

The present results imply that the photolysis of **1** gives dimethylsilylene, which has an absorption spectrum at 350 nm in solution. The large difference in absorption maxima for the spectra reported in solution and in matrices (450 nm) point either to a very large matrix effect or to an incorrect assignment.

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Registry No. I, 4098-30-0; II, 6376-86-9; III, 31732-54-4; IV, 18033-75-5; V, 75462-93-0; VI, 75462-94-1; Et₃SiH, 617-86-7; MeOH, 67-56-1.

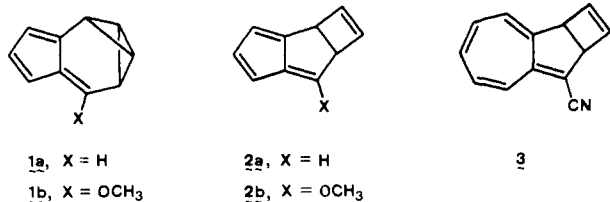
Parent Azulvalene and Dewar Azulene. Syntheses and Isomerizations of Tetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-6,8,10-triene and Tricyclo[5.3.0.0^{2,5}]deca-3,6,8,10-tetraene¹

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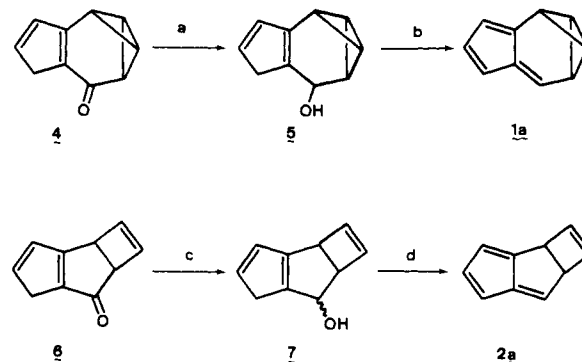
It is well-known that the synthetic achievement of the valence isomers of benzenoid hydrocarbons promoted a better understanding not only of their unique strained structures but also of the potential energy surfaces between these isomers.² Nonalternant hydrocarbons³ hold the complementary position to alternant hydrocarbons as far as the nature of aromatic hydrocarbons is concerned. Therefore, the valence isomers of these nonalternant molecules are of interest especially in the study on their mutual interconversions and isomerizations. While some derivatives of azulvalene (**1b**),⁴ Dewar azulene (**2b**),⁵ and Dewar heptalene (**3**)⁶ have recently been synthesized by us, the methoxy



substitution in **1b** and **2b** causes some perturbation of the electronic structure intrinsic to the azulene isomers. To eliminate this complication the syntheses of the parent compounds **1a** and **2a** have been intended.

After previous unsuccessful approaches toward their syntheses,⁷ **1a** and **2a** have now been prepared following a formal 1,6-dehydration sequence (Scheme I).⁸ Tetracyclic dienone **4**,⁹ was

Scheme I^a



^a (a) 20 equiv of NaBH₄/CH₃OH + C₆H₆ (2:1 v/v), 5 °C; (b) 2.2 equiv of 4-(dimethylamino)pyridine and 1.1 equiv of CH₃COCl/CH₂Cl₂, 0 °C, 2 h (25%); (c) 150 equiv of NaBH₄/CH₃OH + C₆H₆ (2:1 v/v), 0 °C, 0.5 h; (d) 2.4 equiv of *n*-Bu₃P/CH₂Cl₂ + CCl₄, 0 °C, 0.5 h (40%).

reduced to give the alcohol **5**, which was extracted with dichloromethane and used in the next step without purification. To a solution of **5** and 4-(dimethylamino)pyridine in dichloromethane, acetyl chloride was added dropwise at 0 °C. After 2 h the product was extracted into pentane, washed with water, and dried (Mg-SO₄). The solution was filtered through a short column of silica gel (deactivated with 20% H₂O, pentane) to afford **1a**¹⁰ as an acid- and air-sensitive orange oil (25% yield).

Tricyclic ketone **6**¹¹ was reduced to yield the alcohol **7**. Treatment of **7** in a mixture of dichloromethane and carbon tetrachloride with tri-*n*-butylphosphine at 0 °C for 0.5 h produces **2a**¹² as an air-sensitive yellow oil in 40% yield, which can be isolated virtually pure through chromatography on a short column of silica gel (deactivated with 20% H₂O, pentane).

