DOI: 10.1002/ejoc.200500396

Cycloadditions to Alkenyl[2.2]paracyclophanes[‡]

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Keywords: Cyclophanes / Cycloadditions / Annelation / Ene reaction

Cycloadditions between the 4-alkenyl[2.2]paracyclophanes **7**, **16**–**21** and the dienophiles **10a**–**h** have been studied. Whereas **10a**, **b**, **d**, and **g** prefer Diels–Alder addition involving the olefinic double bond and one double bond of a cyclophane benzene ring, **10c**, **e**, **f**, and **h** undergo other cycloadditions such as ene reaction (**10c**), [2+2] cycloaddition to the olefinic double bond (**10e**) and heterodiene addition to the vinyl substituent (**10f**, **h**). Several of the isolated cycloadducts (e.g. **24**–**26**, **52**) are valuable substrates for the preparation of annelated cyclophanes. The mechanisms of several of these cycloadditions are discussed.

Introduction

Cycloadditions – predominantly of the Diels–Alder type – play an important role in [2.2]paracyclophane chemistry. Thus tetra- or disubstituted cyclophanes **3** are obtained by the cycloaddition of triple bond dienophiles **2** to 1,2,4,5-hexatetraene (**1**),[2–4] the tandem process beginning with a [2+4] cycloaddition to produce a *p*-xylylene, which subsequently dimerizes in a [6+6]process to the target molecule **3**. Depending on the substituents R, this can be linearly or angularly annelated to **4**[5] and **5**,[6] respectively, or provide unusual adducts such as the bis-barrelene **6**,[7,8] all three processes involving cycloadditions in their decisive steps (Scheme 1).

In our previous studies in this series we have demonstrated how these cycloadducts can be used to prepare novel layered π-systems,[9] new chiral compounds[10] or serve as substrates for further transformations.[11] To learn more about the mechanistic and preparative details of these cycloadditions, we decided to investigate one of the simplest processes of this type: the addition of various double and triple bond dienophiles to a selection of 4-alkenyl[2.2]paracyclophanes. Indeed, the addition of the simplest diene of this type, 4-vinyl[2.2]paracyclophane (**7**) itself to dehydrobenzene (**8**), provided access to the phenanthrenophane **9**, the parent molecule of the angular systems.[6,12] In order to introduce functional groups into **9** and its derivatives, the dienophile (general structure **10**) must carry appropriate groups. The adducts **11** thus obtained can subsequently be aromatized to **12** or be used in other transformations (Scheme 2).

In the present study we describe the addition of the dienophiles **10a**–**h** to **7** and several other 4-alkenyl[2.2]paracyclophanes.

Preparation of the 4-Alkenyl[2.2]paracyclophanes

The olefinic dienes were prepared from [2.2]paracyclophane (**13**) by standard methods as summarized in Scheme 3. Thus the known carbonyl precursors **14**[13] and **15**[14] were either converted by Wittig reactions into the olefins **7**, **16** and **17** or into **18**–**21** by Grignard reactions followed by acid-catalyzed dehydration (Scheme 3). The structure assignment (see experimental) was also straightforward; whenever diastereo- and regioisomers were produced, these were separated by column chromatography or HPLC.

Cycloaddition Reactions

a) Maleic Anhydride (10a): Heating of **7** in the presence of **10a** at 120 °C for 5 days in acetic acid results in the formation of a single adduct in 72% yield. According to the spectroscopic data given in the Exp. Sect. we assign structure **24** to this product. Since **7** is chiral – the drawn structure has *S* configuration – and two new stereogenic centers are produced during the process, in principle a mixture of diastereomers could be formed. That this is not the case, i.e. that the addition is diastereospecific, can be rationalized by the addition mechanism presented in Scheme 4.

Although the conformation of **7** is unknown, we assume that the required *cis* orientation shown in the Scheme can be achieved readily. The dienophile can then attack the aro-

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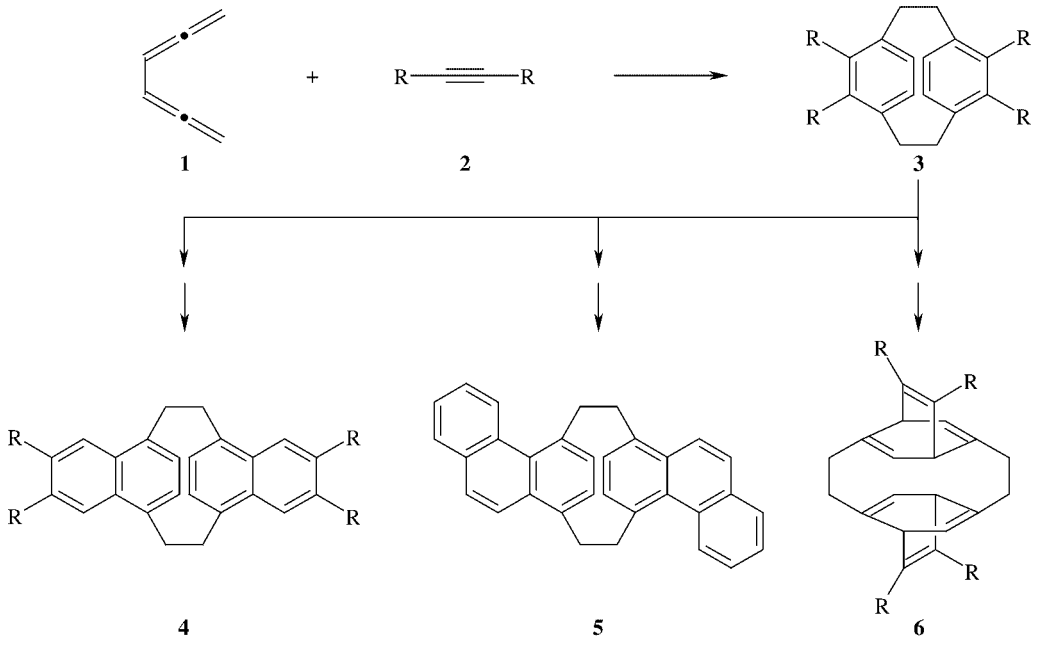
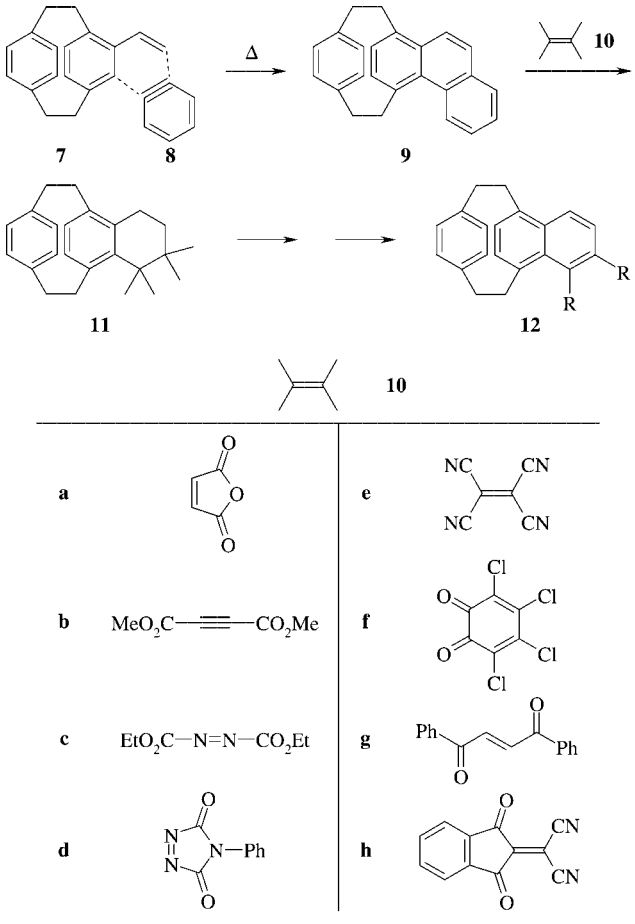
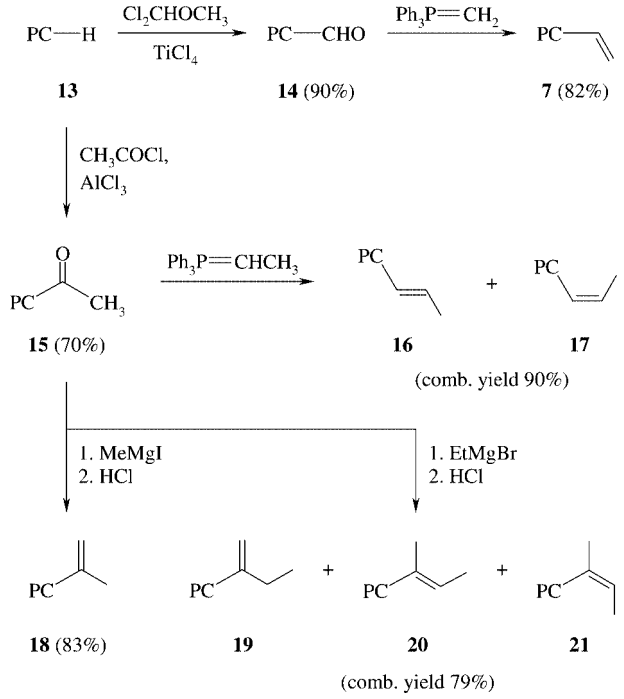


Scheme 1. [2.2]Paracyclophanes as starting materials for novel layered organic compounds.

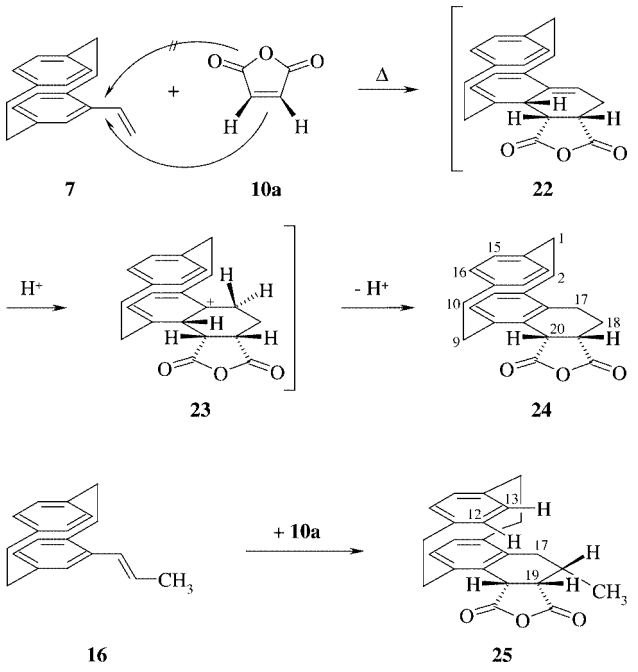


Scheme 2. Cycloadditions to 4-alkenyl[2.2]paracyclophanes.



Scheme 3. Preparation of 4-alkenyl[2.2]paracyclophanes.

matic diene either from the inner or from the outer side of the layered system, and clearly the latter route should be favored. To allow "internal" attack of **10a** would require at least its partial intercalation between the two benzene rings, which is highly unlikely, considering that the intraannular distance between the decks in the cyclophane amounts to only ca. 310 pm. Reaction from the sterically less shielded *exo*-side furnishes adduct **22**, with the anhydride ring pointing away from the phane system. Under the acidic conditions, **22** will be protonated to the cyclohexadienyl cation – a σ complex, incidentally, generated by protonation outside the six-membered ring – which receives transannu-

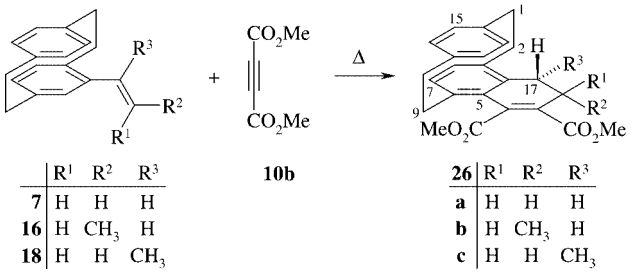


Scheme 4. Cycloadditions of 4-alkenyl[2.2]paracyclophanes and maleic anhydride.

lar stabilization from the intact benzene ring. Such an interaction has been described many times in cyclophane chemistry[15] and also been observed directly by protonation of [2.2]paracyclophane in superacidic media.[16] Finally, deprotonation regenerates the paracyclophane system and furnishes the Diels–Alder adduct **24**. The shown stereochemistry is supported also by the chemical shifts of the bridge protons in the immediate vicinity of the anhydride ring. If this ring was positioned in *endo* orientation (pointing towards the unaffected benzene ring), one of its carbonyl groups would be close to one of the bridge protons, causing a shift to lower field. This effect has been observed for several derivatives of [2.2]paracyclophane carrying a carbonyl-containing substituent in the 4-position.[17] In all these cases the methylene proton facing the carbonyl function is shifted to approximately δ = 4.0 ppm, whereas all other bridge protons absorb below δ = 3.8 ppm. For **24** all bridge protons appear as complex multiplets between δ = 3.7 and 2.75 ppm (see Exp. Sect.).

Cycloaddition between the propenyl derivative **16** in acetic acid (5 d, 120 °C) and maleic anhydride (**10a**) also leads to one product only (54%).[18] To this adduct structure **25** is assigned, the main arguments again being the approach of **10a** to the diene as described above for the parent system and the absence of a Nuclear Overhauser effect on the facing aromatic protons when the signal for the methyl group (δ = 1.00 ppm, J = 6.5 Hz) is saturated. If the methyl group pointed towards the interior of the adduct, i.e. towards the unsubstituted benzene ring, a NOE enhancement could be expected for the aromatic protons 12- and 13-H, respectively; according to molecular models the methyl group and these protons are very close to each other. None of the other alkenyl derivatives **18**–**21** reacts with **10a**. Even after prolonged heating (up to 2 weeks) in high-boiling solvents (acetic acid, toluene) the substrate dienes were recovered unchanged, the only products formed being uncharacterizable "polymeric products". Apart from the increased difficulty with which these dienes achieve the *cisoid*-conformation, this lack of reactivity could also result from the fact that all dienes in this series carry an alkyl group in 1-position of the olefinic substituent. In the decisive, rate-determining initial step (cf. **7** → **22**) this substituent will be forced into close vicinity to one of the ethano bridges. Because of the rigid structure of the phane nucleus, steric compression in the primary adduct cannot be released to the same extent as in an "open" system. For example, α-methyl-*p*-methylstyrene is known to add maleic anhydride (**10a**) in acetic anhydride at 80 °C in the presence of *N*,*N*-dimethylaniline within 24 h.[19] Likewise, 1,1-diphenylethene reacts readily with **10a** (refluxing benzene, 4 h).[20]

b) Dimethyl Acetylenedicarboxylate (10b): Not surprisingly, the cycloaddition behavior of **10b** towards **7** and **16** resembles that of **10a**. Thus, heating the parent system **7** and **10b** in glacial acetic acid at 120 °C for 3 days yields the dihydronaphthalenophane derivative **26a** in 72% yield, easily identified by its spectroscopic data and chemical behavior (see below, Scheme 5).



