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Functionalization Reactions of C_{16}-Hexaquinacene and Related Hemispherical Molecules

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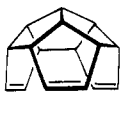
The exhaustive hydroboration of triquinacene (**8**) and C_{16}-hexaquinacene (**1**) has been investigated and the pair of isomeric exo[3]-triols separated in both cases. Whereas **8** reacts with diborane to give 37% of the C_{3v}-symmetric product **10**, **1** affords an amount of **3a** (28%) closer to the statistical value of 25%. Because difficulties were encountered in the oxidation of **3a**, the utility of triketone **4** as a possible precursor of dodecahedrane was not examined further. A four-step conversion of C_{16}-hexaquinacenedione (**26a**) to monoketone **29** was developed. However, this compound was exceptionally susceptible to base-promoted enolization and therefore proved unreactive to homologation reagents designed to give the cyclopentenone **31**. The chemical reactivity of **26a** toward phosphonate reagents was investigated, and a number of homologated derivatives, e.g., **41**, **45**, and **47**, were prepared. However, all attempts to accomplish transannular bond formation with compounds derived from these intermediates were unsuccessful. The diamines **62a** and **63a** also could not be bridged.

C_{16}-Hexaquinacene (**1**), a beautifully symmetric triene of highly convex topology, has played a pivotal role in the advancement of our understanding of neutral homoaromatic character.[2] A second point of interest in this molecule is the relationship it bears to the pentagonal dodecahedrane (**2**).[3,4] With its hexaquinane nature[5] and



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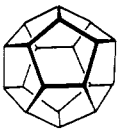

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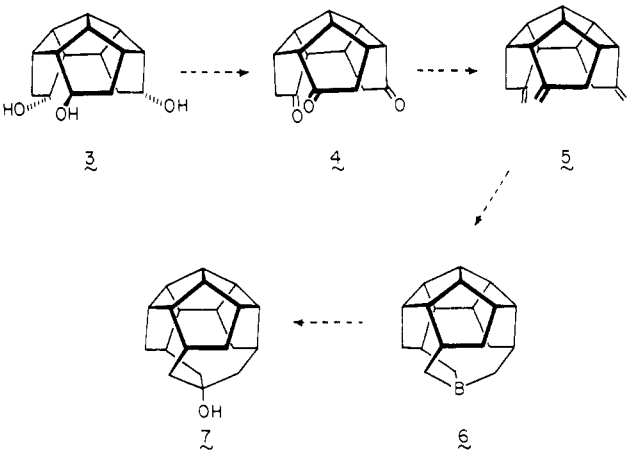
Scheme I



3 4 5 7 6

16 carbon atoms, **1** could serve as a template upon which the four additional methine units might be properly introduced. This approach to **2** gains special appeal because of the relatively ready availability of **1** in eight steps from cyclopentadiene.[2] The development of strategies for the possible conversion of **1** to dodecahedrane requires knowledge of the possibilities for the limitations of functionalization of the C_{16}-hexaquinane framework. Cur-

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(2) (a) Paquette, L. A.; Snow, R. W.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600. (b) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *Ibid.* **1978**, *100*, 7782. (c) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *Ibid.* **1979**, *101*, 6991.

(3) For an excellent recent review of the dodecahedrane field, see: Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

(4) For recent work accomplished in these laboratories, consult: (a) Paquette, L. A.; Balogh, D. W.; Blount, J. F. *J. Am. Chem. Soc.*, **1981**, *103*, 228. (b) Balogh, D. W.; Paquette, L. A.; Engel, P.; Blount, J. F. *Ibid.*, **1981**, *103*, 226. (c) Paquette, L. A.; Balogh, D. W.; Engel, P. *Heterocycles*, **1981**, 271. (d) Balogh, D. W.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3038. (e) Paquette, L. A.; Balogh, D. W.; Uska, R.; Kountz, D.; Christoph, G. G. *Science* **1981**, *211*, 575.

(5) Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.

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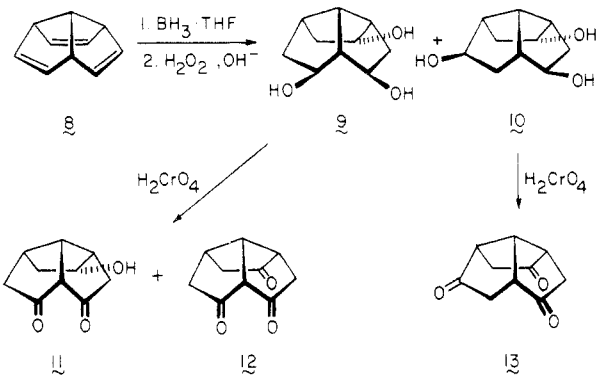
Scheme II



rently, very little information is available concerning chemical reactions which must take place along the fluted perimeter of a hemispherical molecule.[3-7] The added limitation of highly restricted conformational flexibility also has to be given due consideration. As a direct consequence of our interest in **2**, we have sought to effect various chemical transformations on C_{16}-hexaquinane derivatives and detail herein the nature of those complications which have been encountered in dealing with such systems.

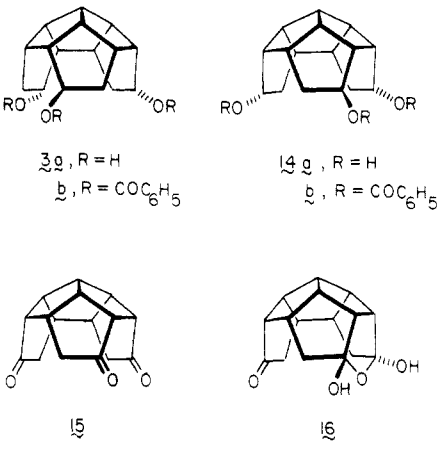
Hydroboration–Oxidation of 1. In our earliest deliberations, it was conceived that **1** might be adapted to serve as a precursor of **2** if symmetrical hydration of its three double bonds as in **3** could be achieved efficiently. Following projected oxidation of **3** to **4** and threefold Wittig olefination to give **5**, we viewed a stiching and riveting scheme[8] mediated by the trisubstituted borane **6** as a potentially short and simple route to carbinol **7** (Scheme I). For this plan to be workable, **3** must be available in reasonable yield and isomerically pure condition.

Initial hydroboration studies were carried out on triquinacene (**8**).[9] If attack by the weakly electrophilic reagent were to occur in completely statistical fashion, a 75:25 ratio of **9** to **10** would be expected (Scheme II). In actuality, treatment of **8** with diborane followed by oxidative workup led to a mixture of triols (71%) whose broad-band decoupled ^{13}C NMR spectrum in D_2O solution was seen to consist of 14 lines. On the assumption that the relative amounts of the two closely related structural isomers are approximated by instrument integration, the product composition was seen to be richer than expected in the more symmetric isomer **10** (37%). The use of disiamylborane favored the formation of **10** even more (41%). Because the triols are sparingly soluble in solvents other than methanol, ethanol, and water (see Experimental Section), their separation required conditions somewhat out of the ordinary. Best success was achieved under high-pressure liquid chromatography conditions with acetone as solvent and silica gel as adsorbent. Gram quantities of **9** and **10** could be cleanly separated in this way.

Although the oxidation of **10** to trione **13** could be achieved with Jones reagent, good yields were realized only as long as very dilute solutions (2–3 mg/mL) of **10** in acetone were utilized. When such conditions were met, an aqueous phase did not separate, and the chromium salts were deposited as a fluffy precipitate. The observation of a distinct water layer inevitably signaled a significant drop-off in yield, perhaps as a consequence of the exceptionally high solubility of **10** in water. Comparable treatment of **9** did not proceed at all smoothly due to incomplete oxidation. Trione **12** was invariably the minor constituent of the product mixture which contained principally the hydroxy diketone **11** or an isomer thereof. This aspect of the work was not pursued further.

Despite the uncommon facets of the oxidation chemistry just described, we were encouraged to pursue the hydroboration of **1** because of the favorable relative amounts of **10** which had been produced. Treatment of **1** with disiamylborane as before and ^{13}C NMR analysis of the triol mixture (70% yield) showed it to contain only 28% of the desired isomer **3**. This reduction in the amount of **3** to a nearly statistical level occurs despite the closer proximity of the double bonds in **1** relative to **8**. Since the addition of boranes to olefins is known to be reversible at more elevated temperatures,[10] heating of the intermediate triboranes formed in this instance was undertaken to determine if higher levels of the less sterically hindered, more symmetric isomer would result. In actuality, treatment of **1** with 9-borabicyclononane in diglyme followed by heating at 148 °C and oxidative workup did not significantly alter the isomer ratio (^{13}C NMR analysis).

Because we were not successful in achieving the chromatographic separation of **3a** and **14a**, the triol mixture



3a, R = H; **b**, R = COC_6H_5

14a, R = H; **b**, R = COC_6H_5

15 **16**

was exhaustively benzoylated. The tribenzoates were readily separated by preparative layer chromatography on silica gel. The slower moving symmetrical isomer **3b** (R_f 0.78, 19% isolated) proved to be a crystalline solid whose ^{13}C NMR spectrum consists of 10 lines. Unsymmetrical tribenzoate **14b** (R_f 0.85, 81%) was isolated as a semisolid; its ^{13}C NMR spectrum comprises 23 lines as expected.

Treatment of the individual tribenzoates with potassium hydroxide in aqueous methanol returned the pure triols. All attempts to convert either isomer to the corresponding

(6) (a) Paquette, L. A. *Org. Synth. Today and Tomorrow (IUPAC)*, **1981**, 335. (b) Sobczak, R. L.; Osborn, M. E.; Paquette, L. A. *J. Org. Chem.* **1979**, *44*, 4886. (c) Hales, N. J.; Paquette, L. A. *Ibid.* **1979**, *44*, 4603. (d) Paquette, L. A.; Begley, W. J.; Balogh, D.; Wyvratt, M. J.; Bremner, D. *Ibid.* **1979**, *44*, 3630. (e) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Muthard, J. L.; Begley, W. J.; Blankenship, R. M.; Balogh, D. *Ibid.* **1979**, *44*, 3616. (f) Balogh, D.; Begley, W. J.; Bremner, D.; Wyvratt, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 749. (g) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Schneider, D. F.; Begley, W. J.; Blankenship, R. M. *Ibid.* **1976**, *98*, 6744.

