

**Figure 1.** Crystal structure of **8**. Si-Si bond lengths (Å): 2.396 [Si(1)-Si(2)], 2.428 [Si(1)-Si(4)], 2.411 [Si(2)-Si(3)], 2.400 [Si(3)-Si(4)]. Ring angles (deg): 80.9° [at Si(1)], 93.9° [Si(2)], 81.2° [Si(3)], 93.4° [Si(4)]. Interatomic distance (Å) between Si(2) and Si(4): 3.13. Dihedral angle between Si(1), Si(2), Si(3) and Si(1), Si(4), Si(3) planes (deg): 143.4°. (The silicon numbering shown above does not conform with the IUPAC system.)

hexane, 25 °C)  $\lambda_{\max}$  256 nm (log  $\epsilon$ , 4.45);  $\lambda_{\text{shoulder}}$  275 (4.36), 304 (4.20); tailing off into the visible region.<sup>5</sup> (3) <sup>1</sup>H NMR (decalin-*d*<sub>18</sub>); the NMR spectra measured at -50-120 °C, all having a singlet assignable to the *tert*-butyl groups of **1**, are temperature dependent and the dynamic behavior of **1** is best analyzed by the inspection of the methylene region ( $\delta$  2.2-3.6). Thus, at -31 °C (250 MHz) more than six partially overlapping, well-defined multiplets (of roughly equal intensity) are discernible in this region (250 MHz).<sup>5</sup> Due to the obvious steric congestion of the substituents, the rotation of the aromatic rings along the axis of the carbon-silicon bond is frozen at -31 °C in terms of the NMR time scale. This rotation proceeds at 2 °C to the extent that the molecule attains roughly 2-fold symmetry as indicated by the appearance of the three broad methylene signals ( $\delta$  2.45, 2.87, 3.34; relative intensity 1:2:1) (see stereostructure **1**). Signals further coalesce in both the methylene (broad singlet,  $\delta$  2.70) and methyl (broad singlet,  $\delta$  0.77) regions as the temperature is raised to 60 °C, and the 90-MHz spectrum taken at 115 °C<sup>5</sup> simply consists of an AB<sub>2</sub> multiplet ( $\delta$  7.06, 6.79;  $J$  = 6.5 Hz) for the aromatic protons, a typical quartet-triplet pair ( $\delta$  0.80, 2.70;  $J$  = 7 Hz) for the ethyl groups, and a singlet ( $\delta$  1.21) for the *tert*-butyl groups. Thus, all the aryl rings have become equivalent. This observation is best explained by reversible ring inversion (Scheme I, **1**  $\rightleftharpoons$  **1a**) involving a planar intermediate or transition state in addition to the rapid rotation of the aryl rings at this temperature.<sup>9</sup> Since the former process is undoubtedly accompanied by significant stretching of the central Si-Si bond, a lower limit for its strength can be roughly estimated to be 15 kcal/mol<sup>10</sup> from the coalescence temperature observed.

**Chemical Properties of 1.** The reactivity of the central bond is extremely high even with the bulky substituents present. Thus, **1** instantly reacts with dioxygen to provide as the major product the corresponding dioxo derivative to which structure **7** is assigned based mainly on its <sup>1</sup>H NMR spectrum.<sup>11</sup> Addition of degassed water to a solution of **1** at room temperature effects quantitative hydration of **1** to provide *cis*-1,3-di-*tert*-butyl-2,2,4,4-tetrakis-

(2,6-diethylphenyl)-1-hydroxycyclotetrasilane (**8**),<sup>12,13</sup> the crystal structure of which is shown in Figure 1.<sup>14</sup> Treatment of **1** with an equimolar amount of Cl<sub>2</sub> in hexane at 0 °C regenerates **6** in high yield. Note that both the hydration and the chlorination proceed in a *cis* fashion. Further studies on the tetrasilabicyclobutane system are in progress.

