Reactions of Singlet Oxygen and *N*-Phenyl-1,2,4-triazoline-3,5-dione with Adamantylidenecyclopentadiene: O–O Homolytic vs C–N Heterolytic Cleavage of the Initial [2 + 4] Cycloadducts

Xiaojun Zhang, Saeed I. Khan, and Christopher S. Foote*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

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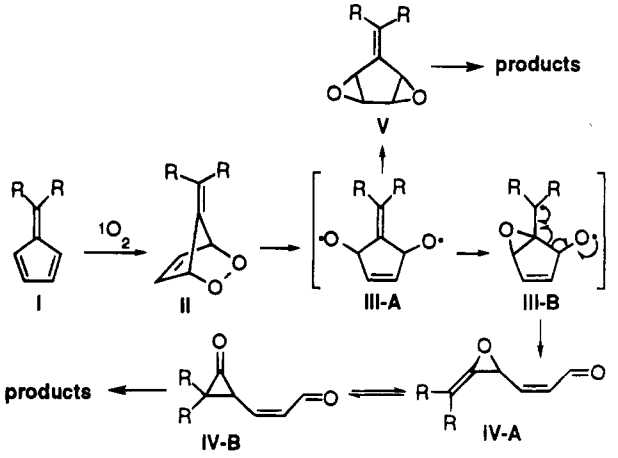
Reaction of $^1O_2$ with adamantylidenecyclopentadiene (**1**) in CH_2Cl_2 at −78 °C initially gave 7-adamantylidene-2,3-dioxabicyclo[2.2.1]hept-5-ene (**2**), which was characterized by low temperature NMR and reduced to the stable adamantylidene-2,3-dioxabicyclo[2.2.1]heptane (**6**). Endoperoxide **2** rearranged at ca. −20 °C to a mixture of oxepinone **3**, keto aldehyde **4**, and cyclopentenone **5**. Peroxide **6** rearranged at a higher temperature (70 °C) to bicycloacetal **7** and keto aldehyde **8**. In contrast, *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) reacted with **1** to give the polycyclic urazoles **9** and **10**, respectively, depending on the conditions. Low temperature NMR experiments detected the intermediate [2 + 4] cycloadduct **11**. A zwitterionic intermediate in the rearrangement of **11** could be trapped by alcohols. Homocleavage of the O–O bond and heterocleavage of the C–N bond, respectively, explain the rearrangement of the initial $^1O_2$ and PTAD cycloadducts with **1**.

Introduction

Singlet oxygen ($^1O_2$) undergoes [4 + 2] cycloaddition with 6-substituted fulvenes to give initially 7-alkylidenebicyclo[2.2.1]endoperoxides, which can rearrange thermally or be chemically transformed to a wide variety of oxygenated products.[1–3] A few intermediate endoperoxides have been characterized by low temperature ^1H NMR,[4–6] or reduced by diazene (HN=NH) reduction to more stable saturated peroxides.[7] Rearrangement of 7-alkylidenebicyclo[2.2.1]endoperoxides is believed to involve homolysis of the O–O bond to a transient diradical (**III-A**, Scheme 1).[8,9] Reorganization of the diradical leads to a second intermediate, an allene oxide (**IV-A**) or its valence tautomer cyclopropanone (**IV-B**). An allene oxide, sterically stabilized by a bulky *tert*-butyl group, was recently prepared by photooxygenation of 6-*tert*-butylfulvene and characterized.[10]

N-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) is a $^1O_2$ mimic.[11,12] It reacts with conjugated dienes in a Diels–Alder fashion, with various olefins in an ene reaction to give *N*-allylurazoles, and with certain olefins in a [2 + 2] reaction to afford 1,2-diazetidines. Because of its remarkable similarity to $^1O_2$, the mechanistic aspects of these reactions have been investigated recently using isotope effects,[13–15] low temperature NMR techniques,[16,17] theoretical calculations, and trapping experiments.[18–20] An aziridinium imide has been proposed as an intermediate in the ene and [2 + 2] cycloaddition reactions[18,21] and has been observed directly in several cases.[16,17]

Scheme 1



In the course of a study of the photooxygenation of 6-heteroatom substituted fulvenes,[6] we also investigated the reaction of adamantylidenecyclopentadiene (**1**) with PTAD. This compound was chosen for two reasons. First, we expected that any intermediate would be stabilized to some extent by the steric effect of the adamantyl group. For example, adamantylideneadamantane-1,2-dioxetane is unusually stable,[22] and the aziridene imide from this compound has been observed

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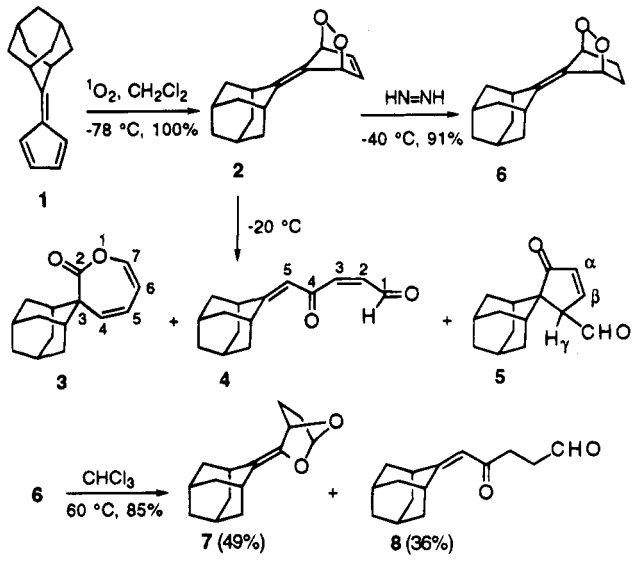
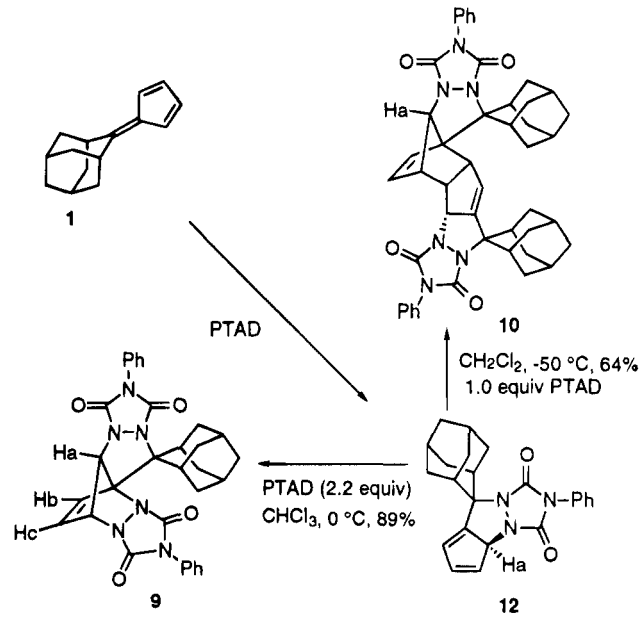
Scheme 2



