mmol) and $SnCl_4$ (10 mg, 0.04 mmol). After 1 h at -78 °C, the reaction was stopped by the addition of saturated aqueous $NaHCO_3$ (0.5 mL) and extracted with EtOAc (3 × 3 mL). After the combined extracts were dried over anhydrous Na_2SO_4 and evaporated under vacuum, the resulting crude reaction product was purified by preparative thin layer silica gel chromatography using EtOAc/hexane (1:10) to give pure **10c** (23 mg, 45%).

10c: ^1H NMR ($CDCl_3$, 200 MHz) δ_H 7.41 (1 H, d, J = 1.7 Hz, H-3), 6.04 (1 H, ddd, J = 5.9, 1.8, 1.8 Hz, H-5 or H-6), 5.68 (1 H, ddd, J = 5.6, 1.9, 1.9 Hz, H-5 or H-6), 5.02 (1 H, d, J = 4.4 Hz, H-1), 3.73 (3 H, s, CO_2CH_3), 3.58-3.33 (10 H, m, two OCH_3, OCH_2CH, H-7 and H-4a), 2.62 (1 H, ddd, J = 8.0, 8.0, 4.2 Hz, H-7a): ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 167.6, 151.5, 134.6, 131.2, 110.6, 100.1, 75.8, 73.2, 58.9, 56.3, 51.3, 47.5, 42.5, 39.4 ppm; MS, m/z (rel abund) 254 (M^+, 4), 223 (10), 222 (10), 209 (8), 190 (3), 177 (67), 162 (17), 149 (51), 145 (16), 121 (30), 105 (13), 91 (25), 77 (21), 44 (100).

Preparation of the Olefin 9. The allylsilane **8a** (40 mg, 0.11 mmol) dissolved in benzene (0.5 mL) containing p-TsOH·H_2O (21 mg, 0.11 mmol) was refluxed for 1.5 h. The reaction mixture was poured into water, and then the organic phase was extracted with saturated aqueous $NaHCO_3$ and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent under vacuum gave a dark residue that was purified by preparative thin-layer chromatography on silica gel using hexane/EtOAc (3:1) to give **9** (20 mg, 73%).

9: ^1H NMR ($CDCl_3$, 270 MHz) δ_H 7.49 (1 H, d, J = 1.2 Hz, H-3), 5.93-5.85, 5.70-5.64, (2 H, m, H-5 and H-6), 4.43 (1 H, d, J = 6.1 Hz, H-1), 3.73 (3 H, s, CO_2CH_3), 3.54 (3 H, s, OCH_3), 2.51-2.41 (3 H, m, H-7, H-7a); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ_C 168.0 (CO_2CH_3), 152.5 (C-3), 134.5 (C-6), 128.7 (C-5), 110.0 (C-4), 102.5 (C-1), 57.3 (C-1, OCH_3), 51.3 (CO_2CH_3), 40.9 (C-4a), 40.0 (C-8), 34.5 (C-7a); MS, m/z (rel abund) 210 (M^+, 36), 179 (29), 178 (44), 150 (22), 149 (26), 147 (36), 146 (44), 139 (44), 121 (30), 120 (20), 119 (36), 118 (44), 108 (44), 107 (40), 91 (65), 84 (44), 77 (32), 71 (43), 66 (60), 45 (100).

Acknowledgment. This research was supported in part by a grant from the National Institutes of Health (CA 25953). We thank Mr. John Hansen for NMR spectral determinations and Mr. Mel Micke and Mr. Gary Girdaukas for mass spectral determinations.

Synthesis of Triannulanes via Intramolecular [2 + 1] Cyclizations of Large-Ring Cycloalkenes

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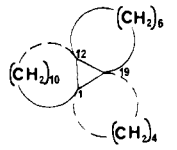
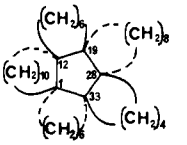
Abstract: Synthetic routes to *trans,cis,cis*-[10.4.3]- and *trans,cis,cis*-[10.4.4]triannulane-16,18-dione (**48** and **60**) are described. The former was prepared via intramolecular [2 + 1] cycloaddition of the carbene generated by photolysis of the α-diazo β-keto ester **43**, followed by Dieckmann cyclization of the derived diester **45**, and subsequent hydrolysis, decarboxylation, and oxidation. The [10.4.4] homologue **60** was prepared via analogous [2 + 1] cyclization of the carbene derived from photolysis of the [10.9]betweenanene α-diazo β-diketone **59**. This intermediate was secured from the acyloin cyclization product **56** of diester **55**, an intermediate in a previously reported synthesis of [10.10]betweenanene. The conversion to dione **58** entailed cyclopropanation of the ene diol bis(trimethylsilyl) ether **56** followed by periodate cleavage of the derived 1,2-cyclopropanediol intermediate. The foregoing sequence was also performed with optically active diester **55** to give optically active triannulanedione **60**. The structures of diones **48** and **60** were confirmed through single-crystal X-ray structure analysis.

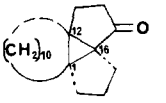
We recently formulated a new class of carbocyclic compounds, "perannulanes", consisting of a central ring whose every side is spanned by bridging chains so as to fashion a ring of fused rings.[1a] The number of bridging chains is indicated by the prefix "tri, tetr, pent, hex, etc.", and the length of each bridging chain is denoted by a bracketed numerical prefix as shown in the following examples. Since each side of the central ring is spanned by a bridging chain, the number of such chains is equal to the central ring size. Thus "triannulanes" have a central three-membered ring, "tetrannulanes" a central four-membered ring, and so forth.[1b] The bracketed chain length designators are arranged in order starting with the longest bridge and proceeding to the longer of the two adjacent bridges and thence to the next contiguous bridge until all bridges have been specified. The stereochemistry of each bridge is indicated by the prefix "cis" or "trans" arranged in the order corresponding to that of the numerical bridge length prefixes. Atoms are numbered starting at the bridgehead common to the longest bridge and the shorter of the two bridges immediately adjacent. Numbering proceeds along the longer bridge and then the next longer adjacent bridge in the order of the bracketed chain length designators until the first numbered position is reached. In the case of functionalized perannulenes, the aforementioned numbering protocol is observed but, if the bridges are symmetrically disposed, the direction of numbering is chosen to accord the lower number to the functional group.



trans, cis, cis-[10.6.4]triannulane
not
trans, cis, cis-[10.4.6]triannulane



trans, cis, cis, cis, cis-[10.6.8.4.6]pentannulane
not
trans, cis, cis, cis, cis-[10.6.4.8.6]pentannulane



trans, cis, cis-[10.3.3]triannulan-15-one
not
trans, cis, cis-[10.3.3]triannulan-17-one

(1) (a) Marshall, J. A.; Peterson, J. C.; Lebioda, L. *J. Am. Chem. Soc.* **1983**, *105*, 6515-6516. (b) Related polycyclic structures "coronanes" have recently been proposed by Fitjer et al. (Fitjer, L.; Giersig, M.; Clegg, W.; Schormann, N.; Sheldrick, G. M. *Tetrahedron Lett.* **1983**, *24*, 5351-5354). Their "[6.4]coronane" is equivalent to *all-cis*-[2.2.2.2.2.2]hexannulane. (c) *trans*-Bicyclo[5.1.0]octanes are relatively stable whereas *trans*-bicyclo-[4.1.0]heptanes are appreciably strained. Likewise, *trans*-cyclooctenes are considerably more stable than *trans*-cycloheptenes. For leading references, see: Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667-669. Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 4550-4555.

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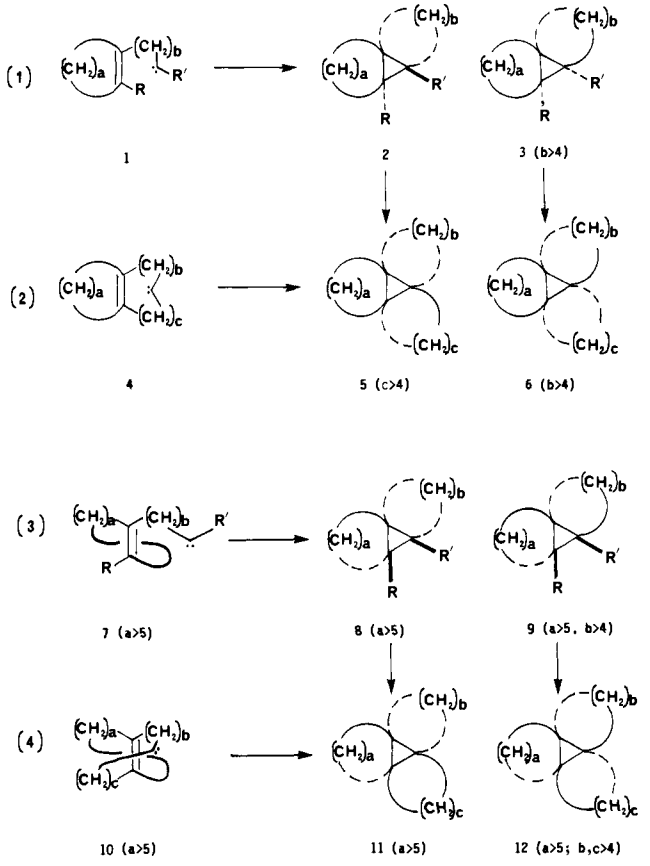
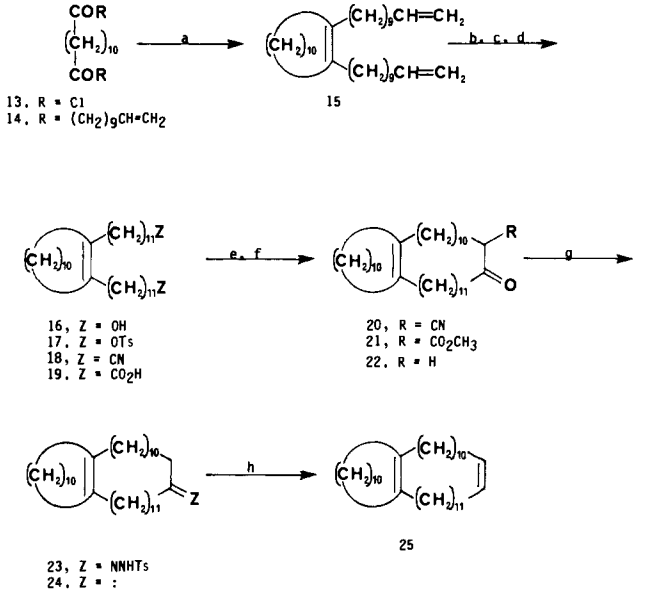
At least one of the bridging chains must be trans fused in perannulanes with odd-numbered central rings. If the central ring is three membered (triannulanes), steric considerations require trans bridging chains to contain at least four atoms.[1c] The synthetic approaches to triannulanes described in this paper are based on intramolecular carbenoid additions to tetrasubstituted double bonds with retention of double bonds stereochemistry as shown in eq 1–4. It is assumed that ring strain will effectively preclude



the formation of trans fused triannulanes such as **3**, **5**, **6**, **9**, and **12** by this [2 + 1] approach unless the newly formed rings are larger than six atoms (i.e., trans-bicyclo[4.1.0] systems).[1c] Those approaches shown in eq 3 and 4 are likewise subject to ring strain considerations insofar as *trans*-cyclooctene is the smallest stable *trans*-cycloalkene (i.e., **7**, **10**; a = 6 or larger).[1c]

Our first efforts were directed along the lines of eq 2 using the readily available triene **15**, prepared as previously reported via McMurry cyclization of dione **14**.[2] The ^{1}H NMR spectrum of this triene was devoid of peaks at 2.2–2.6 ppm, characteristic of the corresponding trans isomer.[3] Hence, the cyclization must proceed with high stereoselectivity. After a number of unsuccessful attempts to convert triene **15** efficiently and directly to ketone **22** via hydroboration–carbonylation methodology,[4] we turned to a more conventional route employing hydroboration–oxidation to diol **16** followed by cyanide displacement of the ditosylate **17** and high dilution Thorpe–Ziegler cyclization of the resulting dinitrile **18**.[5] The hydrolysis product, keto nitrile **20**, underwent unwanted double-bond isomerization during hydrolysis and decarboxylation with hot aqueous sulfuric acid, whereas treatment with strong base effected ring cleavage and hydrolysis to an acid, presumably **19**. Conversion to ketone **22** was finally accomplished through acidic methanolysis to keto ester **21** and saponification–

Scheme I



(a) $TiCl_3$, Li, DME. (b) $(C_6H_{11})_2BH$; H_2O_2, NaOH. (c) *p*-TsCl, C_5H_5N. (d) NaCN, CH_3CN, H_2O, *n*-Bu_3N. (e) $LiN(CH_3)C_6H_5$, THF; H_2O, HCl. (f) CH_3OH, HCl; KOH, H_2O, THF. (g) *p*-$TsNHNH_2$, HCl. (h) $NaOCH_3$, diglyme, 140 °C.

decarboxylation using aqueous potassium hydroxide.

