acetate. Enantiomeric excess was determined by HPLC on a chiral column (CHIRACEL OD from DAICEL, using mixtures of *n*-hexane and 2-propanol). The absolute configuration of the PGA esters was established by comparing optical rotation values of analytical samples obtained by crystallization or flash chromatography of the crude material, with the ones of known compounds. The following enzymes were used: CCL lipase-grade VII and PPL grade II from SIGMA, α-CHT crystalline from SCLAVO, α-CHT on agarose from SIGMA. α-CHT on BIOFIX E_1 was prepared at room temperature by removing the water from a mixture obtained by mixing BIOFIX E_1 with a solution of α-CHT in water. In this way a powder containing 10% of the enzyme was obtained: this preparate was stable to storage and after five uses retained about 30% of the original activity. The following enzymes not mentioned in the text gave negative results or no significant improvement with respect to the one described above: Subtilisin, Trypsin, Papain, Acylase I, lipases from *Pseudomonas fluorescens*, *Rhizzopus arizus*, *Candida lipolitica*, and *Aspergillus niger*. PGA esters were prepared according to the literature.[7]

Hydrolysis of Racemic PGA Methyl Ester with CCL Lipase in CH_2Cl_2/H_2O. CCL (3g) was dissolved in water (75 mL), and the pH was set to 7.5 with a 0.1 N sodium hydroxide solution (1.5 mL). Methyl ester of racemic *trans*-(4-methoxyphenyl)-glycidic acid (1.5 g) in methylene chloride (50 mL) was then added and the mixture stirred at room temperature for 2 h. The organic layer was separated and the water phase extracted again with ethyl acetate. The combined organic phases were dried over sodium sulfate and evaporated to give a yellow oil as a residue (1.28 g) consisting of the methyl ester of (2*R*,3*S*)-*trans*-(4-methoxyphenyl)glycidic acid (50.2% assay, 41.5% yield, 60.4% ee) on the basis of HPLC analysis [Chiracel OD, 4.6 × 250, flow 0.7 mL/min, 35 °C, eluent: hexane/2-propanol = 85/15, t_R 12.2 min for the (2*S*,3*R*)-methyl ester of *trans*-(4-methoxyphenyl)glycidic acid and 9.8 min for the (2*R*,3*S*) enantiomer]. In parallel experiments the oily residue (1.5 g) (85% assay, 60% ee) was crystallized from ethanol to give, after two crystallizations, 0.4 g of the methyl ester of 99% ee. The enrichment in one enantiomer upon crystallization could not be reproduced and remained dependent on undetermined factors.

Hydrolysis of PGA Methyl Ester with CCL Lipase in Cyclohexane/H_2O. PGA methyl ester (10 g) was suspended in 500 mL of cyclohexane and then treated with a CCL lipase solution (10 g) in water (300 mL) at room temperature. After 1.5 h the mixture was treated with ethyl acetate (200 mL) and filtered through a Celite pad. The organic phase was dried and evaporated to give an oil (4.5 g) as a residue which consisted of the methyl ester of (2*R*,3*S*)-*trans*-(4-methoxyphenyl)glycidic acid (47% assay, 35% yield, 98% ee).

Hydrolysis of PGA Methyl Ester with CCL Lipase in Acetonitrile/H_2O. With a procedure analogous to that described, hydrolysis was performed in acetonitrile/water. The reaction arrested at 2 h gave the methyl ester as a 65:35 mixture of the two enantiomers.

Transesterification of PGA Methyl Ester with Ethanol in the Presence of α-CHT. PGA methyl ester (9.3 g) in ethanol (740 mL) was mixed with a solution of α-CHT (7.4 g) in phosphate buffer at pH 7.4 (370 mL), and the resulting biphasic system was stirred at room temperature. The reaction was followed by HPLC (SiO_2 column, *n*-hexane/ethyl acetate (9:1), t_R 8 min for the ethyl ester and 10 min for the methyl ester) which showed that after 5.5 h the ratio of the two esters was 1:1. The solution was rapidly evaporated in vacuum at room temperature to give a mixture of products from which by rapid chromatography crude ethyl ester was obtained (4.5 g). ^1H NMR spectra in the presence of chiral shift reagents showed the product to be a 9:1 mixture of two enantiomers. To this material the (2*R*,3*S*) absolute configuration was assigned on the basis of the negative rotation sign. If the reaction was interrupted at 30% conversion the optical purity of the ester was 85% ee.

