FORMATIONS OF AZAZULANONES AND DIHYDROAZAZULANONES VIA REACTIONS OF TROPONIMINES WITH HETEROCUMULENES

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Abstract—Reactions of troponimines with carbon disulfide, phenyl isocyanate, tosyl isocyanate, or diphenylketene afforded dihydroazazulane and azazulane derivatives through [8+2]-type cycloadducts. Reaction with dimethyl acetylenedicarboxylate gave a dihydroazazulene derivative and a quinoline derivative.

Although the chemistries of tropone (1) and troponthione (2) attracted attention of chemists and were investigated in detail, surprisingly few studies have so far been made the researches on the chemistry of troponimines (3). This may be because 3 have been regarded to be a mere analogue of 1 or 2, and its chemical natures could be deduced easily from those of 1 or 2. However, considering the differences of reactivities between 1 and 2 the study on 3 seems to be worth developing. We investigated the reactions of 3 with heterocumulenes to afford dihydroazazulanonones, azazulanonones and azulenes. Here the results will be reported.

The reaction of tropone phenylhydrazone (3a) with carbon disulfide (4a) afforded a 1:1 adduct (5a) quantitatively. An analogous reaction of 3a with phenyl isocyanate (4b), tosyl isocyanate (4c), diphenylketene (4d) also gave the corresponding 1:1 adducts (5b,5c, and 5d) in almost quantitatively yields, respectively. The similar reactions using tropone tosylhydrazone (3b) with heterocumulenes (4a-4d) produced the corresponding adducts (5e, 5f, 5g, and 5h) in considerable yields, respectively. On the other hand, the reaction of 3b with phenyl isothiocyanate (4e) gave 5i and 6i in 38 and 61% yields, respectively. Upon standing in benzene at room temperature, 5i changed quantitatively to 6i.

The reaction of N-methoxytropionime (3c) with chlorophenyl- (7a) and dichloroketenes (7b) gave azazulanone derivatives (8a) and (8b) in 90 and 62% yields, respectively. Reaction of 3c with chloroketene (7c) afforded 9 in 36% yield. The reaction of 3c with 4e afforded a cycloheptatriene derivative (10 or 10') in 32% yield. Oxidation of 10 or 10' using manganese oxide gave a ketimine derivative (11) in 82% yield.

The reaction of 3c with 4b gave a cycloheptatriene derivative (12) and a 1,3-diazazulanone derivatives (14) in 27 and 43% yields, respectively. The thermal reaction of 12 afforded 13, 14, and a recovery of 12 in 15, 5, and 80% yields, respectively. In contrast, the similar reaction of 12 in the presence of p-chloranil gave 14 in 87% yield. The reaction of 3c with 4e afforded 16 in 60% yield. When a limited quantity of 4c
was used, a [8+2]-type adduct (15) could be detected in $^1$H-nmr spectrum. Reaction of 3c with dimethyl acetylenedicarboxylate (17) afforded a dihydroazazulene derivative (18 or 18') and a quinoline derivative (19) in 12 and 5% yields, respectively. Subsequent oxidation of 18 or 18' afforded an azazulene derivative (20) in 91% yield. These reaction conditions and product yields were summarized in Table 1.

The structures of 5 and 6 were deduced as follows. The molecular ion peaks in mass spectra demonstrated that the products were all 1:1 adducts between the hydrazone and heterocumulenes. Analyses of their $^1$H-nmr spectra and comparisons of the spectra to those of the analogous compounds showed that the products contained 1.7-disubstituted cycloheptatriene moieties. The chemical shifts of the methine protons (H$_a$) of 5a, 5e, and 5i (the neighboring atom of H$_a$ on the heterocyclic moieties are sulfur atom), 5b, 5c, 5f, 5g, and 6i (those are nitrogen atom), and 5d and 5h (those are carbon atom) should be expected to be

![Diagram](image)