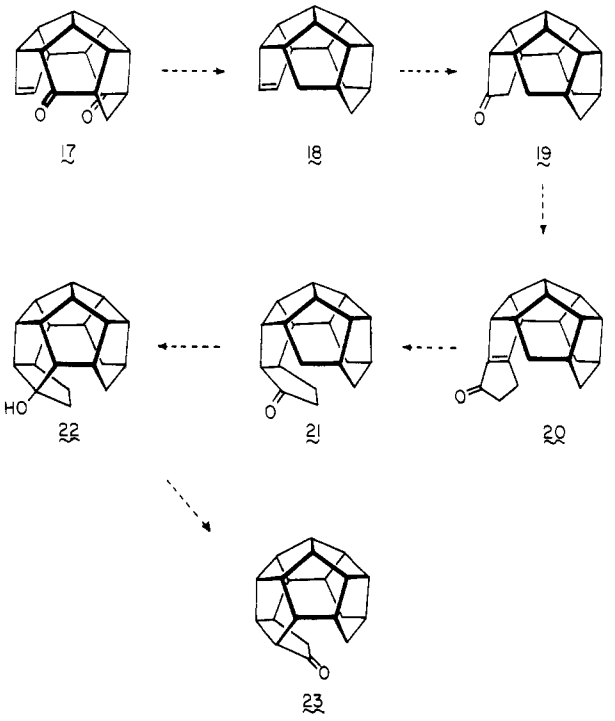
(7) (a) Eaton, P. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 1014. (b) Eaton, P. E.; Mueller, R. H.; Carlson, G. R.; Cullison, D. A.; Copper, G. F.; Chou, T.-C.; Krebs, E.-P. *Ibid.* **1977**, *99*, 2751. (c) Eaton, P. E.; Andrews, G. D.; Krebs, E.-P.; Kunai, A. *J. Org. Chem.* **1979**, *44*, 2824.

(8) (a) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5478. (b) *Ibid.* **1969**, *91*, 1224. (c) Brown, H. C.; Dickason, W. C. *Ibid.* **1969**, *91*, 1226.

(9) (a) Woodward, R. B.; Fukunaga, T.; Kelley, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162. (b) Jacobson, I. T. *Acta Chem. Scand.* **1967**, *21*, 2235. (c) Mercier, C.; Soucy, P.; Rosen, W.; Deslongchamps, P. *Synth. Commun.* **1973**, *3*, 161. (d) Wyvratt, M. J.; Paquette, L. A. *Tetrahedron Lett.* **1974**, 2433. (e) Meyer, L.-U.; de Meijere, A. *Chem. Ber.* **1977**, *110*, 2545.

(10) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1966**, *88*, 1433.

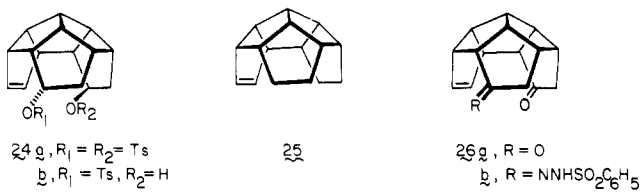
Scheme III



triketone proved unsuccessful. Complex mixtures were invariably obtained. In the case of **14a**, the desired triketone (**15**) may have formed and subsequently experienced hydration to give **16**. This inference is drawn from our observations that hydroxyl signals always persisted in the infrared spectra of the unpurified oxidation mixtures. No characterizable oxidation products were obtained from **3a**. This fact, coupled with the reduced relative yields realized in its formation from **1**, proved to be adequate cause for us to abandon Scheme I.

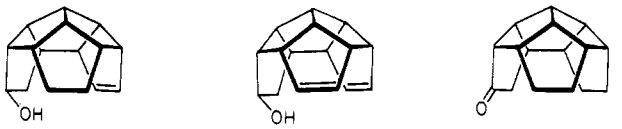
Functional Group Manipulation within C_{16}-Hexaquinacenedione. In an alternative conceptual strategy for the proper deployment of the necessary carbon atoms and bonds, the C_s C_{17}-heptaquinanedione, previously prepared in four steps from **26a**,[6b] was viewed as an attractive starting point (Scheme III). The crux of this projected synthesis was the need to effect (a) reductive removal of the two carbonyl groups without overreduction of the double bond, (b) cyclopentenone annulation of ketone **19**, and (c) photocyclization of **21**. Recently, we described the efficient excited-state ring closure of structurally similar cyclopentanones.[4a] On this basis, the conversion to **22** and the subsequent dehydration of this tertiary alcohol, followed by anti-Markovnikov hydration and oxidation to give **23**, was expected to be problem free. Installation of the remaining two bonds by twofold repetition of this photochemically based sequence was projected to be applicable with an equal level of success. Since the major obstacles to be overcome were thought to exist earlier in the sequence, chemical manipulation of the more readily available C_{16} diketone **26a** was examined first.

The problematic nature of the necessary carbonyl → methylene transformation was first signaled during studies aimed at the reduction of ditosylate **24a**, a known compound readily derived from **26a**.[2] When heated with lithium aluminum hydride in tetrahydrofuran at the reflux temperature for prolonged periods of time, only unreacted **24a** was recovered.[11] Concordant with this low susceptibility of **24a** toward nucleophilic attack, reaction of the ditosylate with lithium triethylborohydride[12] in dry tetrahydrofuran at room temperature gave only half-ester **24b**, with no indication that desired hydrocarbon **25** had been formed in even trace amounts.[11]



24 a, $R_1 = R_2 = Ts$; b, $R_1 = Ts$, $R_2 = H$ — **25** — **26** a, R = O; b, R = $NNHSO_2C_6H_5$

Numerous attempts to effect the Wolff–Kishner reduction of **26a** were equally unsuccessful. As a consequence, we turned out attention to the possibility of reducing a disulfonylhydrazone derivative of **26a**.[13] Unexpectedly, however, heating of the diketone with slightly more than a twofold excess of benzene- or *p*-toluenesulfonylhydrazine delivered products which gave no evidence for the presence of olefinic protons in their ^1H NMR spectra. Under more gentle conditions (25 °C, overnight), conversion to a monosulfonylhydrazone (e.g., **26b**) could be achieved in excellent yield. When **26b** was treated with lithium aluminum hydride in refluxing tetrahydrofuran, conversion to an inseparable mixture of hydroxy olefin **27** and hydroxy diene **28** was observed. If this pair of molecules was first oxidized and then hydrogenated, quite satisfactory conversion to monoketone **26** could be realized. Reversal of the two steps led to serious complications at the oxidation stage much as before. Consequently, diminution of the level of steric hindrance within the cavity of such molecules would appear to be conducive to the enhancement of oxidation efficiency.

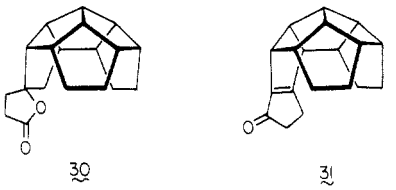


27 **28** **29**

At this point, we proceeded to examine the feasibility of spirolactonization of the carbonyl group in **29**. When this ketone in dimethyl sulfoxide solution was treated with cyclopropyldiphenylsulfonium ylide,[14] the spirocyclobutanone was not obtained satisfactorily. A weakly evident infrared carbonyl absorption at 1775 cm^{-1} in the recovered starting material suggested that a small amount of the desired product may have been produced. However, its level was too low to permit its separation and characterization. The utilization of the lithium and Grignard reagents derived from ethyl 3-bromopropyl acetaldehyde acetal[15] and lithiocyclopropyl phenyl sulfide,[16] all more basic reagents, were unreactive, perhaps because of enolization. With the unavailability of **30**, we were not able to examine the possible rearrangement of **31**. The route outlined in Scheme III was therefore aborted.

Homologation Studies of C_{16}-Hexaquinacenedione. Given the predescribed synthetic constraints, it appeared advantageous to investigate the placement onto diketone

(11) Kuroda, S., unpublished results.
(12) (a) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669. (b) Krishnamurthy, S.; Schubert, R. M.; Brown, H. C. *Ibid.* **1973**, *95*, 8486.
(13) For early reports of this reaction, consult: (a) Caglioti, L. *Tetrahedron* **1966**, *22*, 487. (b) Fischer, M.; Pelah, Z.; Williams, D. H.; Djerassi, C. *Chem. Ber.* **1965**, *98*, 3236.
(14) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5321 and later papers in this series.
(15) Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, R. C. *J. Org. Chem.* **1972**, *37*, 1947.
(16) Trost, B. M.; Keeley, D. E.; Arndt, H. C.; Rigby, J. H.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3080.