Scheme 3



directly.[16] Secondly, the adamantyl substituent cannot give an ene reaction. However, we found that the final products of **1** with PTAD are dramatically different from the simple products of a Diels–Alder reaction, and we observed an interesting structural rearrangement of the primary cycloadduct. In this paper, we report the reactions of both $^1O_2$ and PTAD with **1**, characterization of the products, detection of several intermediates, and their interconversion and interception. Mechanisms explaining the reactions are proposed.

Results

Reaction of $^1O_2$ with Adamantylidenecyclopentadiene (1). To observe the initial product, photooxygenation of **1** was carried out in CD_2Cl_2 at −78 °C in an NMR tube. After 40 min irradiation, NMR at −70 °C showed exclusive formation of the expected endoperoxide, 7-adamantylidene-2,3-dioxabicyclo[2.2.1]hept-5-ene (**2**) (Scheme 2). Endoperoxide **2** was stable at −78 °C and could be stored for days without decomposition, but rearranged rapidly at −25 °C. At 0 °C, no trace of **2** could be detected. TLC analysis of the mixture showed three products, which were separated and shown to be 3-substituted oxepinone **3**, keto aldehyde **4**, and cyclopentenone **5**, in order of increasing polarity. The ratio of **3**:**4**:**5** was 2.3:1.1:1 by ^1H NMR.

The ^1H and ^{13}C NMR spectra of **2** indicated C_s symmetry. Two broad singlets appeared in the ^1H spectrum at 6.70 and 5.49 ppm, corresponding to the vinyl and bridgehead protons, respectively. In the ^{13}C spectrum, besides three sp^2 carbons between 126.0 and 136.8 ppm and five adamantyl carbons between 27.1 and 37.6 ppm, the bridgehead carbons were found at 77.5 ppm. Structural assignments of compounds **3**–**5** are based on extensive NMR experiments, including DEPT, 2D-COSY, and HETCOR. In compound **3**, four vinyl protons were observed at 5.55 (H4), 5.64 (H6), 6.06 (H5) and 6.39 (H7) ppm. In contrast, three vinyl hydrogens in **4** were located at 6.08 (H5), 6.13 (H2), and 6.91 (H3) ppm. Compound **5** showed only two vinyl protons at 7.17 (H_β) and 6.36 (H_α) ppm, both of which couple with the ring proton (H_γ) at 3.95 ppm. H_γ also couples with the aldehydic proton at 9.26 ppm. ^{13}C NMR data for compounds **3**–**5** are also consistent with the assignments (see Experimental Section).

The structure of endoperoxide **2** was further confirmed by diazene reduction to 7-adamantylidene-2,3-dioxabicyclo-[2.2.1]heptane (**6**) at −40 °C. Saturated peroxide **6** is much more stable than endoperoxide **2** and could be handled at room temperature. Thermolysis of **6** at 70 °C in chloroform gave bicycloacetal **7** and keto aldehyde **8**, both of which were isolated and completely characterized (see Experimental Section).

Reaction of PTAD with Adamantylidenecyclopentadiene (1). When a solution of **1** in chloroform was slowly added to 2.2 equiv of PTAD in $CHCl_3$ at 0 °C, the characteristic pink color of PTAD gradually disappeared in 10 min. TLC and ^1H NMR of the crude product indicated formation of a single compound, which had poor solubility in common organic solvents such as $CHCl_3$, methanol, acetonitrile, and acetone. The product was recrystallized from a mixture of CH_2Cl_2 and petroleum ether and found to be the polycyclic urazole **9**, a 2:1 adduct of PTAD and **1** (Scheme 3). In contrast, when a solution of PTAD in chloroform was added to 1.0 equiv of **1** in $CHCl_3$ at −50 °C, adduct **10** (2:2 PTAD and **1**) was isolated in 64% yield, along with 3% of **9**.

The presence of two PTAD units in **9** was indicated by four carbonyl signals at 154.2, 155.5, 157.8, and 158.4 ppm, typical shifts for triazolinediones, and further confirmed by FABMS and elemental analysis. Presence of only one adamantylidenecyclopentadiene unit was clearly seen from the NMR data. Nine adamantyl carbons were well resolved between 27.2 and 38.0 ppm; the tenth, attached to nitrogen, was located at 78.3 ppm. The bridge carbon in **9** appeared at 61.1 ppm. Two bridgehead carbons resonated at 93.1 and 74.1 ppm, the former a singlet and the latter a doublet, from DEPT spectra. The stereochemistry of the bridge carbon was established by NOE experiments: saturation of both vinyl protons (H_b at 6.83 ppm and H_c at 6.46 ppm) produced positive NOEs with the bridge hydrogen H_a (at 4.17 ppm) and vice versa, suggesting that H_a lies above the π-bond (C_b=C_c). This was further confirmed by comparison with the X-ray crystal structure of the related bis-adduct **10** (Figure 1, see below).