The tosylhydrazone **23** was readily prepared via treatment of ketone **22** with (*p*-tolylsulfonyl)hydrazine in acidic THF. Thermal decomposition in basic diglyme[6] led to a hydrocarbon product shown to be a mixture of the cis and trans dienes **25** by ^{1}H and ^{13}C NMR analysis. No cyclopropane carbon resonance indicative of a [2 + 1] cyclization (**5**, a = 10, b = c = 11) could be found in the latter spectrum. Evidently, intramolecular 1,2-hydrogen migration is more favorable than attack on the double bond by the intermediate carbene **24**. This finding prompted a modification of our synthetic strategy.

The intramolecular cycloaddition of α-keto carbenes to olefins is a well-documented route to fused-ring cyclopropanes.[7,8] The most successful examples are those involving five- and six-membered ring closure. Since rings of this size must be cis fused to cyclopropanes and since triannulanes can have no more than two cis-fused rings, the approach shown in eq 4 employing a diazobetweenanene was the clear choice. Acyloin **31**, a likely intermediate for this approach, had served as a key intermediate in our first synthesis of [10.10]betweenanene.[9] An improved route to this acyloin was made possible by our recent work on the coupling of organocopper reagents with large-ring vinyl oxiranes.[10] The sequence is outlined in Scheme II.

Addition of a 1:1 3-butenylmagnesium bromide–copper(I) iodide complex to vinyl oxirane **26** in THF–dimethyl sulfide afforded the trans-allylic alcohol **27** in 90% yield.[10] Further elaboration of this alcohol to triene **29** was found to proceed most efficiently by using a twofold excess of the same complex with phosphate **28** in 1,2-dimethoxyethane (DME)–dimethyl sulfide at −78 to −20 °C. Under these conditions a separable 87:12 mixture of triene **29** and an isomeric triene resulting from S_N2' coupling was obtained in quantitative yield. Selective terminal

(2) Marshall, J. A.; Black, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 7581–7583. Black, T. H. Ph.D. Thesis, Northwestern University, 1980.
(3) Flynn, K. E., unpublished results.
(4) Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5477–5478. Pelter, A.; Smith, K.; Hutchings, M. G.; Rowe, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 129–138.
(5) Allinger, N. L.; Nakazaki, M.; Zalkow, V. *J. Am. Chem. Soc.* **1959**, *81*, 4074–4080.
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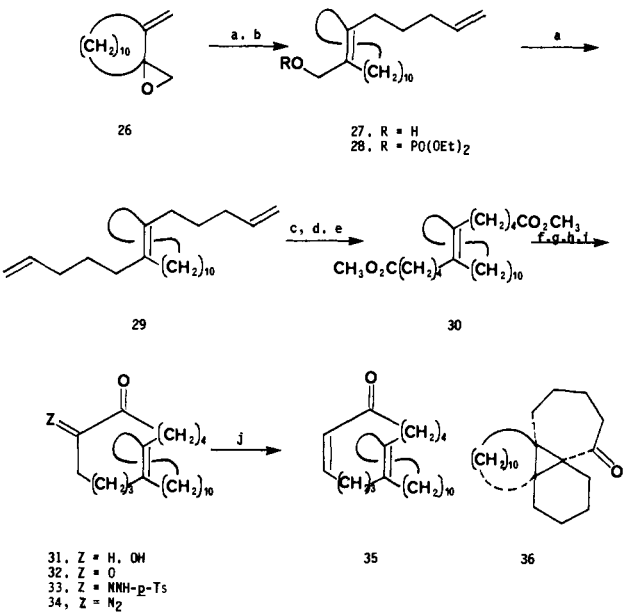
(7) Burke, S. D.; Grieco, P. A. *Org. React. (N.Y.)* **1979**, *26*, 361–475.
(8) (a) White, J. D.; Torii, S.; Nogami, J. *Tetrahedron Lett.* **1974**, 2879–2882. (b) Clark, R. P.; Heathcock, C. H. *Tetrahedron Lett.* **1975**, 529–532.
(9) Marshall, J. A.; Lewellyn, M. *J. Am. Chem. Soc.* **1977**, *99*, 3508–3510.
(10) Marshall, J. A.; Flynn, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 3360–3362; **1984**, *106*, 723–730.

Scheme II



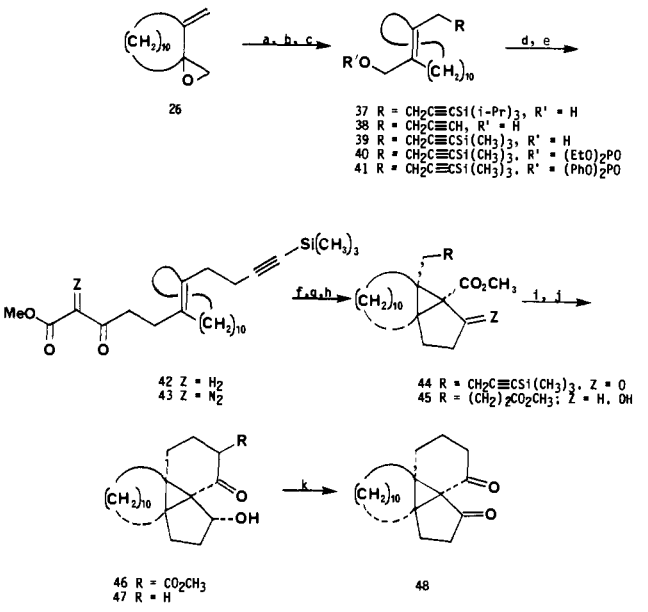
(a) CH_2=$CHCH_2CH_2MgBr$, CuI, DMS. (b) $(EtO)_2POCl$, C_5H_5N. (c) $Siam_2BH$; H_2O_2, NaOH. (d) $(C_5H_5NH)_2Cr_2O_7$, DMF. (e) CH_2N_2. (f) Na–K, Me_3SiCl; n-Bu_4NF. (g) $Cu(OAc)_2$. (h) p-$TsNHNH_2$. (i) KO-t-Bu. (j) Various Cu salts.

hydroboration–oxidation of triene **29** followed by oxidation with pyridinium dichromate and esterification with diazomethane afforded the known diester **30**.[9] Cyclization was effected in 38% yield as previously reported by using sodium–potassium alloy in refluxing xylene in the presence of trimethylsilyl chloride. Cleavage of the intermediate trimethylsilyl enol ether derivative and oxidation of the liberated acyloin **31** with copper(II) acetate afforded dione **32** in 94% yield.[11] The tosylhydrazone derivative **33** upon treatment with potassium *tert*-butoxide gave the diazo ketone **34** in 55% yield.

The cyclization of diazo ketone **34** to triannulanone **36** was attempted with a number of likely catalyst systems including copper(I) iodide–trimethyl phosphite,[8b] rhodium(II) acetate,[13] copper(II) acetylacetonate,[14] copper(II) sulfate,[15] and copper(II) bis(*N*-*n*-butylsalicylideneaminate).[8a,16] All gave mixtures of products, but the last named was the cleanest according to thin-layer chromatography. The major product of that reaction was found to be the dienone **35**, a cis/trans mixture according to ^1H and ^{13}C NMR analysis. That no product corresponding to the triannulanone **36** could be detected showed once again that an intramolecular H shift effectively competes with carbene cycloaddition to the tetrasubstituted double bond even when a six-membered ring is involved in the cyclization. These findings prompted further modifications of our synthetic strategy.

The problem of an unwanted 1,2-hydrogen shift seemed managable through the use of an α-diazo β-dicarbonyl system as the carbene precursor. Such carbenes have been found to participate readily in [2 + 1] cycloadditions to alkenes.[7] To further encourage cycloaddition, we decided to employ a shorter tether leading to a five-membered ring and to postpone introduction of the fourth ring, thus allowing greater freedom of alignment between the pendant carbene and the double bond. The sequence is shown in Scheme III.

Scheme III



(a) $(i\text{-Pr})_3SiC{\equiv}CCH_2MgBr$, CuI, $(CH_3)_2S$. (b) $(n\text{-Bu})_4NF$, HOAc; n-BuLi, $(CH_3)_3SiCl$. (c) $(PhO)_2POCl$, C_5H_5N. (d) $LiCH_2COCH(Li)CO_2CH_3$. (e) p-TsN_3, Et_3N. (f) $h\nu$, Ph_2CO. (g) $(C_6H_{11})_2BH$; H_2O_2, NaOH. (h) CH_2N_2. (i) $LiN(i\text{-Pr})_2$, THF. (j) KOH, H_2O, THF. (k) $(C_5H_5NH)_2Cr_2O_7$, CH_2Cl_2.

Addition of [(triisopropylsilyl)propargyl]magnesium bromide–copper(I) iodide to vinyl oxirane **26**[10] in THF–dimethyl sulfide afforded the trans-allylic alcohol **37** in 79% yield. Addition of the analogous trimethylsilyl reagent gave rise to considerable allenic product resulting from γ-attack by the propargyl reagent. As noted by Corey,[17] the bulky triisopropylsilyl grouping effectively directs coupling to the α-position. Unfortunately, this bulky group also interferes with the subsequent hydroboration step, and in order to facilitate eventual terminal oxidation of the alkyne, the isopropylsilyl substituent in the coupling product **37** had to be replaced with trimethylsilyl. This was best achieved via fluoride cleavage and treatment of the acetylene **38** with *n*-butyllithium and trimethylsilyl chloride. Attempted one-step replacement with methyllithium and trimethylsilyl chloride was not successful.

We had previously found diethyl phosphate derivatives of allylic alcohols such as **39** to be significantly more stable than the corresponding halides and to give higher ratios of S_N2 vs. S_N2' products in coupling reactions with organocopper reagents.[10] Hence, we attempted S_N2 displacement of the diethyl phosphate **40** with the dianion of methyl acetoacetate. The desired product **42** was obtained, but only in low yield. It occurred to us that a competing S_N2 displacement of the ethyl groupings of phosphate **40** might be at fault. Accordingly, we prepared the diphenyl phosphate derivative **41** and subjected it to reaction with excess methyl acetoacetate dianion, whereupon keto ester **42** was secured in 70% yield. Conversion to the diazo derivative **43** was effected with *p*-toluenesulfonyl azide and triethylamine.[18] Of the copper reagents examined, only the *N*-*n*-butylsalicylideneaminato complex[16] was found to effect the desired cyclization to the tricyclic keto ester **44**. Interestingly, treatment of diazo keto ester **43** with copper(II) sulfate in refluxing xylene afforded the isomeric keto ester **49** in 52% yield. This product is thought to arise through 1,3-dipolar addition to the double bond followed by extrusion of nitrogen.[19]

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(19) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32–43.
(20) Thin-layer chromatography (TLC) was carried out by using glass plates precoated (0.25 mm) with E. Merck silica gel 60 F-254.

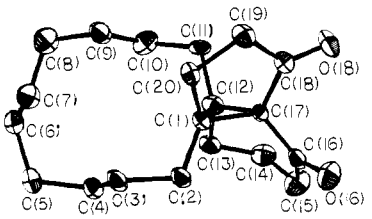
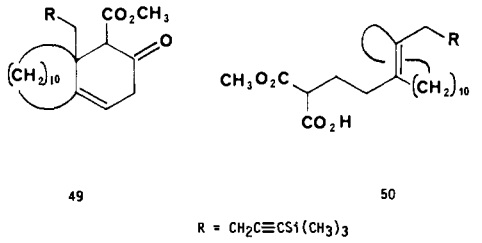


Figure 1. An ORTEP drawing of dione **48**. Thermal ellipsoids are at the 30% probability level.

