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GENERAL APPROACH FOR THE SYNTHESIS OF POLYQUINENES

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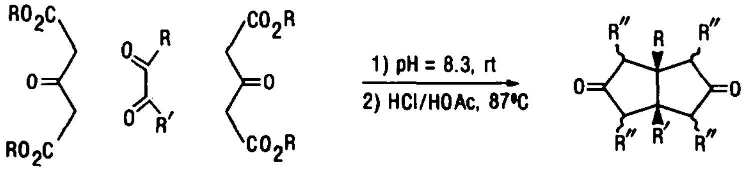
Abstract—The syntheses of tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradeca-3,6,10,13-tetraene **5** and staurane-2,5,8,11-tetraene **6** are described. The key step was the diborane-mediated reduction of the labile β-diketones **13** and **22** to provide the tetrols **11** and **23**, respectively. This was followed by removal of four molecules of water from the corresponding tetrols on heating them in HMPA. This technique has also been employed for preparation of the triquinanetrienes **26** and **27**. The use of the diborane-mediated reduction of strained β-diketones in combination with the HMPA-promoted elimination of the resulting alcohols provides an extremely versatile route to polyquinenes.

For several years we have been involved in the design of a general method for the synthesis of polyquinanes via the reaction of 1,2-dicarbonyl compounds **1** with dimethyl 3-oxoglutarate **2**, as illustrated in Scheme 1.[1–4] This reaction, which is run at room temperature and in aqueous buffer,[1,3] provides the simplest route to 1,5-disubstituted *cis*-bicyclo[3.3.0]octane-3,7-diones, and can be scaled up with ease. Hydrolysis of the 1:2 adduct **3a**, accompanied by decarboxylation, furnishes **3b**. This approach has been employed for the preparation of several natural products[5] and of polyquinane ring systems,[3,4] by simple structural changes in the starting 1,2-dione **1**.

One of the most important features of the *cis*-bicyclo[3.3.0]octane-3,7-dione skeleton has yet to be fully exploited. Although the desired stereospecificity (*cis*) of the condensation is well known,[3] the use of the 3,7-dioxo functionality has received only nominal attention. These carbonyl groups, in theory, could be converted into a variety of substituents; the conversion of these oxo moieties into double bonds would provide a facile route to polyunsaturated cyclopentanoid compounds, as well as to intermediates capable of conversion into polyquinanes. The direction of the present research centers on the design and execution of a general method for the preparation of polyquinenes. This employs the 3,7-dioxo functionality of the bicyclo[3.3.0]octane-3,7-dione system as a handle, the resulting compounds later to be converted into the corresponding polyenes. The initial targets tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradeca-3,6,10,13-tetraene **5** and the [5.5.5.5]fenestrane, staurane-2,5,8,11-tetraene **6**, have been chosen to test the validity of this approach and their structures are depicted in Scheme 2. The reasons for the choice of these polyquinenes for the present work follow below.

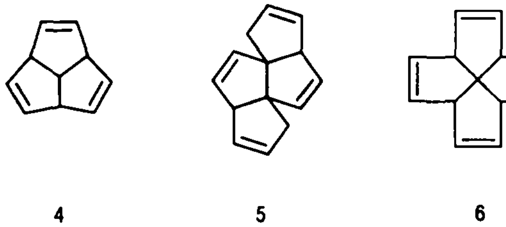
The need for a facile and general route to polyquinenes is well documented;[6–13] a few compounds of interest are shown on the next page. The chemistry of acepentalene[6] (i) has inspired renewed research on triquinacene and isotriquinacene.[7] In regard to this, a short synthesis of triquinacene **4** from **1** and **2** has recently been developed in our laboratory the details of which have been reported elsewhere.[8] In any synthetic method which dares to claim generality, a number of different compounds should be within reach from a common reaction. In this vein the tetraenes, tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradeca-3,6,10,13-tetraene **5** and tetracyclo[5.5.1.0^{4,13}.0^{10,13}]trideca-2,5,8,11-tetraene (staurane tetraene) **6** have been chosen as targets. The interest in **5** stems from its unique shape, as well as the desire to prepare metal complexes of this material. From its geometry this tetraene should be capable, at least in theory, of forming oligomers or polymers with alternating organic and metal subunits in the polymer backbone. However, the most interesting of the three alkenes remains, the [5.5.5.5]fenestrane, staurane-2,5,8,11-tetraene **6**. In



2 **1** **2**

3a, R″ = CO_2CH_3
3b, R″ = H

Scheme 1.



4 5 6

Scheme 2.

addition to the unusual D$_{2d}$ symmetry of **6**,† the impetus for the synthesis of such a molecule rests on the possible conversion of **6** into the related hexaene (**ii**). A number of investigators[9] have vigorously debated whether the central carbon atom of such a hexaene would be either planar or approach a planoid deformation;[9] however, no reports of the synthesis of a molecule closely related to the hexaene (**ii**) have appeared. Certainly a molecule such as this would be severely strained and highly reactive; nonetheless, the pentaene related to it can be easily constructed from models, providing additional stimulus for the design of a facile route to tetraene **6**. There are numerous research groups[9-12] which have reported on both the theoretical aspects and the attempts to synthesize compounds such as the hexaene (**ii**). The tetraene **6**, however, still provides one of the most direct routes to this strained system.‡

Three other polyquinenes **iii**–**v** are potentially within reach via the reaction of **1** with **2**. The 14π annulene (**iii**) has been proposed to be a stable and isolable entity,[13a] while polyquinenes **iv** and **v** have been predicted to be highly unstable.[13b] It is anticipated that the method under investigation here will provide a route to keto functionalized derivatives of **iii**–**v** which can later be employed for synthetic entry into these strained systems.

Earlier we reported the synthesis of tricyclo[6.3.0.0^{1,5}]undecane-3,7,9-trione,[14] tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane-2,6,8,12-tetraone (staurane tetraone)†[11] and tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradecane-4,6,11,13-tetraone,[15] the key steps of which involved the reaction of a suitably substituted 1,2-dione **1** with **2**, followed later by an acid-catalyzed intramolecular acylation sequence. The β-diketones produced by this reaction, however, readily undergo a retro-Claisen reaction on treatment with alkoxide[16] and ring fragmentation on reaction with other nucleophiles. The propensity of such β-diketone systems to undergo cleavage of the β-diketone bond was also observed by Eaton *et al.* in the case of *cis*-bicyclo[3.3.0]octane-2,8-dione.[17] The reactivity of these compounds, consequently, places severe constraints on the transformations which can be successfully carried out. The challenge then remains to develop facile synthetic routes to polyquinenes and polyquinanes which avoid these troublesome ring-cleavage reactions.