**Table 1. Reaction Conditions and Products Yields**

<table>
<thead>
<tr>
<th>Tropon-imine</th>
<th>Heterocumulene</th>
<th>Temperature[°C]</th>
<th>Time [hour]</th>
<th>Solvent</th>
<th>Products</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>4a</td>
<td>60$^1$</td>
<td>13</td>
<td>-</td>
<td>5a</td>
<td>99</td>
</tr>
<tr>
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<td>5b</td>
<td>99</td>
</tr>
<tr>
<td>3a</td>
<td>4c</td>
<td>r. t.</td>
<td>0.5</td>
<td>benzene</td>
<td>5c</td>
<td>(99)</td>
</tr>
<tr>
<td>3a</td>
<td>4d</td>
<td>r. t.</td>
<td>20</td>
<td>ether</td>
<td>5d</td>
<td>(69)</td>
</tr>
<tr>
<td>3b</td>
<td>4a</td>
<td>60$^1$</td>
<td>48</td>
<td>-</td>
<td>5e</td>
<td>(99)</td>
</tr>
<tr>
<td>3b</td>
<td>4b</td>
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<td>2</td>
<td>benzene</td>
<td>5f</td>
<td>(97)</td>
</tr>
<tr>
<td>3b</td>
<td>4c</td>
<td>r. t.</td>
<td>0.5</td>
<td>benzene</td>
<td>5g</td>
<td>(99)</td>
</tr>
<tr>
<td>3b</td>
<td>4d</td>
<td>r. t.</td>
<td>20</td>
<td>ether</td>
<td>5h</td>
<td>(86)</td>
</tr>
<tr>
<td>3b</td>
<td>4e</td>
<td>60</td>
<td>4</td>
<td>benzene</td>
<td>5i</td>
<td>(38)</td>
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<tr>
<td>3c</td>
<td>7a</td>
<td>r. t.</td>
<td>24</td>
<td>CH$_2$Cl$_2$</td>
<td>8a</td>
<td>(90)</td>
</tr>
<tr>
<td>3c</td>
<td>7b</td>
<td>r. t.</td>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>8b</td>
<td>(62)</td>
</tr>
<tr>
<td>3c</td>
<td>7c</td>
<td>r. t.</td>
<td>24</td>
<td>CH$_2$Cl$_2$</td>
<td>9</td>
<td>(36)</td>
</tr>
<tr>
<td>3c</td>
<td>4e</td>
<td>reflux</td>
<td>5</td>
<td>toluene</td>
<td>10</td>
<td>(32)</td>
</tr>
<tr>
<td>3c</td>
<td>4b</td>
<td>reflux</td>
<td>34</td>
<td>toluene</td>
<td>12</td>
<td>(27)</td>
</tr>
<tr>
<td>3c</td>
<td>4c</td>
<td>reflux</td>
<td>0.5</td>
<td>benzene</td>
<td>16</td>
<td>(60)</td>
</tr>
<tr>
<td>3c</td>
<td>17</td>
<td>70</td>
<td>24</td>
<td>benzene</td>
<td>18</td>
<td>(12)</td>
</tr>
</tbody>
</table>

Oxidation of 10: 1) in an autoclave, 2) 80% of 12 was recovered, 3) in the presence of p-chloranil
about 4.20, 4.45, and 3.60 ppm, respectively, referring to the analogous compounds. The observed values of 5a (4.20), 5e (3.98), 5i (3.95), 5b (4.50), 5c (4.58), 5f (4.47), 5g (4.57), 6i (4.72), 5d (3.66), and 5h (3.57) were in good agreement with expected values. IR spectra showed that 5b, 5c, 5d, 5f, 5g, and 5h had carbonyl groups (1720-1740 cm\(^{-1}\)), 5a, 5i, and 6i had thiocarbonyl groups (1290-1330 cm\(^{-1}\)), and 5i had an imino group (1620 cm\(^{-1}\)).