Thermolysis of diazo keto ester **43** led to a complex mixture containing a small amount of the desired cyclopropane **44** according to TLC analysis. Irradiation in benzene with a low-pressure mercury lamp afforded the Wolff rearrangement product, malonate **50**, via the singlet carbene.[21] In the presence of benzophenone, however, the irradiation reaction took a completely different course to give cyclopropane **44** in 42% yield via the triplet carbene intermediate.[22]



49 50

R = $CH_2C{\equiv}CSi(CH_3)_3$

Hydroboration of the acetylenic grouping in **44** with excess dicyclohexylborane[23] was accompanied by reduction of the ketone grouping. Addition of alkaline hydrogen peroxide and esterification of the resultant acid led to the hydroxy diester **45** in 65% yield. Dieckmann cyclization using lithium diisopropylamide in THF at −20 °C and subsequent hydrolysis–decarboxylation of the β-keto ester **46** with potassium hydroxide in refluxing aqueous THF gave the keto alcohol **47** in 63% yield. Oxidation with pyridinium dichromate in methylene chloride afforded *trans,cis,cis*-[10.4.3]triannulane-16,18-dione (**48**) as a highly crystalline solid. The structure assignment was supported by the infrared, ^1H NMR, and ^{13}C NMR spectra and by single-crystal X-ray structure analysis (Figure 1).

The successful cyclization of the carbene derived from the trans-cyclododecenyl α-diazo β-keto ester **43** prompted us to reexamine our betweenanene-based route to triannulanes (Scheme II) with several modifications. A major considerable was the incorporation of a β-dicarbonyl grouping to stabilize the carbene and prevent hydrogen migration. We also decided to employ a nine-carbon bridge to permit the formation of six-membered rings in the cycloaddition step. To that end, dione **58** became our next objective. The sequence is presented in Scheme IV.

The previously described acetylenic alcohol **37** was converted to the diacetylene **52** via addition of [(triisopropylsilyl)-propargyl]magnesium bromide–copper (I) iodide in DME–dimethyl sulfide. As noted above, hydroboration–oxidation of diyne **52** led to mixtures of acidic and ketonic products owing to the large steric bulk of the triisopropylsilyl grouping. The trimethylsilyl derivative **54**, on the other hand, gave the diester **55** in 60–65% yield upon hydroboration–oxidation and direct esterification of the crude acid with diazomethane. Prolonged exposure to alkaline hydrogen peroxide was required for optimal yields of diacid (**55**, R = $CH_2CH_2CO_2H$). On several occasions double bond epoxidation was observed as a side product of this sequence. It is tempting to invoke intramolecular oxygen transfer from an intermediate produced in the borane oxidation step, but no evidence for this possibility could be found.[24]

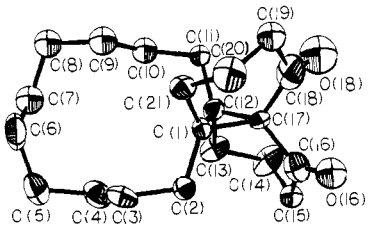
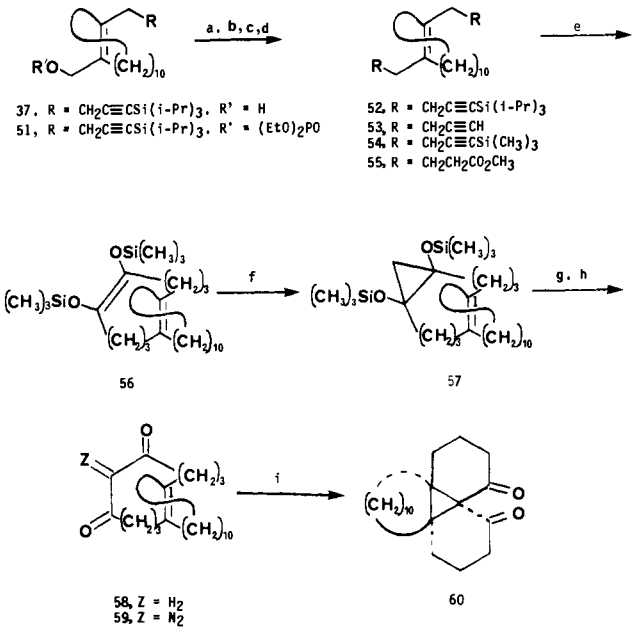


Figure 2. An ORTEP drawing of the A conformer of dione **60**. Thermal ellipsoids are at the 30% probability level.

Scheme IV



37, R = $CH_2C{\equiv}CSi(i\text{-}Pr)_3$, R' = H
51, R = $CH_2C{\equiv}CSi(i\text{-}Pr)_3$, R' = $(EtO)_2PO$

52, R = $CH_2C{\equiv}CSi(i\text{-}Pr)_3$
53, R = $CH_2C{\equiv}CH$
54, R = $CH_2C{\equiv}CSi(CH_3)_3$
55, R = $CH_2CH_2CO_2CH_3$

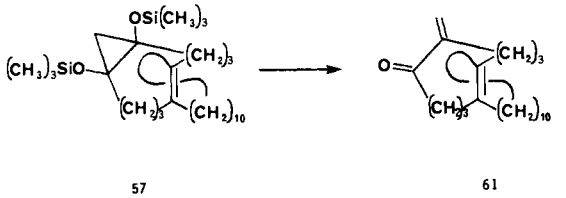
56 57

58, Z = H_2
59, Z = N_2

60

(a) $(i\text{-}Pr)_3SiC{\equiv}CCH_2MgBr$, CuI, DMS. (b) Bu_4NF, THF-H_2O. (c) *n*-BuLi; $(CH_3)_3SiCl$. (d) $(C_6H_{11})_2BH$; H_2O_2, NaOH; CH_2N_2. (e) Na-K, $(CH_3)_3SiCl$. (f) $(C_2H_5)_2Zn$, CH_2I_2. (g) $NaIO_4$. (h) *p*-TsN_3, Et_3N. (i) *hν*, Ph_2CO.

Slow addition of diester **55** and trimethylsilyl chloride to sodium–potassium alloy in refluxing toluene afforded the bis(trimethylsilyl) derivative **56**. Selective cyclopropanation of the exposed double bond of diene **56** was effected with diethylzinc and methylene iodide in refluxing toluene.[25] Other cyclopropanation procedures gave multiple products.[26] Oxidative cleavage of the 1,2-glycol derivative **57** with aqueous sodium periodate afforded the 1,3-dione **58** in 35% overall yield.[27] This oxidation step was best executed with dispatch as cyclopropane **57** underwent pinacol rearrangement to the α-methylene ketone **61** on standing.



57 61

Treatment of dione **58** with *p*-toluenesulfonyl azide and triethylamine led to the desired α-diazo derivative in 65% yield.[18] Irradiation in benzene with benzophenone as the sensitizer afforded *trans,cis,cis*-[10.4.4]triannulane-16,18-dione (**60**) as a crystalline solid in 62% yield. The structure of **60** was fully supported by

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(25) Ito, Y.; Saegusa, T. *J. Org. Chem.* **1977**, *42*, 2326–2327.
(26) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React. (N.Y.)* **1973**, *20*, 1–131.
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infrared, ^1H NMR, and ^{13}C NMR spectra and by single-crystal X-ray structure analysis (Figure 2).

The crystals of dione **60** were found to be partially disordered with four conformers and their enantiomers occupying the unit cell. An ORTEP drawing of the major conformer is shown in Figure 2. Additional details regarding the structure analysis and the conformational preferences of **60** will be published separately.

We briefly examined the synthesis of optically active triannulanedione **60** from allylic alcohol (*S*)-(+)-**37**, prepared via enantioselective Sharpless epoxidation.[10,28] The sample of alcohol (+)-**37** thus obtained was found to be a 75:25 mixture of (*S*)-**37** (70% ee) and the cis isomer according to ^{19}F NMR analysis of the Mosher ester. The alcohol mixture was carried through the homologation sequence of Scheme IV to give dione **58** that could be separated from the related cis isomer via column chromatography.[29] Dione **60**, obtained via irradiation of the α-diazo ketone **59** as described for the racemic series, showed $[\alpha]^{30}_D$ +185°. With the assumption of minimal changes in optical purity for the sequence leading from **37** to **60**,[10] the molecular rotation of pure (+)-**60** can be calculated to be +835°. Initial attempts at removal of the carbonyl groupings of dione **60** have not been successful owing to steric crowding at these positions and facile cleavage of the congested cyclopropane ring.[29]

Experimental Section[30]

1,33-Tetratriacontadiene-12,23-dione (14). The procedure of Sato was modified.[31] To a stirred, cooled (−78 °C) solution of 35.5 mL (148 mmol) of dodecanedioyl chloride **13** in 700 mL of THF was added dropwise 725 mL (326 mmol) of 0.45 M 10-undecenylmagnesium bromide in THF. The solution was allowed to warm to room temperature with stirring over 2 h, and water was added. The aqueous layer was separated, and the product was purified by recrystallization from THF to yield 41.4 g (62%) of dione **14** as a white solid: mp 90–92 °C (lit.[2] mp 88.5–90 °C); IR ($CHCl_3$) ν 2915, 2850, 1705, 1645, 1470, 1465, 1420, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (e), 1.40–2.20 (br m), 2.37 (t, J = 6.9 Hz, $CH_2C{=}O$), 4.95 (m, $CH{=}CH_2$), 5.75 (br m, $CH{=}CH_2$).

(*Z*)-1,2-Bis(10-undecenyl)cyclododecene (15). The procedure of Black was modified.[32] To a stirred mixture of 1.35 g (194 mmol) of lithium and 15 g (97.2 mmol) of titanium(III) chloride was added 125 mL of DME. The black mixture was warmed to reflux for 2 h, whereupon 4.00 g (7.95 mmol) of dione **14** in 150 mL of DME was added dropwise via a Hershberg funnel over 12 h. The stirred solution was then refluxed for 2 h, cooled to room temperature, and filtered through Celite. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, hexane) to yield 3.00 g (80%) of triene **15** as a clear oil: IR (film) ν 2910, 2845, 1560, 1460, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (e), 1.60–2.30 (br m), 4.95 (m, $CH{=}CH_2$), 5.75 (m, $CH{=}CH_2$).

(*Z*)-1,2-Bis(11-hydroxyundecyl)cyclododecene (16). The procedure of Black was modified.[32] To a stirred, cooled (−10 °C) solution of 31.8 mL (31.8 mmol) of 1.0 M borane in THF was added 7.07 mL (69.8 mmol) of cyclohexene in 16 mL of THF. The white heterogeneous mixture was stirred 1 h at −10 °C, whereupon 3.00 g (6.37 mmol) of triene **15** in 16 mL of THF was added dropwise. The solution was stirred at −10 °C for 1 h and at room temperature for 3 h and then cooled to 0 °C, whereupon 1.91 mL of water, 11.7 mL of 3 N sodium hydroxide, and 11.7 mL of 30% hydrogen peroxide were added cautiously. The solution was stirred 1 h at room temperature and 2 h at 45 °C and poured into water. The product was isolated by ethyl acetate extraction. The extracts were washed with brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by recrystallization from hexane to yield 2.40 g (74%) of diol **16** as a white solid: mp 90–92 °C (lit.[32] mp 91–93 °C); IR (film) ν 2920, 2850, 1470, 1045, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (e), 1.50–2.32 (br m), 3.58 (t, J = 6.3 Hz, CH_2OH).

Ditosylate of (*Z*)-1,2-Bis(11-hydroxyundecyl)cyclododecene (17). To a stirred, cooled (0 °C) solution of 1.01 g (2.0 mmol) of diol **16** in 10 mL of pyridine was added 3.81 g (20.0 mmol) of *p*-toluenesulfonyl chloride. The solution was stirred for 2 h at 0 °C and for 1 h at room temperature. Water was then added, and the product was isolated by ethyl acetate extraction. The extracts were washed with 10% hydrochloric acid and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.916 g (56%) of ditosylate **17** as a clear oil: IR (film) ν 2900, 2830, 1480, 1470, 1370, 1190, 1175, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (e), 1.30–2.25 (br m), 2.43 (s, $ArCH_3$), 4.01 (t, J = 6.2 Hz, CH_2O), 7.56 (ABq, $\Delta\nu$ = 39.5 Hz, J_{AB} = 8.7 Hz, Ar*H*).