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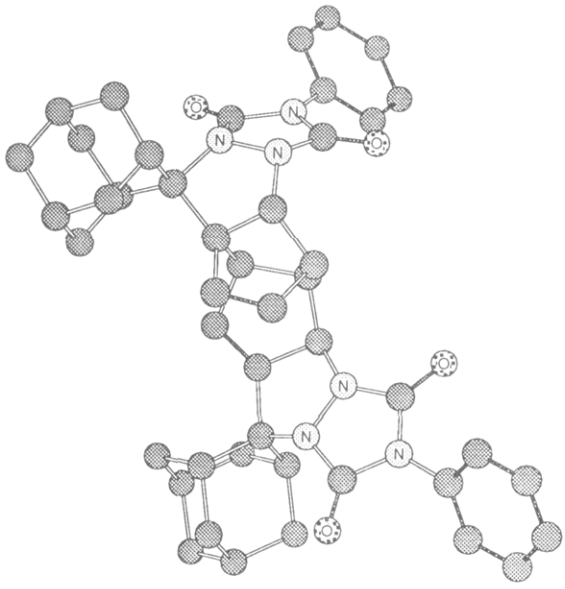
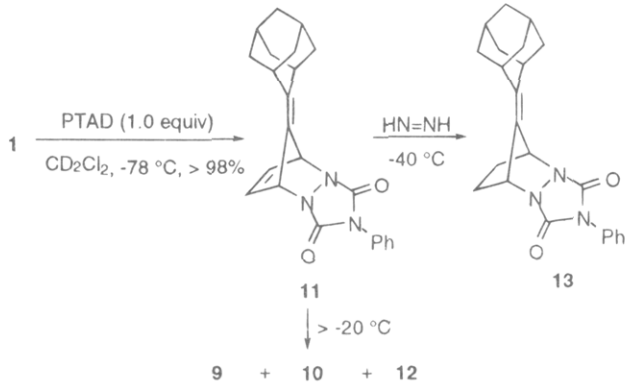


Figure 1. X-ray crystal structure of bis-adduct **10**.

Scheme 4



The structure of bis-adduct **10** was established by 2D-COSY, HETCOR experiments, and unequivocally confirmed by an X-ray crystal structure determination (Figure 1).[23,37] The structure clearly indicates that **10** is a Diels–Alder dimer of urazole **12** (Scheme 3), a [2 + 6] cycloadduct of PTAD and **1**. The sterically less demanding double bond approaches the diene face-specifically *syn* to the triazolinedione moiety to avoid steric interaction with proton H_a, giving the endo bicyclo[2.2.1]heptene exclusively. This X-ray crystal structure also confirmed the assignment of the stereochemistry at the bridge carbon in compound **9**, which is a Diels–Alder adduct of **12** and PTAD (Scheme 3).

To observe urazole **12** and other possible intermediates, 1.0 equiv of PTAD was mixed with **1** in a $CDCl_3$ and CD_2Cl_2 mixture at −70 °C for 40 min. Low temperature ^1H and ^{13}C NMR (−78 °C) detected formation of an intermediate in almost quantitative yield. This compound was shown to be the [4 + 2] cycloadduct **11** (Scheme 4).

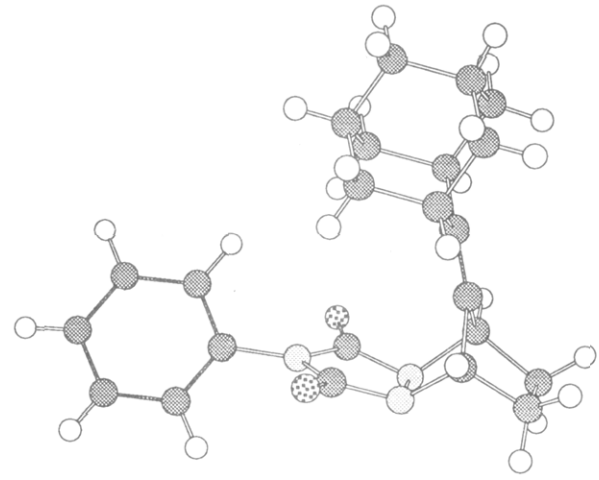


Figure 2. X-ray crystal structure of compound **13**.

Besides the phenyl and adamantyl protons, two vinyl and bridgehead protons appeared at 6.71 and 5.56 ppm, respectively, as triplets (J = 1.0 Hz). ^{13}C NMR of **11** showed a total of 15 resonances, as expected for the symmetrical structure (C_s). The bridgehead carbons were located at 62.2 ppm, a doublet, confirmed by DEPT spectra. As expected, six adamantyl carbons were resolved between 27.2 and 38.2 ppm, and a single carbonyl signal resonated at 158.3 ppm.

At −20 °C, compound **11** began to rearrange to a mixture of **9**, **10** and **12**, with **10** the major product. Compound **12** was characterized only by ^1H NMR, which showed three vinyl protons at 6.70 (1 H) and 6.56 ppm (2 H, unresolved). The singlet at 5.03 ppm was assigned to H_a. The rapid conversion of **11** to **10** on warming (ca. −20 to 25 °C) is remarkable.

Compound **11** was reduced by diazene to give a stable urazole **13** in 80% yield. Both ^1H and ^{13}C NMR are consistent with the C_s symmetry. A single crystal was obtained from methanol and the X-ray structure is shown in Figure 2.[24,37] The phenyl ring is perpendicular to the triazolinedione moiety and bisects the adamantyl cage, the norbornane skeleton, and triazoline ring. The perpendicular arrangement of triazolinedione moiety and phenyl ring can also be seen in the crystal structure of bis-adduct **10** (Figure 1).

