  Bull. Chem. Soc. Jpn., 60, 683—687 (1987)

Preparation, 1,3-Dipolar Cycloaddition, and Thermal and Photochemical Reactions of 3,5-*exo*- and 3,5-*endo*-7-Methylene-4-azatetracyclo[4.2.1.0.^{2,8}0^{3,5}]nona-9-ones[1)]

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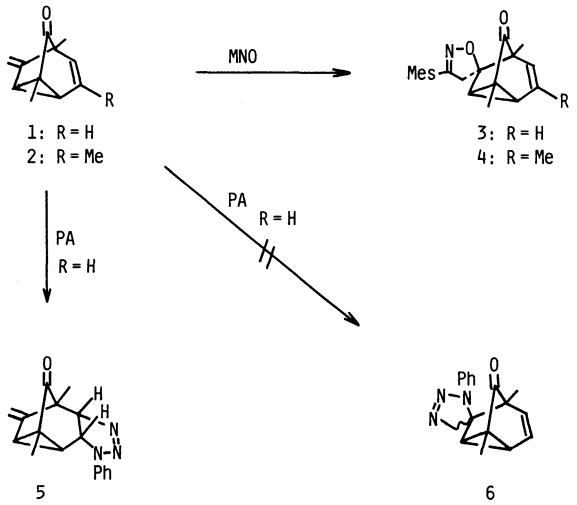
(Received August 6, 1986)

The 1,3-Dipolar cycloaddition of phenyl azide with 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one occurred onto the endocyclic double bond to give the *exo*- and *endo*-adducts (**7** and **8**) in a similar ratio. Upon photoirradiation, **7** and **8** eliminated a nitrogen molecule to give 3,5-*exo*- and 3,5-*endo*-1,3,6-trimethyl-7-methylene-4-azatetracyclo[4.2.1.0.^{2,8}0^{3,5}]nona-9-ones (**9** and **10**) in good yields. The 1,3-Dipolar cycloaddition of 2,4,6-trimethylbenzonitrile oxide with **9** and **10** occurred onto the exocyclic double bond to give two stereoisomers in each case. The stereoselectivity of the reactions is discussed on the basis of the stereoelectronic factor of the aziridine ring. The thermal reaction of **9** and **10** as well as photoirradiation of **9** caused a simple C-N bond cleavage of the aziridine ring. However, photoirradiation of **10** or its dimethyl analogue caused an unusual skeletal rearrangement resulting in the formation of 9-methylene-6-phenyl-6-azatricyclo[3.3.1.0^{2,8}]nona-3-en-7-one ring system. Mechanistic pathways of the rearrangement were postulated.

Previous work in this series has included studies concerning the stereoselectivity and site selectivity of the electrophilic reactions, such as solvomercuration, bromination,[2)] 1,3-dipolar cycloaddition,[3)] and dichlorocarbene addition[4)] of 1,5-diemthyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (**1**)[5)] and its related compounds. Among these reactions, the 1,3-dipolar cycloaddition of **1** and 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (**2**)[5)] with 2,4,6-trimethylbenzonitrile oxide (mesitonitrile oxide, MNO) exhibited remarkable stereoselectivity or site selectivity to give cycloadducts **3** and **4**, while **1** with phenyl azide (PA) afforded adduct **5** (Scheme 1). The formation of the *exo*(to the carbonyl group)-adducts **3** and **4** can been explained by the preferential LUMO(MNO)-HOMO(exocyclic double bond of **1** or **2**) interaction. The prohibited endo attack of MNO onto the exocyclic double bond was ascribed to the repulsive orbital interaction, which could be experienced with the endocyclic double bond as depicted in Fig. 1. In the cycloaddition of PA, on the other hand, the LUMO(PA)-HOMO (exocyclic double bond of **1**) interaction to give *endo*- or *exo*- adduct **6** was prohibited by a repulsive orbital interaction or a large van der Waals nonbonded interaction of the phenyl group. Thus, the cycloaddition occurred onto the endocyclic double bond from the endo side to give **5**.