The structures of the products from 3c were also deduced as follows. Molecular ion peaks of 10, 13, and 18 in mass spectra demonstrated that these products were derived from the addition reactions of 3c with the heterocumulenes followed by the eliminations of methoxy groups. The existences of 1,2- (10 and 18) or 3,4-disubstituted cycloheptatriene moieties (12 and 13) were showed by the coupling constant values and the spin split pattern of the protons on cycloheptatriene moieties in \(^1H\)-nmr spectra. In the IR spectra, the characteristic absorptions of an imino group (10: 1597 cm\(^{-1}\)) and carbonyl groups (12: 1736, 13: 1740, 18: 1732 cm\(^{-1}\)) were observed.

The structures of azazulanone derivatives (8, 9, 11, and 14) and the azazulene derivative (20) were deduced on the basis of their spectral properties. \(\lambda_{max}\) Values in the UV spectra of these compounds (8a: 424, 8b: 418, 9: 412, 11: 414, 14: 390, 20: 455 nm) were in good agreement with those of the analogous
The ir spectra indicated the existences of the carbonyl groups (8a: 1680, 8b:1694, 9: 1682, 14:1667, 20:1736 cm⁻¹) and an imino group (11:1601 cm⁻¹). The dihydroazulano derivative (16) and the quinoline derivative (19) were confirmed by coincidence of their spectral properties to those of the authentic samples.⁶

The reactions of 3a and 3b are considered to proceed through [8+2] cycloadditions, where the electron-rich nitrogen atoms of the troponimine attacked the electron poor central carbon atoms of the heterocumulenes to form ionic intermediates (21), which then cyclized to [8+2] cycloadducts (22). The reactions of 3c are also considered to be initiated by the similar stepwise process to give the adducts of the type (22). An elimination of the methoxy group in 22 formed 10 and 13, which were then oxidized to the corresponding azulane derivatives of type 23 (11 and 14).

The reaction of 3c with 4c is thought to give the initial adduct (15), which then eliminated methoxy isocyanate to give 24. The [8+2] cycloaddition of 24 with 4c could form 16.

The quinoline derivatives (19) is considered to be produced from the [8+2] cycloadduct (25), which cyclized to a norcaradiene-type intermediate (26). The subsequent ring enlargement to 27 followed by an elimination of methanol afforded the final product (19).⁷

These cycloaddition reactions are considered to proceed through a zwitter ionic intermediate (21), which has two anion centers (X and Y). The selectivity of these nucleophiles was explained by HSAB theory.⁸

Tropylium ion is a soft acid and so preferred to react with softer base, therefore, a nitrogen atom in 4b and 4c, a carbon atom in 4d, and a sulfur atom in 4e were selected as the suitable nucleophiles.

In order to clarify the isomerization process of 5i to 6i, their thermodynamic stabilities were evaluated by PM3 MO calculations using model compounds of 5j and 6j. The calculation showed that 6j (heat of formation; 156 kcal/mol) was more stable than 5j (165 kcal/mol), suggesting the formation of the initial product (5i) was kinetically controlled and that of 6i thermodynamically controlled.
EXPERIMENTAL

Melting points were uncorrected. Nmr spectra were measured in deuterio chloroform solution with a Varian XL-200 spectrometer. IR and uv spectra were measured with JASCO FT/IR-5300 and Hitachi 220A spectrophotometers, respectively. Mass spectra were measured with Hitachi M-2000S spectrometer. Only typical experiments are mentioned.

Reaction of Tropone Phenyldrazine (3a) with Carbon Disulfide (4a). A solution of 3a (230 mg, 1.2 mmol) in 4a (20 ml, 330 mmol) was heated at 60°C for 13 h in an autoclave. Removal of excess 4a afforded crystals of 5a (0.32 g, 99%)


Reaction of Tropone Phenyldrazine (3a) with Phenyl Isocyanate (4b). A solution of 3a (0.23 g, 1.2 mmol) and 4b (0.38 g, 3.2 mmol) in benzene (5.0 ml) was heated at 60°C for 15 min under a nitrogen stream. After evaporation of the solvent the residual colorless oil was purified with thin layer chromatography on silica gel using hexane-ethyl acetate 1:2 as a developing solvent to give a colorless oil 5b (370 mg, 99%, Rf= 0.59).


