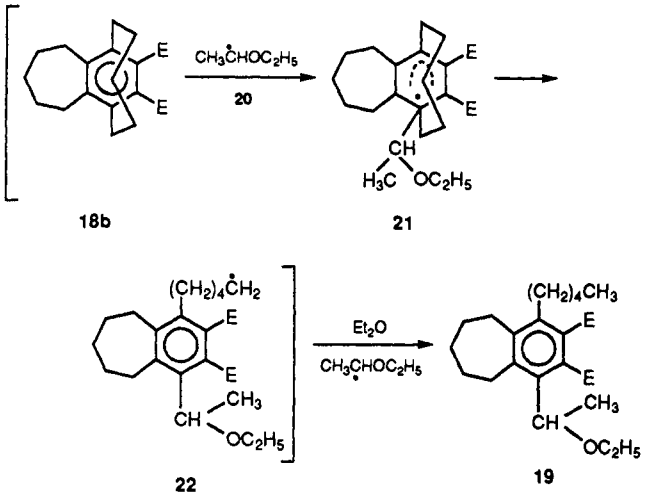
Scheme V. Proposed Mechanism for the Formation of 16



considerable amount of decomposition; after workup only 70% of the material remains, sometimes even less, especially if the irradiation wavelength is decreased. Experiments with wavelengths below 280 nm lead mainly to decomposition. Second, we obtain an unanticipated product with structure **19**.

To rationalize the occurrence of **17b** and **19**, we assume two different reaction paths for **14b**: i) [2 + 2]cycloaddition leading to prismane **17b** and (ii) aromatization affording [5]paracyclophane **18b** as the primary product. On the basis of the work of Bickelhaupt et al., it is reasonable to assume that **18b** is not stable under the given conditions.[26] The attack of ethoxyethyl radical **20** at the bridgehead carbon of **18b** leads to radical π-complex **21**; rearomatization to **22** occurs with cleavage of the highly strained para bridge, and finally abstraction of a hydrogen from a second solvent molecule affords **19** and **20** and maintains the radical chain (see Scheme V). A similar radical sequence has been reported for a thermal addition of diethyl ether to the central C–C bond of [2.1.1]propellane, which is also highly strained.[27] Further experiments done by others have shown that paracyclophane intermediates can be intercepted by the addition of acid[28] or solvent molecules[29] to the 1,4-position. Furthermore, a thermal cleavage of the para bridge has been observed at the benzylic bond.[30] This result is in contrast to our example, in which the cleavage took place at the phenylic bond as a result of the different mechanism. Consequently, the existence of **19** can be considered as indirect evidence for [5]paracyclophane intermediate **18b**. This is the first report of a combination of solvent attack and cleavage of the para bridge, the driving force being the release of strain energy.

(b) Photochemistry of Dewar benzene 14c. The photochemistry of higher homologue **14c**, the Dewar benzene with hexamethylene chains, is determined by the fact that now the product of aromatization, [6]paracyclophane **18c**, is stable (see Scheme VI).[25] Irradiations of Dewar benzene **14c** and paracyclophane **18c** reveal a photochemical equilibrium between these compounds. This equilibrium is independent of the wavelength in the examined range, between 254 and 320 nm, and favors **18c** (80:20). The diagrams in Figure 1 have been constructed from ^{1}H NMR studies of photolyses of **18c** and **14c** at $\lambda \geq 320$ nm.

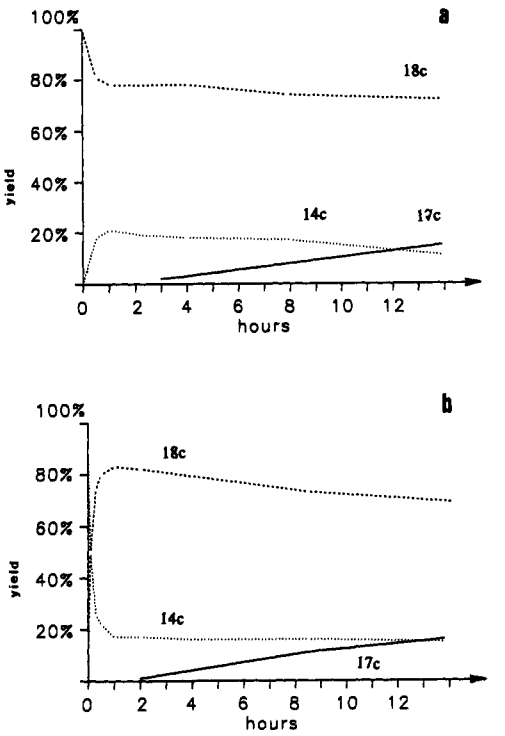


Figure 1. Course of photolyses of (a) **18c** and (b) **14c**.

Scheme VI. Photochemistry of 14c

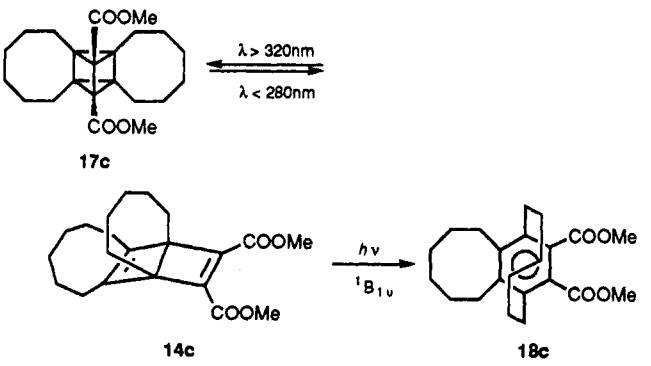
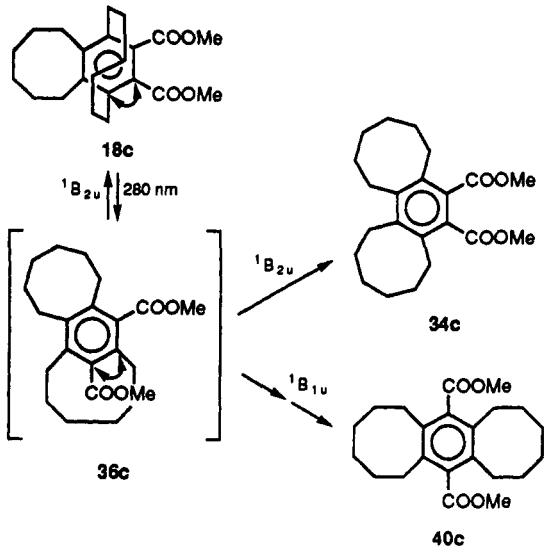


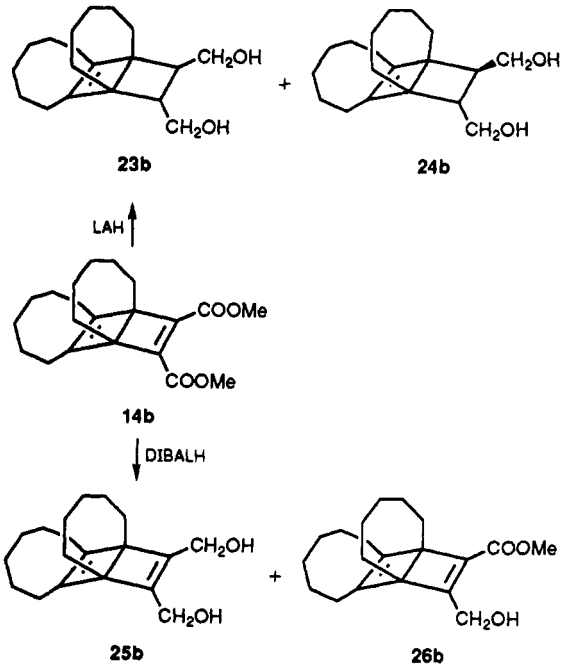
Figure 1a shows that after irradiation of a pure sample of [6]paracyclophane **18c** for about 1 h, a maximum of 20% of **14c** is generated. Analogously, Figure 1b shows a large decrease in Dewar benzene **14c** (containing 10% of **18c**) from 90% initially to 17% after 1 h of irradiation under similar conditions. These figures show that in both experiments equilibrium concentrations are obtained after 30 to 45 min. After 2 h, a new compound is detected by the appearance of a new methoxy resonance. Its concentration increases until after 14 h Dewar benzene **14c** is outstripped; consequently the concentrations of **14c** and **18c** are decreasing. Analytical data and an X-ray study[31] reveal the new compounds to be prismane **17c**. Further studies reveal a photoequilibrium, between Dewar benzene

(25) Gleiter, R.; Treptow, B. *Angew. Chem.* **1990**, *102*, 1452. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1427.
(26) Kostermans, G. B. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1987**, *43*, 2955 and refs cited therein.
(27) Fuchs, J.; Szeimies, G. *Chem. Ber.* **1992**, 2517.
(28) Kostermans, G. B. M.; Kwakman, P. J.; Pouwels, P. J. W.; Somson, G.; de Wolf, W. H.; Bickelhaupt, F. *J. Phys. Org. Chem.* **1989**, 331.
(29) Tsuji, T.; Nishida, S. *Chem. Commun.* **1987**, 1189.
(30) van Straten, J. W.; Turkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 89.
(31) Irngartinger, H.; Oeser, T.; Gleiter, R.; Treptow, B., unpublished.

Scheme VII. Photochemistry of [6]Paracyclophane 18c at λ ≥ 280 nm



Scheme VIII. Hydrogenation of 14b



14c and prismane 17c, which depends strongly on the applied wavelength. At λ ≥ 280 nm, the prismane portion in the mixture amounts to 2%; at shorter wavelengths no prismane 17c is observed. At λ ≥ 320 nm the concentration of 17c increases almost linearly with irradiation time as already demonstrated in Figure 1. On a preparative scale, 17c can be obtained in 30% yield after workup. The reaction should be stopped after 12 h because increasing amounts of byproducts appear. Photolysis of 14c at λ ≥ 280 nm affords two further photoproducts, aromatic species 34c and 40c in 12 and 6% yields, respectively.

A plausible explanation for the observed behavior of prismane 17c is that prismane formation is less efficient than prisame decomposition, or, in other words, the quantum yield for the reaction 14c → 17c is lower than that for the reverse process 17c → 14c. The lower quantum yield for the reaction 14c → 17c implies that at shorter wavelengths almost any prismane molecule generated undergoes a rapid [2 + 2]cycloreversion back into Dewar benzene 14c. At wavelengths higher than 320 nm, the prismane's UV absorption decreases so much that it does not participate in the photostationary state anymore; in this range of UV light, the prismane's absorption is negligibly small, so its amount in the mixture increases with irradiation time.

