Cyclophanes, XLV[‡]
Synthesis of 4-(6-Fulvenyl)[2.2]paracyclophane and Its Derivatives

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Dedicated to Professor Dietrich Spitzner on the occasion of his 60th birthday

Keywords: Fulvenophanes / Fulvenes / Conformation analysis / Cyclophanes / Indenes

Thiele condensation of the [2.2]paracyclophane derivatives **8**, **12**, **22**, and **23** with cyclopentadiene (**9**) led to the monofulvenes **10**, **11**, and **13** and the bis(fulvenes) **24** and **25**. Likewise, condensations of **8** with 1,2,3,4-tetrachlorocyclopentadiene (**14**) and 1,2,3,4-tetraphenylcyclopentadiene (**16**) provided the 4-fulvenyl[2.2]paracyclophanes **15** and **17**. For comparison purposes, **8** was also condensed with lithium fluorenide (**18**) and lithium indenide (**20**) to give the benzoannelated derivatives **19** and **21**, respectively. Reactions of the dialdehydes **22** and **23** led to the bis(indenes) **26** and **27**. 4-(6-Fulvenyl)[2.2]paracyclophane exists as two conformational isomers, **10** (major product) and **11** (minor product). By temperature-dependent NMR spectroscopy, the rotational barrier associated with **11** ⇄ **10** interconversion has been determined as ca. 26 kcal mol^{-1} at 70 °C. The structures of **19** and **27** have been established by single-crystal X-ray crystallography.

Introduction

[2.2]Paracyclophane and ferrocene represent archetypal layered organic and organometallic compounds. Several years ago, we reported on how these two structures can be "merged" to generate novel metallocenophanes such as the tris(iron) derivative **1**.[2−4] These sandwich compounds are characterized by rigid structures and are interesting model systems for studying electronic interactions between metal atoms over large distances. In the present communication, we describe the preparation of several novel hydrocarbon systems with a view to generating a new class of metallocenophanes, as exemplified by structure **2**. In metallocenophanes of this type, the aromatic and organometallic subunits are connected by single bonds, thus making them flexible. Since both monosubstituted [2.2]paracyclophanes and metallocenes are chiral − they possess a plane of chirality − we eventually hope to obtain novel chiral metallocene complexes from the ligands described herein.

The applications of both chiral [2.2]paracyclophanes[5] and chiral metallocene complexes[6] are becoming ever more widespread, not only in stereoselective synthesis in the laboratory but also in the stereocontrolled polymerization of olefins in industry. Among the various methods available for the synthesis of metallocenes, the use of cyclopentadienyl anions, generated either directly from cyclopentadiene or by the addition of hydride[7] or organometallic reagents[8] to substituted fulvenes, e.g. **3**, has proved to be the most useful and widely applicable. The latter routes (formation of **5** via **4** and of **7** via **6**) are represented in Scheme 1.

Fulvenes **3**, bearing substituents in the 6-position, can readily be obtained from cyclopentadiene and an aldehyde by means of the Thiele fulvene synthesis.[9] Addition of organometallic reagents (R′Li or R′MgX) to such substituted fulvenes leads to compounds of type **6** incorporating a chiral centre, as indicated by an asterisk (*), from which either a *d*,*l*- or a *meso*-configured metallocene **7** may be generated (Scheme 1). If the starting aldehyde in the Thiele reaction is chiral, then the overall process generates two pairs of diastereomeric products. 4-Formyl[2.2]paracyclophane (**8**) is such a chiral aldehyde due to the planar chirality of the substituted phane unit. Fulvenes prepared from this aldehyde are thus potential candidates for the preparation of chiral metallocene derivatives. Furthermore, the bis(fulvenes) that may be prepared from [2.2]paracyclophane dialdehydes (see below) represent potentially valuable starting materials for the synthesis of chiral polymeric metallocenes.

Results and Discussion

Synthesis of Monofulvenes

4-Formyl[2.2]paracyclophane (**8**) is readily available in almost quantitative yield through Rieche formylation of the

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[‡] Part XLIV: Ref.[1]