5c: colorless crystals. mp 152-154°C (ethyl acetate). Ms m/z (rel intensity): 393 (M+, 1), 278 (14), 220 (100). IR (KBr): 3350, 1760, 1720, 1350, 1170 cm⁻¹. ¹H-Nmr δ: 2.45 (s, 3H, Me), 4.58 (br s, H₃), 5.52 (m, H₃), 5.84 (br s, H₃), 6.12 (br s, H₃), 6.40 (m, 2H, H₃ and H₃), 7.05-8.05 (m, 9H, aromatic protons). ¹³C-Nmr δ: 21.6, 56.7, 97.2, 118.6, 125.0, 126.6, 127.0, 128.0, 128.4, 129.5, 129.7, 129.9, 130.1, 130.3, 145.1. Anal. Calcd for C₁₉H₁₉N₃O₃S: C, 64.11; H, 4.87. Found: C, 64.01; H, 4.69.

5d: colorless oil. Hrms m/z: 390.1716. Calcd for C₁₉H₁₂N₂O: 390.1730. Ms m/z (rel intensity): 390 (M⁺, 12), 194 (100), 165 (97). IR (oil): 1730, 1650, 1500 cm⁻¹. ¹H-Nmr δ: 3.66 (d, H₆), 4.57 (dd, H₆), 5.92 (d, H₆), 6.02 (dd, H₆), 6.57-7.60 (m, 17H, H₆, H₆ aromatic protons). Coupling constants in Hz; J₆b=4.8, J₆c=9.8, J₆d=6.6, J₆e=10.2, J₆f=6.3. ¹³C-Nmr δ: 46.0, 98.2, 113.6, 120.1, 121.8, 125.9, 126.2, 127.2, 127.9, 128.6, 129.2, 129.3, 132.5, 133.6, 142.9, 145.5, 174.2.

5e: pale yellow crystals. mp 130-132°C (benzene). Ms m/z (rel intensity): 350 (M⁺, 10), 163 (100). Uv (MeOH): 352 nm (log ε, 4.03) 289 (4.21). IR (KBr): 3180, 1350, 1290, 1160 cm⁻¹. ¹H-Nmr δ: 2.39 (s, 3H, Me), 3.98 (br s, H₃), 5.30 (br s, H₆), 6.05-6.80 (m, 4H, H₆, H₆, H₆, and H₆), 7.10-7.80 (m, 4H,
of the solvent the residue was separated with column chromatography on silica gel to give red crystals of water, extracted with dichloromethane, and the organic layer was dried over sodium sulfate. After removal (MeOH): 334 nm (log $\varepsilon$, 3.42), 250 (4.23). IR (KBr): 3100, 2900, 1700, 1640, 1160 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.42 (s, 3H, Me), 4.47 (br s, $H_d$), 4.92 (br s, $H_p$), 6.00-6.80 (m, 4H, $H_e$, $H_g$, $H_c$, and $H_p$). 7.10-7.90 (m, 9H, aromatic protons). $^{13}$C-Nmr $\delta$: 21.6, 55.6, 97.1, 115.7, 118.8, 124.1, 125.8, 128.4, 129.0, 129.1, 129.6, 136.6, 145.0. Analyst. Calcld for C$_{22}$H$_{13}$N$_2$O$_5$S: C, 64.11; H, 4.87. Found: C, 64.12; H, 4.85.

**5f**: colorless crystals. mp 159-160°C (benzene). Ms m/z (rel intensity): 393 (M$^+$, 40), 238 (100), 180 (27). Uv (MeOH): 317 nm (log $\varepsilon$, 3.42), 250 (4.23). IR (KBr): 3100, 2900, 1700, 1640, 1160 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.45 (s, 3H, Me), 2.48 (s, 3H, Me), 4.57 (br s, $H_d$), 5.35 (br s, $H_p$), 6.20-6.62 (m, 4H, $H_e$, $H_g$, $H_c$, and $H_p$). 7.16-7.85 (m, 8H, aromatic protons). $^{13}$C-Nmr $\delta$: 21.8, 56.7, 98.7, 118.0, 125.3, 126.7, 126.9, 128.0, 128.3, 129.7, 129.8, 145.0. Analyst. Calcld for C$_{22}$H$_{19}$N$_3$O$_5$S$_2$: C, 56.15; H, 4.20. Found: C, 56.04; H, 4.49.