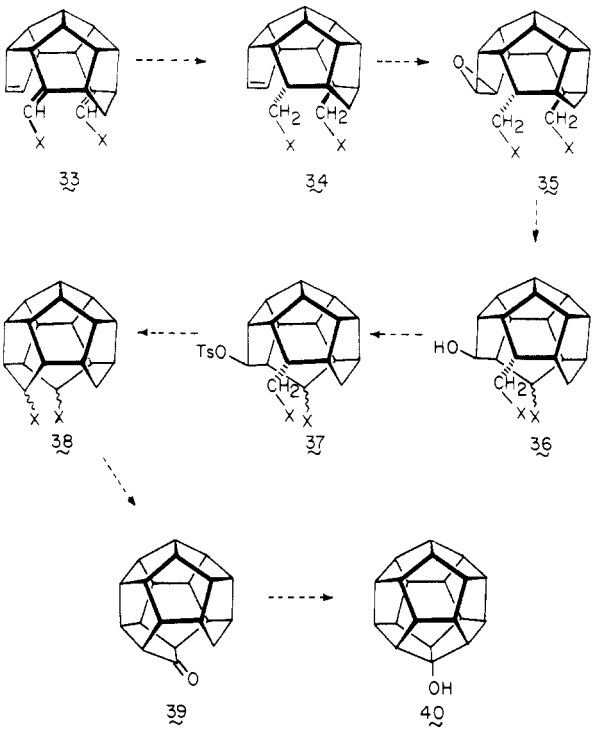
30 31

17 of a pair of identical side chains as in **33**, where X is an electron-withdrawing, carbanion-stabilizing substituent. Subsequent selective reduction of the two conjugated double bonds would serve to remove any need to concern ourselves with syn–anti stereochemistry in **33**. Furthermore, the topology of **33** appeared ideal for guaranteeing that the methine carbons newly formed during conversion to **34** would be configurationally homogeneous as the result of stereospecific exo protonation (Scheme IV). Taken in conjunction with subsequent epoxidation of the remaining double bond from the less hindered direction (cf. **35**), these considerations led us to entertain the possibility of intramolecular carbanionic cyclization.[17] With epoxide ring opening and formation of **36** would come the opportunity for elaboration of tosylate **37** and repetition of the cyclization process. Of course, this scenario assumes that dihedral angle relationships fall within the range acceptable for ready S_N2 displacement. This feature was assessed with Dreiding models and the conclusion reached that, although angles of 180° could not be attained without some conformational distrotion, the matter was too close to call and required testing by experiment. Were **38** to become available, the X groups (e.g., CN, COOR, etc.) would be turned inward (kinetically controlled protonation of the derived anions) and the chemistry adapted for the construction of ketone **39**. Irradiation of this penultimate intermediate was expected to readily provide **40**.[4a]

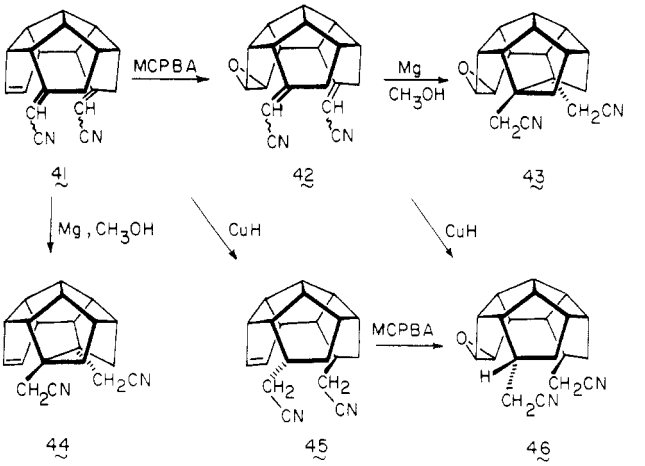
For reasons of expediency, the above sequence of reactions was applied initially to C_{16}-hexaquinacenedione (**26a**). The dicyano triene **41** was produced as a mixture of geometric isomers in 92% yield by reaction with an excess of the anion of diethyl (cyanomethyl)phosphonate. Two separate but convergent protocols were now examined. In the first, epoxidation of **41** with *m*-chloroperbenzoic acid afforded **42** in 75% yield as the sole characterizable product (Scheme V). Reduction of this clear oil with magnesium in methanol, a reagent combination known for its ability reduce α,β-unsaturated nitriles,[18] led to the unstable transannular epoxy nitrile **43** in poor yield. The fact that undesired C–C bond formation had occurred across the interior of the molecular cavity was most apparent in the ^1H NMR spectrum where the two sets of methylene protons α to cyano appear as a sharp four-proton singlet. Maintenance of C_s symmetry was apparent from the simplified ^{13}C NMR spectrum. The high proclivity of these α,β-unsaturated nitriles for coupling of their β-carbon atoms under these conditions became additionally apparent when **41** was treated analogously. The structure of the enedinitrile so obtained (**44**) was established by conventional ^1H and ^{13}C NMR methods, in tandem with mass spectroscopy (see Experimental Section).

These findings made it clear that any reductive method which leads to the buildup of radical or carbanion character at the β-carbon atom would not serve our purposes. This meant that an alternative new procedure had to be developed. We soon found that copper hydride, a reagent which presumably operates by a mechanism akin to Michael reaction (initial β attack), effects the reduction of

Scheme IV



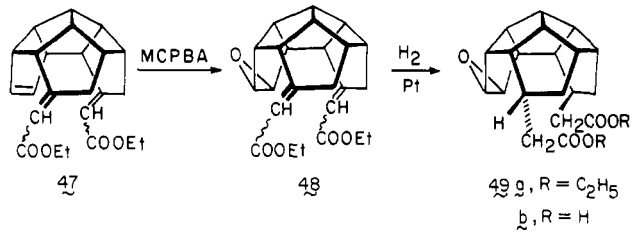
Scheme V



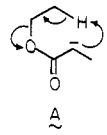
41 to **45** cleanly (70% isolated).[19] This nicely crystalline substance gives **46** quantitatively when subjected to the action of *m*-chloroperbenzoic acid. Of added interest was our observation that **42** can also be converted efficiently to **46** with the copper hydride reagent.

Following the attainment of **46**, numerous attempts were made to cyclize this material with a varied selection of bases under widely differing conditions. All were uniformly unsuccessful. Since it was not clear whether our inability to elaborate an additional five-membered ring within **46** by intramolecular cyclization was of stereoelectronic origin, triene diester **47** was prepared. The condensation of **26a** with triethyl phosphonoacetate proceeded with somewhat less efficiency (60%) than the dinitrile example described earlier. Subsequent chemospecific epoxidation and catalytic hydrogenation provided **49a**. When this epoxy diester was treated with such bases as potassium *tert*-butoxide, sodium hydride, and lithium diisopropylamide in appropriate solvents at ambient temperature, no reaction was

(17) (a) Stork, G.; Cama, L. D.; Coulson, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 5268. (b) Stork, G.; Cohen, J. F. *Ibid.* **1974**, *96*, 5270.
(18) Profitt, J. A.; Watt, D. S.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 127.
(19) Osborn, M. E.; Pegues, J. F.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 167.

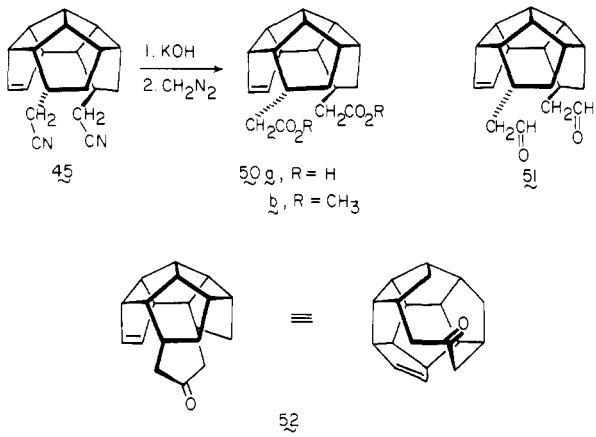


seen. At more elevated temperatures, epoxy diacid **49b** was produced in good yield. The formation of **49b** can be rationalized in terms of a cyclic elimination process involving the extrusion of ethylene as in A. The operation



of this pathway to the apparent exclusion of any cyclization was construed to be indicative that the conformational features of **46** and **49a** are not conducive to facile rearside attack at the epoxide ring.

Molecular models indicated that prior cyclization to give the ketone **52** engenders an appreciable change in spherical contour as well as in the geometric relationship of the enolizable methylene groups and double bond. A reversal of the timing of certain steps in Scheme IV was therefore in order. To this end, enedinitrile **45** was transformed by conventional techniques into enediacid **50a**, enediester **50b**, and enedialdehyde **51**. Dismayingly, all four compounds



proved completely resistant to transannular cyclization. Thus, **45** was unreactive to standard Thorpe–Ziegler conditions, **50b** was recovered intact from various modifications of the Dieckmann reaction, and **51** showed no proclivity either for intramolecular aldol condensation (recovered **51**) or cyclization under McMurry conditions (tar formation).[20] Nor was **52** obtained upon pyrolysis of the barium salt of **50a**.[21] Although less effort was placed on the conversion of this diacid to its anhydride, no indication was found that polyanhydride formation could be bypassed in favor of the monomeric species.

At this juncture, more detailed information on the actual molecular conformation of intermediates such as **45**, **50**, and **51** was sought to enable proper understanding of their inhibited transannular reactivity. To this end, enedinitrile **45** was subjected to X-ray crystal structure analysis. As

(20) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

(21) (a) Rand, L.; Wagner, W.; Warner, P.; Kovac, L. R. *J. Org. Chem.* **1962**, *27*, 1034. (b) Paquette, L. A.; Meisinger, R. H.; Wingard, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 2230.

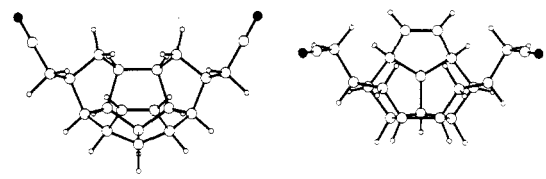


Figure 1. Computer-generated perspective drawings of the final X-ray model for **45**.

