$(CH_3)_2CH$), 2.95 (m, 1 H, TMSC*H*), 3.5 (m, 2 H, NCH_2), 3.65–4.25 (m, 3 H, OCH_2, NC*H*). ^{13}C NMR: δ 160.74, 70.12, 69.91, 69.69, 46.97, 44.95, 33.29, 25.38, 22.84, 18.56, 17.61, −1.0. IR: 1655 (C=N). Anal. ($C_{14}H_{28}N_2OSi$) C, H.

(*S*)-1-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]-2(*R*)-methylpiperidine (5b). The product was obtained in 30% yield, isolated by radial chromatography and purified by distillation, bp 105 °C (0.5 mm). ^1H NMR: δ 0.9 (dd, 6 H, J = 7 Hz, $(CH_3)_2CH$), 1.15 (d, 3 H, J = 8 Hz, $NCHCH_3$), 1.55 (br, 7 H, $CH(CH_3)_2$, $NCH_2(CH_2)_3$), 3.3 (br, 3 H, NCH_2, NC*H*), 3.65 (m, 1 H, C=NC*H*), 3.84–4.25 (m, 2 H, OCH_2). ^{13}C NMR: δ 161.11, 69.83, 47.90, 40.50, 33.24, 29.87, 25.41, 18.72, 18.54, 17.55, 17.33, 14.69. IR: 1650 (C=N). Anal. ($C_{12}H_{22}N_2O$) C, H.

(*R*)-1-(1-Naphthoyl)-2-methylpiperidine. To a solution of 603 mg of **5b** (2.87 mmol) in 8 mL of THF was added dropwise 1.26 g (5 equiv) of acetic formic anhydride.[35] The mixture was refluxed for 48 h and concentrated under reduced pressure. The crude *N*-formylpiperidine was then dissolved in 4 mL of 50% NaOH and refluxed for 18 h. The reaction mixture was cooled to room temperature and diluted with 10 mL of chloroform. 1-Naphthoyl chloride (5 equiv was then added dropwise to the two-phase solution. The mixture was shaken for 20–30 min, and then the layers were separated. The aqueous layer was extracted with chloroform. The combined organic layers were dried over magnesium sulfate, condensed in vacuo. The crude product was purified by radial chromatography. HPLC analysis on a Pirkle column showed this material to be the *R* enantiomer by co-injection with an authentic sample of racemic naphthamide independently prepared from racemic 2-methylpiperidine.[12]

(*S*)-1-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]-2(*R*,*S*)-(6-hexenyl)piperidine (5d) and (*S*)-1-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]-2(*R*,*S*)-(cyclopentylmethyl)-piperidine (5e). Yield: 51% of a 1:1.3 mixture of the two structural isomers, each obtained as a 1:1 mixture of diastereomers. The four isomers were preparatively inseparable but were purified by radial chromatography and distilled from calcium hydride, bp 160 °C (0.05 mm). Anal. ($C_{17}H_{30}N_2O$) C, H. GC–MS confirmed the presence of two pairs of stereoisomers.

(*S*)-1-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]-2(*R*),6-(*R*)-dimethylpiperidine (6). Yield: 46%. The product was isolated by radial chromatography and purified by bulb-to-bulb distillation: bp 93.5 °C (0.1 mm). 500-MHz ^1H NMR: δ 0.9 (dd, 6 H, $(CH_3)_2CH$), 1.7 (m, 1 H, $(CH_3)_2CH$), 1.23 (d, 6 H, CH_3CHN), 1.45 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 1.85 (m, 2 H, CH_2), 3.87 (m, 3 H, C=NC*H*, NC*H*), 4.0–4.2 (m, 2 H, OCH_2). 75-MHz ^{13}C NMR: δ 161.8, 70.89, 69.68, 69.12, 48.90, 33.10, 30.01, 19.50, 18.99, 18.46, 17.98, 17.85, 16.15. IR: 1650 (C=N). Anal. ($C_{13}H_{24}N_2O$) C, H.

(*S*)-1-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]-1,4,5,6-tetrahydropyridine (7). This compound was obtained as a side product from several alkylations of **3**. It was isolated by radial chromatography and purified by bulb-to-bulb distillation: bp 100–103 °C (0.3 mm). ^1H NMR: δ 0.9 (dd, 6 H, J = 7 Hz, $(CH_3)_2CH$), 1.85 (m, 1 H, $CH(CH_3)_2$), 2.05 (m, 4 H, $NCH_2CH_2CH_2$), 3.65 (br t, 2 H, NCH_2), 4.8 (m, 1 H, NCH=C*H*), 6.65 (br d, 1 H, NC*H*=CH). ^{13}C NMR: δ 157.88, 125.82, 103.26, 70.76, 70.11, 43.57, 33.23, 21.48, 21.05, 18.80, 17.70. IR: 1675 (C=C), 1690 (C=N). Anal. ($C_{11}H_{18}NO_2$) C, H.

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Registry No. 1, 17016-83-0; 2, 102922-29-2; 3, 102922-36-1; 5a, 102922-43-0; 5b, 102922-42-9; 5d (isomer 1), 102922-39-4; 5d (isomer 2), 102922-46-3; 5e (isomer 1), 102922-47-4; 5e (isomer 2), 102922-40-7; 6, 102922-38-3; 7, 102922-37-2; (*R*)-1-(1-naphthoyl)-2-methylpiperidine, 90132-88-0; diethyl carbonate, 105-58-8; (*S*)-valinol, 2026-48-4; triethyloxonium tetrafluoroborate, 368-39-8; piperidine, 110-89-4; trimethylsilyl chloride, 75-77-4; 1-naphthoyl chloride, 879-18-5.