	R^1	R^2	R^3
7	H	H	H
16	H	CH_3	H
18	H	H	CH_3

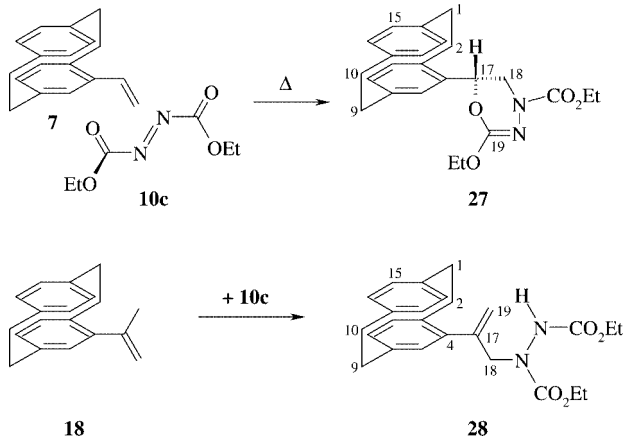
26	R^1	R^2	R^3
a	H	H	H
b	H	CH_3	H
c	H	H	CH_3

Scheme 5. Cycloadditions of 4-alkenyl[2.2]paracyclophanes and dimethyl acetylenedicarboxylate.

Similarly, **16** and **10b** provide the 1:1 adduct **26b** (acetic acid, reflux, 41% yield). When a mixture of **16** and **17** is used in this reaction, only the *E* diastereomer reacts. The orientation of the methyl substituent (δ = 0.88 ppm, J = 6.9 Hz) follows again from a Nuclear Overhauser experiment as described for **25**. In contrast to the above cycloadditions with **10a**, the Diels–Alder addition of **18** and **10b** (acetic acid, 5 d) furnishes the cycloadduct **26c** in 51% yield. If the orientation of R^3 and the hydrogen atom at the same carbon atom were reversed, we would expect an Overhauser effect at 13-H on saturation of the methyl signal (δ = 0.92 ppm, J = 7.2 Hz). This, however, is experimentally not observed, thus the relative orientation is as shown in Scheme 5. The reason for this enhanced reactivity of **18**/**10b** compared to that of the maleic anhydride (**10a**) addition is not clear at present. Molecular models indicate that, with the additional double bond in the newly created six-membered ring, the methyl substituent is farther away from the

ethano bridge in the primary adduct. When a mixture of **19**–**21** is heated with **10b** in acetic acid for several days, no cycloaddition takes place and the starting olefins are recovered unchanged.

c) Diethyl Azodicarboxylate (10c): Heating various styrene derivatives with diethyl azodicarboxylate (**10c**) leads to the expected adducts, Diels–Alder products being produced initially, which stabilize themselves subsequently by an ene reaction.[21] In contrast, neither **7** nor its methyl derivative **18** yield the expected adducts. The parent system **7** provides the oxadiazine **27** on treatment with **10c** in toluene at room temperature for 7 days in the presence of trichloroacetic acid in 18% yield, 21% of the starting material being recovered; if acetic acid is used as the solvent no cycloaddition occurs (Scheme 6).



Scheme 6. Cycloadditions of 4-alkenyl[2.2]paracyclophanes and diethyl azodicarboxylate.

As structure **27** shows, a [2+4] cycloaddition has also taken place in this case; however, the cyclophane has reacted as the dienophile and the N=N–C=O grouping of **10c** plays the role of the diene. That azodicarboxylates react in this manner has been described in the literature several times, a typical example being indene, which also furnishes an oxadiazine with **10c**.[22,23] Although the connectivity of **27** can be derived unambiguously from our spectroscopic data of the cycloadduct (see Exp. Sect.), its relative stereochemistry cannot. Since in the cycloaddition a new stereogenic center is produced, we would expect the formation of diastereomers in the process. These, however, were not observed. Since it is especially unlikely that the NMR signals of both diastereoisomers are identical, we have to assume that the reaction occurs with very high diastereoselectivity.

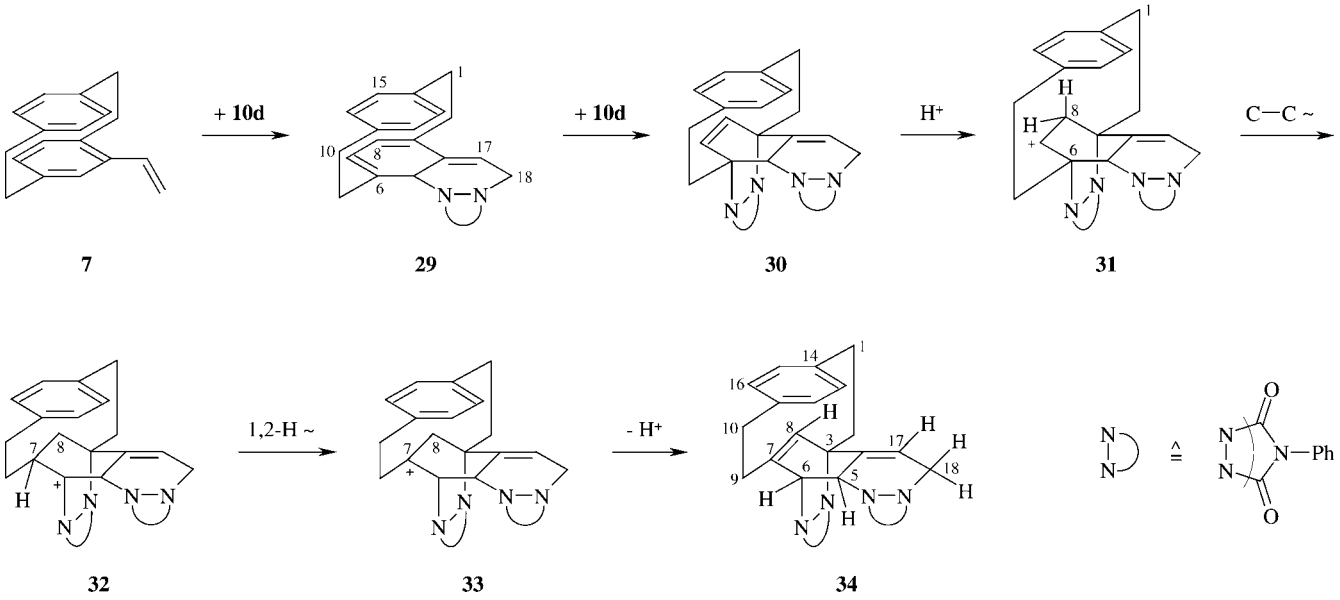
With the reaction between the isopropenyl derivative **18** and **10c**, a third cycloaddition type is observed for the 4-alkenyl[2.2]paracyclophanes: the ene reaction. Under the same conditions as above the 1:1 adduct **28** is obtained in 30% yield, and again the addition is incomplete (recovery of **18**: 31%). In the spectra of **28** the terminal double bond is easily identifiable. The ene-reaction of azodicarboxylates with sterically hindered dienes has been described in the literature.[24,25]

All other olefins (**16**, **17**, **19**–**21**, employed as a mixture of isomers) also reacted with **10c** in varying yields (30–60%), however, in no case could we isolate pure addition products from the oily mixtures either by recrystallization or column chromatography. Mass spectra of these raw adducts indicated the formation of 1:1 products, but their precise structures could not be determined. In the case of **20** and **21** the possibility exists that ene reactions at two different methyl substituents can take place, possibly a reason for the observed product complexity.

d) *N*-Phenyltriazolinedione (10d): The addition of the "record dienophile" **10d** to **17** provides further insight into the mechanism of the Diels–Alder additions to vinyl[2.2]paracyclophanes. When these two components are reacted with each other at room temperature for 7 days in the presence of catalytic amounts of trichloroacetic acid, a 2:1 adduct results in 65% yield, to which we assign the bis-urazole structure **34** (Scheme 7).

Decisive for the assignment are the bridgehead proton at C-6 and the olefinic protons at carbon atoms 8 and 17. The 6-H is registered at δ = 5.96 as a doublet with J = 6.3 Hz, indicating a vicinal coupling partner in *cis*-orientation (5-H, δ = 5.51, m). In the ^{13}C off-resonance spectrum these two carbon atoms absorb as doublets at δ = 60.14 and 58.78 ppm. The proton at C-8 at δ = 4.9 is slightly shifted up-field because of the anisotropy of the facing intact benzene ring and split into a doublet (J = 2.2 Hz) because of the homoallylic coupling with 5-H; 17-H is registered as a multiplet at 6.22 coupling with its neighboring methylene group (18-H) and 5-H. In the off-resonance ^{13}C spectrum these two olefinic carbon atoms absorb as doublets at δ = 123. 47 and 123.74. The complete spectroscopic data of **34** are given in the Exp. Sect.

We explain the formation of this bizarre product by the following route (Scheme 7). Initial monoaddition destroys the aromatic character of the substituted benzene ring of **7** and provides the adduct **29**. Since **10d** is reactive enough, it outpaces the aromatization of **29** – as described above for the addition of **10a** and **10b** – and adds a second equivalent of **10d** to provide the 2:1 product **30**. If this had been the final adduct, its spectra would have shown three monosubstituted olefinic carbon atoms and no bridgehead hydrogen atom, rather than the observed two =CH groups and one bridgehead hydrogen atom (see above and Exp. Sect.). We therefore postulate that the addition reactions are followed by an isomerization process. In this a proton first adds to the C7–C8 double bond of **30** and the resulting cation **31** undergoes a Wagner–Meerwein rearrangement, leading to the less strained carbenium ion **32**. Acid-catalyzed rearrangements of [2.2]paracyclophanes into [2.2]-parametacyclophanes are a well-documented phenomenon in cyclophane chemistry.[26] Intermediate **32** subsequently undergoes a 1,2-hydrogen shift to the tertiary cation **33**, which on loss of a neighboring proton ultimately provides the isolated adduct **34**. The reaction of styrene with the azadienophile **10d** has been investigated by several authors;[27,28] it leads to a mixture of two 2:1 adducts, the one corresponding to **30** (without the phane bridge), the other



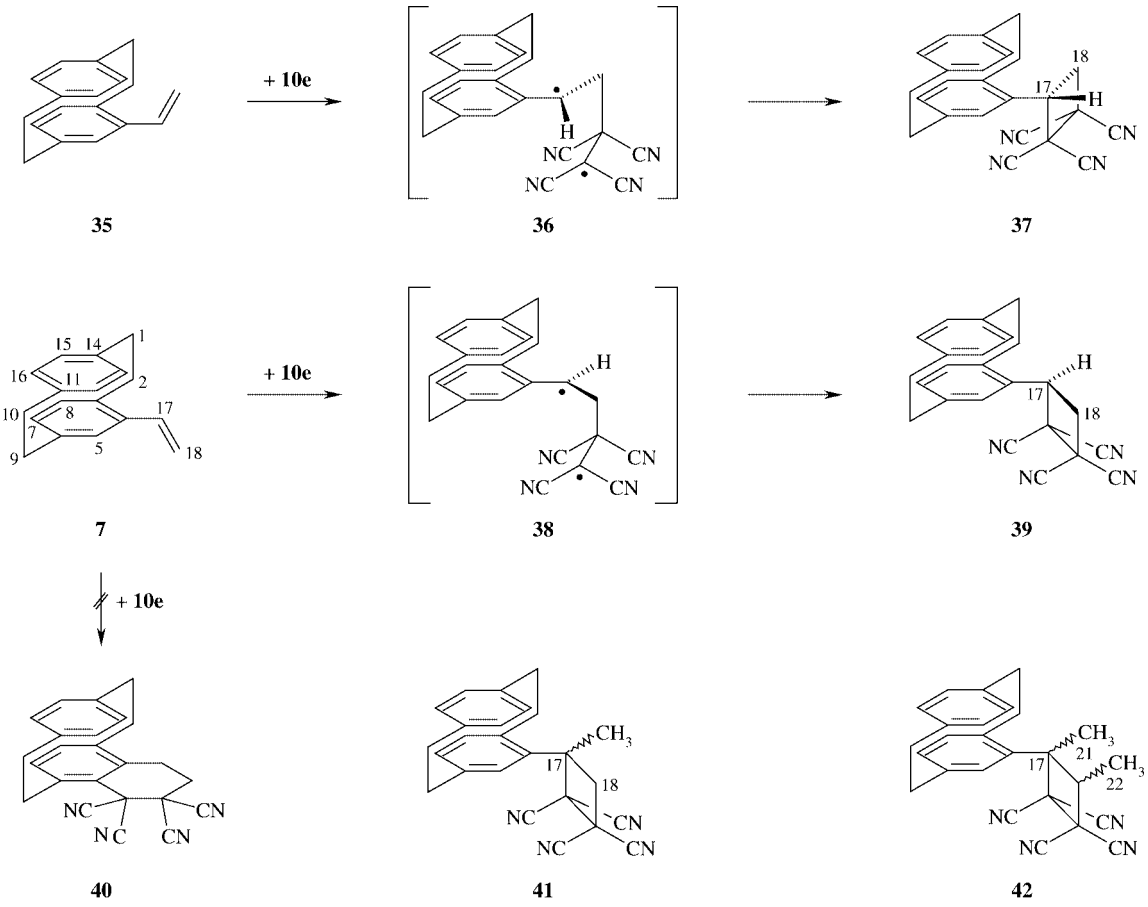
Scheme 7. Cycloaddition of 4-vinyl[2.2]paracyclophane and *N*-phenyltriazolindione.

a product of a tandem sequence beginning with the addition of one equivalent of **10d** (cf. structure **29**) followed by an ene reaction that regenerates the aromatic ring.

e) Tetracyanoethene (10e): Surprisingly, the addition of **10e**, one of the most frequently employed dienophiles, to the parent hydrocarbon 4-vinyl[2.2]paracyclophane (**7**) does not yield the expected [2+4] cycloadduct **40**. Rather, after stirring a mixture of the two components in glacial acetic acid for three days at room temperature, a product is obtained in 33% yield that, according to its spectroscopic data, must contain a four-membered ring. In particular, a doublet at δ = 45.69 and a triplet at 35.23 in the off-resonance ^{13}C NMR spectrum are of diagnostic value (C-17 and C-18), and a doublet of doublets at δ = 4.59 (J_1 = 8.4, J_2 = 12.1 Hz) in the ^{1}H spectrum, caused by the proton at C-17. The multiplet for the methylene group of the four-membered ring overlaps with the signals of the bridge methylene groups and hence cannot be analyzed. All other NMR signals (see Exp. Sect.) support this structure proposal. For the [2+4] cycloadduct **40** not only would the multiplicity of the signals have been different, but the ratio of the aromatic to the non-aromatic protons would have been 6:12 rather than the observed 7:11. Since none of the ^{13}C NMR signals shows any doubling, we can assume that only one diastereomer, either **37** or **39**, has been formed in the cycloaddition, excluding the unlikely possibility that these products possess identical ^{13}C NMR spectra (Scheme 8).[29]