Transesterification of PGA Methyl Ester with *n*-Propanol in the Presence of α-CHT. PGA methyl ester (1 g) in *n*-propanol (80 mL) was mixed with a solution of α-CHT (0.8 g) in phosphate buffer at pH 7.4 (40 mL), and the resulting biphasic system was stirred at room temperature. When the reaction approached 50% conversion the propyl ester was recovered by rapid chromatography and judged to be of 70% ee from chiral HPLC.

Transesterification of PGA Methyl Ester with *n*-Butanol in the Presence of α-CHT. PGA methyl ester (10 g) in *n*-butanol (200 mL) was mixed with a solution of α-CHT (9 g) in phosphate buffer at pH 7.4 (400 mL), and the resulting biphasic system was stirred at room temperature. When the reaction approached 50% conversion (4.5 h) the mixture was extracted with ethyl acetate and evaporated. Cooling of the mixture allowed the recovery of some unreacted methyl ester (3 g). The remainder was partitioned between the two phases obtained upon mixing hexane, ethyl acetate, methanol, acetonitrile, and water in ratios of 30/8/30/8/24, respectively. From the upper phase 92% chemically pure 4 was obtained which resulted of 80% ee from chiral HPLC (*n*-hexane/2-propanol 90/10, t_R 6.5 min for the (2*S*,3*R*) enantiomer and 7.02 min for the (2*R*,3*S*) enantiomer).

Transesterification of PGA Methyl Ester with *n*-Butanol in the Presence of CCL Lipase in *n*-Hexane. PGA methyl ester (4 g) in *n*-hexane containing 20% of *n*-butanol (100 mL) was treated with CCL lipase (10 g) and stirred at room temperature until the ratio of the esters was 1:1 (HPLC). Partition between solvents as above afforded the butyl ester 5 90% chemically pure of 60% ee to which the (2*S*,3*R*) absolute configuration was assigned from the positive rotation sign and the retention time in the HPLC. Other trials with different solvents were also performed: in **cyclohexane** the $t_{1/2}$ is slightly higher then in *n*-hexane. The product obtained is 58% ee. In ***n*-heptane** after 24 h only 15% of the butyl ester is formed with an ee of 70%. In **butyl acetate** the reaction is extremely slow.

Transesterification of PGA Methyl Ester with *n*-Butanol in the Presence of α-CHT on Biofix E_1 in *n*-Hexane. A preparate of α-CHT absorbed on Biofix E_1 as described (10 g) was suspended in *n*-hexane containing 10% of *n*-butanol (100 mL) and the mixture treated with the methyl ester (1 g). After 6 h the enzyme was filtered off and the mixture analyzed. The butyl ester was 70% ee. The preparate was reused several times, and it was evaluated that the loss of activity was approximately 20% for each run. After five times the retained activity was 30%.

Transesterification of PGA Methyl Ester with *n*-Butanol in the Presence of α-CHT Immobilized on Agarose. The preparate (90 mg, 50 U) was mixed with the methyl ester (40 mg), phosphate buffer pH 7.4 (1.6 mL), and 0.8 mL of *n*-butanol. The reaction was complete after 8 h. The product was of 68% ee as judged from HPLC. After seven runs the material had retained 20% of the original activity.

Kiheisterones, New Cytotoxic Steroids from a Maui Sponge

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Marine sponges have proven to be a veritable cornucopia of unusual steroids.[1] We now describe the isolation and structure elucidation of the kiheisterones A and B (1 and 2),[2] each containing an α,β-disubstituted furan in the side chain, cis-fused A/B ring, a monoenolized α-diketone in the A ring, and a C-21 carboxyl group.

