Synthesis of Difunctionalized Iceane Derivatives: 3,13-Dimethylene-8-oxapentacyclo[8.3.1.1^{2,6}.0^{4,12}.0^{6,10}]pentadecane

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Abstract: The propellane 12-oxatricyclo[4.4.3.0^{1,6}]trideca-3,8-diene (**8f**) undergoes two consecutive Diels-Alder reactions, the first intermolecular and the second intramolecular, with the regenerable diene tetrachlorothiophene 1,1-dioxide to give 11-oxa-2,3,4,5-tetrachlorohexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]-3-heptadecane (**4f**). Related propellanes undergo similar reactions. Dissolving metal reductions replace the halogen in these molecules by hydrogen. Catalytic hydrogenation of **4f** gives 11-oxa-2,5-dichlorohexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]heptadecane (**13**) which, on reaction with sodium-potassium alloy, fragments to 16-oxapentacyclo[8.4.3.0^{1,10}.0^{4,13}.0^{7,12}]heptadeca-3,7-diene (**14**). Diene **14** undergoes a Cope rearrangement to the title compound **15**.

Iceane (**1**)[1] is a $C_{12}H_{18}$ hydrocarbon in which there are two six-membered rings in chair configurations and three six-membered rings in nontwist boat configurations. Therefore although a model of iceane is strain free there undoubtably exists nonbonded interactions within the molecule that must be involved in the chemistry of the compound and its derivatives and must be considered during their construction. Three syntheses of iceane have been described[2] and reports of a number of other molecules incorporating the iceane skeleton have also appeared.[3] Because of an interest[4] in the construction of polycyclic molecules we set out to see if the carbon skeleton of iceane could be formed by a more efficient procedure than those reported previously. At the same time, it was hoped that provision could be made to incorporate functionality at the prow and stern positions of one of the boat rings as it was felt that the availability of such a molecule, of interest in its own right, would lead also to further systems with interesting chemical and physical properties.

In our earlier synthesis[2b] of iceane (**1**) a key intermediate

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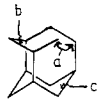

2

containing the substructure **2** was produced by the development of chemistry that involved as one of its steps the formation of the bond labeled "b" in substructure **2**.[5] We wondered, however, if a route could be developed by which such a key intermediate would be built up in a process that involved the formation of the bond labeled "c" to produce substructure **2**.

In principle, there are two ways by which the iceane skeleton might be built up by processes involving the formation of the bonds labeled "a" and "c" and these are by the sequential formation,[6] or by the simultaneous formation, of these bonds. This paper describes the development of chemistry that allows the construction of the iceane skeleton by an intramolecular Diels-Alder reaction in which bonds "a" and "c" are formed simultaneously. Removal of the extra ring system, which this route introduces, leads to iceane derivatives difunctionalized at the prow and stern positions of one of the rings in a boat configuration.

Construction of the Iceane Skeleton. The stereochemistry in the trienes (e.g., **3**), which are required for the intramolecular Diels-Alder reaction, must be cis-syn-cis if cyclization is to occur to give iceane derivatives (e.g., **4**). Addition of a bidentate electrophile from the less-hindered convex face of a tetraene, such as **5**, would be expected to occur preferentially to the most electron rich central double bond to give a triene **3** with the required stereochemistry.

The regenerable diene tetrachlorothiophene 1,1-dioxide[7] reacted cleanly with isotetralin (**6**) to give, in almost quantitative yield, the monoadduct **5**. The only electrophilic addition reaction that was found to be selective for this monoadduct was epoxidation. The addition of dichlorocarbene, generated in several ways,[8] or chlorosulfonyl isocyanate addition gave mixtures in which reaction at either or both double bonds had occurred. Epoxidation of monoadduct **5** at 0 °C proceeded to give predominantly one compound, the spectroscopic data for which were consistent with those for structure **3a**, but for which the stereochemistry was assigned only on the basis of the expected direction of attack of the electrophile. Upon heating, the epoxide **3a** did not undergo an intramolecular Diels-Alder reaction but at elevated temperature gave instead the aromatic compound **7** even under conditions designed to obviate adventitious acid.

Since it appeared that the required regiochemistry could not be introduced at this stage, consideration was given to its introduction at the diene level. A number of propellanes of the general structure **8** are known and it was considered that each of them should undergo a Diels-Alder reaction with tetrachlorothiophene dioxide. The most critical requirement for the formation of

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(1) Müller, E. "Neuere Anshauungen der Organischen Chemie"; Julius Springer: Berlin, 1940; p 30. Fieser, L. F. *J. Chem. Educ.* **1965**, *42*, 408.

(2) (a) Cupas, C. A.; Hadokowski, L. *J. Am. Chem. Soc.* **1974**, *96*, 4668. (b) Hamon, D. P. G.; Taylor, G. F. *Tetrahedron Lett.* **1975**, 155; *Aust. J. Chem.* **1976**, *29*, 1721. (c) Ganter, C.; Klaus, R. O.; Tobler, H. *Helv. Chim. Acta* **1975**, *58*, 1455.

(3) Bundy, F. P.; Kaper, J. S. *J. Chem. Phys.* **1967**, *46*, 3437. Bundy, F. P.; Hanneman, R. E.; Strong, H. M. *Science* **1967**, *155*, 995. Bockelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201. Ōsawa, E.; Schleyer, P. v. R.; Furusaki, A.; Hashiba, N.; Matsumoto, T.; Singh, V.; Tahara, Y.; Wiskott, E.; Farcasiu, M.; Iizuka, T.; Tanaka, N.; Kan, T. *J. Org. Chem.* **1980**, *45*, 2985. Fritz, G.; Marguardt, G.; Sheer, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 654. Ganter, C.; Klaus, R. O.; Tobler, H. *Helv. Chim. Acta* **1954**, *58*, 2517. Hamon, D. P. G.; Taylor, G. F.; Young, R. N. *Tetrahedron Lett.* **1975**, 1623. Hamon, D. P. G.; Taylor, G. F.; Young, R. N. *Aust. J. Chem.* **1977**, *30*, 589. Ganter, C.; Klaus, R. O. *Helv. Chim. Acta* **1980**, *63*, 2559.

(4) Hamon, D. P. G.; Young, R. N. *Aust. J. Chem.* **1976**, *29*, 145 and references cited therein.

(5) The synthesis of ref 2c also involves the formation of the bond labeled "b".

(6) In a formal sense, the synthesis in ref 2a involves the consecutive formation of bond "c" and then bond "a" during the cationic rearrangement involved in that route.

(7) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 856.

(8) Seyferth, D.; Yick-Pui Mui, J.; Gordon, M. E.; Burlitch, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 681. Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1969**, *16*, 21. Hiyama, T.; Sawada, H.; Tsukanaka, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 3013. Banwell, M. G.; Halton, B. *Aust. J. Chem.* **1980**, *33*, 2277.