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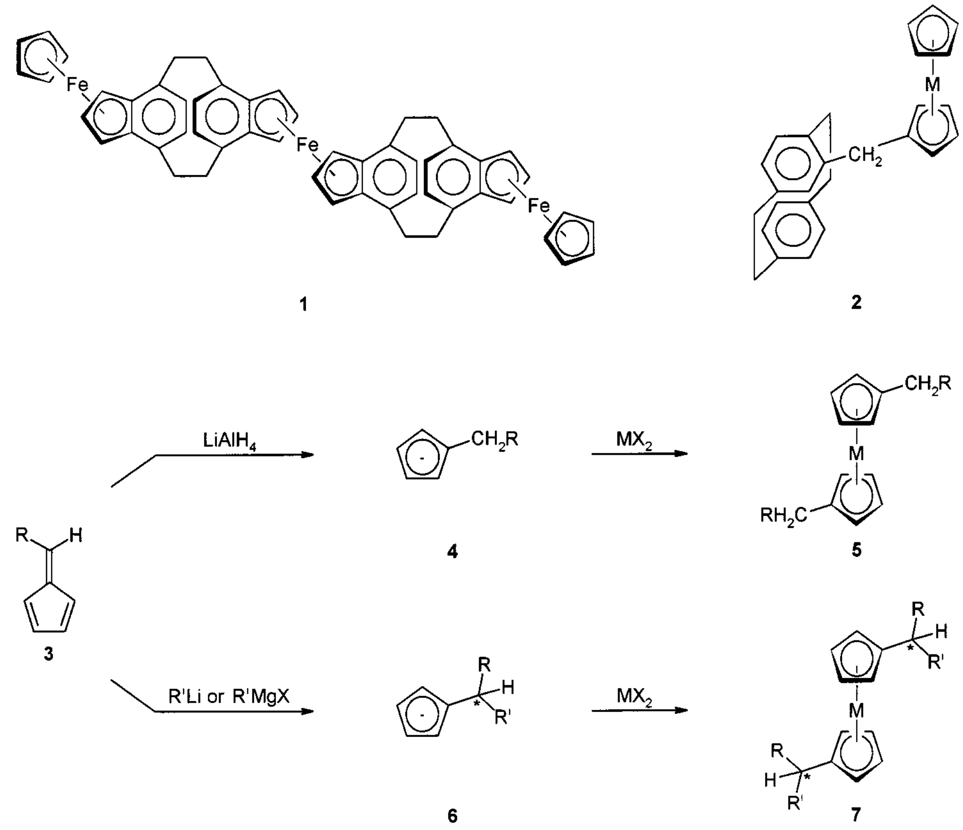
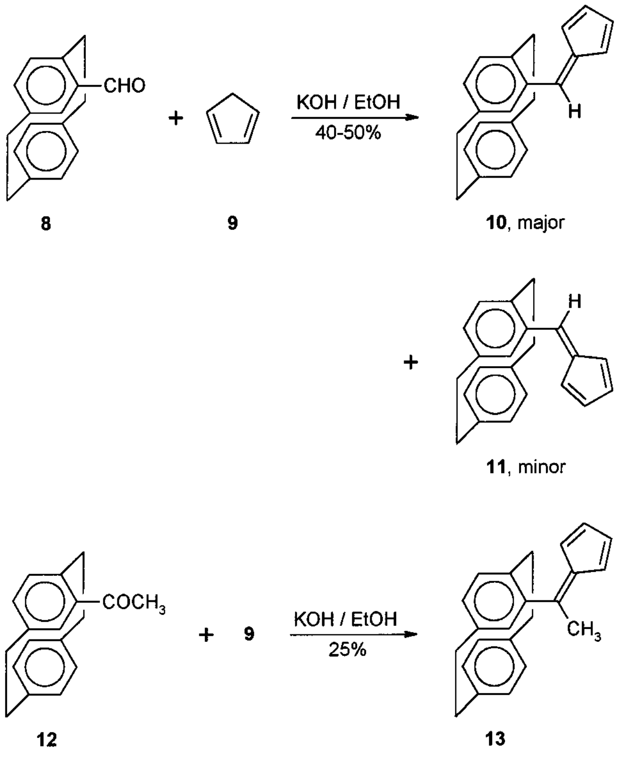


Scheme 1. Metallocenophanes: structural types and preparation from fulvenes (M = Fe, Ni, etc.; X = Hal)

parent hydrocarbon.[10] Condensation of cyclopentadiene (**9**) with **8** under Thiele's conditions using KOH in ethanol furnished two isomers of the corresponding fulvene (**10** and **11**) in an approximately 10:1 ratio in an overall yield of 40−50% (Scheme 2).

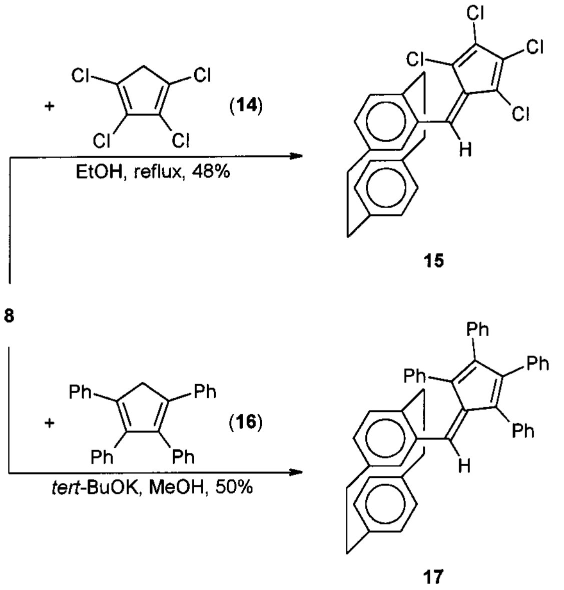


Scheme 2. Preparation of 4-(6-fulvenyl)[2.2]paracyclophane (**10**, **11**) and its 6-methyl derivative **13**

The isomers were carefully separated by either column or radial chromatography on silica gel eluting with dichloromethane/pentane (1:9). A yellow band containing the minor isomer was eluted first, followed by a dark red-orange band containing the major isomer. The minor isomer is a pale-yellow solid, whereas the major component is a dark red-orange solid. The two isomers exhibit identical mass spectra (see Experimental Section), but entirely different ^{1}H NMR and IR spectra. For instance, in the ^{1}H NMR spectrum of the major isomer the signal of the proton in the 6-position of the fulvene ring appears as a sharp singlet at $\delta = 7.25$, whereas in that of the minor isomer the signal of the same proton is coincident with the resonances of the aromatic protons. Similarly, in the spectrum of the major isomer the signal of one of the bridge protons appears as a multiplet at $\delta = 3.56$, distinctly different from the other seven bridge protons, which give rise to an unresolved multiplet in the range $\delta = 2.85{-}3.20$. In the spectrum of the minor isomer, the resonances of all eight bridge protons are accounted for by an unresolved multiplet in the range $\delta = 2.8{-}3.3$. When the yellow minor product was heated in the solid state in a capillary tube, the colour changed to dark red and analysis of the red solid obtained by TLC, ^{1}H NMR, and MS revealed that the minor isomer had been thermally converted to the major isomer, and that this had been accompanied by some polymer formation. Alternatively, when a yellow solution of the minor isomer in $CDCl_3$ was heated to 70 °C in an oil bath, the colour changed to wine-red and the conversion of the minor to the major isomer could be conveniently studied by ^{1}H NMR spectroscopy through monitoring the appearance of new signals at $\delta = 7.25$ and 3.56 attributable to 6-H of the fulvene and one of the bridge protons, respectively. Thermal conversion of the red hydrocarbon into the yellow one was not observed, neither in the solid state nor in solution ($CDCl_3$). We propose that the major isomer corresponds to structure **10** (Scheme 2), in which the aforementioned fulvene proton is located in the interannular space of the cyclophane part of the hydrocarbon and the bulky cyclopentadienyl unit points towards the exterior. In the minor isomer, the opposite situation exists with the bulky cyclopentadienyl unit lying in the interannular space and the fulvene proton pointing outwards. In accordance with these structural assignments, the fulvene proton in **10** (major isomer) is subject to a greater ring current effect and hence is more shielded. Confirmation of these structural assignments for **10** and **11** was provided by crystal structure determinations of the derivatives **19** and **27** (vide infra), both of which have the fulvene proton in the interannular space and show the corresponding resonance in the more highly shielded region of the NMR spectrum. The isomers **10** and **11** arise due to restricted rotation about the C−C bond connecting the fulvenyl substituent to the phane, and the fact that these isomers could be separated at room temperature shows that the activation barrier associated with the conversion is high. The restriction of free rotation stems from unfavourable steric interactions between the fulvenyl substituent and the cyclophane bridge in the course of rotation.[11] The major isomer (**10**), with the bulky cyclopentadienyl substituent pointing towards the exterior of the molecule, is expected to be thermodynamically more stable than the minor isomer **11**. The activation barrier associated with the conversion of **11** to **10** was estimated to be approximately 26 kcal mol^{-1} on the basis of the kinetics of the isomerization as monitored by ^{1}H NMR spectroscopy at 70 °C. The major isomer could be stored for several weeks at 0 °C or below without appreciable decomposition, whereas the minor isomer underwent slow decomposition to give a polymeric material. Full spectral characterization of both conformers is given in the Experimental Section.