A recent collection of marine invertebrates off the island of Maui, Hawaii, provided a sponge of the order Poecilosclerida[3] whose crude extracts were cytotoxic against several cell lines. Silica gel flash and C-18 gravity column

(1) Kerr, R. G.; Baker, B. J. *Nat. Prod. Rep.* **1991**, *8*, 465–497.
(2) The name of the compounds is derived from the town of Kihei in West Maui, the nearest place to the collection site.
(3) We are grateful to Dr. Shirley Pomponi, Harbor Branch Oceanographic Institution, for indentifying the sponge. A voucher specimen is available at HBOI.

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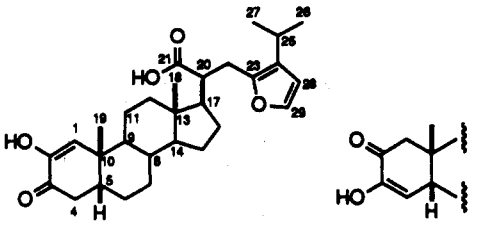

1 2

chromatographies of the lipid extract yielded a fraction which after reversed-phase HPLC afforded 1 and 2 as the cytotoxic compounds.

Kiheisterone A (1) was assigned the molecular formula $C_{29}H_{40}O_5$ by EIMS (M^+ 468.2863 Da, Δ −1.3 mmu), indicating 10 degrees of unsaturation. A fragment ion at m/z 422 (M^+ − 46) showed the loss of H_2O and CO, characteristic of carboxylic acids. A UV maximum at 266 nm (ϵ 10 900) suggested a monoenolized α-diketone.[4] A broad IR absorption near 3450 cm^{-1} was attributable to hydroxyl groups, and strong bands at 1705 and 1670 cm^{-1} provided further evidence for a carboxylic acid and an α,β-unsaturated ketone.

The ^1H NMR spectra showed four typical steroid methyls. Two appeared as singlets at δ 0.76 and 1.18; the other two as doublets at δ 1.04 and 1.09, both coupled (J = 6.8 Hz) to a one-proton septet at δ 2.72, indicating an isolated isopropyl spin system attached to a deshielding moiety. Three olefinic protons, two doublets at δ 6.19 and 7.20 coupled to each other (J = 1.9 Hz), and one singlet at δ 6.07, completed the distinctive features of the proton spectrum.

The ^{13}C NMR spectrum revealed all 29 carbons, including typical signals for an α,β-unsaturated ketone (δ 196.1), a carboxylic acid (180.6), and an α,β-disubstituted furan (146.0, 127.1, 140.8, 108.6). The functional group data from the above spectra accounted for six double-bond equivalents, leaving four for the steroid nucleus. A DEPT experiment indicated four methyl,[5] eight methylene, ten methine, and seven quarternary carbons, which accounted for all 38 nonexchangeable hydrogen atoms. An HMQC experiment established the C–H connectivities, and HMBC and ^1H–^1H COSY experiments were used to determine the C–C connectivities (Table I).

A preliminary inspection of the NMR spectra hinted that 1 had an unconventional side chain. The C-18 methyl protons at δ 0.76 showed a three-bond H–C correlation to a carbon at δ 52.5 (C-17). H-17 (δ 1.71) showed a ^1H–^1H COSY correlation to H-20 (δ 2.66) attached to a carbon resonating at δ 46.8; H-20 in turn was coupled to the protons attached to C-22 (δ 28.6). H-20 also showed HMBC correlations to C-21 (δ 180.6), C-22, and C-23, the furan quarternary α-carbon at δ 146.0. The isopropyl methine proton also showed a three-bond correlation to C-23 and both furan β-carbons (C-24 and -28). H-29 showed correlations across the furan oxygen to C-23 and also to the two furan β-carbons. This information and additional HMQC and HMBC NMR data (Table I) clearly established the structure of the side chain for 1.