Aromatic compounds 34c and 40c can be accounted for as secondary photolysis products of [6]paracyclophane 18c. It must be assumed that ring transposition processes occur via [6]metacyclophane intermediate 36c (see Scheme VII). A plausible mechanism will be presented later in connection with the photochemistry of Dewar benzenes of type 15. An alternative and obvious explanation for the generation of terephthalic ester 40c is the possibility of a cleavage of the distal bonds in prismane 17c resulting in a Dewar benzene of type 28 (Scheme IX, with COOMe instead of CH_2OH), which in turn may aromatize to 40c. This option can be ruled out as photochemical [2 + 2]-cycloreversion occurs exclusively at the distal bonds and affords only original Dewar benzene 14c and its photolysis product [6]paracyclophane (18c).[31]

Investigation of Factors Controlling Prismane Formation. The preliminary conclusion of the preceding section is that 1,4-bridged Dewar benzenes of type 14 are suitable precursors for prismanes. What remains is the elucidation of the nature of the driving force. In the following discussion we will try to determine the roles of steric and electronic factors.

(a) Photochemistry of Strain-Activated Dewar Benzene 25b. We first removed the electronic factor by changing the ester groups to functionalities that are not capable of conjugation. Hydroxymethylene compound 25b meets all the requirements. The transformation of 14b to 25b is not as simple as it appears at first glance because reduction with lithium aluminium hydride (LAH) fails. LAH preferentially hydrogenates the double bond before it attacks the ester groups and affords a 4:1 mixture of unwanted products 23b and 24b.[32] Therefore, we decided to try the "ate" complex composed of diisobutylaluminum hydride (DIBALH) and butyllithium, a sterically hindered reducing agent that has been successfully used in a similar reduction.[33] The reaction of 14b with this complex afforded bis(hydroxymethylene)Dewar benzene 25b as the main product and monoreduced compound 26b as a side product in yields of 62 and 13%, respectively (Scheme VIII).

In 25b because of the isolated double bonds, the absorption spectrum is blue shifted in comparison to that of conjugated diester 14b. Hence, it is not unexpected that we do not observe any photoreaction in the longer wavelength range, above 320 nm, which for the diesters is the typical prismane generation range. At shorter wavelengths, with λ ≥ 280 nm, the experiment is more successful. Following the reaction by ^1H NMR, examination of the hydroxymethylene resonances reveals the consecutive generation of three compounds.

Figure 2 shows the ^1H NMR of a photolysis reaction after 3 h. In addition to the multiplet of 25b, there are three singlets; therefore, all three compounds must be of higher symmetry than 25b. After workup, these new compounds were characterized as prismane 27b, rearranged Dewar benzene 28b, and its aromatic valence isomer 29b (Scheme IX). The amount of prismane reaches a

(32) Meek, J. S.; Stacy, R. D. J. Org. Chem. 1961, 26, 300.
(33) Anantanarayan, A.; Hart, H. J. Org. Chem. 1991, 56, 991.

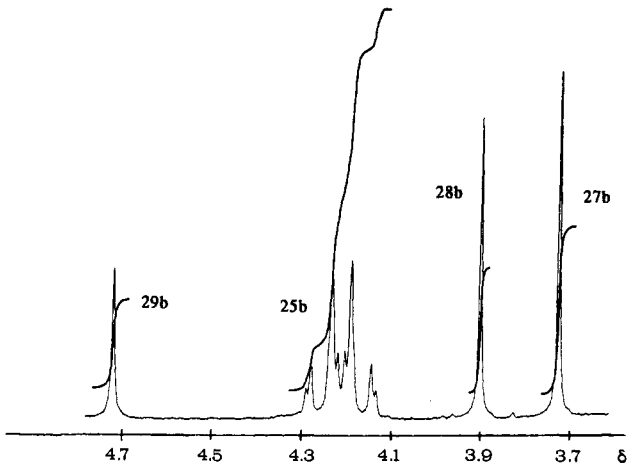
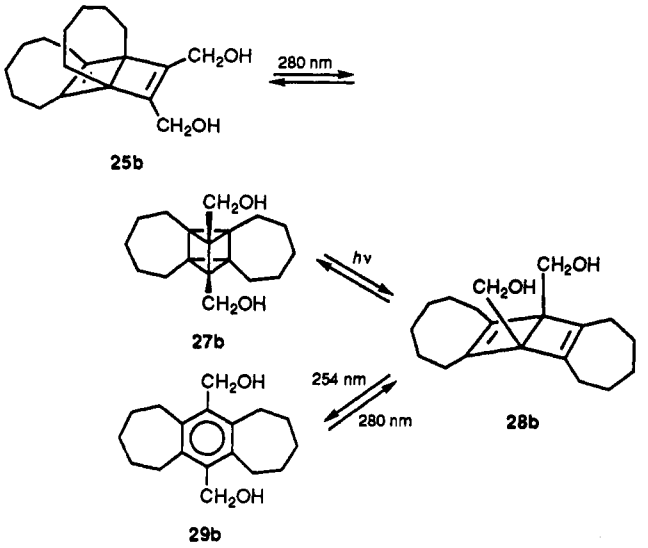


Figure 2. ^{1}H NMR of the (CH_2)OH-section of a photolysis of **25b**.

Scheme IX. Photochemistry of Dewar Benzene 25b

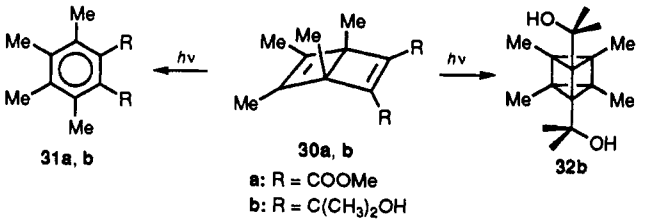


maximum of almost 30% after about 3 h of irradiation and decreases after that in favor of Dewar benzene **28b**, which is derived from **27b** by a cleavage of the distal cyclopropane bonds.

The photochemical behavior of Dewar benzene **28b** is remarkable. Cleavage of the 1,4-bridge in this compound should be strongly thermodynamically favored because this cleavage would lead to the formation of aromatic valence isomer **29b**. However, this does not happen. On the contrary, photolysis of a sample of **28b** at 282 nm reveals instead a slow back-reaction to **25b** via prismane **27b**. Only at 254 nm is considerable conversion into benzene **29b** observed; in addition, the back-reaction still takes place. These results show that the absence of an electronic factor does not inhibit prismane formation, the yield is even higher than in the case of diester **14b**. This higher yield is probably due to a decreased absorption of prismane **27b** in the respective UV range, which shifts the Dewar benzene ⇄ prismane equilibrium further to the prismane side.

(b) Photochemistry of Electronically Activated Dewar Benzenes. In a second experiment, the steric factor in the initial compound was removed. There are several Dewar benzene diesters, without a 1,4-bridge, as suitable model systems. For example tetramethyl derivative **30a** can be considered. This compound was studied

Scheme X. Photochemistry of Tetramethyl Dewar Benzenes 30



31a, b **30a, b** **32b**

a: R = COOMe
b: R = $C(CH_3)_2OH$

in 1966 by Criegee and co-workers. They found that upon photolysis only isomeric phthalic ester **31a** was obtained.[34] However, from **30b**, in which the electronic factor has been exchanged against a steric factor, they obtained prismane **32b** as well as **31b** and further photoproducts (Scheme X).[35]

Dewar benzenes of type **15**, originally only considered as byproducts, are even more appropriate models because of the presence of two bridges. Because the bridges span the 1,2- and 3,4-positions they do not cause too much strain; consequently, in comparison to Dewar benzenes **14**, the steric factor is negligible. Irradiation of compounds **15a**, **15b**, and **15c** in the range above 300 nm always affords rapidly and exclusively the respective phthalic esters, **34a**, **34b**, and **34c**.[36] No trace of prismanes **33** can be detected, nor is there any indication of a photoequilibrium between Dewar benzenes **15** and phthalic esters **34**. A prismane of type **33** would have been a precursor to a propella[n_3]-prismane **C** of C_{2v} symmetry (Scheme II).

Summarizing the results obtained so far, we can state that a steric factor is the main cause for prismane formation and that electronic effects seem to be small. One apparent contradiction should be discussed briefly. As shown above, "non-strained" Dewar benzene **28b** undergoes a cycloaddition to afford prismane **27b** rather than the expected aromatization. A plausible explanation is based on the assumption that a hydrogen bridge bond between the hydroxymethylene groups in **28b** can be involved. Thus, the Dewar benzene would have a pseudo bridge in the 1,4-position, and, consequently, a steric factor would be present. So far we have not succeeded in obtaining an X-ray structure of **28b** to verify this hypothesis.

An Unexpected Phthalic Ester/Terephthalic Ester Rearrangement. The photochemistry of Dewar benzenes **15** in the long wavelength range has already been discussed in the preceding section. During our investigations, we found that in the short wavelength band, below 300 nm, these compounds reveal a complex and fascinating photochemistry.[36] Irradiation of phthalic esters **34b** and **34c** (or their Dewar benzene precursors **15b** and **15c**) at 254 nm unexpectedly affords isomeric terephthalic esters **40b** and **40c** (Scheme XI). In the case of **34a**, no such transformation is observed. It is apparent that ring transposition processes are responsible for these rearrangements, although we could not detect any intermediates under these conditions. Consequently, we had to increase the irradiation wavelength in order to decrease the reaction rate and thus stabilize some of the intermediates. Indeed, irradiation of **34b** at 280 nm yields two other compounds, prismane **38b** and Dewar benzene **39b**. The reaction can be nicely monitored by ^{1}H NMR using

(34) Criegee, R.; Zanker, F. *Chem. Ber.* **1965**, *98*, 3838.
(35) Criegee, R.; Askani, R.; Grüner, H. *Chem. Ber.* **1967**, *100*, 3916.
(36) Gleiter, R.; Treptow, B. *Angew. Chem.* **1992**, *104*, 879. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 862.

