10 Hz, 1 H), 3.59 (s, 3 H), 3.64 (s, 3 H), 7.2–7.6 (m, 5 H).

6: mp 168–171 °C (from ether); IR (KBr) 1725, 1250, 1090, 725, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.2 (m, 12 H), 2.31 (d, J = 16 Hz, 2 H), 2.68 (d, J = 16 Hz, 2 H), 3.56 (s, 6 H), 7.1–7.6 (m, 10 H). Anal. Calcd for $C_{28}H_{32}O_4Se_2$: C, 56.88; H, 5.43. Found: C, 56.96; H, 5.46.

9,11-Bis(methoxycarbonyl)[6.2.2]propella-9,11-diene (2c). To a solution of 310 mg (0.53 mmol) of **6** and 0.17 mL (2.1 mmol) of pyridine in 3.3 mL of dichloromethane was added a mixture of 0.3 mL of 30% hydrogen peroxide (2.6 mmol) and 0.3 mL of water. The mixture was stirred at room temperature for 1.5 h and then heated at 40 °C for 1.5 h. Usual workup followed by flash chromatography (15% ether/petroleum ether) gave 107 mg (73%) of the Dewar benzene **2c**: mp 60–62 °C (from petroleum ether); IR (KBr) 1715, 1580, 1100, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–1.7 (m, 8 H), 2.0–2.2 (m, 4 H), 3.70 (s, 6 H), 7.28 (s, 2 H); ^{13}C NMR δ 163.1 (s), 155.2 (d), 145.7 (s), 61.5 (s), 51.6 (q), 26.5 (t), 25.0 (t), 24.7 (t).

8,11-Bis(methoxycarbonyl)[6]paracyclophane (1c). A degassed solution of 97 mg (0.35 mmol) of **2c** in 100 mL of hexane was sealed in ampules and heated at 50 °C for 95 h. The solvent was evaporated, and subsequent flash chromatography (20% ether/petroleum ether) gave 87 mg (90%) of cyclophane **1c** as white solid. Crystals suitable for X-ray analysis were obtained by recrystallization from cyclohexane.

1c: mp 94–96 °C (from hexane); IR (KBr) 1710, 1265, 1245, 1195, 790, 745, 675 cm^{-1}; MS, m/e (rel intens) 276 (M^+, 25), 217 (38), 205 (100); ^1H NMR ($CDCl_3$, 26 °C) δ −0.7 to +0.1 (m, 2 H), 0.5–1.4 (m, 4 H), 1.5–1.9 (m, 2 H), 1.9–2.4 (m, 2 H), 3.6–3.9 (m, 2 H), 3.92 (s, 6 H), 7.91 (s, 2 H); ^{13}C NMR δ 167.1 (s), 146.5 (s), 136.5 (d), 133.6 (s), 52.2 (q), 37.0 (t), 35.0 (t), 27.0 (t); UV (hexane) [λ_{max}, nm (log ϵ)] 350 (3.2), 270 (3.8), 230 (4.3). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.32; H, 7.33.

Measurement of Valence Isomerization Rates of 2a, 2c, and 7a. The rate of thermal isomerization of **2c** to **1c** was determined by UV spectroscopy,[4] in which the appearance of absorption at 350 nm in degassed hexane (3.4×10^{-4} M) was measured. For the measurement of isomerization rates of **2a** and **7a**, a degassed hexane solution of **1a**[4] or **8a**[7] (1.4×10^{-3} M) was irradiated with a low-pressure mercury lamp at 0 °C for 2–3 h to yield a photostationary mixture of **1a** and **2a** or **7a** and **8a** (ca. 1:1), and the rates were determined by measuring the increase of absorption at 300 and 310 nm, respectively.

X-ray Crystal Structure Analysis of 1c. Crystal data: $C_{16}H_{20}O_4$, M_r = 276.3, monoclinic, space group $C2/c$, a = 19.415 (4) Å, b = 6.975 (1) Å, c = 11.811 (2) Å, β = 112.16 (1)°, V = 1481.4 (4) Å^3, Z = 4, D_c = 1.239 g cm^{-3}, μ(Cu Kα) = 8.4 cm^{-1}, F(000) = 592.

The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Ni-filtered Cu Kα radiation. The crystal with dimensions of 0.3 × 0.25 × 0.2 mm was used for the data measurement. The integrated intensities were measured by the θ–2θ scan technique with background countings at each end of the scan range for 5 s. The scan range was determined as $\Delta 2\theta = (2.0 + 0.3 \tan \theta)°$. The total number of reflections was 1087, among which 948 were observed reflections [$|F_o| > 3\sigma(F_o)$]. Three monitor reflections were measured for each block of 61 reflections to check for radiation damage and for any change of the crystal orientation of the crystal. No radiation damage of the crystal was observed. The measured intensities were corrected for Lorentz and polarization effects but not for absorption, because of the relatively small absorption effects of the compound for Cu Kα radiation. The crystal structure was solved by the direct method (MULTAN 78)[15] and was refined by full-matrix least squares (XRAY SYSTEM).[16] All the hydrogen atoms were searched for on the difference Fourier maps calculated after the anisotropic refinements of non-hydrogen atoms. The weighting scheme applied was $w = [\sigma^2(F_o) + 0.003(F_o)^2]^{-1}$. The final R index defined by $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ was 0.112 for observed reflections. The weighted R index defined by $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was the rather large value of 0.198. All computations were carried out on an ACOS-850S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and interatomic bond distances and angles including hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

(15) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN-78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, England, and Louvain, Belgium, 1978.

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Synthesis and Properties of Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one. A New Entry to the $C_{10}H_{10}$ Manifold

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Starting from 3,8-cyclodecadiene-1,6-dione bis(ethylene acetal) (**4**) a 10-step synthesis is described which leads to the title compound **18**. It is found that **18** rearranges to tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-9-one (**33**) at room temperature. The pyrolysis and photolysis of the tosylhydrazone of **18** and **19** yields the cycloheptatriene derivatives **41** and **42**. From the mesylate of the corresponding alcohol of **18** two dihydroazulenes (**38** and **39**) could be isolated and characterized. In carrying out the Shapiro reaction with **19** we obtained tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (**35**). MNDO calculations concerning the possible reaction path of tricyclo[5.3.0.0^{2,8}]decatriene (**2**) to **35** suggest a radical mechanism and isobullvalene (**34**) as an intermediate.

Introduction

Some time ago we investigated by means of MO calculations the through-bond interaction of two perpendicular π-systems via a four-membered ring system.[1] Evidence for the relay properties of the four-membered ring was found by studying the electronic absorption spectrum of tricyclo[3.3.0.0^{2,6}]octadiene[2] and of tetrabenzotricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene[3] as well as the He I

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(1) Bischof, P.; Gleiter, R.; Haider, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 110; *J. Am. Chem. Soc.* **1978**, *100*, 1036.
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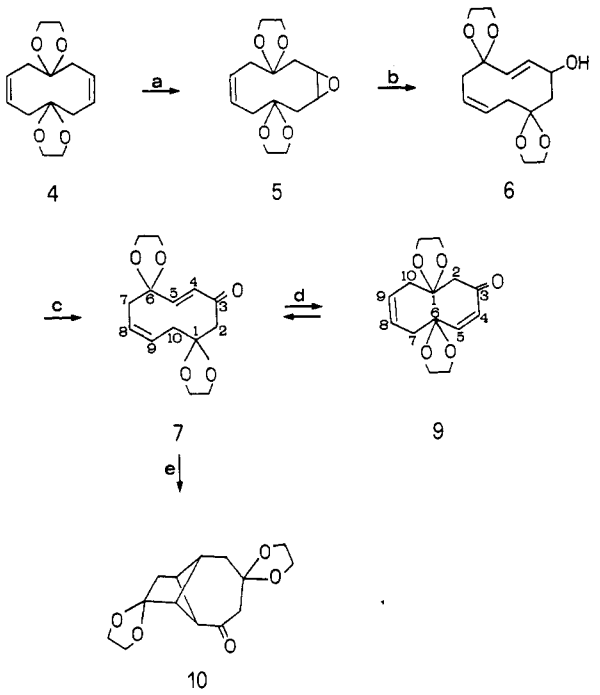
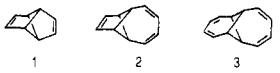
Scheme I[a]



[a] (a) *m*-CPBA, CH_2Cl_2; (b) $(C_6H_5Se)_2$, $NaBH_4$, *n*-BuOH, 120 °C, 24 h; H_2O_2, THF, 0 °C, 20 h; (c) CrO_3, pyridine; (d) *hν*, Et_2O/CH_3CN, −78 °C; (e) *hν*, CH_3CN, 0 °C, 7 h.

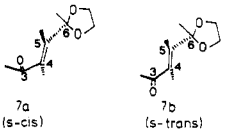
photoelectron spectrum of *trans,trans,trans*-1,2,3,4-tetravinylcyclobutane.[4]

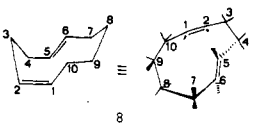
As a result of these investigations we started to explore the synthesis and properties of the homologues of tricyclo[3.3.0.$0^{2,4}$]octadiene (**1**), like tricyclo[5.3.0.$0^{2,8}$]decatriene (**2**)[5a] and tricyclo[5.5.0.$0^{2,8}$]dodecatetraene (**3**).[5b]



Herein we report on our synthetic efforts to generate **2**.[6] The pivot point of our strategy was a photocyclization in which a 2,6-cyclodecadien-1-one derivative was cyclized to a tricyclo[5.3.0.$0^{2,8}$]decan-3-one.[7]

Synthesis of Tricyclo[5.3.0.$0^{2,8}$]decane-3,5,10-trione 5,10-Bis(ethylene acetal). Cyclodeca-3,8-diene-1,6-dione bis(ethylene acetal) (**4**), accessible in good yields from isotetraline,[8] is epoxidized to give **5** (Scheme I). Its rearrangement to alcohol **6** was achieved with diphenyl diselenide.[9] Further oxidation of **6** leads[10] to **7**. The ^1H NMR spectrum of **7** shows a strong line broadening evidently due to the presence of more than one conformer. At low temperatures one can see two conformers (**7a** and **7b** in the ratio 7:5) in the ^1H NMR spectrum. The coupling constants, 16.2 and 16.7 Hz, respectively, for H(4) and H(5) point to the trans conformation of this double bond. Other signals could not be assigned.