(*Z*)-1,2-Bis(11-cyanoundecyl)cyclododecene (18). The procedure of Reeves was modified.[33] To a stirred solution of 1.37 g (27.9 mmol) of sodium cyanide in 2.75 mL of water was added 0.541 g (0.664 mmol) of ditosylate **17** in 4.16 mL of acetonitrile and 0.108 mL (0.453 mmol) of tri-*n*-butylamine. The biphasic solution was stirred vigorously at 80 °C for 18 h and then cooled to room temperature. The product was isolated by ether extraction. The extracts were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by filtration through silica gel (25% ethyl acetate–hexane) to yield 0.334 g (96%) of dicyanide **18** as a clear oil: IR (film) ν 2925, 2850, 2240, 1470, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (e), 1.32–2.20 (br m), 2.31 (t, J = 6.3 Hz, CH_2CN). Anal. Calcd for $C_{36}H_{64}N_2$: C, 82.37; H, 12.29. Found: C, 82.14; H, 12.17.

(*Z*)-12-Cyanobicyclo[23.10.0]-1(25)-pentatriaconten-13-one (20). The procedure of Allinger was modified.[5] To a stirred mixture of 0.286 g (11.9 mmol) of sodium hydride (oil removed by washing with hexane) in 40 mL of THF was added 1.47 mL (13.6 mmol) of *N*-methylaniline. The mixture was warmed to reflux for 2 h, whereupon 0.479 g (0.912 mmol) of nitrile **18** in 10 mL of THF was added dropwise over 20 h to the refluxing solution. The solution was cooled to room temperature, 20 mL of hydrochloric acid was added, and stirring was continued for 1 h. The product was isolated by ether extraction. The extracts were washed with brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.297 g (62%) of cyano ketone **20** as a white solid: mp 109–110.5 °C; IR (KBr) ν 2890, 2835, 2245, 1715, 1470, 1445, 1385, 1090, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (e), 1.33–2.33 (br m), 2.66 (t, J = 7.2 Hz, $CH_2C{=}O$), 3.42 (t, J = 6.3 Hz, CHCN). Anal. Calcd for $C_{36}H_{63}NO$: C, 82.22; H, 12.08. Found: C, 82.16; H, 12.01.

(*Z*)-12-Carbomethoxybicyclo[23.10.0]-1(25)-pentatriaconten-13-one (21). The procedure of Pirkle was modified.[34] An anhydrous solution of hydrochloric acid in methanol was generated by the addition of 9.30 mL (131 mmol) of acetyl chloride to 13.8 mL of methanol at 0 °C. To this stirred, cooled (0 °C) acid solution was added dropwise 0.276 g (0.525 mmol) of cyano ketone **20** in 13.8 mL of THF. The solution was allowed to warm to room temperature and was stirred for 48 h. Water was added, and the product was isolated by ether extraction. The extracts were washed with water and brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the

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(29) A description of these experiments can be found in the Ph.D. Dissertation of J. C. Peterson: "The Synthesis of *trans,cis,cis*-[10.4.3]Triannulane-16,18-dione and *trans,cis,cis*-[10.4.4]Triannulane-16,18-dione", Northwestern University, 1984.

(30) (a) The apparatus and methods described by G. W. Kramer, M. M. Midland, and A. B. Levy [Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; pp 191–202] were used to maintain an argon or nitrogen atmosphere in the reaction flask. (b) Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, and dioxane), calcium hydride (dichloromethane and hexamethylphosphoramide), or sodium (benzene and toluene). (c) Infrared absorption maxima are reported in wavenumbers (cm^{-1}) and are standardized by reference to the 1601-cm^{-1} peak of polystyrene. (d) Proton magnetic resonance spectra were recorded on IBM NR-80 and Varian EM-390 spectrometers. Carbon-13 spectra were recorded at 20 MHz on an IBM NR-80 Fourier transform spectrometer. All samples were prepared as dilute solutions in deuteriochloroform ($CDCl_3$). Chemical shifts (δ) are reported downfield from tetramethylsilane (Me_4Si), in parts per million (ppm) of the applied field. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; envelope, e; multiplet, m. Coupling constants (J) are reported in hertz (Hz). (e) Gas chromatography-mass spectral analysis (GC/MS) was performed on a Finnigan 4021 instrument. High-resolution mass spectra (HRMS) were determined at the Center for Mass Spectrometry, University of Pennsylvania. (f) Combustion microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL. (g) Analytical thin-layer chromatography (TLC) was routinely used to monitor reactions. Plates precoated with E. Merck silica gel 60 F254 of 0.25 mm thickness, supplied by Brinkmann Instruments, were used. (h) Column chromatography was performed by using E. Merck silica gel 60 (230–400 ASTM mesh) according to the procedure of W. C. Still, M. Kahn, and A. Mitra [*J. Org. Chem.* **1978**, *43*, 2923–2925].

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product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.210 g (72%) of keto ester **21** as a white solid: mp 70–82 °C; IR (KBr) ν 2890, 2840, 1745, 1710, 1475, 1445, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (e), 1.40–2.35 (br m), 2.54 (t, J = 6.6 Hz, $CH_2C{=}O$), 3.50 (dd, $J_{1,2}$ = 6.0 Hz, $J_{1,3}$ = 8.4 Hz, $CHCO_2CH_3$), 3.69 (s, CO_2CH_3); ^{13}C NMR ($CDCl_3$) δ 22.5, 23.1, 24.7, 25.4, 25.9, 26.9, 27.7, 28.1, 28.4, 28.8, 28.9, 29.1, 29.2, 29.6, 29.8, 30.0, 30.8, 30.9, 41.6, 52.0, 57.9, 133.6, 170.0, 206.0; high-resolution mass spectrum calcd for $C_{37}H_{66}O_3$ m/e 558.5012, found m/e 558.5021.

(*Z*)-Bicyclo[23.10.0]-1(25)-pentatriaconten-13-one (22). To a solution of 0.100 g (1.78 mmol) of potassium hydroxide in 0.40 mL of water was added 0.100 g (0.179 mmol) of keto ester **21** in 1.40 mL of THF. The biphasic mixture was warmed to reflux and stirred vigorously for 6 h. The mixture was cooled to room temperature, and the product was isolated by ether extraction. The extracts were washed with brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 10% ethyl acetate–hexane) to yield 0.074 g (82%) of ketone **22** as a white solid: mp 83–83.5 °C; IR (KBr) ν 2980, 2830, 1705, 1470, 1405, 1085, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (e), 1.34–2.25 (br m), 2.37 (t, J = 6.0 Hz, $CH_2C{=}O$); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.7, 23.9, 24.9, 25.7, 26.1, 28.0, 28.7, 28.9, 29.2, 29.3, 29.4, 29.6, 30.1, 31.1, 42.3, 133.8, 212.4. Anal. Calcd for $C_{35}H_{64}O$: C, 83.93; H, 12.88. Found: C, 83.67; H, 12.73.

An attempted direct preparation of ketone **22** from cyano ketone **20** (0.105 g) with aqueous potassium hydroxide (1.1 g in 1.6 mL of water) at reflux for 24 h yielded recovered starting material (0.012 g) and diacid **19** (0.057 g): IR (KBr) ν 3600–2600, 1700, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (m, α-CH_2's), 1.30 (e, CH_2's).

Tosylhydrazone of (*Z*)-Bicyclo[23.10.0]-1(25)-pentatriaconten-13-one (23). To a stirred solution of 0.105 g (0.564 mmol) of (*p*-tolylsulfonyl)hydrazine in 0.94 mL of THF was added 0.113 g (0.225 mmol) of enone **22** and 1 drop of concentrated hydrochloric acid. The solution was stirred for 2 h, and the solvent was removed under reduced pressure. The product was purified by filtration through Florisil (chloroform) to yield 0.152 g (101%) of tosylhydrazone **23** as a white solid: mp 112–120 °C; IR ($CHCl_3$) ν 3205, 2910, 2840, 1470, 1335, 1190, 665 cm^{-1}.

(*Z*)-Bicyclo[23.10.0]pentatriaconta-1(25),12-diene (25). The procedure of Casanova was modified.[6] To a stirred, heated (140 °C) solution of 0.0333 g (0.617 mmol) of sodium methoxide in 0.5 mL of 2-methoxyethyl ether was added 0.0412 g (0.0617 mmol) of tosylhydrazone **23** in 0.5 mL of 2-methoxyethyl ether. The stirred solution was heated for 2 h and cooled to room temperature. The product was isolated by hexane extraction. The extracts were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, hexane) to yield 0.0198 g (66%) of a 63:36 mixture of cis and trans dienes **25** as a white solid: mp 64–66 °C; IR (KBr) ν 2870, 2820, 1470, 1440, 975 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (e), 2.00 (m), 5.33 (m, CH=CH). Anal. Calcd for $C_{35}H_{64}$: C, 86.70; H, 13.30. Found: C, 86.73; H, 13.28.

(*E*)-1-(Hydroxymethyl)-2-(4-pentenyl)cyclododecene (27). The procedure of Flynn was modified.[10] To a stirred, cooled (−78 °C) solution of 18.3 g (96.1 mmol) of copper(I) iodide in 43.0 mL (585 mmol) of dimethyl sulfide and 150 mL of THF was added dropwise 120 mL (96.1 mmol) of 0.80 *M* 3-butenylmagnesium bromide in THF. The resultant yellow heterogeneous mixture was stirred at −78 °C for 30 min, whereupon 10.0 g (48.1 mmol) of vinyl oxirane **26** in 40 mL of THF was added dropwise. The mixture was allowed to warm gradually to −20 °C overnight and then poured into saturated ammonium chloride. The product was isolated by ether extraction. The extracts were washed with 3% ammonium hydroxide and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by filtration through silica gel (25% ethyl acetate–hexane) to yield 11.4 g (90%) of alcohol **27** as a viscous oil: IR (film) ν 3300, 2900, 2835, 1640, 1470, 1240, 995, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (e), 1.23–2.70 (br m), 4.18 (ABq, $\Delta\nu$ = 46.5 Hz, J_{AB} = 12 Hz, CH_2OH), 4.81–5.15 (m, $CH{=}CH_2$), 5.52–6.06 (br m, $CH{=}CH_2$). Anal. Calcd for $C_{18}H_{32}O$: C, 81.73; H, 12.22. Found: C, 81.77; H, 12.11.

(*E*)-1-[(Diethylphosphonoxy)methyl]-2-(4-pentenyl)cyclododecene (28). The procedure of Flynn was followed.[10] To a stirred, cooled (−40 °C) solution of 18.6 mL (129 mmol) of diethyl chlorophosphate in 200 mL of pyridine was added dropwise 11.4 g (43.2 mmol) of alcohol **27** in 30 mL of pyridine. The solution was allowed to warm to −20 °C over 2 h. Water was added, and the product was isolated by ether extraction. The extracts were washed with copper(II) sulfate, water, and brine and were dried over potassium carbonate. The solvent was removed at reduced pressure to yield 15.7 g (91%) of phosphate **28** as a viscous oil. This was used without further purification: IR (film) ν 2900, 2820, 1640, 1445, 1275, 1075, 1040, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (e), 1.30 (t, J = 6.4 Hz, P − O − CH_2CH_3), 1.50–2.73 (br m), 4.04 (m, P − O − CH_2CH_3), 4.65 (ABq, $\Delta\nu$ = 33 Hz, J_{AB} = 90 Hz, C=CCH_2O), 4.90 (m, $CH{=}CH_2$), 5.70 (m, $CH{=}CH_2$).