[2+2] cycloadditions of **10e** to various double bond systems have been described in the literature several times,[30,31] and they take place in a stepwise fashion involving either diradical or dipolar intermediates. Regardless which mode is preferred in the case of **7** and **10e**, the bond between the terminus of the alkene (C-18) and **10e** will be formed first, since this process results in the more stable intermediate, even if there is no perfect overlap between the orbital at C-17 and the neighboring benzene ring. In Scheme 8 the intermediacy of diradical intermediates is postulated. Not only can **10e** approach the cyclophane from the outside (see above) or the inside of the phane system but the vinyl substituent can assume two different orientations: *cisoid*, as shown in **7** and mandatory for a Diels–Alder type reaction, and *transoid*, as illustrated by conformation **35**. Assuming that outside attack is favored as discussed for the addition of **10a** and **b**, conformation **35** would lead to the *S*,*R*-diastereomer **37** involving diradical **36**, or, alternatively, from 7 via **38** to the *S*,*S*-diastereomer **39**. Although only one diastereomer is produced in the reaction, no distinction between these two alternatives is possible at present. The actual conformation of 4-vinyl[2.2]paracyclophane is unknown. However, according to a MP2/6-31 G(d) surface scan, conformation **7** is more stable than **35** by about 2.5 kJ/mol.[32]

Cycloaddition of **10e** to the isopropenyl cyclophane **18** (room temperature, acetic acid, 2 d) provides another 1:1 adduct in good yield (81%), shown to possess the cyclobutyl structure **41**. The signal of the methyl group at δ = 2.29 is sharp, indicating again the highly diastereoselective nature of the addition. The fact that the ring-forming process takes place stepwise was shown by the addition of **10e** to the pure diastereomer **20**, which was isolated from the above product mixture (see Scheme 3) by gas chromatography. In the adduct **42** the two methyl groups are registered as two doublets (δ = 1.66, J = 7.0 Hz and δ = 1.76, J = 6.9 Hz, methyl substituents at C-18) and two singlets (δ = 2.16 and 2.17 ppm, methyl substituents at C-17), demonstrating that the stereochemical information of the starting olefin has been lost.[33] Conventional electron-rich styrenes such as 4-methoxy-1-propenylbenzene have also been shown to add **10e** (room temperature, tetrahydrofuran) with formation of cyclobutane derivatives.[34]

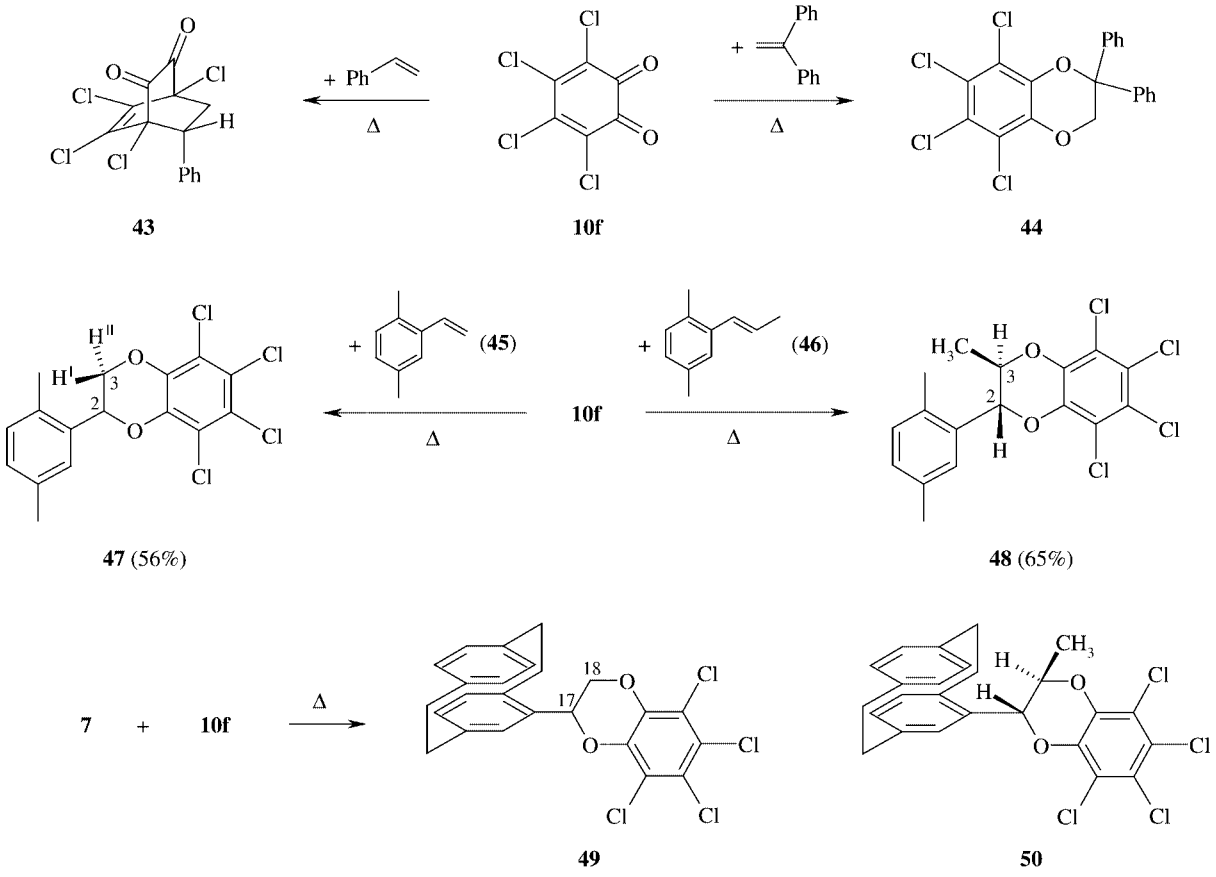


Scheme 8. Cycloadditions of 4-alkenyl[2.2]paracyclophanes and tetracyanoethene.

f) 3,4,5,6-Tetrachloro-1,2-benzoquinone (10f): *ortho*-Quinones are interesting addition partners since in principle they can provide two diene systems: the endocyclic all-carbon diene unit and the semicyclic α-diketo grouping. In a classical investigation Horner and Merz showed that the mode of addition is strongly influenced by the nature of the dienophile.[35] When, for example, styrene and **10f** are brought to reaction, the butadiene systems "wins" and the bicyclic diketone **43** is obtained as the 1:1 cycloadduct. On the other hand, introduction of a second phenyl group in the 1-position (1,1-diphenylethene) favors the formation of the benzodioxane **44**. Whereas indene and phenylacetylene lead to adducts of the former type, tolane again furnishes a benzodioxane derivative; with 1,3-cyclopentadiene a mixture of the two types of adducts is produced. Since structural and spectroscopic data of either of these adducts are lacking in the chemical literature, we first reacted (toluene, reflux) **10f** with 2,5-dimethylstyrene (**45**) and (*E*)-2-propenyl-*p*-xylene (**46**), respectively, as model compounds, hydrocarbons that can be considered as "halves" of [2.2]paracyclophanes. In both cases benzodioxanes, **47** and **48**, are produced as the sole adducts in acceptable yields (Scheme 9).

The most characteristic feature of **47** and **48**, the heterocyclic ring, is easily identified by its NMR spectra. For example, the ^{1}H NMR spectrum of adduct **47** shows three double doublets for the hydrogen atoms in the dioxane ring at δ = 4.02 (J = 11.8 and 9.0 Hz), 4.52 (J = 11.8 and 2.3 Hz), and 5.34 (J = 8.9 and 2.3 Hz), corresponding to 3-H, 3-H′ and 2-H, respectively. In the ^{13}C NMR spectrum, the carbon atoms C-2 and C-3 resonate at δ = 73.09 and 68.53 ppm, and appear as a doublet and a triplet, respectively, in the off-resonance spectrum. In the case of **48**, the ^{1}H NMR spectrum revealed two doublets at δ = 1.00 (J = 6.3 Hz) and 4.52 (J = 8.0 Hz), assigned to the methyl and 2-H protons, while the 3-H proton appears as a multiplet at δ = 4.12–4.18 ppm. The observed ^{13}C NMR signals of **48** confirm its proposed structure by the appearance of the three methyl groups at δ = 15.87, 25.08, and 25.23 ppm, respectively. The two distinctive carbon atoms C-2 and C-3 of the dioxane ring resonate at 67.69 and 76.55 ppm. The complete NMR data together with the other spectroscopic data, all supporting the given structural assignment of the two adducts, can be found in the Exp. Sect. Further structure proof, including the relative configuration of **48**, rests on the single-crystal X-ray structures of **47** and **48** discussed below.

The cycloaddition (refluxing toluene, 2 days) of **10f** to **7** furnishes a single diastereomer in 62% yield to which we assign structure **49** according to its spectroscopic and analytical data (see Exp. Sect.). The structure displayed in Scheme 9 is the result of an "outside" attack of **10f** on the *cisoid* dienophile, **7**; it possesses *S* configuration at its chiral



Scheme 9. Cycloadditions of styrene derivatives and 3,4,5,6-tetrachloro-1,2-benzoquinone.

center. Supporting information on the stereochemical course of the [2+4] cycloaddition is obtained when **16** is reacted with **10f** under the same conditions. Now, cycloadduct **50** is formed in 71% yield, the structure of which not only follows from its spectroscopic data (see Exp. Sect.) but also from an X-ray structural analysis.

The structure of compound **47** is shown in Figure 1 and of **48** in Figure 2, in which the *E* (*trans*) geometry across the single bond C2′–C3′ is clearly shown. The most striking intermolecular contacts in **47** are Cl3···O4 [3.340 Å, operator $x, -1 + y, z$], Cl3···Cl1 [3.645 Å, $1½ - x, ½ + y, ½ - z$] and C3–H3B···Cl4 [2.76 Å, 159°, $x, -1 + y, z$], and in **48** Cl2···Cl2 [3.342 Å, $1 - x, 2 - y, 1 - z$].

Compound **50** crystallizes as a cyclohexane hemisolvate; the cyclohexane molecule is well ordered and displays crystallographic inversion symmetry. The configuration of the substituents across the single bond of the benzodioxane ring is *trans* as in **48** (Figure 3). The molecules associate through several short contacts, in particular the C–H···π contacts C2′-H2′···centroid(C12,13,15,16) [2.64 Å, 165°,

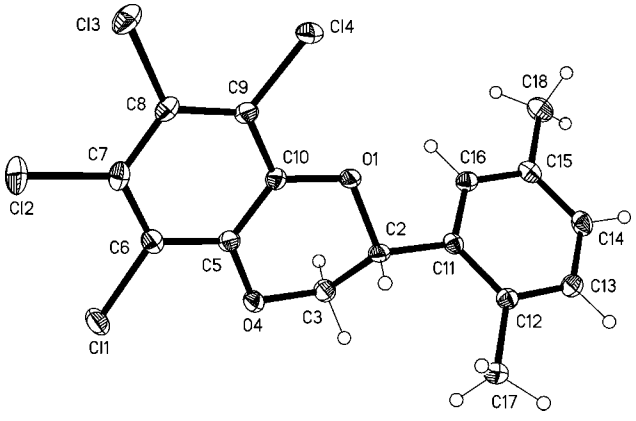


Figure 1. The structure of adduct **47** in the crystal.

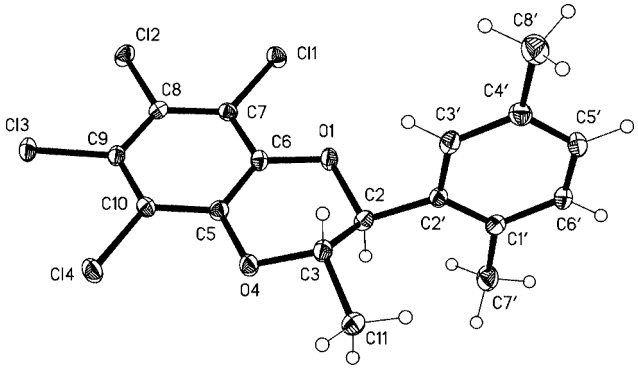


Figure 2. The structure of adduct **48** in the crystal.

operator ½ – *x*, –½ + *y*, 1½ – *z*], Cl2···Cl3 [3.542 Å, –1 – *x*, 1 – *y*, 1 – *z*] and C9–H9B···Cl4 [2.77 Å, 137°, ½ – *x*, –½ + *y*, 1½ – *z*].

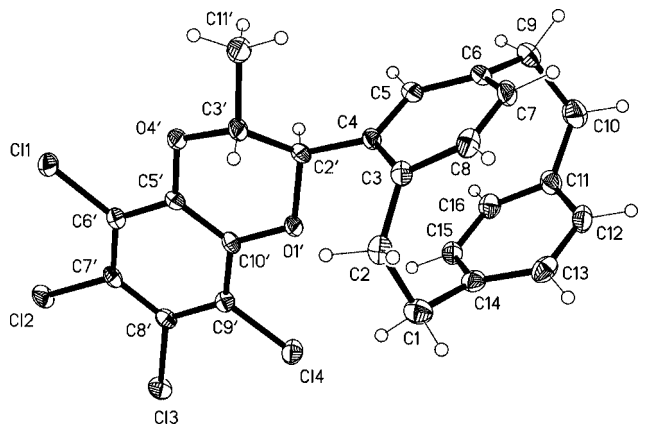
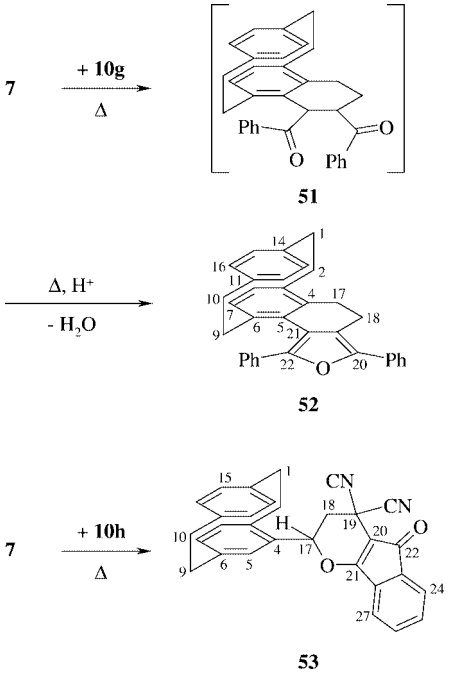


Figure 3. The structure of adduct **50** in the crystal.

g) (*E*)-1,2-Dibenzoylethene (10g), 2-Dicyanomethyleninedan-1,3-dione (10h), and Other Dienophiles: Exploratory experiments were undertaken with **10g** and **10f** as well as several other functionalized dienophiles. Whereas addition of acrylonitrile, fumaronitrile, 1,2-bis(phenylsulfonyl)ethene, propinal and (*p*-tolylsulfonyl)acetylene to **7** failed – in most cases these dienophiles decomposed under the comparatively harsh reaction conditions – refluxing an equimolar mixture of **7** and **10g** in acetic acid/acetic acid anhydride for 3 days resulted in the formation of the furan **52** in 91% yield. Clearly, the primary adduct **51** does not survive the reaction conditions and cyclizes under dehydration to **52**, a reaction that has often been observed for 1,4-diketones (Scheme 10).



