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Received March 8, 1995

Revised June 29, 1995

The application of the Ramberg-Backlund reaction in the conversion of several 3,*n*-dithiabicyclo[*n*.3.1]alkatrienes to the corresponding bicyclo[*n*.3.1]alkapentaenes is reported. Proton magnetic resonance and ultraviolet spectra were utilized in the overall characterization of bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene, bicyclo[9.3.1]pentadeca-2,9,11,1(15)-pentaene, and their precursors. The final step in the synthesis was a Ramberg-Backlund of a *bis*- α,α' -chloro sulfone. The intermediate, 2-chloro-3-thiabicyclo[9.3.1]pentadeca-9,11,13,1(15)-tetraene 3,3-dioxide, was isolated and characterized. The structure and stability of the bridged α,α' -dichloro sulfide intermediates were examined.

J. Heterocyclic Chem., 32, 1467 (1995).

Introduction.

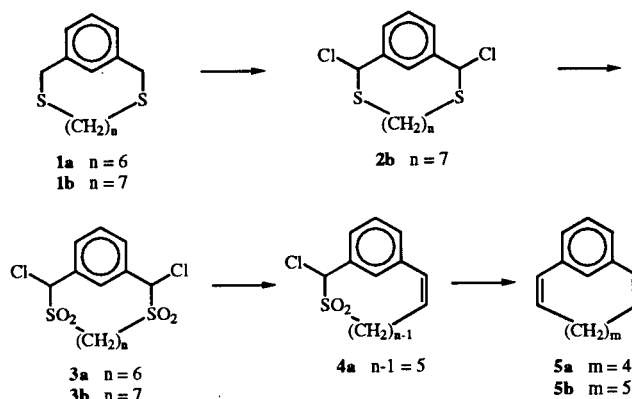
Reviews of the Ramberg-Backlund reaction that include synthetic applications have appeared in the literature [3,4,5]. There is a wealth of evidence that supports a step-wise mechanism, involving the intermediacy of thiirane dioxides, for the reaction of α -haloalkylsulfones with base in protic media [6]. While thiirane dioxides cannot be isolated usually from Ramberg-Backlund reactions due to the facility with which these intermediates lose sulfur dioxide, a highly substituted thiirane dioxide was isolated from the reaction of an α -iodosulfone with base [7,8]. Previously, convincing evidence was presented that indicated the existence of a relatively stable tetrasubstituted thiirane dioxide, *cis*-1,2-dimethyl-1,2-diphenylthiirane 3,3-dioxide, from the reaction of the corresponding α -bromosulfone with base [9].

The Ramberg-Backlund reaction has been utilized to synthesize highly strained alkenes and bridged aromatic systems [10,11,12]. In a previous communication, we reported the synthesis and characterization of several bicyclo[*n*.2.2]alkapentaenes from 3,*n*-dithia[*n*.2.2]alkatrienes *via* the reaction of the corresponding *bis*- α,α' -chlorosulfones with base [13]. The synthesis and availability of the α -halosulfone limit the synthetic utility of the Ramberg-Backlund reaction for bridged aromatic systems. In this paper we describe the chlorination reaction of 3,*n*-dithiabicyclo[*n*.3.1]alkatrienes, the oxidation of the chlorinated intermediates to α,α' -dichlorosulfones, and conversion of the latter compounds to bicyclo[*n*.3.1]alkapolyenes *via* reaction with base.

Results and Discussion.

It has been documented in the literature that the critical step in the synthesis of bridged systems *via* the Ramberg-Backlund method is the halogenation of the sulfide [14]. Thus, the chlorination reaction of 3,*n*-dithia[*n*.3.1]alkatrienes (**1**) was examined carefully. Pmr spectral analysis

Scheme 1



of a reaction mixture of 3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (**1b**) and highly purified *N*-chlorosuccinimide showed that chlorination had occurred,