We next turned our attention to the location and orientation of the monoenolized α-diketone moiety. The C-19 protons showed H–C correlations to the C-1 methine carbon at δ 129.6 and to carbons having typical steroidal chemical shift ranges for C-5 (δ 41.4), C-9 (47.0), and C-10 (38.0).[6] The proton attached to C-1 (δ 129.6) showed only a correlation to C-5, but a set of doublet of doublets at δ 2.25 (J = 17.7, 4.5 Hz) and 2.88 (J = 17.7, 14.6 Hz) clearly showed correlations to the α,β-unsaturated carbonyl C-3 (δ 196.1) and to C-5, C-6, and C-10. The proton at δ 2.88 (H_{ax}-4) also showed a three-bond correlation to C-2 (δ 144.9), thus securing the orientation of the monoenolized diketone in the A ring. The additional HMQC and HMBC NMR data (Table I) are entirely consistent with the conventional steroid portion of 1.

Table I. NMR Data for 1 (in $CDCl_3$)

no.	^{13}C	^1H (J, Hz)	HMBC	COSY
1	129.6 (d)[a]	6.07, 1 H, s	H_3-19	
2	144.9 (s)		H-4ax	
3	196.1 (s)		H-4ax, H-4eq	
4	37.4 (t)	ax 2.88, 1 H, dd (17.7, 14.6)	H-5, H_2-6	4eq, 5
		eq 2.25, 1 H, dd (17.7, 4.5)		4ax, 5
5	41.4 (d)	2.11, 1 H, bd (14.6)	H-1, H-4ax, H-4eq, H_2-6, H_3-19	4ax, 4eq
6	26.0 (t)	eq 1.38, 1 H, m	H-4ax, H-4eq, H_2-5	5
		ax 1.88, 1 H, tt (14.1, 4.6)		5
7	25.9 (t)	ax 1.09, 1 H, m		
		eq 1.54, 1 H, bdq (12.7, 4.6)		
8	35.1 (d)	1.39, 1 H, m	H-9	
9	47.0 (d)	1.31, 1 H, td (10.7, 4.4)	H-8, H-12, H_3-19	
10	38.0 (s)		H-4ax, H-4eq, H-5, H-9, H_3-19	
11	22.3 (t)	1.42, 2 H, m	H-12	
12	37.4 (t)	ax 1.07, 1 H, m	H_3-18	
		eq 1.63, 1 H, m		
13	42.5 (s)		H_2-16, H-17, H_3-18	
14	55.3 (d)	1.08, 1 H, m	H-12, H_3-18	
15	23.6 (t)	1.14, 1 H, m		
		1.68, 1 H, m		
16	27.1 (t)	1.40, 1 H, m	H-17	
		1.97, 1 H, m		
17	52.5 (d)	1.71, 1 H, q (9.7)	H-14, H_2-16, H_3-18	16, 20
18	12.0 (–)[b]	0.76, 3 H, s	H-14, H-17	
19	21.8 (q)	1.18, 3 H, s	H-9	
20	46.8 (d)	2.66, 1 H, td (10.7, 4.5)	H-17, H_2-22	17, 22
21	180.6 (s)		H-17, H-20, H_2-22	
22	28.6 (t)	2.76, 1 H, dd (14.4, 10.7)	H-17, H-20	
		2.79, 1 H, dd (14.4, 4.5)		
23	146.0 (s)		H-20, H_2-22, H-25, H-28, H-29	
24	127.1 (s)		H_2-22, H-25, H_3-26, H_3-27, H-28, H-29	
25	24.2 (d)	2.72, 1 H, septet (6.8)	H_3-26, H_3-27	26, 27
26	23.7 (q)	1.04, 3 H, d (6.8)	H-25	25
27	24.0 (q)	1.09, 3 H, d (6.8)	H-25	25
28	108.6 (d)	6.19, 1 H, d (1.9)	H-25	29
29	140.8 (d)	7.20, 1 H, d (1.9)	H-28	28

[a] Multiplicities were determined by DEPT and HMQC spectra. [b] Reference 5.