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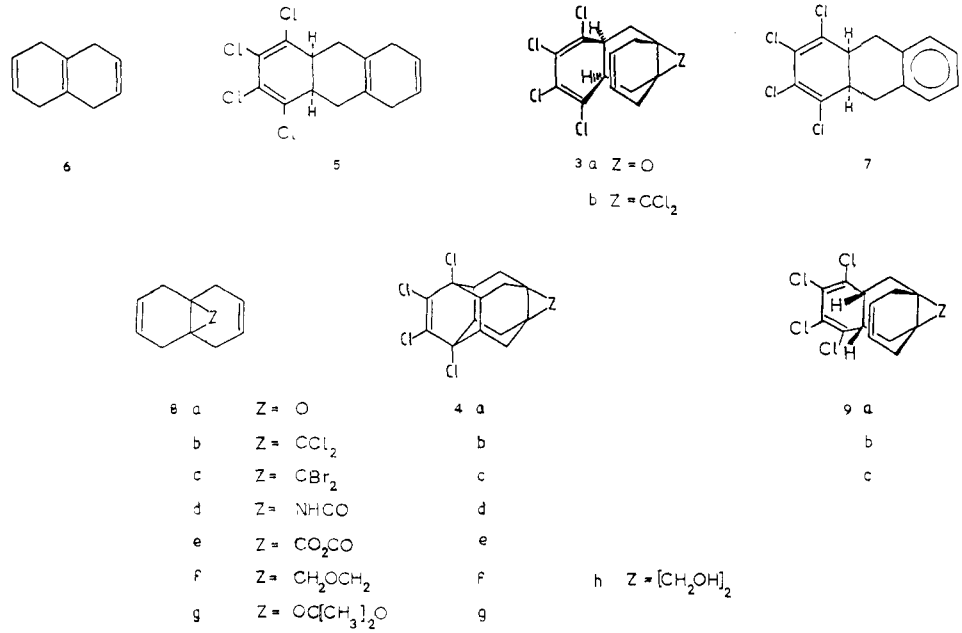
Chart I



compounds with the structure **4** is the control of the stereochemistry of the initial Diels–Alder reaction so that the second intramolecular cyclization can take place. The products **4** can result only by cycloaddition, to the dienes **8**, of the tetrachlorothiophene dioxide on the side anti to the bridge Z. It appeared that at least two factors could affect that approach for each propellane and these effects might be interrelated. These were the conformational preference of the ring system and the size of the bridging group Z. In particular, the larger the size of the bridging group Z, the less favored should be the addition syn to that group and therefore, hopefully, the addition anti would be more favored.

Under carefully controlled conditions, the epoxide **8a**[9] underwent a clean cycloaddition reaction with tetrachlorothiophene dioxide to give a single product, the spectroscopic properties of which were consistent with those for structure **3a**, but the physical properties were different from those for the compound obtained earlier, indicating that they were stereoisomers. For neither of these two epoxides has the stereochemistry been rigorously proven, but one must have the structure **3a** and the other the structure **9a**. The new isomer on heating also rearranged, at elevated temperatures, only to the aromatic compound **7**.

When a mixture of the propellane **8b**[10] and tetrachlorothiophene dioxide was heated[11] in the melt at 120 °C for 7 h, the polycycle **4b** and the triene **9b** were isolated in nearly quantitative yield in a ratio of approximately 1:2 and they could be obtained pure by fractional crystallization. The polycycle **4b** was obtained in 33% yield, mp 242–243 °C. Its structure was shown to be 4,5,6,7,15,15-hexachlorohexacyclo[8.4.1.$0^{1,10}$.$0^{3,8}$.$0^{4,13}$.$0^{7,12}$]-5-pentadecene on the basis of the following data. Elemental analysis and peaks at 402, 404, 406, 408, and 410 in the mass spectrum were consistent with the data for the compound with the molecular formula $C_{15}H_{12}Cl_6$. The ^{1}H NMR spectrum exhibited a broadened singlet at δ 2.35 superimposed on one resonance of an AB quartet at δ 2.22 and 1.48, J = 15 Hz. This spectrum is similar in appearance to that of iceane itself.[2] Six resonances in the broad-band decoupled ^{13}C NMR spectrum were in accordance with the symmetry of compound **4b** and the multiplicities in the off-resonance spectrum were as expected. The isomeric compound **9b**, mp 148–149 °C, showed resonances at δ 5.51 (br s, 2 H) in the ^{1}H NMR and at 123.7 ppm in the ^{13}C NMR spectra which demonstrated the presence of the isolated double bond. In addition, the ^{13}C NMR broad-band and off-resonance decoupled spectra were consistent with the existence of eight different carbon nuclei with the appropriate number of attached hydrogen atoms. The triene **9b** remains unchanged when heated to 170 °C which establishes that it has the wrong stereochemistry for internal cyclization. Evidently under the conditions of its formation the triene **3b**, which must be a precursor to the polycycle **4b**, reacts further and is not isolated.

The reaction between the propellane **8c**[12] and tetrachlorothiophene dioxide afforded an almost equal amount of the triene **9c** and the cyclized compound **4c** as indicated by the NMR spectrum of the crude product. The increse in the amount of the desired product **4c** in the crude product can be attributed to the greater directing effect of the larger *gem*-dihalomethylene group in compound **8c** compared to that in compound **8b**. The effect the size of other Z moieties has on the ratio of the products of the type **4** and **9** has been investigated.

The β-lactam propellane **8d** has been prepared by a modification of the literature method[13] which gives a better yield of product. The acetal propellane **8g**[14] was made by an improved procedure from the corresponding diol.[14] The experimental details required to obtain the anhydride **8e**[15] have not been well described in the past and a procedure is given.

When the β-lactam propellane **8d** in 1,2-dichloroethane, or the anhydride propellane **8e** in toluene, was heated at reflux with tetrachlorothiophene dioxide the hexacyclic products **4d**, or **4e**, crystallized from the reaction mixture, analytically pure, in 65% and 70% yield, respectively. The proof of structure of these compounds relies mainly on the NMR spectra. In each case the ^{1}H NMR spectrum gave a simple pattern consisting of an AB quartet for the methylene groups and a singlet for the bridgehead protons, and in addition the spectrum of **4d** also showed a resonance for the amide hydrogen. The lower symmetry for the product **4d** was not reflected in the proton NMR spectrum but was revealed by the broad-band decoupled ^{13}C NMR spectrum. Although the anhydride **4e** showed only six carbon resonances

(9) Vogel, E.; Klug, W.; Breuer, A. *Org. Synth.* **1975**, *55*, 86.
(10) Vogel, E.; Klug, W.; Breuer, A. *Org. Synth.* **1974**, *54*, 11 and references cited therein.
(11) A preliminary account of this part of the work has been reported: Hamon, D. P. G.; Spurr, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 372. We would like to thank Professor R. N. Warrener, Australian National University, for drawing our attention to errors in nomenclature.
(12) Thompson, G. L.; Heyd, W. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 3177.
(13) Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Philips, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 152.
(14) Ginsburg, D.; Ashkenazi, P.; Kalo, J.; Rüttimann, A. *Tetrahedron* **1978**, *34*, 2161.
(15) Alder, K.; Backendorf, K. H. *Chem. Ber.* **1938**, *71*, 2199. Snatzke, G.; Zanati, G. *Justus Liebigs Ann. Chem.* **1965**, *684*, 62. Scott, W. B.; Pincock, R. E. *J. Org. Chem.* **1967**, *33*, 3374.

in the ^{13}C NMR spectrum, the amide **4d** showed ten resonances. Four of the resonances were clearly in pairs and the chemical shift difference, within these pairs, became smaller the further those carbon atoms were located from the amide group with the effect that the sp^2 carbon atoms bearing chlorine appeared equivalent.