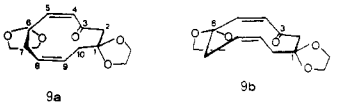




Force-field calculations[11] on cyclodeca-1,5-diene favor a cis–trans conformer (boat–chair) shown in **8**. They predict at somewhat higher energy the presence of two *cis,cis*-1,5-cyclodecadienes. The boat–chair conformation of **8** is supported by an X-ray investigation of eupaformonine,[12] a substituted derivative of **8**. This investigation also shows that the skeleton of **8** is maintained even with fairly large substituents. We consider **7a** as having the s-cis and **7b** as having the s-trans conformation at C(3) to C(5) as shown above (note that the numbering in **7** is different from that in **8**). In the s-cis conformation C(4) and H(4) should be deshielded and C(5) and H(5) should be strongly shielded. We expect the reverse in the s-trans conformation. The assumptions are not conclusive, however, since a bending of the carbonyl group out of the plane of the double bond will cause a similar effect.

Irradiation of **7** causes rearrangement. A single product is obtained as evidenced by an isosbestic point at 314 nm and a linear ED diagram.[13] Irradiation of **7** at −78 °C yields *cis,cis*-4,8-cyclodecadiene-1,3,6-trione 1,6-bis(ethylene acetal) (**9**). The structural assignment is based on the ^1H NMR spectrum of **9**, which shows a coupling $J_{4,5} = J_{8,9} = 13.2$ Hz. The NMR spectrum of **9** shows, analogously to **7**, a broadening of lines.

In the ^{13}C NMR spectrum of one conformer we find 14 signals. The inspection of Dreiding models suggests, that the chair-like, **9a**, and tub-like, **9b**, conformers are likely.



Both correspond to the most stable conformers of *cis,cis*-1,5-cyclodecadiene.[11] Model considerations on **9a** and **9b** suggest, that H···H interactions in **9a** are smaller than those in **9b** and that rearrangement of one conformer into the other should take a considerable activation energy.

Irradiation of **7** at 0 °C in acetonitrile yields at first two products, **9** and a new one, **10**. After 7 h irradiation time, **7** and **9** had disappeared and **10** could be isolated as colorless crystals in 85% yield. The ^1H NMR of **10** revealed no olefinic protons. The structural assignment of **10** is based on spectroscopic information, especially the comparison of NMR data with previously synthesized tricyclo[5.3.0.$0^{2,8}$]decane derivatives.[7] Discrimination between the head-to-tail adduct **10** and the head-to-head adduct **11** is based on the 300-MHz ^1H NMR spectrum of the product. The crucial point is that in **10** a coupling between the protons at positions 1 or 8 with those at positions 2

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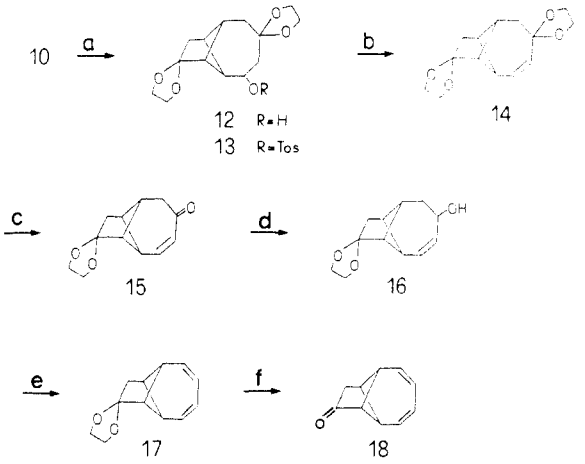
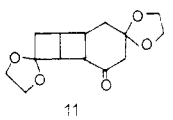
Scheme II[a]



[a] (a) $NaBH_4$, EtOH, TosCl, pyridine; (b) DBN, CH_3CN, 70 °C, 12 h; (c) *p*-TosOH, H_2O/acetone; (d) $LiAlH_4$, ether; (e) $(C_6H_5O)_3PCH_3I$, HMPA, 80 °C, 4 h; (f) 1 N HCl, THF, 24 h.

or 7, respectively is not observed. The long-range coupling constants between H(1) and H(8) are $^4J_{1,8}$ = 7.5 Hz and between H(2) and H(7) are $^4J_{2,7}$ = 5.75 Hz. In case of structure **11** all four protons of the central four-membered ring should couple, and thus a more complex pattern is expected.

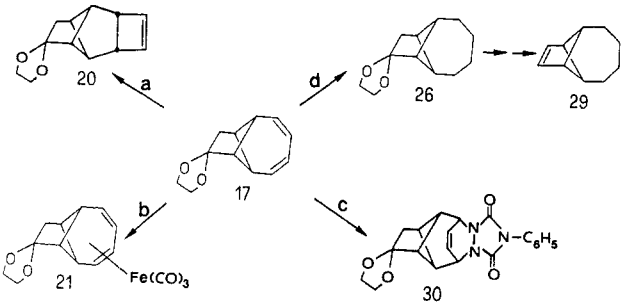


The remaining question, if **10** is formed from **9** or **7**, can be answered with an ED diagram. From the linear slope obtained when **7** is irradiated it can be concluded that **9** and **10** are formed in parallel reactions with about the same quantum yield and the same order. The slower back-reaction of **9** to **7** is not effective during short reaction times. At longer reaction times, however, only the photostable **10** is isolated. The irradiation of **9** yields no linear ED diagram; this can be explained by assuming that **7** is formed as an intermediate. The concentration of **7** is low, however, since it either reacts to form **10** or reverts to **9**. In line with these discussions are considerations of molecular models which reveal that in **7** the double bonds are much more favorably arranged for a ring closure to **10** than in **9**.

Synthesis and Reactions of Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one. The ketone **10** can be easily transformed to the olefin **14** via the alcohol **12** and the corresponding tosylate **13** (Scheme II). The cleavage of both protecting groups in **10** can be achieved with concentrated H_2SO_4 in one step, but the yield is low and the resulting triketone is unstable.[14] Therefore a stepwise path has been followed, by first generating **15**. This enone is transformed via the alcohol **16** to the diene **17**. After cleavage of the second protecting group, tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one (**18**) results.

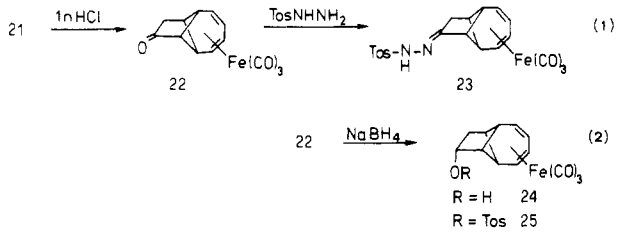
Scheme III summarizes reactions that can be carried out with the diene unit of **17**. Irradiation yields the tetracyclic olefin **20**, whose structural assignment is based on spectroscopic data. Furthermore, the diene unit can be complexed with a $Fe(CO)_3$ fragment as in **21**. As anticipated from other diene–$Fe(CO)_3$ products[15] we find for **21** a

Scheme III[a]

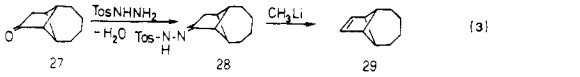


[a] (a) *hν*, CH_3CN; (b) $Fe_3(CO)_{12}$, C_6H_6, 80 °C; (c) PTAD; (d) H_2/PtO_2.

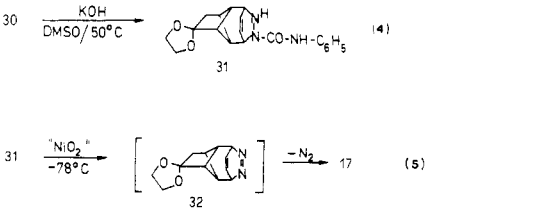
high-field shift of the protons at positions 3 and 6 of the diene unit and a low-field shift of the protons at positions 4 and 5. The IR spectrum of **21** shows the characteristic[16] IR bands of CO groups at 2025, 1980, and 1950 cm^{-1}. As shown below in eq 1 and 2, **21** can be transformed to the corresponding ketone **22**, its tosylhydrazone **23**, the alcohol **24**, and its tosylate **25**.



Reduction of **17** yields tricyclo[5.3.0.0^{2,8}]decan-9-one bis(ethylene acetal) (**26**), which can be transformed via ketone **27** into tricyclo[5.3.0.0^{2,8}]dec-9-ene (**29**) according to Shapiro et al.[17] by treating the tosylhydrazone **28** with excess of CH_3Li (reaction 3). The protons and carbon



atoms at C(2) and C(7) of **29** show the anticipated low-field shifts in the ^1H and ^{13}C NMR spectra.[18] The diene **17** reacts smoothly with phenyltriazolinedione (PTAD) to yield the pentacyclic adduct **30** (Scheme III). Partial hydrolysis of **30** according to eq 4[19] and treatment of the resulting **31** with nickel peroxide at low temperature[20] shows the complete disappearance of **31**. Subsequent



warming of the solution yields **17** (eq 5). This observation can be rationalized by assuming **32** as an intermediate.

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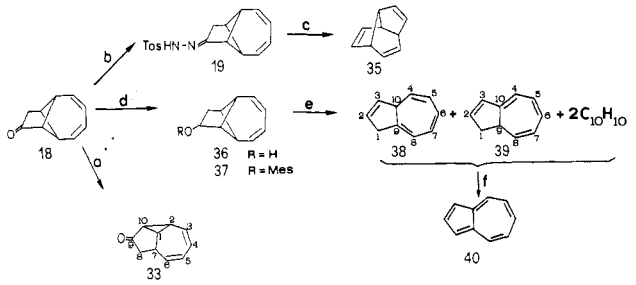
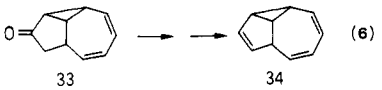
Scheme IV[a]



[a] (a) Al_2O_3, CH_2Cl_2; (b) $TosNHNH_2$; (c) MeLi, ether, 0 °C; (d) $NaBH_4$, MesCl, 0 °C; (e) Me_2SO, *t*-BuOK, 5 h, 20 °C; (f) chloranil.