Discussion

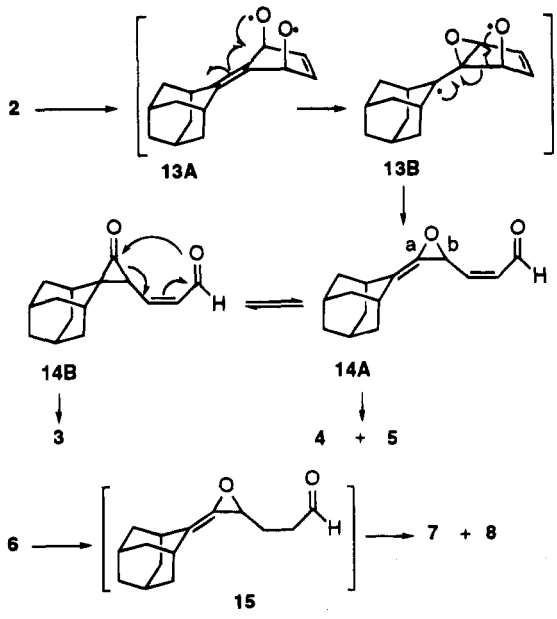
O–O Homocleavage of 7-Adamantylidene-2,3-dioxabicyclo[2.2.1]hept-5-ene (2). Low temperature NMR data and the diazene reduction experiment provide direct evidence that [2 + 4] cycloaddition to form endoperoxide **2** is the initial step in photooxygenation of adamantylidenecyclopentadiene (**1**). Thermal rearrangement products oxepinone **3**, keto aldehyde **4**, and cyclopentenone aldehyde **5** can be most reasonably explained by invoking homolysis of the peroxide bond of endoperoxide **2** (Scheme 5). Closure of diradical **13A** to oxirane carbinyl radical **13B** followed by β-sission of **13B** would produce allene oxide **14A** and/or its valence tautomer

(23) Crystal structure data for **10** (from CH_2Cl_2): formula = $C_{47}H_{50}N_6O_5$, FW = 778.95, monoclinic, space group $p2_1/n$, a = Å 10.576 (2), b = Å 21.957 (3), c = Å 17.352 (3), β = 99.26 (1)°, V = 3976 (1) Å^3, Z = 4, ϱ(calcd) = 1.30 g cm^{-3}, T = 156 K. Anisotropic refinement of all non-hydrogen atoms (except N6 and the carbon atoms of the two phenyl groups which were refined as rigid groups, H fixed and not refined, 440 parameters) using 2466 unique reflections with $F > 5\ \sigma(F)$ from 9152 total data, gave R = 0.083 and R_w = 0.088.

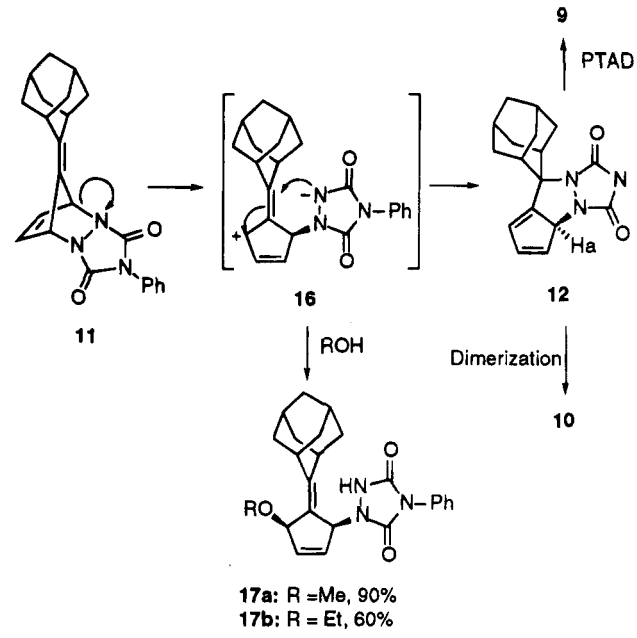
(24) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(25) Crystal structure data for **13** (from methanol): formula = $C_{23}H_{25}N_3O_2$, FW = 375.47, triclinic, space group $p1$ bar, a = Å 13.460 (2), b = Å 8.300 (1), c = Å 10.075 (1), α = 92.92 (1)°, β = 116.80 (1)°, γ = 67.91(1)°, V = 921.3(2) Å^3, Z = 2, ϱ(calcd) = 1.35 g cm^{-3}, T = 156 K. Anisotropic refinement of all non-hydrogen atom (calcd H fixed and not refined; 253 variables) using 1817 unique reflections with $F > 6\ \sigma(F)$ from 3230 total data, gave R = 0.043 and R_w = 0.051.

Scheme 5



Scheme 6



14B. Although an attempt to trap **14A/14B** with acetic acid at −78 °C was unsuccessful, these species are the most reasonable intermediates in rearrangement of endoperoxide **2** and are well precedented. Allene oxide and cyclopropanone were proposed as intermediates in the thermal decomposition of 7-isopropylidene-2,3-dioxabicyclo-[2.2.1]hept-5-ene and were trapped by dienes, furan, and acetic acid.[8] Opening of the epoxide a-bond in **14A**, followed by hydride shift would give rise to keto aldehyde **4**, while opening of the b-bond followed by a Michael-type addition at the carbon α to the carbonyl would produce cyclopentenone aldehyde **5**. On the other hand, intramolecular addition of the aldehyde oxygen to the cyclopropanone in **14B**, followed by bond isomerization, would account for the formation of oxipinone **3**. When photooxygenation of **1** was carried out in a mixture of CH_2Cl_2 and methanol, the product distribution was the same as in CH_2Cl_2. Lack of an effect of methanol on the reaction rate and product distribution further supports the nonpolar diradical pathway.

Saturation of the endocyclic double bond in endoperoxide **2** increases the stability of 7-adamantylidene-2,3-dioxabicyclo[2.2.1]heptane (**6**). However, at higher temperatures, a similar rearrangement occurs, and cycloacetal **7** and keto aldehyde **8** could be accounted for by invoking the analogous intermediate allene oxide **15** shown in Scheme 5.