The ^1H NMR spectrum of the crude product from the reaction of the acetal propellane **8g** with tetrachlorothiophene dioxide showed no vinylic resonances but had absorptions consistent with the hexacyclic acetal **4g** as the only compound present. Thus it appeared that reaction had occurred to give only the hexacyclic material. The acetal group in this molecule is rather labile and it did not survive chromatography, however, the acetal **4g** could be obtained pure by recrystallization.

Under conditions similar to those used to prepare the anhydride **4e**, the ether prepellane **8f**[16] gave only a 40% yield of the hexacyclic material **4f**. In fact this hexacyclic compound can be prepared in better overall yield (85%) by reduction of the anhydride **4e**, with lithium aluminum hydride in ether, to the diol **4h** which on cyclodehydration gives the ether **4f**.

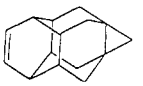
8c

8j

It is possible to rationalize the improvement in the yield of hexacyclic material, on going from the dihalocarbene adducts **8b** and **8c** to the more open propellanes, as being due to greater conformational mobility available when there is no longer the restrictive halogen–double bond interaction (**8i**). That this is so is probably best seen by recourse to models. In particular, it is apparent that little impediment is imposed on the acetal **8g** to prevent it taking up conformations (**8j**) where the diene can approach anti to the bridging group while, at the same time, this bridging group can still provide hindrance to syn attack. It is surprising that there is such an appreciable difference in the yields obtained from the anhydride **8e** and the ether **8f**. Presumably dipolar interactions play a role in the transition state for the initial Diels–Alder reaction of the anhydride **8e** repelling the tetrachlorothiophene dioxide from syn approach.[17a] A similar situation probably pertains for the lactam **8d** also.[17b]

It is perhaps surprising that the epoxide **3a** gives no hexacyclic material at all but rearranges instead at temperatures considerably higher than needed for cyclization in any of the other cases. Dreiding models of the ring system **3a** show the dihedral angle between the two rings bridged by the oxygen atom is considerably expanded over those in the other systems. This has the effect of both misaligning and separating the orbitals of the alkene moiety from those of the diene moiety. Perhaps it is this lack of the appropriate geometry which prevents the intramolecular Diels–Alder reaction in this molecule.

Functionalization at the Prow and Stern Positions. When the hexachloro compound **4b** was reduced with sodium in ethanol,[18] removal of the chlorine atoms was achieved in high yield but two products, which could be separated by reverse phase chromatography, were obtained. The major compound was shown to be the expected monoalkene **10** on the basis of the NMR spectra. In particular the ^{13}C NMR spectrum revealed the presence of six different carbon atoms with only one sp^2 carbon. The ^1H NMR spectrum showed the vinylic protons as a pair of overlapping doublets and the cyclopropyl protons as a sharp singlet. In contrast the ^{13}C NMR spectrum of the minor product showed the presence of eight different carbon atoms, three of which were sp^2, and the ^1H NMR spectrum showed two distinct olefinic regions, one as a singlet the other as a doublet, as well as an AB quartet for the cyclopropyl protons. On the basis of these data, and its molecular weight, the minor compound was assigned the interesting triene structure **11**.



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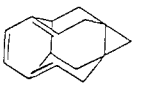
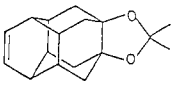


11



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It was considered that the triene **11** arose from compound **4b** by a fragmentation reaction of the type described by Grob[19] and that therefore its formation would be prevented by removal of one or both of the offending bridgehead chlorine atoms from that compound prior to the dissolving metal reduction. The removal of the bridgehead chlorine atoms has been achieved by stannane reductions. In the two cases studied, the crude product from the stannane reaction was treated under the dissolving metal conditions and only the monoalkene (**10** or **12**) was produced. Since no triene is formed by this route it can be implied that the fragmentation reaction does not proceed by way of radicals but must involve anionic intermediates and this is of interest in respect to other studies from this laboratory.[20]

Although clearly a route was available by which the fragmentation reaction[21] could be avoided, alternative chemistry exploiting a fragmentation reaction was pursued.[22] Catalytic hydrogenation of the ether **4f** over Pd in the presence of triethylamine gave the dichloro ether **13**. In principle, reductive fragmentation of compound **13** could give rise to the diene **14** by cleavage of an internal bond or the dimethylene compound **15** by cleavage of the peripheral bond. In practice reaction of the dichloro ether **13** with sodium–potassium alloy in the nonprotonic solvent ether gave diene **14** as the only product[23] of fragmentation. A small amount of the reduction product **16** was also obtained but the two products could be separated by reverse-phase chromatography. The structure of the diene was deduced from spectroscopic data. In particular the ^1H NMR spectrum showed a distorted triplet from the vinylic protons and an AB quartet for the methylene protons of the tetrahydrofuran ring. The broad-band decoupled ^{13}C NMR spectrum showed eight carbon resonances, two of which were for sp^2 carbons, and the off-resonance multiplicites were consistent with this structure.

Flash vacuum pyrolysis of the diene **14** at 500 °C gave cleanly and in high yield the difunctionalized iceane derivative **15**, which is the title compound. This Cope rearrangement could also be followed in solution in D_6 dimethyl sulfoxide in the NMR spectrometer. The product of the rearrangement first appeared at a temperature of ca. 130 °C. The structure of this rearrangement product is established from the NMR spectra. The ^1H NMR shows a singlet at δ 4.46 for the vinylic protons, a singlet at δ 3.47 for the methylene protons of the tetrahydrofuran ring, a broad singlet at δ 2.75 for the bridgehead protons, and an AB quartet at δ 1.91 and 1.22 (J = 12 Hz) for the remaining methylene

(16) Ginsburg, D.; Altman, J.; Babad, E.; Itzchaki, J. *Tetrahedron Suppl., Part 1* **1966**, *8*, 279.

(17) (a) Contrast this with the work of Ginsburg et al., in which orbital steering causes syn approach to propellanes which act as dienes rather than dienophiles: Gleiter, R.; Ginsburg, D. *Pure Appl. Chem.* **1979**, *51*, 1301. (b) See, However: Newkome, G. R.; Fronczek, F. R.; Baker, G. R. *Tetrahedron Lett.* **1982**, 2725.

(18) Lap, B. V.; Padden-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979.

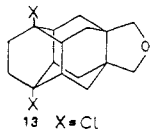
(19) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1.

(20) Hamon, D. P. G.; Richards, K. R. *Aust. J. Chem.* **1983**, *36*, 109.

(21) The dissolving metal reduction has been tried on a number of the hexacyclic compounds **4** and in each case the corresponding triene is formed in an appreciable amount.

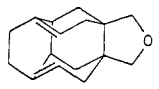
(22) We thank R. R. Smyth for assistance in developing this route.