Although staurane tetraone[3] is insoluble in most organic solvents, it is soluble in pyridine. Attempts to reduce the carbonyl groups, however, with pyridine–borane led to complex mixtures of products, some of which resulted from cleavage of the β-dicarbonyl C—C bonds.[18] On reduction of such β-diketone systems with nucleophilic hydride reagents (LiAlH$_4$ or NaBH$_4$) the compounds suffered a similar fate.[18] In the following report we wish to describe two approaches which were employed to circumvent these difficulties. These routes are termed the "aldol" and "diborane" approaches, both of which were conceived during the synthesis of triquinacene **4** in our laboratory.[8,19]

Outlined in Scheme 3 are the two routes which can be envisaged as potentially viable for synthesis of **5**; these are termed the "aldol" and "diborane" approaches, as pointed out above. Since it had been determined earlier that strained β-diketones in this series[16,17] react extremely readily with nucleophiles, the aldol route to **5** was pursued first. The [6.3.3]propellenedione **7**, which could serve as the key intermediate for both routes, was prepared with ease via the condensation of 5-cyclooctene-1,2-dione with **2**.[3] Oxidation of **7** with ozone in methanol–dichloromethane, followed by reductive workup, gave a 95% yield of the bis-acetal **8**.[20] This protected form of the desired dialdehyde was then stirred in acetic acid in the presence of a trace of concentrated sulfuric acid. These conditions are somewhat similar to those employed by Deslongchamps and co-workers in a different ring system.[21] The acidic medium not only effected cleavage of both acetal functions and catalyzed the desired aldol condensations, but also trapped the intermediate β-hydroxy ketones as the β-acetoxy derivatives **9** and **10**, respectively. This approach, consequently, prevented fragmentation of these tetraquinanes via a retro-aldol reaction! The two diacetates **9** (*trans–trans*) and **10** (*cis–cis*) were obtained as a mixture of diastereomers in 75% yield. Examination of the crude reaction mixture by ^{13}C-NMR spectroscopy with suppressed NOE showed that the two isomers **9** and **10** were present in a ratio of 1 : 3.5.

The ^{1}H-NMR spectra of the two diacetates indicated that both diastereomers contained a C$_2$ symmetry axis perpendicular to the C$_1$, C$_8$ bond of the central *cis*-bicyclo[3.3.0]octane-3,7-dione unit; moreover, the ^{13}C-NMR spectra of both compounds consisted of only nine lines.[20] Because of this symmetry the two isomers must contain the acetate groups in a *cis–cis* or

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† The parent hydrocarbon, staurane, would belong to the D$_{2d}$ point group.

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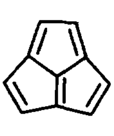
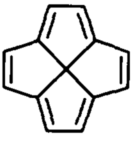
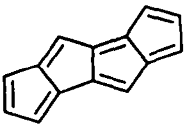


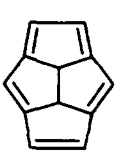
i



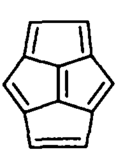
ii



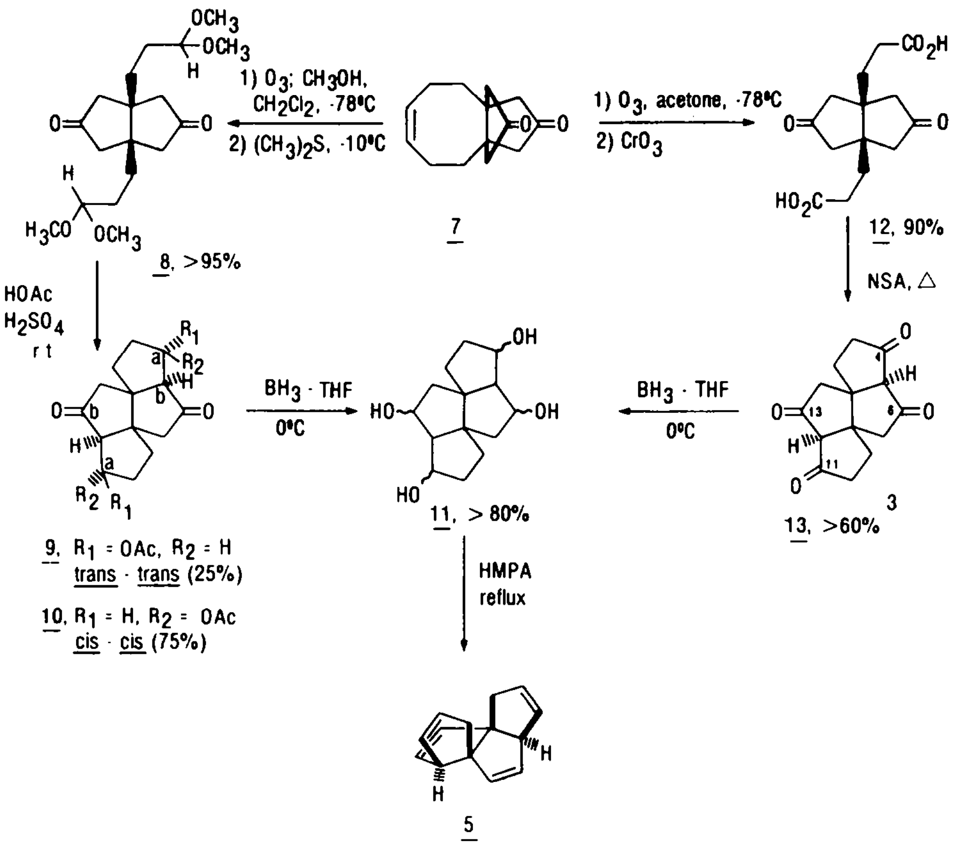
iii



iv



v

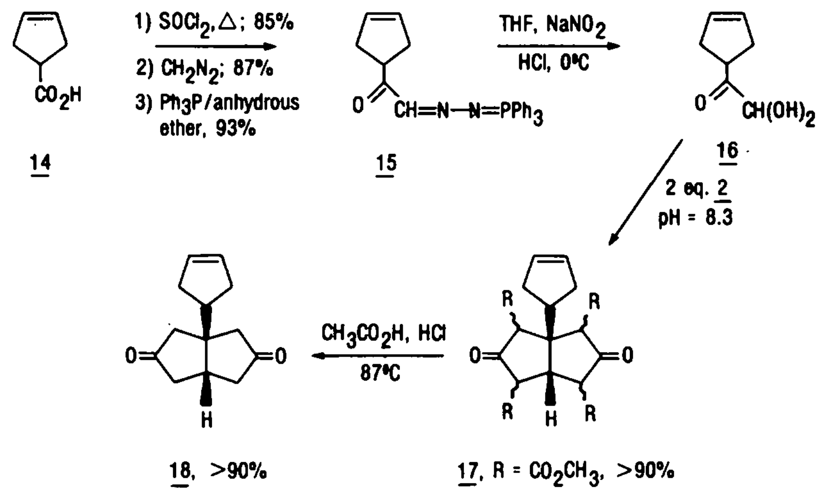


Scheme 3. Synthesis of tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradeca-3,6,10,13-tetraene **5**. The aldol and diborane approaches.

trans–trans relationship with respect to the carbonyl oxygen of the adjacent 5-membered ring. Assignments from the proton spectra were made employing 2-dimensional (COSY) NMR spectroscopy run both in deuteriochloroform and deuteriobenzene. In addition, examination of the proton spectrum of **9** in deuteriobenzene indicated that the coupling constant between proton H_a attached to the acetate-bearing carbon and the proton at the ring juncture (H_b) was very small ($J = 1.8$ Hz), while the coupling constant between H_a and H_b of **10** was 8.5 Hz. On the basis of the ^{1}H-, ^{13}C- and 2D-NMR experiments, it was proposed that **9** and **10** differed only in the stereochemistry at the site of the acetate functionality. In keeping with the Karplus[22] relationship for variation of the 3-bond coupling constant, the first isomer **9** has been determined to possess the C—O acetate bonds *trans* to the carbon bonds bearing the carbonyl group. The *cis–cis* isomer **10**, therefore, contains the two acetate groups in the opposite configuration with respect to that of **9**.[20] The details of the 2D-NMR work will be reported elsewhere.[23]

The mixture of diacetates **9** and **10** was then reacted with diborane in THF, as shown in Scheme 3. Reduction of the carbonyl groups followed by reductive removal of the acetate functionality provided, as expected, a mixture of tetrols represented by structure **11**. The electron impact mass spectrum of the mixture contained the expected parent ion at *m/e* 254. More importantly, examination of the chemical ionization mass spectrum clearly indicated the successive loss of four molecules of water from the parent (P + 1) peak to provide an ion at *m/e* 183 amu.