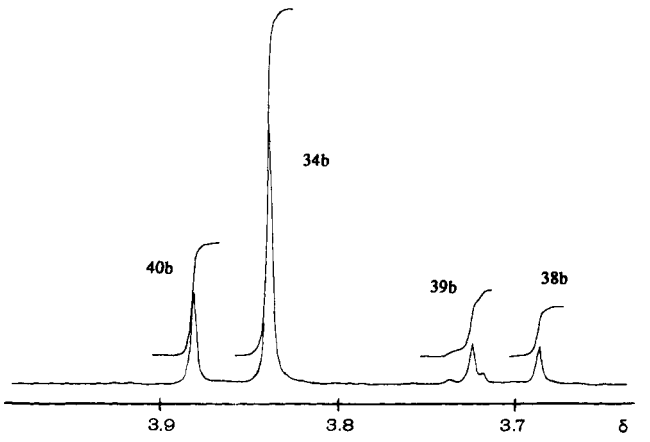
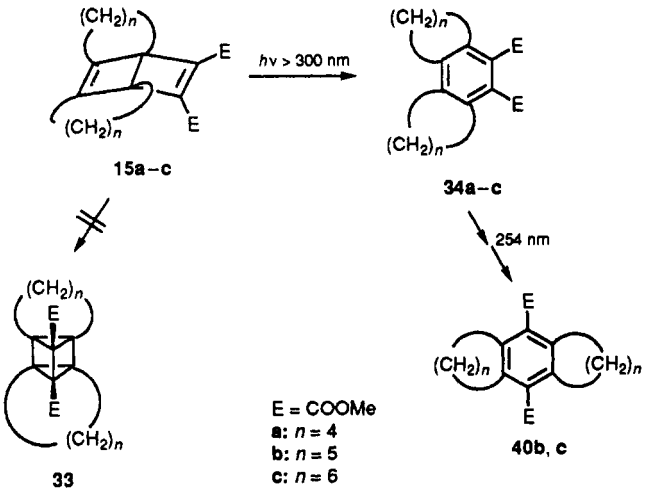


Figure 3. ^{1}H NMR of the COOCH_3-section of a photolysis of **34b**.

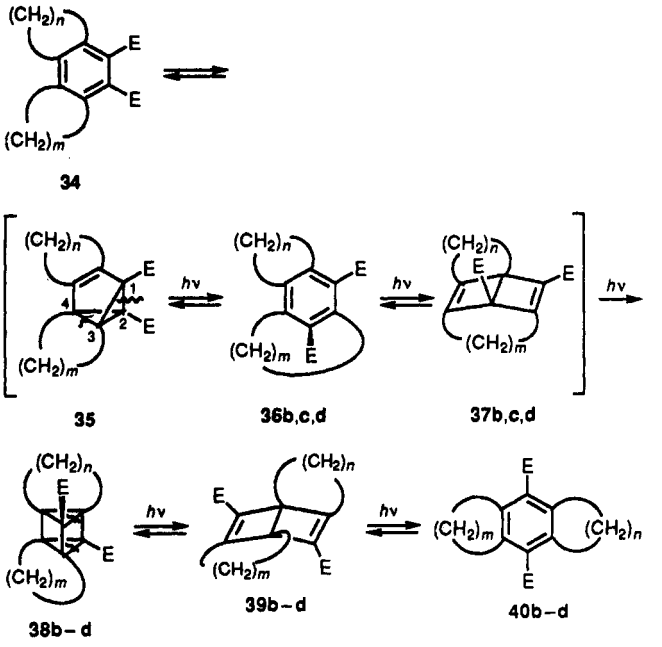
Scheme XI. Photolysis of Dewar Benzenes 15 at λ > 300 nm



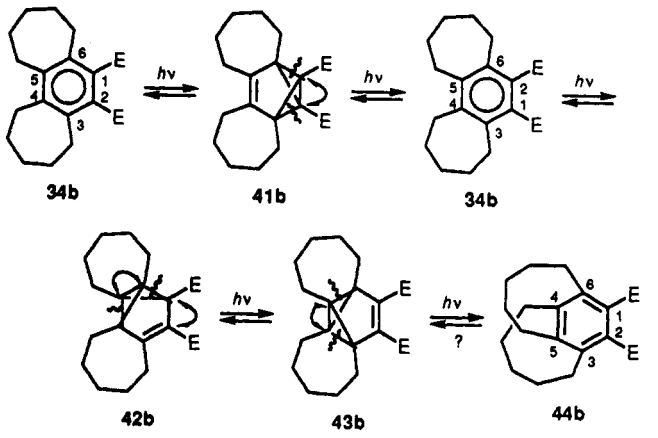
the methoxy singlets as indicators. Figure 3 shows the ^{1}H NMR section of a photolysis of **34b** after 48 h. The amount of intermediates **38b** and **39b** reaches a maximum before it declines in favor of final product **40b**. Because the amount does not exceed 10%, it is important to interrupt the photolysis at the maximum point in intermediate formation. Both compounds **38b** and **39b** prove to be consecutive precursors of **40b**: selective [2 + 2]cycloreversion of **38b**, as shown in Scheme XII, leads to Dewar benzene **39b**, which in turn aromatizes by electrocyclic cleavage of the central 1,4-bond. This result is consistent with the result of irradiation at 282 nm: in the case of Dewar benzene **39b**, 10% starting material **34b** and 90% product **40b** are obtained. It is notable that prismane **38b** is a precursor to a propella[n_3]prismane **D** of C_2 symmetry (Scheme II); hence, it is not a direct valence isomer of phthalic ester **34b**.

To rationalize these findings, a ring transposition process has to be invoked. The ring transposition probably proceeds by means of a 1,2-exchange via a benzvalene intermediate. This process leads to [5]metacyclophane **36b** and its Dewar isomer **37b** as intermediates. The entire sequence is shown in Scheme XII. Photochemical generation of benzvalenes is a common reaction; they arise from the $^1B_{2u}$ state of benzenes (Scheme I). There are two possible routes for aromatization of benzvalene **35b**. The trivial one is the back-reaction to **34b**; the alternative route consists of a cleavage of the bonds between C1–C2 and

Scheme XII. Phthalic/Terephthalic Ester Rearrangement 34 → 40



Scheme XIII. Scheme XIII. Conceivable Benzvalenes Derived from 34b



C3–C4 resulting in [5]metacyclophane **36b**. The reverse sequence is usually invoked to explain the rearrangement of [5]metacyclophanes to 1,2-bridged arenes, although benzvalene intermediates have not been observed directly.[37]

The only reasonable benzvalene arising from **34b** is **35b**. Other conceivable benzvalenes are described in Scheme XIII. It is easy to see that **41b** and **42b** always lead back to **34b**, because bond cleavage as indicated in **41b** results in an interchange of the two ester groups, and cleavage in **42b** results in an interchange of the termini of a pentamethylene bridge. Consequently, **41b** and **42b** are not observable. Only **43b** might afford highly strained system **44b**, whose existence under the given conditions is very questionable.

After the formation of **36b**, the next two steps, the formation of Dewar benzene **37b** and prismane **38b** (Scheme XII), are logical consequences because the bridge-

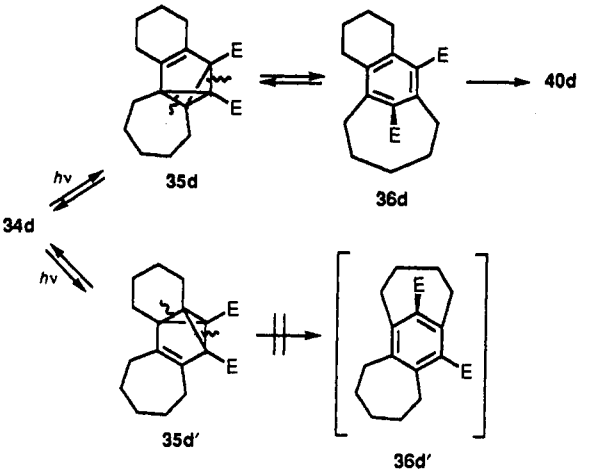
(37) (a) Jenneskens, L. W.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1990**, *112*, 8941. (b) van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977**, 4667.

induced strain is reduced. The geometries of both Dewar benzene **37b** and prismane **38b** are inherent in the assumed boat shaped conformation of **36b**.[38] Prismane formation from a similar bridged Dewar benzene has been described.[18]

So far none of the postulated intermediates in brackets has been isolated and characterized. We attribute this to their low equilibrium concentration and in case of benzvalene **35b**, also to an enhanced reactivity. With the aid of spectroscopy we found the first hint for the existence of **36b** and **37b**. They can be distinguished from the other isomers in this sequence by their lower C_1-symmetry; the ester groups are not equivalent. The ^1H NMR spectrum reveals the presence of two compounds with nonequivalent methoxy groups at an early stage of irradiation. These signals can be considered as the first hint for the presence of **36b** and **37b**, but we still need to devise further experiments to establish their existence.

(a) Modification of the Steric Factor. The steric factor is very important (see the discussion in the preceding section). A steric factor is not present in starting phthalic esters **34**, but is present in metacyclophanes **36**, because of the short 1,3-bridge. Therefore, we altered the chain length and examined the effect of the alternation on the rearrangement. If the bridges are shortened by one CH_2 unit, as in **34a** (m, n = 4), no rearrangement is observed. Even extended irradiation times and shorter wavelengths (254 nm) do not afford **40a**; instead only slow polymerization is observed. The failure of the rearrangement can easily be accounted for with the assumption that potential [4]metacyclophane **36a** is not accessible under the given conditions as a result of its enormous strain energy. Consequently, the entire sequence is interrupted at the second step (**35a** → **36a**). This result is in line with the fact that attempts to synthesize a [4]metacyclophane derivative have not been successful.[18,39] If the bridges are enlarged by one CH_2 unit, as in **34c** (m, n = 6), the rearrangement to **40c** takes place, as mentioned earlier. However, under conditions identical to these used for **34b**, terephthalic ester **40c** is obtained at a reduced rate (30% in comparison to 52% after 12 h) and the equilibrium concentrations of the intermediates are lower. Prismane **38c** could only be detected in the reaction mixture by the typical δ value of protons of the methoxy groups. The explanation could be that, in [6]metacyclophane **36c**, the extended meta-bridge produces less strain, and the strain-releasing steps (steric factor!) leading to **38c** are less important.[40] In Scheme VII, we have already seen this phthalic/terephthalic ester rearrangement in connection with irradiation of [6]paracyclophane **18c** at the same wavelength. The initial step is a 1,2 interchange (via a benzvalene intermediate) converting the highly strained [6]paracyclophane **18c** into less strained [6]metacyclophane **36c**. With this compound as a connecting link, the rearrangement sequence of Scheme XII is entered. Then reactions of **36c** in both directions afford **34c** and **40c**. A similar acid-catalyzed rearrangement of the parent compound [6]paracyclophane to form the ortho isomer has already been reported.[41] These investigations are completed by a third experiment, the irradiation of phthalic ester **34d**, which has a tetra- and a pentamethylene chain (Scheme XIV). In this case, benzvalene **35d'** is responsible for the reduced rate of product formation (24% after 12 h). Although isomer **35d** can react to form **40d** in the usual way, **35d'** represents a dead end because the sequence could only occur via the highly energetic [4]metacyclophane **36d'**.