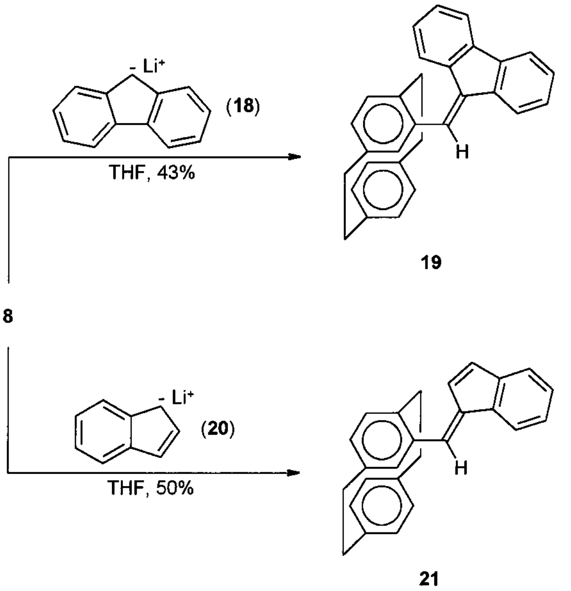
Condensation of 4-acetyl[2.2]paracyclophane (**12**) with **9** using KOH and methanol was much slower, but nevertheless yielded the expected 6-methyl derivative **13** in 25% yield as a dark-red solid (Scheme 2). The use of either sodium methoxide in methanol or potassium *tert*-butoxide did not yield any product and the starting material reacted intractably. Careful examination of the ^{1}H NMR spectrum of the crude **13** revealed it to be a mixture of two isomers, with the signals due to the methyl substituents appearing at $\delta =$ 2.44 and 2.61, respectively. Although the major isomer could be obtained in pure form after column chromatographic separation and recrystallization, the minor isomer was invariably contaminated by some amount of the major component. We assume that the latter has the conformation of **13** shown in Scheme 2, with the methyl substituent in an inward-pointing orientation.

Condensation of 1,2,3,4-tetrachlorocyclopentadiene (**14**) with **8** in refluxing ethanol in the absence of any added base yielded the tetrachlorofulvene **15** in 48% yield after column chromatographic purification as a crimson-red solid (Scheme 3). The fulvene proton in the product gives rise to a sharp singlet at $\delta = 7.57$ in the ^{1}H NMR spectrum. Condensation of 1,2,3,4-tetraphenylcyclopentadiene (**16**) with the aldehyde **8** required a stronger base and heating under reflux (e.g. potassium *tert*-butoxide in boiling methanol). The tetraphenylfulvene **17** precipitated from the crude reaction mixture upon cooling as a dark-red solid (Scheme 3). Although the conversion was only 70%, the yield of the fulvene based on the tetraphenylcyclopentadiene consumed was almost 85%.



Scheme 3. Preparation of the highly substituted fulvenylcyclophanes **15** and **17**

Finally in the monofulvene series, both lithium fluorenide (**18**) and lithium indenide (**20**), generated from the corresponding hydrocarbons by treatment with methyllithium, underwent smooth addition to aldehyde **8** to furnish the corresponding fulvenes **19** and **21** in good yields of 43 and 50%, respectively, as bright-yellow solids (Scheme 4). In all four cases, **15**, **17**, **19**, and **21**, the condensation led only to a single isomer, as shown by ^{1}H NMR spectroscopy, and we propose that these fulvenes are all *exo*-configured as shown in Schemes 3 and 4. Single crystals of **19** suitable for X-ray structural analysis were obtained by slow evaporation of the solvent from the NMR sample. The molecular structure of **19** in the crystal is shown in Figure 1. It clearly shows the stereochemistry of the fulvene proton (17-H), which points towards the interior of the interannular space. The distances between this fulvene proton and the centres of the two benzene rings of the [2.2]paracyclophane moiety amount to 338.2 pm for C3 to C8 and to 394.0 pm for C11 to C15. The mutual orientation of the two parts of the molecule can be described by the torsion angle C5−C4−C17−C18. The C4−C17 bond shows an *ac* conformation [torsion angle −121.61(0.55)°] in contrast to the *transoid* conformation of the C17−C18 bond [torsion angle −174.01(0.45)°]. In the ^{1}H NMR spectrum, the signal due to 17-H appears at δ = 7.58.



