improve signal-to-noise, single-scan methods are also useful to increase digital resolution.

Aurantosides A and B: Cytotoxic Tetramic Acid Glycosides from the Marine Sponge *Theonella* sp.[1]

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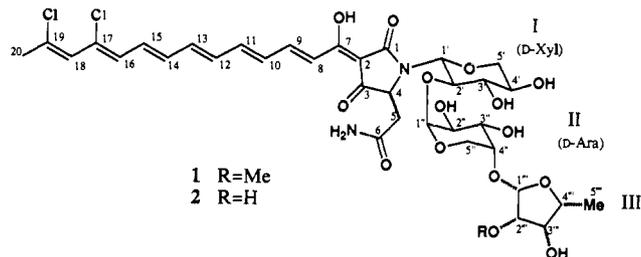*Faculty of Agriculture, University of Tokyo*
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Certain sponges contain microbial symbionts including blue-green algae and bacteria[2] and possess secondary metabolites, some of which may be of microbial origin.[3] A *Theonella* sponge collected off Hachijo Island, from which we isolated bioactive cyclic peptides,[4,5] also contained orange pigments possessing cytotoxic activity. Here we describe the isolation and structure elucidation of the pigments named aurantosides A and B, which are superficially reminiscent of the streptolydigins.[6]

The MeOH extract of the sponge (15 kg) was partitioned between water and ether, and the aqueous phase was extracted with n-BuOH. The n-BuOH phase was gel-filtered over Sephadex LH-20 with MeOH. The cytotoxic orange band was purified by reverse-phase chromatography[7] to furnish aurantoside A (**1**, 1.3 × 10^{-3}% yield based on the wet weight) and aurantoside B (**2**, 1.5 × 10^{-3}% yield),[8] both as orange amorphous powders. They are cytotoxic against P388 and L1210 leukemia cells (**1**, IC_{50} 1.8 and 3.4 μg/mL, respectively; **2**, IC_{50} 3.2 and 3.3 μg/mL).

The UV–visible spectrum of aurantoside A was pH-sensitive.[8] **1** showed intense $(M + Na)^+$ cluster ions with small $(M + H)^+$

(1) Bioactive Marine Metabolites. 38. Part 37: Matsunaga, S.; Fusetani, N. *Tetrahedron Lett.* **1991**, *32*, 5605–5606.

(2) Trench, R. K. *Annu. Rev. Plant Physiol.* **1979**, *30*, 485–531.

(3) (a) Bergquist, P. R.; Wells, R. J. In *Marine Natural Products, Chemical and Biological Perspectives*; Scheuer, P. J., Ed.; Academic Press: New York, 1983; Vol. V., pp 1–50. (b) Hofheinz, W.; Oberhänsli, W. E. *Helv. Chim. Acta* **1977**, *60*, 660–669. (c) Frincke, J. M.; Faulkner, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 265–269. (d) Matsunaga, S.; Fusetani, N.; Hashimoto, K.; Wälchili, M. *J. Am. Chem. Soc.* **1989**, *111*, 2582–2588.

(4) Fusetani, N.; Matsunaga, S.; Matsumoto, H.; Takebayashi, Y. *J. Am. Chem. Soc.* **1990**, *112*, 7053–7054.

(5) Fusetani, N.; Sugawara, T.; Matsunaga, S.; Hirota, H. *J. Am. Chem. Soc.* **1991**, *113*, 7811–7812.

(6) (a) Brill, G. M.; McAlpine, J. B.; Whittern, D. *J. Antibiot.* **1988**, *41*, 36–44. (b) Meyers, E.; Cooper, R.; Dean, L.; Johnson, J. H.; Slusarchyk, D. S.; Trajo, W. H.; Singh, P. D. *J. Antibiot.* **1985**, *38*, 1642–1648 and references cited therein.

(7) The orange solids were first applied to an open column of ODS (70–230 mesh) and eluted with 30, 50, 70, 90, and 100% MeOH in water. The 90 and 100% MeOH fractions were combined and subjected to ODS HPLC with MeCN–H₂O (1:1) with 0.1% TFA to afford **1** and **2**.