Table I

Proton Nuclear Magnetic Resonance Shifts of 3,*n*-Dithia[*n*.3.1]alkatrienes

Compound	Proton Shifts, ppm
3,11-Dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (1b)	7.40 (s, 1H), 7.15 (s, 3H), 3.63 (s, 4H), 2.30 (t, 4H), 1.35 (m, 10H)
3,10-Dithiabicyclo[10.3.1]hexadeca-12,14,1(16)-triene (1a)	7.15 (s, 4H), 3.70 (s, 4H), 2.41 (t, 4H), 1.15 (m, 8H)
3,9-Dithia[9.3.1]bicyclopentadeca-11,13,1(15)-triene (1c)	7.43 (s, 1H), 7.10 (s, 3H), 3.60 (s, 4H), 2.21 (t, 4H), 1.20 (m, 6H)
2,12-Dichloro-3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (1b)	7.40 (s, 1H), 7.10 (s, 3H), 4.47 (s, 2H), 3.60 (t, 4H), 1.34 (m, 10H)
2,12-Dichloro-3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene 3,3,11,11-tetroxide (3b)	7.75 (s, 1H), 7.30 (s, 3H), 4.57 (s, 2H), 3.67 (t, 4H), 1.35 (m, 10H)
2,11-Dichloro-3,10-dithiabicyclo[10.3.1]hexadeca-12,14,1(16)-triene (2a)	7.50 (m), 7.15 (s), 4.70 (m), 3.95 (s), 2.68 (q), 1.80 (m), 1.25 (m)

Table II
Characteristics of Bicyclo[n.3.1]alkapolyenes

Compound	Proton Shifts ppm,	Appearance	Yield
Bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene (5b)	7.75 (s, 1H), 7.00 (m, 3H), 6.28 (d, 2H), 6.00 (m, 2H), 2.25 (q, 4H), 1.43 (m, 6H)	Yellow Oil	25%
Bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene (5a)	7.60 (s, 1H), 7.18 (m, 3H), 6.28 (d, 2H), 5.72 (m, 2H), 1.85 (q, 4H), 1.14 (m, 4H)	Yellow Oil	32%
2-Chloro-3-thiabiacyclo[9.3.1]pentadeca-9,11,13,1(15)-tetraene 3,3-dioxide (4a)	7.20 (m, 3H), 6.40 (d, 1H), 5.80 (m, 1H), 2.98 (m, 2H), 1.92 (m, 2H), 1.30 (m, 6H)	mp 114°	25%

as expected, at the benzylic position (the most acidic proton was replaced) [15]. The *bis*- α -chlorosulfide was unstable at room temperature, yielding a dark resinous material in 24 hours. Previous reports indicate that introduction of a chlorine atom on a carbon *alpha* to a sulfur atom enhances the rate of introduction of a second chlorine atom on the same carbon. The inductive electron withdrawing power of the chlorine atom is presumably responsible for this effect. Contrary to previous reports [15], the same product was obtained from the addition of four and of two equivalents of *N*-chlorosuccinimide to 3,11-dithiabiacyclo[11.3.1]heptadeca-13,15,1(17)-triene. Failure to introduce more than one chlorine atom at each benzylic carbon may reflect the crowded nature of these cyclic systems.

A summary of the proton magnetic resonance spectral data of these intermediates is given in Table III. The chemical shifts of the benzyl protons and the protons attached to the carbon *alpha* to the sulphur atom were compared for the parent sulfide and the chlorinated products. In 3,11-dithiabiacyclo[11.3.1]heptadeca-13,15,1(17)-

triene (1b) the chemical shift of the benzyl proton (b) is 3.63 ppm while the shift of the α -methylene protons (a) is 2.30 ppm. Introduction of the electronegative chlorine atom causes a downfield shift of these protons; the chemical shift of the benzal proton (d) became 4.47 ppm, while the shift of α -methylene protons (c) became 3.60 ppm. Oxidation of the sulfur atoms of the chlorinated compounds causes a slight downfield shift of protons on adjacent carbons; the benzal proton (f) shift became 4.57 ppm and the α -proton (e) shift was 3.67 ppm.

Examination of the proton magnetic resonance spectra of dithiabiacyclo[n.3.1]alkatriene 1b and the intermediates leading to bicyclo[n.3.1]alkapentaene 5a suggest that rotation about the carbon to sulfur single bonds is relatively free in these medium-sized ring systems. If rotation were not relatively free, stereoisomers would have been observed. The α -chloro sulfone was allowed to react with base in tetrahydrofuran to yield the bicyclo[n.3.1]alkapentaene (Scheme I).