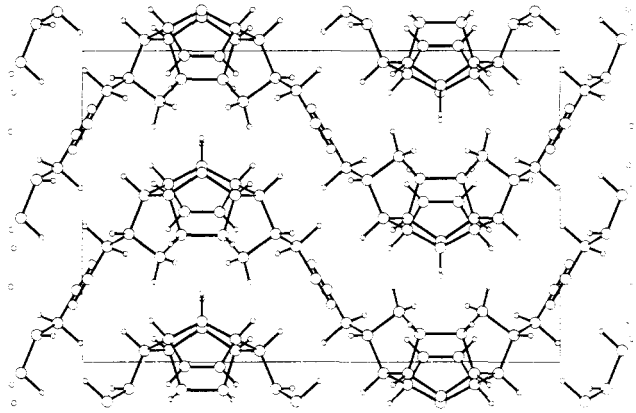
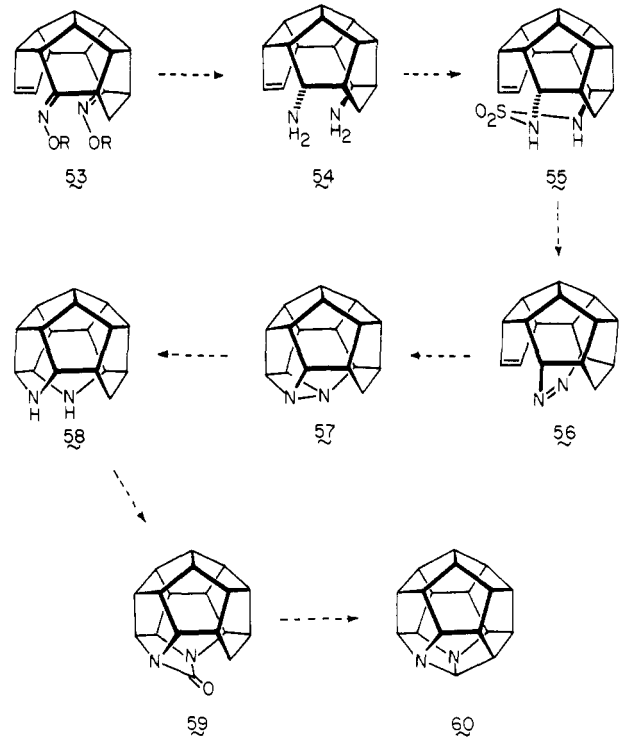


Figure 2. Arrangement of molecules of **45** in the unit cell.

Scheme VI

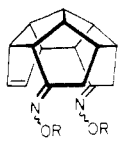


seen in the computer drawings and packing diagrams of this molecule (Figures 1 and 2), the topology adopted by the hexaquinane nucleus is one where the two cyclopentane rings to which the acetonitrile residues are appended exist in envelope conformations with their flaps folded outward. Notwithstanding certain differences between solid-state and solution conformations, the crystallographic data clearly indicate that the functional groups within **45** and related molecules do not find it possible to enter into mutual proximity adequate for bond formation to materialize.

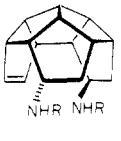
Preliminary Investigation of a Diazadodecahedrane Synthesis. While the preceding studies were in progress, experimental consideration was also being given to the elaboration of a diazadodecahedrane such as **60**. As

Scheme VI points out, the working plan was to transform diketone **17** to *endo,endo*-diamine **54** and to effect conversion to the transannular azo compound **56** by appropriate Ramberg–Bäcklund-type rearrangement[22] of the sulfamide precursor **55**. Once **56** became available, its excited-state [2 + 2] intramolecular cycloaddition[23] to **57** was to be followed by N–N bond fission under conditions of catalytic hydrogenation. Conversion to urea **59** and ultimate cyclization to **60** were to be the final steps.

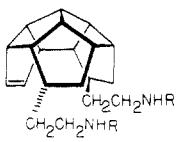
As before, our initial studies were conducted on diketone **26a** which could be dioximated in high yield. Although **61a** proved to be a rather insoluble substance, its reduction to diamine **62a** could be effected with sodium in refluxing *n*-amyl alcohol. Unexpectedly, treatment of the much more soluble dimethoxime **61b** with lithium aluminum



61 a, R = H
b, R = CH_3



62 a, R = H
b, R = OCH_3



63 a, R = H
b, R = Ts

hydride in refluxing ether did not proceed beyond the **62b** stage. As foreshadowed earlier, the air-sensitive diamine **62a** could not be made to deliver the needed cyclic sulfamide. Under all conditions examined, high molecular weight polymeric compounds resulted.

Since dinitrile **45** could be reduced with $LiAlH_4$ to the chain-extended diamine **63a**, attempts were also made along similar lines to cyclize this intermediate with sulfuryl chloride, but to no avail.

Conclusions. Although the C_{16}-hexaquinane framework can be functionalized with a variety of substituents, there exist serious limitations on the subsequent utilization of these groups. Proximity effects and transannular nonbonded steric factors clearly exert a considerable impact on the course of normally straightforward chemical reactions. The difficulty observed in oxidizing alcohols **3a**, **3b**, and **27** is exemplary. Our ability to construct additional fused cyclopentane rings or to achieve transannular bonding was completely thwarted. The first of these goals appears to be disadvantaged by unsatisfactory dihedral angle relationships and the second by the usual difficulties encountered in the cyclization of medium-sized rings located in environments where prevailing conformational features do not allow for close approach of the reactive functional groups. Consequently, alternative approaches are needed to bypass these serious complications if the synthesis of dodecahedranes is to be successfully achieved. The development of more successful protocols is discussed elsewhere.[4,6]

Experimental Section

Proton magnetic resonance spectra were obtained with Varian A-60A, Varian EM-360, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. ^{13}C NMR spectra were recorded with the Bruker instrument. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were obtained with an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory.

Reaction of Triquinacene with Diborane. A solution of triquinacene (200 mg, 1.54 mmol) in 20 mL of dry tetrahydrofuran was treated with 3.2 mL of 2.2 M diborane in tetrahydrofuran at 0 °C. A white solid formed. The mixture was stirred at room temperature for 3 h, treated with 1 mL of water to dissolve the solid, and basified at 0 °C with 2.0 mL of 10% sodium hydroxide solution. The cooling bath was removed, and 2.0 mL of 30% aqueous hydrogen peroxide was added dropwise, causing the reaction mixture to reflux. After being stirred at room temperature for 4 h, the two-phase system was separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were dried and evaporated to yield 300 mg of colorless oil. The oil was dissolved in water and extracted with ehter. The aqueous layer was freeze–dried and gave 200 mg (71%) of viscous, colorless triol mixture: ^{13}C NMR (in D_2O relative to internal dioxane at 67.40 ppm) 79.32, 79.00, 77.71, 76.63, 60.68, 51.51, 51.00, 50.62, 50.30, 39.99, 39.42, 39.13, 38.21, 37.13 ppm. This oil proved to be nearly insoluble in most organic solvents except methanol and was partially soluble in hot acetone or tetrahydrofuran: ^1H NMR (acetone-d_6) series of multiplets between δ 4.0 and 1.0 with maxima at δ 3.5, 2.9, and 1.5.

Reaction of Triquinacene with Disiamylborane. A solution of triquinacene (200 mg, 1.54 mmol) in 15 mL of dry tetrahydrofuran was treated with 3.0 mL of 1.69 M disiamylborane in tetrahydrofuran at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 h and quenched with 1 mL of water. The solution was cooled to 0 °C, and 4.0 mL of 30% hydrogen peroxide was added dropwise. The cooling bath was removed, and an additional 4.0 mL of the H_2O_2 was added at a rate to maintain a gentle reflux. After being stirred at room temperature for 2 h, the mixture was separated into two layers. The organic layer was separated, dried, and evaporated to give 500 mg of colorless oil. Water and ether were added to dissolve the oil, and the aqueous phase was freeze–dried to afford 220 mg (78%) of the **9**/**10** mixture as a viscous gum.

Separation of the Triquinacenetriols 9 and 10. The two isomers were separated by high-pressure liquid chromatography on four 6 ft × 0.75 in. silica gel columns connected in series with acetone as eluant. A solution of the triol mixture for injection into the system was prepared by dissolving the crude product into the minimum amount of methanol and diluting with acetone to an appropriate volume. Complete elution required 6 column volumes (ca. 6000 mL). When a 1.0-g sample was purified, the unsymmetrical isomer **9** was eluted first in fractions 251–311 (14 mL/fraction), and symmetrical isomer **10** appeared in fractions 351–421.

Unsymmetrical isomer **9** was recrystallized from acetone: mp 173–174 °C; ^1H NMR (D_2O, sodium 3-(trimethylsilyl)-1-propanesulfonate) δ 4.3–3.7 (m, 3 H), 3.23 (q, J = 9.0 Hz, 1 H), 3.0–1.9 (series of m, 4 H), 1.9–1.2 (m, 5 H); IR (KBr) 2855, 1083, 1015, 698 cm^{-1}; ^{13}C NMR (D_2O, dioxane signal = 67.40 ppm) 79.00, 77.71, 76.63, 60.68, 50.62, 50.30, 39.99, 39.42, 39.13, 38.21 ppm; mass spectrum, calcd m/e 184.1099, obsd 184.1103.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.93; H, 8.56.

Symmetrical isomer **10** was recrystallized from acetone: mp 200.5–201.5 °C; ^1H NMR (D_2O, sodium 3-(trimethylsilyl)-1-propanesulfonate) δ 4.71 (d of m, J = 4.0 Hz, 3 H), 3.5–2.2 (series of m, 4 H), 2.0–0.9 (series of m, 6 H); IR (KBr) 3310, 1023, 1013, 899 cm^{-1}; ^{13}C NMR (D_2O, dioxane signal = 67.40 ppm) 79.32, 51.51, 51.00, 37.13 ppm; mass spectrum, calcd m/e 184.1099, obsd 184.1103.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.85; H, 8.61.

Oxidation of 10. To a solution of **10** (35 mg, 0.19 mmol) in 30 mL of purified acetone cooled to 0 °C was added dropwise 300 μL of 2.67 M (0.80 mmol) Jones reagent. A flocculent green solid formed which remained suspended in the solvent. The ice bath was removed, and the mixture was stirred for 30 min at room temperature. Dichloromethane (30 mL) was added, causing the

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(23) (a) Borning, W.; Hunig, S. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 777. (b) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.

green solid to coagulate. The mixture was filtered, and the chromium salts were triturated with dichloromethane. The combined organic solutions were dried, filtered, and evaporated to give 58 mg of brown solid. This material was leached with 1 mL of ether, and the residue was taken up in dichloromethane and decolorized with charcoal. Filtration and solvent removal afforded 28 mg (83%) of **13** as a white solid which was recrystallized from acetone: mp 170–170.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.92 (g, J = 9.0 Hz, 1 H), 3.5–2.9 (six-line m, 3 H), 2.9–2.1 (m, 6 H); IR ($CHCl_3$) 3300, 1750, 1411, 1180 cm^{-1}; mass spectrum, calcd m/e 178.0630, obsd 178.0634.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.21; H, 5.64.