Scheme XIV. Reaction Paths for Phthalic Ester 34d



(a) Modification of the Electronic Factor. In this rearrangement series, the electronic factor is not negligible, because of the irreversibility of the prismane formation step (**37** → **38**). Interaction of the carbomethoxy groups with the cyclopropane moieties of a prismane body leads to a stabilization of the distal bonds and a destabilization of the vicinal bonds as indicated by the bond lengths. This interaction was substantiated by X-ray investigations of substituted cyclopropane systems[42] and substituted prismanes.[4,7] In the case of prismane **38b**, a significant shortening of the distal bonds and a lengthening of the vicinal bonds is observed.[31] Photochemical [2 + 2]-cycloreversion takes place in such a way that destabilized bonds are cleaved selectively. A more elaborate discussion of the photochemistry as well as the molecular structures of prismanes **17b**, **17c**, **27b**, and **38b** is in preparation.[31] Here we only note that with prismanes of type **17**, cleavage along either of the two vicinal cyclobutane faces leads back to the original Dewar benzene precursors **14**. However, in the case of prismanes of type **38**, containing exactly one cyclobutane face with two destabilized cyclopropane edges, the reaction leading to Dewar benzenes of type **39** is favored, and back-reaction to precursors **37** is supressed. Thus, the equilibrium is shifted to the product side. In the case of the **34b**/**40b** rearrangement, an educt/product ratio of 1:9 is possible. This reasoning can be supported by an additional experiment. We synthesized compound **45b** by reduction of **34b** with LAH. With hydroxymethyl groups as substituents, no conjugation with the cyclopropane moieties of a hypothetical prismane **47b** is possible, and prismane formation should be reversible. Hence, we expected to obtain **29b** in considerably lower yield, as in the diester case. The experiment reveals that this exchange leads to an even more dramatic change in reactivity: we did not obtain any rearranged product, either at 282 nm or at 254 nm (Scheme XV). We conclude that a tuned

(38) For an X-ray structure of a [5]metacyclophane see: Jenneskens, L. W.; Klamer, J. C.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. *Angew. Chem.* **1984**, *96*, 236. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 238.

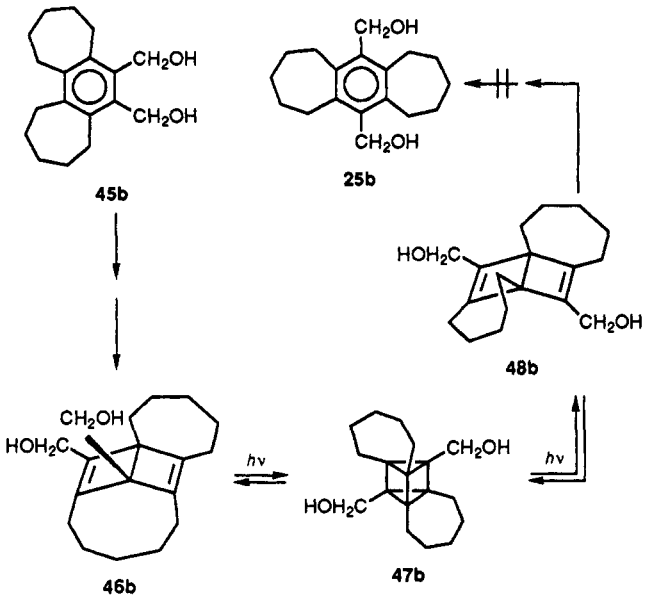
(39) Kostermans, G. B. M.; van Dansik, P.; de Wolf, W. H.; Bickelhaupt, F. *J. Org. Chem.* **1988**, *53*, 4531 an refs cited therein.

(40) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409. Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.

(41) Tobe, Y.; Ueda, K.-I.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron*, **1986**, *42*, 1851.

(42) Allen, F. H. *Acta Crystallogr. Sect. B* **1980**, *36*, 81.

Scheme XV. Photolysis of Benzene Derivative 45b



interplay between steric and electronic factors is responsible for this unexpected rearrangement between doubly bridged phthalic/terephthalic esters.

Conclusion and Outlook

Irradiation of Dewar benzenes with short methylene bridges spanning the 1,4- and 2,3-positions (**14b**, **14c**, **25b**) affords the expected doubly bridged prismanes **17b**, **17c**, and **27b**. A comparison of ester and hydroxymethylene substituents in the 5,6-position shows that, in this case, steric effects dominate prismane generation. However, this domination is changed when Dewar benzenes with bridges spanning the 1,2- and 3,4 positions (**15**) are irradiated. After a rapid aromatization, a phthalic/terephthalic ester rearrangement (**34** → **40**) with the occurrence of prismane intermediates (**38**) follows. This outcome can only be rationalized by the assumption that there is a subtle interplay between electronic and steric factors. The electronic effect induced by the ester substituents is responsible for prismane stability, and the steric factors control prismane formation; the driving force is the release of bridge induced strain in the assumed metacyclophane intermediates (**36**).

Three prismanes (**17b**, **17c**, and **27b**) are precursors to propella[n_3]prismanes ($n = 5, 6$) with the highest symmetry (D_{3h}), and the fourth (**38b**) is a precursor to a prismane with the lowest symmetry (C_2, see Scheme II). Currently we are continuing our work on the construction of the third bridge. Because the doubly bridged Dewar benzenes and prismanes revealed an interesting chemistry, we eagerly anticipate the chemistry of the triply bridged compounds.

Experimental Section

1. General. Unless indicated otherwise, spectra were recorded on the following instruments: NMR, Bruker WM 300 and Bruker AS 200; IR, Perkin-Elmer 580B; UV, Varian Cary 17D and Hewlett Packard 8452A; HRMS, ZAB Vacuum Generators. Elemental analyses were carried out by the Mikroanalytisches Labor, University of Heidelberg. Prior to use, all solvents were dried. All reactions were carried out under an argon atmosphere. Irradiations: All photolyses are carried out in degassed diethyl ether. For the 20-mL vessel, a high-pressure mercury lamp OSRAM HBO 500 W/2 was used in a lamp housing type Oriel Corp. 66187. Wavelength selection was achieved with cutoff filters from Fa. Schott, Mainz. For the 250-mL and 500-mL photoreactors, a high-pressure mercury lamp Philips HPK 125 W was used in water-jacketed immersion wells from Fa. Peschl, Mainz. An immersion well of quartz glass served for the irradiations at $\lambda = 254$ nm, one of modified quartz glass for those at $\lambda \geq 280$ nm, and one of DURAN glass for those at $\lambda \geq 320$ nm.

2. Preparative Experiments. General Procedure for Dewar Benzenes 15a, 15d, 14b, and 15b. A slurry of 1.34 g (10 mmol) of $AlCl_3$ (sublimed) and 10 mL of CH_2Cl_2 is cooled to −40 °C, and a solution of 10 mmol of the cycloalkadiyne (**12a**, **12d**, or **12b**) in 10 mL of CH_2Cl_2 is added slowly. The color of the solution turns to red; the $AlCl_3$ is dissolving. The solution is allowed to warm to rt, stirred for 30 min, and cooled to −20 °C. Solutions of 2.84 g (20 mmol) of dimethyl acetylenedicarboxylate (DMAD) in 10 mL of CH_2Cl_2 and 5 mL of dimethyl sulfoxide (DMSO) in 20 mL CH_2Cl_2 are added successively. The mixture is poured onto 80 mL of ice–water/80 mL of pentane and separated, the aqueous layer is extracted twice with 40 mL of pentane, and the organic layer is dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude products are purified by column chromatography (silica gel, CH_2Cl_2). The two isomeric Dewar benzenes (**14b** and **15b**) usually require a second column chromatographic step to be separated from each other. The second chromatography affords 30% **14b**, 13% **15b**, and 17% mixture.

(a) Dimethyl Tetracyclo[10.2.0.0^{1,6}.0^{7,12}]tetradeca-6,13-diene-13,14-dicarboxylate (15a):[23] yield 1270 mg (42%), viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 6H), 2.4–2.25 (m, 2H), 2.15–1.65 (m, 10H), 1.5–1.0 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 163.8, 150.3, 139.1, 57.6, 52.4, 27.0, 25.2, 24.5, 23.3; UV/vis (acetonitrile) λ_{max} [nm] (log ϵ) 188 (4.23), 235 sh (3.67). Anal. calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.41; H, 7.59.

(b) Dimethyl Tetracyclo[11.2.0.0^{1,6}.0^{7,13}]pentadeca-6,14-diene-14,15-dicarboxylate (15d):[23] yield 820 mg (26%), viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.77 (s, 3H), 2.35–2.25 (m, 2H), 2.2–1.1 (m, 16H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 163.3, 163.25, 150.4, 149.3, 143.5, 141.4, 62.7, 54.5, 51.6, 51.55, 31.1, 28.8, 28.1, 27.7, 27.65, 26.5, 24.4, 24.2 , 22.9; HRMS calcd for $C_{18}H_{20}O_3$ ($M^+ - CH_3OH$) 284.1413, found 284.1386.

(c) Dimethyl Tetracyclo[12.2.0.0^{1,7}.0^{8,14}]hexadeca-7,15-diene-15,16-dicarboxylate (15b):[23] yield 425 mg (13%), viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.77 (s, 6H), 2.4–1.2 (m, 20H); ^{13}C NMR (50.32 MHz, CD_2Cl_2,) δ 163.5, 150.3, 146.5, 60.4, 51.6, 31.1, 28.6, 28.4, 28.1, 27.2; UV/vis (acetonitrile) λ_{max} [nm] (log ϵ) = 196 (4.08), 244 sh (3.05); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) 330.1831, found 330.1842.

(d) Dimethyl Tetracyclo[7.5.2.0.0^{2,8}]hexadeca-2,15-diene-15,16-dicarboxylate (14b):[23] yield 1000 mg (30%), viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.76 (s, 6H), 2.3–1.1 (m, 20H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 162.8, 151.2, 147.7, 61.1, 51.5, 33.2, 29.2, 28.5, 28.4, 27.6, 26.5; UV/vis (acetonitrile) λ_{max} [nm] (log ϵ) 190 (4.41), 240 sh (3.84); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) 330.1831, found 330.1862.