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**Supplementary Material Available:** Detailed information of the X-ray crystal analysis of **8** and listing of physical properties of all new compounds and UV and temperature-dependent <sup>1</sup>H NMR spectra of **1** (12 pages). Ordering information is given on any current masthead page.

(12) **8**: 209-220 °C dec; IR (KBr) 3600 ( $\nu$  SiOH), 2040 ( $\nu$  SiH), 1450 ( $\nu$  SiAr), 1050 cm<sup>-1</sup> ( $\nu$  SiOH); UV (cyclohexane)  $\lambda_{\max}$  274 nm (log  $\epsilon$  4.42), 320 (2.90); <sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.64 (6 H, t, 7 Hz, CH<sub>3</sub>), 0.75, 1.75 (12 H, brs, CH<sub>3</sub>), 1.05 (6 H, t, 7 Hz, CH<sub>3</sub>), 1.08 (9 H, s, *t*-Bu), 1.16 (9 H, s, *t*-Bu), 1.53 (1 H, s, SiOH), 2.75, 3.75 (8 H, brs, CH<sub>2</sub>), 2.87 (8 H, q, CH<sub>2</sub>), 4.63 (1 H, s, SiH), 6.90-7.24 (12 H, m, para Ar); mass spectrum (EI), calc  $m/z$  for C<sub>48</sub>H<sub>72</sub>O<sub>2</sub>Si<sub>4</sub> 776.4660, found 776.4651. The <sup>1</sup>H NMR spectrum indicates that four of the eight ethyl groups are subject to hindered rotation.

(13) Treatment of **5** in dimethoxyethane with 3.5 equiv. of lithium naphthalene at 0 °C followed by aqueous workup gave rise to **8** in ca. 41% yield, whereas the isolation of **6** was successful only to the extent of 7% yield.

(14) Crystals of C<sub>48</sub>H<sub>72</sub>O<sub>2</sub>Si<sub>4</sub> (**8**)  $M$  = 767.3 are monoclinic with  $a$  = 11.468 (3) Å,  $b$  = 24.025 (8) Å,  $c$  = 16.734 (4) Å,  $\beta$  = 94.98 (2)°,  $U$  = 4594 Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z$  = 4,  $\mu$ (Cu K $\alpha$ ) = 14 cm<sup>-1</sup>,  $D_c$  = 1.11 g cm<sup>-3</sup>. Data were measured with Cu K $\alpha$  radiation on a Nicolet R3m diffractometer using  $\omega$  scans. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically by full-matrix least squares to  $R$  = 0.050 for 4477 independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $\theta \leq 50^\circ$ ]. The X-ray analysis reveals a disordered structure which has an approximate, noncrystallographic, 2-fold axis normal to the plane of the cyclotetrasilane ring. The disorder is confined to the axial hydroxy group which has equal (50%) site occupancies on both Si(2) and Si(4).

## Fluxional Behavior in the Solid State: Bullvalene

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The study of dynamical behavior in the crystalline state is of particular interest as—in contrast to the situation in liquid phase—the environment of the single molecule is well-defined and its geometry is often accurately known from X-ray structure studies. In addition, the solid state normally allows a much bigger temperature range to be investigated. In many cases, lattice forces greatly influence the dynamics in solids.<sup>1-6</sup> For example, it has been demonstrated that the Cope rearrangement in semibullvalene, which takes place easily in the liquid state, is drastically hindered in one of the solid phases, whereas in the other phase the de-

(9) Cf.: Gassman, P. G.; Greenlee, M. L.; Dixon, D. A.; Richtsmeier, S.; Gougoutas, J. Z. *J. Am. Chem. Soc.* **1983**, *105*, 5865.

(10) This estimate based on the 2 and 60 °C (250 MHz) spectra is obviously crude since aryl ring rotation is occurring simultaneously. No attempt has been made to separate these processes by line-fitting studies due to the complexity of the system.