C−N Heterocleavage of the [2 + 4] Cycloadduct (11). The outcome of the reaction between PTAD and adamantylidenecyclopentadiene (**1**) depends on the molar ratio of the reagents and the order of the addition of reagents. When **1** was added to 2.0 equiv of PTAD, 2:1 adduct **9** was the sole isolated product. On the other hand, when PTAD was added to 1.0 equiv of **1**, bis-adduct **10** was isolated in 64% yield, along with 3% of **9**. Although the structures of the final products in the reaction of PTAD and **1** are somewhat complex, low temperature NMR data and the diazene reduction experiment unequivocally establish that the initial intermediate is Diels−Alder cycloadduct **11**. Urazole **11** most likely underwent heterocleavage of the C−N bond to give [2 + 6] cycloadduct **12** through zwitterion **16** (Scheme 6). Diene **12** reacts with PTAD to give the 2:1 adduct **9**; in the absence of excess PTAD, it undergoes Diels−Alder dimerization to bis-adduct **10**. This suggests that PTAD is more reactive than **12**, in accord with its well documented high dienophilic reactivity.[25,26] [2 + 6] Cycloadduct **12** was characterized only by ^1H NMR, but its reactions strongly support its structure.

Ionic rearrangements of this type are precedented in reactions of PTAD with strained olefins,[27-31] and with dienes,[18] but, to our knowledge, there is only one example of C−N heterocleavage of the primary Diels−Alder adduct of fulvenes and PTAD in the literature.[32]

Zwitterion **16** is the most likely intermediate in the rearrangement of **11**. The need for allylic stabilization of the cation provided by the double bond was readily demonstrated by the thermal stability of the saturated analogue, **13**. In contrast, endoperoxide **2** and its saturated analogue **6** undergo the same type of rearrangement, because homolysis of the O−O bond does not need allylic stabilization.

Further evidence for zwitterion **16** came from trapping experiments. When methanol was added to a cold (−78 °C) solution of **11** and the solution was allowed to warm to room temperature slowly, methanol trapping product **17a** was isolated in 90% yield (Scheme 6). Similarly, ethanol trapping product **17b** was isolated in 60% yield, along with 12% of **9**. Isolation of high yields of the alcohol adducts strongly supports the intermediacy of zwitterion **16**.

Conclusions

Low temperature NMR measurements and chemical transformations indicate that endoperoxide **2** and urazole **11**, respectively, are intermediates in the reaction of adamantylidenecyclopentadiene (**1**) with $^1O_2$ and PTAD.

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Both intermediates are unstable and start to rearrange at ca. −25 °C, but in different ways. Endoperoxide **2** undergoes homocleavage of the peroxide bond to a nonpolar diradical, which collapses to an allene oxide or cyclopropanone. Rearrangement of this intermediate leads to the final oxygenated products. In contrast, primary PTAD cycloadduct **11** undergoes heterocleavage of the C−N bond to zwitterion **16**, which recloses to [2 + 6] cycloadduct **12**. Such zwitterions are probably common features of reactions with triazolinediones where substrates can support them by appropriate stabilization of the zwitterion or destabilization of the intermediate aziridinium imide. Reaction of **12** with PTAD or its Diels−Alder dimerization gives the final, thermally stable products. The 2:1 adduct **9**, bis-adduct **10**, and urazole **13** are structurally interesting and might be useful precursors for biradical or polyradicals from denitrogenation of the corresponding azoalkanes.[33] Such biradicals and polyradicals are high-spin systems which may function as ferromagnetic coupling units.[34,35]

Experimental Section

General. ^{1}H and ^{13}C NMR data were taken at 360 or 500 MHz. Low temperature NMR experiments were done by cooling the probe to the desired temperature and then inserting the sample, precooled in dry ice−acetone. Usually 10 min or longer was needed before the probe temperature stabilized and good shimming could be achieved. Chemical shift values are in δ (ppm) relative to TMS. Carbon multiplicities were obtained by DEPT experiments. Flash column chromatography was carried out on SiO_2 (Silica gel 60, 40−63 μm). Photooxygenations were performed with a Varian-Eimac Cermax 300-W xenon lamp filtered with a 0.009 M K_2CrO_4 solution (3.5 cm) to remove light below 500 nm. Tetraphenylporphyrin (TPP, ca 1.0×10^{-5} M) in $CHCl_3$ or CH_2Cl_2 was used as sensitizer. Oxygen was passed through activated 4 Å molecular sieves and bubbled through the reaction solution via a Teflon tube.

7-Adamantylidene-2,3-dioxabicyclo[2.2.1]hept-5-ene (2). Adamantylidenecyclopentadiene[36] (**1**) (97 mg, 0.49 mmol) was dissolved in 0.4 mL of CD_2Cl_2 in a 5 mm NMR tube. After 40 min irradiation at −78 °C, low temperature ^{1}H NMR indicated complete conversion of **1** to 7-adamantylidene-2,3-dioxabicyclo-[2,2,1]hept-5-ene (**2**). ^{1}H NMR (500 MHz, CD_2Cl_2, −78 °C) δ 6.70 (br s, 2 H), 5.49 (br s, 2 H), 2.58 (s, 2 H), 1.93 (d, 2 H, J = 14.9 Hz), 1.87 (d, 4 H, J = 12.1 Hz), 1.80 (s, 4 H), 1.65 (d, 2 H, J = 11.5 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2, −78 °C) δ 136.8, 135.1, 125.9, 77.5, 37.6, 37.5, 35.7, 34.1, 27.1. Endoperoxide **2** started to rearrange at ca. −25 °C to oxepinone **3**, keto aldehyde **4**, and cyclopentenone aldehyde **5** in a ratio of 2.3:1.1:1.

Rearrangement of Endoperoxide 2 to Oxepinone 3, Keto Aldehyde 4, and Cyclopentenone Aldehyde 5. Adamantylidenecyclopentadiene (**1**) (310 mg, 1.56 mmol) was dissolved in 30 mL of CH_2Cl_2. Photooxygenation was carried out at −78 °C for 1.5 h. TLC indicated that the starting fulvene reacted completely. The reaction mixture was brought to rt, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2:petroleum ether = 2:4) to give three products, discussed in order of increasing polarity.