Scheme 10. Cycloadditions of 4-vinyl[2.2]paracyclophane and miscellaneous dienophiles.

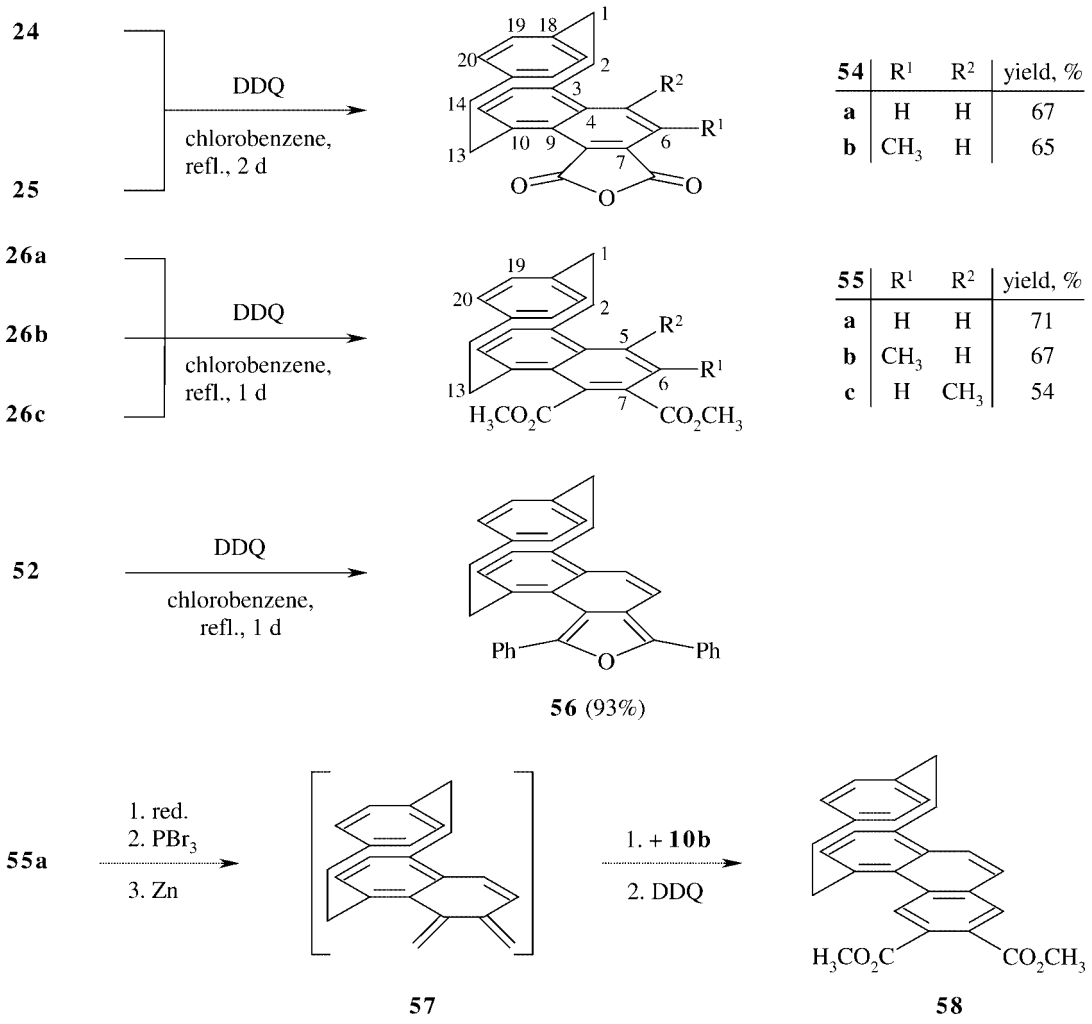
As usual, the structural assignment of **52** is indicated by the spectroscopic data of the adduct. In the ^{1}H NMR spectrum the multiplets for the ethano bridge protons and the methylene groups at C-17 and C-18 overlap, but the ^{13}C signals (triplets) for the corresponding carbon atoms are clearly resolved (δ = 20.09 and 26.40 ppm for C-17 and C-18, and δ = 33.49, 34.53. 34.92. 35.28 ppm for the ethano-bridge carbon atoms). On the basis of COSY H,H and C,H spectra all signals could be unambiguously assigned and the appropriate chemical shifts can be found in the Exp. Sect.

With the efficient π-acceptor **10h**, compound **7** also undergoes a high-yielding cycloaddition (refluxing toluene, 3 days) providing the 1:1 adduct **53** in 93% yield. Its NMR spectra resemble those of related adducts (e.g. **39**, **49**); in particular the protons at C-17 and C-18 are easily assigned. One of the latter is registered at δ = 2.75 ppm as a doublet of doublets with J = 15.2 and 11.6 Hz, whereas the signals of the other proton at this position overlaps with the multiplets of the ethano bridges of the cyclophane. On the other hand 17-H appears at δ = 5.42 ppm as double doublet with J = 11.6 and 1.3 Hz. In the ^{13}C NMR spectrum the dihydro-2*H*-pyran ring is characterized by absorptions at δ = 25.90 (C-18), 36.50 (C-19), 78.65 (C-17), 97.68 (C-20), and 175.95 (C-21) ppm. To rationalize the observed regioselectivity, we again postulate that the *cisoid* olefin (e.g. conformation **7**) is attacked from the "outside" of the phane system.

Further Transformations of the Cycloadducts

The above transformations not only illustrate that 4-alkenyl[2.2]paracyclophanes can participate in a wide spectrum of cycloaddition reactions ([2+4]- and [2+2] cycloadditions, ene reactions, additions to heterodienophiles), but also that the isolated adducts can be used as substrates for further investigations in cyclophane chemistry. In particular, some of the adducts are useful intermediates for functionalized annelated cyclophanes, opening up new routes for the preparation of novel helicenes[36] as illustrated in Scheme 11.

As expected, the aromatization of the anhydrides **24** and **25** and the diesters **26a**–**c** with DDQ in refluxing chlorobenzene did not cause any problems. The naphthalenophane anhydrides **54a** and **b** and the diesters **55a**–**c** were obtained in acceptable yields, and their structures proved by the usual analytical methods (see Exp. Sect.). Oxidation of the furanophane **52** was even achieved in near quantitative yield. The resulting product **56** is already a helicenophane, and the possible preparation of these derivatives in the carbocyclic series is illustrated in the last line of scheme 11, applying a route previously developed by us for linear annelation of [2.2]paracyclophanes.[5] Reduction of **55a** to the diol and subsequent treatment with phosphorus tribromide could provide a dibromide that, on reduction with zinc, could yield the *ortho*-xylylene intermediate **57**. In the presence of a dienophile such as **10b**, this would be trapped to a Diels–Alder adduct that could be aromatized as described above. The resulting benzolog **58** of **55a** could be resubjected to



54	R^1	R^2	yield, %
a	H	H	67
b	CH_3	H	65

55	R^1	R^2	yield, %
a	H	H	71
b	CH_3	H	67
c	H	CH_3	54

56 (93%)

57 **58**

Scheme 11. Aromatization of the primary adducts between 4-alkenyl[2.2]paracyclophanes and various dienophiles.

the same sequence or the intermediate be trapped by other dienophiles. Cylophanes containing differently substituted aromatic "decks" are not readily prepared by the routes of traditional cyclophane chemistry. The approach presented here thus offers a potentially useful alternative.

Experimental Section

General Remarks: Melting points: Kofler hot stage, uncorrected. ^{1}H NMR and ^{13}C NMR spectra: in $CDCl_3$, chemical shifts relative to internal TMS; Bruker AM-300 (300.1 and 75.5 MHz), WM-400 and Bruker AM-400 (400.1 and 100.6 MHz). TLC: Silica gel PF_{254} (Merck), 20×48 cm plates were employed using the solvents listed below. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm UV light. Column chromatography: silica gel 7714 (Merck). Elemental analyses: Microanalysis Laboratory of the Institute of Inorganic Chemistry, Technical University of Braunschweig. MS: Finnigan MAT 8430 spectrometer at 70 eV. IR: Perkin–Elmer 1420, Nicolet 320 FT-IR using KBr pellets and paraffin films. UV: Beckman UV 5230. PC = 4-[2.2]paracyclophanyl. 2,5-Dimethylstyrene (**45**) is a commercially available compound (Aldrich); 1,4-dimethyl-2-propenylbenzene (**46**) has been reported several times in the literature.[37] We prepared it by Wittig reaction from ethyl(triphenyl)phosponium bromide and 2,5-dimethylbenzaldehyde (Aldrich).

1. Preparation of 4-Alkenyl[2.2]paracyclophanes

a) 4-Ethenyl[2.2]paracyclophane (7): To a suspension of methyl(triphenyl)phosphonium bromide (27.2 g, 76.2 mmol) in 250 mL of anhydrous tetrahydrofuran was added at 0 °C 40 mL (76.2 mmol) of *n*-butyllithium (1.9 M in *n*-hexane). After stirring at room temp. for 2 h a solution of 4-formyl[2.2]paracyclophane (**14**)[13] (12.0 g, 51.0 mmol) in 300 mL of tetrahydrofuran was added at 0 °C to the ylid solution. The reaction mixture was stirred at room temp. overnight and hydrolyzed under ice cooling with ca. 200 mL of water. The solution was concentrated to ¼ of its volume and extracted thoroughly with dichloromethane. The combined organic phases were washed with water, dried with sodium sulfate and the solvents were removed in vacuo. The oily residue was purified by silica gel column chromatography with dichloromethane: 9.8 g (82%) of **7**, colorless needles (petroleum ether), m.p. 78 °C. ^{1}H NMR: δ = 2.72–3.53 (m, 8 H, ethano bridges), 5.17–5.61 (m, 2 H, $=CH_2$), 6.29–6.95 (m, 8 H, Ar-H and Ar-CH=) ppm. ^{13}C NMR: δ = 33.60, 34.61, 35.16, 35.41 (t, C-1,-2,-9,-10), 114.14 (t, $=CH_2$), 129.15, 130.12, 131.77, 131.90, 132.97 (2×), 134.71, 135.19 (d, C-5,-7,-8, -12,-13,-15,-16, -CH=), 137.76, 137.85, 139.25 (2×), 139.73 (s, C-3, -4,-6,-11,-14) ppm. IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 2920 (s), 1620

(m), 1585 (m), 1490 (m), 1480 (m), 980 (s), 930 (m), 900 (s), 860 (m), 790 (m). UV (methanol): λ_{max} (lg ε) = 218 nm (4.25), 281 (3.74), 232 (2.69). MS (70 eV): *m*/*z* (%) = 234 (71) [M$^+$], 202 (12), 189 (13), 165 (13), 152 (16), 141 (12), 129 (100), 115 (76), 104 (74), 89 (41), 78 (56), 63 (42). $C_{18}H_{18}$ (234.34): calcd. C 92.26, H 7.74; found C 92.31, H 7.96.

b) 4-(1-Propenyl)[2.2]paracyclophane (16 and 17): To a suspension of ethyl(triphenyl)phoshonium bromide (23.4 g, 63.0 mmol) in 200 mL of anhydrous tetrahydrofuran was added at 0 °C *n*-butyllithium (33.2 mL, 63.0 mmol) in *n*-hexane (1.9 M). After stirring at room temp. for 2 h a solution of **14** (10 g, 42.2 mmol) in 150 mL of tetrahydrofuran was added to the ylid solution. The reaction mixture was stirred at room temp. overnight and worked up as described above for **7**. After silica gel plate chromatography with dichloromethane, 9.42 g (90%) of a colorless amorphous solid was obtained. The diasteromeric mixture of **16** and **17** was separated by HPLC (silica gel, *n*-hexane). The **16**/**17**-isomer ratio varied strongly between 1:1 and 6:1, depending on the quality of the butyllithium solution.

Fraction 1: 17 (*cis*-isomer): Colorless needles (*n*-hexane), m.p. 111 °C. ^{1}H NMR: δ = 1.67 (dd, ^4J = 1.7, ^3J = 7.0 Hz, 3 H, CH_3), 2.72–3.35 (m, 8 H, ethano bridges), 5.72 (dt, J_{cis} = 11.5, ^3J = 7.0 Hz, 1 H, =CH–CH_3), 6.24–6.68 (m, 8 H, Ar-H and Ar-CH=) ppm. ^{13}C NMR: δ = 14.95 (q, CH_3), 33.87, 34.51, 35.21, 35.46 (t, C-1,-2,-9,-10), 126.35, 129.34, 129.79, 131.30, 132.18, 132.98, 133.05, 134.49, 134.74 (d, C-5,-7,-8,-12,-13,-15,-16, -CH=CH-), 136.77, 138.15, 139.11, 139.25, 139.57 (s, C-3,-4,-6,-11,-14) ppm. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (m) cm^{-1}, 3020 (m), 2935 (s), 2860 (m), 1645 (w), 1590 (m), 1560 (m), 1500 (s), 1440 (s), 940 (s), 910 (s), 870 (s), 800 (s), 770 (s), 750 (m), 720 (s). UV (acetonitrile): λ_{max} (lg ε) = 215 nm (4.27), 222 (4.23), 276 (3.67), 311 (2.60). $C_{19}H_{20}$ (248.37): calcd. C 91.88, H 8.12; found C 91.80, H. 8.10.