(*E*)-1,2-Bis(4-pentenyl)cyclododecene (29). The procedure of Flynn was modified.[10] To a stirred, cooled (−78 °C) solution of 15.0 g (78.7 mmol) of copper(I) iodide in 35.2 mL (479 mmol) of dimethyl sulfide and 120 mL of DME was added dropwise 98.0 mL (78.7 mmol) of 0.80 M 3-butenylmagnesium bromide in THF. The resultant yellow heterogeneous mixture was stirred at −78 °C for 30 min, whereupon 15.7 g (39.3 mmol) of phosphate **28** in 30 mL of DME was added dropwise. The mixture was allowed to gradually warm to −20 °C overnight and then poured into saturated ammonium chloride. The product was isolated by ether extraction. The extracts were washed with 3% ammonium hydroxide and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, hexane) to yield 9.71 g (82%) of trienes as an 86:13 mixture of α:γ addition products which could be separated by repeated chromatography: IR (film) ν 2870, 2820, 1630, 1460, 1335, 980, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (e), 1.33–2.62 (br m), 4.95 (m, $CH{=}CH_2$), 5.70 (m, $CH{=}CH_2$). Anal. Calcd for $C_{22}H_{38}$: C, 87.32; H, 12.68. Found: C, 87.56; H, 12.56.

(*E*)-1,2-Bis(4-carbomethoxybutyl)cyclododecene (30). To a stirred, cooled (−12 °C) solution of 0.257 mL (2.57 mmol) of borane–methyl sulfide complex was added dropwise 0.570 mL (5.30 mmol) of 2-methyl-2-butene. The clear solution was stirred for 15 min at −12 °C and for 1.5 h at 0 °C, whereupon 0.200 g (0.622 mmol) of triene **29** in 0.5 mL of ether was added dropwise. After the solution was stirred for 3 h at 0 °C, the solvent was removed at reduced pressure and 1.0 mL of *N*,*N*-dimethylformamide (DMF) was added. The organoborane in DMF was then added dropwise to a stirred, cooled (0 °C) mixture of 4.97 g (13.2 mmol) of pyridinium dichromate in 10 mL of DMF. The mixture was allowed to warm to room temperature and was stirred overnight. The product was isolated by dilution with ethyl acetate and filtration through Celite. The filtrate was washed with 10% hydrochloric acid and brine and dried over magnesium sulfate. The solvent was removed at reduced pressure to yield 0.174 g (72%) of diacid as a brown viscous oil: IR (film) ν 2950, 2940, 2855, 1725, 1465, 1265, 1060 cm^{-1}. This material was esterified without further purification, using the procedure of Arndt.[35] A solution of diazomethane in ether was prepared from 5.5 mL of 50% potassium hydroxide and 0.697 g (6.77 mmol) of *N*-methyl-*N*-nitrosourea in 15 mL of ether. To a stirred, cooled (0 °C) solution of 0.174 g (0.475 mmol) of crude diacid in 15 mL of ethyl acetate was added the ethereal solution of diazomethane. The solution was stirred for 15 min at 0 °C and for 30 min at room temperature, and acetic acid was added. The solution was washed with 10% sodium hydroxide and brine and was dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.097 g (37%) of the known diester **30** as a colorless oil:[9] IR (film) ν 2900, 2840, 1735, 1435, 1200, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (e), 1.29–2.02 (br m), 2.12–2.61 (br m), 2.29 (t, J = 6.9 Hz, CH_2CO_2), 3.63 (s, CO_2CH_3).

(*E*)-6-Hydroxybicyclo[10.10.0]-1(12)-docosen-5-one (31). The procedure of Bloomfield was modified.[36] To a stirred mixture of 0.025 g (1.07 mmol) of sodium in 20 mL of toluene was added 0.042 g (1.07 mmol) of potassium. The vigorously stirred mixture was warmed to reflux for 1 h, whereupon 0.200 g (0.508 mmol) of diester **30** in 0.27 mL (2.13 mmol) of chlorotrimethylsilane and 5 mL of toluene was added slowly over 20 h to the refluxing solution. After the addition was complete, the mixture was refluxed for 4 h, cooled to room temperature, and filtered. The solvent was removed at reduced pressure to yield 0.212 g (87%) of the crude silylated enediolate which was used without further purification: IR (film) ν 2900, 2840, 1670, 1465, 1250, 1220, 1090, 855, 840, 760 cm^{-1}.

To a stirred solution of 0.212 g (0.443 mmol) of the crude silylated enediolate in 1.8 mL of THF was added dropwise 1.33 mL (1.33 mmol) of 1.0 M tetrabutylammonium fluoride in THF. The solution was stirred for 2 h and poured into brine. The product was isolated by ether extraction. The extracts were washed with 10% hydrochloric acid and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.064 g (38%) of known hydroxy ketone **31** as a viscous oil:[9] IR (film) ν 3440, 2900, 1745, 1705, 1465, 1240, 1095, 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (e), 1.60–2.40 (br m), 2.76–3.23 (m, $CH_2C{=}O$), 3.56 (d, J = 5.4 Hz, OH), 4.23–4.47 (m, $CHOH$).

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(*E*)-Bicyclo[10.10.0]-1(12)-docosene-5,6-dione (32). The procedure of Blomquist was followed.[11] To a stirred solution of 0.226 g (0.677 mmol) of hydroxy ketone **31** in 1.05 mL of methanol, 1.34 mL of water, and 1.34 mL of acetic acid was added 0.272 g (1.36 mmol) of copper(II) acetate monohydrate. The solution was warmed to reflux for 10 h and cooled to room temperature. The product was isolated by ether extraction. The extracts were washed with brine and were dried over potassium carbonate. The solvent was removed at reduced pressure to yield 0.212 g (94%) of dione **32** as a yellow semisolid which was used without further purification: IR ($CHCl_3$) ν 2920, 2850, 1710, 1465, 1450, 1105, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (e), 1.31–2.67 (br m), 2.68–3.20 (br m).

Monotosylhydrazone of (*E*)-Bicyclo[10.10.0]-1(12)-docosene-5,6-dione (33). To a stirred solution of 0.212 g (0.639 mmol) of dione **32** in 6.0 mL of methanol and 3.5 mL of dichloromethane was added 0.119 g (0.639 mmol) of (*p*-tolylsulfonyl)hydrazine. The solution was stirred for 18 h, whereupon the solvent was removed at reduced pressure to yield 0.322 g (101%) of monotosylhydrazone **32** as a white foam. This was used without further purification: IR (film) ν 3180, 2990, 2880, 2825, 1685, 1600, 1460, 1350, 1215, 1170, 1160, 1065, 805, 750, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (e), 1.30–2.60 (br m), 3.30 (s, aromatic CH_3), 3.41 (s, NH), 7.24 (m, aromatic H), 7.73 (m, aromatic H).

(*E*)-6-Diazobicyclo[10.10.0]-1(12)-docosen-5-one (34). The procedure of Cava was modified.[12] To a stirred solution of 0.322 g (0.640 mmol) of tosylhydrazone **33** in 5.0 mL of THF was added 0.093 g (0.830 mmol) of potassium *tert*-butoxide. The solution was stirred for 24 h and then poured into water. The product was isolated by ether extraction. The extracts were washed with 2 M potassium hydroxide and brine and were dried over potassium carbonate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 0.120 g (55%) of diazo ketone **34** as a viscous yellow oil: IR ($CHCl_3$) ν 2900, 2825, 2050, 1620, 1460, 1440, 1130, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (e), 1.30–2.80 (br m).

(*E*)-Bicyclo[10.10.0]-1(12),6-docosadien-5-one (35). The procedure of White was modified.[8a] To a stirred solution of 0.082 g (0.239 mmol) of diazo ketone **34** in 4.1 mL of cyclohexane was added 0.139 g (0.120 mmol) of bis(*N*-*n*-butylsalicylideneaminato)copper(II). The stirred solution was warmed to reflux for 6 h. It was then cooled to room temperature, and the product was isolated by ether extraction. The extracts were washed with 10% hydrochloric acid, water, 10% sodium hydroxide, and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 10% ethyl acetate–hexane) to yield 0.031 g (41%) of enone **35** as a clear oil: IR (film) ν 2900, 2840, 1690, 1625, 1465, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (e), 1.25–2.73 (br m), 5.87 (m, CH=CHCO); ^{13}C NMR ($CDCl_3$) δ 23.1, 24.1, 24.7, 24.9, 25.0, 26.1, 26.6, 26.7, 26.9, 27.0, 29.5, 29.9, 32.2, 32.6, 42.6, 130.0, 130.6, 136.8, 142.7, 205.1. Anal. Calcd for $C_{22}H_{36}O$: C, 83.48; H, 11.47. Found: C, 83.34; H, 11.25.

(*E*)-1-(Hydroxymethyl)-2-[4-(triisopropylsilyl)-3-butynyl]cyclododecene (37). The procedure of Flynn was modified.[10] To a stirred, cooled (−78 °C) solution of 9.78 g (51.4 mmol) of copper(I) iodide in 22.7 mL (309 mmol) of dimethyl sulfide and 200 mL of THF was added dropwise 88.6 mL (51.4 mmol) of 0.58 M [1-(triisopropylsilyl)-propargyl]magnesium bromide in THF. The resultant yellow heterogeneous mixture was stirred at −78 °C for 30 min, whereupon 9.73 g (48.8 mmol) of vinyl oxirane **26**[10] in 30 mL of THF was added dropwise. The mixture was allowed to gradually warm to −20 °C overnight; then it was poured into saturated ammonium chloride, and the product was isolated by ether extraction. The extracts were washed with 3% ammonium hydroxide and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 20% ethyl acetate–hexane) to yield 14.9 g (79%) of allylic alcohol **37** as a white waxy solid: mp 74–76 °C; IR ($CHCl_3$) ν 3340, 2920, 2850, 2175, 1470, 1450, 995, 885, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 [s, $SiCH(CH_3)_2$], 1.20 (e), 1.33–2.90 (br m), 4.21 (ABq, $\Delta\nu$ = 47.4 Hz, J_{AB} = 12 Hz, CH_2OH). Anal. Calcd for $C_{26}H_{48}OSi$: C, 77.13; H, 11.98. Found: C, 77.04; H, 11.89.

(*E*)-1-(Hydroxymethyl)-2-(2-butynyl)cyclododecene (38). To a stirred, cooled (0 °C) solution of 10.0 g (25.0 mmol) of allylic alcohol **37** in 50 mL of THF was added 50.0 mL (50.0 mmol) of 1.0 M tetrabutylammonium fluoride in THF. The solution was warmed to room temperature and stirred for 4 h. The solvent was removed at reduced pressure. The residue was partitioned between 10% hydrochloric acid and ether, and the product was isolated by ether extraction. The extracts were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 25% ethyl acetate–hexane) to yield 6.19 g (100%) of ynol **38** as a clear oil: IR (film) ν 3275, 2900, 2850, 2140, 1460, 1445, 1120, 1000, 625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (e), 1.33–2.90 (br m), 4.19 (ABq, $\Delta\nu$ = 32.2 Hz, J_{AB} = 11 Hz, CH_2OH). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.36; H, 11.33.

(*E*)-1-(Hydroxymethyl)-2-[4-(trimethylsilyl)-3-butynyl]cyclododecene (39). The procedure of Audia was followed.[37] To a stirred, cooled (−78 °C) solution of 6.19 g (24.9 mmol) of ynol **38** in 100 mL of THF was added dropwise 23.9 mL (62.2 mmol) of 2.6 M *n*-butyllithium in hexane. The heterogeneous white solution was stirred 30 min at −78 °C, whereupon 9.47 mL (74.7 mmol) of chlorotrimethylsilane was added dropwise. The solution was stirred for 1 h at −78 °C and for 4 h at room temperature, at which time 50 mL of 10% hydrochloric acid was added. The resultant mixture was stirred 1 h and then saturated with sodium chloride. The product was isolated by ether extraction. After the solution was dried over magnesium sulfate, the solvent was removed at reduced pressure and the product was purified by filtration through silica gel (20% ethyl acetate–hexane) to yield 8.00 g (100%) of ynol **39** as a clear oil: IR (film) ν 3325, 2940, 2880, 2200, 1480, 1460, 1285, 875, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, $SiCH_3$), 1.19 (e), 1.33–2.90 (br m), 4.16 (ABq, $\Delta\nu$ = 32.6 Hz, J_{AB} = 11 Hz, CH_2OH). Anal. Calcd for $C_{20}H_{36}OSi$: C, 74.93; H, 11.32. Found: C, 74.96; H, 11.31.