Hydroboration–Oxidation of C_{16}-Hexaquinacene (1). Disiamylborane was prepared by dropwise addition of 2-methyl-2-butene (2.44 mL, 23.04 mmol, freshly distilled from lithium aluminum hydride) to BH_3·THF (11.52 mL, 11.52 mmol, 1 M in tetrahydrofuran) at −78 °C. This solution was stirred at 0 °C for 2 h prior to slow addition to **1** (300 mg, 1.44 mmol) in 10 mL of dry tetrahydrofuran at 0 °C. The resulting clear solution was stirred for 0.5 h at 0 °C and then at room temperature for 21 h before the unreacted borane reagent was quenched with 5 mL of water. The reaction mixture was cooled to 0 °C, and 10% aqueous sodium hydroxide solution (5 mL) was added followed by addition of 30% hydrogen peroxide at room temperature (periodic ice-bath cooling). The reaction mixture was stirred for 3 h at room temperature, at which point solid sodium chloride was added, and the phases were separated. The aqueous layer was extracted with tetrahydrofuran (3 × 25 mL), and the combined organic layers were washed with brine, dried, and concentrated to afford 486 mg of white foam. Purification by preparative thin-layer chromatography on silica gel (elution with tetrahydrofuran) gave 265.2 mg (70%) of a mixture of triols **3a** and **14a**: ^{1}H NMR (pyridine-d_5) δ 5.73 (br s, 3 H), 5.07–4.23 (br m, 3 H), 4.17–1.57 (series of m, 13 H); ^{13}C NMR (pyridine-d_5) 77.75, 77.02, 63.45, 63.38, 58.86, 58.21, 58.02, 55.13, 47.72, 46.92, 46.78, 40.98, 40.22 ppm.

Synthesis and Separation of Tribenzoates 3b and 14b. A mixture of triols **3a** and **14a** (265.2 mg, 1.01 mmol) was dissolved in 20 mL of dry pyridine under nitrogen, treated dropwise with benzoyl chloride (710 μL, 6.10 mmol), and stirred at room temperature for 12.5 h. The reaction mixture was poured into 125 mL of ice–water and extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed with water (50 mL), 10% hydrochloric acid (100 mL), water (50 mL), saturated sodium bicarbonate solution (50 mL), and water (50 mL), dried, and concentrated to afford 913 mg of an oil. Purification by preparative thin-layer chromatography on silica gel (elution twice with 15% ether in dichloromethane) yielded a fast-moving unknown compound, 442 mg of unsymmetrical tribenzoate **14b** (R_f 0.85) as a semisolid [IR (KBr) 2952, 1714, 1280, 1115, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.20–7.73 (m, 6 H), 7.60–7.17 (m, 9 H), 5.80–5.40 (m, 3 H), 3.93–1.67 (series of m, 16 H); ^{13}C NMR ($CDCl_3$) 166.23, 165.84, 132.73, 130.69 (2 C), 129.62, 128.31, 82.58, 81.76, 79.96, 63.31, 62.97, 62.48, 55.34, 54.96, 54.28, 53.84, 47.63, 47.14, 46.22, 37.77, 37.24, 35.97 ppm; mass spectrum, calcd for $M^+ - C_7H_5O$ m/e 469.2015, obsd 469.2024] and 103 mg of symmetrical tribenzoate **3b** (R_f 0.78, 94% total yield) which was recrystallized from ethyl acetate: mp 218–220 °C; IR (KBr) 2953, 1714, 1278, 1118, 1113, 714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.17–7.90 (m, 6 H) 7.58–7.20 (m, 9 H), 5.63–5.40 (m, 3 H), 3.87–2.67 (m, 9 H), 2.33–2.00 (m, 7 H); ^{13}C NMR ($CDCl_3$) 165.94, 132.78, 131.36, 129.58, 128.31, 83.02, 63.60, 55.00, 46.27, 35.68 ppm; mass spectrum, calcd for $M^+ - C_7H_5O$ m/e 469.2015, obsd 469.2024.

Anal. Calcd for $C_{37}H_{34}O_6$: C, 77.33; H, 5.96. Found: C, 77.46; H, 6.10.

Dodecahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,7,9-triol (14a). A solution of **14b** (442 mg, 0.77 mmol) in 60 mL of methanol was treated with 30 mL of potassium hydroxide solution (214 mmol, 40% weight by volume in 5:3 methanol and water), and the mixture was heated at reflux with stirring under a nitrogen atmosphere for 13 h. The reaction mixture was poured into 100 mL of ice–water and extracted with tetrahydrofuran (4 × 75 mL). The combined organic layers were washed with brine (75 mL), dried, and concentrated to afford 248 mg of **14a**. Purification by preparative thin-layer chromatography on silica gel (elution with tetrahydrofuran) gave 182 mg (90%) of **14a** which was recrystallized from ethyl acetate to yield a powdery white solid: mp 223–225 °C; IR (KBr) 3379, 2940, 1025 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 5.62 (br s, 3 H), 5.00–4.27 (m, 3 H), 3.82–1.77 (br m, 16 H); ^{13}C NMR (pyridine-d_5) 77.73, 77.00, 63.40, 58.84, 58.16, 57.97, 55.10, 47.72, 46.75, 40.98, 40.25 ppm; mass spectrum, calcd for $M^+ - H_2O$ m/e 244.1463, obsd 244.1468.

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.11; H, 8.44.

Dodecahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,6,10-triol (3a). A suspension of **3b** (103.4 mg, 0.18 mmol) in 60 mL of methanol was treated with 10 mL of potassium hydroxy solution (71 mmol, 40% weight by volume in 5:3 methanol and water), and the resulting solution was heated at reflux with stirring under a nitrogen atmosphere for 12 h. The reaction mixture was concentrated, and the residue was partitioned between tetrahydrofuran and water. The aqueous phase was extracted with tetrahydrofuran (4 × 50 mL), and the combined organic layers were washed with brine (50 mL), dried, and concentrated to afford 142 mg of **3a**: mp 215 °C dec; ^{1}H NMR (pyridine-d_5) δ 5.97–5.33 (m, 3 H), 5.00–4.40 (m, 3 H), 3.77–1.63 (br m, 16 H); ^{13}C NMR (pyridine-d_5) 77.73, 63.36, 58.79, 55.15, 46.95, 40.30 ppm, mass spectrum, calcd for $M^+ - H_2O$ m/e 244.1463, obsd 244.1468.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,9-dione Benzenesulfonylhydrazone (26b). A solution of **26a** (1.40 g, 5.88 mmol) and benzenesulfonylhydrazine (1.20 g, 7.0 mmol) in 15 mL of methanol was stirred overnight at room temperature. The solvent was evaporated, and the residue was triturated with a small amount of methanol. Filtration and air drying of the solid furnished 2.04 g (90%) of **26b**: mp 186–189 °C; IR (KBr) 3220, 2970, 1650, 1600, 1400, 1345, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90–7.40 (m, 5 H), 5.21 (d, J = 7.0 Hz, 1 H), 4.82 (d, J = 7.0 Hz, 1 H), 3.35 (br s, 3 H), 3.60–1.95 (series of m, 12 H); mass spectrum, calcd m/e 394.1351, obsd 394.1359.

Lithium Aluminum Hydride Reduction of 26b. A solution of **26b** (200 mg, 0.51 mmol) in 20 mL of dry tetrahydrofuran was treated with 1.0 g of lithium aluminum hydride at 25 °C under nitrogen. An additional 20 mL of solvent was introduced, and the mixture was heated at reflux for 1.5 days. With cooling there was added in turn 2.0 mL of ethyl acetate, 5.0 mL of 10% sodium hydroxide solution, 5.0 mL of saturated Rochelle's salt solution, and 40 mL of 5% hydrochloric acid. Extraction of this mixture with chloroform followed by washing of the combined organic phases with several portions of 5% hydrochloric acid, drying, and solvent evaporation gave an essentially pure mixture of **27** and **28** (96 mg, 74%) which was carried on to the next step without further purification: IR (KBr) 3230, 3060, 2950, 1640, 1595, 1390, 1345, 1175, 810, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.82 (m), 5.30 (m), 3.32 (br s), 3.30–1.4 (series of m); mass spectrum, calcd for $C_{16}H_{18}O$ m/e 226.1358, obsd 226.1362; calcd for $C_{16}H_{20}O$ m/e 228.1514, obsd 228.1519.

2,2a,3,4,4a,4b,5,7a,7b,7c,8,9-Dodecahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalen-1-one (29). To a cold (0 °C), magnetically stirred solution of pyridine (1.42 mL, 17.5 mmol) in dry dichloromethane (25 mL) was added under nitrogen 900 mg (9.0 mmol) of chromium trioxide. The amber mixture was stirred at 0 °C for 5 min and at 25 °C for 50 min. To this solution was introduced 250 mg (1.1 mmol) of the **27**/**28** mixture dissolved in 5 mL of dichloromethane. After 1 h at room temperature, the reaction mixture was decanted into 50 mL of water. The residual solid was triturated with ether, and these ether layers were also shaken with the water. After extraction with dichloromethane (4 × 50 mL), the combined organic phases were washed with 1 N hydrochloric acid (50 mL), 1 N sodium hydroxide solution (3 × 50 mL), water (50 mL), and brine (50 mL) prior to drying and solvent evaporation. The resulting mixture of enones (195 mg, 78%) was dissolved in methanol–ethyl acetate (1:1, 15 mL), treated with a pinch of 5% palladium on charcoal, and hydrogenated in a Parr apparatus at 50 psi of H_2 for 36 h. Filtration and evaporation gave 193 mg (95%) of **29**: mp 233–235 °C (from ligroin); IR (KBr) 2960, 1735, 1445, 1300, 1170, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.60–1.0 (series of m, 17 H), 1.52 (br s, 3 H); ^{13}C NMR ($CDCl_3$) 223.4, 64.4 (2 C), 61.1, 56.1,

55.8, 50.0, 49.6, 49.0 (2 C), 44.5, 42.1, 31.0, 30.2, 29.4, 29.0 ppm; mass spectrum, calcd m/e 228.1514, obsd 228.1517.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.21; H, 8.77. Found: C, 83.77; H, 8.85.