Scheme 1.

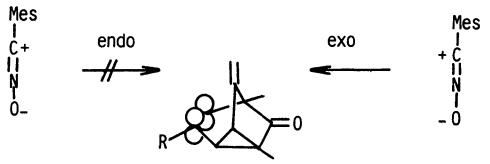


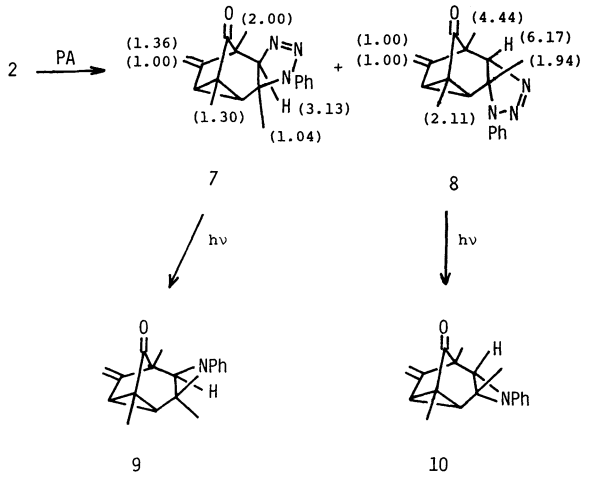
Fig. 1.

In this paper, the 1,3-dipolar cycloaddition of **2** with PA was clarified as occuring onto the endocyclic double bond from the exo and endo sides. These two adducts could eliminate a nitrogen molecule, resulting in the formation of 3,5-*exo*-1,3,5-trimethyl- and 3,5-*endo*-1,3,5-trimethyl-4-azatetracyclo[4.2.1.0.^{3,5}0^{2,8}]nona-9-ones (**9** and **10**) under photoirradiation. The 1,3-dipolar cycloaddition of MNO with the exocyclic double bond of **9** and **10** was interesting from the viewpoint of a comparison of the electronic effect of the aziridine ring of **9** and **10** with that of endocyclic double bond of **1** and **2**, in both of these the endo attack of MNO was completely prohibited (Fig. 1).[3)] Furthermore, thermal and photochemical reactions of **9** and **10** were studied in order to clarify the chemical behaviors, which would be affected by stereochemical arrangements of the aziridine ring. The results are described in this paper.

Results and Discussion

The reaction of **2** with PA under reflux in cyclohexane for 50 h gave an *exo*-adduct **7** and an *endo*-adduct **8** in 32 and 31% yields, respectively. The structural proof was based on elemental analyses and spectroscopic data (see Experimental). Especially, the chemical shifts of the protons on the triazoline moieties of **7** (δ 4.12) and **8** (δ 4.14) are suggestive of the assigned

regioselectivity.[6] The stereochemical arrangement of the triazoline moiety of **7** and **8** was deduced from the pseudo-contact NMR spectra observed by using $Eu(fod)_3$.[7] The relative down-field shifts of δ's of typical protons are give in parentheses in the structural formulae **7** and **8** in Scheme 2. The small values of



Scheme 2.

3.13 and 1.04 for a proton and a methyl group on the triazoline moiety of **7**, as compared with the corresponding values of 6.17 and 1.94 of **8**, suggest the coordination of $Eu(fod)_3$ occurs on the carbonyl-oxygen and support the structural assignment of **7** and **8**. Since the terminus of the methyl-substituted endocyclic double bond (possibly with a large HOMO coefficient) was bound to a nitrogen atom bearing no phenyl group (large LUMO coefficient), the regioselectivity of the adducts **7** and **8** appears to be controlled by the PA(LUMO)-**3**(HOMO) interaction.[3,8] The carbonyl group and the exocyclic double bond of **1** and **2** exist in a similar stereochemical situation in the molecular framework (as depicted in Fig. 2). In the case of **1**, exo (to the carbonyl group) attack of PA was considered to be prohibited, probably by a steric hindrance between the phenyl group of PA and C_1-methyl group.[3] Thus, an addition occurred from the less-hindered side to give only **5**. Similarly, an exo attack in **2** also expected to be sterically hindered. However, the introduction of a C_3-methyl group in **2** resulted in the competition of exo and endo attack to give **7** and **8**. The effect of the methyl group on the stereoselectivity still remained unclear.