(8) The name was coined from the Latin word auranticus, which means orange. **1**: amorphous solid, $[\alpha]^{23}_D$ −568° (c = 0.1, MeOH); UV–vis (H₂O) 414 (ε 46 700), 242 nm (12 100); UV–vis (0.01 N HCl) 456 (ε 32 500), 324 nm (8500); UV–vis (0.01 N NaOH) 412 (ε 52 000), 241 nm (11 500); FAB-MS (positive) m/z 843, 841, 839 (M + Na)⁺, 821, 819, 817 (M + H)⁺; FAB-MS (negative) m/z 819, 817, 815 (M − H)⁻; IR (KBr) 3330, 2920, 1650, 1600, 1540, 1390, 1240, 1130, 1060, and 1000 cm⁻¹. **2**: amorphous solid, $[\alpha]^{23}_D$ −492° (c = 0.1, MeOH); UV–vis (H₂O) 414 (ε 49 100), 242 nm (10 900); UV–vis (0.01 N HCl) 456 (ε 36 100), 301 nm (9800); UV–vis (0.01 N NaOH) 412 (ε 56 200), 242 nm (10900); FAB-MS (positive) m/z 829, 827, 825 (M + Na)⁺, 807, 805, 803 (M + H)⁺; FAB-MS (negative) m/z 805, 803, 801 (M − H)⁻; IR (KBr) 3320, 2900, 1650, 1610, 1540, 1390, 1230, 1130, 1070, 1040, and 995 cm⁻¹.

1 R=Me
2 R=H

3

4

ion species in the FAB mass spectrum. A molecular formula of $C_{36}H_{46}Cl_2N_2O_{15}$ was established by the FAB mass and NMR spectral data, as well as from combustion analysis. A conjugated hexaene (C8–C20) was inferred from the COSY, HMQC, and HMBC spectra. Assignments for the olefinic protons and Me-20 were straightforward: signals were well separated, and long-range couplings were observed between H16 and H18 and between H18 and Me-20 in the normal COSY spectrum. Two chlorine atoms could be placed on C17 and C19 on the basis of their ^{13}C chemical shifts (δ 129.8 and 137.4). Judging from the ^1H–^1H coupling constants and NOESY data, the double bonds have all-trans geometry.

Two apparent anomeric protons were shown in the ^1H and COSY spectra. Starting from the higher field signal (δ 5.04, d, J = 2.8 Hz), we could deduce an arabinopyranose structure (sugar II): H1″ and H4″ were equatorial, whereas H2″ and H3″ were axial. Another anomeric proton at δ 5.06 (H1‴) was that of 5-deoxypentofuranose (sugar III), which had a methoxy group on C2‴ as revealed by the HMBC spectrum. Interpretation of the NMR data for this unit was unexceptional. Though H1′ and H2′ signals of the sugar unit I were both broad and overlapping, ^1H–^1H coupling constants and NOESY data allowed us to assign the xylopyranose with an axial anomeric proton.[9] This was supported by the COSY and NOESY spectra in CD_3OD at −30 °C, which gave well-separated and sharper signals for H1′ and H2′.

The NMR spectra contained signals for a $CHCH_2$ unit (C4, C5) with a broadened methine proton. Two primary amide protons were observed in DMSO-d_6 which showed NOESY correlations with the C5 methylene protons, suggesting that a primary amide was attached to C5. The remaining portion (C1–C3 and C7) consisted of four nonprotonated carbons, generating broad signals at δ 195.0, 176.1, 174.8, and 102.0, one nitrogen and three oxygens. This constellation was reminiscent of a tetramic acid moiety, in which C4 is incorporated into the five-membered ring. The ^{13}C chemical shifts agreed well with those reported for the relevant portion of streptolydigin.[10] The above-mentioned structural units were connected, on the basis of HMBC spectral data (Table I). Structure **1** was fully consistent with the FAB-MS/MS data.[11]

(9) Judging from the coupling constants, H2′, H3′, and H4′ were all axial, so that this unit must be xylopyranose. In the NOESY spectrum, a strong correlation was observed between H5′a and a broad signal at δ 4.52 (H1′ and H2′). H5′a and H2′ project axially in opposite directions from the tetrahydropyran ring; therefore, this cross peak was assignable to the NOE between H5′a and H1′.

(10) Lee V. J.; Rinehart, K. L., Jr. *J. Antibiot.* **1980**, *33*, 408–415.