The chemical shifts for C-18 (δ 12.0) and C-19 (21.8) suggested that the A/B rings are cis-fused.[6] This was confirmed by a ROESY experiment, which clearly showed a correlation between H_3-19 and H-5 and H_{ax}-6.

The mass spectrum of 2 revealed that 2 was an isomer of 1. The ^1H and ^{13}C NMR spectra of 2 resembled those of 1 but showed significant differences in the signals of the A ring. The olefinic proton in the A ring of 2 was shifted upfield to δ 5.70 and appeared as a doublet (J = 2.6 Hz). In 2 both protons (δ 2.18 and 2.62) vicinal to the carbonyl (H_2-1) appeared as geminally coupled doublets (J = 16.5

(4) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 303.

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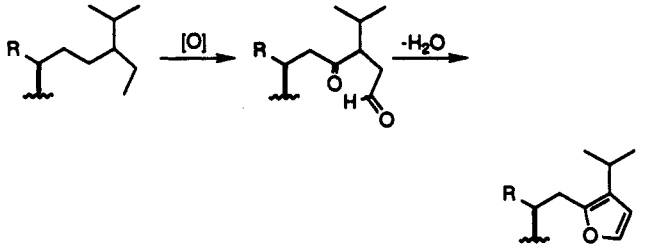
Scheme I. Possible Biogenesis of the Side Chain of 1 and 2

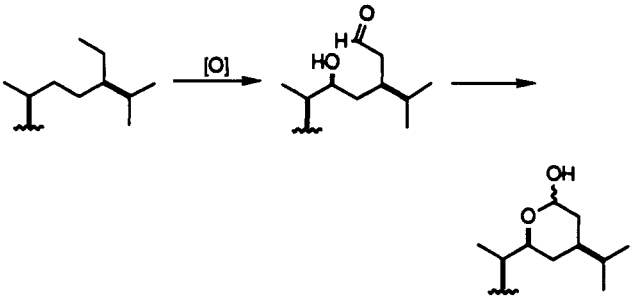


Hz). These data, in addition to full interpretation of the HMQC and HMBC spectra, established the structure as **2**. Both compounds are stable to acid (TFA in $CDCl_3$, rt, 4 d), but both equilibrated to a 1:1 mixture of **1** and **2** in base (triethylamine in $CDCl_3$, rt, 24 h), as evidenced by ^1H NMR spectra and by HPLC.

Steroids with cis-fused A/B rings have been isolated from sponges but are relatively rare.[7-9] They are usually present in relatively large amounts, as is the case with the highly oxygenated sterols from *Dysidea* sp.[7,8] They have also been found in trace amounts, as in the coprostenols isolated from *Petrosia ficiformis*[9] and *Calyx nicaeensis*.[10] In the latter case the occurrence was rationalized by bacterial conversion of Δ^5 sterols which normally occur in these sponges. It has been suggested that unusual steroids present in large quantities in sponges may play a functional role in cell membranes,[11] but it has also been pointed out that highly functionalized sterols, such as the *Dysidea* sterols, probably do not contribute to membrane structure.[8] Since **1** and **2** are present in amounts large enough to be detected in the crude extract by ^1H NMR and are moderately functionalized, it is unlikely that they are produced by indigenous bacteria or involved in cell membrane structure.

Another intriguing feature of **1** and **2** is the oxygenation pattern of the side chain. Oxidation of C-21 to an alcohol is not uncommon in marine sterols, but we are unaware of any sponge sterols oxidized to a C-21 carboxylic acid.[12] While furans are very common in terpenoid marine natural products, their occurrence in the side chain of a sterol is unprecedented. The furan in **1** and **2** is biogenetically derivable from oxidation of C-23 and C-29 to carbonyl groups followed by condensation (Scheme I). While oxidation to a ketone at C-23 is quite common in echinoderm steroid sulfates,[1] and a sponge sterol glycoside with a C-23 alcohol has been described,[13] no C-23 ketone is known to date. It is interesting to note that in contignasterol (**3**), a highly oxygenated sponge steroid which was reported to be the first example of a steroid with a 14β proton configuration,[14,15] C-29 is also oxidized to a carbonyl and forms a hemiacetal with an alcohol at C-22 (Scheme II).