Scheme 4. Preparation of the fluorenyl- and indenylcyclophanes **19** and **21**

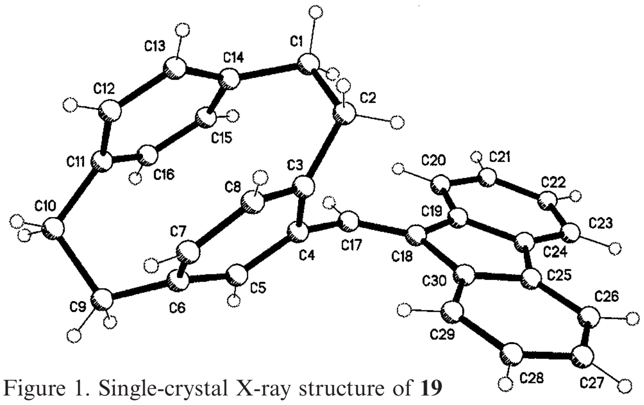
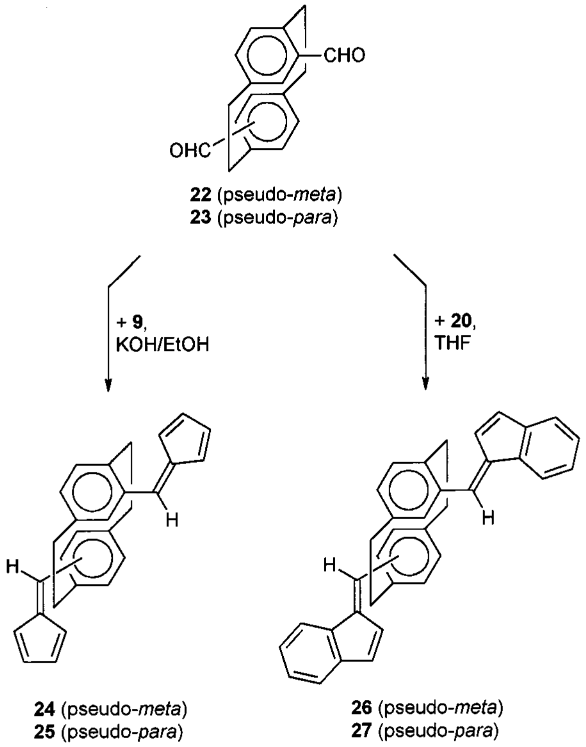


Figure 1. Single-crystal X-ray structure of **19**

Synthesis of the Bis(fulvenes)

The pseudo-*meta* and pseudo-*para* isomers of the dialdehyde of [2.2]paracyclophane, **22** and **23**, respectively, were chosen as condensation partners for the synthesis of bis(fulvenes) from cyclopentadiene (**9**) and indene (Scheme 5). The methodology and the reaction conditions used were identical to those used for preparing the monofulvenes. The bis(fulvenes) **24** and **25** were both obtained as bright-red solids, whereas the bis(indenylfulvenes) **26** and **27** are bright yellow, the yields amounting to 60−70% in these cases.



Scheme 5. Preparation of the bis(fulvenyl)cyclophanes **24**−**27**

Single crystals of **27** suitable for X-ray analysis were obtained by slow diffusion of pentane into a saturated solution of the hydrocarbon in dichloromethane. The molecular structure of this bis(fulvene) is shown in Figure 2. Once again, the stereochemistry at the C−C bond connecting the phane and the fulvenyl unit is clearly revealed. The distances between the 9-H proton and the centres of the aromatic rings of the [2.2]paracyclophane unit in **27** are 339.0 pm (C3 to C8) and 412.5 pm (C11 to C16). The mutual orientation of the two parts of the molecule corresponds to an *sc* conformation considering the C4−C9 bond [torsion angle 42.40(0.21)°] and a *transoid* conformation considering the C9−C10 bond [torsion angle −178.63(0.14)°]. In the ^{1}H NMR spectra, the signals of the fulvenyl protons of **24** and **25** appear at δ = 7.27 and 7.28, respectively, while for both **26** and **27** it appears at δ = 7.55.

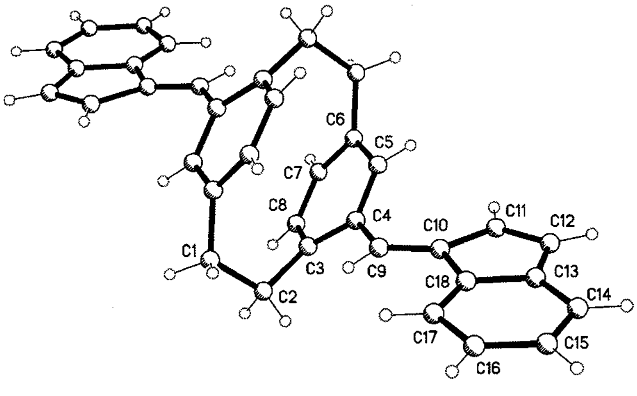


Figure 2. Single-crystal X-ray structure of **27**

Conclusions

Mono- and bis(fulvenes) substituted in the 6-position with the [2.2]paracyclophane moiety have been successfully synthesized from the mono- and two bis(aldehydes) of [2.2]paracyclophane. The parent fulvene was formed as a mixture of two conformers (**10** and **11**) differing in the stereochemistry about the C−C bond connecting the fulvene ring to the aromatic ring. The barrier associated with conversion of the minor isomer **11** to the thermodynamically more stable isomer **10** has been estimated to be 26 kcal mol^{-1}. In view of the planar chiral nature of the substituted [2.2]paracyclophanes, the fulvenes described herein represent potential candidates for starting materials for the synthesis of chiral metallocenes. Two of the fulvenes, **19** and **27**, have been structurally characterized by means of X-ray single-crystal analysis. The molecular structures of these fulvenes clearly show the stereochemistry about the C−C bond connecting the fulvene and cyclophane rings. In both cases, the bulky fulvenyl moiety lies outside the interannular space.