**5g**: colorless crystals. mp 173-175°C (ethyl acetate). Uv (MeOH): 310 nm (log $\varepsilon$, 3.59). IR (KBr): 1760, 1660, 1360, 1150 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.45 (s, 3H, Me), 2.48 (s, 3H, Me), 4.57 (br s, $H_d$), 5.35 (br s, $H_p$), 6.20-6.62 (m, 4H, $H_e$, $H_g$, $H_c$, and $H_p$). 7.16-7.85 (m, 8H, aromatic protons). $^{13}$C-Nmr $\delta$: 21.8, 56.7, 98.7, 118.0, 125.3, 126.7, 126.9, 128.0, 128.3, 129.7, 129.8, 145.0. Analyst. Calcld for C$_{22}$H$_{19}$N$_3$O$_5$S$_2$: C, 56.15; H, 4.20. Found: C, 56.04; H, 4.49.

**5h**: colorless oil. Hrms m/z: 468.1499. Calcld for C$_{28}$H$_{25}$N$_2$O$_5$S: 468.1506. Ms m/z (rel intensity): 468 (M$^+$, 4), 167 (100). Uv (MeOH): 289 nm (log $\varepsilon$, 3.80). IR (oil): 1740, 1650, 1490 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.38 (s, 3H, Me), 3.57 (d, $H_d$), 4.56 (dd, $H_b$), 6.15 (m, 2H, $H_e$ and $H_p$). $^1$H-Nmr $\delta$: 6.59 (dd, $H_g$), 7.60-7.90 (m, 15H, $H_e$ and aromatic protons). Coupling constants in Hz: $J_{ab}$=5.0, $J_{bc}$=9.6, $J_{cd}$=6.8, $J_{de}$=11.2, $J_{ef}$=5.8. $^{13}$C-Nmr $\delta$: 21.7, 46.2, 57.8, 98.8, 119.5, 126.4, 127.2, 127.3, 127.9, 128.1, 128.2, 128.4, 128.5, 128.8, 128.9, 129.1, 129.2, 129.6, 139.3, 142.2, 145.5, 172.0.

**5i**: pale yellow oil. Hrms m/z: 409.0918. Calcld for C$_{28}$H$_{24}$N$_2$O$_5$S: 409.0918. Ms m/z (rel intensity): 409 (M$^+$, 46), 395 (58), 254 (100). Uv (MeOH): 325 nm (log $\varepsilon$, 3.83), 266 (3.89). IR (KBr): 3200, 2900, 1620, 1160 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.40 (s, 3H, Me), 3.95 (br s, $H_d$), 5.15 (br s, $H_p$), 6.00-6.90 (m, 4H, $H_e$, $H_g$, $H_c$, and $H_p$). 7.00-8.00 (m, 9H, aromatic protons). $^{13}$C-Nmr $\delta$: 21.4, 42.2, 110.3, 119.4, 120.8, 124.2, 125.4, 127.3, 128.7, 128.9, 129.3, 129.4, 144.9, 147.4.