Scheme II. Possible Biogenesis of the Side Chain of Contignasterol



Kiheisterones A and B exhibit mild cytotoxicity against several cell lines. IC_{50} values of 5 μg/mL were determined in assays against A-549 lung carcinoma and HT-29 colon adenocarcinoma human tumor cell lines and 2.5 μg/mL against the P388 murine lymphocytic leukemia cell line. Both compounds are more cytotoxic against nontumorous monkey kidney cells, with an IC_{50} of 0.2 μg/mL.

Experimental Section

Isolation. The sponge, order Poecilosclerida,[3] was collected at -10–20 m in Maalaea Bay near Kihei, Maui, on June 4, 1991. A 112.9-g portion of the freeze-dried sponge was extracted overnight with 1.5 L of CH_2Cl_2/2-propanol (1:1). The extract was evaporated in vacuo to yield 6.0 g of a deep red solid, which was partitioned among 1 L of EtOAc/CH_2Cl_2/H_2O (1:1:1). The upper layer was concentrated in vacuo to give 2.8 g, which was partitioned between 300 mL of hexanes/MeOH (2:1). A 0.50-g portion of the MeOH layer residue was subjected to silica gel flash chromatography using a gradient of hexanes to ether. The fraction containing the furanosteroids (62.5 mg) was passed through a C-18 gravity column, eluting with methanol. Final purification was accomplished with reversed-phase HPLC (MeOH/H_2O, 9:1, Phenomenex Ultracarb 5 μm ODS 30, 10- × 250-mm column) to afford 8 mg each of **1** and **2**.

1: hard colorless glass; $[\alpha]_D$ +144° (*c* 1.72, MeOH); EIMS *m/z* 468 (M^+, 7), 422 (1), 285 (1), 137 (5), 123 (100); HR EIMS *m/z* 468.2863 (calcd for $C_{29}H_{40}O_5$ 468.2876); UV (MeOH) λ_{max} 266 nm (ϵ 10300); IR (neat) 3450, 2960, 2930, 2870, 1705, 1670, 1410, 1075 cm^{-1}; ^{13}C NMR and ^1H NMR, see Table I.

2: fine white needles, mp 223–225 °C; $[\alpha]_D$ +19° (*c* 0.70, $CHCl_3$); HR EIMS *m/z* 468.2863 (calcd for $C_{29}H_{40}O_5$ 468.2876); IR (Nujol mull) 3450, 1705, 1670 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 11.8 (C-18), 20.9 (C-11), 22.2 (C-19), 23.4 (C-26), 23.5 (C-27), 23.8 (C-15), 24.1 (C-25), 27.2 (C-16), 27.4 (C-6), 27.4 (C-7), 28.6 (C-22), 35.7 (C-8), 37.2 (C-12), 40.8 (C-10), 41.7 (C-9), 42.2 (C-13), 43.6 (C-5) 47.1 (C-20), 48.4 (C-1), 52.2 (C-17), 55.1 (C-14), 108.4 (C-28), 123.0 (C-4), 126.8 (C-24), 140.5 (C-29), 146.5 (23), 147.0 (C-3), 177.8 (C-21), 195.7 (C-2); ^1H NMR ($CDCl_3$) δ 0.67 (s, 3 H, H-18), 0.95 (m, 1 H, H_{ax}-7), 0.96–1.03 (m, 3 H, H-14, H_{ax}-12, H-15), 1.04 (d, 6 H, *J* = 6.8 Hz, H-26, H-27), 1.05 (s, 3 H, H-19), 1.26–1.33 (m, 4 H, H-8, H-9, H_2-11), 1.35 (m, 1 H, H_a-16), 1.46 (bd, 1 H, *J* = 13.0 Hz, H_{eq}-7), 1.56 (m, 2 H, H_{eq}-6, H-15), 1.60 (m, 1 H, H_{eq}-12), 1.62 (bq, 1 H, *J* = 9.8 Hz, H-17), 1.83 (tt, 1 H, *J* = 14.1, 4.2 Hz, H_{ax}-6), 1.89 (m, 1 H, H_b-16), 2.18 (d, 1 H, *J* = 16.5 Hz, H_a-1), 2.53 (td, 1 H, *J* = 11.1, 4.2 Hz, H-20), 2.61 (bs, 1 H, H-5), 2.62 (d, 1 H, *J* = 16.5 Hz, H_b-1), 2.67–2.76 (m, 3 H, H_2-22, H-25), 5.70 (d, 1 H, *J* = 2.6 Hz, H-4), 6.14 (d, 1 H, *J* = 1.9 Hz, H-28), 7.15 (1 H, d, *J* = 1.9 Hz, H-29).