Experimental Section

General Remarks: The instrumentation used for structure elucidation has been described in the previous publications of this series.[1] Freshly distilled cyclopentadiene (**9**) was used in all fulvene syntheses. Tetrachlorocyclopentadiene (**14**) was obtained by reduction of perchlorocyclopentadiene with zinc according to a literature procedure.[12] 4-Formyl- (**8**),[10] 4-acetyl- (**12**),[13] 4,12-diformyl- (**22**), and 4,13-diformyl[2.2]paracyclophane (**23**)[3,14] were synthesized according to reported procedures.

4-(6-Fulvenyl)[2.2]paracyclophane (10 and 11): Cyclopentadiene (**9**, 0.5 mL) was added to an ice-cold stirred solution of KOH (4 g) in ethanol (20 mL) under nitrogen. The solution turned pale yellow. A solution of aldehyde **8** (0.47 g, 2.00 mmol) in ethanol (20 mL) was then added dropwise and the mixture was stirred at room temp. for ca. 12 h. Thereafter, the dark-red reaction mixture was poured onto ice and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with saturated brine, dried ($MgSO_4$), and the solvent was removed in vacuo to yield a dark-red solid. Chromatographic purification on silica gel eluting with 20% CH_2Cl_2/pentane yielded a yellow fraction (isomer **11**) followed by fractions containing both isomers **10** and **11** and then pure fractions of isomer **10**. The combined yield of the two isomers varied between 0.25 and 0.30 g (40−50%). The isomers were recrystallized from a mixture of CH_2Cl_2/pentane at −30 °C. − **Isomer 10:** Dark red-orange solid; m.p. 124−125 °C. − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1614, 765. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 262 nm (3.88), 350 (4.12). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (s, 1 H), 6.54 (m, 11 H), 3.56 (m, 1 H), 2.85−3.20 (m, 7 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.9 (s), 140.4 (s), 140.0 (s), 139.4 (s), 139.1 (s), 137.0 (d), 136.97 (d), 136.4 (s), 135.0 (d), 134.9 (d), 133.8 (d), 133.1 (d), 132.8 (d), 132.1 (d), 130.8 (d), 130.4 (d), 126.7 (d), 121.1 (d), 35.3 (t), 35.1 (t), 34.7 (t), 33.7 (t). − MS (EI, 70 eV): *m/z* (%) = 285 (3), 284 [M^+] (10), 180 (46), 179 (100), 178 (28), 165 (52), 152 (8). − $C_{22}H_{20}$ (284.4): calcd. C 92.95, H 7.04; found C 92.46, H 7.15. − **Isomer 11:** m.p. 110−115 °C (decomp., colour change from yellow to dark red, cf. text). − IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2851, 1602, 1362, 637. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 348 nm (qualitative). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.2−6.8 (m, 12 H), 3.30 (m, 1 H), 3.0 (m, 7 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.8 (s), 140.4 (s), 140.0 (s), 139.4 (s), 139.1 (s), 137.06 (d), 137.0 (d), 136.38 (s), 134.98 (d), 134.86 (d), 133.85 (d), 133.05 (d), 132.81 (d), 132.10 (d), 130.85 (d), 130.4 (d), 126.6 (d), 121.03 (d), 35.3 (t), 35.04 (t), 34.67 (t), 33.67 (t). − MS (EI, 70 eV): *m/z* (%) = 285 (2), 284 [M^+] (7), 180 (50), 179 (100), 178 (32), 165 (54), 152 (10), 104 (10).

4-(6-Methyl-6-fulvenyl)[2.2]paracyclophane (13): Compound **13** was prepared from ketone **12** (1.0 g, 4.0 mmol), cyclopentadiene (**9**, 5 mL), and NaOH (16 g) in methanol (60 mL). After refluxing the mixture for 6 h, it was worked up and purified as described above for **10** to afford 0.3 g (25%) of **13** as a waxy red-orange solid. − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1601, 768. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 328 nm (3.88). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.5 (m, 4 H), 6.4 (m, 6 H), 6.0 (br. s, 1 H), 3.05 (m, 4 H), 2.88 (m, 4 H), 2.64 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.3 (s), 144.7 (s), 140.8 (s), 139.8 (s), 139.5 (s), 139.3 (s), 138.6 (s), 135.1 (d), 133.8 (d), 132.8 (d), 132.3 (d), 132.27 (d), 131.6 (d), 131.4 (d), 131.0 (d), 130.7 (d), 124.5 (d), 120.8 (d), 35.5 (t), 35.4 (t), 35.2 (t), 34.8 (t), 21.9 (q). − MS (EI, 70 eV): *m/z* (%) = 299 [M^+ + 1] (10), 298 [M^+] (36), 194 (42), 193 (84), 179 (100). − HRMS: *m/z* calcd. for $C_{23}H_{22}$ 298.17215; found 298.1700.