Preparation of Dimethyl Tetracyclo[14.2.0.0^{1,8}0^{9,16}]octadeca-8,17-diene-17,18-dicarboxylate (15c) and Dimethyl Tetracyclo[8.6.2.0.0^{2,9}]octadeca-2(9),17-diene-17,18-dicarboxylate (14c). A slurry of 2 g (0.15 mmol) of $AlCl_3$ (sublimed) and 150 mL of CH_2Cl_2 is cooled to −40 °C, and a solution of 3.18 g (0.29 mmol) of cyclooctyne **16** in 100 mL of CH_2Cl_2 is added slowly. The solution is allowed to warm to rt, stirred for 30 min, and cooled to −20 °C. Solutions of 4.2 g (30 mmol) of DMAD in 50 mL of CH_2Cl_2 and 5 mL of DMSO in 95 mL of CH_2Cl_2 are added successively. The mixture is poured on 150 mL of ice–water/150 mL of pentane and separated; the aqueous layer is extracted twice with 50 mL of pentane, and the organic layer is dried over Na_2SO_4 and concentrated on a rotary evaporator. Purification of the two isomeric Dewar benzenes is difficult and tedious and requires two consecutive column chromatographic steps. First, a separation from side products affords a 32% of a mixture; and second, a separation of the two Dewar benzenes (silica gel, CH_2Cl_2, 35 cm, 50 mm) affords 9% **15c**, 12% **14c**, and 10% mixture.

15c: yield 480 mg (9%), viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.77 (s, 6H), 2.45–2.25 (m, 2H), 2.1–0.8 (m, 22H); ^{13}C NMR

(75.46 MHz, $CDCl_3$) δ 163.3, 151.1, 148.5, 61.5, 51.6, 28.4, 28.0, 25.7, 25.1, 24.5, 23.6; UV/vis (acetonitrile) λ_{max} [nm] (log ε) 208 (3.9), 246 sh (3.51); HRMS calcd for $C_{21}H_{26}O_3$ ($M^+ - CH_3OH$) 326.1882, found 326.1871.

14c: yield 630 mg, viscous oil; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 6H), 2.3–1.8 (m, 8H), 1.8–1.2 (m, 16H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 162.8, 152.3, 147.1, 61.3, 51.6, 26.7, 26.6, 26.2, 25.3, 24.1, 23.8; UV/vis (acetonitrile) λ_{max} [nm] (log ε) 195 (4.12); HRMS calcd for $C_{22}H_{30}O_4$ (M^+) 358.2144, found 358.2115.

Preparation of Dimethyl Hexacyclo[9.5.0.0^{1,5}.0^{2,10}.0^{3,9}.0^{9,11}]-hexadecane-2,10-dicarboxylate (17b) and 19. Dewar benzene **14b** (500 mg, 1.52 mmol) is dissolved in 500 mL of diethyl ether and irradiated for 48–60 h. (λ ≥ 320 nm, 125-W lamp, 10 °C). After removal of the solvent, the crude mixture is separated by column chromatography (neutral alumina III, petroleum ether/ether 4:1) Note: The yield in **17b** depends on the purity of the starting material.

14b: recovered 150 mg (30%).

17b: yield 75 mg (15%); mp 102 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 6H), 1.73 (s, br, 20H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 169.7, 57.0, 51.0, 42.2, 32.2, 30.8, 24.5; UV/vis (acetonitrile): λ_{max} [nm] (log ε) 208 (3.95), 248 sh, (3.34); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) 330.1831, found 330.1822; the molecular structure was obtained by an X-ray analysis.[31]

19: yield 120 mg (24%), viscous, colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 4.64 (q, ^3J(H,H) = 6.7 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.4–3.1 (m, 2H), 3.0–2.8 (m, 4H), 2.7–2.4 (m, 2H), 1.8–1.7 (m, 2H), 1.7–1.4 (m, 6H), 1.57 (d, ^3J(H,H) = 6.7 Hz, 3H), 1.4–1.2 (m, 4H), 1.1 (t, ^3J(H,H) = 7.0 Hz, 3H), 0.9 (m, 3H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 170.3, 169.7, 144.7, 144.0, 136.4, 136.0, 130.5, 129.2, 75.8, 65.1, 52.2, 52.0, 32.1, 31.3, 30.9, 30.8, 28.8, 28.5, 26.9, 26.7, 22.4, 22.3, 14.9, 13.9; UV/vis (ether) λ_{max} (log ε) 212 (4.44), 245 sh (3.72); HRMS calcd for $C_{24}H_{36}O_5$ ($M^+ - CH_3O$) 373.2379, found 373.2389.

Preparation of Dimethyl Hexacyclo[10.6.0.0^{1,5}.0^{2,11}.0^{5,10}.0^{10,12}]-octadecane-2,11-dicarboxylate (17c) and [6]Paracyclophane 18c. Dewar benzene **14c** (500 mg, 1.40 mmol) is dissolved in 500 mL of dry diethyl ether and irradiated for 24–36 h (λ ≥ 320 nm, 125-W lamp, 10 °C). After removal of the solvent, the crude mixture is separated by column chromatography (neutral alumina III, petroleum ether/ether 4:1).

14c: recovered 60 mg (12%).

17c: yield 150 mg (30%); colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 3.64 (s, 6H), 1.95–1.1 (m, 24H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 169.8, 57.0, 51.0, 43.0, 26.6, 25.6, 20.9; UV/vis (acetonitrile) λ_{max} [nm] (log ε) 195 (3.92), 250 sh (3.34); HRMS calcd for $C_{24}H_{30}O_4$ (M^+) 358.2144, found 358.2164; the molecular structure was obtained by an X-ray analysis.[31]

18c: yield 250 mg (50%); slightly yellowish oil; ^1H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 6H), 3.2–3.0 (m, 3H), 3.0–2.6 (m, 5H), 2.0–1.0 (m, 14H), 1.0–0.5 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 169.0, 144.8, 140.9, 50.6, 33.9, 32.3, 31.8, 28.0, 26.4, 26.0(note: the missing aromatic resonance can only be detected in a low-temperature spectrum at 253 K as doublet at 133.9 and 127.4); UV/vis (CH_2Cl_2) λ_{max} [nm] (log ε) 247 (4.25), 280 (3.65), 333 (3.15); HRMS calcd for $C_{24}H_{30}O_4$ (M^+) 358.2144, found 358.2115.

Preparation of *syn*-15,16-Bis(hydroxymethyl)tetracyclo-[7.5.2.0.0^{2,8}]hexadeca-2(8)-ene (23b) and *anti*-15,16-Bis-(hydroxymethyl)tetracyclo[7.5.2.0.0^{2,8}]hexadeca-2(8)-ene (24b). Direct reduction with $LiAlH_4$ is nonuniform; successive reductions with $NaBH_4$ and $LiAlH_4$ afford better yields and easier workup. To a solution of 2.25 g (6.8 mmol) of **14b** in 100 mL of dry ethanol is added 0.26 g (6.8 mmol) of $NaBH_4$ in 15 mL ethanol. The mixture is stirred for 3 h, and some drops of a saturated brine solution are added. Then the mixture is extracted four times with diethyl ether. The extract is dried over Na_2SO_4, and, after removal of the solvent, 2.2 g of crude product are obtained. GC/MS shows three signals with M^+ = 300, 314, and 360 in a ratio of 0.15:0.20:0.65 (note: a partial reesterification with ethanol has taken place). This crude product is dissolved in a little dry diethyl ether and added slowly to a solution of 0.32 g (6.5 mmol) $LiAlH_4$ in 15 mL of ether in a 100-mL flask. The resulting mixture is refluxed for 100 h. Then 0.3 mL of water and 0.3 mL of a sodium hydroxide solution (15%) are added successively with stirring, until a grainy precipitate forms. This precipitate is filtrated and washed with ether, the organic layer is dried (Na_2SO_4), and the solvent is removed. After column chromatography (silica gel, diethyl ether) **23b** and **24b** are obtained in a ratio of 4:1.

23b: yield 1.2 g (64%); ^1H NMR (200 MHz, $CDCl_3$) δ 3.85–3.55 (m, 4H), 3.2–2.8 (s, br, 2H), 2.5–2.3 (m, 2H), 2.1–0.9 (m, 20H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 145.8, 61.7, 52.7, 43.2, 33.7, 33.4, 29.6, 29.1, 29.0, 26.6; UV/vis (ethanol) λ_{max} (log ε) = 198 (3.68); HRMS calcd for $C_{18}H_{28}O_2$ (M^+) 276.2089, found 276.2065.

24b: yield 0.3 g (16%); ^1H NMR (300 MHz, $CDCl_3$) δ 3.85–3.7 (m, 2H), 3.58 (t, ^3J(H,H) = 10.1 Hz, 1H), 3.4 (t, ^3J(H,H) = 10 Hz, 1H), 2.3–0.8 (m, 24H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 149.0, 144.2, 64.5, 64.4, 52.6, 52.55, 50.1, 44.3, 35.5, 33.4, 29.32 (2×), 29.29, 28.8, 27.7, 26.8, 26.6, 26.0; HRMS calcd for $C_{18}H_{28}O_2$ (M^+) 276.2089, found 276.2067.

Preparation of 15,16-Bis(hydroxymethyl)tetracyclo[7.5.2.0.0^{2,8}]hexadeca-2(8),15-diene (25b) and Methyl 15-(Hydroxymethyl)-tetracyclo[7.5.2.0.0^{2,8}]hexadeca-2(8),15-diene-16-carboxylate (26b).[33] In a 250-mL Schlenk tube, a solution of 50 mL of THF and 26 mL of 2.5 M *n*-butyllithium in hexane is cooled to −22 °C. 1 M diisobutylaluminum hydride (65 mL) in hexane is added dropwise under stirring. At the same temperature, stirring is continued for 3 h more. Then, the solution of this "ate complex" is added via cannula into a Schlenk tube containing 4.95 g (15 mmol) **14b** (dissolved in 50 mL of THF) at −78 °C. This procedure takes 1–1.5 h. The mixture is allowed to warm to rt, and stirring is continued for 1 h more. Subsequently the mixture is *cautiously* quenched with 15 mL of 50% aqueous methanol, poured on 13 g of $Na_2SO_4 \cdot 6H_2O$ and 95 mL of THF, slightly warmed for 30 min, and filtered over a pad of Celite. The filter cake is washed once with 100 mL of THF, and the combined organic layers are concentrated on a rotary evaporator. Washing the crude product twice with cold diethyl ether affords 2.05 g of pure **25b** as fine white crystals. The ether extract, after column chromatography (silica gel, diethyl ether), affords another 0.5 g of **25b** and 0.6 g of **26b**.