(11) **7**: Amorphous solid; IR (KBr) 1450 ( $\nu$  SiAr), 1050 cm<sup>-1</sup> ( $\nu$  SiOSi); <sup>1</sup>H NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.43 (3 H, t, 7 Hz, CH<sub>3</sub>), 0.46 (3 H, t, 7 Hz, CH<sub>3</sub>), 0.78 (3 H, t, 7 Hz, CH<sub>3</sub>), 0.97 (3 H, t, 7 Hz, CH<sub>3</sub>), 1.05 (3 H, t, 7 Hz, CH<sub>3</sub>), 1.13 (9 H, s, *t*-Bu), 1.16 (3 H, t, 7 Hz, CH<sub>3</sub>), 1.37 (9 H, s, *t*-Bu), 1.42 (3 H, t, 7 Hz, CH<sub>3</sub>), 1.43 (3 H, t, 7 Hz, CH<sub>3</sub>), 1.82 (2 H, m, 7 Hz, CH<sub>2</sub>), 2.43 (2 H, m, 7 Hz, CH<sub>2</sub>), 2.59 (2 H, q, 7 Hz, CH<sub>2</sub>), 2.83 (4 H, m, CH<sub>2</sub>), 3.08 (2 H, m, CH<sub>2</sub>), 3.45 (2 H, dq, 7 Hz, CH<sub>2</sub>), 3.61 (2 H, m, CH<sub>2</sub>), 6.57, 7.24 (12 H, m, meta, para Ar); mass spectrum (EI), calc'd  $m/z$  for C<sub>48</sub>H<sub>70</sub>O<sub>2</sub>Si<sub>4</sub> 790.4453, found 790.4455. The <sup>1</sup>H NMR spectrum is interpreted as eight nonequivalent methyl and methylene absorptions. Compound **7** is unstable with respect to further oxygenation in solution, so a larger fragment corresponding to C<sub>48</sub>H<sub>70</sub>O<sub>3</sub>Si<sub>4</sub> is detectable in the mass spectrum.

\* Group INC-4, MS-C345.

(1) Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396.

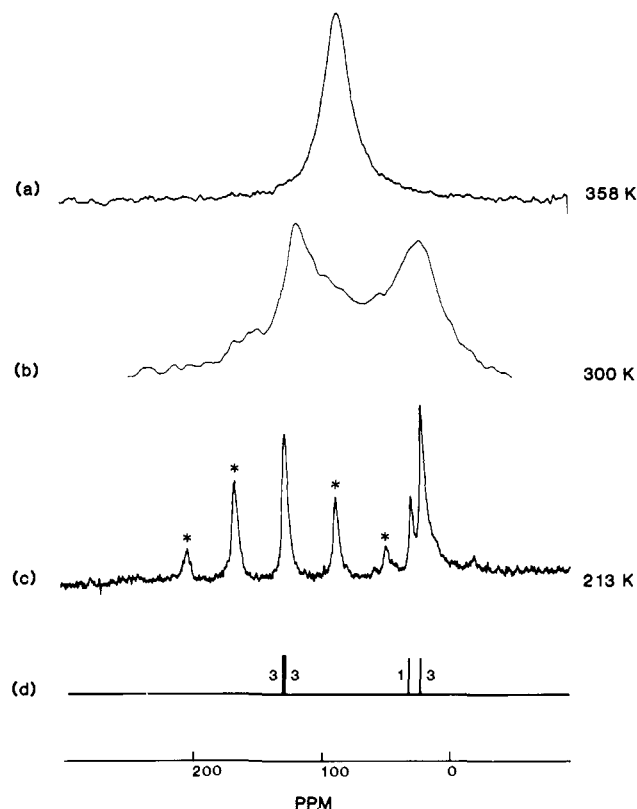
(2) Macho, V.; Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3735.

(3) Fyfe, C. A. "Solid State NMR for Chemists"; C.F.C. Press: Ontario, 1983.

(4) Shiao, W. I.; Duesler, E. N.; Paul, I. C.; Curtin, D. Y.; Blann, W. G.; Fyfe, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 4546.

