modate flipping the aromatic ring of residue 2. We are presently pursuing further experiments to confirm the orientation of the aromatic ring in vancomycin and to delineate the mechanism of the rearrangement process.

CDP-I (M?) has been reported by Marshall to lack antibiotic activity,[2b] and we have confirmed that a mixture of the two forms of CDP-I does not have activity against *Staphylococcus aureus*. This result was difficult to reconcile with the previously held structure **2b** for vancomycin since the structure and that of CDP-I-m (**1b**) were identical except for the carboxamide group, which was distant from the putative site of antibiotic activity. Major differences between the revised structure **3** for vancomycin and the structures of CDP-I-M and -m can account for the absence of activity in CDP-I.

Acknowledgment. We thank Dr. A. M. Thomas (Abbott Laboratories) for helpful discussions, Dr. F. T. Wolf (Vanderbilt University) for the antibiotic assays, and Dr. P. Fletcher (East Carolina University) for the amino acid analyses. This research was supported by the U.S. Public Health Service (GM-25793).

Registry No. Vancomycin, 1404-90-6; vancomycin aglycone, 82198-76-3; O-methylated aglycovancomycin, 82198-77-4.

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(15) Under the conditions for CDP-I formation (pH 4.11, 75 °C) the model peptide Ac-L-Asn-D-Ala showed no detectable reaction after 70 h, but the rate of rearrangement is known to be quite sequence dependent (see, e.g., ref 6i).

Synthesis and Thermal Behavior of 6-Methoxytricyclo[5.3.0.0^{2,5}]deca-3,6,8,10-tetraene (Methoxy-Dewar Azulene). Similarity between Valence Isomers of Azulene and Benzene

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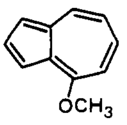
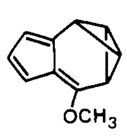
Received April 5, 1982

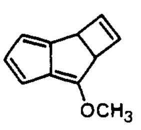
In recent years, keen interest has developed in the chemistry of the valence isomers of benzenoid aromatic hydrocarbons,[1] many of which possess not only novel strained structures[2] but also valued ground- and excited-states properties.[3] However, little is known for the valence isomers of nonalternant hydrocarbons.[4] We have recently reported the synthesis of 6-methoxytetracyclo[5.3.0.0^{2,4}.0^{3,5}]deca-6,8,10-triene (methoxyazulvalene) (**2**)[5] as a first example of the valene-type valence isomer of a representative nonalternant hydrocarbon azulene derivative, **1**. In connection with the study on the thermal and photochemical behavior of **2**, 6-methoxytricyclo[5.3.0.0^{2,5}]deca-3,6,8,10-tetraene (methoxy-Dewar azulene) (**3**) is required. To date known compounds having the Dewar azulene skeleton are confined only to the heavily substituted derivatives prepared through cycloaddition reactions of pentalenes with acetylenes.[6] We report here the synthesis and some properties of **3**.



1

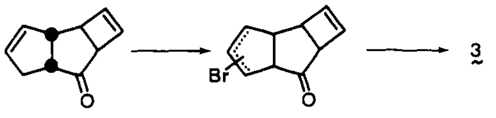


2



3

Scheme I



4 **5**

As outlined in Scheme I, **3** was prepared conveniently from *cis-anti-cis*-tricyclo[5.3.0.0^{2,5}]deca-3,9-dien-6-one (**4**) previously used as a synthetic intermediate for **2**.