Fraction 2: 16 (*trans*-isomer): Colorless needles (*n*-hexane), m.p. 106–108 °C. ^{1}H NMR: δ = 1.93 (dd, ^4J = 1.7, ^3J = 6.6 Hz, 3 H, CH_3), 2.68–3.47 (m, 8 H, ethano bridges), 5.96 (dt, J_{trans} = 15.6, ^3J = 6.6 Hz, 1 H, =CH–CH_3), 6.34–6.69 (m, 8 H, Ar-H and Ar-CH=) ppm. ^{13}C NMR: δ = 18.8 (q, CH_3), 33.74, 34.65, 36.24, 35.49 (t, C-1,-2,-9,-10), 126.22, 129.47, 129.56, 130.95, 130.98, 131.80, 132.94, 132.98, 134.66 (d,-5,-7,-8,-12,-13,-15,-16, Ar-CH, =CH–CH_3), 137.04, 138.01, 139.26, 139.35, 139.60 (s, C-3,-4,-6,-11,-14) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2940 (s), 2860 (m), 1595 (m), 1560 (m), 1440 (s), 1420 (m), 965 (s), 945 (m), 900 (m), 800 (s), 720 (s). UV (acetonitrile): λ_{max} (lg ε) = 218 nm (4.28), 282 (3.79), 317 (2.88). MS (70 eV): *m*/*z* (%) = 248 (43) [M$^+$], 143 (100), 141 (30), 129 (99), 115 (46), 104 (59), 91 (24), 84 (42), 78 (40). $C_{19}H_{20}$ (248.37): calcd. C 91.88, H 8.12; found C 91.87, H 8.12.

c) 4-(2-Propenyl)[2.2]paracyclophane (18): Methylmagnesium iodide was prepared from magnesium (1.46 g, 60.0 mmol) and methyl iodide (3.73 mL, 60.0 mmol) in 45 mL of anhydrous ether. To this solution was added 4-acetyl[2.2]paracyclophane (**15**)[14] (10.0 g, 40.0 mmol) in 500 mL of ether. The reaction mixture was stirred under reflux for 2 h, cooled to room temp. and worked-up as described above. The resulting tertiary alcohol (7.13 g, 67%) was used as obtained in the dehydration step. To a solution of the tertiary alcohol (10.62 g, 40.0 mmol) in 100 mL of trichloromethane was added 70 mL of 6 N hydrochloric acid. After vigorous stirring at room temp. for 12 h, the organic phase was separated, and the aqueous phase carefully extracted with trichloromethane. The combined organic phases were neutralized (hydrogen carbonate), dried (sodium sulfate), and the solvent was removed in vacuo: 8.23 g (83%) of **18**, colorless plates (sublimed at 61 °C, 0.01 Torr), m.p. 75 °C. ^{1}H NMR: δ = 2.04 (br. s, 3 H, CH_3), 2.87–3.37 (m, 8 H, ethano bridges), 5.12–5.18 (m, 2 H, =CH_2), 6.33–6.65 (m, 7 H, Ar-H) ppm. ^{13}C NMR: δ = 23.86 (q, CH_3), 34.40, 35.15, 35.22, 35.42 (t, C-1,-2,-9,-10), 115.30 (t, =CH_2), 130.10, 130.62, 132.13, 132.19, 132.32, 132.94, 135.40 (d, C-5,-7,-8,-12,-13,-15,-16), 136.73, 139.18, 139.29, 139.66, 142.95, 145.37 (s, C-3,-4,-6,-11,-14, Ar-C=) ppm. IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 3025 (w), 2950 (m), 2920 (s), 2850 (m), 1625 (m), 1590 (m), 1500 (m), 940 (m), 900 (s), 850 (s), 825 (m), 715 (s). UV (acetonitrile): λ_{max} (lg ε) = 215 nm (4.25), 225 (4.22), 263(3.53). MS (70 eV): *m*/*z* (%) = 248 (23) [M$^+$], 143 (100), 129 (43), 127 (22), 105 (20). $C_{19}H_{20}$ (248.37): calcd. C 91.88, H 8.12; found C 91.80, H 8.22.

d) 4-(2-Butenyl)[2.2]paracyclophane (19–21): To a solution of ethylmagnesium bromide [from magnesium (0.52 g, 21.4 mmol) and ethyl bromide (1.6 mL, 21.4 mmol)] in 10 mL of anhydrous ether was added at room temp. **15** (3.5 g, 14.0 mmol) in 150 mL of ether. After heating the reaction mixture for 2 h under reflux it was worked-up as described above. The isolated tertiary alcohol (2.7 g, 53%) was dissolved in 50 mL of trichloromethane, and 50 mL of 6 N hydrochloric acid was added. After vigorous stirring for 16 h at room temp. the dehydration mixture was worked-up as described above for **18**: 2.90 g (79%) of a mixture of **19**–**21**. HPLC separation (silica gel, *n*-hexane) provided two fractions in 1:3 ratio.

Fraction 1 19 + 21: ^{1}H NMR: δ = 1.00 (t, J = 7.4 Hz, 3 H, CH_3 of ethyl group), 2.10–2.55 (br. q, 2 H, CH_2 of ethyl group), 2.60–3.64 (m, 8 H, ethano bridges), 5.16 (br. s, 2 H, =CH_2), 5.8–6.9 (m, 7 H, Ar-H); **21** was only present as a trace component.

Fraction 2, 20: Colorless needles (*n*-hexane), m.p. 95 °C. ^{1}H NMR: δ = 1.81–1.83 (m, 3 H, =$CHCH_3$), 1.96 [br. s, 3 H, Ar-C(CH_3)=], 2.87–3.27 (m, 8 H, ethano bridges), 5.65–5.69 (m, 1 H, =CH), 6.31–6.63 (m, 7 H, Ar-H) ppm. ^{13}C NMR: δ = 14.37 (q, =$CHCH_3$), 18.02 [q, Ar-C(CH_3)=], 34.43, 35.19, 35.24, 35.46 (t, C-1,-2,-9,-10), 124.75, 129.94, 130.33, 131.53, 132.13, 132.26, 132.92, 135.29 (d, C-5,-7,-8,-12,-13,-15,-16, =CH–CH_3), 136.68, 136.87, 139.05, 139.25, 139.71, 145.18 (s, C-3,-4,-6,-11,-14, Ar-C=) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2935 (s), 2860 (s), 1590 (m), 1510 (m), 1440 (m), 1420 (w), 1380 (m), 945 (m), 905 (s), 840 (s), 825 (m), 725 (s), 710 (m), 660 (s). UV (acetonitrile): λ_{max} (lg ε) = 216 nm (4.28), 222 (4.26), 265 (3.61). MS (70 eV): *m*/*z* (%) = 262 (81) [M$^+$], 202 (10), 157 (100), 143 (93), 128 (78), 115 (41), 104 (57), 91 (36), 78 (41). $C_{20}H_{22}$ (262.40): calcd. C 91.55, H 8.45; found C 91.51, H 8.64.

2. Cycloadditions

a) Maleic Anhydride (10a) to 7: In 100 mL of glacial acetic acid **7** (1.0 g, 4.3 mmol) and **10a** (0.42 g, 4.3 mmol) were heated under reflux for 5 d. The reaction mixture was cooled to room temp. allowing the anhydride **24** to precipitate. A further crop of adduct was obtained when the solution was concentrated to ca. 1/3 of its volume; total yield: 1.03 g (72%) of **24**, yellowish needles (acetic acid), m.p. 263–265 °C. ^{1}H NMR (CF_3COOH; the adduct is insoluble in other solvents): δ = 1.57–1.67 (m, 1 H, 18-H), 2.31–2.41 (m, 2 H, 17-H), 2.27–3.70 (m, 10 H, 18-, 19-H, ethano bridges), 4.04 (d, ^3J = 8.4 Hz, 1 H, 20-H), 6.39 (dd, J = 7.9 and 1.8 Hz, 1 H, 12-H), 6.49–6.66 (m, 5 H, remaining Ar-H) ppm. Since the anhydride is unstable in trifluoroacetic acid, no ^{13}C NMR spectrum could be obtained. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w), 2940 (s), 1860 (m), 1780 (s), 1500 (m), 1470 (m), 1440 (m), 1415 (m), 1310 (m), 1225 (s), 1070 (s), 960 (s), 920 (s), 720 (s). UV (methanol): λ_{max} (lg ε) = 227 nm (4.20). MS (70 eV): *m*/*z* (%) = 332 (26) [M$^+$], 228 (30), 198 (10), 156 (18), 105 (15), 104 (100). $C_{22}H_{20}O_3$ (332.40): calcd. C 79.50, H 6.06; found C 79. 47, H 6.04.

b) Maleic Anhydride (10a) to 16: In 250 mL of acetic acid compound **16** (2.4 g, 96.0 mmol) and **10a** (1.12 g, 96.0 mmol) were

heated to reflux for 6 d. The solvent was removed in vacuo and the residue taken up in ether; the adduct **25** (1.80 g, 54%) precipitated as a yellowish solid. Recrystallization from ethanol provided analytically pure adduct, colorless needles, m.p. 179–181 °C. ^{1}H NMR: δ = 1.00 (d, ^3J = 6.5 Hz, 3 H, CH_3), 2.38–3.23 and 4.03–4.20 (m, 12 H, ethano bridges, 17-,18-,19-H), 3.87 (d, ^3J = 6.1 Hz, 1 H, 20-H), 6.41–6.60 (m, 6 H, Ar-H) ppm. ^{13}C NMR: δ = 17.82 (q, CH_3), 28.34 (d, C-18), 32.38, 33.32, 33.44, 33.78, 34.00 (t, C-1,-2,-9,-10,-17), 45.31, 46.02 (d, C-19,-20), 127.24, 127.92, 132.07, 133.34, 133.48, 133.59 (d, C-7,-8,-12,-13,-15,-16), 129.60, 134.86, 138.32, 138.76, 139.16, 139.18 (s, C-3,-4,-5,-6,-11,-14), 172.19, 177.73 (s, 2×C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (m), 1750 (s), 1700 (s), 1460 (m), 1450 (m), 1300 (s), 1210 (m), 1170 (s), 1150 (s), 1050 (m), 720 (m). UV (methanol): λ_{max} (lg ε) = 228 nm (4.15). MS (70 eV): *m*/*z* (%) = 346 (30) [M$^+$], 318 (41), 242 (88), 212 (84), 199 (29), 169 (77), 150 (78), 141 (35), 129 (40), 115 (37), 104 (100), 78 (40). $C_{23}H_{22}O_3$ (346.42): calcd. C 79.74, H 6.40; found 79.60, H 6.38.

c) Dimethyl Acetylenedicarboxylate (10b) to 7: A solution of compound **7** (8.0 g, 34.4 mmol) and **10b** (4.2 mL, 34.4 mmol) in 750 mL of glacial acetic acid was refluxed for 3 d. The solvent was removed in vacuo and the oily residue purified by thick layer chromatography (silica gel, dichloromethane): 9.2 g (72%) of diester **26a**, colorless prisms (ether/ethanol), m.p. 129–131 °C. ^{1}H NMR: δ = 2.33–3.43 (m, 12 H, ethano bridges, 17-,18-H), 3.79 (s, 3 H, $COOCH_3$), 3.88 (s, 3 H, $COOCH_3$), 6.37 and 6.41 (AB-q, 2 H, ^3J = 7.8 Hz, 7-,8-H), 6.52–6.62 (m, 4 H, 12-,13-,15-,16-H) ppm. ^{13}C NMR: δ = 23.12 (t, C-18), 24.08 (t, C-17), 32.50, 34.39, 34.82, 35.09 (t, C-1,-2,-9,-10), 51.99 and 52.24 (q, $COOCH_3$), 130.04, 131.34, 132.39, 132.90, 134.34, 135.97 (d, C-7,-8,-12,-13,-15,-16), 128.87, 130.96, 136.10, 136.63, 138.26, 138.82, 139.22, 139.28 (s, C-3,-4,-5,-6,-11,-14,-19,-20), 167.76 and 169.98 (s, ester carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (w), 2950 (m), 2920 (m), 2850 (m), 1730 (s), 1715 (s), 1610 (m), 1265 (s), 1225 (s), 1205 (s), 1110 (m), 790 (m). UV (methanol): λ_{max} (lg ε) = 222 nm (4.24), 329 (3.91). MS (70 eV): *m*/*z* (%) = 376 (80) [M$^+$], 345 (20), 317 (39), 272 (100), 257 (95), 239 (82), 227 (38), 213 (90), 183 (61), 153 (65). $C_{24}H_{24}O_4$ (376.45): calcd. C 76.57, H 6.43; found C 76.89, H 6.62.

d) Dimethyl Acetylenedicarboxylate (10b) to 16: As described for **7**, compound **16** (6.09 g, 24.4 mmol) and **10b** (3.02 mL, 24.6 mmol) were reacted in 750 mL of acetic acid for 5 d to yield 3.91 g (41%) of **26b**, colorless prisms (ethanol), m.p. 152–154 °C. ^{1}H NMR: δ = 0.88 (d, ^3J = 6.9 Hz, 3 H, CH_3), 2.53–3.22 (m, 11 H, ethano bridges, 17-,18-H), 3.80 (s, 3 H, $COOCH_3$), 3.92 (s, 3 H, $COOCH_3$), 6.38 and 6.42 (AB-q, ^3J = 7.8 Hz, 2 H, 7-,8-H), 6.55–6.64 (m, 4 H, 12-,13-,15-,16-H) ppm. ^{13}C NMR: δ = 16.95 (q, CH_3), 27.58 (d, C-18), 32.39, 32.63, 34.22, 34.56, 35.01 (t, C-1,-2,-9,-10,-17), 51.99 (q, $COOCH_3$), 52.33 (q, $COOCH_3$), 128.57, 132.32, 132.63, 134.02, 135.01, 136.75 (d, C-7,-8,-12,-13,-15,-16), 129.44, 131.32, 134.24, 135.98, 137.93, 138.15, 139.19, 139.23 (s, C-3,-4,-5,-6,-11,-14,-19,-20), 167.43 and 170.44 (s, ester carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1} (m), 2890 (m), 2950 (m), 1730 (s), 1720 (s), 1600 (m), 1440 (s), 1310 (s), 1290 (s), 1285 (s), 1255 (s), 1080 (s), 1030 (m), 960 (m), 880 (m), 825 (m), 750 (m). UV (methanol): λ_{max} (lg ε) = 212 nm (4.22), 223 (4.23), 256 (3.92), 3.29 (3.96). MS (70 eV): *m*/*z* (%) = 390 (77) [M$^+$], 331 (16), 286 (100), 271 (89), 253 (47), 227 (63), 195 (83), 186 (36), 104 (70), 78 (18), 59 (35). $C_{25}H_{26}O_4$ (390.48): calcd. C 76.90, H 6.71; found C 76.96, H 6.88.