(*E*)-1-[(Diphenylphosphonoxy)methyl]-2-[4-(trimethylsilyl)-3-butynyl]cyclododecene (41). To a stirred, cooled (−40 °C) solution of 15.5 mL (74.5 mmol) of diphenyl chlorophosphate in 100 mL of pyridine was added dropwise 7.95 g (24.8 mmol) of ynol **39** in 20 mL of pyridine. After the solution was stirred for 1 h at −40 °C, water was added and the product was isolated by ether extraction. The extracts were washed with saturated copper sulfate, water, and brine and were dried over potassium carbonate. The solvent was removed at reduced pressure to yield 12.9 g (94%) of phosphate **41** as a clear oil. This was used without further purification: IR (film) ν 2900, 2840, 2160, 1595, 1495, 1195, 1010, 955, 840, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, $SiCH_3$), 1.15 (e), 1.26–2.90 (br m), 4.35–5.20 (m, OCH_2), 7.15 (m, aromatic).

(*E*)-1-(4-Carbomethoxy-3-oxopentyl)-2-[4-(trimethylsilyl)-3-butynyl]cyclododecene (42). The procedure of Sum and Weiler was modified.[38] To a stirred, cooled (0 °C) mixture of 6.38 g (257 mmol) of 97% sodium hydride and 300 mL of THF was added dropwise 25.2 mL (234 mmol) of methyl acetoacetate. The yellow homogeneous solution was stirred at 0 °C for 30 min, whereupon 89.8 mL (234 mmol) of 2.6 M *n*-butyllithium in hexane was added dropwise. After the solution was stirred an additional 30 min, 12.9 g (23.4 mmol) of phosphate **41** in 50 mL of THF was added dropwise. Stirring was continued for 1 h, and then the mixture was quenched with water and saturated with sodium chloride. The product was isolated by ether extraction and dried over magnesium sulfate. Solvent was removed under reduced pressure, and the product was purified by column chromatography (silica gel, 20% ethyl acetate–hexane) to yield 6.81 g (70%) of β-keto ester **42** as a clear oil: IR (film) ν 2910, 2850, 2165, 1750, 1720, 1630, 1450, 1255, 845, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, $SiCH_3$), 1.20 (e), 1.30–2.85 (br m), 3.40 (s, $COCH_2CO$), 3.66 (s, OCH_3). Anal. Calcd for $C_{25}H_{42}O_3Si$: C, 71.71; H, 10.11. Found: C, 71.91; H, 10.06.

(*E*)-1-(4-Carbomethoxy-4-diazo-3-oxopentyl)-2-[4-(trimethylsilyl)-3-butynyl]cyclododecene (43). The procedure of Regitz was followed.[18] To a stirred, cooled (0 °C) solution of 6.63 g (15.9 mmol) of keto ester **42** in 75 mL of acetonitrile and 2.39 mL (16.5 mmol) of triethylamine was added dropwise 4.42 g (22.6 mmol) of *p*-toluenesulfonyl azide. The solution was allowed to reach room temperature with stirring overnight and was poured into 10% sodium hydroxide and extracted with ether. The extracts were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 20% ethyl acetate–hexane) to yield 6.36 g (90%) of diazo keto ester **43** as a light yellow solid: mp 63–65.5 °C; IR (film) ν 2900, 2850, 2160, 2125, 1725, 1660, 1440, 1320, 1255, 1050, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 [s, $Si(CH_3)_3$], 1.20 (e), 1.30–3.10 (br m), 3.73 (s, OCH_3). Anal. Calcd for $C_{25}H_{40}N_2O_3Si$: C, 67.52; H, 9.07. Found: C, 67.45; H, 9.08.

(1*R,12*R**,16*R**)-1-[4-(trimethylsilyl)-3-butynyl]-16-carbomethoxytricyclo[10.4.0.0^{12,16}]-15-hexadecanone (44).** The procedure of White was modified.[8a] To a stirred solution of 4.47 g (11.2 mmol) of bis(*N*-*n*-butylsalicylideneaminato)copper(II) in 30 mL of xylenes was added 1.00 g (2.25 mmol) of diazo keto ester **43**. The solution was warmed to reflux for 30 min, cooled, diluted with ether, and washed with 10% hydrochloric acid, water, and brine. After the solution was dried over magnesium sulfate, the solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 15% ethyl acetate–hexane) to yield 0.323 g (34%) of cyclopropane **44** as a white solid: mp 124–124.5 °C; IR ($CDCl_3$) ν 2900, 2840, 2160, 1725, 1440, 1255, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 [s, $Si(CH_3)_3$], 1.41 (e), 1.52–2.70 (br

(37) Audia, J. E., unpublished results.
(38) Sum, F.-W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431–1441.

m), 3.67 (s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 0.12, 16.8, 24.0, 24.2, 24.3, 25.5, 26.1, 27.4, 28.1, 28.3, 29.1, 30.4, 39.2, 42.3, 48.2, 52.0, 52.1, 84.6, 106.9, 167.4, 209.9; high-resolution mass spectrum calcd for $C_{25}H_{40}O_3Si$ *m/e* 416.2736, found *m/e* 416.2742.

Keto ester **44** could also be prepared via sensitized irradiation of diazo keto ester **43** using a Pen Ray immersible UV lamp (254 nm). Accordingly, 0.500 g (1.12 mmol) of **43** and 2.05 g (11.2 mmol) of benzophenone in 70 mL of benzene at 10 °C was irradiated under argon overnight with warming to room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography as above to afford 0.197 g (42%) of **44**.

Direct irradiation of diazo keto ester **43** (0.108 g) in benzene (15 mL) with the Pen Ray immersible UV lamp for 4 h at 10 °C to room temperature followed by removal of benzene under reduced pressure afforded 0.98 g of acidic material, mainly **50**. The methyl ester, prepared via treatment with diazomethane,[35] showed the following IR (film) ν 2900, 2850, 1760 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.60 (s, OMe), 3.20 (t, J = 7 Hz, α-CH), 1.10 (s, *t*-Bu).

Thermolysis of diazo keto ester **43** (0.150 g) with copper sulfate (0.108 g) in xylene (5.25 mL) at reflux for 4 h afforded 0.042 g of keto ester **49** as a mixture of stereoisomers: IR (film) ν 2900, 2850, 1740, 1720 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 5.3 (t, J = 6 Hz, vinyl H), 3.62, 3.57 (s, OCH_3), 3.00, 2.88 (s, α-CH), 2.2–1.9 (m, α-CH_2), 1.3 (s, *t*-Bu).

(1*R,12*R**,15*S**,16*R**)-1-(3-Carbomethoxypropyl)-16-carbomethoxytricyclo[10.4.0.0^{12,16}]-15-hexadecanol (45).** The procedure of Zweifel was modified.[23] To a stirred, cooled (0 °C) solution of 3.3 mL (3.3 mmol) of 1.0 M borane in THF was added 0.66 mL (6.6 mmol) of cyclohexene. The cooled, white heterogeneous mixture was stirred 1 h, whereupon 0.273 g (0.655 mmol) of keto ester **44** in 3.0 mL of THF was added dropwise. The solution was stirred at 0 °C for 9 h, and 0.27 mL of methanol, 0.60 mL of 3 N sodium hydroxide, and 0.84 mL of 30% hydrogen peroxide were added dropwise. The mixture was stirred at room temperature for 3 h, poured into brine, acidified, and extracted with ethyl acetate. The solution was dried over magnesium sulfate, and the solvent was removed at reduced pressure to yield 0.371 g of acid as a clear oil which was used without further purification: IR (film) ν 3100, 2875, 1715, 1455, 1060, 975, 895, 660 cm^{-1}.

The above acid was esterified by the procedure of Arndt.[35] A solution of diazomethane in ether was prepared from 7.5 mL of 50% potassium hydroxide and 1.01 g (9.81 mmol) of *N*-methyl-*N*-nitrosourea in 10 mL of ether. To a stirred, cooled (0 °C) solution of 0.371 g (0.655 mmol) of crude acid in 10 mL of ethyl acetate was added the ethereal diazomethane. The yellow solution was stirred 1 h at 0 °C and was quenched with acetic acid. The solution was washed with saturated sodium bicarbonate and dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 50% ethyl acetate–hexane) to yield 0.169 g (65%) of hydroxy diester **45** as a clear oil: IR (film) ν 3400, 2900, 2845, 1740, 1455, 1440, 1260, 1070, 975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (e), 1.50–2.60 (br m), 3.63 (s, CO_2CH_3), 4.89 (dd, J_{AB} = 6.3 Hz, J_{AC} = 9.3 Hz, C*H*OH). Anal. Calcd for $C_{23}H_{38}O_4$: C, 70.01; H, 9.71. Found: C, 70.06; H, 9.73.

***trans,cis,cis*-15-Carbomethoxy-18-hydroxy[10.4.3]triannulan-16-one (46).** To a stirred, cooled (−20 °C) solution of 0.198 mL (1.41 mmol) of diisopropylamine in 4.0 mL of THF was added dropwise 0.88 mL (1.4 mmol) of 1.6 M *n*-butyllithium in hexane. The cooled solution was stirred for 20 min, whereupon 0.185 g (0.470 mmol) of diester **45** in 4.75 mL of THF was added dropwise. The solution was stirred 30 min at −20 °C then quenched with water. The product was isolated by ethyl acetate extraction. The extracts were washed with 10% hydrochloric acid and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure to yield 0.191 g (112%) of keto ester **46** as a yellow oil which was used without further purification: IR (film) ν 3420, 2910, 2850, 1740, 1730, 1650, 1615, 1450, 1375, 1260, 1060, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (e), 1.40–2.50 (br m), 2.70 (br s, OH), 3.64 (s, CO_2CH_3), 5.30 (dd, J_{AB} = 7.5 Hz, J_{AC} = 9.3 Hz, CHOH), 13.30 (s, enolic OH).

***trans,cis,cis*-18-Hydroxy[10.4.3]triannulan-16-one (47).** To a stirred solution of 0.681 g (12.2 mmol) of potassium hydroxide in 4 mL of water was added 0.191 g (0.528 mmol) of crude keto ester **46** in 10 mL of THF. The mixture was warmed to reflux for 6 h. The product was isolated by ethyl acetate extraction. The extracts were washed with water and brine and dried over magnesium sulfate, and the solvent was removed at reduced pressure. The product was purified by column chromatography (silica gel, 50% ethyl acetate–hexane) to yield 0.080 g (63%) of hydroxy ketone **47** as a white crystalline solid: mp 124–125 °C; IR ($CHCl_3$) ν 3400, 2940, 2870, 1680, 1485, 1345, 1290, 1075, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (e), 1.40–2.50 (br m), 5.46 (dd, J_{AB} = 8.1 Hz, J_{AC} = 9.3 Hz, C*H*OH). Anal. Calcd for $C_{22}H_{38}O_2$: C, 78.89; H, 10.60. Found: C, 79.02; H, 10.60.

***trans,cis,cis*-[10.4.3]Triannulane-16,18-dione (48).** The procedure of Corey was followed.[39] To a stirred mixture of 0.117 g (0.311 mmol) of pyridinium dichromate in 0.5 mL of dichloromethane was added 0.0630 g (0.207 mmol) of hydroxy ketone **47** in 0.5 mL of dichloromethane. The mixture was stirred 2 h at room temperature, diluted with ether, and filtered through Celite. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 50% ethyl acetate–hexane) to yield 0.0466 g (75%) of dione **48** as a white crystalline solid: mp 110–111.5 °C; IR ($CHCl_3$) ν 2890, 2840, 1730, 1675, 1460, 1435, 1300, 1155, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (e), 1.66–2.76 (br m); ^{13}C NMR ($CDCl_3$) δ 22.6, 24.2, 24.3, 24.7, 24.8, 25.5, 26.5, 27.7, 28.1, 29.8, 31.2, 39.6, 40.3, 43.2, 52.8, 55.2, 205.4, 211.2. Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.43; H, 10.07.