25b: yield 2.55 g (62%), mp 167 °C, white powder; ^1H NMR (300 MHz, $CDCl_3$) δ 4.23 (m, 4H), 2.2–1.2 (m, 22H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 148.9, 147.2, 59.7, 59.1, 33.5, 29.5, 28.9, 28.7, 28.2, 26.6; UV/vis (diethyl ether) λ_{max} (log ε) 202 (3.69), 228 sh (3.25). Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.79; H, 9.71. Found: C, 78.60; H, 9.55; the molecular structure was obtained by an X-ray analysis.[43]

26b: yield 0.6 g (13%); viscous oil; ^1H NMR (300 MHz, $CDCl_3$) δ 4.9 (t, ^3J(H,H) = 4.9 Hz, 1H), 4.38 (m, 2H), 3.7 (s, 3H), 2.25–1.2 (m, 20H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 173.7, 166.3, 150.1, 146.2, 137.4, 61.7, 60.4, 59.5, 51.6, 33.3, 29.3, 29.2, 28.6, 28.5, 28.4, 28.1, 27.6, 26.43, 26.40; UV/vis (diethyl ether) λ_{max} (log ε) = 196 (3.87), 248 sh (3.46); HRMS calcd for $C_{19}H_{26}O_3$ (M^+) 302.1882, found 302.1848.

Preparation of Hexacyclo[9.5.0.0^{1,5}.0^{2,10}.0^{3,9}.0^{9,11}]hexadecane-2,10-dimethanol (27b) and Tetracyclo[7.7.0.0^{2,8}.0^{10,16}]hexadeca-2(8),10(16)-diene-1,9-dimethanol (28b). A solution of 220 mg (0.80 mmol) of **25b** in 250 mL diethyl ether is irradiated for approximately 3 h (NMR control) at λ ≥ 280 nm (125-W lamp, 10 °C). The solvent is removed on a rotary evaporator, and separation of the mixture by column chromatography (silica gel Merck, diethyl ether) affords 45% starting material **25b**, 27% prismane **27b**, and 20% rearranged **28b**. Notes: (1) solvent and starting material **25b** should be of great purity, otherwise the irradiation leads only to decomposition, (2) silica gel for column chromatography should be deactivated by exposure to air moisture for several days, and (3) prismane **27b** should be eluted from the column within 1 h, otherwise rearrangement during chromatography takes place.

25b: recovered 100 mg (45%).

27b: yield 60 mg (27%), colorless crystals; ^1H NMR (200 MHz, $CDCl_3$) δ 3.72 (s, 4H), 2.0–1.2 (m, 22H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 58.3, 46.7, 45.0, 32.5, 32.0, 25.3; HRMS calcd for $C_{18}H_{26}O_2$ (M^+) 274.1932, found 274.1937; the molecular structure was obtained by an X-ray analysis.[31]

28b: yield 45 mg (20%); white powder, ^1H NMR (300 MHz, CD_2Cl_2) δ 3.85 (s, 4H), 2.85 (s, br, 2H), 2.2–1.2 (m, 20H); ^{13}C NMR

(43) Irngartinger, H.; Oeser, T., unpublished results.

(75.47 MHz, CD_2Cl_2) δ 148.0, 61.3, 59.4, 29.9, 29.42, 29.37; UV/vis (diethyl ether) λ_{max} (log ε) 202 (3.84), 230 sh (3.34); HRMS calcd for $C_{18}H_{26}O_2$ (M^+) 274.1932, found 274.1893.

Preparation of Phthalic Esters 34a, 34b, 34c and 34d. The Dewar benzene precursor (**15a**, **15b**, **15c**, or **15d**) (1.5 mmol) is irradiated in 500 mL of diethyl ether at λ ≥ 320 nm (125-W lamp, 10 °C) until the starting material has disappeared (2–3 h, TLC control). After evaporation of the solvent and silica gel filtration (petroleum ether/ether = 4:1), the corresponding phthalic esters are obtained almost quantitatively.

Dimethyl 1,2,3,4,5,6,7,8-Octahydrophenanthrene-9,10-dicarboxylate (34a): colorless crystals; mp 148–150 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 6H), 2.78 (t, $^3J(H,H)$ = 6.0 Hz, 4H), 2.57 (t, $^3J(H,H)$ = 6.1 Hz, 4H), 1.9–1.6 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 169.9, 139.3, 133.1, 130.1, 52.8, 28.4, 27.7, 23.3, 23.0; UV/vis (acetonitrile) λ_{max} [nm] (log ε) = 213 (4.4), 245 sh (3.45), 287 (2.85). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.5; H, 7.30. Found: C, 71.32; H, 7.40.

Dimethyl 1,2,3,4,5,8,9,10,11,12-Decahydrobenzo[1,2:3,4]biscycloheptene-6,7-dicarboxylate (34b): colorless crystals; mp 105 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 6H), 2.91–2.87 (m, 4H), 2.82–2.78 (m, 4H), 1.8–1.5 (m, 12H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 169.9, 143.3, 139.0, 128.9, 52.2, 31.4, 30.8, 29.4, 27.2, 26.6; UV/vis (acetonitrile) λ_{max} [nm] (log ε) 213 (4.45), 240 sh (3.8), 285 (3.15). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.60; H, 7.99.

Dimethyl-1,2,3,4,5,6,9,10,11,12,13,14-Dodecahydrobenzo-[1,2:3,4]biscyclooctene-7,8-dicarboxylate (34c): colorless crystals; mp 138–140 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.83 (s, 6H), 2.9–2.83 (m, 4H), 2.81–2.75 (m, 4H), 1.85–1.55 (m, 8H), 1.5–1.2 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 170.6, 142.4, 138.1, 130.9, 52.8, 32.1, 31.2, 30.6, 28.0, 27.2, 26.7; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ε) = 215 (4.47), 250 sh (3.65), 282 (3.06). Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.89; H, 8.50.

Dimethyl 2,3,4,5,8,9,10,11,-Octahydro-1*H*-naphtho[1.2]-cyclohexen[3.4]cycloheptene-6,7-dicarboxylate (34d): colorless crystals; mp 86 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 6H), 2.85–2.7 (m, 8H), 1.9–1.5 (m, 10H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 169.8, 169.3, 145.3, 138.4, 136.7, 133.3, 129.4, 129.2, 52.2, 52.1, 31.5, 31.3, 28.6, 27.9, 27.9, 27.2, 26.2 and 23.0; UV/vis (acetonitrile) λ_{max} [nm] (log ε) 216 (4.59), 252 sh (3.79), 288 (3.31). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.64. Found: C, 71.99; H 7.54.

Preparation of Prismane 38b, Dewar Benzene 39b, and Terephthalic Ester 40b. 14b and/or **34b** (325 mg, 0.98 mmol) is irradiated in 500 mL of diethyl ether at λ ≥ 280 nm (125-W lamp, 10 °C). To obtain the maximum yields, the experiment should be interrupted after 24–36 h and after about 48 h for **39b** (NMR control). Workup is carried out by column chromatography (neutral alumina III, petroleum ether/ether = 5:1).

34b: recovered 200 mg (61.5%).

Dimethyl Hexacyclo[9.5.0.0^{1,9}.0^{2,11}.0^{3,9}.0^{5,10}]hexadecane-2,-10-dicarboxylate (38b): 30 mg (9.2%); ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 6H), 2.5–2.35 (m, 2H), 2.25–2.1 (m, 2H), 2.0–1.1 (m, 16H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 170.5, 56.0, 54.5, 50.8, 48.4, 32.3, 28.6, 27.9, 24.5, 24.2; UV/vis (*n*-pentane): λ_{max} [nm] (log ε) = 203 (3.85), 270 sh (2.85); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) 330.1831, found 330.1827; the molecular structure was obtained by an X-ray analysis.[31]

Dimethyl Tetracylo[7.7.0.0^{1,11}.0^{3,9}]hexadeca-2,10-diene-2,-10-dicarboxylate (39b): yield 25 mg (7.7%); ^1H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 6H), 2.9–2.7 (m, 2H), 2.5–2.35 (m, 2H), 2.1–1.4 (m, 16H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 173.9, 164.2, 134.6, 59.3, 50.8, 31.2, 30.9, 27.9, 27.3, 27.2; UV/vis (*n*-pentane) λ_{max} [nm] (log ε) = 218 (4.17), 270 sh (3.47); HRMS calcd for $C_{20}H_{26}O_4$ (M^+) 330.1831, found 330.1819.

Dimethyl 1,2,3,4,5,7,8,9,10,11-Decahydrobenzo[1,2:3,4]biscycloheptene-6,12-dicarboxylate (40b): yield 60 mg (18.5%); colorless needles, mp 149 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 6H), 2.7–2.55 (m, 8H), 1.9–1.7 (m, 4H), 1.7–1.5 (m, 8H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 171.1, 137.2, 134.4, 51.9, 32.3, 31.8, 27.2; UV/vis (acetonitrile) λ_{max} [nm] (log ε) = 208 (4.27), 230 sh (3.70), 282 (3.06). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.37; H, 8.21.

Preparation of Dewar Benzene 39c and Terephthalic Ester 40c: photolysis of 250 mg (0.7 mmol) of **15c** and/or **34c** in 500 mL of diethyl ether (λ ≥ 282 nm, 125-W lamp, 10 °C) for 30 h; column chromatography (neutral alumina III, petroleum ether/ether 5:1).

34c: recovered 140 mg (56%).

Dimethyl Tetracyclo[8.8.0.0^{1,12}.0^{3,10}]octadeca-2,11-diene-2,11-dicarboxylate (39c): yield 12 mg (5%); ^1H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 6H), 3.0–2.8 (m, 2H), 2.4–2.15 (m, 4H), 2.15–1.3 (m, 18H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 174.2, 164.1, 136.8, 60.3, 50.7, 30.4, 27.3, 26.6, 25.9, 24.6, 24.2; HRMS calcd for $C_{22}H_{30}O_4$ (M^+) 358.2144, found 358.2169.

Dimethyl 1,2,3,4,5,6,8,9,10,11,12,13-Dodecahydrobenzo[1,2:4,5]biscyclooctene-7,14-dicarboxylate (40c): yield 60 mg (24%); colorless needles, mp 169 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.88 (s, 6H), 2.7–2.6 (m, 8H), 1.8–1.6 (m, 8H), 1.45–1.25 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 171.1, 135.5, 135.3, 51.8, 31.0, 29.2, 26.1; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ε) = 206 (4.62), 230 sh (3.91), 280 (3.19). Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.61; H, 8.46.