The implications of the synthesis of the tetrol **11** and the behavior on mass spectrometry were far-reaching. For the first time a tetracyclic system such as **11** had been formed without ring fragmentation and its behavior (TLC, ^{1}H-NMR, ^{13}C-NMR, etc.) characterized. Immediately we set about to prepare more of the tetracyclic tetraketone **13**, which had been synthesized earlier in our laboratory.[3] To this end the [6.3.3]propellene dione **7** was treated with ozone and the ozonide which resulted was oxidized with Jones' reagent. This gave a 90% yield of diacid **12**, a compound which had been prepared less efficiently much earlier.[3] The diacid **12** was subsequently cyclized to the tetraketone **13** by published procedures.[3] Although the tetraketone was not soluble in tetrahydrofuran, a slurry of **13** was stirred at 0° in diborane–THF until the material dissolved (2 days). The solution was worked up to provide an 80% yield of the mixture of stereoisomeric tetrols represented by structure **11**. The chemical ionization mass spectrum of the two mixtures of tetrols **11** prepared by the "aldol" approach and the "diborane" route were virtually identical. Furthermore, none of the product from the fragmentation of the 5-membered rings via either a retro-Claisen or retro-aldol reaction was observed. This result illustrates the fact that, indeed, certain Lewis acid-catalyzed reactions of these strained β-diketones



Scheme 4. Preparation of key intermediate, 1-(3′-cyclopentenyl)-*cis*-bicyclo[3.3.0]octane-3,7-dione **18**.

could be effected in high yield with absolutely no cleavage of the β-dicarbonyl C—C bonds. The reasons for the success in the diborane reduction vs previous difficulties with other nucleophiles in this system have been communicated.[24]

In the description of the synthesis[8] of triquinacene **4** it was pointed out that the HMPA-mediated dehydration, according to the method of Monson,[25] was extremely effective in converting the triquinane triol intermediate[8] into triquinacene **4**. Similar treatment of the mixture of stereoisomeric tetrols **11** from both the aldol approach and the diborane approach, separately, in refluxing HMPA (cold finger condenser, dry ice–acetone) for 24 h gave, within experimental error, an 80% yield of the desired tetraene **5** accompanied by 18% of the bridgehead isomer (**vi**).† The combined yield of the two alkenes from this sequence was greater than 65%. The tetraenes were isolated by extraction of the HMPA solution with pentane. The pentane layer was washed with water to remove residual HMPA and the desired tetraene **5** was purified by flash chromatography on silica gel.[20] The ^{1}H-NMR, mass and IR spectra of **5** strongly supported the structure as assigned; conclusive confirmation of the assignment was obtained on examination of the ^{13}C-NMR spectrum of the tetraene. The spectrum contained only seven lines, in agreement with the C_2 symmetry of the molecule; moreover, these signals appeared at chemical shifts consistent with the assignment. Conversion of **11** into **5** also serves to verify the structures of **9–11**, since rearrangements are not expected to occur for 2° alcohols when HMPA is employed as the dehydrating agent.[25]

Although **5**, an oil, is stable under argon in a sealed tube for several weeks, it forms a polymer after several days on exposure to air. The IR spectrum of this polymer shows the presence of OH (3400 cm^{-1}), and CO bands (1700 cm^{-1}). In addition, elemental analysis of the insoluble solid (found: C, 63.60; H, 5.40; O, 31.20%) also indicates the presence of oxygen.[23] As anticipated, **5** does react with rhodium trichloride trihydrate to form an insoluble polymer-like material which appears to contain a backbone composed of alternating metal organic subunits. This material has not been completely characterized but elemental analysis for C, H, and Cl supports this hypothesis.‡ The interesting properties of the tetraene **5** with regard to chirality and reactions with electrophiles, including other transition metal cations, will be reported in due course. In addition, interaction of the diene system (via PES) in terms of homoconjugation is also of interest with regard to **5**.

Since the aldol approach to the tetrol **11** (Scheme 3) was completed prior to the diborane route, it was felt initially that the synthesis of staurane-2,5,8,11-tetraene **6** might best be accomplished by the former method. An intermediate, (1 - (3′ - cyclopentenyl) - *cis* - bicyclo[3.3.0]octane - 3,7 - dione **18** (Scheme 4), was therefore prepared in which the bisaldehyde functionality, required for the aldol approach, was masked as a cyclopentene unit. The importance of such an intermediate was twofold since oxidation of the double bond could alternatively lead to the corresponding glutaric acid derivative earlier employed for preparation of staurane - 2,6,8,12 - tetraketone.[3,11] Cyclopentene-3-carboxylic acid **14**, which can be prepared on a 200 g scale[27] and which is also commercially available, was chosen as the starting material. The acid **14** was converted in three steps into

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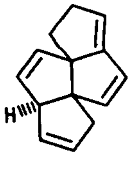
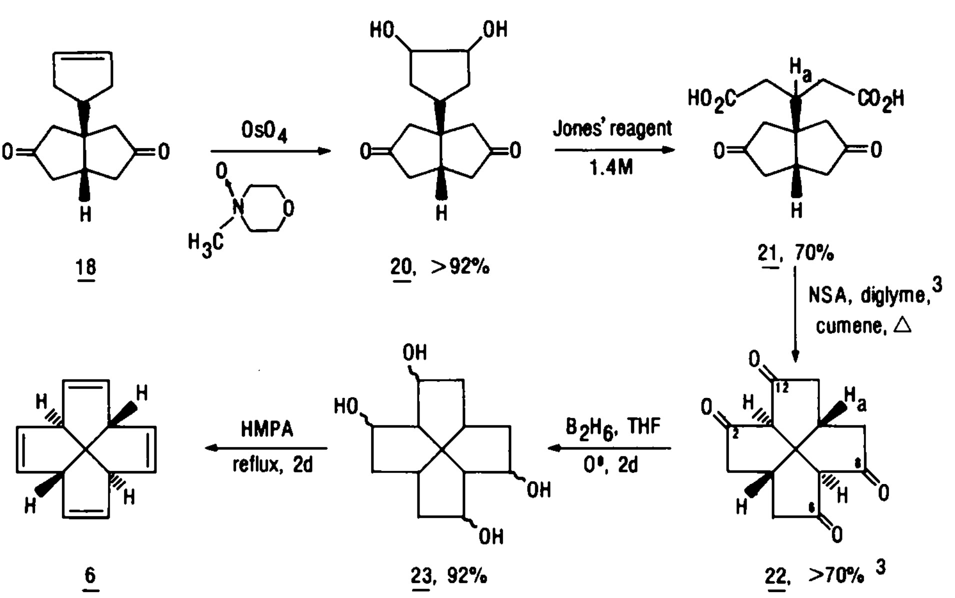
† ^{13}C-NMR (CDCl$_3$) δ 30.25 (t), 34.56 (t), 36.34 (t), 62.10 (d), 115.88 (d), 124.69 (d), 128.05 (d), 132.33 (d), 136.5 (d), 142.0 (d), 147.9 (d). The two quaternary carbons and the carbon atom of the bridgehead alkene were not observed because of the small quantity of **vi** available for analysis.



vi

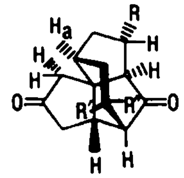
‡ A polymer composed of repeating subunits which contains two rhodium atoms and two chlorine atoms per molecule of **5** would require: C, 36.60; H, 3.05; Cl, 15.47 and Rh, 44.86. The values found for C(35.5), H(3.15), Cl(14.24) are within 1.2% of those predicted for the polymer, albeit the value for rhodium was about 6% too low.