(23) Marshall, J. A. *Synthesis* **1971**, 229.



13 X = Cl

16 X = H



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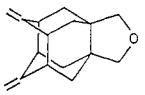

15

groups. The ^{13}C NMR spectrum reveals the presence of six different carbon atoms.

In conclusion it can be stated that a route to difunctionalized iceane derivatives has been demonstrated which makes these compounds available for further study.

Experimental Section

1,2,3,4-Tetrachloro-*cis*-4a,5,8,9,9a,10-hexahydroanthracene (5). A solution of 1,4,5,8-tetrahydronaphthalene[24] (**6**) (1.32 g, 10.0 mmol) and tetrachlorothiophene 1,1-dioxide[7] (2.54 g, 10.0 mmol) in carbon tetrachloride (12 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (5 mg) was heated at reflux for 3.5 h under a nitrogen atmosphere. The solvent was removed to leave a white solid (3.3 g, ~100%) which was of satisfactory purity for subsequent use. Flash chromatography on silica gel with petroleum ether as the eluent provided the pure adduct **5**: mp 105–107 °C; IR ($CDCl_3$) 3040, 1660, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.56 (s, 2 H), 3.05 (m, 2 H), 2.44 (s, 4 H), 2.17 (m, 4 H); ^{13}C NMR ($CDCl_3$) 134.4, 134.0, 124.6, 124.1, 40.7, 30.9, 29.7 ppm; MS, *m/e* 320, 322, 324, 326 (M^+). Anal. Calcd for $C_{14}H_{12}Cl_4$: C, 52.21; H, 3.76. Found: C, 52.47; H, 3.85.

***meso*-(4a*R*,10a*R*,8a*S*,9a*S*)-5,6,7,8-Tetrachloro-1,4,4a,8a,9,9a,10,10a-octahydro-4a,9a-oxidoanthracene (3a).** A solution of 85% *m*-chloroperbenzoic acid (225 mg, 1.1 mmol) in dichloromethane (10 mL) was added over 10 min to a stirred suspension of the adduct of **5** (322 mg, 1.0 mmol) and anhydrous sodium acetate (123 mg, 1.5 mmol) in dichloromethane (5 mL) and cooled to −5 °C. The mixture was stirred for 3.5 h at 0 °C then treated with 10% aqueous sodium hydroxide solution (10 mL). The aqueous layer was separated and extracted with dichloromethane (10 mL) and the organic phase was washed with brine (10 mL), dried ($MgSO_4$), and evaporated to give a white solid (332 mg) which was purified by flash chromatography on silica gel. Elution with 25% dichloromethane/petroleum ether (~350 mL) followed by 50% dichloromethane/petroleum ether (~150 mL) provided the epoxide **3a** (200 mg, 59%). Recrystallization from chloroform/petroleum ether afforded an analytical sample, mp 181–183 °C dec. The epoxide was judged to be a single isomer by TLC on silica gel (R_f 0.26 with 50% dichloromethane/petroleum ether) and by HPLC on a Waters Radial PAK B column (17% dichloromethane/petroleum ether at 3 mL/min): IR ($CDCl_3$) 3030, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.36 (br s, 2 H), 2.97 (7, 2 H), 2.43 (br s, 4 H), 2.16 (m, 4 H); ^{13}C NMR ($CDCl_3$) 133.6, 124.5, 122.3, 60.3, 38.8, 30.9, 29.4 ppm; MS, *m/e* 336, 338, 340, 342 (M^+). Anal. Calcd for $C_{14}H_{12}Cl_4O$: C, 49.74; H, 3.58. Found: C, 49.76; H, 3.71.

***meso*-(4a*S*,10a*R*,8a*S*,9a*R*)-5,6,7,8-Tetrachloro-1,4,4a,8a,9,9a,10,10a-octahydro-4a,9a-oxidoanthracene (9a).** A solution of 11-oxatricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**8a**) (296 mg, 2.0 mmol) and tetrachlorothiophene dioxide (508 mg, 2.0 mmol) in carbon tetrachloride (5 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (2 mg) and anhydrous sodium bicarbonate (336 mg, 4.0 mmol) was heated for 12 h at reflux under a nitrogen atmosphere. The mixture was filtered while hot and evaporated to give a white solid (730 mg) which was purified by flash chromatography on silica gel. Elution with 25% dichloromethane/petroleum ether provided the epoxide **9a** (377 mg, 56%). Recrystallization from chloroform/petroleum ether afforded an analytical sample, mp 159–161 °C. The epoxide was judged to be a single isomer by TLC on silica gel (R_f 0.29 with 50% dichloromethane/petroleum ether) and by HPLC on a Waters Radial PAK B column (17% dichloromethane/petroleum ether at 3 mL/min): IR ($CDCl_3$) 3025, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) 5.38 (br s, 2 H), 2.76 (m, 2 H), 2.41 (br s, 4 H), 2.16 (m, 4 H); ^{13}C NMR ($CDCl_3$) 133.7 (s), 123.7 (s), 122.4 (d), 58.6 (s), 38.9 (d), 30.8 (t) ppm; MS, *m/e* 336, 338, 340, 342 (M^+). Anal. Calcd for $C_{14}H_{12}Cl_4O$: C, 49.74; H, 3.58. Found: C, 49.70; H, 3.76.

1,2,3,4-Tetrachloro-4a,9,9a,10-tetrahydroanthracene (7). Method 1. A mixture of 11-oxatricyclo[4.4.1.$0^{1,6}$]undeca-1,3-diene[11] (**8a**) (148 mg, 1.0 mmol) and tetrachlorothiophene dioxide (254 mg, 1.0 mmol) was heated for 2 h at 120 °C. After the mixture had melted, a vigorous evolution of sulfur dioxide ensued. A yellow-orange oil was produced which was purified by flash chromatography on silica gel. Elution with petroleum ether (150 mL) followed by 10% dichloromethane/petroleum ether (150 mL) and 20% dichloromethane/petroleum ether (300 mL) provided the tetrahydroanthracene **7** (190 mg, 59%). Recrystallization from methanol afforded an analytical sample: mp 125–126 °C; IR ($CDCl_3$) 3050, 3010, 1595, 1580, 1500, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (s, 4 H), 3.05 (br s, 6 H); MS, *m/e* 318, 320, 322, 324 (M^+). Anal. Calcd for $C_{14}H_{10}Cl_4$: C, 49.74; H, 3.58. Found: C, 49.70; H, 3.76.

Method 2. A solution of the epoxide **3a** (67 mg, 0.2 mmol) in 1,2-dichlorobenzene (3 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (1 mg) and sodium bicarbonate (42 mg, 0.5 mmol) was heated for 4.5 h at reflux under an atmosphere of nitrogen. TLC analysis showed that no reaction had occurred. The mixture was filtered and heated for 18 h at 250 °C in a sealed tube after which time the solution had become turbid. Analysis by TLC and ^1H NMR showed that the aromatic compound **7** had been produced.

A similar result was obtained when the epoxide **9a** was subjected to the same conditions described above.