Bromination of **4** with *N*-bromosuccinimide in dry carbon tetrachloride in the presence of azodiisobutyronitrile under reflux for 1.5 h gave a mixture of allylic bromides **5** ($\nu_{C=O}$ 1720 cm^{-1}) which, without separation, was treated with 2 equiv of potassium *tert*-butoxide in HMPA at 0 °C for 5 min and then quenched with freshly distilled methyl fluorosulfonate for 5 min to give **3** as a yellow oil in 60% yield.[7] Dewar azulene **3** was too unstable to allow its combustion analysis (highly sensitive to air and acids; however, it could be stored at ambient temperature under argon atmosphere); however, available spectroscopic data are consistent with the proposed structure; MS, *m/e* 158 (M$^+$, 64%), 128 (azulene cation, 66%), 115 (indenium ion, 100%); ^{1}H NMR (100 MHz, CDCl$_3$) δ 4.11 (s, 3 H, OCH$_3$), 4.11 (m, 1 H, H-2), 4.24 (dd, 1 H, J = 2.7, 1.0 Hz, H-5), 6.02 (m, 1 H, H-10), 6.25 (dd, 1 H, J = 4.8, 1.1 Hz, H-8), 6.49 (dd, 1 H, J = 2.6, 1.0 Hz, H-3 or -4), 6.55 (dd, 1 H, J = 2.6, 1.0 Hz, H-4 or -3), 6.73 (dd, 1 H, J = 4.8, 2.2 Hz, H-9); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 44.8, 59.9, 60.1, 110.2, 113.2, 124.9, 135.2, 138.6, 144.1, 146.3, 172.4; UV (cyclohexane) λ_{max} 289 nm (ϵ 12000), 357 (950). The ultraviolet spectrum of **3** needs comment. In spite of the increased strain involved in the fulvene chromophore, the long-wavelength maximum of **3** exhibits a blue shift by 10 nm compared to that of **2**. This finding implies that there is a conjugation effect between the fulvene and bicyclobutane moieties in **2** to some extent.[8]

In sharp contrast to **2**, which undergoes clean isomerization to **1** on irradiation, photolysis of **3** resulted in slow decomposition instead of isomerization to **1**.[9] On the other hand, the thermal

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[1] For Dewar benzenes, see: (a) van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1963**, *85*, 3297. (b) Breslow, R.; Napierski, J.; Schmidt, A. H. *Ibid.* **1972**, *94*, 5906. van Tamelen, E. E.; Carty, D. *Ibid.* **1967**, *89*, 3922, **1971**, *93*, 6102. (c) McDonald, R. N.; Frickey, D. G. *Ibid.* **1968**, *90*, 5315. (d) Yang, N. C.; Carr, R. V.; Li, E.; McVey, J. J.; Rice, S. A. *Ibid.* **1974**, *96*, 2297. For benzvalenes, see: (e) Katz, T. J.; Wang, E. J.; Acton, N. *Ibid.* **1971**, *93*, 3782. (f) Gandillon, G.; Bianco, B.; Burger, U. *Tetrahedron Lett.* **1981**, 51. (g) Burger, U. *Chimia* **1979**, *33*, 147. For prismane, see: (h) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

[2] For a review, see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

[3] (a) For degenerate photoinduced valence isomerizations and quantum chain processes, see: Renner, C. A.; Katz, T. J.; Pouliquen, J.; Turro, N. J.; Waddel, W. H. *J. Am. Chem. Soc.* **1975**, *97*, 2596. Turro, N. J.; Ramamurthy, V.; Katz, T. J. *Nouv. J. Chim.* **1977**, *1*, 363. (b) For adiabatic photoreaction, see: Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 572. (c) For chemoexcitations, see: Lechtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3025.

[4] Notable early examples of such isomers were naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene ((a) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47. (b) Pagni, R. M.; Watson, C. R., Jr. *Ibid.* **1973**, 59. (c) Pagni, R. M.; Burnett, K.; Hasell, A. C. *Ibid.* **1977**, 163; *J. Org. Chem.* **1978**, *43*, 2750) and naphtho[1,8]bicyclo[3.2.0]heptene ((d) Meinwald, J.; Samuelson, G. E.; Ikeda, M. *J. Am. Chem. Soc.* **1970**, *92*, 7604. (e) Gleiter, R.; Haider, R.; Murata, I.; Pagni, R. M. *J.Chem. Res., Synop.* **1979**, 72. (f) Watson, R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 2551. (g) Turro, N. J.; Ramamurthy, V.; Pagni, R. M.; Butcher, J. A., Jr. *J. Org. Chem.* **1977**, *42*, 92).

[5] Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1981**, *103*, 6738.

[6] Suda, M.; Hafner, K. *Tetrahedron Lett.* **1977**, 2453. For examples of intermediate formation of Dewar azulene skeleton, see: Hafner, K.; Diehl, H.; Suss, H. U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 104. LeGoff, E. *J. Am. Chem. Soc.* **1962**, *84*, 3975.