The photoirradiation of **7** and **8** with RPR-350 nm lamps underwent a clear elimination of a nitrogen molecule to give aziridine **9** or **10**, respectively (Scheme 2).[9,10] The structures of **9** and **10** were also confirmed on the basis of the spectral data.

Compounds **9** and **10** contain an aziridine ring instead of a π bond of **2**, the cycloaddition of which occured to give only an *exo*-adduct **4**.[3] Thus, the cycloaddition of MNO with **9** and **10** was investigated in order to gain a further insight into the stereoelectronic control of the aziridine ring, as compared with the endocyclic π bond (Fig. 1). The reaction of **9** with MNO afforded *exo*-adduct **11** and *endo*-adduct **12** in 58 and 23% yields. Similarly, a reaction of **10** afforded two adducts (**13** and **14**) in 79 and 10% yields. The structures of these adducts were deduced from the spectroscopic data. Especially, the chemcial shifts of the

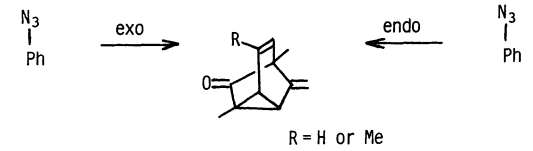
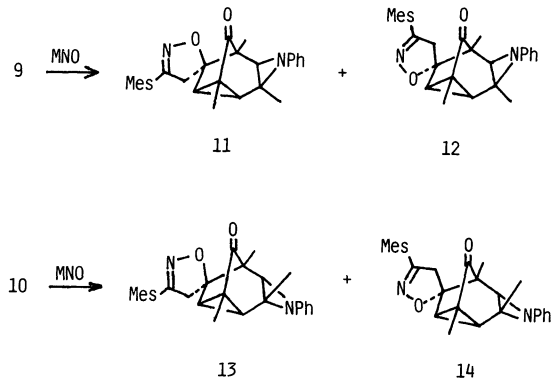


Fig. 2.



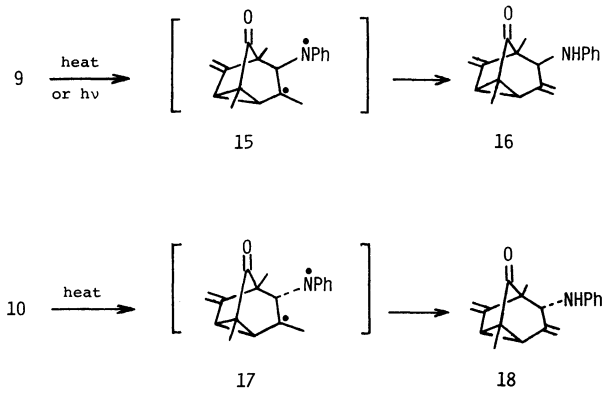
Scheme 3.

methylene group on the isoxazoline moieties were helpful in determining the stereochemistry. In the cases of *endo*-adducts **12** (δ 3.22, 3.29) and **13** (δ 3.03, 3.14), chemical shifts of these protons appeared at higher fields compared with those of *exo*-adducts, **11** (δ 3.24, 3.34) and **13** (δ 3.23, 3.29). This fact could be ascribed to the anisotropy effect of the carbonyl group. Thus, the stereochemical arrangement of the isoxazoline moieties of **11**—**14** were established.

Consequently, in the cycloaddition of MNO with **9**, the stereoelectronic control of the aziridine bent bond seemed to be much reduced compared with that of the endocyclic double bond in **2** (Fig. 1). Thus, the *endo*-adduct **12** was obtained in an appreciable amount. The steric hindrance of the methyl group at C_3 does not seem so significant in the cycloaddition of **9**. The product ratio of **13**/**14** was larger than that of **11**/**12**. This fact is suggestive of a repulsive interaction of MNO with the bent σ (C-N) bonds of the aziridine ring of **10**.