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Supplementary Material Available: ^1H, ^{13}C, HMQC, and HMBC NMR spectra for **1** and ^1H and ^{13}C NMR spectra for **2**

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Highly Functionalized Benzobarrelene Derivatives. Bromination of 2-Bromo-5,6-benzobicyclo[2.2.2]octa-2,6-diene: High Temperature Bromination. 3.[1]

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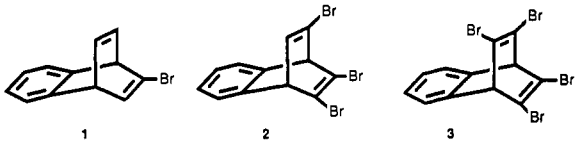
Introduction

In a continuation of our investigation of high-temperature bromination[3] of bicyclic systems we report on the addition of bromine to 2-bromobenzobarrelene (1). Recent work has revealed that bromination of 1 gives five rearranged products via Wagner–Meerwein rearrangement with accompanying aryl and alkyl migration. However, the bromination of 1 at 78 °C resulted in the formation of nonrearranged products with the bicyclo[2.2.2]skeleton. In this paper, we describe the high-temperature reaction of 1 with 2 equiv of Br_2 and the synthesis of tri- and tetrasubstituted benzobarrelene derivatives 2 and 3. These have potential importance for exploring the effect of different substituents in the same molecule on the course of the di-π-methane rearrangement.[4]