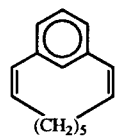
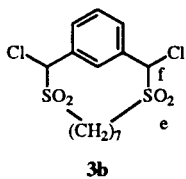
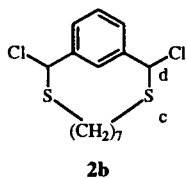
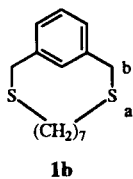
Proton magnetic resonance spectroscopy was utilized in the identification of the structures of the bicyclo[n.3.1]-alkapentaenes 5a and 5b, and the related tetraene 4a. The spectral data is summarized in Table II. The 60 MHz spectrum of 5b contained multiplets at 1.43 ppm for the six methylene protons, a quartet for the four allyl protons at 2.25 ppm, a multiplet at 6.00 ppm for the two vinyl protons, a doublet for the two benzal protons at 6.28 ppm and a multiplet at 7.00 ppm for three of the aromatic protons and a singlet at 7.75 ppm for the remaining aromatic proton. The spectrum of 5a contained similar shifts. The chemical shifts observed were consistent with the assigned structures and could be interpreted in terms of a single conformation in solution.

The ultraviolet spectra for bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene (5b) and bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene (5a) were obtained in connection with an analysis of their conformations. Wavelengths of maximum absorbance (λ_{\max}) and molar absorptivities for pertinent structures are listed in Table IV. The uv data indicate that the two double bonds in the aliphatic bridge of bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene (5b) are coplanar and conjugated with the benzene ring as illustrated in 5a. The vinyl linkages and the benzene nucleus may assume coplanarity.

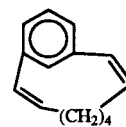
Table III

Chemical Shifts of Benzylic and Alpha Protons in 3,*n*-Dithiabiacyclo[n.3.1]alkatriene Derivatives

Proton	Chemical Shift, ppm	
a	2.30	$\delta v_{ac} = 1.30$
b	3.63	$\delta v_{ac} = 0.84$
c	3.60	$\delta v_{ce} = 0.07$
d	4.47	$\delta v_{df} = 0.10$
e	3.67	
f	4.57	



5a-conformer



5b-conformer

The molar absorptivity of pentaene 5b is 25,381 while the reference, *cis*- β -methylstyrene, has a molar absorptivity of 12,589. When more than one absorbing chro-

mophore is present, the observed ultraviolet absorption spectrum will be the sum of the uv spectra of the individual chromophores if there is no direct electronic interaction between chromophores [16]. Since vinyl linkages are attached (1,3)- to each other in bicyclo[n.3.1]alkapentaene **5b**, this system may be regarded as being composed of two independent substituted styrene units. Thus one would expect, for **5b**, the same approximate wavelength of maximum absorption and twice the molar absorptivity of *cis*- β -methylstyrene. Experimental data support this hypothesis since the observed molar absorptivity of **5b** is approximately twice that observed for β -methylstyrene (see Table IV).

In the more strained system, bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene (**5a**), the aliphatic bridge is more likely to assume the less crowded puckered conformation, **5a**-conformer, with the aliphatic bridge slightly tilted above the face of the benzene ring. The molar absorptivity of this diene **5a** is 14,286, which is greater than the value of the molar absorptivity of the reference, *cis*- β -methylstyrene, but considerably less than the molar absorptivity observed for the less strained bicyclo[9.3.1]pentadecapentaene (**5b**). Molar absorptivities for both systems **5b** ($\lambda_{\max} = 248$, $\epsilon = 25,381$) and **5a**, ($\lambda_{\max} = 242$, $\epsilon = 14,286$) indicate that the vinyl linkages are conjugated with the benzene ring. A more planar conjugated conformation, **5a**-conformer, would be expected to have a longer wavelength for maximum absorbance than one, **5b**-conformer, tilted out of plane. The wavelength of maximum absorbance observed for **5a** and **5b** indicate that conjugation in the less strained diene **5a** is more extensive. Although it is difficult to predict absorption maxima for complex systems such as the ones considered here, comparison of data on closely related systems, **5a** and **5b**, is informative [17].

The ultraviolet spectra for the bicyclo[n.3.1]alkapentaenes support our previous interpretation of ultraviolet data for bicyclo[n.2.2]alkapentaenes [13]. In each case, ultraviolet data indicate that the more highly strained bicycloalkapentaene adopts the less planar conformation (with the aliphatic bridge above the face of the aromatic ring).

Table IV

Ultraviolet Absorption Characteristics of Structurally Related Systems

Compound	Maximum Wavelength, nm	Molar Absorptivity
Bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene	248	25,381
Bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene	242	14,286
Bicyclo[11.2.2]heptadeca-2,11,13,15,16-pentaene	251	10,710
<i>cis</i> - β -Methylstyrene	241	12,589

Dreiding molecular models of these systems suggest that the bicyclo[11.2.2]heptadecapentaene (**1c**) would assume the nonplanar conformation while the bicyclo[n.3.1]alkapentaenes **5a** and **5b** would assume a more planar conjugated conformation.