4,5,6,7,15,15-Hexachlorohexacyclo[8.4.1.$0^{1,10}$.$0^{3,8}$.$0^{4,13}$.$0^{7,12}$]-5-pentadecene (4b) and *meso*-(4a*R*,10a*S*,8a*R*,9a*S*)-5,6,7,8,11,11-Hexachloro-1,4,4a,8a,9,9a,10,10a-octahydro-4a,9a-methanoanthracene (9b). A mixture of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene[10] (**8b**) (2.15 g, 10.0 mmol) and tetrachlorothiophene dioxide (2.54 g, 10.0 mmol) was heated for 7 h at 120 °C. The mixture became homogeneous and sulfur dioxide evolution commenced within a few minutes and after ca. 2 h a crystalline solid was deposited. The solidified mass which formed on cooling was recrystallized once from carbon tetrachloride/petroleum ether to give the hexacyclic product **4b** (1.56 g, 33%): mp 242–243 °C; IR ($CDCl_3$) 1603 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (br s, 4 H), 2.22 and 1.48 (ABq, *J* 15 Hz, 8 H); ^{13}C NMR ($CDCl_3$) 131.8 (s), 82.8 (s), 74.7 (s), 46.1 (d), 28.7 (s), 24.6 (t) ppm; MS, *m/e* 402, 404, 406, 408, 410 (M^+). Anal. Calcd for $C_{15}H_{12}Cl_6$: C, 44.48; H, 2.99. Found: C, 44.18; H, 2.94.

The mother liquors from the crystallization of the carbocycle **4b** were concentrated and the residue was recrystallized three times from petroleum ether to give the isomeric triene **9b**: mp 148–149 °C; IR ($CDCl_3$) 3060, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (br s, 2 H), 1.4–3.2 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 132.0 (s), 123.7 (s), 123.7 (d), 74.0 (s), 39.1 (d), 31.3 (t), 26.2 (t), 25.5 (s) ppm; MS, *m/e* 402, 404, 406, 408, 410 (M^+). Anal. Calcd for $C_{15}H_{12}Cl_6$: C, 44.48; C, 44.48; H, 2.99. Found: C, 44.27; H, 2.93.

11,11-Dibromotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (8c). This dibromide was prepared from isotetralin (**6**) by an adaptation of the method of Vogel, Klug, and Breuer[10] with the workup procedure of Paquette et al.[12] A product of satisfactory purity for subsequent use was obtained, in 27% yield, by sublimation at 100 °C (1 mm).

15,15-Dibromo-4,5,6,7-tetrachlorohexacyclo[8.4.1.$0^{1,10}$.$0^{3,8}$.$0^{4,13}$.$0^{7,12}$]-5-pentadecene (4c). A solution of the diene **8c** (1.21 g, 4.0 mmol) and tetrachlorothiophene dioxide (1.01 g, 4.0 mmol) in *p*-xylene (2 mL) was heated for 24 h at reflux under a nitrogen atmosphere. The mixture was partially cooled and petroleum ether (3 mL) was added. Cooling to room temperature then to 0 °C precipitated a brown solid (1.11 g) which was filtered and recrystallized from carbon tetrachloride/petroleum ether to yield the hexacyclic product **4c** (0.58 g, 29%). A second recrystallization provided an analytical sample: mp 216–217 °C; IR ($CDCl_3$) 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (br s, 4 H), 2.15 and 1.43 (ABq, *J* = 13 Hz, 8 H); ^{13}C NMR ($CDCl_3$) 131.5, 96.2, 74.8, 46.1, 28.3, 26.5 ppm; MS, *m/e* 490, 492, 494, 496, 498, 500 (M^+). Anal. Calcd for $C_{15}H_{12}Br_2Cl_4$: C, 36.48; H, 2.45. Found: C, 36.58; H, 2.51.

11-Aza-11-chlorosulfonyl-12-oxotricyclo[4.4.2.$0^{1,6}$]dodeca-3,8-diene. A solution of chlorosulfonyl isocyanate (3.0 g, 21.0 mmol, 4.8 mL) in anhydrous ether (5 mL) was added, dropwise over 5 min, to a solution of isotetralin (2.64 g, 20 mmol) in ether (5 mL) and cooled to 0 °C. The mixture was warmed to ambient temperature and stood overnight (16 h) by which time the adduct had crystallized. The product was filtered and washed with ether/petroleum ether (1:1) to give the *N*-chlorosulfonyl β-lactam, analytically pure, 3.0 g, (86%): mp 120–121 °C; IR ($CDCl_3$) 3070, 1810, 1645, 1400, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.61–6.10 (m, 4 H), 1.82–3.31 (complex, 8 H). Anal. Calcd for $C_{11}H_{12}ClNO_3S$: C, 48.27; H, 4.42. Found: C, 48.24; H, 4.47.

11-Aza-12-oxotricyclo[4.4.2.$0^{1,6}$]dodeca-3,8-diene (8d). The above *N*-chlorosulfonyl β-lactam was dissolved in ether/acetone (2:1, 15 mL) and added, dropwise, to a vigorously stirred mixture of ether/acetone (2:1, 15 mL) and 25% sodium sulfite solution.[25] The aqueous phase was kept between pH 7 and 8 (phenolphthalein) by the addition of 10%

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(25) Durst, T.; O'Sullivan, M. J. *J. Org. Chem.* **1970**, *35*, 2043.

sodium hydroxide solution. After 1.5 h, the layers were separated and the aqueous phase was extracted with ether (20 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to yield a colorless oil, 1.47 g (88%), which crystallized on standing. This material was not purified further. It had identical spectral properties with those published.[13]

15-Aza-4,5,6,7-tetrachlorohexacyclo[8.4.2.0^{1,10}.0^{3,8}.0^{4,13}.0^{7,12}]hexadec-5-en-16-one (4d). A solution of diene **8d** (5.0 g, 28.6 mmol) and tetrachlorothiophene dioxide (7.30 g, 28.7 mmol) in 1,2-dichloroethane (25 mL) was heated for 14 h at reflux. During this time, a fine precipitate was formed. The mixture was cooled and the product was filtered and washed with ether to give the lactam **4d**, analytically pure (6.87 g, 66%): mp >310 °C dec; IR (Nujol) 3160, 3090, 1750, 1705, 1610 cm^{-1}; ^{1}H NMR (80 MHz) (Me_2SO-d_6) δ 8.30 (s, 1 H), 1.98 (s, 4 H), 2.12 and 1.75 (ABq, J = 13 Hz, 8 H); ^{13}C NMR (Me_2SO-d_6) 175.4, 130.6, 74.1, 73.9, 52.5, 51.3, 45.2, 42.7, 29.3, 24.5 ppm; MS, m/e 322, 324, 326, 328 (M^+ - NHCO). Anal. Calcd for $C_{15}H_{13}Cl_4NO$: C, 49.35; H, 3.59. Found: C, 49.42; H, 3.71.

1,4,4a,5,8,8a-Hexahydronaphthalene-4a,8a-dicarboxylic Anhydride (8e). The monopotassium salt of acetylene dicarboxylic acid (60 g, 0.39 mmol) was added to 20% sulfuric acid solution (500 mL). After the salt had completely dissolved, the aqueous solution was extracted with ether (2 × 500 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to yield the free acid (45 g, ca. 100%) as an off-white solid which was used immediately for the next step.