Oxepinone **3** (153 mg, 46%): mp 84−85° C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (d, 1 H, J = 6.8 Hz), 6.13 (dd, 1 H, J = 10.3, 6.1 Hz), 5.64 (dd, 1 H, J = 6.7, 6.4 Hz), 5.55 (d, 1 H, J = 10.3 Hz), 2.36 (br s, 2 H), 1.87 − 1.83 (m, 2 H), 1.72 (br s, 10 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 164.4 (s), 140.1 (d), 132.1 (d), 124.1 (d), 107.0 (d), 56.8 (s), 37.3 (t), 33.6 (t), 26.9 (d), 26.8 (d); FT-IR ($NaCl/CDCl_3$) cm^{-1} 2904 (s), 1745 (s), 1728 (s), 1635 (m), 1269 (s), 727 (m); MS m/z (rel intensity) 230 (M, 19), 202 (M − 28, 100), HRMS calcd for $C_{15}H_{18}O_2$ 230.1307, obsd 230.1317.

5-Adamantylidene-4-oxopentenal (4) (66 mg, 19%): mp 44 − 46 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.28 (d, 1 H, J = 7.3 Hz), 6.91 (d, 1 H, J = 11.7 Hz), 6.13 (dd, 1 H, J = 11.7, 7.2 Hz), 6.08 (s, 1 H), 4.04 (br s, 1 H), 2.40 (br s, 1 H), 2.03 − 1.95 (m, 6 H), 1.88 − 1.82 (m, 6 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 193.2 (d), 190.2 (s), 177.0 (s), 143.5 (d), 137.2 (d), 117.0 (d), 42.0 (d), 40.5 (t, 2 C), 39.5 (t, 2 C), 36.6 (t), 33.8 (d), 27.7 (d, 2 C); FT-IR ($NaCl/CDCl_3$) cm^{-1} 2910 (s), 1682 (s), 1665 (m), 1615 (s); MS m/z (rel intensity) 230 (M, 19), 202 (M − 28, 97), 175 (M − 55, 40), HRMS calcd for $C_{15}H_{18}O_2$ 230.1307, obsd 230.1307.

Cyclopentenone **5** (72 mg, 20%): mp 64−65 °C, ^{1}H NMR (360 MHz, $CDCl_3$) δ 9.26 (d, 1 H, J = 4.9 Hz), 7.17 (dd, 1 H, J = 5.8, 3.6 Hz), 6.36 (dd, 1 H, J = 5.8, 1.1 Hz), 3.95 (m, 1 H), 3.14 (d, 1 H, J = 12.8 Hz), 2.12 − 1.48 (m, 13 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 210.2 (s), 198.7 (d), 152.9 (d), 137.1 (d), 65.0 (d), 57.9 (s), 38.1 (t), 35.6 (t), 35.0 (d), 34.1 (t), 32.2 (t), 31.4 (t), 29.4 (d), 26.9 (d); FT-IR (KBr) cm^{-1} 2910 (s), 1723 (s), 1701 (s); MS m/z (rel intensity) 230 (M, 80), 202 (M − 28, 100), HRMS calcd for $C_{15}H_{18}O_2$ 230.1307, obsd 230.1308.

7-Adamantylidene-2,3-dioxabicyclo[2.2.1]heptane (6). Adamantylidenecyclopentadiene (**1**) (106 mg, 0.55 mmol) in 50 mL of CH_2Cl_2 was photooxygenated at −78 °C for 1.0 h. At the same temperature, potassium azodicarboxylate (0.5 g, 2.7 mmol) was introduced. Then, acetic acid (0.3 mL, 5.7 mmol) in 2.0 mL of CH_2Cl_2 was slowly added to the mixture through a dropping funnel at −50 °C during 10 min. The reaction was left at −40 °C for 1.0 h, and the temperature was gradually raised to 25 °C. The precipitate was filtered and washed with 10 mL of CH_2Cl_2. The filtrate was condensed to give 110 mg (91%) of 7-adamantylidene-2,3-dioxabicyclo[2.2.1]heptane (**6**) in above 96% purity as a colorless oil. Further SiO_2 flash column chromatography did not improve the purity. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (t, 2 H, J = 1.4 Hz), 2.63 (br s, 2 H), 1.92−1.66 (m, 16 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 135.4 (s), 130.9 (s), 74.7 (d, 2 C), 39.5 (t, 2 C), 38.5 (t, 2 C), 36.8 (t), 36.2 (d, 2 C), 29.5 (t, 2 C), 28.2 (d), 28.0 (d).

2-Adamantylidene-1,7-dioxabicyclo[2.2.1]heptane (7) and 5-Adamantylidene-4-oxopentanal (8). Compound **6** (250 mg, 1.07 mmol) in 0.5 mL of $CDCl_3$ was heated to 70 °C for 10 min. ^{1}H NMR indicated formation of **7** and **8**, which were isolated by flash column chromatography (petroleum ether:ethyl acetate = 10:1). **7** (123 mg, 49%, oil): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (dd, 1 H, J = 1.8, 0.9 Hz), 5.16 (dd, 1 H, J = 3.1, 1.0 Hz), 2.75 (br s, 1 H), 2.39 (br s, 1 H), 1.95−1.59 (m, 16 H); ^{13}C NMR (90 MHz, CDCl3) δ 140.5 (s), 112.8 (s), 101.7 (d), 75.1 (d), 39.6 (t), 38.6 (t), 38.5 (t), 37.9 (t), 37.2 (t), 33.0 (d), 31.7 (t), 29.8 (d), 28.4 (d), 28.4 (d), 27.1 (t); FT-IR ($NaCl/CDCl_3$) cm^{-1} 2905 (s), 2847 (s), 1147 (s), 1076 (s), 976 (s), 877 (s); MS m/z (rel intensity) 232 (M, 100), 204 (M − 28, 37), 148 (M − 84, 85), HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, obsd 232.1456. **8** (90 mg, 36%, colorless oil): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (t, 1 H, J = 0.6 Hz), 5.99 (s, 1 H), 4.05 (br s, 1 H), 2.79 (m, 2 H), 2.73 (m, 2 H), 2.37 (s 1 H), 1.99−1.78 (m, 12 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 201.1 (d), 198.9 (s), 172.1 (s), 116.1 (d), 41.5 (d), 40.3 (t, 2 C), 39.3 (t, 2 C), 37.6 (t), 36.8 (t), 36.5 (t), 33.1 (d), 27.8 (d, 2 C); FT-IR ($NaCl/CDCl_3$) cm^{-1} 2907 (s), 1723 (s), 1685 (s), 1617 (s); MS m/z (rel intensity) 232 (M, 12), 204 (M − 28, 32), 188 (M − 44, 100), 175 (M − 57, 96), HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, obsd 232.1463.