On thermolysis, **1a** undergoes quantitative isomerization to azulene with first-order kinetics.¹³ From an Arrhenius plot ($r = 0.9995$) of the data, the activation parameters, $\Delta H^\ddagger = 27.5 \pm 0.5$ kcal/mol, $\Delta S^\ddagger = -4.8 \pm 1.1$ eu, $E_a = 28.6 \pm 0.5$ kcal/mol, and $\log A = 12.3 \pm 0.3$, are obtained. **2a** was also converted (60–80%) thermally to azulene with partial decomposition. From the several runs the activation energy for the process was roughly estimated to be ~ 32 kcal/mol, deduced from the decay rate of **2a**.¹³ The activation energy for the thermolysis of **1a** is substantially smaller than that of **1b**.⁴ Furthermore comparison of the activation energies for **1a** and **2a** shows that **1a** directly

(8) All the reactions were carried out in argon atmosphere. All solvents used for the reactions and workup were deaerated by bubbling with argon and distilled under argon before use. It should be noted that the synthetic methods described in the text provide azulene-free **1a** and **2a**. This makes the purification of these labile molecules easier. **1a** and **2a** were too unstable to allow their combustion analyses; however, these structures were unequivocally established by their characteristic NMR spectra.^{10,12}

(9) **4** is now available conveniently from 9-chlorotetracyclo[5.3.0.0^{2,4}.0^{3,5}]dec-1(7)-en-6-one, colorless needles, mp 55.5–56.6 °C, which can be stored in a refrigerator without decomposition.¹

(10) ¹H NMR (100 MHz, CDCl₃) δ 6.67 (dd, 1 H, $J = 4.8, 1.7$ Hz, H-6), 6.31 (dd, 1 H, $J = 5.3, 2.0$ Hz, H-9), 5.90 (m, 1 H, H-10), 5.83 (ddd, 1 H, $J = 5.3, 1.1, 0.8$ Hz, H-8), 3.47 (t, 2 H, $J = 2.4$ Hz, H-3,4), 3.03 (ddd, 1 H, $J = 3.9, 2.4, 0.8$ Hz, H-2), 2.49 (m, 1 H, H-5); ¹³C NMR (22.5 MHz, CDCl₃) δ 137.4, 133.2, 121.3, 116.9, 40.1, 38.5, 36.0; UV (cyclohexane) λ_{max} 281 (ϵ 11 000), 400 nm (370).

(11) **6** was obtained from tricyclo[5.3.0.0^{2,5}]dec-9-en-6-one⁴ through allylic bromination with NBS/ABIBN/CCl₄ followed by dehydrobromination with KO-*t*-Bu in ether.¹

(12) ¹H NMR (100 MHz, CDCl₃) δ 6.83 (dd, 1 H, $J = 4.8, 2.0$ Hz, H-6), 6.81 (dd, 1 H, $J = 5.2, 2.1$ Hz, H-9), 6.48 (dd, 1 H, $J = 2.4, 0.8$ Hz, H-4), 6.41 (dm, 1 H, $J = 2.4$ Hz, H-3), 6.13 (dd, 1 H, $J = 5.2, 0.8$ Hz, H-8), 6.04 (m, 1 H, H-10), 4.48 (m, 1 H, H-5), 4.00 (m, 1 H, H-2); ¹³C NMR (22.5 MHz, CCl₄) δ 140.9 (2 carbons), 140.7, 139.7, 116.9, 113.3, 64.1, 46.2; UV (cyclohexane) λ_{max} 270 (ϵ 17 000), 384 nm (1400).

(13) A solution of **1a** or **2a** in toluene-*d*₆ in the presence of a small amount of TMEDA was degassed and sealed in vacuo in an NMR tube, and thermolyses were performed in an NMR cavity. The disappearance of **1a** and the appearance of azulene were monitored by NMR integration. First-order rate constants for **1a** are $k^{363} = 1.78 \times 10^{-5}$, $k^{373} = 4.85 \times 10^{-5}$, $k^{383} = 1.44 \times 10^{-4}$, and $k^{393} = 3.44 \times 10^{-4}$ s⁻¹. For the thermolysis of **2a**, half-lives are found to be 10 h (393 K), 2 h (403 K), and 50 min (413 K).

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isomerizes to azulene without any intervention of **2a**. These findings support our previous assumption^{5,14} on the role of the pentafulvene moiety during the ring opening of azulvalene. The activation energy for **2a** is also small as compared with that of **2b** (36.7 kcal/mol).⁵ The observed rate retardation by methoxy substitution in **2b** is mainly due to the increase in repulsive force with the progress of the disrotatory bond fission of **2b** with antiaromatic transition state.¹⁵