(11) The pseudomolecular ion peak at m/z 817 gave rise to ions at m/z 685, 555, and 423, which were generated by the cleavage of the three glycosidic bonds. Though the NMR data with broad ^1H and ^{13}C signals indicate that aurantoside A exists as a mixture of four possible tautomers (2,3 enol or 2,7 enol with cis or trans 2,7 bond), X-ray study of a tetramic acid (Nolte, M. J.; Steyn, P. S.; Wessels, P. L. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1057–1065) suggests that the tautomer depicted in formula **1** is the predominant one.

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Table I. NMR Data for Aurantosides A and B (MeOH-d_4)

	aurantoside A (1)				aurantoside B (2)		
	^{13}C mult	^{1}H mult	*J*, Hz	HMBC (C no.)	^{13}C mult	^{1}H mult	*J*, Hz
1	174.8 s				174.9 s		
2	102.0 s				102.0 s		
3	195.0 s				195.1 s		
4	65.5 d	4.33 br			65.3 d	4.32 br	
5a	38.5 t	2.67 dd	7.0, 16.0	4, 6	38.1 t	2.67 dd	7.2, 16.0
5b		2.79 dd	4.5, 16.0	3, 4, 6		2.79 dd	4.1, 16.0
6	174.3 s				174.3 s		
7	176.1 s				176.2 s		
8	122.1 d	7.21 br d	15.1		122.0 d	7.22 br d	15.4
9	146.4 d	7.59 dd	10.9, 15.1	10, 11	146.5 d	7.61 dd	11.4, 15.4
10	133.4 d	6.59 dd	10.9, 14.6	8, 9, 12	133.4 d	6.61 dd	11.4, 14.5
11	145.2 d	6.87 dd	11.2, 14.6	12, 13	145.2 d	6.88 dd	11.3, 14.5
12	135.8 d	6.56 dd	11.2, 14.5	10, 11, 13	135.7 d	6.57 dd	11.3, 14.6
13	140.1 d	6.68 dd	11.1, 14.5	12, 15	140.1 d	6.69 dd	11.2, 14.6
14	137.6 d	6.59 dd	11.1, 14.6	12, 16	137.6 d	6.61 dd	11.2, 14.5
15	132.0 d	6.76 dd	10.7, 14.6	14, 16, 17	131.9 d	6.77 dd	10.7, 14.5
16	131.5 d	6.44 d	10.7	14, 15, 18	131.4 d	6.45 d	10.7
17	129.8 s				129.7 s		
18	127.8 d	6.32 s		16, 17, 19	127.8 d	6.33 s	
19	137.4 s				137.4 s		
20	23.6 q	2.38 d	1.1	18, 19	23.5 q	2.39 br s	
1′	86.5 d	4.52 br			86.0 d	4.52 br	
2′	81.5 d	4.52 br			81.1 d	4.52 br	
3′	79.2 d	3.48 dd	9.0, 9.0	2′, 4′	79.2 d	3.48 t	9.0
4′	70.4 d	3.63 ddd	5.4, 9.0, 10.5	3′	70.5 d	3.62 m	
5′a	69.4 t	3.22 dd	10.5, 11.3	3′, 4′	69.2 t	3.21 t	11.0
5′b		3.88 dd	5.4, 11.3	1′, 3′, 4′		3.88 m	
1″	103.8 d	5.04 d	2.8	2′, 3″, 5″	103.9 d	5.04 d	2.5
2″	71.5 d	3.79 dd	2.8, 9.4	3″	71.7 d	3.79 dd	2.5, 9.4
3″	70.7 d	3.77 dd	2.9, 9.4	2″	70.7 d	3.77 m	
4″	75.9 d	3.90 ddd	1.4, 2.9, 3.9	2″, 3″, 1‴	76.5 d	3.92 m	
5″a	61.4 t	3.57 dd	3.9, 12.6	1″, 3″, 4″	61.9 t	3.61 m	
5″b		3.71 dd	1.4, 12.6	1″, 4″		3.75 m	
1‴	98.7 d	5.06 d	4.4	4″, 3‴, 4‴	100.7 d	4.92 d	4.7
2‴	87.2 d	3.65 dd	4.4, 7.9	4‴, OMe	78.9 d	3.88 m	
3‴	79.7 d	3.88 dd	6.6, 7.9	2‴, 4‴	79.5 d	3.76 m	
4‴	79.5 d	3.74 dq	6.6, 6.4	1‴, 3‴	81.1 d	3.78 m	
5‴	20.9 q	1.31 d	6.4	3‴, 4‴	20.7 q	1.31 d	6.0
OMe	58.3 q	3.35 s		2‴			