[7] Preparation of **3** has to be done under very strictly controlled conditions. All solvents used were deoxygenated by bubbling with dry argon before use. Potassium *tert*-butoxide and methyl fluorosulfonate were purified by sublimations and distillations, respectively, just before use.

[8] Conjugation effects between bicyclobutane and some π systems have been suggested in benzvalene (Griffith, D. W. T.; Kent, J. E.; O'Dwyer, M. F. *Aust. J. Chem.* **1975**, *28*, 1397. Griffith, D. W. T.; Kent, J. E.; O'Dwyer, M. F. *J. Mol. Spectrosc.* **1975**, *58*, 427. Harmon, P. J.; Kent, J. E.; O'Dwyer, M. F.; Smith, M. H. *Ibid.* **1979**, *32*, 2579) and in tropovalene (Sugihara, Y.; Morokoshi, N.; Murata, I. *Tetrahedron Lett.* **1977**, 3887).

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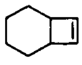
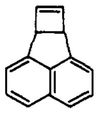
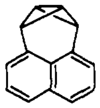
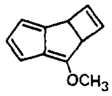
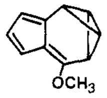
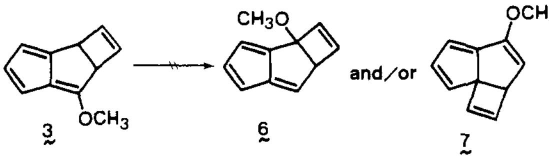
Table I. Activation Energies for Cyclobutene and Bicyclobutane Ring Openings

compd	E_a, kcal/mol	ref	compd	E_a, kcal/mol	ref
	45.9	*a*		38.8	*g*
	43.2	*b*		32.4	*g*
	39.5	*c*			
	39.3	*d*		32.9	*d*
	23.0	*e*		25.9	*h*
	36.7	*f*		~31	*f*

[a] Branton, G. R.; Frey, H. M.; Montagne, D. C.; Stevens, D. D. R. *Trans. Faraday Soc.* 1966, *62*, 659. [b] Branton, G. R.; Frey, H. M.; Skinner, R. F. *Ibid.* 1966, *62*, 1546. [c] Willcott, M. R.; Coerland, E. *Tetrahedron Lett.* 1966, 6341. [d] Reference 4g. [e] Reference 1b. [f] This work. [g] Christl, M.; Heinemann, V.; Kristof, W. *J. Am. Chem. Soc.* 1975, *97*, 2299. [h] Reference 11.

behavior of **2** and **3** is of particular interest. It should be noted that **3** was found to be thermally stable up to 120 °C in dodecane or benzene for 48 h; consequently the intervention of **3** during the thermal isomerization of **2** to **1** can be eliminated. However, at elevated temperature **3** undergoes clean isomerization to **1** quantitatively with first-order kinetics in the temperature range 428–455 K (by ^{1}H NMR monitoring in benzene-d_6).[10] From an Arrhenius plot ($r = 0.9986$) of the data the activation parameters, $\Delta H^\ddagger = 35.8 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = 2.1 \pm 1.0$ eu, $E_a = 36.7 \pm 0.6$ kcal/mol, and $\log A = 13.9 \pm 0.2$ are obtained. The azulvalene **2** also converted (70–80%) thermally to **1** accompanied by partial decomposition. From the several runs the activation energy for the process was roughly estimated to be 31 kcal/mol, deduced from the decay rate of **2** in dodecane (temperature range 110–140 °C) monitored by UV spectroscopy. In Table I available data of activation energies for the related compounds are compared. Inspection of these data indicate that the activation energies for the ring opening of both **2** and **3** are substantially higher than those of benzvalene and Dewar benzene, respectively; however, the values found for **2** and **3** are smaller than those of the other compounds in Table I.

In conclusion, two points we believe are worth making. First, although most bicyclobutanes incorporated into a cyclic framework are known to be thermally converted to the corresponding cyclobutene isomer, the thermolysis of **2** gives rise directly to **1** without any intervention of **3**. The plausible explanation for the process is that the fulvene π system (6π) in **2** does not play a passive role during this ring opening but assists in the fission of the bicyclobutane ring.[11] Second, in spite of the fact that the activation enthalpy for aromatization of **3** is greater than that of Dewar benzene, **3** did not give any detectable amount of either **6** or **7** through a [3,7] sigmatropic shift during the thermolysis of **3**.[12,13] These facts found for **2** and **3** are, at least phenomenalistically, parallel to the thermal behavior of benzvalene and Dewar benzene, respectively. The possibility of realizing the synthesis of both parent azulvalene and Dewar azulene and the study on the ground- and excited-states properties of these intriguing molecules are currently under investigation.