4-(1,2,3,4-Tetrachloro-6-fulvenyl)[2.2]paracyclophane (15): A mixture of aldehyde **8** (2.36 g, 10.00 mmol) and 1,2,3,4-tetrachlorocyclopentadiene (**14**, 2.0 g, 10.0 mmol) in ethanol (150 mL) was refluxed under nitrogen for 48 h; the solution turned dark red. After removal of the solvent, the crude product was purified by column chromatography on silica gel eluting with 20% CH_2Cl_2/pentane. Initial fractions contained some unchanged **14** (pungent smell!), but were followed by a yellow band consisting of pure **15**. Removal of the solvent afforded a dark-red solid (0.83 g, 48% based on recovered aldehyde **8**, 1.4 g), which was recrystallized by slow diffusion of pentane into a CH_2Cl_2 solution to give dark-red crystals; m.p. 151−152 °C. − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1613, 720. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 284 nm (3.95), 386 nm (4.17). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (s, 1 H), 6.62 (two overlapping doublets, 2 H, *J* = 7.9 Hz), 6.56 (br. s, 3 H), 6.51 (d, 1 H, *J* = 7.9 Hz), 6.41 (d, 1 H, *J* = 8.0 Hz), 3.48 (m, 1 H), 3.10 (m, 7 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.5 (s), 140.8 (d), 139.6 (s), 139.3 (s), 138.9 (s), 138.2 (d), 135.8 (d), 134.9 (d), 133.1 (d), 132.2 (s), 132.0 (d), 131.8 (s), 131.1 (s), 130.6 (d), 125.8 (s), 120.1 (s), 115.9 (s), 35.2 (t), 34.8 (t), 34.5 (t), 33.4 (t). − MS (EI, 70 eV): *m/z* (%) = 426 (4), 424 (18), 422 (44), 420 (28), 387 (20), 385 (20), 285 (30), 284 (32), 283 (96), 281 (98), 280 (60), 248 (62), 246 (100), 210 (24), 176 (25), 104 (48). − HRMS: *m/z* calcd. for $C_{22}H_{16}{}^{35}Cl_4$ 420.00061; found 420.0004. − $C_{22}H_{16}Cl_4$ (422.2): calcd. C 62.56, H 3.79, Cl 33.65; found C 62.46, H 3.81, Cl 33.07.

4-(1,2,3,4-Tetraphenyl-6-fulvenyl)[2.2]paracyclophane (17): A mixture of aldehyde **8** (0.24 g, 1.00 mmol), 1,2,3,4-tetraphenylcyclopentadiene (**16**, 0.37 g, 1.00 mmol), and potassium *tert*-butoxide (0.55 g, 5.00 mmol) in methanol (20 mL) was heated to reflux for 16 h using an oil bath. After the addition of a second portion of potassium *tert*-butoxide (0.5 g), reflux was continued for a further 12 h under nitrogen. The crude mixture was subsequently cooled in an ice bath and filtered to afford a crimson-red solid (0.33 g) consisting of the fulvene **17** and some unchanged tetraphenylcyclopentadiene. Chromatographic purification on silica gel eluting with 20% CH_2Cl_2/pentane yielded first the unchanged starting material (0.11 g) followed by a dark-red fraction containing the pure product (0.2 g, 50% based on recovered starting material). The product was recrystallized from a CH_2Cl_2/pentane mixture to give crimson-red crystals; m.p. 120 °C. − IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 2927, 1597, 699. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 372 nm (4.19). − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.35 (m, 2 H), 7.26 (m, 1 H), 7.22 (s, 1 H), 6.95 (m, 7 H), 6.80 (m, 2 H), 6.69 (m, 3 H), 6.60 (m, 6 H), 6.30 (m, 3 H), 6.12 (dd, 1 H, *J* = 1.8 and 7.8 Hz), 5.99 (d, 1 H, *J* = 7.8 Hz), 5.8 (d, 1 H, *J* = 1.8 Hz), 3.25 (m, 1 H), 2.8 (m, 5 H), 2.45 (m, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.3 (s), 143.5 (s), 141.2 (d), 141.1 (s), 139.4 (s), 139.3 (s), 139.2 (s), 138.0 (s), 137.5 (d), 136.4 (s), 135.8 (s), 135.7 (s), 135.4 (s), 134.7 (s), 133.7 (d), 133.0 (d), 132.98 (d), 132.95 (d), 131.8 (d), 131.6 (d), 131.5 (s), 130.9 (d), 130.5 (d), 130.3 (d), 130.2 (d), 127.8 (d), 127.3 (d), 127.0 (d), 126.7 (d), 126.6 (d), 126.2 (d), 125.1 (d), 35.1 (t), 34.4 (t), 34.3 (t), 33.8 (t). − MS (EI, 70 eV): *m*/*z* (%) = 588 [M$^+$] (1.5), 483 (1.5), 371 (32), 370 (100), 291 (14), 215 (12). − HRMS: *m*/*z* calcd. for $C_{46}H_{36}$ 588.2817; found 588.2808.

4-(9-Fluorenylidene)[2.2]paracyclophane (19): To a stirred solution of fluorene (0.42 g, 2.50 mmol) in anhydrous THF (15 mL), methyllithium (1.56 mL of a 1.6 M solution in hexane) was added under nitrogen at room temp. The solution turned orange with the liberation of a gas, presumably methane. After 10 min, a solution of aldehyde **8** (0.5 g, 2.5 mmol) in anhydrous THF (10 mL) was added and the reaction mixture was stirred at room temp. for 12 h. Thereafter, saturated NH_4Cl solution was added and the mixture was extracted with CH_2Cl_2. Chromatographic separation on silica gel eluting with 20% CH_2Cl_2/pentane yielded first some unchanged fluorene, followed by the product (0.25 g, 43% based on recovered fluorene). Recrystallization from CH_2Cl_2/pentane yielded yellow crystals; m.p. 180−181 °C. − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1448, 774, 729. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 260 nm (4.47), 350 (4.12). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (m, 1 H), 7.72 (m, 1 H), 7.67 (d, 1 H, *J* = 6.8 Hz), 7.58 (s, 1 H), 7.39 (m, 3 H), 7.25 (dt, 1 H, *J* = 7.4 and 1.0 Hz), 6.96 (dt, 1 H, *J* = 7.6 and 1.0 Hz), 6.86 (dd, 1 H, *J* = 1.8 and 7.8 Hz), 6.57 (m, 5 H), 6.46 (dd, 1 H, *J* = 1.8 and 7.8 Hz), 3.45 (m, 1 H), 3.10 (m, 5 H), 2.98 (m, 1 H), 2.84 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.8 (s), 139.7 (s), 139.6 (s), 139.5 (s), 139.4 (s), 139.2 (s), 136.7 (s), 135.74 (s), 135.71 (s), 135.7 (d), 135.0 (d), 133.2 (d), 133.1 (d), 133.0 (d), 132.1 (d), 129.5 (d), 128.4 (d), 128.0 (d), 126.9 (d), 126.8 (d), 126.7 (d), 124.2 (d), 120.0 (d), 119.6 (d), 119.4 (d), 35.3 (t), 35.0 (t), 34.6 (t), 33.9 (t). − MS (EI, 70 eV): *m*/*z* = 385 (12), 384 [M$^+$] (42), 280 (30), 279 (100), 265 (26), 86 (35), 84 (56). − HRMS: *m*/*z* calcd. for $C_{30}H_{24}$ 384.1878; found 384.1872. − $C_{30}H_{24}$ (384.5): calcd. C 93.75, H 6.25; found C 93.52, H 6.34.