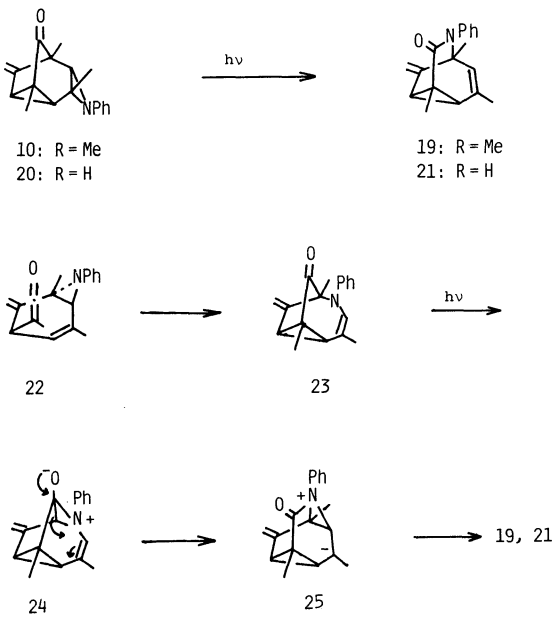
Studies of the thermal reaction[10] of **9** and **10** in 1,2-dimethylbenzene indicated that this fragmentation of the aziridine ring gave the corresponding exo and endo amino compounds **16** and **18** in 15 and 21% yields, leaving unreacted starting materials **9** and **10** in 85 and 79% yields. The structures of products **16** and **18** were unequivocally assigned on the basis of the spectral data. Similarly, a photoirradiation of **9** with RPR-254 nm lamps afforded **16** in a 35% yield. Thus, the reaction seems to proceed via diradical intermediates

15 and **17** formed by homolytic rupture of the C-N bond.[11]



Scheme 4.

However, a similar photoreaction of **10** gave only **19** in an 18% yield, in addition to large amounts of extremely decomposed materials. Similarly, the irradiation of the dimethyl derivative **20**[3] also gave **21** in a 30% yield. The structures of **19** and **21** were assigned on the basis of the spectral data. The ^{1}H NMR spectra of **19** and **21** exhibited typical chemical shifts and coupling patterns of the divinylcyclopropane moiety observed in compounds **1**, **2**,[5] and 5,8-dimethyl-9-methylenetricyclo[3.3.1.0^{2,8}]non-3-en-7-one.[12] The IR spectra suggest the existence of a six-membered amide function. Furthermore, the mass spectra of **19** and **21** exhibited an ion with *m/z* 119 (phenyl isocyanate). Thus, the structures of **19** and **21** could be deduced.



Scheme 5.

Compounds **10** and **20** have a skeleton similar to photolabile tricyclo[3.2.1.0^{2,7}]oct-3-en-8-one derivatives, which have been shown to photoisomerize to ketene derivatives.[13] Therefore, a ketene **22** is postulated to be a possible intermediate. Then, the addition of the ketene to the vinylaziridine moiety gives **23**, the photoreaction of which possibly gives zwitter ion **24**. The photoreaction initiated by the attack of a lone pair electron on nitrogen onto the carbonyl group has been previously reported regarding the rearrangement of the 8-azabicyclo[3.2.1]octa-3,6-dien-2-one ring system.[14] The reaction pathway of **24** may involve a formal intermediate **25** to give **19** and **21**. The reaction sequences postulated above are purely speculative, and evidence has not been obtained. The exo isomer **9** gives only **16** possibly via a diradical intermediate. This fact and the photorearrangement of endo isomers **10** or **20** to give **19** or **21** may stand in contrast to a thermal rearrangement of 3-arylsulfonyl-3-azatricyclo-[3.2.1.0^{2,4}]oct-6-ens.[15]

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The mass spectral studies were conducted using a Shimadzu GCMS-QP1000 and JEOL JMS-DX300 mass spectrometers. The ^{1}H NMR spectra (60 MHz) were recorded on a Hitachi R-24 spectrometer using Me_4Si as internal standard. The photoirradiations were carried out using Rayonet photoreactor fitted with appropriate lamps. All of the thermal and photochemical reactions were carried out under nitrogen atmosphere. Mesitonitrile oxide (MNO)[16] and phenyl azide (PA)[17] were prepared by the standard methods. All of the melting points are uncorrected.