Preparation of Terephthalic Ester 40d: photolysis of 265 mg (0.84 of mmol) of **15d** and/or **34d** in 250 mL of diethyl ether (λ ≥ 282 nm, 125-W lamp, 10 °C) for 12 h; column chromatography (silica gel, petroleum ether/ether 5:1).

34d: recovered 170 mg (64%).

Dimethyl 2,3,4,5,7,8,9,10-Octahydro-1*H*-naphtho[1,2]cycloheptene-6,11-dicarboxylate (40d): yield 40 mg (15%), colorless crystals, mp 118–119 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.88 (s, 6H), 2.7–2.55 (m, 8H), 1.85–1.5 (m, 10H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 170.8, 137.2, 134.8, 131.0, 52.0, 32.2, 31.8, 27.4, 26.7, 22.4; UV/vis (acetonitrile) λ_{max} [nm] (log ε) = 206 (4.59), 228 sh (3.94), 282 (3.29). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.64. Found: C, 72.02; H, 7.59.

Preparation of 1,2,3,4,5,8,9,10,11,12-Decahydrobenzo[1,2:3,4]biscycloheptene-6,7-dimethanol (45b). $LiAlH_4$ (0.71 g, 18.7 mmol) is dissolved in 20 mL of diethyl ether, and a solution of 4.1 g (12.4 mmol) of **34b** in 80 mL of diethyl ether is added under stirring so slowly that the mixture is slightly simmering. After 4 d of refluxing, workup is carried out as follows: after successive addition of 1.4 mL of water, 1.4 mL of a sodium hydroxide solution (15%), and 4.2 mL of water, the precipitate is filtered and washed with ether, and the combined organic phases are concentrated on a rotary evaporator to afford crude **45b**. Purification is achieved by recrystallization from diethyl ether.

45b: yield 2.6 g (77%), white crystals; ^1H NMR (300 MHz, $CDCl_3$) δ 4.83 (d, $^3J(H,H)$ = 4.7 Hz, 4H), 2.99 (m, 4H), 2.92 (m, 4H), 2.18 (t, $^3J(H,H)$ = 4.7 Hz, 2H), 1.8–1.7 (m, 4H), 1.7–1.5 (m, 8H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 141.1, 140.7, 134.0, 59.6, 30.7, 29.4, 29.3, 27.5, 27.0; UV/vis (diethyl ether) λ_{max} [nm] (log ε) = 212 (4.68), 230 sh (4.05), 280 (2.15); HRMS calcd for $C_{18}H_{26}O_2$ (M^+) 274.1933, found 274.1896.

3. Photochemical Experiments. Photolyses of [6]paracyclophane 18c. (1) Compound **18c** (185 mg, 0.52 mmol) is irradiated at λ ≥ 320 nm (125-W lamp, 10 °C) in 250 mL of diethyl ether for a total of 14 h. To examine the course of reaction, samples of 5 mL are drawn from the mixture after certain periods and investigated by ^1H NMR (200 MHz, $CDCl_3$). The methoxy resonances serve as satellites. Estimated relative margin of error of NMR evaluation: 10%. Result (time, % of **18c**, % of **14c**, % of **17c**): 0 h 100%, 0%, 0%; 30 min, 81%, 19%, 0%; 1 h, 78%, 22%, 0%; 2.25 h, 81%, 19%, 0%; 3 h, 79%, 18%, ≈2%; 4 h, 80%, 17%, ≈3%; 8 h, 75%, 18%, 8%; 14 h, 73%, 12%, 15%; this outcome is graphically represented in Figure 1a. (2) 185 mg (0.52 mmol) of **18c**, 250 mL of diethyl ether, λ ≥ 280 nm, 125-W lamp, 10 °C, 12 h, further procedure as in 1. Estimated relative margin of error of NMR evaluation: 10%. Result (time, % of **18c**, % of **14c**, % of **17c**, % of **34c**, % of **40c**): 0 h, 100%, 0%, 0%, 0%, 0%; (30 min, 78%, 20%, ≈2%, 0%, 0%; (2 h, 80%, 18%, ≈2%, 0%, 0%; 4 h, 79%, 19%, ≈2%, traces, traces; (8 h, 73%, 15%, 0%, 8%, 4%; 12 h, 62%, 14%, 0%, 18%, 6%. Chromatographic workup (neutral alumina III, petroleum ether/ether = 4:1) affords 80 mg (43%) of **18c**, 40 mg (21%) of **14c**, 22 mg (12%) of **34c** and 10 mg (5.4%) of **40c**. (3) 130 mg (0.36 mmol) of **18c**, 250 mL of diethyl ether, λ = 254 nm, 125-W lamp, 10 °C, 1 h, further procedure as in 1. Estimated relative margin of error of NMR evaluation: 10%. Result (time, % of **18c**, % of **14c**, % of **17c**): 0 h, 93%, 7%, 0%; 15 min, 79%, 21%, 0%; 30 min, 81%, 19%, 0%; 1 h, 76%, 24%, 0%.

Photolysis of Dewar Benzene 14c: 105 mg (0.29 mmol) of **14c** (containing 10% of **18c**), 250 mL of diethyl ether, $\lambda \geq 320$ nm, 125-W lamp, 10 °C, 14 h. The course of reaction is monitored by ^{1}H NMR as described for the photolyses of [6]paracyclophane **18c** (1) (see above). Estimated relative margin of error of NMR evaluation: 10%. Result (time, % of **18c**, % of **14c**, % of **17c**): 0 h, 10%, 90%, 0%; 5 min, 50%, 50%, 0%; 15 min, 74%, 26%, 0%; 30 min, 80%, 20%, 0%; 1 h, 83%, 17%, traces; (2 h, 80%; 17%; ≈2%; 4.5 h, 79%, 16%, ≈5%; 8.5 h, 73%, 16%, 11%; 14 h, 69%, 15%, 16%; this outcome is graphically represented in Figure 1b.

Photolysis of Dewar Benzene 28b: (1) 10 mg (0.036 mmol) of **28b**, 20 mL of diethyl ether, 280-nm cutoff filter, 500-W lamp, 10 °C, 8 h. ^{1}H NMR evaluation (300 MHz, $CDCl_3$, the hydroxymethylene resonances serve as satellites) affords 85% of starting material **28b**, 10% of **25b**, ≈2% of **27b**, and only traces of **29b**.

(2) 10 mg (0.036 mmol) **28b**, 20 mL of diethyl ether, $\lambda = 254$ nm, 500-W lamp, 10 °C, 4 h. ^{1}H NMR evaluation as in (1) affords 38% of starting material **28b**, 28% of **25b**, traces of **27b**, and 29% of **29b**.

Photolysis of Dewar Benzene 39b: 4 mg (0.012 mmol) of **39b** in ≈0.5 mL of $CDCl_3$ in an NMR tube, 280-nm cutoff filter, 500-W lamp, 25 °C, 1 h. ^{1}H NMR analysis (300 MHz, $CDCl_3$, the methoxy resonances serve as satellites) affords 87% of terephthalic ester **40b** and 13% of phthalic ester **34b**.

Comparative Photolyses of Phthalic Esters 34a–34d: (1a) 500 mg (1.66 mmol) of **34a**, 500 mL of diethyl ether, $\lambda \geq 280$ nm, 125-W lamp, 10 °C, 75 h. ^{1}H NMR analysis shows no conversion. (1b) 500 mg (1.66 mmol) of **34a**, 500 mL of diethyl ether, $\lambda = 254$ nm, 125-W lamp, 10 °C, 75 h. ^{1}H NMR analysis shows only slow decomposition of starting material. (2) 210 mg (0.64 mmol) of **34b**, 250 mL of diethyl ether, $\lambda \geq 280$ nm, 125-W lamp, 10 °C, 12 h. ^{1}H NMR evaluation (300 MHz, $CDCl_3$, the methoxy resonances serve as satellites) affords 52% of terephthalic ester **40b** and 48% of phthalic ester **34b**. (3) 185 mg (0.52 mmol) of **34c**, 250 mL of diethyl ether, $\lambda \geq 280$ nm, 125-W lamp, 10 °C, 13 h. ^{1}H NMR evaluation (300 MHz, $CDCl_3$) affords 30% of terephthalic ester **40c** and 70% of phthalic ester **34c**. (4) 265 mg (0.84 mmol) of **34d**, 250 mL of diethyl ether, $\lambda \geq 280$ nm, 125-W lamp, 10 °C, 12 h. ^{1}H NMR analysis (300 MHz, $CDCl_3$) affords 24% of terephthalic ester **40d** and 76% of phthalic ester **34d**.

Photolysis of 45b: (1) 252 mg (0.92 mmol) of **45b**, 250 mL of diethyl ether, $\lambda \geq 280$ nm, 125-W lamp, 10 °C, 12 h. ^{1}H NMR analysis (300 MHz, $CDCl_3$, the hydroxymethylene resonances serve as satellites) shows no conversion. (2) 10 mg (0.036 mmol) of **45b**, 20 mL of diethyl ether, $\lambda = 254$ nm, 500-W lamp, 10 °C, 12 h. ^{1}H NMR analysis (300 MHz, $CDCl_3$) shows only slow decomposition of starting material.

Acknowledgment. Our work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, the BASF Aktiengesellschaft, Ludwigshafen, DEGUSSA and Metallgesellschaft in Frankfurt. We thank Karen Treptow for typing this manuscript.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds **14b**, **14c**, **15b–17b**, **17c**, **18c**, **19**, **23b**, **24b**, **26b**, **27b**, **28b**, **38b**, **39b**, **39c**, and **45b** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see current masthead page for ordering information.