4-(1-Indenylidene)[2.2]paracyclophane (21): In analogy to the above preparation, condensation of the aldehyde **8** (1.0 g, 4.2 mmol) with indene (0.6 g, 5.0 mmol) yielded 0.68 g (50%) of **21**. Recrystallization from CH_2Cl_2/pentane afforded dark-yellow crystals; m.p. 92−93 °C. − IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1}, 1617, 1448, 759. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 252 nm (4.27), 366 (4.27). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (m, 1 H), 7.51 (s, 1 H), 7.32 (m, 1 H), 7.27 (m, 2 H), 6.97 (dd, 1 H, *J* = 5.4 and 1.3 Hz), 6.79 (d, 1 H, *J* = 5.5 Hz), 6.63 (m, 2 H), 6.56 (m, 2 H), 6.52 (m, 2 H), 6.43 (d, 1 H, *J* = 6.9 Hz), 3.61 (m, 1 H), 3.10 (m, 6 H), 2.90 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.2 (s), 139.9 (s), 139.8 (s), 139.7 (s), 139.4 (s), 139.2 (s), 137.3 (s), 136.5 (d), 135.1 (d), 133.9 (d), 133.1 (d), 132.9 (d), 132.1 (d), 130.7 (d), 127.5 (d), 127.4 (d), 126.9 (d), 124.98 (d), 118.98 (d), 35.4 (t), 35.1 (t), 34.8 (t), 33.98 (t). − MS (EI, 70 eV): *m*/*z* (%) = 335 (5), 334 [M$^+$] (14), 230 (42), 229 (100), 215 (44). − HRMS: *m*/*z* calcd. for $C_{26}H_{22}$ 334.17215; found 334.1716. − $C_{26}H_{22}$ (334.5): calcd. C 93.41, H 6.58; found C 93.38, H 6.60.

4,13-Bis(6-fulvenyl)[2.2]paracyclophane (24): According to the procedure described for the preparation of **10**, reaction of the pseudo-*meta*-dialdehyde **22** (1.0 g, 3.7 mmol), cyclopentadiene (**9**, 1.0 mL), and KOH (6 g) in methanol (60 mL) yielded 0.76 g (60%) of **24** as a bright-yellow solid; m.p. > 360 °C. − IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1}, 1615, 766, 626. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 342 nm (4.48). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (s, 2 H), 6.3−6.8 (m, 14 H), 3.55 (m, 2 H), 2.8−3.2 (m, 6 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.0 (s), 140.2 (s), 139.5 (s), 137.0 (d), 136.8 (d), 136.6 (s), 135.1 (d), 134.0 (d), 131.8 (d), 130.6 (d), 126.6 (d), 121.0 (d), 34.2 (t), 33.0 (t). − MS (EI, 70 eV): *m*/*z* (%) = 360 [M$^+$] (26), 181 (52), 180 (42), 179 (100), 165 (66). − HRMS: *m*/*z* calcd. for $C_{28}H_{24}$ 360.1878; found 360.1871.

4,12-Bis(6-fulvenyl)[2.2]paracyclophane (25): According to the procedure described for the preparation of **10**, reaction of the pseudo-*para*-dialdehyde **23** (1.0 g, 3.7 mmol), cyclopentadiene (**9**, 1.0 mL), and KOH (6 g) in methanol (60 mL) gave 1.34 g of crude **25** as a red solid. Purification of the product by means of column chromatography on silica gel eluting with 20% CH_2Cl_2/pentane yielded **25** (0.85 g, 64%) as dark red-orange crystals; m.p. > 360 °C (colour change from red to dark brown; decomp.). − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1616, 1587, 896, 766, 627. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 340 nm (4.53). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.28 (s, 2 H), 6.72 (d, 2 H, *J* = 1.6 Hz), 6.65 (m, 4 H), 6.54 (m, 2 H), 6.44 (d, 4 H, *J* = 7.7 Hz), 6.39 (m, 2 H), 3.56 (m, 2 H), 3.12 (m, 4 H), 2.94 (m, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 145.2 (s), 140.2 (s), 139.5 (s), 136.9 (d), 136.8 (d), 136.6 (s), 135.0 (d), 134.0 (d), 131.8 (d), 130.6 (d), 126.6 (d), 121.0 (d), 34.2 (t), 33.0 (t). − MS (EI, 70 eV): *m*/*z* (%) = 361 (10), 360 [M$^+$] (30), 182 (10), 181 (62), 180 (50), 179 (100), 178 (54), 166 (32), 165 (76). − HRMS: *m*/*z* calcd. for $C_{28}H_{24}$ 360.1878; found 360.1872. − $C_{28}H_{24}$ (360.5): calcd. C 93.33, H 6.66; found C 93.28, H 6.64.