Cycloaddition of 2 with PA. A solution of **2** (2.36 g, 13.6 mmol) and PA (2.78 g, 23.4 mmol) in cyclohexane (12 cm^3) was heated under reflux for 50 h. After the solvent was evaporated, the residue was separated by column chromatography on alumina. The fractions eluted with hexane afforded **2** (377 mg, 16%). The fractions eluted with benzene afforded **7** (1.28 g, 32%). The fractions eluted with dichloromethane afforded **8** (1.25 g, 31%). For **7**: Mp 86—87 °C (from hexane); IR ($CHCl_3$) 1733 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.26 (6H, s), 1.44 (3H, s), 2.10 (1H, d, J=7.2 Hz), 2.37 (1H, d, J=7.2 Hz), 4.12 (1H, s), 4.67 (1H, s), 4.86 (1H, s), 6.80—7.32 (5H, m); MS *m/z* (rel intensity) 265 (M^+-N_2, 9), 77 (100). Found: C, 73.77; H, 6.38; N, 14.41%. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.33%. For **8**: Mp 114—115 °C (from hexane); IR ($CHCl_3$) 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, s), 1.36 (3H, s), 1.52 (3H, s), 2.17 (1H, d, J=7.8 Hz), 2.64 (1H, d, J=7.8 Hz), 4.14 (1H, s), 4.90 (1H, s), 5.03 (1H, s), 6.8—7.5 (5H, m); MS *m/z* (rel intensity) 265 (M^+-N_2, 6), 118 (100). Found: C, 73.84; H, 6.46; N, 14.24%. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.33%.

Photoirradiation of 7. A solution of **7** (2.0 g, 6.83 mmol) in anhydrous acetonitrile (200 cm^3) was irradiated with RPR-350-nm lamps through a Pyrex filter for 5 h. After the solvent was evaporated, the resulting residue was crystallized from ethanol to give colorless crystals of **9** (1.32 g, 73%): Mp 105—106 °C (from EtOH); IR ($CHCl_3$) 1736 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.14 (3H, s), 1.25 (3H, s), 1.27 (3H, s), 1.94 (1H, dXd, J=7.4, 0.8 Hz), 2.04 (1H, d, J=0.8 Hz), 2.40 (1H, d, J=7.4 Hz), 4.53 (1H, s), 4.79 (1H, s), 6.42—7.22 (5H, m); UV (EtOH) 244 (ε 11700) and 291 (2300). Found: *m/z* 265.1472. Calcd for $C_{18}H_{19}NO$: M, 265.1467.

Photoirradiation of 8. A solution of **8** (947 mg, 3.3 mmol) in anhydrous acetonitrile (200 cm^3) was irradiated

with RPR-350 nm lamps through a Pyrex filter. After the solvent was evaporated, the resulting residue was crystallized from hexane to give colorless crystals of **10** (760 mg, 88%): Mp 118—119 °C (from hexane); IR ($CHCl_3$) 1739 cm^{-1}; ^1H NMR (CCl_4) δ=1.19 (3H, s), 1.26 (6H, s), 1.98 (1H, d, J=1.8 Hz), 2.01 (1H, d×d, J=8.0, 1.8 Hz), 2.43 (1H, d, J=8.0 Hz), 4.72 (1H, s), 4.84 (1H, s), 6.54—7.28 (5H, m); UV (EtOH) 236 (ε 14800), 275 (sh, 2120), and 284 (sh, 1480). Found: m/z 265, 1451. Calcd for $C_{18}H_{19}NO$: M, 265.1467.