The assumed instability of **32** is in line with observations on structurally related azo compounds.[21]

Reactions of Tricyclo[5.3.0.$0^{2,8}$]deca-3,5-dien-9-one (18). The method of purifying **18** led to unexpected results. We obtained an isomer, tricyclo[5.3.0.$0^{2,10}$]deca-3,5-dien-9-one (**33**) (c.f. Scheme IV). Compound **33** was first synthesized by Doering et al. in 1967.[22] Although its reported UV spectrum is identical with that of our sample and the CO stretching frequency found at 1700 cm^{-1} is compatible with the given structure, we undertook a detailed investigation of its ^1H NMR spectrum. The ^1H NMR spectrum of **33** has been analyzed by applying simulation and correlation spectroscopy (COSY).[24] The ^1H NMR spectrum of **33** and its ^1H shift-correlated NMR spectrum (COSY) is provided as supplementary material. The availability of **33** from **18** provides a new access to isobullvalene (**34**)[23] (eq 6). In carrying out the Shapiro



(6)

reaction[17] with **19** we did not obtain the anticipated **2** but an isomer. The ^1H NMR spectrum of the product shows six olefinic protons (6.6 (2 H), 5.9 (2 H) 5.6 (2 H) ppm) and four protons between 3.2 (2 H) and 2.4 (2 H) ppm. Identical data are reported for tricyclo[5.3.0.$0^{4,8}$]deca-2,5,9-triene (**35**)[25] (see Scheme IV). The structure of **35** is further assured by its ^{13}C NMR spectrum which is consistent with twofold symmetry and its IR spectrum, which is identical with that obtained by Jones.[25]

The preparation of the alcohol **36** and its mesylate **38** was undertaken to obtain **2** by an elimination reaction. Treatment of **37** with potassium *tert*-butoxide (*t*-BuOK) yielded a mixture of four isomeric hydrocarbons of the formula $C_{10}H_{10}$; two of which, **38** and **39** (Scheme IV), could be separated by preparative GC and investigated. The other two could not be separated. The oxidation of **38**, **39**, and the mixture with chloranil gave azulene (**40**).

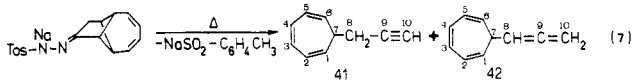
The isomers show different UV absorption spectra. Compound **38** shows a maximum at 276 nm, while **39** shows two maxima at 318 and 218 nm in *n*-hexane. These values are in agreement with those for three and four conjugated double bonds, respectively, as suggested by model calculations.[26] In the ^1H NMR spectra of **38** and **39** the signals of seven olefinic protons between 2.5 and 3.3 ppm are recorded.

Table I. Calculated Bond Lengths (Å) for 2, 34 and 44 according to the MNDO Method[a]

bond	2	44	34
1–2	1.59	2.53	3.60
1–6	2.66	2.61	1.55
2–3	1.49	1.41	1.35
3–4	1.35	1.37	1.46
4–5	1.46	1.43	1.35
5–6	1.35	1.36	1.48
6–7	1.59	1.49	1.53
7–8	1.59	1.57	1.55
8–9	1.53	1.53	1.53
9–10	1.36	1.38	1.35
1–7	1.58	1.52	1.55
1–10	1.53	1.44	1.50

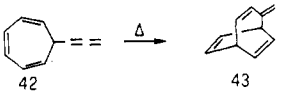
[a] The numbering of the atoms is given in Figure 1.

Thermolysis and Photolysis of the Sodium Salt of 19. In view of the thermal behavior of the Li salt of **19** in ether, we studied the thermolysis of the sodium salt of **19** without solvent and base. By heating the sodium salt of **19** to 120–125 °C a vigorous thermolysis was observed. The vapor was condensed together with Ar on a cold finger (10 K). The IR spectrum obtained from the trapped products is provided as supplementary material. We observe strong bands at 3322, 2190, and 1969 cm^{-1}. These bands are characteristic for the C–H stretching frequency of an acetylenic hydrogen (3322 cm^{-1}), the C–C stretching frequency of a triple bond (2190 cm^{-1}), and the antisymmetric stretching frequency of an allenic fragment (1969 cm^{-1}). When carrying out the thermolysis on a larger scale we could identify the cycloheptatriene derivatives **41** and **42** in the ratio 2:1 (eq 7). Attempts to separate the



(7)

mixture of **41** and **42** by preparative GC yield only **41** and a further $C_{10}H_{10}$ isomer, 2-*exo*-methylenebicyclo[3.2.2]-deca-3,6,8-triene (**43**) (eq 8). The spectral data of **41** and



(8)

43 are identical with those reported in the literature.[27] The irradiation of a degassed solution of the sodium salt of **19** in THF at room temperature yields **41** and **42** in the ratio of 2:1 as primary products.

Discussion

During our synthesis of the tricyclo[5.3.0.$0^{2,8}$]deca-3,5-diene system substituted at the 9-position, we encountered several rearrangements which deserve comment.

The properties of **1** and its reactions[28] revealed several rearrangements that can be rationalized by a homolytic rupture of one of the strained bonds of the four-membered ring moiety.[29] Model calculations on **1**–**3**[1,2] confirm this insofar as the bond lengths of the four-membered ring are predicted to be relatively long. To contribute further to this problem we have carried out a model calculation using

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(29) Gold, A.; Borden, W. T. *J. Am. Chem. Soc.* **1972**, *94*, 7179.

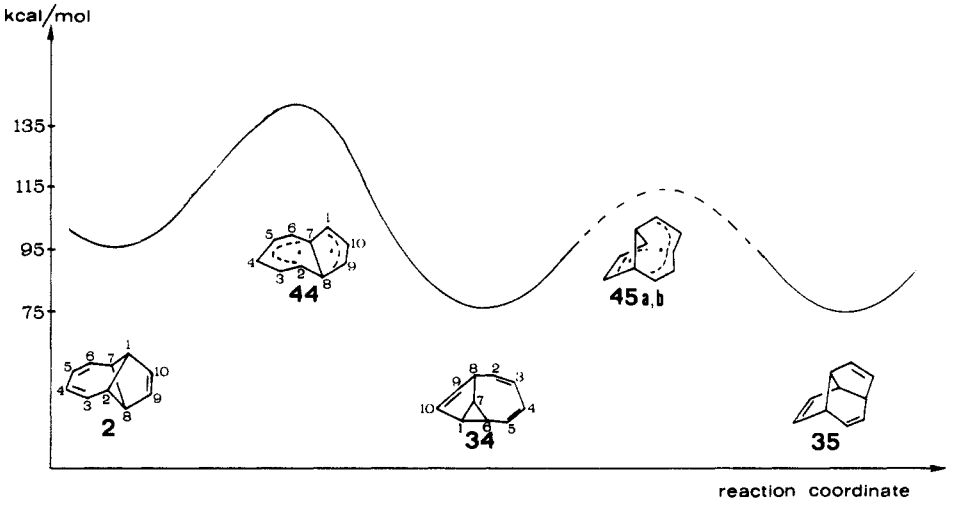
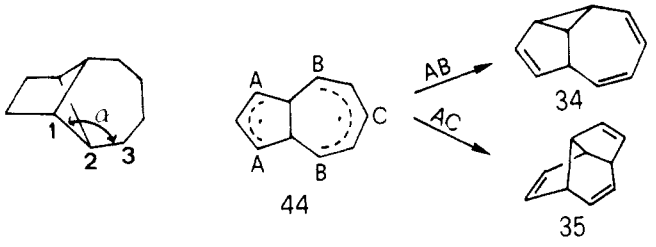


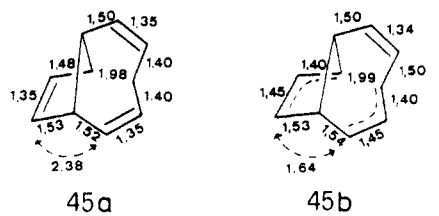
Figure 1. Calculated reaction coordinate for the rearrangement of **2** to **34** and **35** according to MNDO.

the MNDO method.[30] The starting point was **2**, whose geometrical parameters were optimized with respect to the total energy by using the MNDO method. The bond lengths obtained for **2** are given in Table I. As the reaction coordinate we choose the lengthening of one bond (C(1)–C(2)) of the cyclobutane ring (see below). The structure of maximal energy was found when C(1)–C(2) was lengthened to 2.528 Å. The structure **44** obtained satisfies the criteria of McIver and Komornicki[31] for a transition state; it is shown in Figure 1. A slight variation of the geometry of **44** along the reaction coordinate will yield either to **2** or **34**. The same result is obtained when we varied the angle between atoms 1, 2, and 3 as reaction coordinate (see below). In Figure 1 we have shown the calculated reaction coordinate as well as the heats of formation obtained for **2**, **44**, and **34**. The most relevant bond length of all three structures are given in Table I. The reason for the preference of **34** over **35** can be found when considering the geometry of the biradical **44**. A ring



closure between A and C will lead to **35**, while the connection of adjacent A and B will give rise to **34**. In **44** the distance AC is found to be 3.70 Å, while for the distance AB 2.61 Å is calculated.

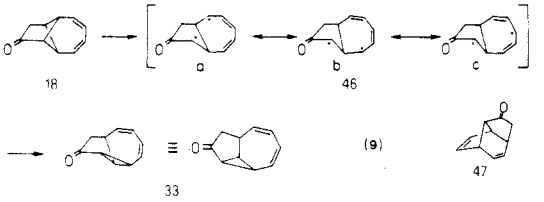
A similar search for the reaction path between **34** and **35** was hampered by convergence problems. Starting out from **34** or **35** will lead to two closely related transition states (**45a** and **45b**) whose most relevant geometrical



parameters are indicated as shown. Furthermore it is found that **35** is by 1.0 kcal/mol more stable than **34**. The activation energy for the conversion of **34** to **35** can only be estimated; values between 34 and 50 kcal/mol are obtained.

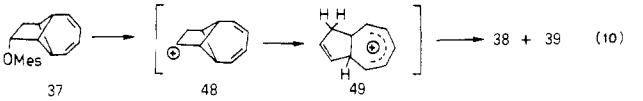
The predicted activation energies for both reaction paths just discussed are too high. The reason for this is that we did not include CI. The energy of the biradical intermediates **44** and **45** will be drastically lowered when CI is included. Nevertheless our results clearly point out that the rearrangement of **2** to **35** should be a two-step mechanism via **34** as an intermediate.

The rearrangement of **18** to **33** can be rationalized by assuming a homolytic or heterolytic bond rupture of the four-membered ring in **18** to yield a biradical or a dipolar intermediate **46** (see eq 9). From the valence structure



46b the recombination to **33** can be understood. If this reaction scheme holds, further investigations on the thermal and photochemical behavior of **18** and **33** have to show if **47** cannot be detected.

For the rearrangement of the mesylate **37** to the dihydroazulenes a ionic mechanism seems likely. This assumption is supported by the observation that treatment of **37** with traces of H_2O in Me_2SO yields a mixture of isomeric alcohols. We assume that the primarily formed cation, **48** in eq 10, is stabilized by ring opening to **49** which yields after deprotonation **38** and **39**. This explains the



observation that **38** and **39** are found in 85% yield. Further (1,*n*) H shifts from **38** and **39** can yield to other dihydroazulene isomers. Labeling experiments with deuterium at positions 9 and 10 of **37** should give us more information about the proposed mechanism.