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Bromination of (1*RS*,2*RS*,5*RS*)-2,3-Dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene. A New and Convenient Synthesis of Disubstituted Benzobarrelenes

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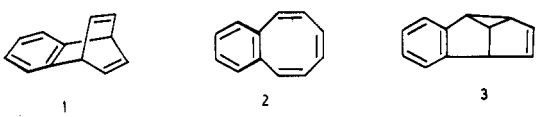
Bromination of (1*RS*,2*RS*,5*RS*)-2,3-dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene (**1**) at −20 °C has been found to give only one product, the tetrabromide **10** via Wagner–Meerwein rearrangement with accompanying aryl migration. Radicalic bromination at room temperature produced nonrearranged tetrabromides, the rearranged tetrabromide **10**, the ketones **13** and **14**, and addition–elimination products **11** and **12**. Structures of the products were determined by ^1H and ^{13}C NMR data and chemical means. The double dehydrobromination of **10** was achieved by using potassium *tert*-butoxide to give 2,3-dibromobenzobarrelene (**20**). Reaction of **20** with *n*-BuLi and subsequent quenching with CH_3I, CO_2, and H_2O afforded the corresponding substituted benzobarrelenes.

Introduction

Benzobarrelene (**1**) is a molecule of considerable potential mechanistic interest. Zimmerman et al.[1] have reported that benzobarrelene (**1**) undergoes two types of photochemical reactions, one leading to benzocyclooctatetraene (**2**) proceeding from the singlet state of **1** via (2π + 2π)-cycloaddition and the other leading to semibulvalene (**3**) from the triplet excited state via di-π-methane rearrangement. Furthermore, deuterium labeling studies revealed that of the two bonding routes; vinyl–vinyl bridging and vinyl–aryl bridging, the last one is mainly utilized. However, di-π-methane rearrangement was uniquely provided by the vinyl–vinyl bridging. By the



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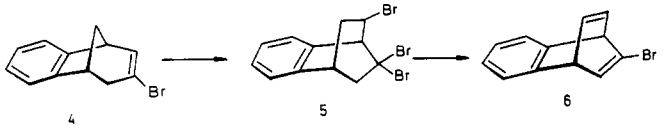
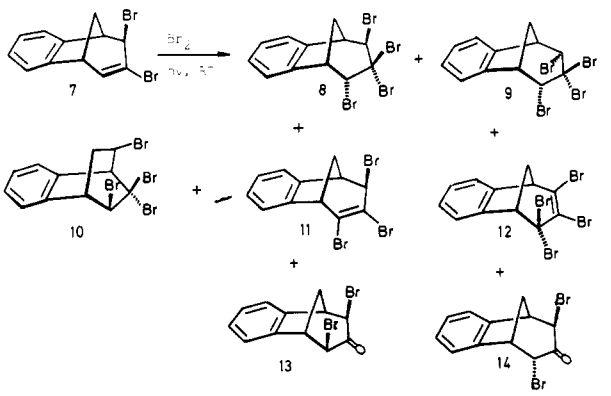
0022-3263/89/1954-0181$01.50/0

Scheme I



Scheme II



introduction of a substituent in a vinyl location the symmetry of benzobarrelene skeleton is destroyed. Therefore, the number of possible initial bonding modes is increased to three ($2\pi + 2\pi$)-cycloadditions and six di-π-methane rearrangements. On this basis, vinyl-substituted benzobarrelenes gain importance by elucidation of the mechanism of the ($2\pi + 2\pi$)-cycloaddition reaction and di-π-methane rearrangement. Some monosubstituted benzobarrelenes[2] have been synthesized by reaction of benzyne with substituted benzenes. From these reactions resulted a complex mixture that could not be separated easily and the reported yields were very low. Recently, we presented an alternative large-scale preparation of substituted benzobarrelenes[3] by bromination of **4** at −50 °C followed by dehydrobromination (Scheme I). Reaction of **6** with *n*-BuLi and subsequent quenching with various electrophiles afforded the corresponding substituted benzobarrelenes in high yields.

In a continuation of our investigation of the electrophilic addition of bromine to bicyclic systems,[4] we report on the addition of bromine to the (1*RS*,2*RS*,5*RS*)-2,3-dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene (**7**) and synthesis of some disubstituted benzobarrelenes that have potential importance to explore the substituent effect in the di-π-methane rearrangement.

Results and Discussion

The starting material **7** was synthesized by addition of dibromocarbene to the readily available benzonorbornadiene[5] as reported in the literature.[6] We observed that **7** and bromine reacted in the dark and at room temperature very slowly compared to the reaction of **4** with bromine to give addition products. We have already shown that the *exo*-bromonium ion was formed exclusively as an intermediate by the reaction of **4** with bromine. The exo orientation of the bromine at the C_2 carbon in **7** provides a sufficient bulk for an incoming bromine from the exo face of the molecule, which results in decreasing the reaction rate.

When the solution of **7** and bromine in CH_2Cl_2 was irradiated with a sunlamp (150 W) at room temperature, the starting material was consumed completely in 3.5 h. We assume that these reactions are occurring by a radical mechanism. The reaction led to a considerably complex mixture. After repeated and careful silica gel chromatography, we isolated seven products (Scheme II). These structural assignments follow mainly from ^1H and ^{13}C NMR and mass spectral data and chemical transformations (Table I).

It has been already shown[7] that the addition of bromine to unsaturated benzobicyclic systems can lead to a multiplicity of products. The intermediate formed by addition of bromine ion or bromine radical to the double bond can give nonrearranged products or undergo Wagner–Meerwein rearrangement involving either an aryl group or alkyl group. All products isolated by this reaction, except **10**, show no skeleton rearrangement.