The absolute stereochemistry of arabinose and xylose were determined to be D by GC analysis of the hydrolysis product on a Chirasil Val III column.[12] Acid hydrolysis of **1**, followed by *p*-bromobenzoylation, yielded the 1,3-bis-*O*-(*p*-bromobenzyl) derivative of the 5-deoxypentose (**3**).[13] ^{1}H NMR coupling constants and NOE data indicated that this sugar unit was 5-deoxy-2-*O*-methylarabinofuranose.[14] NaIO$_4$/KMnO$_4$ oxidation of **1**, followed by acid hydrolysis, provided L-Asp as identified by HPLC after derivatization with Marfey's reagent,[15] thereby revealing that aurantoside A had 4*S* stereochemistry.

NMR spectra of aurantoside B, which is more polar than **1**, were almost superimposable on those of aurantoside A, except for the absence of a methoxy signal. Interpretation of the NMR and FAB mass data indicated that **2** was the 2‴-des-*O*-methyl derivative of aurantoside A.[16] Acidic methanolysis, followed by *p*-bromobenzoylation and HPLC separation, afforded 1-*O*-methyl-2,3-bis-*O*-(*p*-bromobenzoyl)-5-deoxyarabinose (**4**).[17] The

CD spectrum of **4** exhibited a negative exciton split, indicating that this sugar unit was in the D form.[18] Thus, it is most likely that 5-deoxy-2-*O*-methylarabinose in **1** is in the D form.

Aurantosides are the first tetramic acid glycosides isolated from a marine organism. While the tetramic acid moiety is reminiscent of some terrestrial microbial metabolites,[19] the acetamide and 14-carbon side chains as well as the *N*-trisaccharide-derivatized tetramic acid are unique structural features of the aurantosides.[21]

(12) König, W. A.; Benecke, I.; Bretting, H. *Angew. Chem., Int. Ed. Eng.* **1981**, *20*, 693–694.

(13) ^{1}H NMR data for **3** (CDCl$_3$): δ 6.48 (s, H1), 5.08 (d, *J* = 3.3 Hz, H3), 4.51 (dq, *J* = 3.3, 6.6 Hz, H4), 4.10 (s, H2), 3.55 (3 H, s, 2-OMe), 1.49 (3 H, d, *J* = 6.6 Hz, H$_3$5). Aromatic protons are omitted.

(14) Stevens, J. D.; Fetcher, H. G., Jr. *J. Org. Chem.* **1968**, *33*, 1799–1805. Small coupling constants between H1 and H2 and between H2 and H3 in **3** indicated that both H1/H2 and H2/H3 are trans. An NOE observed for H1 on irradiation of Me-5 showed that they were on the same face of the molecule. ^{1}H–^{1}H coupling constants of the 5-deoxy-2-*O*-methylarabinose residue in aurantoside A revealed that H1‴ and H2‴ are cis.

(15) Marfey, P. *Carlsberg Res. Commun.* **1984**, *49*, 591–596.

(16) 2D NMR data (COSY, ROESY, HMQC, and HMBC) supported the structure **2** for aurantoside B. C4 stereochemistry and the configuration of Ara and Xyl residues were established as in the case of **1**.

(17) ^{1}H NMR data for **4** (CDCl$_3$): δ 5.40 (s, H2), 5.14 (d, *J* = 5.0 Hz, H3), 5.05 (s, H1), 4.34 (dq, *J* = 5.0, 6.5 Hz, H4), 3.44 (3 H, s, 1-OMe), 1.51 (3 H, d, *J* = 6.5 Hz, H$_3$5). Aromatic protons are omitted. CD spectrum (MeCN): 251 (Δε = −27.2), 240 (0), 234 (+6.9) nm.

(18) Nakanishi, K.; Kuroyanagi, M.; Nambu, H.; Oltz, E. M.; Takeda, R.; Verdine, G. L.; Zask, A. *Pure Appl. Chem.* **1984**, *56*, 1031–1048.

(19) Aurantosides have a conjugated polyene structure similar to the structures of erythroskyrine, lipomycins, and olefficin,[20] none of which are chlorinated.