Further rearrangements occur during the thermal decomposition of the alkali salts of **19**. The rearrangement of **19** in the presence of an excess of methyllithium at −20 °C may involve **2** as an intermediate. In favor of this view

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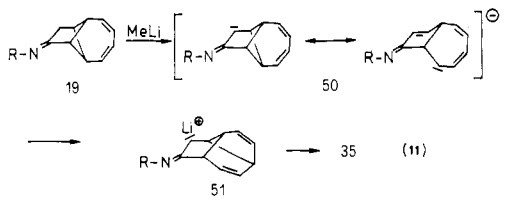
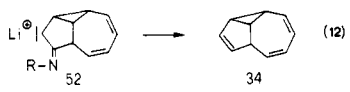
(31) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

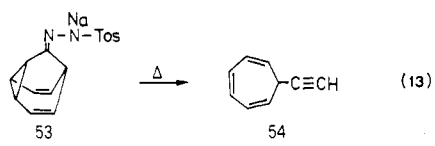
is the observation that **28** reacts under the same conditions to yield **29** (see eq 3). Counterarguments stem from the results of MO calculations which predict that **34** should be an intermediate. The latter could not be detected although a half-life time of about 13 h under the reaction conditions applied (−20 °C) has been reported.[32] An other alternative to rationalize the occurrence of **35** is given by an anionic intermediate (**50**) as shown in eq 11. This



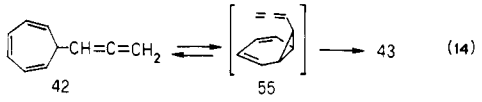
mechanism does not exclude the formation of **34**, however. From **50** one also might imagine the rearrangement to **52**, which might lead to **34** (see eq 12). The synthesis of **2** and studies on **33** and **34** might clarify the remaining questions.



Finally a comment is needed on the thermal and photochemical decomposition of the sodium salt of **19**. Examination of other thermolysis experiments of sodium salts of tosylhydrazones like **53**[33] leads us to the assumption that the acetylene **41** (see eq 7) is produced as a primary product (eq 13). In the presence of base **41** rearranges



to **42**. The rearrangement of **42** to **43** (see eq 5) can be formulated via a Cope rearrangement when we assume an equilibrium with the norcaradiene isomer **55** (eq 14).



Investigations on the equilibrium between cycloheptatriene and norcaradiene[34] as well as the Cope rearrangement of divinylcyclopropanes[35] show that under the conditions applied to isolate the mixture **41**/**42** (160 °C) the above rearrangement seems very likely.

Conclusions

Although our original goal of synthesizing **2** could only be partially achieved, our synthetic efforts have been rewarded by several new rearrangements leading to new entrances on the $C_{10}H_{10}$ manifold. We obtained new access to tricyclo[5.3.0.$0^{4,8}$]deca-2,5,9-triene (**35**), to the two new dihydroazulenes **38** and **39**, and to isobullvalene (**34**) via the ketone **33**. Furthermore the thermal rearrangement of the sodium salt of **19** yielded two cycloheptatrienes (**41**, **42**) one of which (**42**) rearranged to methylenehomobarrelene (**43**).

Experimental Section

General. Melting points are uncorrected. ^{1}H NMR spectra were measured on a 300-MHz instrument with the exception of **33**, for which a 500-MHz spectrometer was used with Me_4Si as internal standard. The 500-MHz spectrum as well as a COSY spectrum of **33** is given as supplementary material. In the COSY experiment a spectral width of 2304 Hz in both dimensions was used with quadrature detection, to collect a 256 × 1024 data matrix. The matrix was zero-filled in the t_1 dimension and transformed in the magnitude mode by using the sine bell function in both dimensions. Digital resolution in the resulting 512 × 512 data matrix was 4.5 Hz per point. ^{13}C NMR spectra were obtained with a 75.46-MHz instrument with Me_4Si as internal standard. High-resolution mass spectra (MSHR) were recorded at an ionization energy of 70 eV. The IR spectra were carried out with a Beckmann IR 4200 spectrometer; relative intensities are indicated as follow: strong (s), medium (m), weak (w), broad (br). Electronic absorption spectra were recorded on a Cary 17 D (Varian) spectrometer. Elemental analyses were performed by Microanalytical Laboratory, University of Heidelberg.

8,9-Epoxy-3-cyclodecene-1,6-dione Bis(ethylene acetal) (5). To a suspension of 35.3 g (0.14 mol) of **4**[8] dissolved in 1 L of methylene chloride and 15 g of sodium hydrogencarbonate was added dropwise a solution of 26.4 g (0.13 mol) *m*-chloroperoxybenzoic acid (80–85%) in 250 mL of CH_2Cl_2, while being stirred mechanically. After being stirred for 40 h, the suspension was filtered and washed three times with a 5% aqueous sodium hydrogen carbonate solution and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized from ethyl acetate by fractional crystallization to yield 23 g (61%) of epoxide **5**: mp 214–215 °C; ^{1}H NMR ($CDCl_3$) δ 1.4–2.3 (m, 6 H), 2.4–2.91 (m, 2 H), 3.0–3.28 (m, 2 H), 4.02 (s, 8 H), 5.35–5.83 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 127.5 (d), 110.2 (s), 64.7 (t), 64.5 (t), 54.8 (d), 35.4 (t), 33.7 (t); MSHR, (M^+) calcd 268.1311, obsd 268.1322.

4-Hydroxy-2,8-cyclodecadiene-1,6-dione Bis(ethylene acetal) (6). To a solution of 6 g (20 mmol) of diphenyl diselenide in 200 mL of dry *n*-butanol was added 1.6 g (42 mmol) of $NaBH_4$ in batches under N_2 until the bright yellow solution turned colorless. After addition of 10 g of **5** (37 mmol) the solution was refluxed for 20 h. After the solution was cooled, 200 mL of THF was added. To this solution was added 40 mL of 30% aqueous H_2O_2 over 1 h under ice cooling. After 16 h the resulting slurry was filtered and washed twice with an aqueous $FeSO_4$ solution and a 5% aqueous $NaHCO_3$ solution. After drying (Na_2SO_4) and removal of the solvent, the residue was crystallized from ether/pentane (1:1). White crystals, (55%), 5.5 g of **6** were obtained: mp 115–117 °C; ^{1}H NMR ($CDCl_3$) δ 1.7–2.7 (m, 6 H), 3.08 (m, br, 1 H), 3.95 (m, 8 H), 4.55 (br, 1 H), 5.2–5.7 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 136.5 (d), 128.8 (d), 127.7–127.3 (br), 125.0 (d), 110.0 (br), 109.9 (s), 69.8 (br), 67.6–67.3 (br), 64.3 (int.), 45.2 (br), 37.1–36.9 (br), 36.4 (t), 34.8 (br); MSHR, (M^+) calcd 268.1311, obsd 268.1291. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.78; H, 7.65.

***cis,trans*-4,8-Cyclodecadiene-1,3,6-trione 1,6-Bis(ethylene acetal) (7).** Chromium trioxide (6 g, 60 mmol) was added to a stirred solution of 9.5 mL (120 mmol) of dry pyridine in 150 mL of dry methylene chloride. After the burgundy-colored solution was stirred for 30 min at room temperature, a solution of the alcohol **6** (2.7 g, 10 mmol) in 20 mL of dry methylene chloride was added in one portion. A tarry, black residue separated immediately. After being stirred 36 h, the solution was decanted from the residue and mixed with 200 mL of ether. The organic solution was filtered through a small portion of silica gel. Evaporation of the solvent afforded the crude ketone, which was recrystallized from ether to give 1.35 g (50%) of **7** as colorless needles: mp 129–130 °C; IR (KBr) $\tilde{\nu}_{max}$ 1680 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05–2.85 (m, br, 5 H), 3.22 (br, 1 H), 3.7–4.2 (m, 8 H), 5.5–6.83 (m, 2 H), 6.22 (d, 1 H, J = 16.8 Hz), 6.65 (br, 0.5 H). At −50 °C the following assignments can be made: **7a** [($CDCl_3$) δ], H(4) 6.27, H(5) 6.85, H(8,9) 5.49–5.89; **7b** [($CDCl_3$) δ], H(4) 5.97, H(5) 6.33, H(8,9) 5.70–5.88. ^{13}C NMR ($CDCl_3$) δ 199.3 (s), 150.0 (br), 129.0 (d), 128.0 (br), 125.1 (d), 109.7 (s), 107.0 (br), 64.7 (t),

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(35) v. E. Doering, W.; Roth, W. R. *Angew. Chem.* **1963**, *75*, 27.

64.6 (t), 49.9 (t), 38.0 (br), 37.1 (t). At −50 °C the following assignments can be made: **7a** [($CDCl_3$) δ], C(4) 134.88, C(5) 152.22, C(8) 128.44, C(9) 124.81; **7b** [($CDCl_3$) δ], C(4) 128.89, C(5) 136.68, C(8) 127.33, C(9) 124.63. UV (CH_3CN) λ_{max} (ε) 217 (6000), 328 (65); MSHR, (M^+) calcd 266.1154, obsd 266.1174. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.0; H, 6.94.

***cis,cis*-4,8-Cyclodecadiene-1,3,6-trione 1,6-Bis(ethylene acetal) (9).** A solution of 300 mg (1.1 mmol) of **7** in 100 mL of dry acetonitrile and 450 mL of dry ether was cooled to −78 °C, degassed, and irradiated in a Pyrex reactor with a HPK 125-W lamp for 2 h. After removal of the solvent the residue was recrystallized from ether to yield 265 mg of colorless crystals (88%): mp 109–110 °C; IR (KBr) $\tilde{\nu}_{max}$ 3020 (w), 2980 (m), 2890 (m), 1695 (s), 1405 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3–3.2 (4 H, m), 2.92 (2 H, m), 3.98 (8 H, m), 5.52–5.95 (2 H, m), 5.58 (1 H, d, J = 13.2 Hz), 6.1 (1 H, d, J = 13.2 Hz); ^{13}C NMR ($CDCl_3$) δ 201.9 (s), 134.3 (d), 132.2 (d), 128.0 (d), 127.6 (d), 111.1 (s), 107.6 (s), 64.8 (t, double intensity), 64.5 (t, double intensity), 49.3 (t), 35.7 (t), 34.9 (t); UV (acetonitrile) λ_{max} (ε) 305 (35) nm; MSHR, (M^+) calcd 266.1154, obsd 266.1151.

