_{17}H_{17}ON_3$: C, 73.19; H, 6.31; N, 14.04%.

*Photoirradiation of the Adduct **8a**.* A solution of **8a** (100 mg, 0.36 mmol) in 10 cm^3 of acetonitrile was irradiated with a high pressure mercury lamp (400 W) through a Pyrex filter for 24 h under a nitrogen atmosphere. After the removal

of the solvent, the residue was chromatographed on Florisil using dichloromethane as the eluent to give 80 mg (85%) of **9**: mp 128—129 °C (from hexane-benzene, 1/1); IR (CCl_4), 1751, 1664, 1601, 1492, 1407 cm^{-1}; NMR ($CDCl_3$), δ=1.29 (3H, s), 1.34 (3H, s), 2.28 (1H, d, J= 6.0 Hz), 2.36—2.55 (2H, m), 2.68 (1H, d×d, J=6.0, 3.0 Hz), 4.72 (1H, s), 4.83 (1H, s), 6.66—7.17 (5H, m). Found: C, 81.28; H, 6.66; N, 5.86%. Calcd for $C_{17}H_{17}ON$: C, 81.24; H, 6.82; N, 5.57%.

Cycloaddition of ***1b*** *with PA.* A solution of **1b** (100 mg, 0.62 mmol) and PA (147 mg, 1.24 mmol) in 5 cm^3 of cyclohexane was refluxed for 7 d. The reaction mixture was then recrystallized from hexane-CCl_4 to give 48 mg (28%) of the adduct **8b**. The filtrate contained 44 mg (44%) of **1b**. For **8b**: mp 172—174 °C (dec): IR ($CHCl_3$), 3625, 1601, 1491, 1113, 1096, 1065 cm^{-1}; NMR ($CDCl_3$), δ=1.32 (3H, s), 1.43 (3H, s), 1.58—1.79 (2H, m), 2.32—2.45 (1H, broad s), 3.76 (1H, broad s), 4.46 (1H, d×d, J=12.0, 2.4 Hz), 4.57 (1H, d, J=12.0 Hz), 4.57 (1H, s), 4.77 (1H, s). 6.86—7.40 (5H, m), MS, m/z (rel intensity), 281 (M^+, absent), 253 (28), 119 (100). Found: C, 72.99; H, 6.82; N, 14.68%. Calcd for $C_{17}H_{19}ON_3$. C, 72.57; H, 6.81; N, 14.94%.

Cycloaddition of ***1c*** *with PA.* A solution of **1c** (100 mg, 0.57 mmol) and PA (136 mg, 1.14 mmol) in 5 cm^3 of cyclohexane was refluxed for 7 d. After the removal of the solvent, the residue was recrystallized from hexane-benzene to give 50 mg (30%) of the adduct **8c**. The filtrate contained the recovered **1c** (30 mg, 30%). For **8c**: mp 145—146 °C (dec): IR ($CHCl_3$), 3549, 1600, 1494, 1110 cm^{-1}; NMR ($CDCl_3$), δ=1.20 (3H, s), 1.24 (3H, s), 1.33 (3H, s), 1.57—1.81 (2H, m), 4.51 (1H, d×d, J=12.0, 3.0 Hz), 4.55 (1H, s), 4.63 (1H, d, J=12.0 Hz), 4.73 (1H, s), 6.83—7.40 (5H, m); MS, m/z (rel intensity), 295 (M^+, absent), 267 (100). Found: C, 73.42; H, 7.17; N, 14.23%. Calcd for $C_{18}H_{21}ON_3$: C, 73.19; H, 7.17; N, 14.23%.