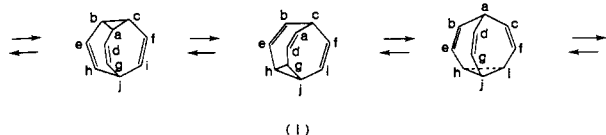
(5) Szeverini, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Reson.* **1982**, *47*, 462.

(6) Meier, B. H.; Graf, F.; Ernst, R. R. *J. Chem. Phys.* **1982**, *76*, 767.



**Figure 1.**  $^{13}\text{C}$  CP-MAS spectra of bullvalene powder at (a) 358, (b) 300, and (c) 213 K. Spectra were obtained on a Bruker CXP 200 spectrometer with a probe built by DOTY SCIENTIFIC. The cross-polarization times, chosen according to the  $T_{1\rho}$  values of the sample, were 800, 500, and 1000  $\mu\text{s}$  in (a), (b), and (c), respectively. The low-temperature spectrum (c) consists of three lines, the low-field one showing a sideband pattern. Spinning sidebands are marked by asterisks. The chemical shifts, observed in the low-temperature spectrum, are very similar to those found for the dissolved molecule.<sup>10</sup> Trace (d) of the figure shows the line positions for bullvalene in isotropic solution. The high-temperature spectrum (a) consists of a single line at a resonance position equal to the weighted average of the low-temperature lines, indicating a fast Cope rearrangement (relative to the difference in chemical shifts) taking place. Spectrum (b) shows an exchange-broadened spectrum (see text).

generacy of the rearrangement is removed by intermolecular interactions.<sup>1-2</sup> Because of the nearly spherical shape of the molecule, the Cope rearrangement in bullvalene (I) is a candidate



for a reaction where the dynamics in liquid and crystalline phase are governed by intramolecular forces. A sensitive test for that behavior is the comparison of dynamics in liquid and solid phase. Liquid-state NMR spectroscopy and solid-state NMR using magic angle sample spinning offer a unique possibility to observe the same molecular properties in both states. The occurrence of a degenerate Cope rearrangement between the 1 209 600 isomers of bullvalene is well established for the liquid state.<sup>7-13</sup> Although several studies have been performed previously,<sup>14-16</sup> little is known

about the possible Cope rearrangement in the solid state. A wide-line NMR study<sup>13</sup> indicated that some motion, either the Cope rearrangement or a reorientation of the whole molecule about a molecular axis, takes place at room temperature. Two X-ray structure studies,<sup>15,16</sup> however, insist on the absence of the Cope rearrangement at this temperature. We present high-resolution NMR spectra which prove that the Cope rearrangement takes place in the crystalline solid.

Cross polarization-magic angle spinning  $^{13}\text{C}$  spectra of a bullvalene powder at 213, 300, and 358 K are shown in Figure 1. Since the proton relaxation time  $T_1$  of bullvalene gets rather long at applied fields of 4.7 T and temperatures below room temperature (longer than 400 s), one of the samples has been treated with  $\gamma$  radiation to generate relaxation centers.<sup>17</sup> The spectra at 213 and 300 K were obtained with the irradiated sample. The spectrum at 213 K clearly shows three resonance lines (one of them showing sideband structure) at positions near the four lines in the spectrum of dissolved bullvalene. The two lines at 128 ppm in the liquid state are separated by only 0.2 ppm and are therefore not resolved in the MAS spectrum. Not all the carbons which are chemically equivalent in the liquid state have an identical environment in the crystalline solid ( $Z = 4$ ), but the effect of the crystalline environment is obviously not big enough to give rise to resolved lines in the MAS spectrum. However, this probably is the reason for the relatively broad lines, which are not due to residual exchange broadening, as the line width stays constant on further cooling. At 358 K, the spectrum consists of a single line, indicative of fast chemical exchange. The observed averaging of the resonance positions shows that all the carbons sample a chemically identical environment and can be explained only by a Cope rearrangement and not by a rotation of the rigid molecule. The observation that the position of the high-temperature resonance line is exactly at the weighted average of the low-temperature resonance positions suggests that the degeneracy of the Cope rearrangement is preserved in the solid state. Together with the results of the X-ray studies where an essentially ordered structure was found, this suggests a mechanism where the Cope rearrangement is combined with a rotation of the whole molecule in such a way that the translational symmetry of the crystal is maintained in the equilibrium structures. The line width of the high-temperature resonance is dominated by exchange broadening. A quantitative description of the line shape of exchange-broadened MAS spectra, however, is more involved than of similar liquid-state spectra because the chemical exchange rate is comparable to the spectral separation between the lines and to the spinning speed.<sup>18</sup> Additional line broadening arises if the chemical exchange rate is comparable to the strength of the decoupler field expressed in frequency units.<sup>19,20</sup> Furthermore, rotational motion of the rigid molecule can influence the line width through these "spinning-speed" or "proton-decoupling" effects. As noted above, the Cope rearrangement must be combined with molecular rotation to explain the ordered X-ray structure. In addition, there may be rotational motion of the rigid molecule such as rotation about the threefold axis of the single molecule which is another activated process. The same remarks apply to the spectrum at 300 K which is strongly broadened, mainly by chemical exchange and by the effect of the spinning speed. A detailed analysis of the center and sideband line shape in the MAS spectrum lies outside the scope of this paper. Our crude preliminary analysis, however, indicates that the activation enthalpy as well as the preexponential factor