Scheme 5. Synthesis of staurane-2,5,8,11-tetraene **6**. The diborane approach.

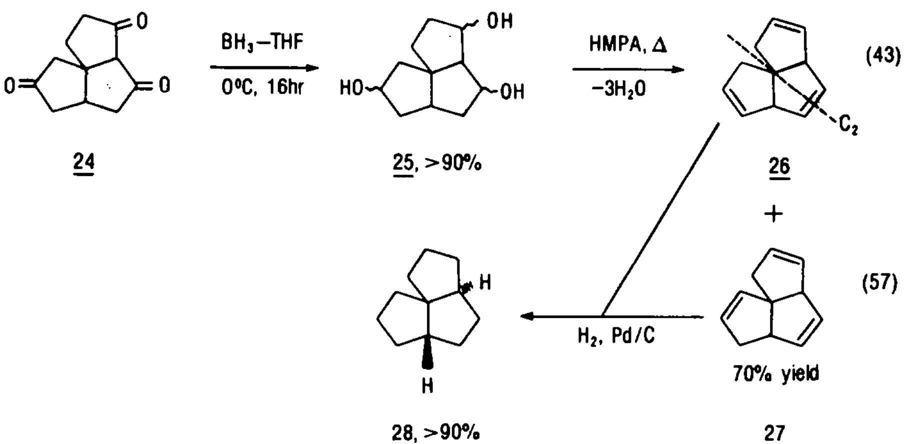
the phosphazine **15**, by the method of Bestmann *et al.*,[28] as illustrated in Scheme 4. Generally, 200 g of **15** could be prepared in a matter of days. The phosphazine **15** was then stirred with nitrous acid to provide the cyclopentene-3-glyoxal **16** in yields ranging from 60 to 80%. Glyoxal **16**, present as the hydrate, was dissolved immediately in methanol and added at room temperature to a solution of **2** dissolved in aqueous sodium bicarbonate. After stirring for 12 h, the white precipitate which had formed was filtered off to give the 1 : 2 adduct **17**. While the yields in this step vary from 80 to 92%, depending on the purity of the glyoxal **16**, this condensation occurs much faster and in better yield than that of the corresponding glutaric acid diethylester derivative reported earlier from our laboratory.[11] The yields are higher and as much as 65 g of tetraester **17** have been prepared in one step. The improved success with **16** in comparison to glyoxals substituted with larger groups results from fewer steric interactions in the intermediates on the pathway to **17**,[4] in contrast to those which occurred when the diester was employed.[4,11] This has been shown to hold for numerous 1,2-dicarbonyl compounds and a detailed study has recently been completed.[29] Hydrolysis of the ester functions, accompanied by decarboxylation, provided the desired 1 - (3' - cyclopentenyl) - *cis* - bicyclo[3.3.0]octane - 3,7 - dione **18** in excellent yield (Scheme 5).

With the 3,7-dione **18** in hand, the aldol approach to the desired [5.5.5.5]fenestrane system present in tetraene **6** could now be attempted. Conversion (O_3; DMS) of **18** into the diketodialdehyde, followed by treatment with a solution of acetic acid–sulfuric acid, analogous to conversion of **8** into **9** and **10**, gave two epimeric diacetates **19a** and **b**. Unfortunately, the two diketodiacetates were the products of transannular cyclization presumably arising from rotation of the glutaraldehyde side chain by 180° (see **19a**, H_a = alpha), followed by aldolization. The details of this reaction have been communicated in preliminary form;[24] the full discussion of these results will be reported elsewhere.[30] Although the unique ring system present in **19a** and **b** is interesting in its own right, it will not lead to the desired [5.5.5.5] system, and hence, the aldol approach was discontinued.



19a, R=R' = $OCOCH_3$, R''= H (62%)
19b, R=R'' = $OCOCH_3$, R'= H (38%)
overall yield 75%

Even though the pyridine–borane route had failed earlier,[18] the success encountered in the conversion of **13** into the tetrol **11** (Scheme 3) prompted a reinvestigation of this approach. In this vein, 1 - (3' - cyclopentene) - *cis* - bicyclo[3.3.0]octane - 3,7 - dione **18** was stirred with osmium tetroxide, followed by addition of Jones' reagent, to provide a 70% yield of the diacid **21** (Scheme 5). This acid had been prepared earlier by a less efficient route.[3] It was subjected to acid-catalyzed cyclization to provide the tetraone **22** with the stereochemistry indicated (H_a = beta, see **22**), as reported earlier.[3,11] The highest yield obtained to date was 78%, while yields normally ranged from 50 to 70%; unreacted diacid comprises much of the remainder of the material and can be recycled if desired. Although the crystalline [5.5.5.5]fenestrane (staurane tetraketone **22**) was insoluble in THF, it was stirred at 0° in borane–THF, by analogy to the conversion of **13** into **11** (Scheme 3). This procedure, after workup, gave a 92% yield of the desired staurane-2,6,8,12-tetrol **23** as a mixture of stereoisomers. One of these crystallized and was characterized as a white solid, while the remainder of the material was obtained as an oil. In keeping with the successful dehydration procedure[25] employed in



Scheme 6.

the syntheses of **4** and **5**, the stereoisomeric mixture of tetrols was simply heated in refluxing HMPA for 48 h. This procedure cleanly gave staurane-2,5,8,11-tetraene **6** (80%) accompanied by the bridgehead alkene (20%, see vii) in 61% overall yield.† Staurane-2,5,8,11-tetraene **6** was separated from the bridgehead isomer by flash chromatography on silica gel. The product which resulted was triturated with pentane and further purified by sublimation; it is a white solid (m.p. 90°, sealed capillary) which sublimes at atmospheric pressure on mild heating. The ^{1}H-NMR spectrum of **6**, as expected, is very simple, consisting of two singlets at δ 3.48 and 5.33, respectively. The IR spectrum of **6** is completely consistent with the assigned structure; moreover, the ^{13}C-NMR spectrum [($CDCl_3$) 66.00 (s), 66.36 (d), 131.83 (d)] is definitive for **6** (D_{2d} symmetry). Further work is in progress to convert **6** into the stable [5.5.5.5]pentaene, a potential precursor of the [5.5.5.5]hexaene (see ii).[9,10]