Conclusions.

The dithiabicyclo[n.3.1]alkatrienes were prepared, utilizing 1,*n*-alkanediisothiuronium salts as dithiol synthons in yields comparable to or greater than those reported in the literature [18,19]. Elemental analytical data and the proton magnetic resonance spectral analysis of the bicyclo[n.3.1]-alkapentaenes provided proof of the structures. Also, the structures of the intermediate dithiabicyclo[n.3.1]-alkatrienes **1**, the corresponding α,α' -dichlorosulfides **2** and α,α' -dichlorosulfones **3** were confirmed by proton magnetic resonance spectral analysis. The chlorination of the dithiabicyclo[n.3.1]alkatrienes was the critical step in synthetic sequence, as previously reported in the literature [14,20]. Data on *N*-chlorosuccinimide chlorination of 3,*n*-dithiabicyclo[n.3.1]alkatrienes support the findings of Tuleen and Stephens [15] that the most acidic proton, the benzylic hydrogen, is replaced by a chlorine atom. Paquette [21] and others [15] reported that geminal dihalogenation is enhanced by the introduction of the first halogen atom, since the α -hydrogen becomes more acidic [22]. An examination of reaction mixtures of dithiabicyclo[n.3.1]alkatriene with two and with four equivalents of *N*-chlorosuccinimide indicated the presence of the same dichlorosulfide. This indicates that dichlorination at an α -carbon is not enhanced by introduction of the first chlorine atom. The instability of the *bis*- α,α' -chlorosulfide intermediates **2** was demonstrated during this investigation.

The oxidation of the *bis*- α,α' -chlorosulfides **2** to the corresponding *bis*- α -chlorosulfones **3** was efficiently done with *m*-chloroperoxybenzoic acid. Dehydrochlorination of the *bis*-chlorosulfone **3** to diene is efficient when carried out with potassium *t*-butylate in tetrahydrofuran. Therefore, the Ramberg-Backlund synthetic procedure is a suitable method for the preparation of bicyclo[n.2.2]-alkapentaenes.

The conformational analysis of bicyclo[n.3.1]alkapentaenes by ultraviolet spectrophotometry supported the previously published analysis of bicyclo[n.2.2]alkapentaenes [13]. The more strained hydrocarbon, bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene (**5a**), assumed a more puckered conformation.

EXPERIMENTAL

Melting points were determined by the capillary method on a Mel-temp apparatus and are uncorrected. All chemicals and reagents were reagent grade unless otherwise stated. Proton

nuclear magnetic resonance spectra were determined on a Varian EM-360 NMR spectrometer (60 MHz). Chemical shifts are reported in parts per million downfield from an internal standard, tetramethylsilane, and were determined in chloroform-d solution. Ultraviolet spectra were run in acetonitrile on a Beckman Model 24 spectrophotometer. Elemental analyses were obtained at Instranal Laboratory, Inc., Rensselaer, NY.

1,7-Heptanedithiouronium Dibromide (1) [22].

A 29 g (0.38 mole) sample of thiourea was dissolved in 350 ml of 100% ethanol by heating. A 50 g (0.19 mole) sample of 1,7-dibromoheptane was dissolved in 50 ml of ethanol. The two solutions were combined and refluxed for 18 hours. The ethanol was then evaporated under reduced pressure on a rotary evaporator. A solid was isolated from a medium of diethyl ether-ethanol (80:40). A crystalline solid was obtained (78 g, 67%), mp 238-239°.

3,11-Dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene.

A 16.4 g (0.040 mole) sample of 1,7-heptanedithiouronium dibromide was added to 200 ml of water that contained 8 g (0.20 mole) of sodium hydroxide. The mixture was heated at 90° for 2 hours and allowed to stand for at least 18 hours to form the corresponding dimercaptide in solution. A 7.0 g (0.040 mole) sample of *bis*-1,3-(chloromethyl)benzene was dissolved in 200 ml of benzene. This solution and the above dimercaptide solution were added simultaneously (dropwise with precision dropping funnels) to 1.4 liters of refluxing ethanol over a 4 hour period. The solution was allowed to reflux overnight. The total volume of the reaction mixture was reduced to approximately 100 ml under reduced pressure. The solution was then extracted with two 100 ml portions of chloroform. The chloroform was evaporated, leaving a yellow oil. This oil was recrystallized from methanol. White crystals of (1b) were obtained (4.3 g, 40%, mp 56-58°, lit mp 58° [18]). Utilizing the appropriate dithiouronium salt and dimercaptide, 3,10-dithiabicyclo[10.3.1]hexadeca-12,14,1(16)-triene (1a) were prepared by the same procedure in thirty-eight percent (3.8 g, mp 64-66°, lit mp 64° [18]). Data on the dithiabicyclo[n.3.1]alkatriene are summarized in Table I.