The mass spectra of **8** and **9** (M^+ = 470/472/474/476/478) and analysis of the ^1H and ^{13}C NMR spectra indicated the existence of four bromine atoms in **8** and **9**. That **8** is unsymmetrically substituted was evident from its 12-line ^{13}C NMR spectrum. On the other hand, a seven-line ^{13}C NMR spectrum is in good agreement with the structure **9**, which possesses a symmetry element. However, ^{13}C NMR does not give any indication about the stereochemistry of the bromine atoms at the C_2 and C_4 carbon atoms in **9**. Normally one has to expect from the exo configuration of bromine in the starting material **7** that the bromine atoms at C_2 and C_4 also have to be in the exo positions due to the symmetrical structure. The configuration of these bromines at the C_2 and C_4 carbons has been established by analysis of the AB system arising from the bridge methylene protons H_{8e} and H_{8i}. The bridge protons at C_8 in **8** and **9** appear as an AB system. B parts of these AB systems (H_{8e}) show in both cases a doublet. There is no further measurable coupling with the adjacent bridge head protons H_1 and H_5 due to nearly 90° dihedral angles between H_{8e} and H_1 and H_5. However, the A part of the AB system in **8** is split into triplets of doublets of doublets. The second doublet splitting ($^4J_{28e}$ = 1.9 Hz) originates from the proton on C_4 which is in the endo position. In the case of ^4J in the bicyclic systems one speaks of the M or W arrangement. The bonding arrangement of the coupled protons H_2 and H_{8i} meets the M criterion. In the case of **9** we do not observe any measurable coupling between H_{8i} and H_2 and H_4, which indicates the exo orientation of the protons, in other words endo orientation of the bromine atoms in **9**. Furthermore, the chemical shift differences between the external bridge protons H_{8e} ($\Delta\delta$ = 0.76 ppm) in **8** and **9** also support the proposed configuration of the bromine atoms. There is no considerable chemical shift difference between the resonances of the internal hydrogens H_{8i} ($\Delta\delta$ = 0.05 Hz) in **8** and **9**. H_{8e} in **8** resonates at lower field (2.96 ppm) compared to the H_{8e} (2.20 ppm) in **9**. This fact can be explained on the basis of strong steric repulsion between H_{8e} in **8** and neighboring

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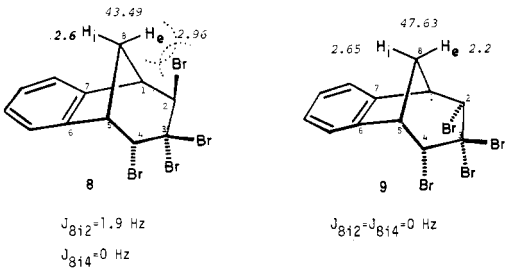
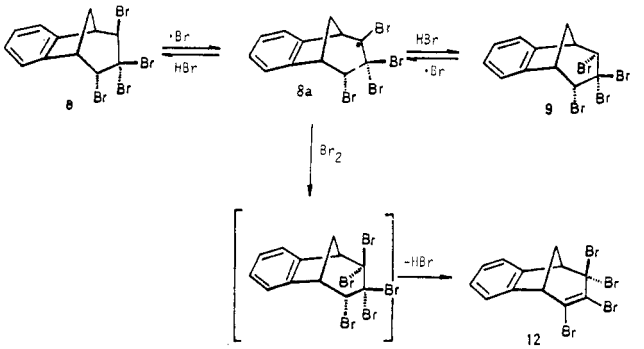


bromine in the exo position. Any steric repulsion between H_{8e} and geminal bromines is out of the question due to the chair conformation of the cyclohexane ring. It is well known that interactions related to the van der Waals effect cause a paramagnetic contribution to the shielding constants, which results in a shift to lower field.[8] Moreover, this configurational finding was also supported by ^{13}C NMR chemical shifts of the methylene carbons. Tori et al.[9] discovered the remarkable γ-syn (shielding) and γ-anti (deshielding) effects exerted by a cyclopropane ring annulated to the bicyclo[2.2.1]heptane skeleton upon its bridging carbon atoms, C_8. More recently, new examples were discovered.[10] Typical γ-gauche effects are also observed in methylnorbornanes. Other substituents, e.g., the halogens, cause γ-effects up to −7 ppm. Downfield chemical shift of the methylene carbon in **9** compared to the chemical shift of the methylene carbon in **8** is associated with the endo configuration of the bromine atom in **9**.

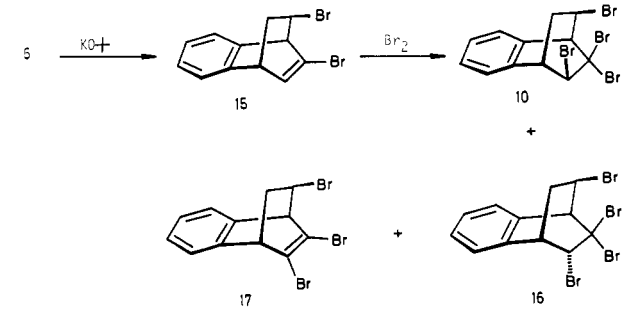
A symmetrically substituted tetrabromo compound, expected from this reaction, must have the exo–exo configuration instead of the isolated endo–endo product **9**. In order to shed light into the formation mechanism of **9**, we studied the chemical behavior and stability of all isolated products under the applied reaction conditions and noticed that the bromine-catalyzed irradiation of the tetrabromo compound **8** provided **9** and **12**. For this conversion we suggest the following mechanism[12] (Scheme III). Bromine radical produced by irradiation of bromine can abstract a hydrogen atom at the C_2 carbon, forming the tetrabromo radical **8a** with a planar structure.[13] **8a** can form in a reversible manner the endo–endo tetrabromide **9** and the starting material **8**. Reaction of **8a** with bromine can provide the pentabromide, which can be converted easily to the tetrabromide **12**.

The only isolated rearrangement product (**10**) was formed in a yield of 1.6%. The proton and carbon NMR assignments for this structure were readily rationalized and an authentic sample was prepared by an independent route starting from **5**, whose structure was determined by X-ray structural analysis.[14] Dehydrobromination of **5** with 1 mol

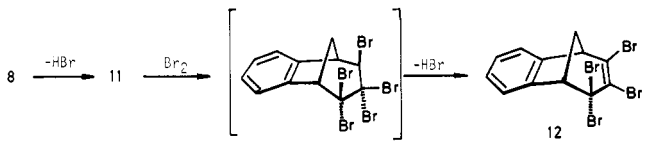
Scheme III



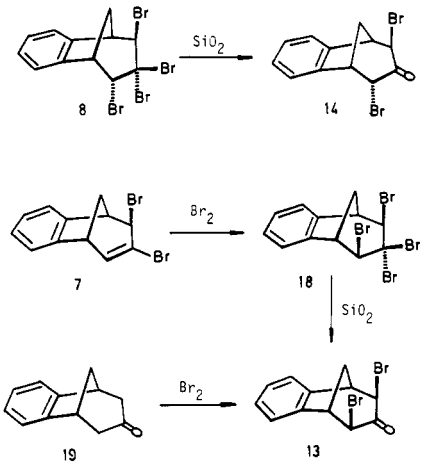
Scheme IV



Scheme V



Scheme VI



of potassium *tert*-butoxide gave the expected dibromo compound **15** with the exo configuration (Scheme IV). Bromination of the double bond in **15** provided two isomers **10** and **16** from which the major isomer was identical with that obtained by bromination of **7**. The correct stereochemical assignments to **10** and **16** were made by proton NMR spectroscopy (Table I).