The successful use of the diborane approach to circumvent nucleophile-mediated cleavage of the β-dicarbonyl C—C bonds of 2,8-dioxo-substituted *cis*-bicyclo[3.3.0]octanediones (see **11** and **23**) represents a significant advance in the use of the methods reported here for the preparation of polyquinenes. This technique has recently been successfully exploited in the case of other labile β-diketones and one final example will be presented (Scheme 6). The triquinane trione **24** was prepared in our laboratory[14] but readily underwent retro-Claisen reactions on treatment with alkoxide, as described before.[3] However, simply stirring the trione **24** in borane–THF, under conditions analogous to preparation of **23**, resulted in a 90% yield of a mixture of stereoisomeric triols. These are represented by structure **25** (Scheme 6). The mixture of triols was heated in HMPA and then purified, according to the procedure employed with **5**. After chromatography, two alkenes **26** and **27** were isolated in 70% overall yield. They were present in the ratio of 43 : 57, respectively. The structures of both alkenes were readily confirmed by mass spectrometry and ^{13}C-NMR spectroscopy. A C_2 axis of symmetry was present in triene **26**, consequently, the ^{13}C-NMR spectrum of this isomer contained only six lines, while the spectrum of the triene of lower symmetry exhibited eleven signals, as expected (Experimental). This mixture of trienes polymerized on exposure to air; however, catalytic reduction (H_2, Pd/C) of a freshly prepared sample gave the parent hydrocarbon, tricyclo[6.3.0.0^{1,5}]undecane **28** in 92% yield. The parent hydrocarbons in the case of **5** and **6** were prepared via the same procedure.[26] It is interesting to note that both trienes **26** and **27** and the tetraene **5** reacted on exposure to air (presumably with oxygen) over a 3 day period to provide a polymeric material. However, staurane tetraene **6** did not readily undergo this reaction. It is felt the reasons for the lesser reactivity of the staurane system **6** are steric in nature and parallel the conclusions regarding the lesser reactivity of staurane tetraketone **22** described earlier.[16] The trienes **26** and **27** as well as the tetraene **5** were quite stable for weeks when stored under argon.

Although the initial challenge was to design a general route to polyquinenes which employed the condensation of 1,2-dicarbonyl compounds **1** with **2** as the key step, the rewards reach far beyond this objective. In fact, the recently discovered "diborane" approach permits, for the first time, the successful reduction of labile *cis*-bicyclo[3.3.0]octane-2,8-dione systems to the corresponding hydroxyl derivatives without cleavage of the C—C bonds contained in the β-diketone system. This development is significant, since it allows conversion of compounds which contain these strained β-dicarbonyl groups into polyquinenes (for example, **5** and **6**) and eventually into the parent hydrocarbons.[26] This result also serves to strengthen the use of the reaction of **1** with **2** as a simple, general approach for preparation of polyquinenes and polyquinanes.[26] Combination of the diborane approach to provide the tetrols, coupled with the HMPA-mediated dehydration procedure of Monson[25] now permits the removal of several hydroxyl groups in a one-pot reaction to furnish good yields of the corresponding polyunsaturated cyclopentanoid compounds. The

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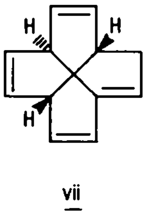

vii

advantage of this method is obvious, since it provides a simple route to gram quantities of **4** and **6**, from which more strained polyquinenes such as **i** and **ii** should become accessible. When this technique is coupled with the aldol-epimerization approach recently employed for the synthesis of triquinacene,[8] a facile route to the carbon skeletons of tetraquinenes **iv** and **v** should be within reach.

EXPERIMENTAL

Microanalyses were performed on an F. and M. Scientific Corp. Model 185 C, H and N analyzer. M.ps were taken on a Thomas–Hoover m.p. apparatus; they are uncorrected. Low-resolution NMR spectra were recorded on a Varian EM-360 spectrometer, while the high-resolution spectra were run on a Bruker 250 mHz multiple-probe instrument. Chemical ionization (CI) mass spectra and electron impact (EI) mass spectra were obtained on either a Finnigan GC/MS or a Hewlett Packard 5985 gas chromatograph–mass spectrometer. The IR spectra were obtained on a Beckman Acculab 1 instrument or a Nicolet FT IR.

1,5-(*Bis*-3-*propionaldehyde dimethyl acetal*)cis - *bicyclo*-[3.3.0]*octane* - 3,7 - *dione* **8**. Compound **7**[3] (5 g, 23 mmol) was dissolved in a mixture of dry MeOH (100 ml) and CH_2Cl_2 (200 ml). The soln was cooled to −78° in a dry ice–acetone bath and O_3 was passed through the mixture until a deep blue coloration was observed. The soln was stirred for 5 min and the excess O_3 purged from the medium with a stream of N_2 (15 min). The mixture then became colorless. It was allowed to warm to −10°, after which Me_2S (2.85 g, 46 mmol) was added slowly. The mixture was stirred at −10° for 1 h, and then at ice bath temp for 1 h. The soln was next allowed to warm to room temp and stirred overnight. The solvent was removed under reduced pressure and the residue was treated with water (100 ml) and subsequently extracted with $CHCl_3$ (3 × 100 ml). The dimethyl sulfoxide produced in the reduction remained in the water layer. The combined organic layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure to provide **8** (7.5 g, 95.1% yield) as a white solid. This material was recrystallized from MeOH to provide **8**: m.p. 110–111° (CH_3OH); IR (KBr) 1740 cm^{-1}; ^{13}C-NMR (62.9 mHz, $CDCl_3$) δ 28.51 (t), 28.86 (t), 48.18 (q), 49.18 (s), 53.04 (t), 104.32 (d), 215.48 (s); ^1H-NMR (250 mHz, $CDCl_3$) δ 1.45–1.46 (8H, m), 2.25 (8H, q), 3.20 (12H, s), 4.25 (broad 2H); mass spectrum (EI, 15 eV) *m/e* 342 (2.1), 310 (1.1), 278 (75.1), 246 (100), 214 (13). (Found: C, 62.94; H, 8.77. Calc for $C_{18}H_{30}O_6$: C, 63.16; H, 8.77%.)

Preparation of trans–trans *and* cis–cis - 4,11 - *diacetoxy-tetracyclo*$[6.6.0.0^{1,5}.0^{8,12}]$*tetradecane* - 6,13 - *dione*, **9** *and* **10**. The bisacetal **8** (7.5 g, 21.9 mmol) was stirred for 3 d in freshly distilled glacial AcOH (150 ml) in the presence of 4 drops of conc H_2SO_4. An additional 3 drops of conc H_2SO_4 was added and the mixture stirred for 48 h. It was then brought to pH 4 with Na_2CO_3 and the AcOH was removed under reduced pressure. To the residue, water (100 ml) was added and the soln was extracted with $CHCl_3$ (3 × 100 ml). The combined extracts were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The spongy solid which resulted was dissolved in EtOAc and purified by flash column chromatography on silica gel (grade 60, 230–400 mesh, Aldrich; hexane–EtOAc gradient elution) to provide the first isomer, **9**, designated *trans–trans*. The second isomer was then eluted from the column; it has been designated *cis–cis*, **10**. The overall yield of this sequence was 75.1% and the two isomers were present in a ratio of **9** (1) to **10** (3.5). They were purified by crystallization from EtOAc–hexane. Compound **9**: (*trans–trans*) m.p. 180–181°; IR (KBr) 1741 cm^{-1}; ^1H-NMR (250 mHz, $CDCl_3$) δ 1.90–2.00 (8H, m), 1.95 (6H, s), 2.40–2.60 (6H, m), 5.50 (2H, m, J α to acetate = 1.8 Hz); ^{13}C-NMR (62.9 mHz, $CDCl_3$) δ 20.81 (q), 23.10 (t), 33.41 (t), 49.33 (t), 54.92 (s), 66.07 (d), 78.19 (d), 169.72 (s), 214.60 (s); mass spectrum (CI, CH_4) 335 (P + 1, 18), 275 (90), 233 (57), 215 (100). Compound **10**: (*cis–cis*) m.p. 162–163°; IR (KBr) 1742 cm^{-1}; ^1H-NMR (250 mHz, $CDCl_3$) δ 1.93–2.21 (8H, m), 1.97 (6H, s), 2.48–2.54 (6H, m), 5.44 (2H, m, J α to acetate = 8.5 Hz); ^{13}C-NMR (62.9 mHz, $CDCl_3$) δ 20.86 (q), 32.51 (t), 34.07 (t), 52.28 (t), 55.45 (s), 62.01 (d), 76.44 (d), 169.69 (s), 211.54 (s); mass spectrum (CI, CH_4) 335 (P + 1, 55), 275 (73), 233 (100), 215 (61). (Found: C, 64.93; H, 6.70. Calc for $C_{18}H_{22}O_6$: C, 64.70; H, 6.60%.)