(20) (a) Shoji, J.; Shibata, S.; Sankawa, U.; Taguchi, H.; Shibanuma, Y. *Chem. Pharm. Bull.* **1965**, *13*, 1240–1246. (b) Schabacher, K.; Zeeck, A. *Tetrahedron Lett.* **1973**, 2691–2694. (c) Gyimesi, J.; Mehasfalvi-Vajna, Zs.; Horváth, Gy. *J. Antibiot.* **1978**, *31*, 626–627.

(21) After we submitted this paper, a tetramic acid from a marine sponge was reported. Gunasekara, S. P.; Gunasekera, M.; McCarthy, P. *J. Org. Chem.* **1991**, *56*, 4830–4833.

Automerization of Naphthalene. New Evidence Consistent with the Intermediacy of Benzofulvene[1]

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We first reported the thermal interconversion of [α-^{13}C]-naphthalene (**1α**) and [β-^{13}C]naphthalene (**1β**) in 1977[2] and have subsequently observed the 1,2-scrambling of carbon atoms at high temperatures in a variety of other aromatic hydrocarbons,[3–8] as well as in benzene-^{13}C$_2$.[9] Considerable evidence suggests that the mechanism of these "automerization" reactions and related thermal rearrangements of benzenoid hydrocarbons involves reversible contraction of a benzene nucleus to a five-membered-ring intermediate.[7,10,11] Herein we present new evidence that deposes the previously proposed carbene **2** as a candidate for that intermediate in favor of benzofulvene (**3**); Scheme I depicts plausible pathways to **3** via ring contractions of carbenes **4** and **5**.

R. F. C. Brown et al. have reported that flash vacuum pyrolysis (FVP) of benzofulvene gives naphthalene as the exclusive product.[12] We have now repeated this reaction using isotopically labeled benzofulvene, enriched to 99% ^{13}C in the methylene group (**3**).[13] At 900 °C/10^{-3} Torr, labeled benzofulvene **3** yields [α-^{13}C]naphthalene (**1α**) and [β-^{13}C]naphthalene (**1β**) in a ratio of 21:79 ± 3.[14,15] Control experiments (repyrolysis of the labeled

naphthalene mixture) confirm that **1α** and **1β** do not interconvert (≤3%) under these conditions.[16]

We believe that the disparate product distribution in this experiment argues strongly against carbene **2** as an intermediate *on the pathway from benzofulvene to naphthalene.* Our reasoning is as follows: At 900 °C, a kinetically controlled product ratio of 21:79 requires a difference in free energy of activation (ΔΔ*G*‡) of ca. 3.1 kcal/mol between two competing pathways.[15] If carbene **2** were the intermediate in the aromatization of benzofulvene (Scheme I), then these two competing pathways would be the aryl shift (**2** → **1α**) and the vinyl shift (**2** → **1β**).[17] Such rearrangements of carbenes, however, are extremely exothermic reactions with very low energy barriers (Figure 1A)[18] and should be characterized by quite early (carbene-like) transition states.[19] Given two equally exothermic pathways (**2** → **1α** vs **1β**),[20] both with very low energy barriers, it seems highly unlikely that they could differ in Δ*G*‡ by as much as 3.1 kcal/mol. Thus, carbene **2** appears improbable as an intermediate *on the pathway from benzofulvene to naphthalene.*

Brown et al. originally proposed an alternate pathway for the aromatization of benzofulvene via carbene **4** (Scheme 1).[12] This mechanism would certainly account for the minor product (**1α**) we obtain from labeled benzofulvene **3**, and the major product (**1β**) could presumably arise by an analogous pathway via carbene **5**. It would be reasonable to assume that the initial ring expansions, rather than the subsequent hydrogen shifts, represent the rate-limiting steps on these two competing pathways.

This proposal has the virtue that the product-determining branch point in the mechanism involves highly endothermic reactions with very high energy barriers (Figure 1B) that should be characterized by quite late (carbene-like) transition states.[19] These two competing pathways, which lead to different carbenes, could more easily differ in Δ*G*‡ by 3.1 kcal/mol. Indeed, Dewar and Merz place carbene **5** lower in energy than carbene **4** by 3.4 kcal/mol on the basis of MNDO calculations.[21] This calculated difference in energy not only qualitatively predicts the preferential formation of **1β** from **3** via carbene **5** but even agrees quantitatively with the product ratio we observe.