The tribromo compound **11** is formed by dehydrobromination of **8** during the reaction. Independent bromination of the isolated pure sample of **11** followed by spontaneous dehydrobromination provided **12** as sole product. With this reaction we established the origin of the tetrabromide **12** (Scheme V).

The formation mechanism of the dibromo ketones **13** and **14** is given in Scheme VI. We assume that the primarily formed tetrabromide **8** partly and tetrabromide **18**

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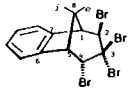
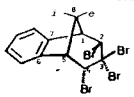
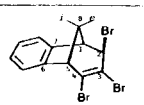
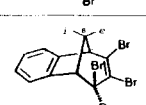
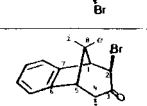
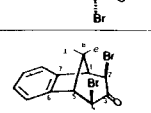
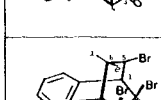
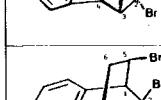
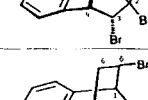
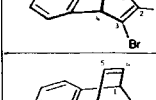
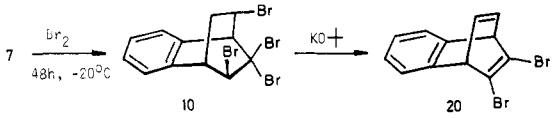
Table I. ^1H and ^{13}C NMR Spectral Data of the Compounds 8, 9, 10, 11, 12, 13, 14, 16, 17, and 20 (All Values Are in ppm, Downfield from Internal Me_4Si, in $CDCl_3$ Solutions)

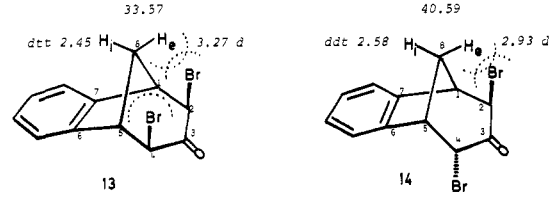
Compound	C/H 1	2	3	4	5	6	8i	8e	Aromatic prot.	Other ^{13}C-Values	Coupling Constants
 [a] 8	3.84 t 50.69	5.57 dd 62.99	--- 67.60	4.9 d 61.54	3.63 dd 49.66	---	2.60 ddt AB-System 43.49	2.96 d	7.42 m 1H 7.26 m 3H	143.95 140.36 128.42 128.35 125.99 124.26	$J_{12} = J_{45} = 2.2$ Hz $J_{58i} = J_{18i} = 4.8$ Hz $J_{8i8e} = 11.8$ Hz, $J_{8i2} = 1.9$ Hz
 [d] 9	3.60 dd 50.76	4.95 d 62.92	--- 70.67	4.95 d 62.92	3.60 dd 50.76	---	2.65 dt AB-System 47.63	2.20 d	7.40 m 2H 7.25 m 2H AA'BB'-Sys.	140.15 128.29 125.71	$J_{12} = J_{45} = 2.2$ Hz $J_{8i5} = J_{8i1} = 4.8$ Hz $J_{8i8e} = 11.8$ Hz
 [b] 11	3.85 d 53.05	--- 	--- 	4.75 dd 56.71	3.80 dd 50.17	---	2.4 ddt AB-System 39.45	2.83 d	7.15-7.30 m 4H	149.69 140.87 134.37 127.81 127.60 125.08 121.82 120.15	$J_{45} = 2$ Hz $J_{58i} = J_{18i} = 4.5$ Hz $J_{8i8e} = 11.5$ Hz, $J_{48i} = 1.5$ Hz
 [d] 12	4.25 d	---	---	---	3.70 d	---	2.40 dt AB-System	2.85	7.00-7.60 m 4H		$J_{18i} = J_{58i} = 4.6$ Hz $J_{8i8e} = 11.6$ Hz
 [d] 14	3.64 t 49.77	4.45 t 51.38	--- 193.71	5.42 d 57.65	3.75 t 48.06	---	2.58 ddt AB-System 40.40	2.93 d	7.25-7.45 m 4H	141.68 141.28 128.92 128.42 126.40 124.20	$J_{12} = 3.2$ Hz, $J_{45} = 3.0$ Hz $J_{18i} = J_{58i} = 4.6$ Hz $J_{8i8e} = 12.0$ Hz, $J_{20i} = 2.3$ Hz
 [b] 13	3.65 dd 47.44	4.30 dd 47.86	--- 198.54	4.30 dd 47.86	3.65 dd 47.44	--- ---	2.45 dtt AB-System 33.57	3.27 d	7.25-7.35 AA'BB'-Sys. 4H	142.45 129.44 124.92	$J_{12} = J_{45} = 2.9$ Hz, $J_{8i8e} = 12.7$ Hz $J_{18i} = J_{58i} = 5.0$ Hz $J_{20i} = J_{48i} = 2.1$ Hz
 [c] 10	4.17 s 46.21[e]	--- 63.18	4.95 t 65.00	3.25 ddd 44.67[e]	4.13 m 59.41	6e 2.25 dddd AB-System 27.15	6i 2.59 ddd	---	7.15-7.35 m 4H	139.57 136.52 128.92 128.30 125.69 124.85	$J_{36i} = 2.1$ Hz
 [c] 16	4.25 s 46.23	--- 64.59	5.31 d 64.85	3.28 m 42.94	4.24 m 59.70	2.3-2.5 m AB-System 37.38		---	7.16-7.35 m 4H	139.41 132.95 128.68 128.07 126.98 125.98	$J_{34} = 2.13$ Hz $J_{36i} = 0.0$ Hz
 [a] 17	4.52 d 51.93	--- 124.72[e]	--- 122.96[e]	4.20 t 45.54	4.11 m 59.21	2.27-2.38 m 38.42		---	7.15-7.39 4H	140.15 138.79 127.33 126.76 124.00 123.23	$J_{15} = 2.76$ Hz $J_{46i} = J_{46e} = 2.70$ Hz
 [c] 20	4.95 58.56	--- 129.41	--- 129.41	4.95 A-part of AA'XX'-sys 58.56	6.93 X-part of AA'XX' sys. 138.69	6.93 138.69	---	---	6.96-7.22 AA'BB'-Sys. 4H	144.54 124.58 122.61	

[a] 400-MHz ^1H NMR, 100-MHz ^{13}C NMR. [b] 360-MHz ^1H NMR, 90-MHz ^{13}C NMR. [c] 300-MHz ^1H NMR, 75-MHz ^{13}C NMR. [d] 60-MHz ^1HNMR. [e] Interchangeable.