A solution of acetylene dicarboxylic acid (35 g, 0.31 mol) and butadiene (90 g, 145 mL, 1.67 mol) in dioxane (75 mL) was stirred and heated for 20 h at 140 °C in an autoclave. The mixture was cooled to about 100 °C and excess butadiene and dioxane were vented. On further cooling, the residual yellow syrup was poured into saturated sodium carbonate solution (450 mL) and the mixture was heated for 2 h at 75 °C. The solution was cooled, extracted with ether (4 × 250 mL), and acidified with concentrated hydrochloric acid. The white precipitate that formed was separated from a small amount of brown gum and filtered to give the crude product, 1,4,4a,5,8,8a-hexahydronaphthalene-*cis*-4a,8a-dicarboxylic acid (40.7 g, 65%), as a white solid. A small portion was recrystallized from acetonitrile, mp 190–195 °C (lit.[15a] mp 225 °C).

A mixture of the crude diacid (38.7 g, 0.174 mol) and *p*-toluenesulfonic acid (0.5 g) in toluene (100 mL) was heated for 48 h at reflux under a nitrogen atmosphere (Dean–Stark apparatus). Undissolved material (3.0 g) was filtered at ambient temperature and the filtrate was evaporated to leave a yellow-brown solid which on recrystallization from dichloromethane/petroleum ether afforded the anhydride **8e** (19.56 g, 55%), mp 98–99 °C (lit.[15a] mp 102–103 °C). Spectral data of this compound were identical with those published.[15b]

4,5,6,7-Tetrachloropentacyclo[8.4.0.0^{3,8}.0^{4,13}.0^{7,12}]-5-tetradecene-1,10-dicarboxylic Anhydride (4e). A solution of anhydride (**8e**) (7.62 g, 30.0 mmol) and tetrachlorothiophene dioxide (6.12 g, 30.0 mmol) in toluene (15 mL) was heated for 15 h at reflux. The product, which precipitated from solution as it formed, was filtered from the cooled reaction mixture and washed with ether. In this way, the anhydride **4e** was isolated, analytically pure, as colorless granules (8.32 g, 70%): mp 344–345 °C; IR (Nujol) 1870, 1850, 1835, 1775, 1605, 1235, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (br s, 4 H), 2.51 and 1.86 (ABq, J = 13 Hz, 8 H); ^{13}C NMR ($CDCl_3$) 174.2 (s), 132.1 (s), 72.1 (s), 43.4 (s), 41.7 (d), 27.1 (t) ppm; MS, m/e 392, 394, 396, 398, 400 (M^+). Anal. Calcd for $C_{16}H_{12}Cl_4O_3$: C, 48.77; H, 3.07. Found: C, 48.34; H, 3.10.

12,12-Dimethyl-11,13-dioxatricyclo[4.4.3.0^{1,6}]trideca-2,8-diene (8g). A solution of recrystallized *cis*-4a,8a-dihydroxy-1,4,4a,5,8,8a-hexahydronaphthalene[14] (1.88 g, 11.3 mmol) and *p*-toluenesulfonic acid (50 mg) in 2,2-dimethoxypropane and acetone (5:1, 30 mL) was heated at 130 °C for 5 h in a sealed tube. The almost colorless solution was cooled to ambient temperature and vigorously stirred for 5 min over powdered anhydrous potassium carbonate. The solvent was evaporated and the residual pale yellow oil was bulb-to-bulb distilled at 80–90 °C (0.5 mm). The ketal **8g** (2.0 g, 87%) was obtained as a colorless oil which was not purified further. Spectral data of this compound were identical with those reported.[14]

11,11-Dimethyl-10,12-dioxa-2,3,4,5-tetrachlorohexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]-3-heptadecene (4g). A solution of the crude diene **8g** (2.354 g, 11.42 mmol) and tetrachlorothiophene dioxide (2.91 g, 11.46 mmol) in toluene (15 mL), containing anhydrous potassium carbonate (3.146 g, 22.8 mmol), was heated for 16 h at reflux. The resultant pink-orange solution was cooled, filtered, and evaporated to give a moist solid which was recrystallized from carbon tetrachloride/petroleum ether to give the ketal **4g** (1.84 g, 41%), mp 215–216 °C. Attempted chromatography of the mother liquors on silica gel caused extensive loss of material. IR ($CDCl_3$) 1610, 1100, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (br s, 4 H), 2.33 and 1.88 (ABq, J = 12 Hz, 8 H), 1.42 (s, 6 H); ^{13}C NMR ($CDCl_3$) 131.0 (s), 108.3 (s), 79.4 (s), 72.8 (s), 44.2 (d), 32.7 (t), 30.0 (q) ppm; MS, m/e 379, 381, 383, 385, 387 (M^+ - CH_3). Anal. Calcd for $C_{17}H_{18}Cl_4O_2$: C, 51.54; H, 4.53. Found: C, 51.69; H, 4.44.

Hexacyclo[8.4.1.0^{1,10}.0^{3,8}.0^{4,13}.0^{7,12}]-5-pentadecene (10). Method 1. To a partial solution of the hexachloride **4b** (162 mg, 0.4 mmol) and sodium borohydride (150 mg, 4.0 mmol) in 95% ethanol (4 mL) was added tri-*n*-butylstannyl chloride (15 mg, 46 μmol)[26] and azobis(isobutyronitrile) (2 mg). The mixture was heated for 36 h at reflux under a nitrogen atmosphere and then cooled to ambient temperature and treated with oxalic acid (30 mg). After the solution was stirred for 0.25 h, water (10 mL) was added and the organic material was extracted into dichloromethane (3 × 7 mL), washed with 10% sodium bicarbonate solution (10 mL) and saturated sodium chloride solution (10 mL), dried ($MgSO_4$), and evaporated to give crude tetrachloride (~180 mg). The residue was dissolved in 95% ethanol (5 mL) heated at reflux and sodium metal (736 mg, 32.0 mmol) was added portionwise over 1 h. Refluxing was continued for 4 h and the mixture was worked up as in method 2 below to yield a pale yellow solid (120 mg). An analysis of the crude product by ^{1}H NMR showed that no triene **11** had been formed. Recrystallization from methanol followed by sublimation at 120 °C (12 mm) provided the olefin **10** (50 mg 63%): mp 166–167 °C; IR (CCl_4) 3050, 1620 cm^{-1}; ^{1}H NMR (CCl_4) δ 6.11 (dd, J = 5 and 2.5 Hz, 2 H), 2.07 (br s, 2 H), 1.82 (br s, 4 H), 1.34 and 1.04 (ABq, J = 12 Hz, 8 H), 0.40 (s, 2 H); ^{13}C NMR ($CDCl_3$) 135.1 (d), 40.5 (d), 36.0 (d), 32.5 (t), 20.0 (t), 15.5 (s) ppm; MS, m/e 198 (M^+). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 91.05; H, 9.14.