Cycloaddition of 9 with MNO. A solution of **9** (200 mg, 0.78 mmol) and MNO (122 mg, 0.78 mmol) in anhydrous benzene (5 cm^3) was heated under reflux for 6 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using chloroform-benzene (1/1) as developer. The first band from the TLC plates contained 186 mg (58%) of the adduct **11**. The second band from the TLC plates gave 75 mg (23%) of the adduct **12**. For **11**: Mp 162—163 °C (from EtOH); IR ($CHCl_3$) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (3H, s), 1.36 (3H, s), 1.37 (3H, s), 1.50 (1H, s), 2.05 (1H, d, J=2.5 Hz), 2.07 (1H, d, J=2.5 Hz), 2.25 (9H, s), 3.24 (1H, d, J=19.4 Hz), 3.34 (1H, d, J=19.4 Hz), 6.56—7.17 (7H, m); MS m/z (rel intensity) 426 (M^+, 62), 77 (100). Found: C, 78.84; H, 7.04; N, 6.70%. Calcd for $C_{28}H_{30}N_2O_2$: C, 78.84; H, 7.09; N, 6.57%. For **12**: Mp 214—216 °C (from EtOH); IR ($CHCl_3$) 1747 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.23 (3H, s), 1.34 (3H, s), 1.37 (3H, s), 1.57 (1H, s), 2.08 (1H, d, J=1.8 Hz), 2.17 (1H, d, J=1.8 Hz), 2.32 (9H, s), 3.22 (1H, d, J=17.4 Hz), 3.29 (1H, d, J=17.4 Hz), 6.60—7.24 (7H, m); MS m/z (rel intensity) 426 (M^+, 19), 118 (100). Found: m/z 426. 2338. Calcd for $C_{28}H_{30}N_2O_2$: M, 426.2307.

Cycloaddition of 10 with MNO. A solution of **10** (265 mg, 1 mmol) and MNO (161 mg, 1 mmol) in anhydrous benzene (5 cm^3) was heated under reflux for 5 h. After the solvent was evaporated, the resulting residue was separated by TLC on silica gel using dichloromethane-benzene (2/1) as developer to give the adducts, **13** (323 mg, 76%) and **14** (43 mg, 10%). For **13**: Mp 196—198 °C (from EtOH); IR ($CHCl_3$) 1744 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, s), 1.34 (3H, s), 1.38 (3H, s), 1.61 (1H, s), 2.09 (1H, d, J=2.0 Hz), 2.17 (1H, d, J=2.0 Hz), 2.32 (9H, s), 3.23 (1H, d, J=17.6 Hz), 3.29 (1H, d, J=17.6 Hz), 6.69—7.42 (7H, m) Found: m/z 426.2314. Calcd for $C_{28}H_{30}N_2O_2$: M, 426.2307. For **14**: Mp 191—192 °C (from EtOH); IR ($CHCl_3$) 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (3H, s), 1.37 (3H, s), 1.41 (3H, s), 1.69 (1H, s), 2.28 (9H, s), 2.21—2.45 (2H, m), 3.03 (1H, d, J=17.4 Hz), 3.14 (1H, d, J= 17.4 Hz), 6.72—7.41 (7H, m). Found: m/z 426.2314. Calcd for $C_{28}H_{30}N_2O_2$: M, 426.2307.

Thermal Reaction of 9. A solution of **9** (100 mg, 0.38 mmol) in 1,2-dimethylbenzene (2 cm^3) was heated under reflux for 20 min. After the solvent was evaporated, the mixture was then separated by TLC on alumina using hexane as developer. The first band from the TLC plates contained **16** (15 mg, 15%). The second band from the TLC plates contained **9** (77 mg, 77%). For **16**: Mp 105—106 °C (from Et_2O); IR (CCl_4) 1742 cm^{-1}; ^1H NMR (CCl_4) δ=1.03 (3H, s), 1.35 (3H, s), 2.33 (1H, d, J=7.3 Hz), 2.71 (1H, d, J=7.3 Hz), 3.51 (1H, d, J=10.3 Hz), 4.12 (1H, d×d×d, J=10.3, 3.2, 2.0 Hz), 4.75 (1H, s), 4.97 (1H, s), 5.06 (1H, d, J=3.2 Hz), 5.10 (1H, d, J=2.0 Hz), 6.35—7.25 (5H, m). Found: m/z 265.1440. Calcd for $C_{18}H_{19}NO$: M, 265.1467.