Tricyclo[5.3.0.$0^{2,8}$]decane-3,5,10-trione 5,10-Bis(ethylene acetal) (10). An ice-cooled solution of 2 g (7.5 mmol) of **7** in 500 mL of dry acetonitrile was irradiated under nitrogen for 14 h with a Philips HPK 125-W lamp. After complete removal of the solvent, the residual oil solidified. Recrystallization from ether yielded 1.7 g (85%) of colorless crystals: mp 85 °C; IR (KBr) $\tilde{\nu}_{max}$ 1680 (s), 1310 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03–2.12 (m, 2 H), 2.33–2.42 (m, 3 H), 2.73 (1 H, J = 2.5 Hz), 2.78 (d, 1 H, J = 7.5 Hz), 2.84 (d, 1 H, J = 5.75 Hz), 2.92 (d, 1 H, J = 13.3 Hz), 2.98 (d, 1 H, J = 13.3 Hz), 3.89–4.04 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 207.0 (s), 114.7 (s), 106.7 (s), 64.7 (t), 64.5 (t), 64.4 (t), 64.3 (d), 53.5 (d), 51.7 (t), 47.3 (d), 44.2 (t), 42.9 (d), 38.8 (t); MSHR, (M^+) calcd 266.1154, obsd 266.1129. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.15; H, 6.90.

6-Hydroxytricyclo[5.3.0.$0^{2,8}$]decane-4,9-dione Bis(ethylene acetal) (12). A suspension of 180 mg (4.5 mmol) of sodium borohydride in 20 mL of dry ethanol was added dropwise to a stirred solution of the ketone **10** (2.1 g, 7.89 mmol) in 50 mL of dry ethanol. After 12 h of being stirred and addition of 10 mL of H_2O, the reaction mixture was filtered. The precipitated salts were washed two times with methylene chloride and the organic layer was dried ($MgSO_4$). Evaporation of the solvent yielded 2 g (95%) of product, which crystallized on standing (mixture of two isomeric alcohols): mp 75 °C; IR (KBr) $\tilde{\nu}_{max}$ 3440 (br), 2950 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (s, 2 H), 2.09–2.22 (m, 5 H), 2.26 (dd, 1 H, J = 7.5 Hz), 2.48 (tt, 1 H, J = 5.7 Hz), 2.63 (dd, 1 H, J = 5.7 Hz), 3.0 (br, 1 H), 3.88–4.06 (m, 8 H), 4.16 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 115.8 (s), 110.2 (s), 67.3 (d), 64.4 (t), 64.2 (t), 63.8 (t), 57.0 (d), 51.6 (d), 49.2 (d), 47.2 (d), 44.9 (t), 41.2 (t), 40.4 (d), 38.4 (t), 37.9 (d); MSHR, (M^+) calcd 268.1321, obsd 268.1316. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.75; H, 7.50.

6-[(*p*-Tolylsulfonyl)oxy]tricyclo[5.3.0.$0^{2,8}$]decane-4,9-dione Bis(ethylene acetal) (13). A solution of 2 g (7.4 mmol) of **12** and 2.17 g (11.4 mmol) of *p*-toluenesulfonyl chloride in 25 mL of pyridine was left for 5 days at 5 °C. After the addition of a small piece of ice, the reaction mixture was poured into 200 mL of ice–water. The white precipitate was filtered, washed with water, and dried ($MgSO_4$) to yield 2.64 g (79%) of tosylate **13** (two isomers): mp 105–115 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 1360 (s), 1305 (s); ^1H NMR ($CDCl_3$) δ 1.89–2.16 (m, 7 H), 2.28 (m, 1 H), 2.42–2.50 (m, 5 H), 3.8–4.0 (m, 8 H), 4.96 (m, 1 H), 7.33 (d, 2 H), 7.80 (dd, 2 H); ^{13}C NMR δ 144.5 (s), 134.4 (s), 129.8 (d), 127.8 (d), 115.3 (s), 107.4 (s), 80.0 (d), 64.7 (t), 64.5 (t), 55.5 (d), 51.3 (d), 50.2 (d), 47.2 (d), 44.8 (t), 44.1 (t), 40.4 (d), 40.4 (t), 39.0 (d), 38.4 (t), 21.6 (q); MSHR, (M^+) calcd 422.1367, obsd 422.1383. Anal. Calcd for $C_{21}H_{26}O_7S$: C, 59.7; H, 6.2; S, 7.5. Found: C, 59.67; H, 6.36; S, 7.35.

Tricyclo[5.3.0.$0^{2,8}$]dec-5-ene-4,9-dione Bis(ethylene acetal) (14). A solution of the tosylate **13** (2.5 g, 6 mmol) in 75 mL of dry acetonitrile and 4 mL of 1.5-diazabicyclo[4.3.0]non-5-ene was heated to 80 °C for 15 h, cooled to room temperature, and poured into 300 mL of water. The aqueous mixture was extracted with methylene chloride and dried over $MgSO_4$. Removal of the solvent gave 975 mg (65%) of **14**: mp 77–78 °C; IR (KBr) $\tilde{\nu}_{max}$ 2960 (s), 1640 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (s, 2 H), 2.29 (s, 2 H), 2.28 (m, 1 H), 2.50–2.60 (m, 1 H), 2.60 (s, 2 H), 3.90–4.05 (m, 8 H), 5.71–5.75 (d, 1 H, J = 11.4 Hz), 5.92–5.99 (dd, 1 H, J = 11.4 Hz, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 132.8 (d), 132.3 (d), 115.3 (s), 108.9 (s), 64.5 (t), 64.1 (t), 56.0 (d), 50.4 (d), 46.7 (d), 45.4 (d), 44.2 (t), 38.0 (t); MSHR, (M^+) calcd 250.1215, obsd 250.1210. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24. Found: C, 66.97; H, 7.45.

Tricyclo[5.3.0.$0^{2,8}$]dec-5-ene-4,9-dione 9-Ethylene Acetal (15). A solution of **14** (975 mg 3.7 mmol) and *p*-toluenesulfonic acid monohydrate (200 mg, 1 mmol) in 5 mL of water and 10 mL of acetone was stirred for 20 min at room temperature. Most of the acetone was removed under reduced pressure, and the residue was poured into 50 mL of water. After extraction with ether, the combined extracts were washed successively with water, an aqueous $NaHCO_3$ solution, and a saturated sodium chloride solution and dried. Removal of the solvent gave the crude ketone **15**, which was purified by column chromatography, using silica gel. Elution with methylene chloride/ethyl acetate (10:1) yielded 684 mg (90%) of crystalline ketone **15**: mp 68 °C; IR (KBr) $\tilde{\nu}_{max}$ 2941 (m), 1680 (s), 1310 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 2 H), 2.36–2.41 (tt, 1 H, J = 4.4 Hz), 2.45–2.50 (dd, 2 H, J = 7.4 Hz), 2.71–2.77 (dd, 1 H, J = 6.6 Hz, J = 8.8 Hz), 2.97–2.99 (d, 2 H, J = 4.4 Hz), 3.90–4.05 (m, 4 H), 6.03–6.06 (d, 1 H, J = 11.7 Hz), 6.82–6.89 (dd, 1 H, J = 11.7 Hz, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 201.3 (s), 148.0 (d), 131.8 (d), 115.0 (s), 64.8 (t), 56.0 (d), 50.3 (d), 46.6 (d), 45.1 (d), 44.7 (t), 42.7 (t); MS, (M^+) calcd 206.09, obsd 206.08. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.07; H, 7.06.

4-Hydroxytricyclo[5.3.0.$0^{2,8}$]dec-5-en-9-one Ethylene Acetal (16). A solution of **15** (684 mg, 3.3 mmol) in 30 mL of dry ether was added dropwise to 70 mg (2 mmol) of lithium aluminium hydride in 10 mL of ether. The reaction mixture was refluxed for 3 h. Then water was added cautiously. After being stirred for a further 30 min, the reaction mixture was filtered, and the precipitated salts were washed two times with ether. After the etheral solution was dried ($MgSO_4$), the solvent was removed to yield a colorless oil, which crystallized on standing. Column chromatography, using silica gel and elution with methylene chloride/ethyl acetate (10:1), yielded 631 mg (91%) of crystalline (two isomers) alcohol **16**: mp 80 °C; IR (KBr) $\tilde{\nu}_{max}$ 3290 (br), 3025 (w), 2950 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (s, br, 1 H), 1.91–1.93 (dd, 1 H, J = 1.3 Hz, J = 5.3 Hz), 1.97–2.08 (m, 2 H), 2.20–2.37 (m, 3 H), 2.50 (t, 1 H, J = 7.1 Hz), 2.65–2.69 (2 d, 1 H, J = 7.1 Hz), 3.87–4.01 (m, 4 H), 4.66–4.79 (m, 1 H), 5.70–5.83 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 136.6 (d), 136.55 (d), 128.5 (d), 115.7 (s), 114.5 (s), 69.1 (d), 69.06 (d), 64.5 (t), 58.3 (d), 52.7 (d), 50.9 (d), 47.6 (d), 47.2 (d), 47.0 (d), 43.8 (t), 41.7 (d), 37.7 (t), 36.5 (t); MS, (M^+) calcd 208.11, obsd 208.03. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.20; H, 7.74. Found: C, 68.93; H, 7.83.

Tricyclo[5.3.0.$0^{2,8}$]deca-3,5-dien-9-one Ethylene Acetal (17). A solution containing allylic alcohol **16** (631 mg, 3.0 mmol) in 10 mL of hexamethylphosphoramide was stirred under nitrogen, while methyltriphenoxyphosphonium iodide (3 g, 7.4 mmol) was added in one portion. The resulting mixture was heated for 5 h at 95 °C. After cooling to room temperature, it was poured into 200 mL of 2.7 N potassium hydroxide solution and extracted with 1:1 ether/pentane (800 mL). The organic solvent was washed with water, dried over $MgSO_4$, and evaporated. The remaining oil was chromatographed on silica gel. Elution with CH_2Cl_2 yielded 490 mg (85%) of crystalline diene **17**: mp 64–65 °C; ^1H NMR ($CDCl_3$) δ 1.17–1.19 (d, 1 H, J = 7.0 Hz), 1.26–1.29 (dt, 1 H, J = 7.0 Hz, J = 1.1 Hz), 2.10 (dd, 2 H, J = 1.1 Hz), 2.83–2.89 (dd, 2 H, J = 7.0 Hz, J = 1.8 Hz), 3.89–4.05 (m, 4 H), 5.95–6.11 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 132.5 (d), 125.3 (d), 116.4 (s), 64.6 (t), 50.6 (d), 43.6 (t), 33.7 (d), 24.0 (d); UV (CH_3CN) λ_{max} (ε) 275 (3680) nm; MSHR, (M^+) calcd 190.0982, obsd 190.0988. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.50; H, 7.55.