Under the strictly selected irradiations with monochromatic light,¹⁶ **1a** isomerizes almost quantitatively throughout the overall reaction whereas **2a** isomerizes in ~60%, at least in the initial stage of the photolysis. It should be pointed out that the quantum yields for isomerizations of **1a** and **2a** in argon-purged cyclohexane with the irradiation in their first and second absorption bands are Φ_{s_1} (excited at 460 nm) = 5×10^{-4} and Φ_{s_2} (excited at 300 nm) = 0.35 for **1a**; Φ_{s_1} (excited at 400 nm) ~ 10^{-6} and Φ_{s_2} (excited at 280 nm) = 1.8×10^{-2} for **2a**.¹⁶ Since addition of isoprene ($E_T = 60.1$ kcal/mol) or 1,3-cyclohexadiene ($E_T = 52.4$ kcal/mol) does not affect the above data, **1a** and **2a** presumably isomerize from their two distinct singlet excited states. The higher quantum yields in excitation of upper states of each compound should be ascribed to the longer lifetimes of these states as compared with those of S_1 states.¹⁷

This synthetic achievement permits access to a full understanding of the ground- and excited-state properties of these prototype molecules. We plan to examine such matters in due course.

Registry No. **1a**, 92622-71-4; **2a**, 92622-72-5; **4**, 73566-86-6; **5**, 92622-73-6; **6**, 92622-74-7; **7**, 92622-75-8; azulene, 275-51-4; 9-chlorotetracyclo[5.3.0.0.2⁴.0.3⁵]dec-1(7)-en-6-one, 92622-76-9; tricyclo[5.3.0.0.3⁵]deca-3,9-dien-6-one, 73566-88-8; 7-bromotricyclo[5.3.0.0.2⁵]deca-3,9-dien-6-one, 92622-77-0.

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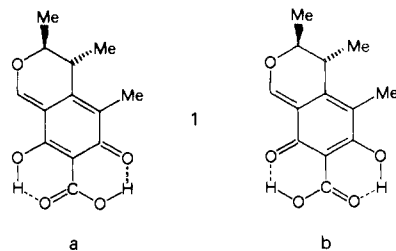
Temperature Dependence of Tautomeric Equilibria in the Solid State: The Case of Citrinin

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Citrinin (**1**) is an extensively studied² fungal metabolite, whose



chemical structure was determined years ago by degradative,

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Table I. Crystal Data for Citrinin (**1**)^a

	290 (2) K	147 (5) K
<i>a</i> , Å	13.441 (3)	13.358 (4)
<i>b</i> , Å	7.291 (2)	7.226 (5)
<i>c</i> , Å	12.241 (3)	12.170 (3)
<i>V</i> , Å ³	1199.6 (5)	1174.8 (9)
<i>D_m</i> , g cm ⁻³	1.385	
<i>D_x</i> , g cm ⁻³	1.386	1.415

^a C₁₃H₁₄O₅, fw 250.25, *Z* = 4, orthorhombic, space group *P*2₁2₁- (*D*₂⁴), $\mu(\text{Mo K}\alpha) = 1.00 \text{ cm}^{-1}$.

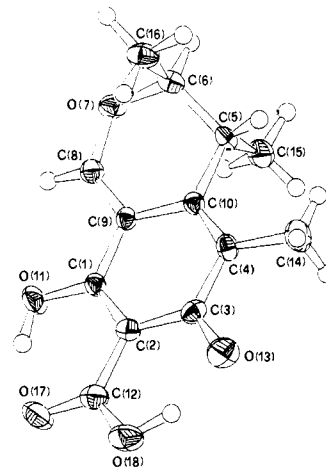


Figure 1. Perspective view of the molecule of citrinin at 147 K, with atomic numbering scheme. The thermal ellipsoids are drawn at a 50% probability level.

synthetic and spectroscopic techniques.³⁻⁶ The absolute configurations of its asymmetric centers have also been established,^{7,8} but no experimental evidence could be found to distinguish between the *p*-quinonemethide formulation **1a**, usually adopted as the true structure, and the *o*-quinone form **1b**. The results of an early investigation by single-crystal X-ray diffraction have been interpreted⁹ in terms of structure **1a**, but anomalous values for some of the few published molecular dimensions seem rather in favor of either a resonance hybrid between the extreme structures **1a** and **1b**, as recently proposed,¹⁰ or, more likely, a disordered structure corresponding to the superimposition of different amounts of **1a** and **1b**. Indeed, the position of the carboxylic group with respect to the hydroxyl and quinonoid oxygen atoms strongly suggests the occurrence of intramolecular proton exchange, reminiscent of the well-known case of naphthazarin,¹¹ and hence the existence of a tautomeric equilibrium between the para and the ortho isomers. If both forms are present in the crystal (i.e., the structure is disordered), two distinct positions for each proton involved in the intramolecular hydrogen bonds should be found, while the formulation of the structure as a resonance hybrid would require the detection of each hydrogen atom in a single position.

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