Scheme VII



completely hydrolyze to **14** and **13**, respectively. Inspection of the models indicates that the isomer **18** has the most steric interaction between the bromines and other groups. Due to this effect it was not possible to isolate this isomer (**18**). The structure of **14** was established unambiguously by ^1H and ^{13}C NMR spectra. Asymmetry in the molecule supported exo and endo configuration of the bromine atoms. Finally, x-ray structural analysis of **14** confirms the structural findings.[15] The ^1H NMR and ^{13}C NMR spectra of **13** were highly characteristic. Analysis of the AB system arising from the bridge methylene protons shows that the high field part (2.45 ppm, H_{8i}) is split into doublets of triplets of triplets (J = 12.7, 5.0, 2.1 Hz). The second triplet splitting is reconcilable only with an exo–exo arrangement of the two substituents. ^{13}C NMR chemical shifts in **13** and **14** were also completely in agreement with the structures and results obtained by ^{13}C NMR spectra of **8** and **9**. Independently, bromination of **19** in CCl_4 gave **13** quantitatively.



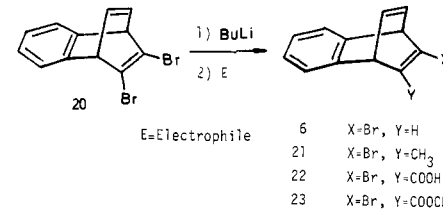
For the synthesis of the benzobarrelenes, we were interested in the rearranged product **10**. During the bromination reaction of **7**, **10** was formed in a yield of only 1.6%. Recently, we have observed[4] that the product distribution in the bromination of **4** is dependent strongly on the reaction temperature. Therefore, we studied the bromination of **7** at different temperatures and reaction conditions and found out that the bromination in dichloromethane solution at −20 °C, in the dark and 48 h, led to quantitative yield to **10** (Scheme VII).

It is evident from the bromine configuration in **10** that the initial attack by the bromine has occurred from the sterically less favored side of the π-system. The homoconjugative interaction between the developing cationic center and the aryl π-electron center plays an important role in promoting attack from the less favored side of the double bond. This reasoning explains the sole formation of **10**. In the case of endo attack, we should expect either unrearranged products or products involving alkyl bridge shift.

This key step serves both to bring about the requisite skeletal rearrangement and to provide the functionality that permits easy introduction of the double bonds. In the final step, the double dehydrobromination of **10** was achieved with surprising efficiency by using potassium *tert*-butoxide. With 2 mol of potassium *tert*-butoxide we isolated dibromobenzobarrelene (**19**) in a yield of 88%. The proton and carbon NMR spectra showed the expected symmetry in the molecule. The ^1H NMR spectrum consists of an AA′BB′ system (aromatic protons) and an AA′XX′ system arising from the bridgehead protons and the double-bond protons. A six-line ^{13}C NMR spectrum

(15) Büyükgüngör, O., to be published.

Scheme VIII



is in good agreement with structure **19**.

Dibromobenzobarrelene (**20**) was the key compound for the synthesis of the other disubstituted benzobarrelene derivatives. When **20** was treated with 1.2 equiv of *n*-BuLi/THF at −78 °C for $^1/_2$ h, followed by H_2O, CH_3I, and CO_2, the product are as shown in Scheme VIII.

The presently described synthesis offers advantages. It begins with a readily available starting material, benzonorbornadiene, and subsequent steps are all efficient and readily applicable to large-scale preparation. On the other hand, this route offers several possibilities for isotopically labeling the bicyclic skeleton and introduction of different substituents by replacing the second bromine atom.

Experimental Section

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from solution in 0.1-mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The ^1H NMR spectra were recorded on EM 360 Varian, Bruker WM 300, Bruker WM 360, and Bruker WM 400 spectrometers and reported in δ units with Me_4Si as internal standard. Apparent splittings are given in all cases. Mass spectra were recorded on a Finnigan-MAT MS Model 4000 mass spectrometer at an ionizing voltage 70 eV. Analytical thin-layer chromatography (TLC) was performed on silica gel 60_{254} plates. Column chromatography was done on silica gel (60–200 mesh) from Merck Company.

Bromination of (1*RS*,2*RS*,5*RS*)-2,3-Dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene (7).[6] To a solution of 2 g (6.37 mmol) of *exo*-dibromide **7** in 60 mL of CH_2Cl_2 was added dropwise, with stirring and during 3.5 h, a solution of 1.1 g (6.9 mmol) of bromine in 25 mL of CH_2Cl_2 at room temperature. The reaction flask was irradiated during the reaction with a 150-W sunlamp. The reaction mixture was allowed to stir $^1/_2$ h and the solvent was removed under reduced pressure. The oily residue was crystallized from CH_2Cl_2/petroleum ether (3:1) to give tetrabromide **8** (1540 mg, 51%).

(1*RS*,2*RS*,4*RS*,5*SR*)-2,3,3,4-Tetrabromo-6,7-benzobicyclo[3.2.1]oct-6-ene (8): colorless crystals, mp 130–131 °C; MS, m/e 470/472/474/476/478 (M^+); IR (KBr, cm^{-1}) 2940, 1470, 1460, 1295, 1185, 1130, 1250, 980, 790. Anal. Calcd for $C_{12}H_{10}Br_4$: C, 30.42; H, 2.13; Br, 67.46. Found: C, 30.25; H, 2.36; Br, 66.98.