Tetracyclo$[6.6.0.0^{1,5}.0^{8,12}]$*tetradeca* - 4,6,11,13 - *tetrol* **11**. The diketodiacetates **9** and **10** (5 g, 15 mmol) were dissolved in dry THF (30 ml) and cooled in an ice bath. While the soln was stirred at 0° a cooled soln of borane–THF in THF (1.0 M, 75 ml) was added slowly. After the addition, the mixture which resulted was stirred for 24 h, at which time the starting material had completely disappeared (TLC). Dry MeOH (60 ml, cold) was added dropwise to the cold mixture with stirring. The mixture which resulted was stirred for 15 min. The solvents were subsequently removed under reduced pressure to yield a product which contained **11** and the corresponding borate ester. The crude product was repeatedly heated with dry MeOH and the solvent removed under reduced pressure (Buchi rotavapor) to remove the borate ester as trimethoxyborane. The residue which remained was passed through a short column of silica gel and then allowed to stand in MeOH overnight. A white crystalline (25%) ppt from the soln was washed with MeOH, dried (Na_2SO_4) and characterized: compound **11**: m.p. 280°; IR (KBr) 3500–3100 (broad), 3010 and 1500 cm^{-1}; ^1H-NMR (250 mHz, DMSO-d_6) δ 1.30–1.90 (m, 14H), 4.40 (4, H), 4.42 (broad s, 4H); ^{13}C-NMR (62.9 mHz, DMSO-d_6) δ 31.21 (t), 35.21 (t), 47.67 (t), 56.70 (s), 62.75 (d), 69.89 (d), 72.18 (d); mass spectrum (CI, CH_4) *m/e* 255 (P + 1, 5), 237 (10), 219 (64), 201 (100), 183 (16). (Found: C, 65.70; H, 8.66. Calc for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66%.) The oil (75%) which remained had ^1H-NMR, IR and mass spectra virtually identical with those of the white solid. The tetrol **11** is a mixture of stereoisomers; it was used directly in the next step.

Tetracyclo$[6.6.0.0^{1,5}.0^{8,12}]$*tetradeca* - 3,6,10,13 - *tetraene* **5**. A mixture of isomeric tetrols **11** (2 g, 7.9 mmol) was heated to reflux in a hexamethylphosphoryltriamide (30 ml, HMPA) with stirring. The soln, originally colorless, turned yellow just below 200° and then darkened. The evolution of Me_2NH could readily be observed. The mixture was then held at reflux for 24 h under two water cooled spiral condensers which were also attached to a dry ice–acetone trap. During this time, the starting material disappeared and a dark brown mixture was obtained. After cooling, the HMPA soln was extracted with a large excess of pentane. The pentane layer was washed three times with brine and dried (Na_2SO_4). The pentane was removed by careful distillation, the oil which remained was chromatographed on silica gel (pentane). Although **5** and the bridgehead alkene were present in the original mixture in a ratio of 85:15, after chromatography a ratio of 92:8 was observed in a combined yield of 65%. The tetraene **5** was further purified by chromatography on silica gel to provide a colorless oil: IR (FT, neat) 3047 and 2930 cm^{-1}; ^1H-NMR (250 mHz, $CDCl_3$) δ 2.15–2.35 (m, 4H), 3.40 (q, 2H), 5.50–5.70 (m, 4H); ^{13}C-NMR (62.9 mHz, $CDCl_3$) 40.08 (t), 62.31 (d), 67.11 (s), 128.88 (d), 130.08 (d), 134.23 (d), 139.11 (d); mass spectrum (EI, 15 eV) 182 (59), 167 (100), 149 (58), 125 (58). High resolution mass spectrum calc for $C_{14}H_{14}$: 182.1095; found: 182.1084. (Found: C, 92.05; H, 7.60. Calc for $C_{14}H_{14}$: C, 92.30; H, 7.70%.) The tetraene **5** can be stored under Ar for several weeks; however, on exposure to air it polymerizes to a solid which contains C, H and O. Anal. C, 63.60; H, 5.40; O, 31.20. This solid does not vaporize under conditions of EI or CI mass spectroscopy even at temps above 250°. The bridgehead alkene was present in too small a quantity for full characterization. The carbon spectrum of this material is described in the footnote on p. 1600.

Preparation of tetracyclo$[6.6.0.0^{1,5}.0^{8,12}]$*tetradeca-4,6,11,13-tetrol* **11** *from tetracyclo*$[6.6.0.0^{1,5}.0^{8,12}]$*tetradecane-4,6,11,13-tetraone* **13**. To a suspension of **13**[3] (0.5 g, 2 mmol) in dry THF (15 ml) which had been cooled to ice bath temp, was slowly added a cold soln of borane–THF complex in THF (1.0 M, 10 ml). After the addition, the slurry which resulted was stirred for 36 h at 0°. Dry, cold MeOH (25 ml) was then added dropwise, with stirring, to the cold soln to destroy excess diborane. The mixture was then stirred for 15 min, after which time the solvent was removed under reduced pressure. This procedure gave **11** accompanied by its borate ester. The boron compound was removed by repeated heating of the material in MeOH followed by the removal of solvent and trimethoxyborane under reduced pressure. The oily residue from this procedure was passed through a short column of silica gel (1 : 1, EtOAc–EtOH) and then subjected to the HMPA-mediated dehydration as described in the previous experiment. In the mixture so produced, the two isomers were present in a ratio of 85 : 15 before purification. Chromatography on silica gel (pentane) gave the tetraene **5** and the bridgehead isomer, both of which were identical (GC analysis, mass spectrometry, TLC and ^{13}C-NMR spectroscopy) with the two tetraenes obtained in the previous dehydration. Consequently, **11** produced from the aldol approach and the diborane approach gave the same two tetraenes in the same ratios (GC) within experimental error.

Preparation of the ozonide of 1 - (3′ - *cyclopentene*) - cis - *bicyclo*[3.3.0]*octane* - 3,7 - *dione* **18** *to provide the diketodialdehyde*

The cyclopentene substituted compound **18** (500 mg, 2.44 mmol) was dissolved in EtOAc (50 ml). The mixture was cooled to −50° and O_3 was passed through the soln until the mixture turned blue. N_2 was then passed through the soln for 15 min, after which the solvent was removed at room temp under reduced pressure. This procedure gave a white solid (610 mg, 99%) which melted at 142–146°. Recrystallization from EtOAc provided the pure ozonide: m.p. 154–155°; IR (KBr) 2958, 2895, 1733, 1411 and 1400 cm^{-1}; ^{1}H-NMR (60 mHz, $CDCl_3$) δ 0.70–2.90 (m, 14H), 5.75 (d, 1H, J = 5 Hz), 5.80 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 30.49 (d), 32.19 (t), 38.80 (d), 44.44 (t), 46.83 (t), 49.62 (s), 98.06 (d), 215.49 (s); mass spectrum (CI, CH_4) *m/e* 253 (P+1), 235, 207 (100), 179, 165, 137. (Found: C, 61.81; H, 6.43. Calc for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39%.)