If benzofulvene isomerizes to naphthalene via the six-membered-ring carbenes **4** and **5**, as we now propose, rather than via the indenyl carbene **2**, then a strong case can be made that the automerization of naphthalene is also more likely to proceed via **4**, **5**, and benzofulvene rather than via simple ring contraction to **2**. A crucial element of this argument is the postulate that the transition state between **2** and **3** lie lower in energy than the transition states separating **2** from either **1α** or **1β**. This seems reasonable, since 1,2-hydrogen shifts in carbenes almost always occur more readily than 1,2-carbon shifts.[18] Furthermore, Kjell and Sheridan have actually observed that carbene **2**, when generated in a frozen matrix at low temperatures, rearranges exclusively to benzofulvene and gives no naphthalene.[22] Conse-

[†] Visiting scholar from Sharif University of Technology, Tehran, Iran.
[‡] Undergraduate summer research student from Northwestern University.
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(2) Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* 1977, *99*, 4506.
(3) Scott, L. T.; Highsmith, J. R. *Tetrahedron Lett.* 1980, *21*, 4703.
(4) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* 1981, *103*, 5875.
(5) Scott, L. T. *Acc. Chem. Res.* 1982, *15*, 52.
(6) Scott, L. T.; Kirms, M. A.; Berg, A.; Hansen, P. E. *Tetrahedron Lett.* 1982, *23*, 1859.
(7) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* 1984, *25*, 1661.
(8) Scott, L. T. *Chem. Aust.* 1987, *54*, 298.
(9) Scott, L. T.; Roelofs, N. H.; Tsang, T.-H. *J. Am. Chem. Soc.* 1987, *109*, 5456.
(10) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* 1987, *109*, 5461.
(11) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* 1988, *29*, 6857.
(12) Brown, R. F. C.; Gream, G. E.; Peters, D. E.; Solly, R. K. *Aust. J. Chem.* 1968, *21*, 2223-2236.
(13) Benzofulvene enriched to 99% ^{13}C in the methylene group (**3**) was synthesized by (a) quenching the lithium salt of indene in ether with ^{13}CO$_2$ generated from 99%-^{13}C-enriched BaCO$_3$, (b) esterification of the resulting indenecarboxylic acid (SOCl$_2$/CHCl$_3$, then EtOH/THF), (c) reduction of the ester with LiAlH$_4$/AlCl$_3$/Et$_2$O, and (d) dehydration of the indenylmethanol in benzene at 10 °C with methanesulfonyl chloride (1.0 equiv) and triethylamine (9 equiv). The indene derivatives in this synthetic sequence are known compounds in their unlabeled form: see ref 12 and citations therein.
(14) Flash vacuum pyrolyses were conducted in a commercially available Trahanovsky pyrolysis apparatus purchased from Kontes, Inc., Vineland, NJ 08360. Polymerization of **3** in the sample chamber was suppressed by matrix-isolating the material in frozen benzene at 0 °C; a portion of the benzene dimerizes to biphenyl in the pyrolysis tube. The pyrolysate was doubly sublimed prior to quantitative ^{13}C NMR analysis; the appropriate correction was made for unequal α and β ^{13}C signal intensities in the NMR spectrum of unenriched naphthalene.

(15) The 900 °C temperature we report here is the thermocouple reading inside the oven at the midpoint of, but external to, the pyrolysis tube.
(16) The automerization of naphthalene has a half-life of approximately 2 s at 1035 °C in a nitrogen flow system.[2]
(17) Cyclization of carbene **2** to naphthvalene would not account for formation of **1α**.
(18) Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* 1980, *102*, 7817-7818. Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Paike, N. *Tetrahedron Lett.* 1989, *30*, 481-484. Moss, R. A.; Ho, G.-J. *Tetrahedron Lett.* 1990, *31*, 1225-1228. Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* 1990, *112*, 5642-5644. Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* 1990, *112*, 9148-9156 and references cited therein.
(19) Hammond, G. S. *J. Am. Chem. Soc.* 1955, *77*, 334. For a modern discussion of the Hammond postulate, see: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed., Plenum Press: New York, 1990; Part A, pp 211-215.
(20) The thermodynamic product ratio **1α**:**1β** is essentially 50:50.[2]
(21) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* 1986, *108*, 5146-5153. The tricyclic tetraenes proposed by these authors as intermediates separating benzofulvene from carbenes **4** and **5** not only are superfluous but also are incompatible with the experimental observation that naphthalene (with a greater total resonance energy) automerizes significantly more readily than does benzene.[9]