(15) Johnson, S. M.; McKechnie, J. S.; Lin, B. T.-S.; Paul, I. C. *J. Am. Chem. Soc.* **1967**, *89*, 7123.

(16) Amit, A.; Huber, R.; Hoppe, W. *Acta Crystallogr., Sect. B* **1968**, *B24*, 865.

(17) A sample was inserted in the core of the Omega West Reactor at Los Alamos shortly after shutdown for about 14 h to get a broad energy spectrum of  $\gamma$  irradiation, which resulted in a  $T_1$  of 5 s.

(18) Suwelack, D.; Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1980**, *73*, 2559.

(19) Garroway, A. N.; Moniz, W. B.; Resing, H. A. *ACS Symp. Ser.* **1979**, *No. 103*.

(20) Vanderhart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361.

(7) Doering, W. v. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715.

(8) Saunders, M. *Tetrahedron Lett.* **1963**, 1699.

(9) Allerhand, A.; Gutowsky, H. S. *J. Am. Chem. Soc.* **1965**, *87*, 4092.

(10) Oth, J. F. M.; Mullen, K.; Gilles, J.-M.; Schroeder, G. *Helv. Chim. Acta* **1974**, *57*, 1415.

(11) Huang, Y.; Macura, S.; Ernst, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5327.

(12) Yannoni, C. S. *J. Am. Chem. Soc.* **1970**, *92*, 5237.

(13) Poupko, P.; Zimmerman, H.; Luz Z. *J. Am. Chem. Soc.* **1984**, *106*, 5391.

(14) Graham, J. D.; Santee, E. R. *J. Am. Chem. Soc.* **1966**, *88*, 3453.

for the Cope rearrangement are very similar to the ones found in isotropic solution<sup>10</sup> and liquid-crystalline solution.<sup>13</sup> These results are supported by a  $T_1$  study of a nonirradiated sample, where an activation energy of 60 kJ/mol, very close to the 55 kJ/mol observed in liquid phase,<sup>10</sup> was found.<sup>21</sup> Although the agreement may be fortuitous we tentatively interpret this to mean that the dynamics of the Cope rearrangement in the solid is governed by the same intramolecular forces as in the liquid phase.

In conclusion, the Cope rearrangement can be clearly identified and described by chemical shift resolved NMR spectroscopy, an aim that cannot be achieved by X-ray or wide-line NMR spectroscopy.

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(21) Meier, B. H.; Earl, W. L., unpublished results.