This ozonide was treated with Me_2S in MeOH to provide the methoxy hemiacetal in greater than 95% yield. This hemiacetal was in equilibrium with the diketodialdehyde. The diketodialdehyde was reacted with AcOH–H_2SO_4 as described in previous experiments to provide **19a** and **b**. The details of the investigation of **19a** and **b** will be reported elsewhere.[30]

Tetracyclo[5.5.1.0^{4,13}.0^{10,13}]*tridecane* - 2,6,8,12 - *tetrol* **23**. To a suspension of **22** (0.5 g, 2.2 mmol) in dry THF (70 ml), a soln of diborane–THF (1.0 M, 65 ml) was added at 0° over a 30 min period. The mixture was stirred at 8° for 48 h and then at room temp for 1.5 h. MeOH (50 ml) was added slowly to the cold mixture with stirring. The solvents were removed under reduced pressure to yield the crude **23**, accompanied by borate esters. The esters were removed by dissolving the crude product in MeOH and heating the mixture under reduced pressure. In this manner trimethoxyborane and the MeOH were both removed. The process was repeated five times to provide **23** (0.48 g, 93%) free of borate esters. The crude product was purified by column chromatography on silica gel (40% EtOH–EtOAc) to give a stereoisomeric mixture of **23** (0.38 g, 73.5%) present as an oil, and a pure crystalline **23** (0.095 g, 18.4%): m.p. 228–229°; IR (FT, KBr) 3301.40 (broad), 3229.10 (broad), 2932.98, 2891.50 and 2872.21 cm^{-1}; ^{1}H-NMR (CD_3OD) δ 1.72 (quintet, 4H, J = 5.5 Hz), 2.01–2.18 (m, 6H, overlap of CH and CH_2s), 2.30 (t, 2H, J = 5.0 Hz), 3.88 (q, 4H, J = 5.3 Hz), 4.87 (s, 4H); ^{13}C-NMR (CD_3OD) δ 42.33 (t), 49.38 (d), 69.75 (s), 69.91 (d), and 78.31 (d); mass spectrum (CI, CH_4) 241 (P+1, 8%), 223 (5.5), 205 (33.5), 187 (100), 169 (33). (Found: C, 65.44; H, 8.20. Calc for $C_{13}H_{20}O_4$: C, 65.00; H, 8.3%.)

Tetracyclo[5.5.1.0^{4,13}.0^{10,13}]*trideca* - 2,5,8,11 - *tetraene* **6**. A soln of **23** (stereoisomeric mixture, 0.38 g, 1.6 mmol) and anhyd HMPA (30 ml) was heated to reflux with stirring for 48 h. This experiment was carried out with two condensers, one of which was a cold-finger type (dry ice–acetone). After cooling the soln to room temp, the soln was poured into pentane (400 ml) and the pentane layer was washed consecutively with water (3 × 50 ml) and brine (3 × 50 ml), and then dried (Na_2SO_4). Removal of the pentane by fractional distillation gave a crude solid, which was purified by flash column chromatography [230–400 mesh, SiO_2, pentane]. This gave **6** (80%) accompanied by the bridgehead tetraene (20%) in a combined yield of 61%. The tetraene **6** was obtained as a white solid when the mixture of alkenes was triturated with pentane at −30°. This material was subsequently sublimed at 60–80° at atmospheric pressure to provide pure **6**: m.p. 90° (sealed capillary); IR (FT, KBr) 3070, 2900 and 1610 cm^{-1} (weak); ^{1}H-NMR ($CDCl_3$) δ 3.48 (s, 4H), 5.33 (s, 8H); ^{13}C-NMR ($CDCl_3$) δ 66.00 (s), 66.36 (d), 131.83 (d); mass spectrum (EI, 15 eV) 168 (P, 67), 167 (P−1, 100), 166 (17), 165 (52) and 164 (7.1). High resolution mass spectrum calc for $C_{13}H_{12}$: 168.0939; found: 168.0958. Mass spectrum of bridgehead tetraene (EI, 15 eV) 168 (M^+, 62), 167 (100), 166 (17.4), 165 (52) and 164; ^{13}C-NMR (bridgehead tetraene,[41] $CDCl_3$) δ 46.24, 54.25, 59.72, 64.06, 112.18, 115.66, 125.52, 130.41, 131.60, 134.35, 135.38, 141.53. The quaternary C atom was not observed in the ^{13}C-NMR spectrum due to the very small quantity of sample available for analysis.

Tricyclo[6.3.0.0^{1,5}]*undeca* - 3,6,9 - *triene* **26** *and tricyclo*[6.3.0.0^{1,5}]*undeca* - 2,6,9 - *triene* **27**. The trione **24** prepared by the method of Oehldrich *et al.*[14] was stirred at 0° in borane–THF. After the analogous workup described for **18** was completed, a mixture of stereoisomeric triols represented by **25** was obtained in 90% yield, compound **25**: oil (IR, neat) 3600–3200 cm^{-1}; mass spectrum (CI, CH_4) P+1 199 (20), 181 (10), 163 (100), 145 (90). (Found: C, 66.24; H, 9.02. Calc for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09%.)

The epimeric mixture of **25** was heated in HMPA, under the analogous conditions to those reported for preparation of **5**. After workup and flash chromatography (SiO_2) the two trienes **26** and **27** were isolated in a combined yield of 70%, compound **26**: oil; IR (FT, neat) 3047, 2930 and 802 cm^{-1}; ^{13}C-NMR (62.9 mHz, $CDCl_3$) 48.26 (t), 65.50 (s), 66.92 (d), 128.78 (d), 131.69 (d), and 131.78 (d); mass spectrum (EI, 15 eV) 144 (P, 100), 129 (95), 115 (35), 105 (28), 91 (20). High resolution mass spectrum calc for $C_{11}H_{12}$: 144.0939; found: 144.0923. Compound **27**: oil; ^{13}C-NMR (62.9 mHz, $CDCl_3$) 36.99 (t), 44.17 (t), 56.40 (d), 56.46 (s), 63.15 (d), 127.49 (d), 128.09 (d), 130.64 (d), 132.87 (d), 135.48 (d), 137.22 (d).

Analysis was performed on the mixture of **26** and **27**. (Found: C, 91.54; H, 8.29. Calc for $C_{11}H_{12}$: C, 91.66; H, 8.33%.)

The mixture of **26** and **27** was then converted into the parent hydrocarbon, **28**, by catalytic hydrogenation (H_2, Pd/C, 53 psi) in MeOH. This procedure gave a 92% yield of **28** present as an oil. Compound **28**: IR (FT, neat) 2937, 2859 and 501 cm^{-1}; ^{1}H-NMR (250 mHz, $CDCl_3$) δ 0.90–2.10 (m); ^{13}C-NMR (C_2 axis of symmetry) (62.9 mHz, $CDCl_3$) 26.77 (t), 33.44 (t), 33.49 (t), 42.08 (t), 52.32 (d), 61.93 (s); mass spectrum (EI, 15 eV) 150 (7.6), 135 (13.3), 122 (100), 107 (72.7), 93 (30.1). High resolution mass spectrum calc for $C_{11}H_{18}$: 150.1408; found: 150.1401. (Found: C, 87.79; H, 11.98. Calc for $C_{11}H_{18}$: C, 88.00; H, 12.00%.)