Method 2. Small pieces of cleaned (ethanol) sodium metal (736 mg, 32.0 mmol) were added over 0.75 h to a partial solution of the hexachloride **4b** (162 mg, 0.4 mmol) in ethanol (5 mL) heated at reflux. The mixture was refluxed for a further 4 h and then cooled and treated with iced water (20 mL). The organic material was extracted into petroleum ether (3 × 10 mL), washed with water (2 × 10 mL) and saturated sodium chloride solution (10 mL), dried ($MgSO_4$), and evaporated to give a solid (80 mg, ~100%) which consisted of an ca. 1:3 mixture of the triene **11** and the olefin **10** by NMR. GLC-MS (15% OV101, 190 °C) showed that the molecular weights of these compounds differed by two mass units. The two components were separated by either reverse-phase HPLC on a Waters Radial Pak A column (5% aqueous methanol, 4 mL/min) or by medium-pressure chromatography on a reverse-phase Merck RP8 Lobar size B column (5% aqueous methanol, 8 mL/min). First to elute was pentacyclo[8.4.1.0^{1,10}.0^{4,13}.0^{7,12}]penta-3,5,7-triene (**11**) which was contaminated with a small amount of the olefin **10**. IR (CCl_4) 3050, 3030, 1620 cm^{-1}; ^{1}H NMR (80 MHz, CCl_4) δ 6.42 (s, 2 H), 5.26 (d, J = 6.5 Hz, 2 H), 2.56 (br s, 2 H), 2.47 and 1.40 (ABq, J = 18 Hz, 4 H), 1.60 and 1.13 (ABq, J = 13 Hz, 4 H), 0.59, 0.47 (ABq, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 146.3 (s), 134.3 (d), 125.3 (d), 44.2 (d), 31.9 (t), 29.1 (t), 21.3 (s), 19.0 (t) ppm; MS, m/e 196 (M^+), M^+ calcd for $C_{15}H_{16}$ 196.125194, found 196.125078. The olefin **10**, which eluted second, was identical in all respects with the product isolated in method 1.

11-Oxa-2,3,4,5-tetrachlorohexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]-3-heptadecene (4f). Method 1. A solution of 12-oxatricyclo[4.4.3.0^{1,6}]trideca-3,8-diene[16] (**8f**) (352 mg, 2.0 mmol) and tetrachlorothiophene dioxide (508 mg, 2.0 mmol in toluene (3 mL) was heated for 15 h at reflux. The solvent was evaporated to leave an oil which partly crystallized on standing. Crystallization of the residue from carbon tetrachloride/petroleum ether provided the ether **4f** (293 mg, 40%). An analytical sample, mp 201–203 °C, was obtained by two recrystallizations from chloroform/petroleum ether followed by sublimation at 190 °C (0.1 mm): IR ($CDCl_3$) 1605, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.43 (s, 4 H), 2.25 (br s, 4 H), 1.93 and 1.67 (ABq, J = 13 Hz, 8 H); ^{13}C NMR ($CDCl_3$) 131.5 (s), 80.0 (t), 74.5 (s), 43.1 (d), 40.6 (s), 29.4 (t) ppm; MS, m/e 364, 366, 368, 370 (M^+). Anal. Calcd for $C_{16}H_{16}Cl_4O$: C, 52.49; H, 4.41. Found: C, 52.53; H, 4.44.

Method 2. The anhydride **4e** (1.576 g, 4.0 mmol) was added portionwise over 0.25 h to lithium aluminum hydride (0.38 g, 10.0 mmol) in tetrahydrofuran (15 mL). The mixture was heated for 2 h at reflux under N_2 then cooled to ambient temperature. Water (0.5 mL), 15% NaOH (0.5 mL), and then more water (1.0 mL) were added dropwise. The inorganic salts were filtered through Celite and the filtercake was washed thoroughly with tetrahydrofuran. The filtrate was dried ($MgSO_4$) and evaporated to give 1,10-bis(hydroxymethyl)-4,5,6,7-tetrachloropentacyclo[8.4.0.0^{3,8}.0^{4,13}.0^{7,12}]-5-tetradecene (**4h**) as a white foam (1.332 g, 87%) which was not purified further. IR (Nujol) 3250, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD, 1:1) δ 4.29 (s, 2 H, exchangeable), 3.52 (s, 4 H), 2.25 (br s, 4 H), 1.88 and 1.58 (ABq, J = 14 Hz, 8 H); MS, m/e 382, 384, 386, 388 (M^+). A suspension of this diol (1.2 g, 3.1 mmol) in toluene (25 mL) containing *p*-toluenesulfonic acid (70 mg) was heated

(26) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554.

for 16 h at reflux under an atmosphere of nitrogen (Dean–Stark apparatus). The solution was cooled and vigorously stirred over anhydrous potassium carbonate for 5 min and then the mixture was filtered and the solvent evaporated to give a pale yellow solid (1.16 g, ca. 100%). Recrystallization from dichloromethane/petroleum ether provided a solid which was identical in all respects with the ether adduct **4f** obtained by method 1.

11,11-Dimethyl-10,12-dioxahexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]-3-heptadecene (12). A solution of the ketal **4g** (198 mg, 0.5 mmol, tri-*n*-butylstannane (320 mg, 1.1 mmol), and azobis(isobutyronitrile) (2 mg) in toluene (1 mL) was heated for 23 h at reflux under an atmosphere of nitrogen. Carbon tetrachloride (1 mL) was added and refluxing was continued for 2 h. The solution was cooled to ambient temperature and diluted with ether/dichloromethane (2:1, 15 mL). The mixture was treated with a solution of potassium fluoride (2 g) in water (10 mL) and was vigorously stirred for 0.25 h. The suspension of tri-*n*-butylstannyl fluoride was filtered and the aqueous layer was separated and extracted with ether/dichloromethane (2:1, 10 mL). The organic extracts were washed with 10% aqueous sodium bicarbonate (15 mL), dried ($MgSO_4$), and concentrated. The residue was dissolved in 95% ethanol (5 mL) heated at reflux and sodium metal (805 mg, 35.0 mmol) was added in portions over 1.5 h. More 95% ethanol (2 mL) was added to the thick mixture and refluxing was continued for 2.5 h. The solution was cooled to ambient temperature and poured into ice water (15 mL). The organic material was extracted into petroleum ether (3 × 10 mL), washed with water (10 mL) and saturated sodium chloride solution (10 mL), dried ($MgSO_4$), and evaporated to give a yellow oil (180 mg). Chromatography on neutral alumina (Woelm, activity 1) with dichloromethane/petroleum ether (1:1) as the eluent afforded the ketal **12**: mp 84–86 °C; IR (CCl_4) 3050, 1365, 1375 cm^{-1}; ^{1}H NMR (CCl_4) δ 6.03 (dd, J = 5 and 2 Hz, 2 H), 1.96 (br s, 2 H), 1.87 and 1.39 (ABq, J = 9 Hz, 8 H), 1.30 (s, 6 H); MS, m/e 258 (M^+), 243 ($M^+ - CH_3$), $M^+ - CH_3$ calcd for $C_{17}H_{22}O_2$ 243.138496, found 243.138077.