Registry No. 1, 58000-25-2; **2**, 79794-93-7; **3**, 82182-27-2; **4**, 79815-07-9.

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[9] We examined here direct irradiation in hexane and acetone-sensitized irradiation and low-temperature irradiation in methylcyclohexane–isopentane (1:4) at 77 K; all resulted in decomposition. In all cases, irradiations were conducted with a high-pressure Hg lamp through Pyrex and/or quartz filter.

[10] A solution of **3** in benzene-d_6 was degassed and sealed in vacuo in an NMR tube. The tube was immersed in a thermostated and stirred oil bath. The tube was removed at appropriate intervals and immediately cooled to room temperature. The disappearance of **3** and the appearance of **1** were monitored by NMR integration. First-order rate constants are $k^{428} = 1.24 \times 10^{-5}$, $k^{438} = 3.66 \times 10^{-5}$, $k^{447} = 8.00 \times 10^{-5}$, and $k^{455} = 1.66 \times 10^{-4}$ s^{-1}.

[11] In the case of thermal conversion of benzvalene to benzene it was suggested that the extra double bond does not play a appearance of in this process: Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932. Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 4133.

[12] Previous studies by Goldstein and Leight have shown that ^{1}H NMR spectra of deuterated Dewar benzene recovered after half thermal cyclodissociation revealed less than 5% contamination by any isotopic isomer: Goldstein, M. J.; Leight, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 8112.

[13] For a general discussion of a formal [3,3] sigmatropic shift, see: Otterbacher, E. W.; Gajewsky, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5862 and references cited therein. In view of the facts that the fulvene acts as a 6π component in pericyclic reactions and that Dewar benzene isomerizes to benzene even at room temperature whereas Dewar azulene **3** isomerizes only at elevated temperature, a [3,7] sigmatropic shift in **3** would have, a priori, been expected.

Long-Distance (25 Å) Electron Transfer by Triplet Excited States in Rigid Media[1]

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Received April 22, 1982

We report measurements of phosphorescence quenching in rigid media by two types of electron-transfer reactions (see Table I for data and key to abbreviations):

$$\mathrm{TMPD(T_1) + PA \rightarrow TMPD^+ + PA^-} \qquad (1)$$

$$\mathrm{HMTI + PMDA(T_1) \rightarrow HMTI^+ + PMDA^-} \qquad (2)$$

In reaction 1 the first triplet excited state (T_1) of TMPD transfers an electron *to* phthalic anhydride (PA); in reaction 2 triplet PMDA captures an electron *from* an unexcited molecule of HMTI. These reactions show similar 25-Å quenching distances obtained by using eq 3 below. Although back reactions are expected to prevent a measurable buildup of the ions in reactions 1 and 2 and no ions were found, the data are in excellent accord with the electron-transfer mechanism while alternatives may be eliminated (see below). Charge-transfer processes of triplets occur in fluid solutions[3-6] where the reactants may collide with each other, but long-distance electron transfer (ET) by triplets has not been previously reported. The 25-Å quenching radii found here are the largest reported for ET by excited molecules.

Quenching data for reaction 1 appear in Figure 1. The phosphorescence and fluorescence intensities were measured in

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[1] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract No. W-31-109-ENG-38.

[2] Undergraduate research participants from (a) University of Michigan at Flint and (b) University of Chicago.

[3] Ibar, S.; Linschitz, H.; Cohen, S. *J. Am. Chem. Soc.* **1980**, *102*, 1419.

[4] Periasamy, N.; Linschitz, H. *Chem. Phys. Lett.* **1979**, *64*, 281.

[5] Cheddar, G.; Castelli, F.; Tollin, G. *Photochem. Photobiol.* **1980**, *32*, 71.

[6] Cheddar, G.; Tollin, G. *Photobiochem. Photobiophys.* **1980**, *1*, 235.

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