Triene Dinitrile 41. To a suspension of oil-free sodium hydride (60 mg, 2.5 mmol) in 25 mL of dry benzene under nitrogen was slowly added 720 μL (658 mg, 3.72 mmol) of diethyl (cyanomethyl)phosphonate over a period of 1 h. The fel which formed was broken up by adding more benzene (10 mL), stirring, and shaking. After being stirred for 3 h at room temperature, the mixture was treated with a solution of **26a** (200 mg, 0.83 mmol) in 5 mL of benzene. An almost immediate precipitation was observed. After 3 h, the contents were rinsed with chloroform and water into a 250-mL Erlenmeyer flask to generate a total volume of ca. 100 mL. The aqueous phase was extracted with chloroform (4 × 50 mL), and the combined organic layers were dried and concentrated. The residue was purified by thick-layer chromatography on silica gel (ether elution). There was isolated 220 mg (92%) of **41**: mp 183–189 °C (from methanol); IR ($CHCl_3$) 2980, 2250, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (br s, 2 H), 5.11 (br s, 2 H), 3.8–3.2 (m, 8 H), 3.0–2.2 (m, 6 H); ^{13}C NMR ($CDCl_3$) 176.3, 131.9, 131.8, 131.3, 131.0, 128.4, 91.6, 91.0, 90.3, 63.1, 62.9, 62.0, 61.0, 60.7, 57.2, 56.9, 56.8, 56.5, 56.4, 56.3, 55.6, 55.4, 54.5, 46.2, 45.2, 38.5, 38.0, 37.2, 20.0 ppm; mass spectrum, calcd m/e 286.1470, obsd 286.1478.

Anal. Calcd for $C_{20}H_{18}H_2$: C, 83.92; H, 6.29. Found: C, 83.67; H, 6.34.

Peracid Epoxidation of 41. A solution of **41** (290 mg, 1.0 mmol) and *m*-chloroperbenzoic acid (300 mg of 85% purity, 1.48 mmol) in 10 mL of dichloromethane was stirred at room temperature for 15 h and diluted with 50 mL of chloroform. This solution was washed with 10% potassium carbonate solution (5 × 50 mL), dried, and concentrated. The residue was purified by layer chromatography on silica gel (ether elution). There was obtained 207 mg (75%) of **42** as a light oil: IR ($CHCl_3$) 2980, 2120, 1640, 1235–1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (br s, 2 H), 3.50 (s, 2 H), 3.7–3.0 (series of m, 8 H), 3.0–2.3 (m, 6 H); ^{13}C NMR ($CDCl_3$) 174.7, 119.7 (2 C), 93.4, 93.1, 92.7, 77.3, 64.0, 63.7, 63.5, 63.1, 62.1, 61.6, 61.3, 61.0, 60.4, 57.2, 56.2, 55.9, 53.9, 52.8, 52.2, 51.6, 51.2, 51.0, 50.8, 47.3, 47.0, 45.0, 38.6, 38.0, 37.6, 36.9 ppm; mass spectrum, calcd m/e 302.1419, obsd 302.1425.

Reduction of 41 with Magnesium in Methanol. To a nitrogen-blanketed magnetically stirred solution of **41** (75 mg, 0.26 mmol) in methanol (6 mL) was added 400 mg of magnesium turnings during 30 min. Gas evolution was observed, and an ice bath was alternately applied and removed to maintain a reaction temperature of ca. 10 °C. Six hours later, the ice bath was again applied while 20 mL of 6 N hydrochloride acid was introduced via syringe over a 40-min period. The reaction mixture was extracted with ether (4 × 25 mL), and the combined organic phases were washed with brine prior to drying and concentration. There was obtained 25 mg (33%) of the relatively unstable (discoloration to brown) oily **44**: IR ($CHCl_3$) 2980, 2240, 1610, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (s, 2 H), 3.15 (br s, 4 H), 2.22 (br s, 4 H), 3.6–1.6 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 131.7, 63.7, 63.0, 55.8, 54.6, 54.2, 53.5, 40.0, 36.6, 22.6, 22.0 ppm; mass spectrum, calcd for $C_{20}H_{20}N_2$ m/e 228.1626, obsd 228.1633.

Reduction of 42 with Magnesium in Methanol. Application of the identical procedure to **42** (85.0 mg) furnished 10.5 mg (12%) of the unstable oil **43**: IR ($CHCl_3$) 2980, 2260, 1640, 1430; ^1H NMR ($CDCl_3$) δ 2.35 (s, 4 H), 3.6–1.6 (series of m, 16 H); mass spectrum, calcd for $C_{20}H_{20}N_2O_4$ m/e 304.1576, obsd 304.1583.

Copper Hydride Reduction of 41. To a cold (0 °C) magnetically stirred suspension of cuprous bromide (1.5 g, 10.4 mmol) in 10 mL of dry tetrahydrofuran was added 3.5 mL of a 70% solution of Vitride [sodium bis(2-methoxyethoxy)aluminum hydride, 12.25 mmol] in benzene. The resulting dark solution was stirred for 30 min at 0 °C and 30 min at −78 °C. At this point, 2-butanol (1.8 mL, 24.3 mmol) was cautiously added, followed by 200 mg (0.7 mmol) of **41** dissolved in 10 mL of dry tetrahydrofuran. The mixture was allowed to warm to room temperature during 4 h, recooled to −78 °C, at which point 6 mL of saturated ammonium chloride solution was added, and warmed to room temperature where it was poured into 75 mL of the NH_4Cl solution. Extraction with chloroform (5 × 30 mL) followed by drying and solvent evaporation left an oil which was purified by TLC on silica gel (ether elution). There was isolated 140 mg (70%) of **45**: mp 114–115 °C (from methanol); IR ($CHCl_3$) 2980, 2240, 1450, 1415, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.65 (s, 2 H), 2.58 (br s, 4 H), 3.4–1.8 (series of m, 16 H); ^{13}C NMR ($CDCl_3$) 131.7, 119.3, 63.8, 62.7, 53.4, 52.8, 52.3, 45.6, 43.7, 33.2, 18.7 ppm; mass spectrum, calcd m/e 290.1783, obsd 290.1791.

Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.76; H, 7.59. Found: C, 82.58; H, 7.55.

Epoxydinitrile 46. (A) By Epoxidation of 45. A solution of **45** (40 mg, 0.133 mmol) and *m*-chloroperbenzoic acid (40 mg of 85% purity, 0.20 mmol) in 10 mL of chloroform was stirred at room temperature for 15 h and poured into 75 mL of water. The aqueous layer was extracted with chloroform (4 × 50 mL), and the combined organic phases were washed with 10% potassium carbonate solution (4 × 50 mL) prior to drying and solvent evaporation. The residual oil was purified by TLC on silica gel (ether elution) to give 45 mg (100%) of **46** as a clear, colorless oil: IR ($CHCl_3$) 2980, 2240, 1760, 1720, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (s, 2 H), 3.5–2.3 (m, 16 H), 1.8–1.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) 118.9, 65.6, 64.9, 61.8, 52.5, 51.5, 49.3, 45.9, 43.3, 32.7, 18.4 ppm; mass spectrum, calcd for $C_{20}H_{22}N_2O$ m/e 306.1732, obsd. 306.1738.

(B) Copper Hydride Reduction of 42. Reaction of **42** with copper hydride under the predescribed conditions gave **46** in 69% yield. The spectra of the samples prepared by the two methods were superimposable.

Triene Diester 47. Sodium hydride (63 mg of 50% oil dispersion, 1.31 mmol) was washed with two 1-mL portions of dry benzene, slurried in 2 mL of the same solvent, and treated dropwise with 300 μL (339 mg, 1.51 mmol) of triethyl phosphonoacetate. This mixing was stirred under argon at room temperature for 1 h. A solution of **26a** (100 mg, 0.42 mmol) in 2 mL of benzene was introduced, and the reaction mixture was stirred at room temperature for 1.5 days and transferred directly to two silica gel plates (40 × 20 cm). Elution with 10% ethyl acetate in hexane afforded 96 mg (60%) of **47** as a mixture of isomers: ^1H NMR ($CDCl_3$) δ 5.7–5.1 (m, 4 H), 4.08 and 4.07 (overlapping q, J = 7.0 Hz, 4 H), 4.0–1.9 (series of m, 4 H), 1.20 (t, J = 7.0 Hz, 6 H); mass spectrum, calcd (M^+) m/e 380.1987, obsd 380.1995.

To substantiate that a mixture of isomeric α,β-unsaturated esters had been produced, a 34-mg sample of the mixture was hydrogenated at 50 psi of H_2 in a Parr apparatus over 10% palladium on charcoal (14 mg) in ethyl acetate (15 mL) for 1.5 days. After filtration of the reaction mixture through Celite and evaporation of the filtrate, there was obtained 30 mg of a single symmetric hexahydro derivative: IR (CCl_4) 2940, 1735, 1175, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.13 (q, J = 7.0 Hz, 4 H), 4.0–1.5 (series of m, 24 H), 1.25 (t, J = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$) 173.8, 67.2, 65.7, 60.2, 52.9, 48.3, 46.6, 43.7, 36.2, 34.7, 30.9, 14.3 ppm.

Epoxidation of 47. A dichloromethane solution (5 mL) of *m*-chloroperbenzoic acid (160 mg of 85% purity, 0.8 mmol) was added under nitrogen to a solution of **47** (200 mg, 0.53 mmol) in 5 mL of the same solvent. After 15 h, the reaction mixture was poured into water (100 mL), and the aqueous phase was extracted with dichloromethane (70 mL). Workup in the predescribed manner, including preparative TLC on silica gel (elution with ether–hexane 1:1), gave **48** as an oily mixture of geometric isomers: 107 mg (50%); IR ($CHCl_3$) 2980, 1730, 1390, 1170, 1050; ^1H NMR ($CDCl_3$) δ 5.78 (br s, 2 H), 4.18 (q, J = 7.5 Hz, 4 H), 3.58 (s, 2 H), 3.6–2.2 (series of m, 14 H), 1.30 (t, J = 7.5 Hz, 6 H).