e) Dimethyl Acetylenedicarboxylate (10b) to 18: As described for **7**, compound **18** (7.0 g, 28.0 mmol) and **10b** (3.44 mL, 28.0 mmol) were reacted in 700 mL of acetic acid for 5 d to yield 5.57 g (51%) of **26c**, colorless needles (ether/ethanol), m.p. 135–137 °C. ^{1}H NMR: δ = 0.92 (d, ^3J = 7.2 Hz, 3 H, CH_3), 2.46 (m, 1 H, 18-H), 2.76–3.31 (m, 10 H, ethano bridges, 17-,18-H), 3.80 (s, 3 H, $COOCH_3$), 3.82 (s, 3 H, $COOCH_3$), 6.38 and 6.43 (AB-q, ^3J = 7.7 Hz, 2 H, 7-,8-H), 6.46–6.57 (m, 4 H, 12-,13-,15-,16-H) ppm. ^{13}C NMR: δ = 20.70 (q, CH_3), 28.07 (d, C-17), 30.57, 32.18, 34.43, 34.84, 34.93 (t, C-1,-2,-9,-10,-18), 52.07 (q, $COOCH_3$), 52.25 (q, $COOCH_3$), 127.45, 129.98, 131.03, 131.22, 132.21, 135.31 (d, C-7,-8,-12,-13,-15,-16), 133.27, 134.18, 136.15, 136.48, 139.24, 139.31, 139.36, 141.22 (s, C-3,-4,-5,-6,-11,-14,-19,-20), 168.52 and 169.58 (s, ester carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2960 (s), 2880 (m), 1750 (s), 1725 (s), 1630 (m), 1575 (m), 1460 (s), 1440 (s), 1310 (s), 1265 (s), 1230 (s), 1125 (s), 1080 (s), 1040 (m), 985 (m), 880 (m), 800 (m), 780 (m). UV (methanol): λ_{max} (lg ε) = 213 nm (4.22), 222 (4.20), 245 (3.86), 330 (3.84). MS (70 eV): *m*/*z* (%) = 390 (7) [M$^+$], 375 (14), 121 (12), 119 (15), 90 (28), 88 (92), 84 (100), 49 (25). $C_{25}H_{26}O_4$ (390.48): calcd. C 76.90, H 6.71; found C 76.20, H 6.73.

f) Diethyl Azodicarboxylate (10c) to 7: A mixture of **7** (1.00 g, 4.3 mmol), **10c** (0.67 mL, 4.3 mmol), and trichloroacetic acid (0.1 g, 6.0 mmol) in 100 mL of toluene was kept at room temp. for 7 d. After washing with water and drying with magnesium sulfate, the solvent was removed in vacuo and the remaining oil separated by plate chromatography (silica gel, dichloromethane): 0.26 g (19%) of **27**, colorless prisms (ether), m.p. 185–187 °C; 0.21 g of **7** were recovered unchanged. ^{1}H NMR: δ = 1.30–1.39 (overlapping q, 6 H, 2×CH_3), 2.90–3.54 (m, 10 H, ethano bridges and 18-H), 4.17–4.35 (m, 4 H, –OCH_2–), 5.18 (dd, *J* = 9.1 and 2.6 Hz, 1 H, 17-H), 6.32–6.56 (m, 7 H, 5-,7-,8-,12-,13-,15-,16-H) ppm. ^{13}C NMR: δ = 14.22 (q, CH_3), 14.72 (q, CH_3), 33.67, 34.88, 35.02, 35.21 (t, C-1,-2,-9,-10), 43.09 (t, C-18), 62.28 (t, –OCH_2–), 64.29 (t, –OCH_2–), 76.24 (d, C-17), 130.64, 130.75, 132.08, 133.04, 133.27, 134.17, 136.25 (d, C-5,-7,-8,-12,-13,-15,-16), 132.82, 139.14, 139.32, 139.56, 140.33 (s, C-3,-4,-6,-11,-14) ppm; the signals for C-19 (line broadening, possibly because of rotation about the urethane C–N bond at intermediate rate) and the ester carbonyl group could not be observed. IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (br., w), 3000 (m), 2930 (m), 1700 (s), 1665 (s), 1495 (m), 1450 (s), 1390 (m), 1380 (s), 1355 (m), 1300 (s), 1040 (m), 1000 (m), 900 (m), 875 (m). UV (methanol): λ_{max} (lg ε) = 225 nm (4.32), 285 (2.83). MS (70 eV): *m*/*z* (%) = 408 (14) [M$^+$], 231 (13), 143 (24), 129 (100), 115 (31), 104 (86), 86 (74), 84 (86), 78 (21). $C_{24}H_{28}N_2O_4$ (408.50): calcd. C 70.57, H 6.91, N 6.86; found C 70.46, H 7.00, N 6.63.

g) Diethyl Azodicarboxylate (10c) to 18: A solution of **18** (1.0 g, 4.0 mmol), trichloroacetic acid (0.1 g, 6.0 mmol) and **10c** (0.63 mL, 4.0 mmol) in 100 mL of toluene was kept at room temp. for 7 d. Work-up as described above for **7** provided 0.34 g (30%) of **28**, while 0.31 g of **18** was revovered; white-yellow prisms (ethanol), m.p. 120–122 °C. ^{1}H NMR: δ = 1.20–1.25 (overlapping q, 6 H, 2×CH_3), 2.92–3.06 (m, 8 H, ethano bridges and –NCH_2–), 4.10–4.19 (m, 6 H, 2×–OCH_2– and ethano bridges), 5.30 and 5.40 (m, 2 H, =CH_2), 6.34–6.65 (m, 8 H, Ar-H, –NH) ppm. ^{13}C NMR: δ = 15.40 (q, 2×CH_3), 34.10, 35.04, 35.25, 35.31 (t, C-1,-2,-9,-10), 55.90 (br. t, –NCH_2–), 61.90 (t, –OCH_2–), 62.45 (t, –OCH_2–), 115.73 (br. t, =CH_2), 129.59 (2×), 131.33, 132.10, 132.28, 133.05, 135.24 (d, C-5,-7,-8,-12,-13,-15,-16), 138.94, 139.34, 139.47, 139.56 (2×), 145.31 (s, C-3,-4,-6,-11,-14,-7) ppm; the C=O signals were not observed. IR (KBr): $\tilde{\nu}$ = 3260 cm^{-1} (s), 3000 (m), 2950 (m), 1770 (s), 1535 (s), 1495 (m), 1480 (m), 1450 (s), 1390 (m), 1295 (s), 1270 (s), 1225 (br., s), 1080 (s), 915 (m), 800 (m), 790 (m). UV (methanol): λ_{max} (lg ε) = 215 nm (4.25), 223 (4.24). MS (70 eV): *m*/*z* (%) = 422 (17) [M$^+$], 349 (16), 320 (18), 262 (37), 246 (58), 228 (64), 200 (21), 184 (21), 157 (72), 141 (100), 128 (72), 105 (68), 104 (68), 91 (24). $C_{25}H_{30}N_2O_4$ (422.52): calcd. C 71.07, H 7.16, N 6.63; found C 71.03, H 7.19, N 6.56.

h) 1-Phenyl-1,3,4-triazolin-2,4-dione (10d) to 7: A solution of **7** (1.00 g, 4.3 mmol), **10d** (0.75 g, 4.3 mmol) and trichloroacetic acid (100 mg, 6.0 mmol) in 100 mL of toluene was kept at room temp. for 7 d. The reaction mixture was washed with water, dried with magnesium sulfate, and the solvent was removed in vacuo. When the oily residue was taken up in ethanol, the 2:1 adduct **34** precipitated as a colorless, amorphous solid (0.81 g, 32%), m.p. 214–216 °C. ^{1}H NMR: δ = 1.56–1.67, 2.27–2.62, 2.81–3.20 (m, 8 H, ethano bridges), 4.26 (dd, J = 18.1 and 4.7 Hz, 1 H, 18-H), 4.67 (dd, J = 18.1 and 2.2 Hz, 1 H, 18-H), 4.90 (d, J = 2.2 Hz, 1 H, 8-H), 5.51 (dt, J = 6.3 and 2.2 Hz, 1 H, 5-H), 5.96 (d, J = 6.3 Hz, 1 H, 6-H), 6.22 (dd, J = 4.7 and 2.2 Hz, 1 H, 17-H), 6.84 and 6.99 (AB-q, J = 7.8 Hz, 2 H, 15-,16-H), 7.12–7.56 (m, 12 H, 2×C_6H_5, 12-,13-H) ppm. ^{13}C NMR: δ = 31.95, 33.86, 37.91, 43.88 (t, C-1, -2,-9,-10), 44.03 (t, C-18), 58.78 (d, C-5), 60.14 (d, C-6), 65.01 (s, C-3), 123.47, 123.74, 125.21 (2×), 125.42 (2×), 126.62, 128.24, 128.28, 129.07 (2×), 129.09 (2×), 130.35, 130.74, 135.24 (d, C-10,-12,-13, -15,-16,-17, 2×C_6H_5), 131.25 (2×), 136.61, 137.84, 141.35, 141.66 (s, C-4,-7,-11,-14, 2×N–Ph), 151.63, 151.95, 155.60, 156.15 (s, 4×C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 2920 (m), 1770 (m), 1720 (s), 1620 (m), 1600 (m), 1500 (s), 1410 (s), 900 (w), 760 (m), 720 (m), 690 (m). UV (methanol): λ_{max} (lg ε) = 224 nm (4.49), 300 (3.45). MS (70 eV): m/z (%) = 584 (10) [M$^+$], 409 (19), 290 (9), 178 (8), 177 (50), 129 (14), 120 (24), 119 (100), 92 (12), 91 (53), 77 (18). $C_{34}H_{28}N_6O_4$ (584.63): calcd. C 69.85, H 4.83, N 14.38; found C 69.70, H 4.78, N 14.20.

i) Tetracyanoethene (10e) to 7: A solution of **7** (0.8 g, 3.4 mmol) **10e** (0.435 g, 3.4 mmol) in 60 mL of glacial acetic acid was kept at room temp. for 3 d. When the solvent was removed in vacuo the [2+2] adduct **37** or **39** precipitated (0.41 g, 33%) as a violet solid; recrystallization from ethanol provided colorless needles (m.p. 193–196 °C) which soon turned yellow. ^{1}H NMR: δ = 2.99–3.50 (m, 10 H, ethano bridges and 18-H), 4.59 (dd, J = 12.1 and 8.4 Hz, 1 H, 17-H), 6.18 (br. s, 1 H, H-5), 6.26–6.68 (m, 6 H, 7-,8-,12-,13-,15-, 16-H) ppm. ^{13}C NMR: δ = 33.62, 34.51, 34.95, 35.23 (2×) (t, C-1, -2,-9,-10, C-18), 43.88 (2×) (s, C-19,-20), 45.69 (d, C-17), 108.03, 109.84, 110.39, 111.09 (s, 4×CN), 129.54, 131.53, 132.03, 133.57, 133.87, 134.97, 136.57 (d, C-5,-7,-8,-12,-13,-15,-16), 130.73, 137.91, 138.81, 139.88, 141.64 (s, C-3,-4,-6,-11,-14). IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2960 (s), 2940 (s), 2860 (m), 1595 (s), 1500 (s), 1490 (m), 1440 (m), 960 (m), 940 (m), 900 (s), 850 (m). UV (methanol): λ_{max} (lg ε) = 227 nm (4.28). MS (70 eV): m/z (%) = 362 (5) [M$^+$], 335 (2), 192 (6), 130 (12), 129 (23), 105 (23), 104 (100), 78 (11). $C_{24}H_{18}N_4$ (362.43): calcd. C 79.54, H 5.00, N 15.46; found C 79.70, H 4.93, N 15.67.

j) Tetracyanoethene (10e) to 18: As described above for **7**, a solution of **18** (0.8 g, 3.2 mmol) and **10e** (0.41 g, 3.2 mmol) in 60 mL of acetic acid was kept at room temp. for 2 d. The adduct **41** crystallized from the solution as colorless needles: 0.97 g (81%); m.p. 126 –128 °C. ^{1}H NMR: δ = 2.29 (s, 3 H, CH_3), 2.45–2.58 and 2.93–3.27 (m, 8 H, ethano bridges), 3.30 and 3.47 (AB, J = 12.6 Hz, 2 H, 18-H), 6.26–6.49 and 6.67–6.76 (m, 7 H, 5-,7-,8-,12-,13-,15-,16-H) ppm. ^{13}C NMR: δ = 20.55 (q, CH_3), 32.87 (s, C-17), 33.45, 35.12, 35.23, 35.85, 44.27 (t, C-1,-2,-9,-10,-18), 51.55 (2×) (s, C-19,-20), 108.68, 109.30, 110.35, 111.79 (s, 4×CN), 127.03, 131.17, 132.12, 132.40, 133.23, 135.04, 136.73 (d, C-5,-7,-8,-12,-13,-15,-16), 134.65, 138.16, 139.15, 140.07, 140.79 (s, C-3,-4,-6,-11,-14) ppm. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (m), 2980 (m), 2920 (s), 2850 (m), 2250 (w), 1900 (w), 1590 (m), 1450 (s), 1385 (s), 1300 (m), 1260 (m), 900 (s), 790 (s), 720 (s). UV (methanol): λ_{max} (lg ε) = 226 nm (4.21). MS (70 eV): m/z (%) = 248 (58) [M$^+$ – 128 (TCNE)], 143 (100), 129 (62), 128 (62), 105 (20), 76 (16). $C_{25}H_{20}N_4$ (376.46): calcd. C 79.76, H 5.35, N 14.88; C 79.70, H 5.30, N 14.76.

k) Tetracyanoethene (10e) to 20: From compound **20** (0.7 g, 2.7 mmol) and **10e** (0.35 g, 2.7 mmol) in 55 mL of acetic acid under the above conditions was obtained **42** (0.47 g, 44%) as a mixture of diastereomers; colorless needles (ethanol), m.p. 173–175 °C. ^{1}H NMR: δ = 1.66 (d, ^3J = 7.0 Hz, 3 H, CH_3, H-22), 1.76 (d, ^3J = 6.9 Hz, 3 H, CH_3, H-22), 2.16 and 2.17 (2×s, 3 H, CH_3, H-21), 2.78–3.38 (m, 8 H, ethano bridges), 3.79 (q, ^3J = 6.9 Hz, 1 H, 18-H), 6.05–6.74 (m, 7 H, H-5,-7,-8,-12,-13,-15,-16) ppm. ^{13}C NMR: δ = 13.12 and 13.70 (q, CH_3), 22.05 (q, CH_3), 33.84, 34.57, 34.96, 35.11 (2×), 35.22, 35.71, 35.89 (t, C-1,-2,-9,-10), 38.56 (s, C-17), 46.56 and 47.67 (d, C-18), 54.37, 55.32 (s, C-19,-20), 110.28, 110.36 (s, CN), 126.23, 127.77, 131.22, 131.56, 131.76, 131.87, 132.73, 132.90, 134.48, 134.58, 137.18, 137.27 (d, C-5,-7,-8,-12,-13,-15,-16), 135.97, 138.05, 138.33, 139.82, 139.97, 140.09, 140.87, 141.03 (s, C-3,-4,-6,-11,-14) ppm. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w), 2980 (m), 2920 (s), 2850 (m), 2250 (w), 1590 (m), 1460 (s), 1410 (m), 1400 (m), 1120 (m), 900 (m), 880 (m), 800 (m), 720 (s). UV (methanol): λ_{max} (lg ε) = 227 nm (4.26). MS (70 eV): m/z (%) = 390 (10) [M$^+$], 158 (27), 157 (100), 143 (49), 128 (39), 105 (16), 104 (74). $C_{26}H_{22}N_4$ (390.49): calcd. C 79.97, H 5.68, N 14.35; C 79.88, H 5.85, N 14.27.