Tricyclo[5.3.0.$0^{2,8}$]deca-3,5-dien-9-one (18). A solution of 490 mg (2.6 mmol) of **17** in 100 mL of THF was cooled to 0 °C and treated with 45 mL of 1 N hydrochloric acid. After warming to room temperature and being stirred for 24 h, the reaction mixture was neutralized with 1 N sodium hydroxide solution. The product was extracted with ethyl acetate, and the combined organic layers were washed with water and brine, dried over $MgSO_4$, and evaporated at room temperature, leaving 365 mg of a colorless oil, which was purified on silica gel. Elution with methylene chloride gave 350 mg (93%) of pure **18**: IR (film) $\tilde{\nu}_{max}$ 3040 (m),

1755 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (s, 2 H), 2.45 (s, 2 H), 2.96 (d, 2 H, J = 5.8 Hz), 6.11–6.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 212.4 (s), 132.3 (d), 126.8 (d), 52.1 (d), 45.8 (t), 43.0 (d), 23.9 (d); UV (CH_3CN) λ_{max} (ϵ) 275 (3870) nm; MSHR, (M^+) calcd 146.0704, obsd 146.0718.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one (*p*-Tolylsulfonyl)hydrazone (19). A mixture of 180 mg (1.23 mmol) of **18** and 270 mg (1.45 mmol) tosylhydrazine in 15 mL of dry ethanol was stirred at room temperature for 24 h. A white precipitate formed, which was filtered and identified as pure desired product **19** (180 mg). The ethanol was evaporated and the residue was chromatographed on silica gel. Elution with methylene chloride/ethyl acetate gave 75 mg of **19**. A total of 255 mg (66%) of white crystalline tosylhydrazone was obtained. **19**: mp 142 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 3200 (s), 3030 (w), 1340 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.51–1.54 (d, 1 H, J = 7.0 Hz), 1.81–1.84 (d, 1 H, J = 7.0 Hz), 2.45 (s, 5 H), 2.65–2.70 (br, 2 H), 5.98–6.05 (m, 4 H), 7.32–7.35 (d, 2 H, J = 8 Hz), 7.39 (s, 1 H), 7.86–7.89 (d, 2 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 167.3 (s), 143.9 (s), 135.5 (s), 131.9 (d), 129.5 (d), 128.0 (d), 126.2 (d), 53.3 (d), 36.7 (d), 36.7 (t), 23.8 (d), 21.5 (q); UV (CH_3CN) λ_{max} (ϵ) 225 (19 800), 275 (3680) nm; MSHR, (M^+) calcd 314.1080, obsd 314.1083. Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.94; H, 5.77; N, 8.91; S, 10.20. Found: C, 64.61; H, 6.0; N, 8.76; S, 10.16.

Tetracyclo[5.3.0.0^{2,8}.0^{3,6}]dec-4-en-9-one Ethylene Acetal (20). A solution of **17** (20 mg; 0.11 mmol) in 15 mL of dry acetonitrile was irradiated under argon atmosphere for 5 h with a mercury lamp (250 W) using a cutoff filter (WG 305). After completion (GC control), the solvent was removed, and the residue was chromatographed on silica gel to yield 15 mg (75%) of liquid **20**: ^1H NMR ($CDCl_3$) δ 2.00–2.09 (m, 3 H), 2.20–2.28 (m, 3 H), 3.26 (s, 2 H), 3.9–4.0 (m, 4 H), 6.09 (s, 2 H); IR (film) $\tilde{\nu}_{max}$ 3025 (s), 2950 (m) cm^{-1}; MSHR, (M^+) calcd 190.0982, obsd 190.0985.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one Ethylene Acetal Tricarbonyliron (21). A solution of 680 mg (1.35 mmol) of dodecacarbonyltriiron and 220 mg (1.16 mmol) of **17** in 20 mL of dry benzene was refluxed under nitrogen for 18 h. After filtration and evaporation of the solvent, the residue was dissolved in methylene chloride and chromatographed on silica gel. Elution with CH_2Cl_2 gave 300 mg (77%) of the yellow crystalline complex **21**: mp 74 °C dec; two isomers; IR (KBr) $\tilde{\nu}_{max}$ 2025 (s), 1985 (s), 1950 (s), 1305 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (d, 1 H, J = 1.1 Hz), 1.92 (d, 1 H, J = 1.1 Hz), 1.83–1.94 (dd, 2 H, J = 7.0 Hz), 2.10–2.14 (dd, 1 H, J = 7.0 Hz, J = 12.5 Hz), 2.38–2.46 (m, 2 H, J = 16.1 Hz, J = 6.2 Hz, J = 2.2 Hz), 3.23–3.25 (m, 2 H), 3.77–3.94 (m, 4 H), 5.37–5.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 211.4 (s), 211.3 (s), 113.2 (s), 87.6 (d), 65.5 (t), 64.5 (t), 64.4 (t), 60.6 (d), 60.4 (d), 54.3 (d), 53.1 (d), 48.7 (d), 25.1 (t), 23.1 (t); MSHR, (M^+) calcd 330.0190, obsd 330.0191. Anal. Calcd for $C_{15}H_{14}O_5Fe$: C, 54.58; H, 4.27. Found: C, 54.32; H, 4.26.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one Tricarbonyliron (22). To a solution of 300 mg (0.91 mmol) **21** in 50 mL of THF (freshly distilled over Na) was added 14 mL of 1 N HCl under N_2 with stirring and cooling (0 °C), over a period of 30 min. The stirring was continued over 10 h at room temperature. After neutralization with 1 N sodium hydroxide solution, the solvent was extracted twice with ethyl acetate. The organic layer was washed with water and dried ($MgSO_4$). After removal of the solvent the residue was chromatographed on alumina. Elution with CH_2Cl_2 yielded 130 mg (50%) of **22**: mp 72–75 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 2040 (s), 1940–1950 (br, s), 1755 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 2 H), 2.46–2.62 (m, 4 H), 3.22–3.25 (m, 2 H), 5.47–5.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 210.6 (s), 208.6 (s), 88.1 (d), 59.3 (d), 57.8 (d), 50.8 (d), 50.2 (d), 49.0 (d), 43.7 (t); MSHR, (M^+) calcd 285.9928, obsd 285.9880. Anal. Calcd for $C_{13}H_{10}O_4Fe$: C, 54.58; H, 3.52. Found: C, 54.22; H, 3.67.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one (*p*-Tolylsulfonyl)hydrazone Tricarbonyliron (23). The preparation of the ironcarbonyl derivate **23** was identical with that described for the tosylhydrazone **19**. Compound **22** (60 mg; 0.21 mmol) was converted to 86 mg (90%) of tosylhydrazone **23**: mp 160 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 3200 (m), 2040 (s), 1990 (s), 1970 (s), 1335 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22–2.23 (d, 2 H, J = 0.9 Hz), 2.31–2.42 (m, 3 H), 2.35 (s, 3 H), 2.5–2.6 (d, 1 H, J = 7.3 Hz), 3.05–3.25 (m, 2 H), 5.38–5.49 (dd, 2 H, J = 5.5 Hz, J = 2.7 Hz), 6.96 (s, 1 H), 7.24–7.38 (m, 2 H), 7.75–7.86 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 210.8 (s), 164.1 (s), 144.0 (s), 135.6 (s), 129.7 (d), 127.8 (d), 88.0 (d), 66.8 (d), 58.1 (d), 51.4 (d), 50.7 (d), 34.5 (t), 21.7 (q); UV (CH_3CN) λ_{max} (ϵ) 230 (28 100), 275 (4320) nm. Anal. Calcd for $C_{20}H_{18}O_5N_2SFe$: C, 52.88; H, 4.0; N, 6.17; S, 7.06. Found: C, 52.20; H, 4.21; N, 5.95; S, 7.03.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-ol Tricarbonyliron (24). The ironcarbonyl derivate **24** was prepared by a procedure identical with that described for the preparation of the alcohol **36**. Ketone **22** (60 mg, 0.21 mmol) was converted to 50 mg (90%) of the alcohol **24**: IR (KBr) $\tilde{\nu}_{max}$ 3200 (br), 2040 (s) 1960–1950 (br, s), 1350 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23–1.33 (br, 2 H), 1.62 (s, 1 H), 1.99–2.16 (m, 4 H), 2.50 (1 H), 3.21–3.33 (2 H), 3.94 (1 H), 5.40 (2 H); ^{13}C NMR ($CDCl_3$) δ 211.4 (s), 87.9 (d), 87.6 (d), 70.4 (d), 64.7 (d), 60.8 (d), 60.5 (d), 56.0 (d), 48.1 (d), 44.4 (d), 38.7 (t). Anal. Calcd for $C_{13}H_{12}O_4Fe$: C, 54.20; H, 4.19. Found: C, 54.48; H, 3.91.

9-[(*p*-Tolylsulfonyl)oxy]tricyclo[5.3.0.0^{2,8}]deca-3,5-diene Tricarbonyliron (25). To a solution of *p*-toluenesulfonyl chloride (55 mg, 0.29 mmol) in 1.5 mL of dry pyridine was added 55 mg (0.2 mmol) of **24**. After 48 h at 5 °C, pieces of ice were added until yellow crystals began to precipitate. The solid was filtered, washed with water, and dried to yield 55 mg (62%) of yellow tosylate **25**: mp 160 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 2040 (s), 1950 (br, s), 1360 (s), 1340 (s), 1190 (s), 1180 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (1 H), 1.96–1.98 (2 H), 2.12 (2 H), 2.43–2.45 (4 H), 3.11–3.21 (2 H), 4.47 (1 H), 5.36 (2 H), 7.33–7.34 (2 H), 7.73–7.76 (2 H); ^{13}C NMR ($CDCl_3$) δ 144.5 (s), 137.5 (s), 129.8 (d), 127.7 (d), 88.1 (d), 87.7 (d), 80.1 (d), 62.1 (d), 59.2 (d), 58.9 (d), 54.7 (d), 47.3 (d), 44.9 (d), 36.1 (t), 21.6 (q); UV (CH_3CN) λ_{max} (ϵ) 230 (28 100), 275 (3920) nm. Anal. Calcd for $C_{20}H_{18}O_6SFe$: C, 54.34; H, 4.10; S, 7.52. Found: C, 54.60; H, 4.11; S, 7.49.