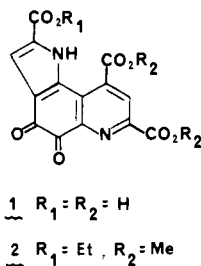
## A Synthesis of Methoxatin

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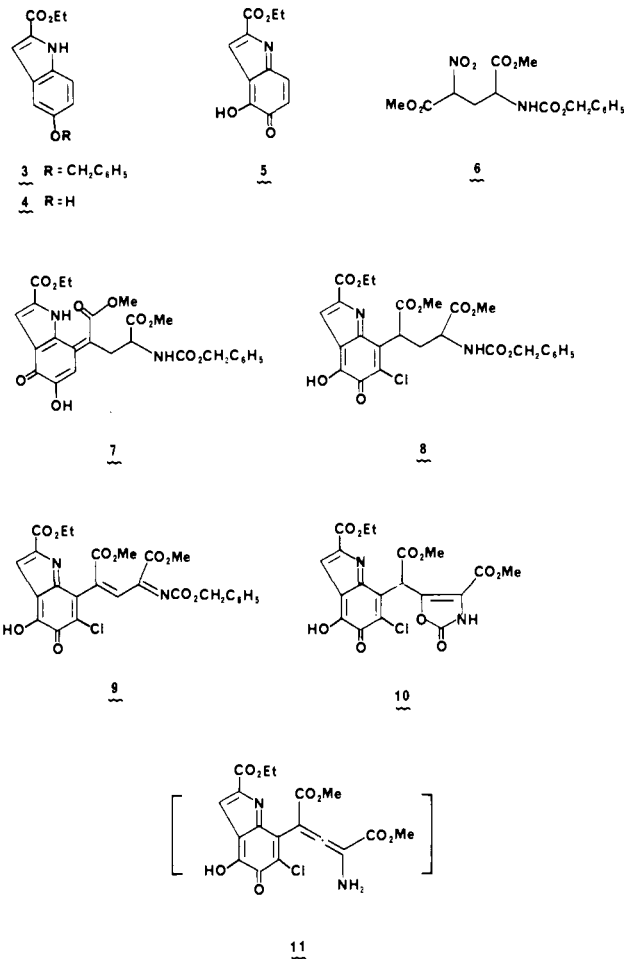
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Methylotrophic bacteria use one-carbon compounds as their sole source of energy. The function of the critical enzyme methanol dehydrogenase was found to be dependent on a cofactor called methoxatin. An X-ray diffraction study of a derivative revealed structure **1**<sup>1</sup> for methoxatin, and syntheses were accomplished subsequently.<sup>2-5</sup>



To our knowledge the biosynthetic pathway to methoxatin remains unknown but phenylalanine or *o*-tyrosine and glutamic acid appear to be attractive precursors. We describe a total synthesis of methoxatin (**1**) from derivatives of these hypothetical forerunners. Oxidation of the hydrochloride of *o*-tyrosine ethyl ester with Fremy's salt gave the quinone imine **5**<sup>6</sup> (mp >270 °C, orange needles) but in poor yield. Intermediate **5** was produced more efficiently when phenol **4**,<sup>7</sup> prepared by debenzilation of



commercial **3**, was oxidized with Fremy's salt (2.2 equiv,  $CH_3CN$ ,  $H_2O$ ,  $KH_2PO_4$ , 20 °C, 30 min, 94% yield).<sup>8</sup> To render one hydrogen atom adjacent to the  $\gamma$ -carboxy group of glutamic acid more acidic and to simultaneously introduce a leaving group we prepared a mixture of diastereomeric nitro esters **6** by adding methyl nitroacetate to *N*-(benzyloxycarbonyl)dehydroalanine methyl ester<sup>9</sup> ( $1/2$  equiv of  $Et_3N$ , 3 equiv of nitro ester, 20 °C, 3 days, 75% yield). Michael addition of **6** to **5** ( $Et_3N$ , THF, 20 °C, 1 h, 47% yield) afforded **7**<sup>10</sup> (yellow needles, mp 180–182 °C, dec). When a solution of **7** in methylene chloride containing triethylamine (1 equiv) was treated with *N*-chlorosuccinimide (1 equiv, 20 °C, 30 min), followed by addition of DDQ (5 equiv) or  $MnO_2$  (30 equiv) and  $Et_3N$  (1 equiv) (20 °C, 90 min), two diastereomeric chlorides **8** (mp 126–129 °C dec and 171–174 °C dec) and the bright red imine **9**<sup>11</sup> (mp 88–91 °C dec) were formed in 35–50% and 27–31% yield, respectively. Dehydrogenation of **8** to **9** could be accomplished with  $MnO_2$  or NiO ( $CH_2Cl_2$ ,  $Et_3N$ , 1 equiv). Absence of intramolecular hydrogen bonding and lack of indole  $NH-C_3$  proton coupling demand the presence of tautomer **9** and suggest nonplanarity of quinone imine and azadiene chromophores.