11-Oxa-2,5-dichlorohexacyclo[7.6.1.1^6,13.0^2,7.0^{5,15}.0^{9,13}]heptadecane (13). To a solution of the ether **4f** (1.464 g, 4.0 mmol) in ethyl acetate (40 mL) was added 5% palladium on carbon catalyst (75 mg) and triethylamine (1.01 g, 10 mmol). The mixture was stirred for 3 h at ambient temperature and pressure under a hydrogen atmosphere. The catalyst and triethylamine hydrochloride were removed by filtration through Celite and the filtrate was evaporated to give the dichloro ether **13** (0.957 g, 80%). An analytical sample, mp 98–99 °C, was prepared by sublimation at 90 °C (0.5 mm) ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 4 H), 2.41 (br s, 4 H), 2.29 (s, 4 H), 1.80 (center of a merging ABq, J = 14 Hz, 8 H); MS, m/e 298, 300, 302 (M^+). Anal. Calcd for $C_{16}H_{20}Cl_2O$: C, 64.22; H, 6.74. Found: C, 64.47; H, 6.99.

16-Oxapentacyclo[8.4.3.0^{1,10}.0^{4,13}.0^{7,12}]heptadeca-3,7-diene (14) and 11-Oxahexacyclo[7.6.1.1^{6,13}.0^{2,7}.0^{5,15}.0^{9,13}]heptadecane (16). To a suspension of sodium–potassium alloy (0.4 mL, 346 mg, ~9.6 mmol) in ether (25 mL) was added the dichloro ether **13** (530 mg, 1.77 mmol) in one portion. The mixture turned dark blue and was stirred for 16 h at room temperature under a nitrogen atmosphere. Excess alloy was destroyed by the cautious addition of ethanol (2 mL). Water (50 mL) was added, the aqueous layer was extracted with ether (2 × 50 mL), and the organic layer was dried ($MgSO_4$) and evaporated to give a solid (380 mg, 94%) which consisted of a mixture of the diene **14** and the ether **16**, (ca. 3:1). The two components were separated (Merck Lobar RP8 column, 7.5% aqueous methanol). The diene **14** eluted first: mp 91–94 °C; IR ($CDCl_3$) 3040, 1650, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.11 (t, J = 4 Hz, 2 H), 3.68 and 3.30 (ABq, J = 10 Hz, 4 H), 2.51 (br s, 2 H), 1.5–2.4 (complex, 10 H), 1.18 (d of ABq, J = 12 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 142.1 (s), 120.5 (d), 79.5 (t), 41.6 (s), 38.0 (d), 34.0 (t), 29.6 (t), 28.9 (t) ppm; MS, m/e 228 (M^+), M^+ calcd for $C_{16}H_{20}O$ 228.151406, found 228.151629.

The ether **16** eluted second: mp 51–53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 4 H), 1.95 (br s, 4 H), 1.75 (d, J = 12 Hz, 1.48 (br s, 4 H), 0.99 (br s, 2 H), 0.92 (d, J = 12 Hz, 4 H); ^{13}C NMR ($CDCl_3$) 81.2 (t), 41.9 (s), 35.2 (d), 34.6 (d), 33.7 (t), 26.1 (t) ppm; MS, m/e 230 (M^+), M^+ calcd for $C_{16}H_{22}O$ 230.167055, found 230.167785.

3,13-Dimethylene-8-oxapentacyclo[8.3.1.1^{2,6}.0^{4,12}.0^{6,10}]pentadecane (15). The diene **14** (120 mg, 0.53 mmol) was vaporized at 120 °C (0.4 mm) and passed through a hollow quartz tube (40 × 3 cm) heated at 500 °C. The pyrolysate condensed on a cold finger at 15 °C (100 mg, 83%). Flash chromatography of the condensate on silica gel, with 50% dichloromethane/petroleum ether as the eluent, afforded the diene **15** as a white solid: mp 93–96 °C; IR ($CDCl_3$) 3080, 1650, 1050, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) 4.46 (s, 4 H), 3.47 (s, 4 H), 2.75 (br s, 4 H), 1.91 and 1.22 (ABq, J = 12 Hz, 8 H); ^{13}C NMR ($CDCl_3$) 153.9, 104.2, 80.5, 42.7, 41.0, 36.2 ppm; MS, m/e 228 (M^+), M^+ calcd for $C_{16}H_{20}O$ 228.151406, found 228.151629.

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Registry No. 3a, 85710-40-3; **3b**, 85760-84-5; **4a**, 85710-41-4; **4b**, 82491-28-9; **4c**, 82491-31-4; **4d**, 85710-42-5; **4e**, 85710-43-6; **4f**, 85710-44-7; **4g**, 85710-45-8; **4h**, 85710-46-9; **5**, 85710-47-0; **6**, 493-04-9; **7**, 85710-48-1; **8a**, 16573-72-1; **8b**, 39623-22-8; **8c**, 4578-96-5; **8d**, 30483-18-2; **8e**, 3642-06-6; **8f**, 15405-67-1; **8g**, 69998-91-0; **9a**, 85760-85-6; **9b**, 82491-29-0; **9c**, 82491-30-3; **10**, 85710-49-2; **11**, 85710-50-5; **12**, 85710-51-6; **13**, 85710-52-7; **14**, 85710-53-8; **15**, 85710-54-9; **16**, 85710-55-0; tetrachlorothiophene 1,1-dioxide, 72448-17-0; 11-aza-11-chlorosulfonyl-12-oxotricyclo[4.4.2.0^{1,6}]dodeca-3,8-diene, 85710-56-1; acetylene dicarboxylic acid, 142-45-0; butadiene, 106-99-0; 1,4,4a,5,8,8a-hexahydronaphthalene-*cis*-4a,8a-dicarboxylic acid, 3642-04-4; *cis*-4a,8a-dihydroxy-1,4,4a,5,8,8a-hexahydronaphthalene, 69998-88-5.

Indole-2,3-quinodimethanes: A New Strategy for the Synthesis of Tetracyclic Systems of Indole Alkaloids

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Abstract: The imine **7**, derived from *N*-[(4-methoxyphenyl)sulfonyl]-2-methylindole-3-carboxaldehyde (**6**) and 4-pentenylamine, on treatment with a range of chloroformates gave *cis*-octahydropyridocarbazoles **8**, in yields ranging from 43 to 92%. Similarly the series of imines **18–24** derived from **6** and the corresponding amine gave, on treatment with the mixed carbonic anhyride from ethyl chloroformate and 4-pentenoic acid **25**, the tetracyclic amides **26–31**. The equivalent series of transformations with a 4a-ethyl group present leads directly to cis-fused tetracyclic precursors **40–42** and **45**. The structure and relative stereochemistry of the tetracyclic carbamate **43** is confirmed by single-crystal X-ray crystallography. Some general examples of indole-2,3-quinodimethane cyclizations that give fused pentacyclic and spirocyclic compounds **49**, **50**, and **51** directly are described.

Historically speaking, the area of indole alkaloids has fascinated organic chemists for the last 100 years.[1] It is only relatively recently that modern methods of spectroscopy, and X-ray crystallography, have removed the onerous burden of structural elu-

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