Polycyclic Urazole 9. PTAD (234 mg, 1.34 mmol) was dissolved in 20 mL of $CHCl_3$ at 0 °C under argon. Adamantylidenecyclopentadiene (**1**) (117 mg, 0.59 mmol) in 5 mL of $CHCl_3$ was slowly introduced through a dropping funnel. The pink PTAD color gradually disappeared at 0 °C after 15 min stirring. TLC indicated complete conversion of **1** to a single product. The crude reaction mixture was condensed. Recrystallization from CH_2Cl_2:petroleum ether (3:7) gave urazole **9** (288 mg, 89%) mp 190−192 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.48−7.33 (m, 10 H), 6.83 (d, 1 H, J = 5.6 Hz), 6.46 (dd, 1 H, J = 5.6, 2.4 Hz), 5.50 (br s, 1 H), 4.17 (d, 1 H, J = 1.4 Hz),

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3.20 (br s, 1 H), 2.93 (d, 1 H, J = 11.3 Hz), 2.37 (d, 1 H, J = 13.0 Hz), 2.27 (d, 1 H, J = 11.4 Hz), 2.13 (s, 1 H), 2.05 – 2.00 (m, 4 H), 1.90–1.85 (m, 5 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 158.4 (s), 157.8 (s), 155.5 (s), 154.2 (s), 132.9 (d), 132.4 (d), 132.2 (s), 131.4 (s), 129.5 (d, 2 C), 129.3 (d, 2 C), 129.2 (d), 128.6 (d), 126.7 (d, 2 C), 126.1 (d, 2 C), 93.1 (s), 78.3 (s), 74.1 (d), 61.1 (d), 38.0 (t), 36.6 (d), 36.1 (t), 35.5 (t), 34.7 (t), 33.9 (t), 32.0 (d), 27.6 (d), 27.2 (d); FT-IR (KBr) cm^{-1} 1785 (m), 1774 (m), 1731 (s), 1410 (s); FAB HRMS obsd 549.2256, calcd for $C_{31}H_{29}N_6O_4$ 549.2250. Anal. Calcd for $C_{31}H_{28}N_6O_4$: C, 67.86, H, 5.15, N, 15.33. Found: C, 67.19, H, 4.93, N, 14.94.

Bis-Adduct 10. Adamantylidenecyclopentadiene (**1**) (142 mg, 0.72 mmol) in 6.0 mL of $CHCl_3$ was cooled to −40 °C under argon. Upon stirring, PTAD (126 mg, 0.72 mmol) in 10 mL of $CHCl_3$ was slowly added via a syringe. After 1.5 h stirring below −20 °C, the reaction was brought to 25 °C and stirred for an additional 30 min. The crude reaction mixture was condensed to give a solid. Recrystallization from acetone: petroleum ether (1:3) gave **10** (117 mg, 64%): mp 224–225 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.52–7.43 (m, 8 H), 7.37–7.34 (m, 2 H), 6.19 (d, 1 H, J = 5.9 Hz), 5.87 (dd, 1 H, J = 5.8, 3.1 Hz), 5.80 (s, 1 H), 4.84 (d, 1 H, J = 8.6 Hz), 3.93 (m, 1 H), 3.83 (d, 1 H, J = 7.2 Hz), 3.75 (d, 1 H, J = 1.7 Hz), 3.59 (d, 1 H, J = 12.8 Hz), 3.48 (d, 1 H, J = 13.0 Hz), 3.41 (m, 1 H), 2.57 (s 1 H), 2.41–1.69 (m, 25 H); ^{13}C NMR (90 MHz, CD_2Cl_2) δ 150.9, 149.9, 148.8, 148.7, 148.4, 134.6 134.3, 132.8, 132.7, 129.2, 129.0, 128.3, 126.6, 80.9, 77.3, 76.8, 70.9, 61.3, 60.6, 45.0, 42.5, 38.7, 38.2, 37.8, 36.5, 36.4, 35.7, 35.6, 35.0, 34.6, 34.2, 34.1, 33.6, 32.1, 30.9, 27.1, 27.0, 26.7, 26.6. FT-IR (KBr) cm^{-1} 2911 (s), 1761 (s), 1701 (vs), 1695 (s); HRFAB-MS: calcd for $C_{46}H_{47}N_6O_4$ 747.3659, obsd 747.3286.

10-Adamantylidene-2,4,6-triazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (11). Adamantylidenecyclopentadiene (**1**) (14 mg, 0.07 mmol) was dissolved in 0.3 mL of CD_2Cl_2 in an NMR tube, and the tube was cooled to −78 °C under argon. PTAD (12.4 mg, 0.07 mmol) in 0.3 mL of CD_2Cl_2 was slowly added under argon, and the bubbling was maintained at −78 °C for 1.0 h. Low temperature ^{1}H NMR indicated quantitative formation of Diels–Alder adduct **11**. ^{1}H NMR (500 MHz, CD_2Cl_2, −76 °C) δ 7.51 (t, 2 H, J = 7.4 Hz), 7.45 (t, 1 H, J = 7.2 Hz), 7.34 (d, 2 H, J = 7.6 Hz), 6.71 (s, 2 H), 5.56 (s, 2 H), 2.67 (br s, 2 H), 1.96–1.87 (m, 6 H), 1.81 (s, 2 H), 1.73 (d, 2 H, J = 11.4 Hz), 1.66 (d, 2 H, J = 11.2 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2, −65 °C) δ 158.3 (s, 2 C), 133.1 (d, 2 C), 130.9 (s), 130.3 (s), 129.3 (s), 128.8 (d, 2 C), 128.4 (d), 125.4 (d, 2 C), 62.2 (d, 2 C), 38.2 (t, 2 C), 37.6 (t, 2 C), 35.8 (t), 33.8 (d, 2 C), 27.4 (d), 27.2 (d). Compound **11** started to rearrange at −20 °C to give 89% of bis-adduct **10** and 10% of adduct **9** by ^{1}H NMR. In the process of rearrangement, an intermediate **12** was also observed: ^{1}H NMR (360 MHz, CD_2Cl_2) δ 7.53–7.40 (m, 5 H), 6.70 (dd, 1 H, J = 6.1, 1.3 Hz), 6.56 (m, 2 H), 5.03 (s, 1 H), 3.28 (d, 2 H, J = 13.7 Hz), 2.48 (br s, 2 H), 2.40 (br s, 2 H), 2.07–1.85 (m, 8 H).