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REFERENCES

[1] U. Weiss and J. M. Edwards, *Tetrahedron Lett.* 4885 (1968).
[2] R. W. Weber and J. M. Cook, *Can. J. Chem.* **56**, 189 (1978).
[3] R. Mitschka, J. Oehldrich, K. Takahashi, U. Weiss, J. V. Silverton and J. M. Cook, *Tetrahedron* **37**, 4521 (1981).

[4] G. Kubiak, U. Weiss and J. M. Cook, *J. Org. Chem.* **49**, 561 (1984).

[5] *Gymnomitrol*: R. M. Coates, S. K. Shaw and R. W. Mason, *J. Am. Chem. Soc.* **101**, 6765 (1979); Y.-K. Han and L. Paquette, *J. Org. Chem.* **44**, 3731 (1979). *Isocomene*: W. G. Dauben and D. M. Walker, *Ibid.* **46**, 1103 (1981). *Modhephene*: J. Wrobel, K. Takahashi, V. Honkan, G. Lannoye, S. H. Bertz and J. M. Cook, *Ibid.* **48**, 139 (1983). *Pentalenene*: E. Piers and V. Karunaratne, *J. Chem. Soc. Chem. Commun.* 959 (1984).

[6a] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, p. 290f. Wiley, New York (1961); [b] R. B. Woodward, T. Fukunaga and R. C. Kelly, *J. Am. Chem. Soc.* **86**, 3162 (1964); [c] M. A. McKervey, J. J. Rooney and N. G. Samman, *J. Chem. Soc. Chem. Commun.* 1185 (1972); [d] H. Butenschön and A. de Meijere, *Tetrahedron Lett.* **24**, 4563 (1983); *Ibid.* **25**, 1693 (1984); [e] I. Gutman, M. Milu and N. Trinajstic, *J. Am. Chem. Soc.* **99**, 1692 (1977).

[7] L. A. Paquette and J. D. Kramer, *J. Org. Chem.* **49**, 1445 (1984).

[8] S. H. Bertz, G. Lannoye and J. M. Cook, *Tetrahedron Lett.* **26**, 4695 (1985). For a preliminary report see Ref. 19.

[9] R. Hoffmann, R. W. Alder and C. F. Wilcox, Jr., *J. Am. Chem. Soc.* **92**, 4992 (1970); R. Hoffmann, *Pure Appl. Chem.* **28**, 181 (1971); R. Keese, A. Pfenninger and A. Roesle, *Helv. Chim. Acta* **62**, 326 (1979); M. C. Böhm, R. Gleiter and P. Schang, *Tetrahedron Lett.* 2575 (1979); J. Chandrasekhar, E.-U. Würthwein and P. v. R. Schleyer, *Tetrahedron* **37**, 921 (1981).

[10] H. Schori, B. B. Patil and R. Keese, *Ibid.* **37**, 4457 (1981); M. Luyten and R. Keese, *Angew. Chem. Int. Ed. Engl.* **23**, 390 (1984); R. Keese, *Nachr. Chem. Tech. Lab.* **30**, 844 (1982); K. Krogh-Jespersen, D. Cremer, D. Poppinger, J. A. Pople, P. v. R. Schleyer and J. Chandrasekhar, *J. Am. Chem. Soc.* **101**, 4843 (1979); P. v. R. Schleyer and E.-U. Würthwein, *J. Chem. Soc. Chem. Commun.* 542 (1982); D. C. Crans and J. P. Snyder, *J. Am. Chem. Soc.* **102**, 7152 (1980); W. T. Hoeve and H. Wynberg, *J. Org. Chem.* **45**, 2930 (1980); J. Mani and R. Keese, *Synthesis of* 2,3 - *Dimethyl* - *tetracyclo*$[5.5.1.0^{4,13}.0^{10,13}]$*trideca* - 2,5 - *dien* - 9 - *one, a New Derivative of all* - cis - [5.5.5.5]*Fenestrane*, submitted. We thank Professor Keese for a preprint of this manuscript.

[11] R. Mitschka, U. Weiss and J. M. Cook, *J. Am. Chem. Soc.* **100**, 3973 (1978).

[12] W. G. Dauben and D. M. Walker, *Tetrahedron Lett.* **23**, 711 (1982); V. B. Rao, S. Wolff and W. C. Agosta, *J. Chem. Soc. Chem. Commun.* 293 (1984); M. T. Crimmins, S. W. Mascarella and L. Bredon, *Tetrahedron Lett.* **26**, 997 (1985).

[13a] I. Willner and M. Rabinovitz, *J. Am. Chem. Soc.* **100**, 337 (1978); [b] B. Hess, Jr. and L. J. Schaad, *J. Org. Chem.* **36**, 3418 (1971).

[14] J. Oehldrich, J. M. Cook and U. Weiss, *Tetrahedron Lett.* 4549 (1976).

[15] A. Gawish, R. Mitschka, U. Weiss and J. M. Cook, *Ibid.* **22**, 211 (1981).

[16] W. C. Han, K. Takahashi, J. M. Cook, U. Weiss and J. V. Silverton, *J. Am. Chem. Soc.* **104**, 318 (1982).

[17] P. E. Eaton, R. H. Mueller, G. R. Carlson, D. A. Cullison, G. F. Cooper, T.-C. Chou and E.-P. Krebs, *Ibid.* **99**, 2751 (1977).

[18] C. Weringa and J. M. Cook, unpublished results.

[19] G. Lannoye, V. Honkan, U. Weiss, S. Bertz and J. M. Cook, Abstracts of Papers, 16th Annual Meeting, Great Lakes American Chemical Society Region, Illinois State University, Normal, Illinois, 7–9 June (1982), No. 201.

[20] This work has been reported in preliminary form: M. Venkatachalam, M. Jawdosiuk, M. Deshpande and J. M. Cook, *Tetrahedron Lett.* **26**, 2275 (1985).

[21] A. Belanger, J. Poupant and P. Deslongchamps, *Ibid.* 2127 (1968).

[22] M. Karplus and J. A. Pople, *J. Chem. Phys.* **38**, 2803 (1963); M. Karplus, *Ibid.* **30**, 11 (1959).

[23] M. Venkatachalam, M. Deshpande, S. Wehrli and J. M. Cook, manuscript in preparation.

[24] M. N. Deshpande, M. Jawdosiuk, G. Kubiak, M. Venkatachalam, U. Weiss and J. M. Cook, *J. Am. Chem. Soc.* **107**, 4786 (1985).

[25] R. S. Monson, *Tetrahedron Lett.* 567 (1971); J. S. Lomas, D. S. Sagatys and J. E. Dubois, *Ibid.* 165 (1972); R. S. Monson and D. N. Priest, *J. Org. Chem.* **36**, 3826 (1971).

[26] M. Venkatachalam, G. Kubiak, J. M. Cook and U. Weiss, *Tetrahedron Lett.* **26**, 4863 (1985).

[27] G. H. Schmid and A. W. Wolkoff, *J. Org. Chem.* **32**, 254 (1967); K. C. Murdock and R. B. Angier, *Ibid.* **27**, 2395 (1962).

[28] H. J. Bestmann, O. Klein, L. Gothlich and H. Buckschewski, *Chem. Ber.* **96**, 2259 (1963); F. Weygand and H. J. Bestmann, *Ibid.* **90**, 1230 (1957).

[29] G. Kubiak, K. Avasthi and J. M. Cook, manuscript in preparation.

[30] M. N. Deshpande, S. Wehrli, M. Jawdosink, J. T. Guy, Jr., D. W. Bennett, J. M. Cook, M. R. Depp and U. Weiss, *J. Org. Chem.* (1986), in press.