Thermal Reaction of 10. A solution of **10** (100 mg, 0.38 mmol) in 1,2-dimethylbenzene (1.5 cm^3) was heated under reflux for 2.5 h. After the solvent was evaporated, the residue was separated by TLC on alumina using hexane-benzene (2/1). The first band from the TLC plates gave **18** (21 mg, 21%). The second band from the TLC plates contained **10** (79 mg, 79%). For **18**: Mp 119—120 °C (from Et_2O); IR ($CHCl_3$) 1735 cm^{-1}; ^1H NMR (CCl_4) δ=1.06 (3H, s), 1.36 (3H, s), 2.39 (1H, d, J=7.2 Hz), 2.70 (1H, d, J=7.2 Hz), 3.35 (1H, broad d, J=10.8 Hz), 4.08 (1H, broad d, J=10.8 Hz), 4.79 (1H, s), 4.92 (1H, s), 5.12 (2H, m), 6.34—7.28 (5H, m). Found: m/z 265.1451. Calcd for $C_{18}H_{19}NO$: M, 265.1467.

Photochemical Reaction of 9. A solution of **9** (810 mg, 3.06 mmol) in anhydrous acetonitrile (50 cm^3) was irradiated with RPR-254 nm lamps in a quartz tube for 4 h. After the solvent was evaporated, the residue was separated by TLC on alumina using hexane-dichloromethane (2/1) as developer to give **16** (285 mg, 35%), the spectral data of which was identical with those of the authentic specimen.

Photochemical Reaction of 10. A solution of **10** (62 mg, 0.23 mmol) in anhydrous acetonitrile (10 cm^3) was irradiated with RPR-254 nm lamps in a quartz tube for 3 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using chloroform-ethyl acetate (5/1) as developer to give **19** (11 mg, 18%): Bp 94 °C (bath temp)/93 Pa; IR (CCl_4) 2978, 2926, 1691, 1601, 1503, 1382, 1143, 900, 700 cm^{-1}; ^1H NMR (CCl_4) δ=1.49 (3H, s), 1.51 (3H, s), 1.85 (3H, d, J=1.6 Hz), 1.94—2.10 (2H, m), 5.27—5.50 (3H, m), 6.67—7.74 (5H, m); MS. m/z (rel intensity) 265 (M^+ 12), 250 (14), 146 (22), 119 (15), 77 (100). Found: m/z 265.1491. Calcd for $C_{18}H_{19}NO$: M, 265.1467.

Photochmeical Reaction of 20. A solution of **20** (100 mg, 0.4 mmol) in anhydrous acetonitrile (10 cm^3) was irradiated with RPR-254 nm lamps in a quartz tube for 14 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using benzene-ethyl acetate (2/1) as developer to give **20** (53 mg, 53%) and **21** (30 mg, 30%). For **21**: Bp 110 °C (bath temp)/528 Pa; IR (CCl_4) 3030, 2985, 2915, 1656, 1597, 1492, 1385, 1121, 891 cm^{-1}; ^1H NMR (CCl_4) δ=1.02 (3H, s), 1.33 (3H, s), 1.86—2.13 (1H, m), 2.36 (1H, d, J=6.0 Hz), 4.71 (1H, s), 4.76 (1H, s), 5.54 (1H, d, J=8.0 Hz), 5.70 (1H, d×d, J=8.0, 6.0 Hz), 6.51—7.11 (5H, m); MS, m/z (rel intensity), 251 (M^+, 100), 236 (74), 132 (65), 119 (79). Found: m/z 251.1328. Calcd for $C_{17}H_{16}NO$: M, 251.1310.

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