Trifluoroacetic acid (20 °C, 1 h, 85% yield) caused cleavage of the benzyl group in **9** with formation of the yellow 4-oxazolin-2-one **10**,<sup>12</sup> mp 182–184 °C dec. Heating **10** in chlorobenzene

(1) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B. T.; Kennard, O. *Nature (London)* **1979**, *280*, 843.

(2) Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc.* **1981**, *103*, 5599.

(3) Gainor, J. A.; Weinreb, S. M. *J. Org. Chem.* **1982**, *47*, 2833.

(4) Hendrickson, J. B.; deVries, J. G. *J. Org. Chem.* **1982**, *47*, 1148.

(5) MacKenzie, A. R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1983**, 1372.

(6) <sup>1</sup>H NMR ( $CDCl_3$ )  $\delta$  1.40 (t, 3 H,  $J = 7.2$  Hz), 4.38 (q, 2 H,  $J = 7.2$  Hz), 6.25 (d, 1 H,  $J = 10$  Hz), 7.27 (s, 1 H), 7.28 (d, 1 H,  $J = 10$  Hz), 10.23 (br, 1 H, exchanged with  $D_2O$ ); UV  $\lambda_{max}$  ( $C_2H_5OH$ ) 272, 331, 465 nm.

(7) Alvarez, E. F.; Lora-Tamayo, M.; Monge, A. *Bull. Soc. Chim. Fr.* **1969**, 1932.

(8) 2-Phenyl-5-hydroxyindole was oxidized to an analogous quinone by: Teuber, H. J.; Staiger, G. B. *Chem. Ber.* **1956**, *89*, 489.

(9) Kolar, A. J.; Olsen, R. K. *Synthesis* **1979**, 457.

(10) <sup>1</sup>H NMR ( $CDCl_3$ ) revealed a hydroxy proton  $\delta$  7.11 (s, 1 H, exchanged with  $D_2O$ ). An indole proton at  $\delta$  7.35 (d, 1 H,  $J = 1.9$  Hz) and a hydrogen bonded indole NH at  $\delta$  12.76 (br, 1 H, exchanged with  $D_2O$ ); UV  $\lambda_{max}$  ( $C_2H_5OH$ ) 273 (log  $\epsilon$  4.4), 311 (4.0), 330 (4.0), 367 (4.2), 540 nm (3.2).

(11) <sup>1</sup>H NMR (acetone- $d_6$ )  $\delta$  6.76 (s, 1 H) vinyl proton; 7.40 (br, 1 H, exchanged with  $D_2O$ ), 7.43 (s, 1 H) indole proton; UV  $\lambda_{max}$  ( $C_2H_5OH$ ) 286 (log  $\epsilon$  4.5), 332 (3.7), 490 nm (3.3).

(12) <sup>1</sup>H NMR ( $CDCl_3$ )  $\delta$  5.74 (s, 1 H), 7.50 (s, 1 H), 7.30 (s, 1 H) and 7.6 (br, 1 H), both exchanged with  $D_2O$ ; UV  $\lambda_{max}$  ( $C_2H_5OH$ ) 274 (log  $\epsilon$  4.4), 359 (3.7), 568 nm (3.5); IR ( $CHCl_3$ ) 3400, 1790, 1760, 1727  $cm^{-1}$ .