Tricyclo[5.3.0.0^{2,8}]decan-9-one Ethylene Acetal (26). A solution of 100 mg (0.53 mmol) of diene **17** in 6 mL of ethanol was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After the theoretical amount of hydrogen had been absorbed (10 h), the reaction mixture was filtered and the solvent removed. The remaining liquid was chromatographed on silica gel. Elution with ether gave 92 mg (89%) of a colorless liquid: IR (film) $\tilde{\nu}_{max}$ 2920 (s), 1300 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56–1.58 (br, 4 H), 1.80–1.84 (br, 4 H), 1.96 (s, 2 H), 2.21–2.23 (m, 4 H), 3.88–4.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 116.4 (s), 64.5 (t), 52.8 (d), 51.4 (d), 45.1 (t), 41.3 (d), 29.6 (t), 27.1 (t); MSHR, (M^+) calcd 194.1303, obsd 194.1305.

Tricyclo[5.3.0.0^{2,8}]decan-9-one (27). A solution of **26** (92 mg, 0.47 mmol) in 20 mL of THF was cooled to 0 °C and treated with 7 mL of 1 N HCl. The reaction was warmed to room temperature, and stirring was continued for 18 h. The reaction mixture was neutralized with 1 N sodium hydroxide solution, and the product was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and evaporated, leaving 70 mg of a colorless oil, which was purified on silica gel. Elution with CH_2Cl_2 gave 67 mg (95%) of pure liquid ketone **27**: IR (film) $\tilde{\nu}_{max}$ 2940 (s), 1765 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55–2.00 (m, 8 H), 2.25–2.40 (m, 4 H), 2.5–2.8 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 219.9 (s), 61.8 (d), 53.2 (d), 47.6 (t), 40.4 (d), 30.0 (t), 26.8 (t); MSHR, (M^+) calcd 150.1045, obsd 150.1062.

Tricyclo[5.3.0.0^{2,8}]decan-9-one (*p*-Tolylsulfonyl)hydrazone (28). A mixture of 67 mg (0.45 mmol) of **27** and 84 mg (0.45 mmol) of tosylhydrazine in 4 mL of dry ethanol was stirred at room temperature for 24 h. A white precipitate was formed, which was filtered and identified as pure **28** (30 mg). The ethanol was removed, and the residue was chromatographed on silica gel. Elution with methylene chloride/ethyl acetate (10:1) gave 60 mg of **28**. A total of 90 mg (63%) of white, crystalline tosylhydrazone **28** was obtained: mp 217 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 3240 (s), 2920 (s), 1329 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–1.61 (m, 4 H), 1.75–1.87 (br, m, 4 H), 2.02–2.08 (m, 2 H), 2.32 (d, 2 H, J = 1.7 Hz), 2.42–2.45 (m, 1 H), 2.43 (s, 3 H), 2.83 (d, 2 H, J = 7.0 Hz), 7.23 (s, 1 H), 7.32 (d, 2 H, J = 8.0 Hz), 7.85 (m, 2 H, J = 8.0 Hz); MSCI, m/e 319 (M + 1).

Tricyclo[5.3.0.0^{2,8}]dec-9-ene (29). To a stirred suspension of 90 mg (0.28 mmol) of **28** in 3 mL of dry ether (ice cooling) was added 0.63 mL (1 mmol) of 1.6 N methyllithium in dry ether during 10 min. Stirring was continued at room temperature for 16 h, during which time the reaction mixture developed a deep red–orange color. A small amount of water was added to destroy the excess CH_3Li, and then an additional 5 mL was added. The

layers were separated and the organic layer was washed with water and dried. The solvent was removed by alumina distillation. The residue was chromatographed on aluminia (elution with ether) to give 23 mg (62%) of the tricyclic compound **29**: IR (GC/IR) $\tilde{\nu}_{max}$ 3043 (m), 1650 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52 (m, 4 H), 1.72 (m, 4 H), 2.48 (s, 2 H), 2.87 (s, 2 H), 7.05 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 147.4 (d), 80.7 (d), 48.9 (d), 31.3 (t), 27.2 (t); MSHR, (M^+) calcd 134.0962, obsd 134.1114.

4-Phenyl-2,4,6-triazapentacyclo[6.5.2.0^{2,6}.0^{8,12}.0^{9,13}]pentadec-14-ene-3,5,10-trione 10-Ethylene Acetal (30). To a solution of 100 mg (0.53 mmol) of **17** in dry methylene chloride (5 mL) was added dropwise phenyltriazolinedione (92 mg, 0.53 mmol) in 2 mL of CH_2Cl_2. The color of the red mixture disappeared quickly. After the mixture was stirred for 3 h at room temperature, the solvent was evaporated, and the residue was chromatographed on silica gel; elution with methylene chloride/ethyl acetate (1:1) gave 163 mg (85%) of **30** as a mixture of two isomers: mp 65 °C dec; IR (KBr) $\tilde{\nu}_{max}$ 1770 (s), 1720 (s), 1405 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–2.1 (m, 3 H), 2.60–2.85 (m, 2 H), 2.9–3.05 (m, 1 H), 3.85–4.0 (m, 4 H), 5.0–5.3 (m, 2 H), 6.3–6.45 (t, 2 H), 7.3–7.55 (m, 5 H); ^{13}C NMR δ 154.5 (s), 131.8 (s), 129.7 (d), 128.1 (d), 125.5 (d), 114.3 (s), 114.0 (s), 64.8 (t), 60.9 (d), 54.5 (d), 53.3 (d), 53.1 (d), 51.1 (d), 50.8 (d), 49.8 (d), 43.5 (t), 43.1 (d), 41.1 (t); MSHR, (M^+) calcd 365.1373, obsd 365.1345.

2-(*N*-Phenylcarbamoyl)-2,3-diazatetracyclo[6.2.2.0^{5,9}.0^{6,10}]dodec-11-en-7-one Ethylene Acetal (31). To a mixture of 104 mg (0.45 mmol) of **30** and 180 mg of powdered KOH were added 10 mL of Me_2SO and 10 mL of water. The reaction mixture was stirred under nitrogen for 3 h, while being heated to 50 °C. The colorless solution was cooled to 0 °C and diluted with saturated aqueous NH_4Cl. The aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. The solvent was removed, and the residue was chromatographed on silica gel by elution with CH_2Cl_2/ether (2:1) to yield 122 mg (80%) of two isomers (**31**): mp 115–118 °C; IR (KBr) $\tilde{\nu}_{max}$ 3340 (m), 3220 (m), 1660 (s), 1510 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85–2.08 (m, 3 H), 2.50–2.67 (m, 1 H), 2.60 (s, 2 H), 2.72–2.87 (m, 1 H), 3.80–4.0 (m, 4 H), 4.02–4.08 (m, 1 H), 5.35–5.42 (m, 1 H), 6.35–6.45 (m, 2 H), 7.0 (t, 1 H), 7.28 (d, 2 H), 8.35 (br, 1 H); MSHR, (M^+) calcd 339.1583, obsd 339.1578.

Tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-9-one (33). **18** (40 mg) was dissolved in methylene chloride and chromatographed on aluminia (neutral, act I). The resulting isomeric ketone **33** showed the following spectroscopic properties: IR (film) $\tilde{\nu}_{max}$ 1700 cm^{-1}; UV ($CDCl_3$) λ_{max} (ϵ) 258 (4200) nm; MS, (M^+) calcd 146.07, obsd 146.06. ^1H NMR ($CDCl_3$) δ 2.57 (H(1), $J_{1,2}$ = 5.4 Hz, $J_{1,7}$ = 6.4 Hz, $J_{1,10}$ = 4.9 Hz), 2.16 (H(2), $J_{2,3}$ = 3.9 Hz, $J_{2,7}$ = 1.1 Hz, $J_{2,10}$ = 10.3 Hz), 6.21 (H(3), $J_{3,4}$ = 11.4 Hz), 6.04 (H(4), $J_{4,5}$ = 5.8 Hz), 5.82 (H(5), $J_{5,6}$ = 10.6 Hz), 6.19 (H(6), $J_{6,7}$ = 8.1 Hz), 3.28 (H(7), $J_{7,8a}$ = 10.6 Hz, $J_{7,8b}$ = 8.0 Hz), 2.48 (H(8a), $J_{8a,8b}$ = −19.2 Hz, $J_{8a,10}$ = 1.1 Hz), 219 (H(86)), 1.82 (H(10)).

Tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (35). To a stirred suspension of 350 mg (1 mmol) **19** in 10 mL of dry ether (ice cooling) was added 3 mL (4.5 mmol) of 1.5 N methyllithium in ether during 15 min. Stirring was continued at room temperature for 16 h, during which time the reaction mixture developed a deep red-orange color. A small amount of water was added to destroy the excess methyllithium, and then an additional 25 mL was added. The layers were separated, and the organic layer was washed with water and dried. Most of the solvent was removed by careful distillation. The residue, which contained one main hydrocarbon (85 mg; 65%), was subjected to preparative GC to give 26 mg (20%) of **35**:[25] ^{13}C NMR ($CDCl_3$) δ 145.5 (d), 133.3 (d), 129.4 (d), 60.3 (d), 41.6 (d); MS, (M^+) calcd 130.08, obsd 130.07. When the reaction was carried out at 0 or −20 °C the same result was obtained.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-ol (36). To a solution of 100 mg (0.68 mmol) **18** in 5 mL of dry ethanol was added 12 mg (0.32 mmol) of $NaBH_4$ in one portion. The reaction mixture was stirred at room temperature for 2 h. Water was added, and the solution was extracted three times with ether. The combined organic layers were dried ($MgSO_4$) and evaporated to give a colorless oil (100 mg), which crystallized on standing in a refrigerator. When the reaction product was chromatographed on silica gel by elution with methylene chloride, it yielded 93 mg (92%) of the alcohol **36**: mp 62 °C; IR (KBr) $\tilde{\nu}_{max}$ 3240 (br), 1335 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, 2 H, J = 1.7 Hz), 1.52–1.55 (dd, 1 H, J = 1.7 Hz, J = 11.5 Hz), 1.86 (s, br, 1 H), 2.23–2.29 (dd, 1 H, J = 7.0 Hz, J = 11.5 Hz), 2.37–2.42 (m, 1 H), 2.92–2.97 (dd, 1 H, J = 6.6 Hz, J = 8.3 Hz), 4.59–4.62 (d, 1 H, J = 7.0 Hz), 5.95–6.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 133.2 (d), 132.4 (d), 125.4 (d), 124.9 (d), 73.2 (d), 50.9 (d), 46.3 (d), 40.2 (t), 32.8 (d), 26.6 (d); UV (CH_3CN) λ_{max} (ϵ) 278 (2750) nm; MSHR, (M^+) calcd 148.0904, obsd 148.0896. Anal. Calcd for $C_{10}H_{12}O$: C, 79.99; H, 8.16. Found: C, 79.20; H, 8.34.

Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-yl Methanesulfonate (37). To a solution of 93 mg (0.63 mmol) of **36** in 3 mL of dry methylene chloride, containing 0.5 mL of triethylamine, was added 80 mg (0.7 mmol) of methanesulfonyl chloride at 0 °C. Stirring for 1 h completed the reaction. The mixture was first extracted with ice–water, followed by 5% $NaHCO_3$ solution and brine. Drying of the organic solution ($MgSO_4$) followed by solvent removal gave 124 mg (87%) of **37**, which was pure enough for most uses: mp 48–53 °C; IR (KBr) $\tilde{\nu}_{max}$ 1345 (s), 1180 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31–1.33 (m, 1 H, J = 6.6 Hz), 1.57–1.60 (dd, 1 H, J = 6.6 Hz, J = 1.8 Hz), 1.89–1.94 (dt, 1 H, J = 1.8 Hz, J = 12.4 Hz), 2.36–2.47 (m, 2 H, J = 12.4 Hz, J = 7.5 Hz, J = 6.6 Hz), 2.93–3.00 (m, 1 H, J = 6.6 Hz, J = 8.0 Hz), 5.28–5.34 (m, 1 H, J = 7.5 Hz), 5.94–6.14 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 131.9 (d), 131.1 (d), 126.1 (d), 125.6 (d), 82.9 (d), 50.0 (d), 46.9 (d), 38.6 (q), 38.2 (t), 32.6 (d), 26.3 (d); UV (CH_3CN) λ_{max} (ϵ) 275 (3240) nm; MSHR, (M^+) calcd 226.0657, obsd 226.0660.

Dihydroazulenes 38 and 39. To a solution of **37** (124 mg, 0.55 mmol) in Me_2SO (2 mL) was added potassium *tert*-butoxide (123 mg, 1.1 mmol) under N_2. The reaction mixture was stirred at room temperature for 5 h, then was poured into water (5 mL), extracted with ether (3 × 20 mL), dried, and evaporated to leave 60 mg (85%) of a mixture of four isomeric $C_{10}H_{10}$ hydrocarbons. Preparative GC isolation (Carbowax, 125 °C) afforded **38** and **39** as colorless liquids. **39**: IR (GC/IR) $\tilde{\nu}_{max}$ 3063 (s), 3024 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.54–2.61 (dd, H(1b), $J_{1a,1b}$ = 18.6 Hz, $J_{1b,9}$ = 4.0 Hz), 2.70–2.90 (m, H(9), $J_{9,1a}$ = 9.3 Hz), 3.12–3.27 (dd, H(1a), $J_{1a,9}$ = 9.3 Hz), 5.36–5.39 (dd, H(8), $J_{7,8}$ = 9.7 Hz, $J_{8,9}$ = 3.7 Hz), 6.01–6.09 (m, H(4), H(7)), 6.19 (s, H(2), H(3)), 6.23–6.25 (dd, H(5), $J_{5,6}$ = 11.1 Hz, $J_{5,4}$ = 6.2 Hz), 6.43–6.48 (dd, H(6), $J_{5,6}$ = 11.1 Hz, $J_{4,6}$ = 6.2 Hz); UV (hexane) λ_{max} 318, 218 nm; MSHR, (M^+) calcd 130.0783, obsd 130.0798. **38**: IR (GC/IR) $\tilde{\nu}_{max}$ 3066 (s), 3028 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06–3.10 (d, H(10), $J_{4,10}$ = 4.4 Hz), 3.30 (m, H(1a)), 5.00–5.04 (dd, H(4), $J_{4,5}$ = 9.7 Hz, $J_{4,10}$ = 4.4 Hz), 5.92–5.96 (m, H(2)), 6.00–6.06 (H(5), H(8), $J_{5,6}$ = 5.7 Hz, $J_{5,4}$ = 9.7 Hz, $J_{8,7}$ = 5.7 Hz), 6.19–6.21 (br, H(3)), 6.43–6.48 (dd, H(6), $J_{5,6}$ = 5.7 Hz, $J_{6,7}$ = 11.5 Hz), 6.52–6.58 (dd, H(7), $J_{6,7}$ = 11.5 Hz, $J_{7,8}$ = 5.7 Hz); UV (hexane) λ_{max} 276 nm; MSHR, (M^+) calcd 130.0783 obsd 130.0775.

Preparation of the Sodium Salt of 19. To a solution of 60 mg (0.19 mmol) of **19** in 3 mL of dry methylene chloride was added 9 mg (0.3 mmol) of 80% NaH. After stirring for 2.5 h under N_2 the solution was diluted with 25 mL of *n*-hexane. A white precipitate formed and was filtered and washed with *n*-hexane (50 mL). Drying in vaccuum yielded 61 mg (95%) of the sodium salt of **19**.

Thermolysis of the Sodium Salt of 19. The sodium salt of **19** (50 mg, 0.15 mmol) was heated to 130 °C under reduced pressure (10^{-4} torr). The volatile products were collected in a cold trap and identified by ^1H NMR spectroscopy as the compounds **41** and **42** (2:1). Preparative GC isolation yielded **41** and **43**[27] (Carbowax, 160 °C). **41**: IR (matrix, 10 K) $\tilde{\nu}_{max}$ 3329 (s), 3028 (s), 2928 (w), 1254 (m), 741 (m), 706 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (m, H(7), $J_{1,7}$ = 5.3 Hz), 2.0 (t, H(10), $J_{8,10}$ = 2.7 Hz), 2.55–2.60 (dd, H(8), $J_{8,10}$ = 2.7 Hz, $J_{7,8}$ = 7.0 Hz), 5.3 (dd, H(1), H(6), $J_{1,2}$ = 9.3 Hz, $J_{1,7}$ = 5.3 Hz), 6.2–6.3 (dd, H(2), H(5), $J_{2,3}$ = 3.1 Hz, $J_{2,1}$ = 9.3 Hz), 6.6–6.7 (dd, H(3), H(4), $J_{3,4}$ = 3.1 Hz, $J_{2,3}$ = 3.1 Hz). **42**: IR (matrix, 10 K) $\tilde{\nu}_{max}$ 1969 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (m, H(7)), 4.85–4.9 (dd, H(10), $J_{10,8}$ = 6.5 Hz, $J_{10,7}$ = 3.2 Hz), 5.3 (dd, H(1), H(6)), 5.48–5.5 (dt, H(8), $J_{8,10}$ = 6.5 Hz, $J_{7,8}$ = 6.5 Hz), 6.2–6.3 (dd, H(2), H(5)), 6.6–6.7 (dd, H(3), H(4)).

Photolysis of the Sodium Salt of 19. To a solution of 10 mg (0.03 mmol) of **19** in 10 mL of freshly distilled THF was added 1 mg (0.04 mmol) NaH. The mixture was stirred for several hours under argon. The resulting suspension was irradiated for 2 h (Hg lamp, WG 305), diluted with water, and extracted twice with ether

(2 × 10 mL). The combined ether extracts were washed with water and dried over $MgSO_4$. The solvent was removed by careful distillation. The resulting products showed the same properties as those obtained by thermolysis.

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Note added in proof: After completion of this paper, J. Dressel and L. A. Paquette informed us about their successful synthesis of **2**.[5b] According to their findings the thermal behavior of **2** is in line with the predictions of our calculations.

Supplementary Material Available: ^1H NMR spectrum and ^1H shift-correlated NMR spectrum (COSY) of **33** as well as the IR spectrum of the pyrolysis products of the sodium salt of **19** (4 pages). Ordering information is given on any current masthead page.

[3.3]Orthocyclophanes with Facing Benzene and Naphthalene Rings[1]

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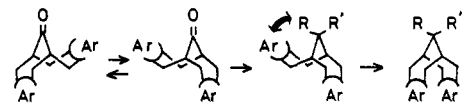
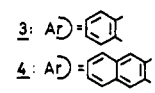
Dibenzo-, dinaphtho-, and benzonaphthobicyclo[4.4.1]undecan-11-ones **3**, **4**, and **6a** were converted into [3.3]orthocyclophanes **8–10** and **12** by the reaction of the carbonyl group at the bridge with ethylene and propylene glycol, ethane-1,2-dithiol, and Grignard reagents. Compared with those of the corresponding ketones, upfield shifts of aromatic protons of **8–10** and **12** were observed in ^1H NMR spectra. Their electronic spectra have an absorption tail that extends to about a 10 nm higher wavelength. X-ray crystallography of dibenzo derivatives **8a** and **9a** disclosed that the closest intramolecular distances of two benzene rings is 3.03–3.07 Å and the dihedral angle between two benzenes is 25°.

Meta- and paracyclophanes have attracted much attention in the last two decades because of their layered structures with facing aromatic rings.[2] On the other hand, orthocyclophanes generally possess a rather flattened structure and have been less studied. Several compounds that contain [2.2]- and [3.3]orthocyclophane moieties are known;[3] however, there are only a few examples of orthocyclophanes that exhibit a "π–π" interaction of the two facing aromatic rings. Janusene (**1**)[4] and the related com-

pound **2**[5] are [3.3]orthocyclophanes whose electronic spectra show a characteristic band that reflects a throughspace interaction of the two facing benzene rings.

We reported the preparation of dibenzo- (**3**) and dinaphtho[4.4.1]undecan-11-one (**4**), which are flexible and exist as two equivalent conformers with $\Delta G^{\ddagger}$ = 10–15 kcal mol^{-1}.[7] The introduction of bulky substituents onto the C1 bridge of **3** resulted in increased repulsion between the substituents and the two benzene rings, forcing the rings to take a facing conformation (eq 1). We describe the preparation and characterization of [3.3]orthocyclophanes that have facing benzene and naphthalene rings.





Results and Discussion

Preparation of [3.3]Orthocyclophanes. Dibenzo- and dinaphthobicyclo[4.4.1]undecan-11-one (**3** and **4**) were prepared as reported.[6] Benzocycloheptenonedicarboxylate **5a** and its naphtho analogue **5b** were needed to prepare benzo–naphtho derivative **6a**. Although some preparative methods have been reported,[7] we synthesized **5a** and **5b** by the reaction of the bis(bromomethyl)arenes **7a** and **7b**

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