Stereospecific Construction of Multiple Contiguous Quaternary Carbons. Total Synthesis of (±)-*cis, anti, cis*-1,8,12,12-Tetramethyl-4-oxatricyclo[6.4.0.0^{2,6}]dodecan-3-ol, a Thapsane Isolated from *Thapsia villosa* var *minor*†

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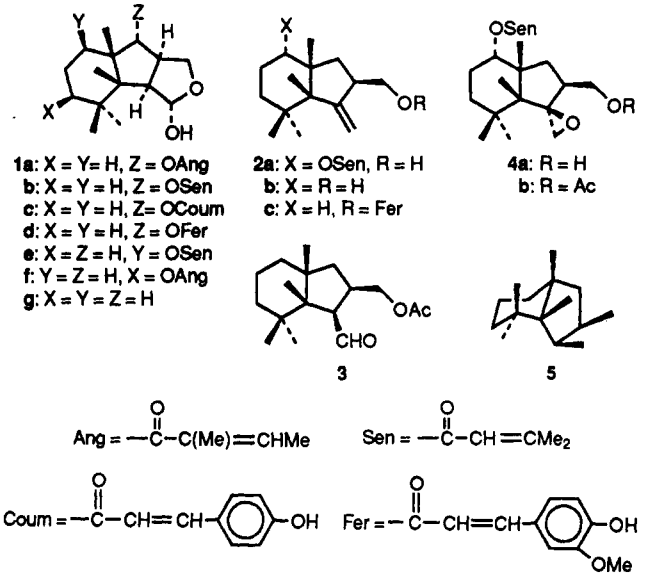
Received May 4, 1993®

The details of the first total synthesis of a natural thapsane **1g** containing three contiguous quaternary carbon atoms, starting from cyclogeraniol (**9**) is described. The Claisen rearrangement of **9** with methoxypropene in the presence of a catalytic amount of propionic acid produced ketone **10**. Rhodium acetate-catalyzed intramolecular cyclopropanation of α-diazo-β-keto ester **12**, obtained from **10** via β-keto ester **8**, furnished cyclopropyl keto ester **7**. Lithium in liquid ammonia reductive cleavage of cyclopropyl compound **7** gave a 1:1 mixture of hydrindanone **6** and ketol **13**. Wittig methylenation of **6** furnished ester **21**. Epoxidation of **21**, followed by BF_3–OEt_2-catalyzed rearrangement of epoxide **23** afforded hemiacetal **25**. Treatment of hemiacetal **25** with triethylsilane in trifluoroacetic acid furnished lactone **22**, a degradation product of various thapsanes. Finally, DIBAH reduction of lactone **22** generated the thapsane **1g**.

In 1984, Rasmussen *et al.*[1] reported the isolation of a new sesquiterpene containing a new carbon skeleton, from the ethanolic extract of the roots of a Mediterranean umbelliferous plant, *Thapsia villosa L.* The structure as well as the absolute configuration of this new sesquiterpene was established as **1a**, by spectral and single crystal X-ray analysis. Shortly thereafter, Grande *et al.* reported the isolation of the corresponding senicioate ester **1b** from the benzene extract of the roots of *Thapsia villosa* var *minor*, along with four other hemiacetalic (**1c–f**), four nonacetalic (**2a–4a,4b**), and a dimeric thapsane as minor components having the same carbon framework.[2,3] The trivial name Thapsane was suggested for the bicyclic carbon skeleton, 2,3,3a,4,4,7a-hexamethylhydrindan (**5**), present in these compounds. Recently, Christensen *et al.* have reported the isolation of three additional thapsanes[4] (**2b,c, 1g**) from *Thapsia villosa* var *minor* collected near Capo Espichel (Chart I). The presence of an unique *cis,anti,cis*-3b,4,4,-7a-tetramethylperhydroindeno[1,2-*c*]furan framework,[1-4] containing three contiguous quaternary carbon atoms and five to six chiral centers makes thapsanes attractive synthetic targets. The generation of three contiguous quaternary carbons in the hydrindan framework to build the thapsane skeleton, poses a synthetic challenge. In continuation of our interest in the synthesis of sesquiterpenes containing multiple contiguous quaternary carbon atoms,[5,6] we report the first total synthesis of a natural thapsane (**1g**),[6] featuring a Claisen rearrangement and an intramolecular diazo ketone cyclopropanation reaction for the construction of vicinal quaternary carbon atoms.

Chart I



The retrosynthetic analysis of thapsane, based on the Claisen rearrangement[7] and intramolecular diazo ketone cyclopropanation[8] reactions, readily identified the hydrindanone **6**, cyclopropyl β-keto ester **7**, and β-keto ester **8** as key intermediates with cyclogeraniol (**9**) as the starting material (Scheme I). Cyclogeraniol (**9**) which contains a single quaternary carbon atom was obtained from β-ionone by controlled ozonation[9] followed by direct reduction of the ozonide with sodium borohydride.[5g] The second quaternary carbon atom was introduced using a Claisen rearrangement (Scheme II). Thus, Claisen rear-

† Dedicated to Professor Gilbert Stork.

® Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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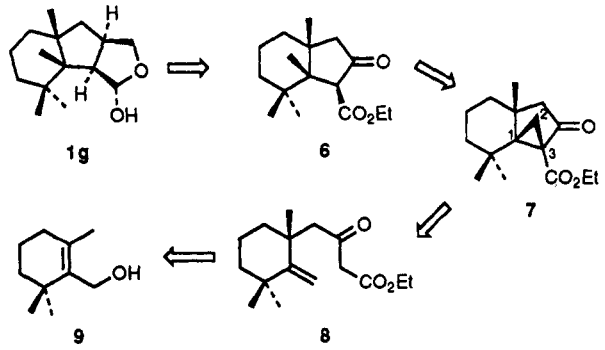
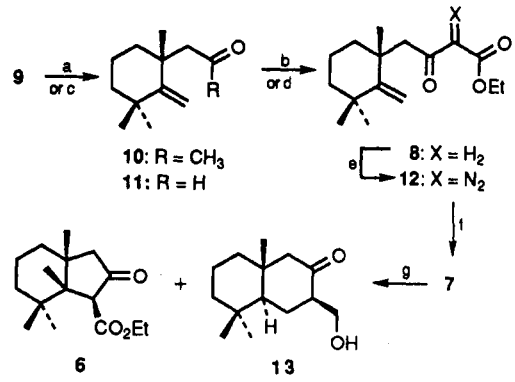
Scheme I



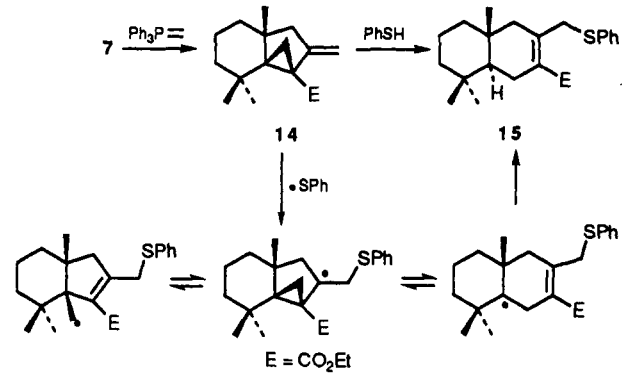
Scheme II[a]



[a] Conditions: (a) CH_2=C(OMe)CH_3, EtCOOH, PhMe, 160 °C (for **10**); (b) LHMDS, THF, ClCOOEt, −78 °C → rt (from **10**); (c) CH_2=CHOEt, $Hg(OAc)_2$, PhMe, 180 °C (for **11**); (d) $N_2CHCOOEt$, $SnCl_2$, CH_2Cl_2 (from **11**); (e) TsN_3, Et_3N, MeCN; (f) $Rh_2(OAc)_4$, C_6H_6, rt; (g) Li, liquid NH_3, THF.

rangement[5c,7b] of cyclogeraniol (**9**) with methoxypropene and a catalytic amount of propionic acid in toluene in a sealed tube (150–160 °C) furnished ketone **10** in 65% yield. Generation of the kinetic enolate of ketone **10** with lithium hexamethyldisilazide in dry THF at −78 °C, followed by quenching with ethyl chloroformate, furnished β-keto ester **8** in 80% yield. Alternatively, **8** was also obtained via the Lewis acid[10] catalyzed intermolecular insertion of ethyl diazoacetate to aldehyde **11**. Treatment of aldehyde **11** (obtained from **9** via the Claisen rearrangement with ethyl vinyl ether and mercuric acetate)[11] with ethyl diazoacetate in the presence of $SnCl_2$ furnished β-keto ester **8** in 70% yield. The third quaternary carbon was introduced in a stereospecific manner using an intramolecular diazo ketone cyclopropanation reaction. Diazo transfer reaction of β-keto ester **8** with tosyl azide in the presence of triethylamine in acetonitrile, afforded diazo compound **12** in 83% yield. Rhodium acetate-catalyzed decomposition of **12** in benzene at room temperature[12] furnished stereospecifically cyclopropyl compound **7**, in 65% yield. The reductive cleavage of the cyclopropane ring in keto ester **7** with lithium in liquid ammonia at −33 °C furnished a 1:1 mixture of hydrindanone **6** and ketol **13** in 64% yield. Products **6** and **13** were formed by the selective cleavage

Scheme III



of either C_3–C_2 or C_3–C_1 bonds of cyclopropane. It is well established[13] that in the lithium–liquid ammonia reductive cleavage of cyclopropyl ketones, the cyclopropane bond which overlaps best with the p-orbital of the carbonyl carbon will be cleaved. Accordingly, transfer of an electron to the ketone carbonyl results in the cleavage of the C_3–C_2 bond leading to β-keto ester **6**. On the other hand, transfer of an electron to the ester carbonyl results in the cleavage of the C_3–C_1 bond, because in the sterically less-hindered conformation the C_3–C_1 bond has better overlap with the π-system of the carbonyl of ester, followed by further reduction leading to ketol **13**. This is further supported by the fact that a primary alcohol was obtained from the ester, analogous to the lithium–ammonia reduction of α,β-unsaturated esters to the corresponding primary alcohols.[14] The trans ring junction was assigned based on analogy with known octalone reductions[15] and the stereochemistry at C_4 was assigned based on thermodynamic considerations.[13d]

It was anticipated that the generation of a radical at C-4 of the tricyclo[4.4.0.$0^{1,3}$]decane system would lead to opening of the cyclopropane in the desired fashion, generating a hydrindane with a methyl group at the ring junction. Addition of •SPh to the vinyl cyclopropane moiety of ester **14** was explored for the generation of the radical at C-4 (Scheme III). Ester **14** was prepared from **7** via Wittig olefination, with methylenetriphenylphosphorane[17] at room temperature in 75% yield. Treatment of vinyl cyclopropane **14** with 1 equiv of thiophenol in refluxing benzene for 12 h afforded ester **15** in 72% yield. The formation of product **15** can be explained by a homoallyl–cyclopropylmethyl–homoallyl radical rearrangement.[18] The cyclopropylmethyl radical generated by the addition of thiophenol leads to the formation of a homoallyl radical which is in equilibrium with the thermodynamically more stable homoallyl radical leading to the formation of ester **15**.

Alternatively, treatment of ketol **16**[13d] with lithium–ammonia furnished hydrindanone **17**. The hydroxy group in ketol **17** was protected as its TBDMS ether **18** and the final carbon atom required for the thapsane framework was introduced using a Wittig methylenation (Scheme IV).

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