Catalytic Hydrogenation of 48. A solution of **48** (77 mg) in 10 mL of ethyl acetate containing 15 mg of 15% palladium on charcoal was hydrogenated in a Parr apparatus at a pressure of 3 atm. The reaction mixture was filtered through Celite, and the filtrate was evaporated to give 60 mg (78%) of **49a**: IR ($CHCl_3$) 2980, 1745, 1190, 700–500; ^1H NMR ($CDCl_3$) δ 4.18 (q, J = 7.5 Hz, 4 H), 3.80 (s, 2 H), 3.6–2.5 (series of m, 10 H), 2.70 (br s, 4 H), 2.0–1.5 (m, 6 H), 1.35 (t, J = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) 173.1 (s), 65.2 (d), 65.0 (d), 62.4 (d), 60.4 (t), 52.6 (d), 52.1 (d), 49.9 (d), 46.0 (d), 43.4 (d), 35.8 (t), 33.1 (t), 14.3 ppm (q); mass spectrum, calcd for $C_{24}H_{32}O_5$ m/e 400.2250, obsd 400.2256.

Attempted Cyclization of 49a. A variety of bases served to transform **49a** to the corresponding diacid **49b**. For example, heating **49a** (30 mg, 0.08 mmol) with potassium *tert*-butoxide (100 mg, 0.9 mmol) in 4 mL of *tert*-butyl alcohol under anhydrous conditions furnished 21 mg (83%) of **49b**: mp 240 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 3.79 (s, 2 H), 3.8–1.0 (series of m, 20 H); ^{13}C NMR (Me_2SO-d_6) 174.0, 64.4, 61.3, 51.5, 49.3, 45.4, 42.9, 42.7, 36.5, 35.1, 32.6 ppm.

Hydrolysis–Esterification of 45. A solution of **45** (120 mg), potassium hydroxide (700 mg), and water (2 mL) in 2 mL of ethylene glycol monomethyl ether was heated at reflux for 6 h. After cooling, the reaction mixture was acidified with dilute hydrochloric acid. The precipitated solid was filtered and air-dried to give 110 mg (79%) of **50a**: IR (KBr) 1700 cm^{-1}; mass spectrum, calcd m/e 328, obsd 328.

A solution of **50a** (110 mg, 0.34 mmol) in 5 mL of tetrahydrofuran was chilled to 0 °C and treated with a fourfold excess of ethereal diazomethane. Removal of solvent several hours later furnished 110 mg (75%) of diester **50b**: IR ($CHCl_3$) 2940, 1725, 1445, 1360, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.62 (s, 2 H), 3.56 (s, 6 H), 3.5–2.3 (series of m, 12 H), 1.62–1.22 (m, 8 H).

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.84. Found: C, 73.68; H, 7.74.

Ene Dialdehyde 51. A cold (−78 °C) solution of **45** (890 mg, 3.1 mmol) in 3 mL of dry tetrahydrofuran was treated under nitrogen with 6.75 mL (12.0 mmol) of diisobutylaluminum hydride (25% in hexane). The reaction mixture was stirred at −78 °C for 2 h and at room temperature for 1.5 h prior to being poured into water. The product was extracted into dichloromethane (4 × 30 mL), and the combined organic layers were washed with 1 N hydrochloric acid, dried, and concentrated. There was obtained 50 mg (6%) of **51** as a colorless oil: IR ($CHCl_3$) 2960, 1730, 1590, 1445 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.66 (t, 2 H), 5.71 (s, 2 H), 4.0–1.0 (series of m, 20 H); mass spectrum, calcd for $C_{20}H_{24}O_2$ m/e 296.1776, obsd 296.1781.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,9-dione Dioxime (61a). A solution of **26a** (100 mg, 0.42 mmol), hydroxylamine hydrochloride (1.0 g, 14.5 mmol), and pyridine (1 mL) in 20 mL of absolute ethanol was heated at the reflux temperature for 2 h and stirred at 25 °C for 10 h. Following solvent evaporation, the residue was triturated with tetrahydrofuran (ca. 7 mL) and filtered. The filtrate was concentrated and the crystalline solid recrystallized from acetone. There was obtained 110 mg (98%) of **61a**: mp 236 °C dec; IR ($CHCl_3$) 3250, 3100, 1660, 1425, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.58 (d, J = 7 Hz, 2 H), 3.8–3.3 (m, 10 H), 2.9–2.2 (m, 6 H); mass spectrum, calcd m/e 270.1368, obsd 270.1375.

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.11; H, 6.67. Found: C, 70.70; H, 6.76.

2,2a,3,4,4a,4b,5,7a,7b,7c-Decahydro-3,4,5-[1]-propanyl[3]ylidene-1*H*-dicyclopenta[*a*,*cd*]pentalene-1,9-dione Dimethoxime (61b). A solution of **26a** (100 mg, 0.42 mmol), methoxylamine hydrochloride (1.0 g, 12.0 mmol), and pyridine (1 mL) in 10 mL of absolute ethanol was stirred at 25 °C for 16 h and concentrated in vacuo. The solid residue was partitioned between water and chloroform, and the aqueous phase was extracted with chloroform (4 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), dried, and concentrated to give 115 mg (93%) of **61b**: mp 113–116 °C (from hexane); IR (KBr) 2960, 1730, 1650, 1440, 1180, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.49 (dd, J = 18, 4.5 Hz, 2 H), 3.82 (s, 6 H), 3.6–2.2 (series of m, 14 H); ^{13}C NMR ($CDCl_3$) 168.8, 168.3, 132.7, 132.2, 131.7, 131.3, 61.4, 61.3, 60.6, 60.5, 60.3, 59.8, 57.3, 57.0, 55.8, 53.1, 52.8, 50.5, 45.5, 44.6, 34.6, 34.1, 31.6, 31.0 ppm; mass spectrum, calcd m/e 298.1681, obsd 298.1687.

Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.48; H, 7.38. Found: C, 72.57; H, 7.44.

Reduction of 61a to Diamine 62a. To a nitrogen-blanketed, refluxing solution of **61a** (100 mg, 0.34 mmol) in 5 mL of *n*-amyl alcohol was added 1 g of sodium metal in small pieces during 4 h. Additional amounts of solvent were added as needed to keep the solids dissolved (total of 10 mL). When the sodium was consumed, the reaction mixture was cooled to 0 °C, and 10 mL of concentrated hydrochloric acid was added slowly. Chloroform (75 mL) was added, and this solution was washed extensively with water (7 × 75 mL). The organic phase was dried and evaporated, and the residual oil was dried overnight in vacuo. There was obtained 76.5 mg (94%) of **62a** which proved to be unstable under various conditions of attempted purification: IR ($CHCl_3$) 3350, 2960, 1570, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 131.7, 61.3, 59.6, 55.6, 54.2, 53.9, 44.1, 37.0, 29.7; mass spectrum, calcd for $C_{16}H_{22}N_2$ m/e 242.1783, obsd 242.1788.

Reduction of 61b to 62b. To lithium aluminum hydride (200 mg, 5.3 mmol) in 15 mL of anhydrous ether was added 200 mg (0.67 mmol) of **61b**. The stirred mixture was heated at reflux for 1.5 h, cooled, and treated slowly with 5 mL of ethyl acetate, 1 mL of 10% sodium hydroxide solution, and 2 mL of 20% potassium sodium tartrate (Rochelle's salt) solution. The resulting white suspension was extracted with ether (5 × 50 mL), and the combined organic layers were dried and evaporated to leave 165 mg (77%) of **62b** as a tan oil: IR ($CHCl_3$) 2960, 1455, 1430, 1355, 1250, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.05 (s, 2 H), 3.81 (br s, 2 H), 3.60 (s, 6 H), 4.0–2.4 (series of m, 10 H), 2.0–1.3 (m, 6 H); ^{13}C NMR ($CDCl_3$) 131.7, 68.1, 62.0, 61.6, 55.5, 54.4, 53.7, 52.0, 44.0, 31.3 ppm; mass spectrum, calcd for $C_{18}H_{26}N_2O_2$ m/e 302.1994, obsd 302.2002.

Hydride Reduction of 45. Lithium aluminum hydride (150 mg, 3.9 mmol) was added to a stirred tetrahydrofuran solution (75 mL) of dinitrile **45** (100 mg, 0.34 mmol), and the mixture was stirred at room temperature for 24 h. Following the addition of ethyl acetate (2 mL), 10% sodium hydroxide solution (1 mL), and 20% Rochelle's salt solution (2 mL), the product was extracted into chloroform (4 × 50 mL). The combined organic layers were dried and concentrated to give 50 mg (49%) of diamine **63a**: ^{1}H NMR ($CDCl_3$) δ 5.82 (s, 2 H), 3.15 (complex t, 6 H), 3.0–1.2 (series of m, 18 H), 1.53 (br s, 4 H).

To a nitrogen-blanketed solution of this product (50 mg, 0.17 mmol) in 5 mL of pyridine at 0 °C was added 64 mg (0.34 mmol) of *p*-toluenesulfonyl chloride. After 1.5 h, the reaction mixture was poured into chloroform, and this solution was washed several times with water. The organic phase was dried and evaporated to furnish a solid which was purified by preparative layer chromatography on silica gel (elution with ethyl acetate–hexane, 4:1). There was obtained 173 mg (85%) of **63b**: mp 120–122 °C (from ethyl acetate–hexane); IR ($CHCl_3$) 3360, 2940, 2860, 1590, 1400, 1325, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 8 Hz, 4 H), 7.20 (d, J = 8 Hz, 4 H), 5.48 (s, 2 H), 5.00 (t, J = 7 Hz, 2 H), 2.41 (s, 6 H), 3.3–1.2 (series of m, 20 H), 1.25 (br s, 4 H); ^{13}C NMR ($CDCl_3$) 143.4, 131.7, 129.7, 128.0, 127.3, 64.0, 54.0, 53.1, 52.1, 45.5, 45.3, 43.3, 33.3, 31.1, 29.7, 21.5 ppm.