l) Tetrachloro-*o*-quinone (10f) to 2-Vinyl-*p*-xylene (45): To a refluxing solution of **45** (0.27 g, 2 mmol) in dry toluene (30 mL), a solution of **10f** (0.49 g, 2 mmol) in dry toluene (20 mL) was added dropwise under N_2 during 30 min; the mixture was refluxed for 3 d. The solvent was concentrated in vacuo and the residue was separated by plate chromatography (silica gel, cyclohexane) to give adduct **47** (0.43 g, 56%) as colorless crystals (cyclohexane), m.p. 163 °C. ^{1}H NMR: δ = 2.36 (s, 6 H, 2 CH_3), 4.02 (dd, J = 11.8 and 9.0 Hz, 1 H, 3-H), 4.52 (dd, J = 11.8 and 2.3 Hz, 1 H, 3-H′), 5.34 (dd, J = 8.9 and 2.3 Hz, 1 H, 2-H), 7.12–7.14 (m, 2 H, Ar-H), 7.35 (s, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 18.55, 21.08 (q, 2×CH_3), 68.53 (C-3), 73.09 (C-2), 120.36, 120.88 (Ar-C-Cl, C-6 and/or C-9), 124.61, 124.71 (Ar-C-Cl, C-7 and/or C-8), 126.72 (Ar-C), 128.28, 129.83, 130.77 (Ar-CH), 132.14, 132.16 (Ar-C), 139.36 (C-5), 139.63 (Ar-C-10) ppm. IR (KBr): $\tilde{\nu}$ = 3020–3000 cm^{-1} (w), 2949–2865 (w), 1590 (s), 1438 (m), 1380 (s), 1554 (s), 1380 (m), 1330 (w), 1280 (m), 1080 (s). MS (70 eV): m/z (%) = 382 [M$^+$ + 4] (20), 380 [M$^+$ + 2] (36), 378 [M$^+$] (100), 376 (82), 261 (12), 259 (30), 132 (40), 117 (52), 115 (22). $C_{16}H_{12}Cl_4O_2$ (378.09): calcd. C 50.83, H 3.20, Cl 37.51; found C 50.70, H 3.16, Cl 37.44.

m) Tetrachloro-*o*-quinone (10f) to 2-(*E*-1-Propenyl)-*p*-xylene (46): As described for **45**, a solution of **46** (0.29 g, 2 mmol) and **10f** (0.49 g, 2 mmol) in anhydrous toluene (50 mL) was refluxed under N_2 for 3 d. The solvent was removed in vacuo and the residue was separated by plate chromatography (silica gel, cyclohexane) to give **48** (0.46 g, 65%), as colorless crystals (cyclohexane), m.p. 120–122 °C. ^{1}H NMR: δ = 1.00 (d, J = 6.3 Hz, 3 H, CH_3), 2.17 (s, 6 H, 2×CH_3), 4.12–4.18 (m, 1 H, 3-H), 4.52 (d, J = 8.00 Hz, 1 H, 2-H), 6.36–7.35 (m, 3 H, Ar-H) ppm. ^{13}C NMR: δ = 15.87 (CH_3), 25.08, 25.23 (2 CH_3, *p*-xylene), 67.69 (C-3), 76.65 (C-2), 122.60, 124.61 (Ar-C-Cl, C-6 and/or C-8), 131.00, 132.40 (Ar-C-Cl, C-7 and/or C-8), 132.48, 132.71, 134.56 (Ar-CH), 135.87, 136.40 (Ar-C), 139.56 (*p*-xylene-C), 139.78 (C-5), 140.46 (C-10) ppm. IR (KBr): $\tilde{\nu}$ = 3025–3006 cm^{-1} (m), 2985–2855 (m), 1557 (s), 1060 (s). MS (70 eV): m/z (%) = 396 [M$^+$ + 4] (24), 394 [M$^+$ + 2] (50), 392 [M$^+$] (100), 390 (18), 349 (6), 275 (10), 273 (22), 271 (18), 147 (12), 146 (80), 131 (52), 105 (10), 91 (12). $C_{17}H_{14}Cl_4O_2$ (392.12): calcd. C 52.07, H 3.60, Cl 36.17; found C 51.90, H 3.54, Cl 36.00.

n) Tetrachloro-*o*-quinone (10f) to 7: To a refluxing solution of **7** (0.47 g, 2.0 mmol) in anhydrous toluene (50 mL), a solution of **10f** (0.49 g, 2 mmol) in anhydrous toluene (50 mL) was added dropwise under N_2 during 30 min. After further refluxing for 2 d (the reac-

tion was monitored by TLC), the solvent was removed in vacuo and the residue was subjected to plate chromatography (silica gel, hexane): adduct **49** was obtained (0.60 g, 62%) as colorless needles (cyclohexane), m.p. 210–212 °C. ^{1}H NMR: δ = 2.80–3.20 (m, 6 H, ethano bridges), 3.28–3.54 (m, 2 H, ethano bridges), 4.30 (dd, J = 11.9 and 8.9 Hz, 1 H, 18-H), 4.40 (dd, J = 11.9 and 2.3 Hz, 1 H, 18-H′), 5.03 (dd, J = 9.0 and 2.3 Hz, 1 H, 17-H), 6.38–6.54 (m, 5 H, H-PC), 6.58 (br., s, 1 H, 5-H), 6.88 (d, J = 8.0 Hz, 1 H, 8-H) ppm. ^{13}C NMR: δ = 28.00, 34.88, 35.01, 35.22 (t, C-1,-2,-9,-10), 67.69 (C-18), 77.28 (C-17), 120.10, 120.19 (Ar-C-Cl, C-21 and/or C-24), 124.18, 124.50 (C-22 and/or C-23), 130.12, 132.31, 132.44, 132.58, 134.08, 134.38, 134.47 (PC-C), 134.72, 137.04, 138.44, 138.52 (PC-C), 139.99 (C-4), 141.50 (C-20), 142.16 (C-25) ppm. IR (KBr): $\tilde{\nu}$ = 3010–3000 cm^{-1} (m), 2974–2951 (m), 1580 (s), 1556 (s), 1390 (s), 1280 (m), 1095 (s). MS (70 eV): m/z (%) = 484 [M$^+$ + 4] (12), 482 [M$^+$ + 2] (48), 480 [M$^+$] (100), 478 (24), 447 (10), 445 (24), 443 (26), 223 (10), 149 (22), 129 (52), 104 (60), 84 (74), 51 (38), 49 (76). $C_{24}H_{18}Cl_4O_2$ (480.209): calcd. C 60.03, H 3.78, Cl 29.53; found C 59.88, H 3.70, Cl 29.48.

o) Tetrachloro-*o*-quinone (10f) to 16: From **16** (0.5 g, 2. 0 mmol) in 50 mL of toluene and **10f** (0.49 g, 2 mmol) in toluene (50 mL, reflux for 2 d) adduct **50** (0.7 g, 71%) was obtained according to the above procedure as colorless crystals (cyclohexane), m.p. 185 °C. ^{1}H NMR: δ = 0.88 (d, J = 6.4 Hz, 3 H, CH_3), 2.80–3.10 (m, 4 H, ethano bridges), 3.18–3.30 (m, 2 H, ethano bridges), 3.35–3.55 (m, 2 H, ethano bridges), 4.25–4.32 (m, 1 H, 18-H), 4.51 (d, J = 8.0 Hz, 1 H, 17-H), 6.43–6.55 (m, 5 H, PC-H), 6.58 (s, 1 H, 5-H), 7.11 (d, J = 8.0 Hz, 1 H, 8-H) ppm. ^{13}C NMR: δ = 17.07 (CH_3), 34.19, 35.00, 35.29, 35.38 (t, C-1,-2,-9,-10), 73.81 (C-18), 83.92 (C-17), 120.10, 120.35 (Ar-C-Cl, C-21 and/or C-24), 124.37, 124.62 (Ar-C-Cl, C-22 and/or C-23), 130.58, 132.20, 132.29, 132.89, 134.15, 134.65, 134.81 (PC-CH), 137.32, 138.31, 139.62, 139.71 (PC-C), 140.08 (C-4), 140.28 (C-20), 140.34 (C-25) ppm. IR (KBr): $\tilde{\nu}$ = 3015–3000 cm^{-1} (w), 2974–2851 (w), 1557 (s), 1508 (m), 1430 (vs), 1405 (s), 1378 (s), 1364 (m), 1337 (m), 1325 (m), 1073 (s), 970 (s). MS (70 eV): m/z (%) = 499 [M$^+$ + 4] (8), 497 [M$^+$ + 3] (22), 496 [M$^+$ + 2] (58), 494 [M$^+$] (100), 492 (80), 460 (30), 459 (94), 456 (24), 390 (20), 389 (24), 317 (24), 247 (10), 231 (12), 145 (24), 143 (62), 129 (54), 104 (80), 91 (18), 78 (10). $C_{25}H_{20}Cl_4O_2$ (494.26): calcd. C 60.75, H 4.08, Cl 28.69; found C 60.65, H 4.00, Cl 28.55.

p) (*E*)-1,2-Dibenzoylethene (10g) to 7: A mixture of **7** (0.47 g, 2 mmol) and **10g** (0.47 g, 2 mmol) in glacial acetic acid (50 mL) and acetic anhydride (5 mL) was refluxed under N_2 for 3 d. The solid precipitate formed after cooling was collected by filtration and washed several times by water and then with cyclohexane. After drying in vacuo, compound **52** (0.82 g, 91%) was obtained as pale yellow crystals (acetonitrile), m.p. 262–264 °C. ^{1}H NMR: δ = 2.41–2.61 (m, 2 H, ethano bridges), 2.63–2.95 (m, 3 H, ethano bridges), 3.00–3.36 (m, 6 H, ethano bridges), 3.44–3.47 (m, 1 H, ethano bridges), 6.26–6.35 (m, 3 H, 7-, 8-,13-H), 6.37 (dd, J = 8.0 and 1.2 Hz, 1 H, 12-H), 6.48 (dd, J = 8.9 and 1.8 Hz, 1 H, 15-H), 6.68 (dd, J = 8.4 and 1.4 Hz, 1 H, 16-H), 7.24–7.30 (m, 2 H, Ph-*para*-H), 7.40–7.58 (m, 2 H, Ph-*meta*-H), 7.68–7.80 (m, 2 H, Ph-*ortho*-H) ppm. ^{13}C NMR: δ = 20.09 (t, C-18), 26.40 (t, C-17), 33.49, 34.53, 34.92, 35.28 (t, C-1,-2,-9, and –10), 121.00 (s), 121.02 (s), 125.14, 125.35 (d each, Ph-H-*ortho*), 126.90, 127.56 (d each, Ph-H-*para*), 128.32, 128.72 (d, each, Ph-H-*meta*), 129.47 (s), 130.44 (d), 131.30 (s), 131.38 (d), 132.23 (d), 132.46 (s), 133.40 (d), 133.42 (d), 134.28 (d), 135.88 (s, 2 C), 137.22 (s, Ph-C), 139.05 (s, C-19), 140.26 (s, C-21), 145.81 (s, C-20), 147.35 (s, C-22). IR (KBr): $\tilde{\nu}$ = 3047–3007 cm^{-1} (m), 2966–2849 (m), 1575 (m-s), 1050 (s). MS (70 eV): m/z (%) = 453 [M$^+$ + 1] (40), 452 [M$^+$] (100), 348 (30), 347 (70), 243 (12), 105 (20). $C_{34}H_{28}O$ (452.60): calcd. C 90.23, H 6.23; found C 90.10, H 6.20.

q) 2-Dicyanomethylenindane-1,3-dione (10h) to 7: A mixture of **7** (0.47 g, 2 mmol) and **10h** (0.42 g, 2 mmol) in anhydrous toluene (150 mL) was refluxed under N_2 for 10 d. The toluene was evaporated in vacuo and the residue was subjected to silica gel column chromatography with benzene/hexane (1:1) to give **53** (0.82 g, 93%) as yellow crystals (benzene/cyclohexane), m.p. 130–132 °C. ^{1}H NMR: δ = 2.75 (dd, J = 15.2 and 11.6 Hz, 1 H, 18-H), 2.99–3.39 (m, 8 H, ethano bridges and 18-H′), 3.42–3.50 (m, 1 H, ethano bridges), 5.42 (dd, J = 11.6 and 1.3 Hz, 1 H, 17-H), 6.42 (s, 1 H, 5-H), 6.46 (d, J = 7.6 Hz, 1 H, PC-H), 6.54–6.62 (m, 5 H, PC-H), 7.35 (dd, J = 8.7 and 1.8 Hz, 1 H, 27-H), 7.42–7.46 (m, 2 H, 25-, 26-H), 7.60 (dd, J = 8.8 and 2.0 Hz, 1 H, 24-H) ppm. ^{13}C NMR: δ = 25.90 (C-19), 32.80, 34.50, 35.30, 35.70 (t, C-1,-2,-9,-10), 36.50 (C-18), 78.65 (C-17), 97.68 (C-20), 115.66, 116.25 (2×CN), 126.50, 128.00, 128.65 (Ar-CH), 128.78, 129.40, 130.89 (PC-CH), 131.29 (Ar-CH), 131.68 (PC-C), 131.97, 132.25, 132.31, 132.98 (PC-CH), 133.14, 133.30, 133.58, 135.25 (PC-C), 135.77, 138.90 (Ar-C), 175.95 (C-28), 187.23 (C-22) ppm. IR (KBr): $\tilde{\nu}$ = 3032–3010 cm^{-1} (s), 2925–2853 (s), 2220 (w), 1711 (s), 1626 (s), 1586 (s), 1407 (s), 1306 (m), 1080 (s). MS (70 eV): m/z (%) = 442 [M$^+$] (38), 415 (8), 311 (14), 310 (12), 284 (10), 130 (32), 129 (80), 105 (50), 104 (100), 78 (20). $C_{30}H_{22}N_2O_2$ (442.52): calcd: C 81.43, H 5.01, N 6.37; found C 81.30, H 5.00, N 6.30.