After filtration of the tetrabromide **8**, the organic solvent was evaporated and the oily residue (1.5 g) was subjected to silica gel (100 g) chromatography, eluting with petoleum ether. The first component isolated was identified as **12**.

(1*RS*,5*RS*)-2,3,4,4-Tetrabromo-6,7-benzobicyclo[3.2.1]-octa-2,6-diene (12) (110 mg, 3.6%): colorless crystals, mp 115–116 °C from $CHCl_3$/*n*-hexane (1:3); MS, m/e (relative intensity) 468/470/472/474/476 (M^+, 12), 389/391/393/395 (M^+ − Br, 8), 310/312/314 (M^+ − 2Br, 11), 231/233 (M^+ − 3Br, 10), 152 (naphthalene, 100); IR (KBr, cm^{-1}) 2940, 1565, 1465, 1440, 1300, 1180, 1120, 1030, 940, 750. Anal. Calcd for $C_{12}H_8Br_4$: C, 30.54; H, 1.71; Br, 67.75. Found: C, 30.38; H, 1.63; Br, 67.38.

The second component proved to be **11**.

(1*RS*,4*SR*,5*SR*)-2,3,4-Tribromo-6,7-benzobicyclo[3.2.1]-octa-3,6-diene (**11**) (300 mg, 10%). A pure sample of this compound was obtained by recrystallization from $CHCl_3$/hexane as a colorless crystalline solid, mp 100–101 °C: MS, m/e 390/392/394/396 (M^+); IR (KBr, cm^{-1}) 2940, 1580, 1465, 1295, 1230, 1160, 1125, 1100, 1025. Anal. Calcd for $C_{12}H_9Br_3$: C, 36.68; H, 2.31; Br, 61.01. Found: C, 36.43; H, 2.26; Br, 60.23.

As third fraction we isolated the tetrabromide **8** (430 mg, 14%, total yield 65%). Continued elution with the same solvent afforded the rearranged product **10**.

(1*SR*,3*SR*,4*SR*,10*RS*)-2,2,3,10-Tetrabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (48 mg, 1.6%): colorless crystals, mp 141–142 °C (from dichloromethane–hexane); MS, *m/e* (relative intensity) 470/472/474/476/478 (M^+, 5), 391/393/395/397 (M^+ – Br, 3), 311/313/315 (M^+ – Br, – HBr, 7), 284/286/288 (M^+ – Br, – HBr, –HC≡CH, 100), 206/208 (naphthalene dibromide, 64), 152 (95); IR (KBr, cm^{-1}) 2940, 1310, 1250, 1225, 1190, 1100, 1000, 945, 860. Anal. Calcd for $C_{12}H_{10}Br_4$: C, 30.42; H, 2.13; Br, 67.46. Found: C, 30.55; H, 2.27; Br, 66.31.

Further elution with petroleum ether furnished **9**.

(1*RS*,2*SR*,4*RS*,5*SR*)-2,3,3,4-Tetrabromo-6,7-benzobicyclo[3.2.1]oct-6-ene (80 mg, 2.7%): mp 170–171 °C, colorless crystals from chloroform–hexane; MS, *m/e* (relative intensity) 470/472/474/476/478 (M^+, 6), 391/393/395/397 (M^+ – Br, 2), 311/313/315 (M^+ – Br, – HBr, 8), 287 (13), 264 (30), 153 (80), 73 (100); IR (KBr, cm^{-1}) 2935, 1460, 1210, 990, 795, 760.

Elution with $CHCl_3$–petroleum ether (2:1) gave as the sixth fraction the symmetric dibromo ketone **13**.

(1*RS*,2*RS*,4*SR*,5*SR*)-2,4-Dibromo-3-oxo-6,7-benzobicyclo[3.2.1]oct-6-ene (13) (64 mg, 2.2%): mp 156–157 °C, colorless crystals from CH_2Cl_2–petroleum ether; IR (KBr, cm^{-1}) 2995, 1710, 1450, 1305, 1195, 1000, 860, 760. Anal. Calcd for $C_{12}H_{10}OBr_2$: C, 43.67; H, 3.05; Br, 48.43. Found: C, 43.41; H, 3.15; Br, 48.63.

Finally, elution with $CHCl_3$–petroleum ether gave as the last fraction **14**.

(1*RS*,2*RS*,4*RS*,5*SR*)-2,4-Dibromo-3-oxo-6,7-benzobicyclo[3.2.1]oct-6-ene (14) (170 mg, 5.8%): mp 128–130 °C, colorless crystals from CH_2Cl_2–hexane; MS, *m/e* (relative intensity) 328/330/332 (M^+, 3), 249/251 (M^+ – Br, 68), 170 (M^+ – 2Br, 83), 151 (90), 128 (75), 115 (100); IR (KBr, cm^{-1}) 2960, 2910, 1720, 1470, 1455, 1340, 1200, 1155, 1105, 1075, 970, 855, 800, 765.

Bromination of 7 at –20 °C. A solution of bromine (4.9 g, 30.0 mmol) in 20 mL of CH_2Cl_2 was added dropwise and during $^1/_2$ h to a CH_2Cl_2 solution (40 mL) of dibromide (3.14 g, 10.0 mmol) **7** at –20 °C in the dark. The mixture was stirred for 48 h at –20 °C and the solvent was evaporated. The ^1H and ^{13}C NMR data of the crude material indicated that only one product was formed quantitatively and this product (**10**) was identical with that obtained by reaction of bromine with **7** at room temperature as the third fraction. An analytical pure sample was obtained by crystallization from $CHCl_3$/*n*-hexane (2:3): colorless crystals, mp 141–142 °C.