Anal. Calcd for $C_{34}H_{42}N_2O_4S$: C, 71.05; H, 7.37. Found: C, 70.82; H, 7.43.

Structure Determination of 45. Colorless crystals of **45**, 0.3–0.7 mm in size, were used. Most of the larger crystals were shown to be nonsingle crystals. Preliminary Weissenberg photographs with Cu Kα radiation indicate that the crystals belong to the orthorhombic system. Systematic extinctions are $0kl$, $k + l = 2n + 1$, h_k0, $h = 2n + 1$, $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$, thus defining the extinction unit Pn-a comprising the two space groups $pn2_1a$ and $Pnma$.

The determination of lattice parameters and the intensity measurements were made with a Nonius CAD4 diffractometer. A small crystal fragment with approximate dimensions 0.10 × 0.13 × 0.14 mm was mounted on a fiber of Lindemann glass (ϕ = 0.08 mm) with colorless nail polish (Cutex). Twenty-five reflections determined with the Nonius peak-hunting procedure in the range $8° \leq 2\theta \leq 22°$ were carefully centered. Accurate cell parameters were calculated by a least-squares procedure and led to the orthorhombic cell constants a = 11.588 (5), b = 17.847 (10), and c = 7.451 (3) Å. The calculated density for four molecules of formula $N_2C_{20}H_{22}$ is 1.25 g cm^{-3}.

Intensity data were measured at T = 20 (1) °C by the ω–2θ scan technique with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). All independent reflections in the range $2° \leq 2\theta \leq 50°$ were measured. For every 100 reflections, the orientation of the crystal was controlled, and every 2.5 h the intensity of the 122 reflection was checked. During the measurement, no significant deviation (less than 3σ) could be observed. A total of 1230 reflections were measured. After multiple measurements were averaged, 1212 independent reflections remained, of which 596 were unobserved with $J \leq 2.58\sigma(I)$. The standard deviation was calculated as $\sigma^2(I) = P + m^2(B_1 + B_2)$, wherein P is the peak

Table I. Fractional Atomic Coordinates, with Standard Deviations in Parentheses

atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
N(1)	0.8140 (5)	0.5211 (4)	0.1373 (8)	0.0115 (6)	0.0058 (3)	0.026 (2)	−0.0056 (7)	−0.009 (2)	0.001 (1)
C(1)	0.5868 (5)	0.4032 (3)	0.0402 (8)	0.0073 (5)	0.0030 (2)	0.015 (1)	0.0008 (5)	−0.003 (1)	0.002 (1)
C(2)	0.6617 (4)	0.3373 (3)	−0.0122 (8)	0.0046 (4)	0.0033 (2)	0.016 (1)	−0.0013 (5)	−0.001 (1)	0.000 (1)
C(3)	0.5893 (5)	0.2936 (3)	−0.1509 (7)	0.0058 (4)	0.0038 (2)	0.012 (1)	0.0001 (5)	−0.000 (1)	0.003 (1)
C(4)	0.4624 (5)	0.3192 (3)	−0.1198 (8)	0.0060 (4)	0.0035 (2)	0.018 (1)	−0.0014 (5)	−0.006 (1)	0.001 (1)
C(5)	0.4643 (4)	0.3703 (3)	0.0446 (8)	0.0051 (4)	0.0029 (2)	0.021 (1)	0.0019 (5)	−0.001 (2)	0.000 (1)
C(6)	0.3905 (7)	0.2500 (0)	−0.078 (1)	0.0046 (6)	0.0042 (3)	0.024 (2)	0.0000 (0)	−0.001 (2)	0.000 (0)
C(7)	0.3678 (7)	0.2500 (0)	0.123 (1)	0.0062 (7)	0.0036 (3)	0.024 (2)	0.0000 (0)	0.005 (2)	0.000 (0)
C(8)	0.4277 (5)	0.3205 (3)	0.2073 (9)	0.0061 (5)	0.0032 (2)	0.021 (2)	0.0014 (5)	0.007 (1)	−0.001 (1)
C(9)	0.5148 (6)	0.2874 (4)	0.3304 (8)	0.0105 (6)	0.0036 (2)	0.014 (1)	−0.0006 (6)	0.007 (1)	0.001 (1)
C(10)	0.6266 (5)	0.4482 (3)	0.2024 (8)	0.0082 (5)	0.0033 (2)	0.019 (1)	−0.0001 (6)	−0.001 (1)	−0.002 (1)
C(11)	0.7330 (5)	0.4889 (3)	0.1670 (8)	0.0103 (6)	0.0031 (2)	0.022 (2)	−0.0015 (6)	−0.009 (2)	0.002 (1)

atom	x	y	z	atom	x	y	z
H(11)	0.585 (5)	0.433 (3)	−0.048 (7)	H(61)	0.309 (7)	0.250 (0)	−0.136 (10)
H(21)	0.726 (5)	0.353 (3)	−0.076 (7)	H(71)	0.281 (7)	0.250 (0)	0.181 (10)
H(22)	0.677 (5)	0.306 (3)	0.102 (7)	H(81)	0.375 (6)	0.353 (3)	0.282 (9)
H(31)	0.608 (5)	0.312 (3)	−0.264 (8)	H(91)	0.577 (5)	0.322 (3)	0.412 (7)
H(41)	0.407 (5)	0.346 (3)	−0.239 (9)	H(101)	0.636 (4)	0.416 (3)	0.310 (7)
H(51)	0.413 (4)	0.412 (3)	0.047 (7)	H(102)	0.560 (5)	0.486 (4)	0.240 (9)

Table II. Bond Lengths (Å), with Estimated Standard Deviations in Parentheses

N(1)-C(11)	1.12 (1)	C(4)-C(6)	1.52 (1)
C(1)-C(2)	1.51 (1)	C(5)-C(8)	1.56 (1)
C(1)-C(5)	1.54 (1)	C(6)-C(7)	1.52 (1)
C(1)-C(10)	1.52 (1)	C(7)-C(8)	1.57 (1)
C(2)-C(3)	1.54 (1)	C(9)-C(8)	1.49 (1)
C(3)-C(4)	1.56 (1)	C(9)-C(9′)	1.34 (1)
C(4)-C(5)	1.53 (1)	C(10)-C(11)	1.46 (1)

Table III. Interbond Angles (deg), with Estimated Standard Deviations in Parentheses

C(2)-C(1)-C(5)	103.8 (5)	C(1)-C(5)-C(8)	119.0 (5)
C(2)-C(1)-C(10)	116.2 (5)	C(4)-C(5)-C(8)	106.3 (5)
C(5)-C(1)-C(10)	117.7 (5)	C(4)-C(6)-C(4′)	108.5 (6)
C(1)-C(2)-C(3)	104.7 (5)	C(4)-C(6)-C(7)	107.1 (6)
C(2)-C(3)-C(4)	105.4 (5)	C(4′)-C(6)-C(7)	107.1 (6)
C(2)-C(3)-C(3′)	120.3 (5)	C(6)-C(7)-C(8)	108.6 (5)
C(4)-C(3)-C(3′)	107.1 (5)	C(6)-C(7)-C(8′)	108.6 (5)
C(3)-C(4)-C(5)	106.4 (5)	C(8)-C(7)-C(8′)	106.7 (5)
C(3)-C(4)-C(6)	108.0 (5)	C(8)-C(9)-C(9′)	113.4 (6)
C(5)-C(4)-C(6)	109.2 (5)	C(1)-C(10)-C(11)	112.1 (5)
C(1)-C(5)-C(4)	102.9 (5)	N(1)-C(11)-C(10)	179 (12)

scan and B_1 and B_2 are the background measurements for $1/2m$ of the time of the peak scan (m = 2). The intensities were corrected for Lorenz and polarization effects,[24] but no absorption correction was applied (μ(Mo K$\bar{\alpha}$) = 0.793 cm^{-1}).

Statistical tests indicated that the structure is centrosymmetric with $\langle E \rangle$ = 0.802, $\langle E^2 \rangle$ = 1.030, and $\langle E^2 - 1 \rangle$ = 0.959. The space group should therefore be *Pnma* with the molecule lying on the crystallographic mirror plane. The structure was solved with direct phasing according to the symbolic addition procedure. The complete structure was then determined with structure factor and Fourier calculations and refined with block-diagonal least-squares calculations. The hydrogen atoms could all be seen in a difference Fourier synthesis. In the last few cycles of refinement, the hydrogen atoms were included with isotropic temperature factors; anisotropic temperature factors for the nitrogen and carbon atoms were also applied. The function minimized was $\sum w(F_o - F_c)^2$ and $w = 1/(6 + F_o + 0.02F_o^2)$. The atomic scattering factors were taken from the literature.[25] The final agreement factor was (F) = 0.064) $R(wF^2)$ = 0.096 for observed reflections and $R(F)$ = 0.139 for all reflections (Tables I–III). A final difference Fourier synthesis did not show any peak higher than ±0.3 e/A^3. All calculations and drawings were done using the program system KRIPROG.[26]

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Registry No. **1**, 66081-13-8; **3a**, 78168-44-2; **3b**, 78168-45-3; **8**, 6053-74-3; **9**, 78168-46-4; **10**, 78168-47-5; **13**, 78168-48-6; **14a**, 78168-49-7; **14b**, 78168-50-0; **26a**, 66081-14-9; **26b**, 78168-51-1; **27**, 78168-52-2; **28**, 78168-53-3; **29**, 78168-54-4; **41**, 78168-55-5; **42**, 78168-56-6; **43**, 78168-57-7; **44**, 78168-58-8; **45**, 72017-14-2; **46**, 78168-59-9; **47**, 78168-60-2; **48**, 78168-61-3; **49a**, 78168-62-4; **49b**, 78168-63-5; **50a**, 78168-64-6; **50b**, 78168-65-7; **51**, 78168-66-8; **61a**, 78168-67-9; **61b**, 78168-68-0; **62a**, 78168-69-1; **62b**, 78168-70-4; **63a**, 78168-71-5; **63b**, 78168-72-6; diisoamylborane, 6838-83-1; 2-methyl-2-butene, 513-35-9; BH_3·THF, 14044-65-6.

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