3. Aromatization Reactions

a) of Anhydrides 24 and 25: A solution of **24** (0.30 g, 0.9 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.41 g, 1.8 mmol) in 100 mL of chlorobenzene was refluxed for 2 d. On cooling to room temp., the hydroquinone precipitated. It was removed by filtration and washed thoroughly with dichloromethane. The solvent of the combined organic phases was removed in vacuo and the resulting residue purified by plate chromatography (silica gel, dichloromethane): 0.20 g (67%) of **54a**, colorless prisms (methanol), m.p. 282 –283 °C. ^{1}H NMR: δ = 2.75–3.31 (m, 6 H, ethano bridges), 3.81–3.91 (m, 1 H, ethano bridge), 4.50–4.59 (m, 1 H, ethano bridge), 5.50–5.60 (m, 2 H, 16-,17-H), 6.46–6.62 (m, 2 H, 19-,20-H), 7.00 and 7.08 (AB-q, J = 7.4 Hz, 2 H, 11-,12-H), 7.93 and 8.24 (AB-q, J = 8.4 Hz, 2 H, 5-,6-H) ppm. ^{13}C NMR: δ = 33.74, 34.21, 34.95, 36.72 (t, C-1,-2,-13,-14), 119.01, 128.89, 130.00, 132.02, 132.22, 133.81, 135.05, 137.37 (d, C-5,-6,-11,-12,-16,-17, -19,-20), 127.02, 130.05, 130.80, 137.84, 137.85, 138.17, 139.34, 140.62 (s, C-3,-4,-7,-8,-9,-10,-15,-18), 162.88 and 163.80 (s, carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (m), 1845 (m), 1770 (s), 1570 (m), 1440 (m), 1285 (s), 1180 (s), 1160 (m), 920 (s), 880 (m), 740 (s). UV (methanol): λ_{max} (lg ε) = 213 nm (4.39), 275 (4.25), 303 (3.58), 351 (3.18). MS (70 eV): m/z (%) = 328 (87) [M$^+$], 252 (12), 239 (14), 224 (46), 196 (31), 168 (18), 152 (42), 126 (24), 104 (100), 103 (63), 78 (56), 77 (36). $C_{22}H_{16}O_3$ (328.37): calcd. C 80.47, H 4.91; found C 80.84, H 4.91.

By the same procedure from **25** (0.50 g, 1.4 mmol) and DDQ (0.635 g, 2.8 mmol) was prepared 0.312 g (65%) of the methyl derivative **54b**, yellowish prisms (methanol), m.p. 273–275 °C. ^{1}H NMR: δ = 2.87 (s, 3 H, CH_3), 2.74–3.29 (m, 6 H, ethano bridges), 3.78–3.85 (m, 1 H, ethano bridge), 4.44–4.54 (m, 1 H, ethano bridge), 5.52–5.61 (m, 2 H, 16-,17-H), 6.57 (br. s, 2 H, 19-,20-H), 6.94 and 7.00 (AB-q, J = 7.4 Hz, 2 H, 11-,12-H), 7.95 (s, 1 H, 5-H) ppm. ^{13}C NMR: δ = 18.25 (q, CH_3), 33.58, 34.43, 34.96, 36.70 (t, C-1,-2,-13,-14), 122.45, 130.20, 131.92, 132.23, 134.52, 135.06, 136.47 (d, C-5,-11,-12,-16,-17,-19,-20), 127.54, 129.21, 132.76, 137.01, 137.52, 137.87, 139.27, 140.77 (s, C-3,-4,-6,-7,-8,-9,-10,-15, -18), 162.80 and 163.80 (s, carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ =

2930 cm^{-1} (m), 2860 (m), 1900 (s), 1840 (s), 1770 (s), 1500 (m), 1440 (m), 1350 (m), 1290 (s), 1180 (m), 1150 (m), 930 (s), 890 (m). UV (acetonitrile): λ_{max} (lg ε) = 213 nm (4.44), 236 (4.19), 304 (4.08), 380 (3.51), 401 (3.40). MS (70 eV): *m*/*z* (%) = 342 (83) [M^+], 238 (46), 210 (14), 165 (22), 105 (46), 104 (100), 78 (29), 57 (18). $C_{23}H_{18}O_3$ (342.39): calcd. C 80.68, H 5.30; found C 80.70, H 5.30.

b) of Diesters 26a–c: A mixture of DDQ (3.15 g, 14.0 mmol) and the diester **26a** (5.2 g, 14.0 mol) in 400 mL of chlorobenzene was refluxed for 2 h. After cooling to room temp. the produced hydroquinone was removed by filtration and thoroughly washed with dichloromethane: 3.74 g (71%) of **55a**, colorless plates (ethanol/ether), m.p. 130–131 °C. ^{1}H NMR: δ = 2.86–3.83 (m, 8 H, ethano bridges), 3.96 (s, 3 H, $COOCH_3$), 4.06 (s, 3 H, $COOCH_3$), 5.71 (br. s, 2 H, 16-, 17-H), 6.45–6.54 (m, 2 H, 19-,20-H), 6.81 and 6.83 (AB-q, *J* = 7.4 Hz, 2 H, 2 H, 11-,12-H), 7.82 and 7.92 (AB, *J* = 8.7 Hz, 2 H, 5-,6-H) ppm. ^{13}C NMR: δ = 32.88, 34.31, 34.79, 36.03 (t, C-1,-2,-13,-14), 52.40 (q, $-OCH_3$), 52.57 (q, $-OCH_3$), 124.13, 129.18, 129.66, 131.22, 131.62, 131.97, 133.05, 134.80 (d, C-5,-6, -11,-12,-16,-17,-19,-20), 126.00 (2×), 136.89, 136.97, 137.95 (2×), 138.16, 138.58 (s, C-3,-4,-7,-8,-9,-10,-15,-18), 166.96 and 170.53 (s, carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (m), 2900 (m), 2840 (m), 1740 (s), 1725 (s), 1590 (m), 1580 (m), 1450 (s), 1400 (m), 1270 (s), 1230 (s), 1190 (s), 1155 (s), 1140 (m), 1080 (s), 980 (m), 950 (m). UV (methanol): λ_{max} (lg ε) = 213 nm (4.36), 231 (4.35), 276 (4.24), 312 (3.56), 350 (3.22). MS (70 eV): *m*/*z* (%) = 374 (72) [M^+], 270 (100), 239 (48), 226 (17), 152 (32), 140 (18), 105 (22), 104 (31), 103 (32), 78 (32). $C_{24}H_{22}O_4$ (374.44): calcd. C 76.99, H 5.92; found C 77.18, H 5.89.

By the same procedure from **26b** (2.34 g, 6.0 mmol) and DDQ (1.36 g, 6.0 mmol) in 160 mL of chlorobenzene was obtained **55b** (1.56 g, 67%) within 28 h as colorless needles (ethanol), m.p. 154–155 °C. ^{1}H NMR: δ = 2.56 (s, 3 H, CH_3), 2.74–3.77 (m, 8 H, ethano bridges), 3.93 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 5.69 (br. s, 2 H, 16-,17-H), 6.44–6.51 (m, 2 H, 19-,20-H), 6.75 and 6.77 (AB-q, *J* = 7.3 Hz, 2 H, 11-,12-H), 7.59 (s, 1 H, 5-H) ppm. ^{13}C NMR: δ = 20.32 (q, CH_3), 32.87, 34.31, 34.79, 35.84 (t, C-1,-2,-13,-14), 52.38 (q, OCH_3), 52.67 (q, OCH_3), 128.19, 128.35, 129.38, 131.67, 131.81, 132.79, 133.90 (d, C-5,-11,-12,-16,-17,-19,-20), 129.63, 130.47, 130.67, 130.85, 136.03, 136.37, 136.84, 137.78, 138.12 (s, C-3,-4,-6,-7,-8,-9,-10,-15,-18), 169.12 and 170.23 (s, carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} (w), 2860 (w), 1725 (s), 1430 (m), 1285 (s), 1230 (s), 1200 (s), 1170 (m), 1100 (m), 880 (m), 800 (m). UV (methanol): λ_{max} (lg ε) = 213 nm (4.12), 230 (4.36), 274 (4.31), 311 (3.54). MS (70 eV): *m*/*z* (%) = 388 (92) [M^+], 374 (21), 357 (15), 284 (100), 269 (52), 240 (43), 225 (24), 221 (39), 105 (41), 78 (37). $C_{25}H_{24}O_4$ (388.46): calcd. C 77.30, H 6.23; found C 77.64, H 6.33.

By the same procedure from diester **26c** (4 g, 10.0 mmol) DDQ (2.27 g, 10.0 mmol) in 20 mL of chlorobenzene was prepared **55c** (2.11, 54%) as colorless needles (ethanol), m.p. 136–137 °C. ^{1}H NMR: δ = 2.79 (s, 3 H, CH_3), 2.67–3.99 (m, 8 H, ethano bridges), 3.94 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 5.64–5.87 (m, 2 H, 16-, 17-H), 6.50–6.56 (m, 2 H, 19-,20-H), 6.76 and 6.81 (AB-q, 2 H, *J* = 7.4 Hz, 11-,12-H), 7.68 (s, 1 H, 6-H) ppm. ^{13}C NMR: δ = 24.20 (q, CH_3), 34.73, 35.40, 36.61, 38.73 (t, C-1,-2,-13,-14), 52.44 (q, OCH_3), 52.56 (q, OCH_3), 129.80, 130.79, 131.02, 131.37, 135.62, 136.28, 136.72 (d, C-6,-11,-12, 16,-17,-19,-20), 125.14, 127.96, 129.51, 132.92, 134.59, 137.71, 137.96, 138.41, 138.71 (s, C-3,-4, -5,-7,-8,-9,-10,-15,-18), 167.18 and 170.97 (s, carbonyl groups) ppm. IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1} (m), 2950 (m), 1735 (s), 1725 (s), 1580 (m), 1435 (s), 1370 (m), 1290 (m), 1260 (s), 1225 (s), 1190 (m), 880 (m), 800 (m), 785 (m). UV (methanol): λ_{max} (lg ε) = 213 nm (4.36), 227 (4.33), 275 (4.31), 344 (3.38). MS (70 eV): *m*/*z* (%) = 388 (49)

Table 1. Crystal data collection and refinement parameters for compounds **47**, **48**, and **50**.

Compound	**47**	**48**	**50**·½C_6H_{14}
Formula	$C_{16}H_{12}Cl_4O_2$	$C_{17}H_{14}Cl_4O_2$	$C_{28}H_{26}Cl_4O_2$
M_r	378.06	392.08	536.29
Crystal habitus	colorless prism	colorless prism	colorless prism
Crystal size [mm]	0.58×0.26×0.24	0.55×0.42×0.24	0.44×0.42×0.38
Crystal system	monoclinic	monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/n$
Cell constants			
a [Å]	16.210(2)	8.892(3)	8.5964(8)
b [Å]	8.7869(8)	23.990(6)	10.9965(14)
c [Å]	23.255(3)	7.902(2)	26.667(3)
α [°]	90	90	90
β [°]	109.162(8)	97.34(3)	98.498(8)
γ [°]	90	90	90
V [Å^3]	3128.7	1671.9	2493.2
Z	8	4	4
D_x [Mg·m^{-3}]	1.605	1.558	1.429
μ [mm^{-1}]	0.759	0.713	0.500
Transmissions	0.89–0.98	0.80–0.96	0.85–0.91
F(000)	1536	800	1112
T [°C]	–100	–130	–100
$2\theta_{max}$	50	50	50
No. of reflections			
measured	2854	3321	4939
unique	2745	2952	4381
R_{int}	0.018	0.017	0.016
Parameters	201	211	308
$wR(F^2$, all reflections)	0.084	0.083	0.075
$R[F, >4\sigma(F)]$	0.033	0.033	0.032
S	0.92	1.09	0.92
max. $\Delta\rho$ (e/Å^3)	0.31	0.26	0.23

[M^+], 284 (100), 269 (32), 240 (21), 213 (14), 195 (14), 165 (40), 152 (32), 131 (21), 104 (64), 91 (14), 78 (32). $C_{25}H_{24}O_4$ (388.46): calcd. C 77.30, H 6.23; found C 77.32, H 6.29.

c) of Furan 52: A solution of **52** (0.45 g, 1 mmol) and DDQ (0.23 g, 1 mmol) in chlorobenzene (120 mL) was refluxed for 1 d. The mixture was cooled to room temp. and dichloromethane (200 mL) was added, causing the precipitation of DDQ-H_2. The precipitate was filtered off and washed several times with dichloromethane until the filtrate became colorless. The filtrates were combined and concentrated below 50 °C in vacuo. The product was collected, recrystallized from trichloromethane/cyclohexane (1:3, v/v) and stored in the dark under dry conditions until the spectral measurements could be taken: 0.42 g (93%) of furanophane **56**, yellow needles, m.p. 220–222 °C. ^{1}H NMR: δ = 2.55–2.65 (m, 2 H, ethano bridges), 2.72–2.80 (m, 1 H, ethano bridge), 2.87–3.00 (m, 2 H, ethano bridges), 3.08–3.22 (m, 2 H, ethano bridges), 3.65–3.70 (m, 1 H, ethano bridge), 5.78 (dd, J = 7.8 and 1.7 Hz, 1 H, 13-H), 6.22 (dd, J = 7.8 and 1.8 Hz, 1 H, 12-H), 6.55 (dd, J = 8.0 and 1.8 Hz, 1 H, 15-H), 6.60–6.72 (m, 3 H, 7-,8-,16-H), 7.22 (d, J = 9.3 Hz, 1 H, 18-H), 7.33–7.38 (m, 2 H, Ph-*para*-H), 7.40–7.45 (m, 2 H, Ph-*meta*-H), 7.47–7.54 (m, 2 H, Ph-*meta*-H), 7.72 (d, J = 9.3 Hz, 1 H, 17-H), 7.79–7.84 (m, 2 H, Ph-*ortho*-H), 7.98–8.03 (m, 2 H, Ph-*ortho*-H) ppm. ^{13}C NMR: δ = 34.17, 34.63, 35.19, 36.11 (t, C-1,-2,-9,-10), 117.44, 118.64, 120.56, 120.97, 125.29, 126.85 (d each, Ph-H-*ortho*), 127.69, 127.93 (d each, Ph-H-*para*), 128.40 (d, C-18), 128.50, 128.90 (d each, Ph-H-*meta*), 129.03 (Ar-C), 131.23, 131.52, 133.25, 133.30 (PC-CH), 133.41, 133.39, 133.98 (Ar-C), 134.28, 136.62 (PC-CH), 136.98 (d, C-17), 138.31 (s, C-19), 139.50 (s, C-21), 147.80 (s, C-20), 148.90 (s, C-22) ppm. IR (KBr): $\tilde{\nu}$ = 3058–3006 cm^{-1} (m), 2988–2851 (m), 1580 (s), 1480 (s), 1460 (s), 1290 (m), 1070 (m). MS (70 eV): *m*/*z* (%) = 451 [M^+ + 1] (50), 450 [M^+] (76), 346 (76), 345 (100), 241 (14), 228 (32), 202 (14), 105 (24), 77 (30). $C_{34}H_{26}O$ (450.58): calcd. C 90.63, H 5.82; found C 90.50, H 5.80.

X-ray Crystallography: A summary of the crystal data, data collection and refinement parameters for the three crystal structures reported in this paper is given in Table 1. **Structure Determination of 47 and 50:** Intensities were registered with Mo-K_α radiation (λ = 0.71073 Å) with a Siemens P4 diffractometer fitted with an LT-2 low-temperature attachment. Absorption corrections were based on ψ scans. Structures were refined anisotropically by full-matrix least-squares on F^2, using the program SHELXL-97.[38] The hydrogen atoms were refined with rigid methyl groups or a riding model. **Structure determination of 48:** Measurements were made with a Stoe STADI-4 diffractometer. All other details as above.

CCDC-238102 (for **50**), -238103 (for **47**), -238104 (for **48**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: June 3, 2005
Published Online: November 10, 2005