Bromination of (1*SR*,4*RS*,10*RS*)-2,10-Dibromo-1,4-dihydro-1,4-ethanonaphthalene (15). A magnetically stirred solution of **15** (628 mg, 2 mmol) in 20 mL of dry chloroform cooled to 0 °C was treated dropwise with a solution of bromine (320 mg, 2 mmol) in 10 mL of chloroform during 45 min. After completion of the addition, the solution was allowed to warm to 20 °C. The solvent was evaporated and the residue was subjected to chromatography on silica gel (70 g). Elution with petroleum ether afforded 44 mg (5%) of (1*SR*,4*SR*,10*RS*)-2,3,10-tribromo-1,4-dihydro-1,4-ethanonaphthalene (**17**), which was recrystallized from $CHCl_3$–hexane (1:3). The colorless crystals had the following: mp 134–135 °C; MS, *m/e* (relative intensity) 390/392/394/396 (M^+, 6), 284/286/288 (M^+ – HBr, – HC≡CH, 55), 205/207 (M^+ – Br, – HBr, – HC≡CH, 8), 152 (56), 76 (100); IR (KBr, cm^{-1}) 2970, 1610, 1480, 1465, 1090, 965, 850.

The second component isolated was identified as **10** (642 mg, 65%).

Lastly, 242 mg (24.5%) of (1*SR*,3*RS*,4*SR*,10*RS*)-2,2,3,10-tetrabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**16**) was isolated: white needles, mp 177–178 °C (from $CHCl_3$–hexane); IR (KBr, cm^{-1}) 2960, 1475, 1460, 1350, 1190, 1100, 950, 860, 750. Anal. Calcd for $C_{12}H_{10}Br_4$: C, 30.42; H, 2.13; Br, 67.46. Found: C, 30.13; H, 2.28; Br, 66.21.

Reaction of 8 with Bromine. To a solution of 474 mg (1 mmol) of tetrabromide **8** in 15 mL of $CHCl_3$ was added 160 mg (1 mmol) of bromine. The reaction mixture was stirred magnetically while being irradiated with a 150-W sunlamp for 17 h at room temperature. The solvent was removed under reduced pressure. The residue was subjected to chromatography on silica gel (35 g). Elution with petroleum ether gave as the first fraction the tetrabromide **12** (255 mg, 53%). Continued elution with the same solvent afforded **11** as the second fraction (40 mg, 10%). Further elution with petroleum ether furnished **9** (115 mg, 24%) as the last fraction.

Bromination of 11 (Synthesis of 12). To a magnetically stirred solution of **11** (79 mg, 0.2 mmol) in 10 mL of CCl_4 was added bromine (50 mg, 0.3 mmol) in 2 mL of CCl_4. The resulting reaction mixture was irradiated with a sunlamp (150 W) for 2.5 h at room temperature. Evaporation of solvent gave **12** as sole product in a yield of 97%. The spectral data of this compound was in full agreement with those obtained by bromination of **7** as first fraction.

Dibromo Ketone 13. A solution of **19** (86 mg, 0.5 mmol) in 10 mL of dry chloroform cooled to 0 °C was treated with a solution of bromine (160 mg, 1 mmol) in 2 mL of chloroform while being stirred magnetically. After completion of the addition the solution was stirred for $^1/_2$ h. Evaporation of the solvent gave **13** as single product (157 mg, 95%). An analytically pure sample was obtained by recrystallization from CH_2Cl_2–hexane. This product was identical with those obtained by bromination of **7** as the sixth fraction.

2,3-Dibromo-1,4-dihydro-1,4-ethenonaphthalene (20). To a solution of 2.5 g (22 mmol) of potassium *tert*-butoxide in 150 mL of dry and freshly distilled tetrahydrofuran was added dropwise a solution of **10** (4.74 g, 10 mmol) in 20 mL of dry THF while stirring mechanically. The resulting reaction mixture was refluxed for 4 h. After being cooled to room temperature, the solution was poured into a mixture of petroleum ether (100 mL) and water (100 mL). The layers were separated and the aqueous phase was extracted with petroleum ether. The combined organic layers were washed with water (2 × 50 mL), dried, and evaporated to leave a pale yellow oil, which was distilled at reduced pressure (1 mmHg, 120 °C) to give the dibromobenzobarrelene **20** (2.74 g, 88%): mp 71–72 °C, colorless needles from dichloromethane–pentane (2:5); MS, *m/e* (relative intensity) 310/312/314 (M^+, 9), 231/233 (M^+ – Br, 6), 152 (M^+ – 2Br, 100); IR (KBr, cm^{-1}) 1610, 1460, 1450, 1310, 1260, 1215, 1185, 1060, 980, 910, 840, 755. Anal. Calcd for $C_{12}H_8Br_2$: C, 46.20; H, 2.58; Br, 51.22. Found: C, 46.10; H, 2.42; Br, 50.93.

2-Bromo-3-methyl-1,4-dihydro-1,4-ethenonaphthalene (21). To a solution of **20** (624 mg, 2 mmol) in 15 mL of freshly distilled THF was added dropwise a solution of butyllithium (3.6 mL, 2.4 mmol) in hexane under a nitrogen atmosphere at –70 °C. The reaction mixture was stirred for an additional 15 min. At the same temperature was added a solution of CH_3I (320 mg, 2.2 mmol) in 5 mL of THF during 30 min. After allowing the reaction to come to room temperature, a part of the THF was removed under reduced pressure. To the resulting mixture were added 50 mL of H_2O and 50 mL of petroleum ether, and the combined organic layers were washed with water and dried. After removal of solvent the oily residue was subjected to bulb-to-bulb distillation at 150 °C and 1 mmHg. The distillate was crystallized from diethyl ether/*n*-pentane (1:6). **21**: 341 mg (69%), mp 44–45 °C; ^1H NMR (60 MHz, CCl_4) δ 6.6–7.2 (m, 6 H), 4.45–4.8 (m, 2 H), 1.8 (s, 3 H); IR (KBr, cm^{-1}) 3080, 2960, 1450, 1310, 1270, 1130, 990, 800, 750.