**5j**: pale yellow crystals. mp 194-195°C (benzene). Ms m/z (rel intensity): 409 (M$^+$, 41), 254 (100). Uv (MeOH): 334 nm (log $\varepsilon$, 3.76), 276 (4.13). IR (KBr): 3200, 1440, 1170 cm$^{-1}$. $^1$H-Nmr $\delta$: 2.45 (s, 3H, Me), 4.72 (br s, $H_d$), 4.87 (br s, $H_p$), 6.10-6.42 (m, 4H, $H_e$, $H_g$, $H_c$, and $H_p$). 7.20-7.90 (m, 9H, aromatic protons), 8.00 (br s, NH). $^{13}$C-Nmr $\delta$: 21.8, 61.4, 98.6, 113.8, 124.9, 125.9, 127.5, 128.2, 129.2, 129.5, 129.7, 137.2, 145.4. Analyst. Calcld for C$_{25}$H$_{19}$N$_3$O$_5$S$_2$: C, 56.10; H, 4.68. Found: C, 61.47; H, 4.60.

**Reaction of N-Methoxytroponimine (3c) with Chlorophenylethene (7a).** To a solution of 3c (135 mg, 1.0 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (1.5 ml) was slowly added a solution of chlorophenylethene chloride (570 mg, 3.0 mmol) in dichloromethane (1.0 ml) at room temperature. After the addition was completed, the mixture was stirred at room temperature for 24 h and then poured into water, extracted with dichloromethane, and the organic layer was dried over sodium sulfate. After removal of the solvent the residue was separated with column chromatography on silica gel to give red crystals of 8a (91 mg, 90%, hexane-ethyl acetate 65:35 as an eluent).

**8a**: orange crystals. mp 128-130°C (ethyl acetate). Ms m/z (rel intensity): 251 (M$^+$, 100), 178 (50), 165 (52). Uv (MeOH): 424 nm (log $\varepsilon$, 3.75), 288 (4.22). IR (KBr): 1680, 1583 cm$^{-1}$. $^1$H-Nmr $\delta$: 4.18 (s, 3H,
OMe), 6.90-7.90 (m, 10H, olefinic protons). 13C-Nmr δ: 65.1, 110.4, 127.6, 127.8, 128.6, 129.0, 130.1, 131.0, 131.6, 135.6, 139.0. Anal. Calcd for C16H13NO2: C, 76.48; H, 5.21. Found: C, 76.46; H, 5.20.


9: yellow crystals. mp 190-192°C (ethyl acetate). Hrms m/z: 253.0337. Calcd for C12H10NO2Cl: 253.0319. Ms m/z (rel intensity): 253 (M+, 15), 202 (100). Uv (MeOH): 436 nm (log ε, 3.84). Ir (KBr): 1682, 1651, 1607 cm⁻¹. 1H-Nmr δ: 4.20 (s, 3H, Me), 4.95 (s, 2H, CH2), 7.50-7.85 (m, 4H, Hα, Hβ, Hε and Hδ), 9.54 (d, Hε, Jde=11.0 Hz). 13C-Nmr δ: 49.7, 65.3, 116.8, 132.8, 134.3, 136.3, 138.7.

10: pale yellow crystals. mp 126-128°C (benzene). Ms m/z (rel intensity): 240 (M+, 100), 137 (85). Uv (MeOH): 343 nm (log ε, 4.22), 293 (3.90), 273 (3.90). Ir (KBr): 1597, 1568, 1520, 1424 cm⁻¹. 1H-Nmr δ: 4.15 (d, 2H, Hα and Hδ), 5.49 (dt, Hβ), 6.38 (dd, Hδ), 6.69 (d, Hε), 7.02-7.42 (m, 5H, aromatic protons). Coupling constants in Hz: Jαβ=Jαδ=6.9, Jεc=10.1, Jεd=5.7, Jεδ=11.5. 13C-Nmr δ: 29.6, 118.9, 119.0, 121.4, 121.9, 123.5, 126.7, 127.3, 129.6, 140.3, 143.4, 167.1. Anal. Calcd for C14H12N2S: C, 69.97; H, 5.03. Found: C, 70.00; H, 5.01.


Thermal reaction of 12. A solution of 12 (66 mg, 0.19 mmol) in toluene (4.0 ml) was refluxed for 48 h and then separated with thin layer chromatography on silica gel using methanol-ethyl acetate 1:4 as a developing solvent to give a colorless oil 13 (Rf=0.82, 6 mg, 15%), recovered 12 (Rf= 0.94, 53 mg, 80%), and 14 (Rf=0.41, 2mg, 5%).