(*E*)-1-[(Diethylphosphonoxy)methyl]-2-[4-(triisopropylsilyl)-3-butynyl]cyclododecene (51). To a stirred, cooled (−40 °C) solution of 3.72 g (9.30 mmol) of alcohol **37** in 50 mL of pyridine was added dropwise 4.01 mL (27.7 mmol) of diethyl chlorophosphate. The white heterogeneous mixture was stirred for 1 h at −40 °C, and then water was added. The mixture was poured into water, and the product was isolated by ether extraction. The extracts were washed with saturated copper(II) sulfate, water, and brine and were dried over potassium carbonate. The solvent was removed at reduced pressure to yield 4.55 g (92%) of phosphate **51** as a yellow oil which was used without further purification: IR (film) ν 2890, 2840, 2150, 1465, 1280, 1030, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 [s, Si[CH(CH_3)$_2$]$_3$], 1.20 (e), 1.32 (t, J = 7.0 Hz, $POCH_2CH_3$), 1.67–2.90 (br m), 4.70 (m, $POCH_2CH_3$), 4.30–4.60 (m, C=CCH_2O), 4.66–5.00 (m, C=CCH_2O).

(*E*)-1,2-Bis[4-(triisopropylsilyl)-3-butynyl]cyclododecene (52). The procedure of Flynn was followed.[10] To a stirred, cooled (−78 °C) solution of 3.53 g (18.6 mmol) of copper(I) iodide in 8.15 mL (111 mmol) of dimethyl sulfide and 120 mL of DME was added dropwise 33.8 mL (18.6 mmol) of 0.55 M [3-(triisopropylsilyl)propargyl]magnesium bromide in THF. The yellow heterogeneous mixture was stirred for 30 min at −78 °C, whereupon 4.54 g (8.47 mmol) of phosphate **51** in 10 mL of DME was added dropwise. The solution was allowed to gradually warm to −20 °C overnight and then was poured into saturated ammonium chloride. The product was isolated by ether extraction; the extracts were washed with 3% ammonium hydroxide and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, hexane) to yield 4.74 g (96%) of diyne **52** as a clear oil: IR (film) ν 2900, 2840, 2150, 1465, 1380, 1365, 1025, 995, 895, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 [s, Si[CH(CH_3)$_2$]$_3$], 1.23 (e), 1.35–2.85 (br m). Anal. Calcd for $C_{38}H_{70}Si_2$: C, 78.27; H, 12.10. Found: C, 78.22; H, 12.21.

(*E*)-1,2-Bis(3-butynyl)cyclododecene (53). To a stirred, cooled (0 °C) solution of 4.87 g (8.38 mmol) of diyne **52** in 25 mL of THF was added dropwise 25.1 mL (25.1 mmol) of 1.0 M tetrabutylammonium fluoride in THF. The solution was allowed to warm to room temperature and was stirred for 36 h. It was then poured into 10% hydrochloric acid, and the product was isolated by ether extraction. The extracts were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 2% ethyl acetate–hexane) to yield 1.97 g (87%) of diyne **53** as a clear oil: IR (film) ν 3275, 2900, 2845, 2110, 1470, 1450, 1245, 1055, 890, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (e), 1.35–3.00 (br m). Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.88; H, 11.29.

(*E*)-1,2-Bis[4-(trimethylsilyl)-3-butynyl]cyclododecene (54). The procedure of Audia was followed.[37] To a stirred, cooled (−78 °C) solution of 1.82 g (6.74 mmol) of diyne **53** in 25 mL of THF was added dropwise 6.46 mL (16.8 mmol) of 2.60 M *n*-butyllithium in hexane. The white heterogeneous mixture was stirred at −78 °C for 30 min, whereupon 2.57 mL (20.2 mmol) of chlorotrimethylsilane was added dropwise. The mixture was allowed to warm to room temperature and was stirred overnight. Water was then added. The product was isolated by ether extraction, and the extracts were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, hexane) to yield 2.56 g (92%) of diyne **54** as a clear oil: IR (film) ν 2880, 2830, 2160, 1465, 1250, 1040, 840, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 [s, Si(CH_3)$_3$], 1.30 (e), 1.50–2.90 (br m). Anal. Calcd for $C_{26}H_{46}Si_2$: C, 75.28; H, 11.18. Found: C, 75.48; H 11.18.

(*E*)-1,2-Bis(3-carbomethoxypropyl)cyclododecene (55). The procedure of Zweifel was modified.[23] To a stirred, cooled (0 °C) solution of 19.3 mL (19.3 mmol) of 1.0 M borane in THF was added dropwise 4.20 mL (38.6 mmol) of cyclohexene. The white heterogeneous mixture was stirred at 0 °C for 1 h, whereupon 2.00 g (4.84 mmol) of diyne **54** in 8.0

(39) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399–402.

mL of THF was added dropwise. The solution was then stirred at 0 °C overnight, and 3.0 mL of methanol, 7.6 mL of 3 N sodium hydroxide, and 9.2 mL of 30% hydrogen peroxide were added cautiously. The mixture was warmed to 60 °C for 2.5 h and poured into 10% NaOH and ether. The ether layer was washed with 10% NaOH, and the combined basic extracts were acidified with concentrated hydrochloric acid at 0 °C. The product was isolated by ethyl acetate extraction. The extracts were washed with brine and dried over magnesium sulfate. The solvent was removed at reduced pressure to yield 1.80 g of crude diacid as a milky semisolid: IR (film) ν 3175, 2900, 2850, 1710, 1080, 1055 cm^{-1}.

The above acid was esterified following the procedure of Arndt.[35] An ethereal solution of diazomethane was prepared from 4.96 g (48.1 mmol) of *N*-methyl-*N*-nitrosourea, 37.2 mL of 50% potassium hydroxide, and 48 mL of ether at 0 °C. To a stirred, cooled (0 °C) solution of 1.80 g (4.84 mmol) of crude diacid in 48 mL of ethyl acetate was added the yellow ethereal diazomethane. The yellow solution was washed with saturated sodium bicarbonate and dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 10% ethyl acetate–hexane) to yield 1.16 g (66%) of diester **55** as a clear oil: IR (film) ν 2900, 2840, 1740, 1440, 1370, 1205, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (e), 1.33–2.06 (br m), 2.24 (t, J = 6.6 Hz, CH_2CO_2), 3.64 (s, CO_2CH_3); ^{13}C NMR ($CDCl_3$) δ 24.4, 24.7, 24.8, 26.0, 26.6, 29.3, 31.1, 33.6, 51.3, 134.0, 174.0. Anal. Calcd for $C_{22}H_{38}O_4$: C, 72.09; H, 10.45. Found: C, 71.97; H, 10.44.

(*E*)-16,18-Bis(trimethylsiloxy)bicyclo[10.8.0]eicosa-1(12),16-diene (56). The procedure of Bloomfield was modified.[36] To a vigorously stirred mixture of 0.075 g (3.3 mmol) of sodium in 60 mL of toluene was added 0.13 g (3.3 mmol) of potassium. The stirred mixture was warmed to reflux for 1 h, whereupon 0.200 g (0.546 mmol) of diester **55** in 1.00 mL (7.88 mmol) of chlorotrimethylsilane and 8.0 mL of toluene was added dropwise to the refluxing mixture over 13 h. After the addition was complete, the stirred purple mixture was refluxed for 2 h, cooled to room temperture, and filtered under argon. The solvent was removed at reduced pressure to yield 0.249 g of crude silylated enediolate **56** as a yellow oil which was used without further purification: IR (film) ν 2850, 1670, 1470, 1450, 1045, 915, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 [s, $Si(CH_3)_3$], 1.19 (e), 1.36–2.80 (br m).

(*E*)-16,18-Bis(trimethylsiloxy)tricyclo[10.9.0.0^{16,18}]-1(12)-heneicosene (57). The procedure of Ito and Saegusa was modified.[25] To a stirred solution of 0.249 g (0.546 mmol) of crude silylated enediolate **56** in 1.10 mL of toluene was added 1.10 mL (1.10 mmol) of 1.0 M diethylzinc in toluene and 0.094 mL (1.17 mmol) of diiodomethane. The stirred solution was warmed to 80 °C for 2.5 h, cooled to room temperature, and poured into a dilute solution of ammonium chloride. The product was isolated by ether extraction, and the extracts were washed with brine and dried over potassium carbonate. The solvent was removed at reduced pressure to yield 0.293 g of cyclopropane **57** as a yellow oil which was used without further purification: IR (film) ν 2880, 1465, 1445, 1250, 1100, 840, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 [s, $Si(CH_3)_3$], 1.21 (e) 1.53–2.80 (br m).

(*E*)-Bicyclo[10.9.0]-1(12)-heneicosane-16,18-dione (58). The procedure of Van Audenhove was modified.[27] To a stirred mixture of 0.293 g (0.546 mmol) of crude cyclopropane **57** in 1.05 mL of THF, 0.45 mL of methanol, and 0.84 mL of water was added 0.270 g (1.26 mmol) of sodium periodate. The mixture was stirred for 3 h then diluted with water, and the product was isolated by ether extraction. The extracts were washed with brine and dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by column chromatography (silica gel, 15% ethyl acetate–hexane) to yield 0.0638 g (37% from diester) of dione **58** as a clear oil: IR (film) ν 2910, 2850, 1705, 1475, 1415, 1370, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (e), 1.50–2.70 (br m), 3.46 [s, $CH_2(CO)_2$]; ^{13}C NMR ($CDCl_3$) δ 21.3, 23.9, 26.8, 28.7, 31.6, 39.9, 62.4, 136.4, 200.0. Anal. Calcd for $C_{21}H_{35}O$: C, 79.19; H, 10.76. Found: C, 79.05; H, 10.61.

(*E*)-Bicyclo[10.9.0]-17-diazo-1(12)-heneicosane-16,18-dione (59). The procedure of Regitz was modified.[18] To a stirred, cooled (0 °C) solution of 0.0638 g (0.210 mmol) of dione **58** in 1.0 mL of acetonitrile, 0.2 mL of dichloromethane, and 0.056 mL (0.401 mmol) of triethylamine was added dropwise 0.0792 g (0.401 mmol) of *p*-toluenesulfonyl azide. The yellow solution was allowed to warm to room temperature and was stirred for 36 h. The solvent was removed at reduced pressure, and the residue was filtered through silica gel (25% ethyl acetate–hexane) to yield 0.0447 g (65%) of diazo dione **59** as a yellow oil: IR (film) ν 2880, 2830, 2090, 1675, 1640, 1465, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (e), 1.33–3.00 (br m); high-resolution mass spectrum. Calcd for $C_{21}H_{32}N_2O_2$ m/e 316.2404 ($M^+ - N_2$), found m/e 316.2405 ($M^+ - N_2$).

***trans*,*cis*,*cis*-[10.4.4]Triannulane-16,18-dione (60).** The procedure of Jones was modified.[21] Nitrogen was bubbled through a solution of 0.0756 g (0.220 mmol) of diazo dione **59** and 0.601 g (3.30 mmol) of benzophenone in 10 mL of benzene for 30 min. The cooled (15 °C) solution was then irradiated with a Pen Ray immersible UV lamp (254 nm) for 2 h. The solvent was removed under reduced pressure, and the product was purified by column chromatography (silica gel, 15% ethyl acetate–hexane) to yield 0.0432 g (62%) of dione **60** as a white crystalline solid: mp 109–110 °C (crystal change 85–85.5 °C); IR (film) ν 2890, 2830, 1695, 1670, 1465, 1450, 1320, 1270, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (e), 1.50–2.70 (br m); ^{13}C NMR ($CDCl_3$) δ 22.6, 24.1, 24.2, 24.5, 26.9, 28.3, 29.6, 40.3, 40.8, 47.0, 210.0. Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.98; H, 10.32.