10-Adamantylidene-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione (13). Adamantylidenecyclopentadiene (**1**) (142 mg, 0.72 mmol) was dissolved in 10 mL of CH_2Cl_2 at −50 °C. PTAD (132 mg, 0.72 mmol) in 10 mL of CH_2Cl_2 was slowly added over 15 min. Stirring was continued at −50 °C for 1.5 h to ensure complete conversion of starting material. Potassium azodicarboxylate (781 mg, 4.0 mmol) was added to the above solution, followed by slow addition of acetic acid (0.52 mL) in 5.0 mL of CH_2Cl_2. After addition, the mixture was stirred at −50 °C for 1.5 h and then gradually returned to 25 °C. The precipitate was filtered and washed with CH_2Cl_2. The filtrate was condensed to give a crude white solid. Recrystallization from methanol gave **13** (210 mg, 80%): mp 160–162 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.47–7.34 (m, 5 H), 4.91 (t, 2 H, J = 1.8 Hz), 2.67 (br s, 2 H), 2.12–2.07 (m, 2 H), 1.95–1.86 (m, 8 H), 1.82 (s, 2 H), 1.73 (d, 2 H, J = 11.2 Hz), 1.59 (d, 2 H, J = 11.2 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 159.2 (s), 140.3 (s), 131.3 (s), 128.9 (d, 2 C), 128.0 (d), 125.1 (d, 2 C), 124.3 (s), 59.2 (d, 2 C), 40.0 (t, 2 C), 38.5 (t, 2 C), 36.3 (t), 35.3 (d, 2 C), 27.7 (d), 27.6 (t, 2 C), 27.6 (d); FT-IR (NaCl/$CDCl_3$) cm^{-1} 2919 (s), 1778 (m), 1722 (s), 1402 (s), 733 (s); FABMS 376.7 (M + 1).

Trapping of Zwitterion 16 by Alcohol. Adamantylidenecyclopentadiene (**1**) (117 mg, 0.59 mmol) dissolved in 10 mL of methanol was cooled to −50 °C under argon. PTAD (114 mg, 0.60 mmol) in 10 mL of CH_2Cl_2 was slowly added to the above solution with stirring. The reaction was left at −50 °C for 1.5 h and then brought to RT. The solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate:MeOH = 2.3:2.5:0.2) to give the methanol adduct **17a** (212 mg, 90%): mp 142–143 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.15 (br s, 1 H), 7.52–7.44 (m, 4 H), 7.38–7.33 (m, 1 H), 6.50 (ddd, 1 H, J = 5.9, 2.3, 1.1 Hz), 6.12 (dd, 1 H, J = 6.0, 2.7 Hz), 5.72 (dd, 1 H, J = 2.6, 1.1 Hz), 4.67 (d, 1 H, J = 2.4 Hz), 3.44 (s, 3 H), 2.85 (br s, 2 H), 2.01–1.80 (m, 11 H), 1.55 (d, 1 H, J = 10.9 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 153.9 (s), 150.8 (s), 149.8 (s), 136.0 (d), 133.4 (d), 131.5 (s), 129.1 (d), 128.0 (d), 125.7 (d), 121.1 (s), 79.8 (d), 57.4 (d), 56.2 (q), 39.8 (t), 39.1 (t), 38.6 (t), 38.5 (t), 36.6 (t), 35.2 (d), 34.9 (d), 27.8 (d), 27.7 (d); FT-IR (NaCl/$CDCl_3$) cm^{-1} 3450 (w), 2910 (s), 1768 (s), 1703 (s), 1420 (s); HRMS calcd for $C_{24}H_{27}N_3O_3$ 405.2052, obsd 373.1782 (M − CH_3OH).

Similarly, ethanol trapping adduct **17b** (60%) was obtained: mp 141–142 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.19 (br s, 1 H), 7.52–7.43 (m, 4 H), 7.37–7.33 (m, 1 H), 6.46 (ddd, 1 H, J = 5.9, 2.3, 1.1 Hz), 6.11 (dd, 1 H, J = 6.0, 2.6 Hz), 5.72 (dd, 1 H, J = 2.5, 0.9 Hz), 4.76 (d, 1 H, J = 2.4 Hz), 3.69 (m, 1 H, a part of AB), 3.59 (m,1 H, a part of AB), 2.85 (br s, 2 H), 2.04–1.76 (m, 11 H), 1.57 (d, 1 H, J = 11.6 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ 153.4 (s), 150.7 (s), 149.8 (s), 136.5 (d), 133.0 (d), 131.6 (s), 129.0 (d, 2 C), 127.9 (d), 125.6 (d, 2 C), 121.3 (s), 78.3 (d), 64.2 (t), 57.4 (d), 39.6 (t), 39.2 (t), 38.6 (t), 38.4 (t), 36.7 (t), 35.2 (d), 34.9 (d), 27.8 (d), 27.7 (d), 15.7 (q); FT-IR (NaCl/$CDCl_3$) cm^{-1} 3461 (w), 2903 (s), 2852 (s), 1767 (s), 1704 (s), 1452 (s); Anal. Calcd for $C_{25}H_{29}N_3O_3$: C, 71.56, H, 6.97, N, 10.02. Found: C, 71.29, H, 6.92, N, 9.88.

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of **2–10**, **11**, **13**, **17a**, and **17b** (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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