1 2 3

Results and Discussion

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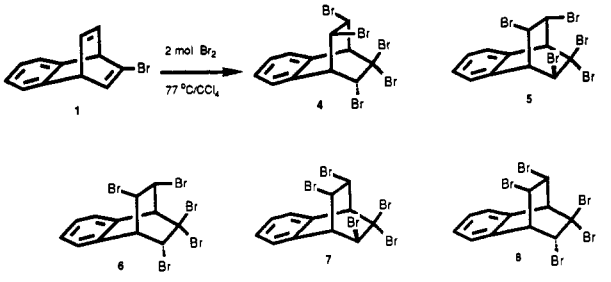
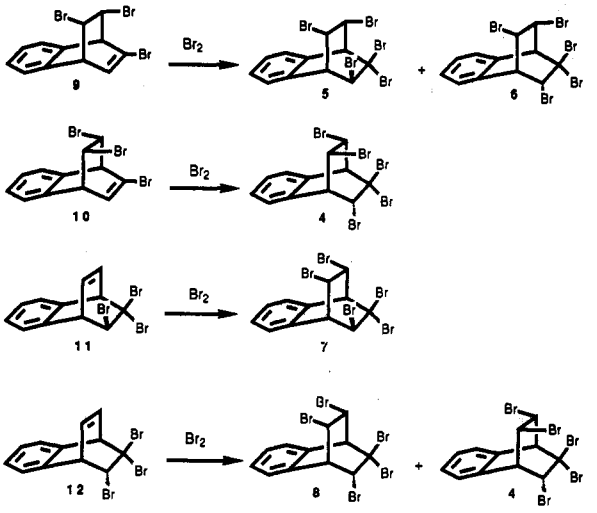
The starting material 1 was prepared by our published method[5] starting from benzonorbornadiene and was subjected to bromination[6] in refluxing carbon tetrachloride. The reaction mixture was kept for 15 min at reflux temperature and led to a considerably complex mixture consisting of five products. The resulting mixture was crystallized from methylene chloride/carbon tetrachloride, and we isolated 4 as the major product in a yield of 36%. The rest of the mixture was subjected to repeated column chromatography, and we isolated four additional products 5–8 in yields of 9, 18, 5, and 7%, respectively (Scheme I). The structure of these compounds has been elucidated on the basis of the spectral data obtained by ^1H NMR and ^{13}C NMR experiments (Table I) and chemical transformations. The ^1H and ^{13}C NMR spectra indicated that only nonrearranged products were formed during this reaction. Because of the very close structural similarity we were not able to make a clear-cut differentiation between the stereochemistry in any of these materials containing five bromine atoms. Therefore, we carried out an X-ray

Scheme I



Scheme II



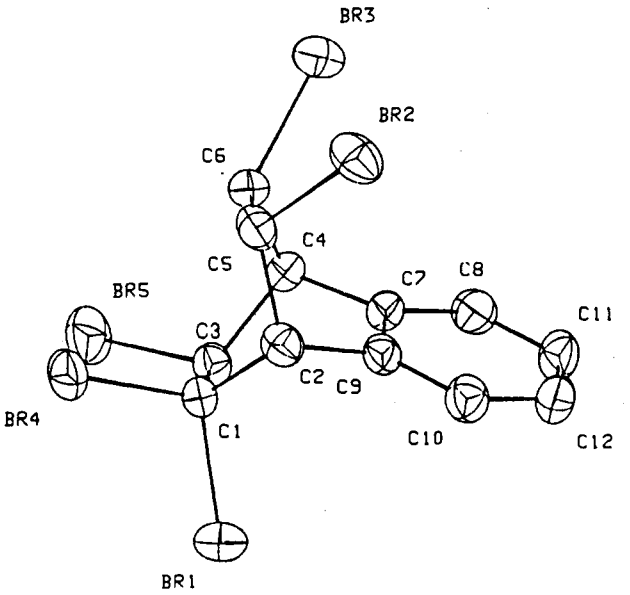


Figure 1. X-ray crystal structure of 7.

(1) For part 2 see: Balci, M.; Çakmak, O.; Hökelek, T. *Tetrahedron*, in press.

(2) Author to whom inquiries regarding the X-ray crystallographic analysis should be addressed.

(3) (a) Çakmak, O.; Balci, M. *Tetrahedron Lett.* **1989**, *31*, 2349. (b) Çakmak, O.; Hökelek, T.; Büyükgüngör, O.; Balci, M. *Tetrahedron Lett.* **1990**, *31*, 2345.

(4) (a) Hixon, S. S.; Mariano, P. S.; Zimmermann, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmermann, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; New York, 1991.

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(6) For bromination of similar systems see: (a) Lobanova, T. P.; Benus, E. I.; Barkash, V. A. *Zh. Obsch. Khim.* **1960**, *39*, 2332. (b) Lobanova, T. P.; Slyko, N. M.; Derendyaev, B. G.; Barkash, V. A. *Zh. Org. Khim.* **1970**, *6*, 2473. (c) Lobanova, T. P.; Derendyaev, B. G.; Kollegova, M. I.; Barkash, V. A. *Zh. Org. Khim.* **1973**, *9*, 1883. (d) Smith, W. B. *J. Org. Chem.* **1985**, *50*, 5731.

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