2,12-Dichloro-3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (2b).

A 0.20 g (0.0007 mole) sample of 3,11-dithiabicyclo[11.3.1]hepta-13,15,1(17)-triene (1b) was dissolved in 20 ml of carbon tetrachloride. A 0.20 g (0.0015 mole) sample of purified, powdered *N*-chlorosuccinimide was added and the mixture was stirred magnetically for two hours. The mixture was filtered to remove the suspended succinimide. The solvent was evaporated under pressure at 30-35°. 2,11-Dichloro-3,10-dithiabicyclo[10.3.1]hexadeca-12,14,1(16)-triene (2a) was prepared by the same procedure and on the same molar scale. Deuterated chloroform was added and proton nuclear magnetic spectrum was run. The nmr data are summarized in Tables I and II.

3,11-Dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene-3,3,11,11-tetroxide (3c).

A 0.20 g (0.0006 mole) sample of 3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (1b) was dissolved in 15 ml of dichloromethane. A 0.65 g (0.0050 mole) sample of *m*-chloroperoxybenzoic acid was added and the solution was stirred magnetically for 48 hours. A 15 ml portion of saturated sodium bicarbonate solution was added and the solution was

stirred three more hours. The bilayered solution was filtered by suction to remove a white solid mp 260°. This solid was insoluble in both chloroform-d and acetonitrile-d. The nmr spectrum could not be determined.

2,12-Dichloro-3,11-dithiabicyclo[11.3.1]heptadeca-13,15,1(17)-triene-3,3,11,11-tetroxide (3b).

A 0.27 g (0.0005 mole) sample of 3,11-dithiabicyclo[11.3.1]heptadeca-13,1,1(17)-triene (1b) was dissolved in 15 ml of dichloromethane. A 0.65 g (0.0050 mole) sample of *m*-chloroperoxybenzoic acid was added and the solution was magnetically stirred for 24 hours. A 15 ml portion of saturated sodium bicarbonate solution was added and the solution was stirred two more hours. The bilayered solution was filtered by suction. The product was dissolved in deuterated chloroform and the proton nuclear magnetic resonance spectrum was run. The nmr data are summarized in Table I.

Bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene (5b).

A 1.6 g (0.0060 mole) sample of dithiabicyclo[11.3.1]heptadecatriene (1b) and 1.8 g (0.0130 mole) purified, powdered *N*-chlorosuccinimide (freshly recrystallize from eight parts of water) were allowed to react in 75 ml of carbon tetrachloride for 2 hours. A 5.0 g (0.024 mole) sample of *m*-chloroperoxybenzoic acid was dissolved in 100 ml chloroform. The carbon tetrachloride solution was filtered into the chloroform solution. The combined solution was magnetically stirred for 18 hours. The solution was then extracted with 100 ml saturated sodium bicarbonate. The organic layer was dried over magnesium sulfate and the solvent was evaporated. A 100 ml portion of tetrahydrofuran and 3.5 g (0.031 mole) of potassium butylate were added. This mixture was magnetically stirred for 21 hours. The solvent was evaporated and 70 ml of water were added. The resulting solution was extracted with two 100 ml portions of chloroform and dried over magnesium sulfate. The solvent was evaporated leaving a yellow oil (1.6 g crude yield). This oil was dissolved in 25 ml of carbon tetrachloride, filtered, and the solvent evaporated. A proton NMR spectrum of the crude mixture gave evidence of pentaene formation. For purification, the product (in 5 ml of chloroform) was placed on an alumina column (d = 2 cm), and chromatographed with carbon tetrachloride as the eluting solvent. Five 40 ml fractions of eluent were collected. The pure diene was eluted in fractions two and three (0.31 g, 25%). A proton nuclear magnetic resonance spectrum was run to confirm the structure and determine the purity of the pentaene. NMR data is listed in Table II.

Bicyclo[8.3.1]tetradeca-2,8,10,12,1(14)-pentaene (5a) and 2-Chloro-3-thiabicyclo[9.3.1]pentadeca-9,11,13,1(15)-tetraene 3,3-Dioxide (4a).