Cycloaddition of ***11*** *with MNO.* A solution of **11** (200 mg, 1.04 mmol) and MNO (168 mg, 1.04 mmol) in 8 cm^3 of benzene was refluxed for 6 h. After the removal of the solvent, the residue was separated by TLC on silica gel using benzene-ethyl acetate (4/1) as the eluent to give **11** (139 mg, 70%), the adduct **12** (47 mg, 13%), and the adduct **13** (36 mg, 10%). For **12**: mp 170—171 °C (from hexane-benzene); IR ($CHCl_3$), 2949, 1732, 869 cm^{-1}; NMR ($CDCl_3$), δ= 1.16 (3H, s), 1.22 (3H, s), 1.30 (3H, s), 1.53—1.68 (1H, m), 2.18—2.48 (1H, m), 2.28 (9H, s), 3.19 (3H, s), 4.04 (1H, d×d, J= 10.5, 3.0 Hz), 4.64 (1H, d, J=10.5 Hz), 6.84 (2H, broad s); MS, m/z (rel intensity), 353 (M^+, 82), 338 (32), 43 (100). Found: C, 74.76; H, 7.79; N, 3.87%. Calcd for $C_{22}H_{27}O_3N$: C, 74.75; H, 7.70; N, 3.96%. For **13**: mp 195—196 °C (from benzene); IR ($CHCl_3$), 2930, 1729, 875 cm^{-1}; NMR ($CDCl_3$), δ=0.50 (3H, s), 1.26 (3H, s), 1.35 (3H, s), 2.15 (3H, s), 2.19 (3H, s), 2.28 (3H, s), 2.28—2.38 (2H, m), 3.26 (3H, s), 3.84 (1H, d, J=10.2 Hz), 5.09 (1H, d×d, J=10.2, 3.0 Hz), 6.71 (1H, broad s), 6.84 (1H, broad s). MS, m/z (rel intensity), 353 (M^+, 68), 43 (100). Found: C, 74.68; H, 7.69; N, 3.40%. Calcd for $C_{22}H_{27}O_3N$: C, 74.75; H, 7.70; N, 3.96%.

Cycloaddition of ***11*** *with PA.* A solution of **11** (100 mg, 0.52 mmol) and PA (124 mg, 1.04 mmol) in 5 cm^3 of cyclohexane was refluxed for 7 d. After the removal of the solvent, the residue was recrystallized from hexane-benzene to give 65 mg (40%) of the adduct **14**. The filtrate contained 23 mg (23%) of **11**. For **14**: 178—179 °C (decomp); IR ($CHCl_3$), 1735, 1601, 1487, 1108, 1095 cm^{-1}; NMR (acetone-d_6), δ=1.00 (3H, s), 1.25 (3H, s), 1.44 (3H, s), 2.37—2.70 (2H, m), 3.26 (3H, s), 4.77 (2H, s), 6.87—7.50 (5H, m); MS, m/z (rel intensity), 311 (M^+, absent), 285 (85), 267 (100). Found: C, 69.07; H, 6.85; N, 13.77%. Calcd for $C_{18}H_{21}O_2N_3$: C, 69.43; H, 6.80; N, 13.50%.

Photoirradiation of ***14****.* A solution of **14** (100 mg, 0.32 mmol) in 10 cm^3 of acetonitrile was irradiated with a Rayonet Photoreactor (MGR-100) fitted with RPR-350 nm lamps through a Pyrex filter for 2 h under a nitrogen atmosphere. After the removal of the solvent, the residue was chromatographed on Florisil using dichloromethane as the eluent to give 81 mg (89%) of 15: mp 129—132 °C; IR ($CHCl_3$), 1733, 1592, 1482, 1448, 1111, 1047 cm^{-1}; NMR ($CDCl_3$), δ= 1.21 (3H, s), 1.27 (3H, s), 1.64 (3H, s), 2.03—2.57 (3H, m), 2.71 (1H, d×d, J=5.8, 3.6 Hz), 3.17 (3H, s), 6.58—7.27 (5H, m); MS, m/z (rel intensity), 283 (M^+, 12), 118 (100). Found: C, 75.43; H, 7.33; N, 5.23%. Calcd for $C_{18}H_{21}O_2N$: C, 76.29; H, 7.47; N, 4.94%.

Methoxymercuration of ***9****.* A suspension of **9** (502 mg, 2 mmol), mercury(II) acetate (638 mg, 2 mmol) in methanol (8 cm^3) was stirred for 30 min. To this reaction mixture, 8 cm^3 of 3 mol dm^{-3} sodium hydroxide solution was added and followed by reduction with 38 mg (1 mmol) of sodium borohydride in 2 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide. To this mixture, 10 cm^3 of brine and 10 cm^3 of benzene was added and then filtered. The filtrate was extracted with benzene, and the benzene extract was dried over sodium sulfate. After the removal of the solvent *in vacuo*, 439 mg (78%) of **15** was obtained.

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