Thermal Reaction of 12 in the Presence of p-Chloranil. A mixture of 12 (90 mg, 0.26 mmol) and p-chloranil (100 mg, 0.41 mmol) in toluene (3.0 ml) was refluxed for 2 h and then separated with thin layer chromatography on silica gel using ethyl acetate-methanol 4:1 as a developing solvent to give 14 (50 mg,
87%).

18: colorless oil. Hrsm/z: 247.0859. Calcd for C_{13}H_{13}NO_4: C_{13}H_{13}NO_4. Ms m/z (rel intensity): 247 (M^+, 68), 215 (100), 157 (77). Ir (oil): 1732, 1693, 1589 cm\(^{-1}\). \(^1H\)-Nmr \(\delta\): 3.21 (d, 2H, \(H_a\) and \(H_d\)), 3.84 (s, 3H, Me), 3.85 (s, 3H, Me), 5.48 (dt, \(H_b\)), 6.04 (dd, \(H_c\)), 6.23 (dd, \(H_d\)), 6.93 (d, \(H_e\)), 9.23 (br s, NH). Coupling constants in Hz; \(J_{ab}=J_{ad}=6.7, J_{bc}=9.4, J_{cd}=10.5, J_{de}=9.7\). Oxidation of 10. To a solution of 10 (86 mg, 0.36 mmol) in dichloromethane (5.0 ml) was added manganese oxide (900 mg, 7.6 mmol) and the mixture was stirred at room temperature for 1 h. After filtration the solvent was removed to give crystals of 11 (70 mg, 82%).

11: red yellow crystals. mp 138-140°C (dichloromethane-ethyl acetate 1:1). Ms m/z (rel intensity): 238 (M^+, 100), 135 (52). Uv (MeOH): 414 nm (log \(\epsilon\), 4.17), 265 (4.48). Ir (KBr): 1601, 1580, 1444 cm\(^{-1}\). \(^1H\)-Nmr \(\delta\): 6.90-7.65 (m, 10H, olefinic and aromatic protons). \(^13C\)-Nmr \(\delta\): 120.4, 126.7, 129.6, 130.9, 133.0, 133.8, 138.2, 151.2, 156.9, 172.7. Anal. Calcd for C_{14}H_{11}N_2S: C, 70.56; H, 4.23. Found: C, 70.50; H, 4.20.

20: yellow crystals. mp 151-153°C (ethyl acetate). Ms m/z (rel intensity): 245 (M^+, 88), 214 (83, 100). Uv (MeOH): 455 nm (log \(\epsilon\), 3.03), 316 (3.88), 281 (4.67), 215 (4.34). Ir (KBr): 1736, 1709 cm\(^{-1}\). \(^1H\)-Nmr \(\delta\): 3.98 (s, 3H, Me), 4.07 (s, 3H, Me), 8.01 (dd, \(H_a\)), 8.04 (dd, \(H_d\)), 8.19 (dd, \(H_c\)), 8.95 (d, \(H_e\)), 9.69 (d, \(H_f\)). Coupling constants in Hz; \(J_{de}=10.2, J_{bc}=9.4, J_{ab}=10.5, J_{cd}=9.7\). Anal. Calcd for C_{13}H_{13}NO_4: C, 63.67; H, 4.52. Found: C, 63.70; H, 4.55.

REFERENCES AND NOTES
4. \(^1H\)-Nmr spectrum of 15 was as follows: \(^1H\)-Nmr \(\delta\): 2.38 (s, 3H, Me), 3.88 (s, 3H, OMe), 4.41 (br s, \(H_a\)), 5.30 (br s, \(H_b\)), 5.58-6.53 (m, 4H, \(H_e\), \(H_f\), \(H_c\), and \(H_d\)), 7.10-8.20 (m, 4H, aromatic protons). Compound (15) could not be isolated, since it easily decomposed under the reaction conditions and during the purification process.

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