4,13-Bis(indenylidene)[2.2]paracyclophane (26): In analogy to the preparation of **19**, reaction of pseudo-*meta*-dialdehyde **22** (0.26 g, 1.00 mmol), indene (0.35 g, 3.00 mmol), and methyllithium (1.87 mL of 1.6 M hexane solution) gave 0.29 g (65%) of **26** as a dark red-orange solid; m.p. 135−138 °C. − IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 1605, 1457, 771. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 256 nm (4.44), 366 (4.09). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (m, 2 H), 7.55 (s, 2 H), 7.35 (m, 2 H), 7.28 (m, 4 H), 7.03 (dd, 2 H, *J* = 1.1 and 5.52 Hz), 6.84 (d, 2 H, *J* = 5.5 Hz), 6.7 (d, 2 H, *J* = 1.8 Hz), 6.7 (d, 2 H, *J* = 7.8 Hz), 6.50 (dd, 2 H, *J* = 1.8 and 7.8 Hz), 3.63 (m, 2 H), 3.20 (m, 2 H), 3.03 (m, 4 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.1 (s), 139.8 (s), 139.4 (s), 137.3 (s), 136.9 (s), 136.3 (d), 134.3 (d), 132.45 (d), 132.4 (d), 127.52 (d), 126.86 (d), 126.77 (d), 125.0 (d), 120.96 (d), 119.0 (d), 34.89 (t), 33.29 (t). − MS (EI, 70 eV): *m*/*z* (%) = 460 [M$^+$] (16), 231 (34), 230 (36), 229 (100), 215 (40). − HRMS: *m*/*z* calcd. for $C_{36}H_{28}$ 460.2192; found 460.2184. − $C_{36}H_{28}$ (460.6): calcd. C 93.91, H 6.09; found C 93.08, H 6.18.

4,12-Bis(indenylidene)[2.2]paracyclophane (27): In analogy to the preparation of **19**, reaction of pseudo-*para*-dialdehyde **23** (0.26 g, 1.00 mmol), indene (0.23 g, 2.00 mmol), and methyllithium (1.25 mL of 1.6 M hexane solution) gave 0.32 g (70%) of **27** as dark red-orange crystals; m.p. > 360 °C (colour change from red to dark brown; decomp.). − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1618, 1449, 758. − UV/Vis ($CHCl_3$): λ_{max} (log ε) = 282 nm (4.33), 362 (4.60). − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (m, 2 H), 7.55 (s, 2 H), 7.34 (m, 2 H), 7.28 (m, 4 H), 7.01 (d, 2 H, *J* = 5.56 Hz), 6.79 (d, 2 H, *J* = 5.4 Hz), 6.70 (m, 4 H), 6.50 (d, 2 H, *J* = 7.8 Hz), 3.63 (m, 2 H), 3.14 (m, 4 H), 2.95 (m, 2 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.2 (s), 140.0 (s), 139.53 (s), 139.51 (s), 137.2 (s), 136.7 (s), 136.4 (d), 134.14 (d), 134.10 (d), 131.0 (d), 127.5 (d), 127.3 (d), 126.8 (d), 125.0 (d), 120.9 (d), 119.0 (d), 34.3 (t), 33.3 (t). − MS (EI, 70 eV): *m*/*z* (%) = 461 (16), 460 [M$^+$] (38), 232 (10), 231 (72), 229 (100), 215 (58). − HRMS: *m*/*z* calcd. for $C_{36}H_{28}$ 460.2192; found 460.2184. − $C_{36}H_{28}$ (460.6): calcd. C 93.91 H 6.09; found C 93.90, H 6.18.

X-ray Crystallography of 19 and 27. − Structure Determination of 19: A cut needle was mounted on a glass fibre in inert oil and transferred to the cold gas stream of a Siemens P4 diffractometer fitted with a Siemens LT-2 low-temperature attachment. Data were collected by the ω-scan method using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). All unique data were used for calculations (program SHELXL-97: G. M. Sheldrick, University of Göttingen). The structure was solved by direct methods and refined anisotropically by full-matrix least-squares methods on F^2. The hydrogen atoms were refined with a riding model. The structure was found to contain a $CDCl_3$ molecule for every three molecules of **19**, this being disordered over two positions with occupancies of 0.60 and 0.40. − **Structure Determination of 27:** A cut tablet was mounted in inert oil and measured by ω/θ scans with a Stoe STADI-4 diffractometer. All other details were as above. − A summary of the crystal data, data collection, and refinement parameters for the two crystal structures reported in this paper is given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-135528 (**19**) and -135529 (**27**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Summary of crystal data, data collection, and refinement parameters for **19** and **21**

Compound	**19**	**27**
Empirical formula	$C_{30.33}H_{24}D_{0.33}Cl$	$C_{36}H_{28}$
M_r	424.62	460.58
Crystal habit	colourless needle	yellow tablet
Crystal size (mm)	0.82×0.24×0.24	0.92×0.38×0.23
Crystal system	trigonal	orthorhombic
Space group	*P*31*c*	*Pbca*
Cell constants:		
a (Å)	22.149(4)	13.8363(10)
b (Å)	22.149(4)	10.2172(10)
c (Å)	7.7369(10)	17.172(2)
α (°)	90	90
β (°)	90	90
γ (°)	120	90
V (Å^3)	3286.9	2427.5
Z	6	4
D_x (Mg m^{-3})	1.287	1.260
μ (mm^{-1})	0.190	0.071
Transmissions		
$F(000)$	1338	976
T (°C)	−100	−130
$2\theta_{max}$	55	50
No. of reflections:		
measured	5756	4208
unique	2580	2145
R_{int}	0.062	0.024
Parameters	288	163
Restraints	310	0
$wR(F^2$, all refl.)	0.141	0.106
$R[F, > 4\sigma(F)]$	0.058	0.041
S	0.83	1.05
max. Δρ (e Å^{-3})	0.17	0.24

Acknowledgments

One of us (S. S.) thanks the Alexander von Humboldt Foundation, Bonn, for a fellowship, and the Indian Institute of Technology, Madras, India, for sabbatical leave. We thank Prof. Dr. L. Ernst for useful discussions, especially for his help with the kinetics of the isomerization of **11** using NMR techniques, and the Fonds der Chemischen Industrie for continuous support of our studies.

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Received December 30, 1999
[O99695]