3-Bromo-1,4-dihydro-1,4-ethenonaphthalene-2-carboxylic Acid (22). A stirred solution of **20** (936 mg, 3 mmol) in dry THF (20 mL) was cooled to –70 °C under a nitrogen atmosphere and treated dropwise with a solution of butyllithium (2.8 mL, 3.2 mmol) in hexane. After completion of the addition, stirring was continued for 15 min; 1 g of CO_2 was added at –70 °C and the solution was stirred for a further 15 min, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. A part of the THF was removed under reduced pressure and 30 mL of H_2O was added. To the aqueous phase was added dilute HCl until pH 1 and then the solution was extracted two times with 50 mL of diethyl ether. The combined organic layers were dried and evaporated. The oily residue was subjected to column chromatography (20 g, Al_2O_3). Elution with petroleum ether afforded bromobenzobarrelene **6** as the first fraction (75 mg, 8%). Further elution with diethyl ether gave a mixture of **22** and benzobarrelene-2-carboxylic acid (**25**).[3a] The acid mixture was separated by repeated crystallization. **22**: (581 mg, 70%), mp 167–168 °C, colorless crystals from diethyl ether–pentane (5:1); ^1H NMR (60 MHz, $CDCl_3$) δ 10.5 (br s, 1 H), 6.75–7.4 (m, 6 H), 5.50 (t, 1 H), 5.05 (t, 1 H); IR (KBr, cm^{-1})

3500–2700, 1660, 1580, 1430, 1310, 1250.

25 was formed in a yield of 7% (40 mg). This compound was identical with that reported in the literature.[3a]

2-Carbomethoxy-3-bromo-1,4-dihydro-1,4-ethenonaphthalene (23). The acid **22** (277 mg, 1 mmol) was esterified with diazomethane and the derived ester was purified by filtration through a short silica gel (5 g) column: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.7–7.3 (m, 4 H), 6.9 (t, 2 H), 5.5 (t, 1 H), 4.95 (t, 1 H), 3.7 (s, 3 H); IR (NaCl, film, cm^{-1}) 3080, 2960, 1720, 1620, 1590, 1440, 1320, 1310, 1250.

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Registry No. (±)-**6**, 117269-28-0; (±)-**7**, 117404-71-4; (±)-**8**, 117269-29-1; **9**, 117404-72-5; (±)-**10**, 117405-97-7; (±)-**11**, 117269-30-4; (±)-**12**, 117269-31-5; **13**, 54143-22-5; (±)-**14**, 117404-73-6; (±)-**15**, 117404-74-7; (±)-**16**, 117269-32-6; (±)-**17**, 117269-33-7; **19**, 13351-26-3; **20**, 117269-34-8; (±)-**21**, 117269-35-9; (±)-**22**, 117269-36-0; (±)-**23**, 117269-37-1; (±)-**25**, 117269-38-2.

Lewis Acid Promoted Reactions of Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones with Ethyl Diazoacetate[1]

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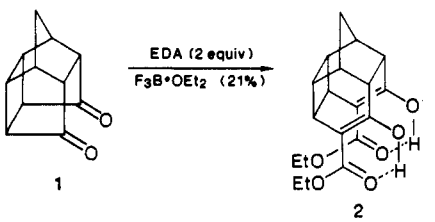
Reaction of 1-X-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones [X = CH_3 (**3**), phenyl (**4**), *p*-cyanophenyl (**9**), and *p*-methoxyphenyl (**13**)] with 1 equiv of EDA in the presence of $F_3B{\cdot}OEt_2$ affords the corresponding monohomologation products [**5** (25%), **6** (25%), **10** (61%), and **14** (37%), respectively]. The structures of **5**, **6**, **10**, and **15** (the product formed via decarboxylation of **14**) were determined by single-crystal X-ray structural analysis. Reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**1**) with 1 equiv of ethyl diazoacetate (EDA) in the presence of boron trifluoride etherate affords ethyl 2,6-dioxopentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane-3-carboxylate (**16a**, 21%) as the major monohomologation product along with ethyl 4,10-dioxotetracyclo[6.4.0.0^{2,6}.0^{5,9}]dodec-11-ene-11-carboxylate (**19**, 17%). Decarboxylation of **16a** with NaCl–DMSO afforded **17** (79%). Subsequent Friedlaender condensation of **17** with *o*-aminobenzaldehyde in the presence of base afforded **18** (73%). The structure of **18** was established by single-crystal X-ray structural analysis.

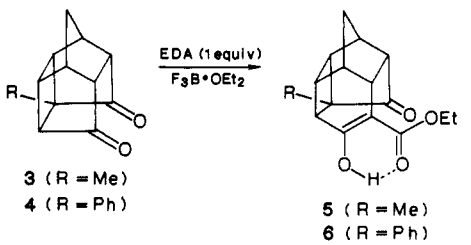
As part of a program designed to explore the synthesis and chemistry of novel functionalized polycyclic cage molecules,[2] we recently reported the results of a study of the Lewis acid promoted reaction of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (PCUD-8,11-dione, **1**) with ethyl diazoacetate (EDA).[3] A single, substituted pentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]tridecane, **2** (Scheme I), was isolated from the reaction of **1** with 2 equiv of EDA in the presence of boron trifluoride etherate. The structure of **2** was established via single-crystal X-ray structural analysis.[3]

In an effort to extend this reaction to synthesize new derivatives of the pentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodecane ring system, we have undertaken a study of the corresponding boron trifluoride promoted reaction of unsymmetrically substituted PCUD-8,11-diones (i.e., **3** and **4**, Scheme II) with 1 equiv of EDA.[4] In each case, a single monohomologation product was isolated. Not surprisingly, the less hindered of the two carbonyl groups in both **3** and **4** suffered attack by EDA. However, the regiochemistry of the ring-expanded products (**5** and **6**, respectively) thereby obtained in each case is *opposite* of that which we reported earlier[3] for the corresponding bishomologation product, which is formed when **1** is reacted with 2 equiv of EDA in the presence of boron trifluoride etherate. Confirmation of the structures of ring-expanded products **5** and **6** (which served to define the regiochemistry of homologation) was obtained via single-crystal X-ray structural analysis (vide infra).

Scheme I



Scheme II



In the light of our previously published observation[3] regarding the regiochemistry of EDA–$F_3B{\cdot}OEt_2$-promoted

(1) Dedicated to Professor Michael J. S. Dewar on the occasion of his 70th birthday.

(2) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT, Vol. 1, in press.

(3) Marchand, A. P.; Arney, B. E., Jr.; Gilardi, R.; Flippen-Anderson, J. L. *J. Org. Chem.* **1987**, *52*, 3455.

(4) Marchand, A. P.; Annapurna, G. S. *Abstracts of Papers*; 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 30–Sept 4, 1987; American Chemical Society: Washington, DC, 1987; Abstr ORGN 9.

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