Table I. Crystal Data and Data Collection Parameters for [10.4.3]- and [10.4.4]Triannulanes

	[10.4.3] (**48**)	[10.4.4] (**60**)
system, space group	monoclinic, $P2_1/c$, Z = 4	monoclinic, $P2_1/a$, Z = 8
a, Å	9.743 (2)	18.483 (5)
b, Å	21.439 (6)	10.933 (3)
c, Å	8.472 (2)	18.373 (4)
β, deg	106.25 (2)	97.31 (3)
V, Å^3	1697 (1)	3681 (2)
μ, cm^{-1}	0.69	0.66
cryst size, mm	0.4 × 0.3 × 0.1	0.5 × 0.4 × 0.3
2θ max, deg	43	42
no. of reflctns measd	2106	3623
independent	1946, R_{merge} = 0.021	3496, R_{merge} = 0.016
with $I \geq 2\sigma(I)$	1115	1974

(*S*)-(*E*)-1-(Hydroxymethyl)-2-[4-(triisopropylsilyl)-3-butynyl]cyclododecene [(*S*)-37)]. The procedure of Flynn was followed.[10] To a cooled (−23 °C), stirred solution of 5.74 mL (19.3 mmol) of titanium(IV) tetraisopropoxide in 73 mL of dichloromethane was added 4.00 mL of (+)-diethyl tartrate. The solution was stirred for 10 min, whereupon 7.71 g (19.3 mmol) of alcohol **37** in 15 mL of dichloromethane and 3.24 mL (10.6 mmol) of 3.29 M *tert*-butyl hydroperoxide in dichloromethane were added dropwise. The solution was stirred at −23 °C for 30 min, and a small aliquot was removed and quenched with 10% tartaric acid. HPLC analysis indicated the reaction was less than half completed, so an additional 0.78 mL (2.55 mmol) of 3.29 M *tert*-butyl hydroperoxide was added. The cooled (−23 °C) solution was stirred for 2 h, and 46.3 mL of 10% tartaric acid was added. The biphasic mixture was stirred for 15 min at −23 °C and for 1 h at room temperature. The layers were separated, and the aqueous layer was extracted with dichloromethane. The extracts were dried over potassium carbonate, the solvent was removed at reduced pressure, and the product was purified by column chromatography on silica gel to yield 3.49 g (45%) of alcohol (*S*)-**37**, a 75:25 trans/cis mixture: IR (film) ν 3325, 2900, 2845, 2160, 1470, 1000, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 [s, $SiCH(CH_3)_3$], 1.19 (e), 1.33–2.90 (br m), 4.20 (ABq, $\Delta\nu$ = 47.4 Hz, J_{AB} = 12 Hz, CH_2OH); high-resolution mass spectrum calcd for $C_{26}H_{48}OSi$ m/e 404.3476, found m/e 404.3477; $[\alpha]^{30}_D$ +39.4°.

Mosher Ester Derivative of (*S*)-(*E*)-1-(Hydroxymethyl)-2-[4-(triisopropylsilyl)-3-butynyl]cyclododecene. To a stirred solution of 0.100 g (0.250 mmol) of alcohol (*S*)-**37** and 0.034 g (0.277 mmol) of 4-(dimethylamino)pyridine in 0.5 mL of dichloromethane was added 0.064 g (0.252 mmol) of (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetyl chloride. The solution was stirred for 2 h, and water was added. The product was isolated by ether extraction and dried over magnesium sulfate. The solvent was removed at reduced pressure, and the product was purified by filtration through silica gel to yield 1.38 g (90%) of ester as a clear oil: IR (film) ν 2890, 2840, 2160, 1740, 1455, 1275, 1180, 1030, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.11 [s, $SiCH(CH_3)_3$], 1.23 (e), 1.30–2.80 (br m), 3.53 (br s, OCH_3), 4.85 (apparent d, J = 5 Hz, CH_2O of cis isomer), 4.90 (ABq, $\Delta\nu$ = 43.4 Hz, J_{AB} = 12 Hz, CH_2O of trans isomer), 7.34 (m, aromatic H); ^{19}F NMR ($CHCl_3$) δ 4.15, 4.37, 4.41 (ratio 25:11:64).

X-ray Structure Analysis. The same basic procedures were used for data collection for both [10.4.3]- and [10.4.4]triannulane-16,18-diones. The intensities were measured at room temperature on a CAD-4 diffractometer using graphite-monochromated Mo Kα radiation and ω–2θ scan. The unit cell dimensions obtained from setting angles of 25 general reflections are given in Table I together with the relevant data collection parameters. The structure of **48** was solved by means of MULTAN 11/82[40] using 262 structure amplitudes with $E > 1.54$. The E map

(40) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. "Multan 11/80", a System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, incorporated in: "Enraf-Nonius Structure Determination Package"; Frenz, B. A., Ed.; 1982.

produced from the set of phases with the best combined figure of merit yielded the positions of all non-hydrogen atoms. A full-matrix, least-squares refinement with calculated and fixed positions of hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms was carried out. The quantity minimized by a normal unconstrained least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = (\sigma^2(F_o) + (0.02F_o)^2)^{-1}$. The refinement converged to $R = 0.045$ and $R_w = 0.043$ with the highest maximum on the final difference Fourier map 0.26 e Å^{-3}.[41]

The structure of **60** was solved by means of MULTAN 11/82[40] using 450 structure amplitudes with $E > 1.45$. The knowledge of structure of **48** was utilized to normalize structure factors by assuming two symmetry-independent, randomly oriented molecules in the unit cell. Earlier attempts to solve the structure with the structure factors normalized on the assumption of randomly distributed atoms were not successful. The E map produced from the set of phases with the best combined figure of merit yielded the positions of almost all atoms. The two missing, one in each molecule, were revealed in a subsequent difference Fourier map. A full-matrix least-squares refinement was then carried out based on the assumption of two ordered molecules A and B in the unit cell. Calculated positions of hydrogen atoms with the C-H distance of 1.00 Å were periodically updated and used in structure factors calculations. The refinement with isotropic atomic temperature factors converged at $R = 0.22$, with anisotropic at $R = 0.16$. At this stage it was apparent that the structure was partially disordered. We again carried out refinement with isotropic temperature factors, but this time we used elastic restraints on bond lengths and some of the angles utilizing the program SHELX-76.[42] The target values for the bond lengths were those given by Ermer[43] with $\sigma = 0.004$ Å. The angles were restrained only in the macrocycle by targeting the distance between the second neighboring carbon atoms with the average value of 2.558 Å and $\sigma = 0.010$ Å found in **48**. The angles at C(1) and C(12), atoms which also form the strained cyclopropane ring, were not restrained. After several refinement/difference Fourier calculations we were able to find molecule C overlapping with B by connecting peaks in the difference Fourier maps and atoms with unusually low-temperature factors. Molecule C as discussed above is essentially the enantiomer of molecule A. In the final model only one atom C(17) was common to molecules B and C. There is also a partial disorder in the site occupied by molecule A, but this is just the superposition of two different conformers. We allowed for it by introducing molecule D with nine separate atoms and 14 atoms common with molecule A. The same restraints were used for molecules C and the independent part of D as for molecules A and B; however, we did not introduce any restraints at the joints of A and D. The refinement of the model with isotropic thermal parameters for all atoms converged at $R = 0.120$. At this stage we introduced anisotropic thermal parameters for 15 atoms with full occupancy. The refinement of this model with 77 isotropic and 15 anisotropic atoms and 446 parameters against 1973 observations and 116 restraints were carried out in two blocks that included the pairs of overlapping molecules. The occupancies of the molecules were allowed to refine with the sums A + D and B + C constrained to 1.0. Their final values were 0.600 (21) and 0.662 (6) for A and B, respectively. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (\sigma^2(F_o) + 0.0004F_o^2)^{-1}$ and $\sigma(F_o)$ is from the counting statistics. The refinement converged except for strongly correlated temperature factors of C(2B) and C(2C) that had in the last cycle shift/esd ratios of 1.6. The average shift/esd ratio was <0.1, final $R = 0.108$, $R_w = 0.131$, and the highest peak on the difference Fourier map was 0.44 e Å^{-3}. The largest violation of a bond length restraint was 0.005 Å and of a second neighbor distance was 0.04 Å. A series of Laue photographs did not show significant diffuse scattering that would indicate short term order.

(41) Calculations were carried out by using: Frenz, B. A., Ed. "Enraf-Nonius Structure Determination Package", 1982.
(42) Sheldrick, G. SHELX-76, a Program for Crystal Structure Determination; Cambridge University: England, 1976.
(43) Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161.

Acknowledgment. Support from the National Science Foundation through a research grant (CHE-8026013) is gratefully acknowledged.

Registry No. 13, 4834-94-4; **13**, 4834-94-4; **14**, 76128-04-6; **15**, 76128-06-8; **16**, 76128-08-0; **17**, 91410-29-6; **18**, 91410-30-9; **19**, 91410-34-3; **20**, 91410-31-0; **21**, 91410-32-1; **22**, 91410-33-2; **23**, 91410-35-4; (*E*)-**25**, 91410-37-6; (*Z*)-**25**, 91410-36-5; **26**, 87336-89-8; **27**, 91464-50-5; **28**, 91464-51-6; **29**, 91464-52-7; **30**, 63240-90-4; **30** (diacid), 63240-88-0; **31**, 63240-92-6; **31** (enediol disilyl ether), 91410-38-7; **32**, 91410-39-8; **33**, 91410-40-1; **34**, 91410-41-2; (*E,E*)-**35**, 91410-43-4; (*Z,E*)-**35**, 91410-42-3; (±)-**37**, 91410-44-5; (+)-**37**, 91464-54-9; (*Z*)-**37**, 91443-16-2; (+)-**37** ((+)-Mosher ester), 91423-99-3; (*Z*)-**37** ((+)-Mosher ester), 91465-55-3; **38**, 91410-45-6; **39**, 91410-46-7; **41**, 91410-47-8; **42**, 91410-48-9; **43**, 91410-49-0; **44**, 91410-50-3; **45**, 91410-54-7; **45** (diacid), 91410-55-8; **46**, 91410-56-9; **47**, 91410-57-0; **48**, 91410-58-1; *cis*-**49**, 91410-53-6; *trans*-**49**, 91464-55-0; **50**, 91410-51-4; **50** (diester), 91410-52-5; **51**, 91410-59-2; **52**, 87336-92-3; **53**, 91410-60-5; **54**, 87336-93-4; **55**, 87336-95-6; **55** (diacid), 87336-94-5; **56**, 87336-96-7; **57**, 91464-53-8; **58**, 87350-59-2; **59**, 87336-98-9; (±)-**60**, 87336-99-0; (+)-**60**, 91465-56-4; $BrMg(CH_2)_9CH{=}CH_2$, 88476-93-1; *p*-$TsNHNH_2$, 1576-35-8; $CH_2{=}CH(CH_2)_2MgBr$, 7103-09-5; $(EtO)_2POCl$, 814-49-3; $CH_3CH{=}C(CH_3)_2$, 513-35-9; $(i\text{-}Pr)_3SiC{\equiv}CCH_2MgBr$, 87350-60-5; $(CH_3)_3SiCl$, 75-77-4; $(PhO)_2POCl$, 2524-64-3; $CH_3COCH_2CO_2CH_3$, 105-45-3; *p*-TsN_3, 941-55-9; 1-methylene-2-(3-butenyl)-2-(4-pentenyl)-cyclododecane, 91423-98-2; (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 20445-33-4.

Ylide vs. 1,4-Cycloaddition in the Interaction of an Alkylidenecarbene with Azoarenes and the Formation of 2*H*-Indazoles and Tetrahydrotetrazoles[1]

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Abstract: Reaction of substituted azobenzenes with isopropylidenecarbene $(CH_3)_2C{=}C{:}$, generated from either 2-methyl-1-propenyl triflate and *t*-BuOK or silylvinyl triflate $(CH_3)_2C{=}C(OTf)SiMe_3$ and benzyltrimethylammonium fluoride (BTAF), gave 2*H*-indazoles in moderate yield. Indazoles were identified by spectral means as well as independent synthesis. A two-step mechanism, involving an ylide-type intermediate, is proposed for these reactions. Interaction of 3,3′,5,5′-tetrakis(trifluoromethyl)azobenzene and 4,4-bis(trifluoromethyl)azobenzene with the carbene derived from silylvinyl triflate gave tetrahydrotetrazoles, a new class of compounds, consistent with trapping of the proposed ylide. 2*H*-Indazoles react with methyl triflate to form the N-methylated salt, but they do not undergo Diels-Alder reactions.

We had previously reported[3] that the reaction of isopropylidenecarbene **2** with azobenzene gave 2-phenyl-3-isopropylindazole (**3**), an unusual and little known heterocyclic ring system. In order to provide further mechanistic insight as well

0002-7863/84/1506-6015$01.50/0