A 1.30 g (0.0050 mole) sample of dithia[10.3.1]hexadecatriene 1a and 1.40 g (0.0105 mole) crushed *N*-chlorosuccinimide were stirred magnetically in 75 ml of carbon tetrachloride for 2 hours. A 4.3 g (0.020 mole) sample of 85% *m*-chloroperoxybenzoic acid was dissolved in 100 ml of chloroform. The carbon tetrachloride solution was filtered into the chloroform solution and magnetically stirred for 18 hours. The solution was then extracted with 100 ml of saturated sodium bicarbonate, 50 ml of 10% sodium bisulfate and again with 100 ml of saturated sodium bicarbonate. The extracted solution was dried over magnesium sulfate and evaporated completely. A 60 ml portion of dimethoxyethane and 3.5 g (0.031 mole) of potassium butylate

were added and the mixture was stirred for 21 hours. The solution was evaporated to approximately 20 ml and 75 ml of water was added. The solution was then extracted twice with 75 ml of chloroform. The chloroform portion was washed with 50 ml of water and dried over magnesium sulfate. The solution was evaporated completely, leaving a yellow oil. This oil was dissolved in 35 ml of carbon tetrachloride, and 2 g alumina was added. The sample was filtered and evaporated (0.6 g crude yield). A proton nmr spectrum of the crude mixture indicated the presence of both pentaene and tetraene. The tetraene **4a** was recrystallized from methanol, 0.20 g, mp 114°; nmr spectral data for **4a** are summarized in Table II.

Anal. Calcd. for C₁₄H₁₇ClSO₂: C, 59.04; H, 6.02. Found: C, 58.80; H, 6.04.

The filtrate was evaporated, leaving a yellow oil. This oil was placed on an alumina column (d = 2 cm) in 5 ml of chloroform. The eluting solvent was carbon tetrachloride. Five 40 ml fractions of eluent were collected with the pure pentaene **5a** in fractions two and three (0.29 g, 32%). The pentaene was isolated by evaporation of the eluting solvent. Deuterated chloroform was added and the proton nmr spectrum run. The nmr data are summarized in Table II.

This pentaene **5a** was also prepared by the same procedure utilizing a different base. The procedure for the reaction was identical through the chlorination of 3,10-dithiabicyclo[10.3.1]hexadeca-12,14,1(16)-triene (**1a**). The oxidized chlorinated compound **3a** was extracted in the same manner with saturated sodium bicarbonate and 10% sodium bisulfate. After drying and complete evaporation, 2.0 g (0.040 mole) of potassium hydroxide were dissolved in 10 ml of water, and added to the *bis*-chlorosulfone derived from the dithiabicyclo[10.3.1]-hexadecatriene along with 50 ml of dimethoxyethane. This solution was magnetically stirred for 23 hours. The solution was evaporated to approximately 20 ml, and 75 ml of water were added. This solution was extracted with two 75 ml portions of chloroform and dried over magnesium sulfate. The solution was evaporated, leaving a yellow oil (0.90 g crude yield). The proton nmr spectra of the crude mixture indicated the presence of both pentaene and tetraene, **5a** and **4a**, respectively. The tetraene **4a** was recrystallized from methanol (0.50 g). The filtrate was evaporated leaving a yellow oil. The oil was placed on an alumina column (d = 2 cm). Five 40 ml fractions of eluent were collected. After evaporation, the pure diene was obtained from fractions two and three (0.30 g, 32%). A proton nmr spectrum was run to confirm the diene structure and its purity. The nmr spectral data are summarized in Table II.

Anal. Calcd. for C₁₄H₁₆: C, 91.25; H, 8.75. Found: C, 91.40; H, 8.60.

Ultraviolet spectra of the bicyclo[*n*.3.1]alkapentaenes **5a** and **5b** were determined in acetonitrile. The concentrations of the bicyclo[9.3.1]pentadeca-2,9,11,13,1(15)-pentaene (**5a**) and of bicyclo[8.3.1]tetradeca-2,8,10,12,1(13)-pentaene (**5b**) utilized were in the range of 8 × 10⁻⁵ moles per liter. Wavelengths of maximum absorbance and absorbencies were obtained directly from the spectra. The molar absorptivities were calculated from the absorbances and concentrations. The ultraviolet spectro-

metric data are summarized in Table IV, and discussed in the Results and Discussion section of this paper.

Acknowledgement.

This work was supported by a Minority Biomedical Research Support grant from the National Institutes of Health (Grant No. S06-RR-08025), and supported in part by a Research Centers in Minority Institutions award, RR-09104, from the National Center for Research Resources, National Institutes of Health.

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