Unusual Reactions of Halo[5]metacyclophanes

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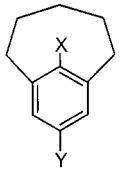
The synthesis of novel [5]metacyclophanes **1** has been achieved either by an improved version of the general approach starting from halobicyclo[5.3.0]dec-1(7)-enes **2** or by nucleophilic substitution of 11-chloro[5]metacyclophanes. Conformational analysis of **1** revealed that the *exo* conformation, in which the pentamethylene bridge is pointing away from the aromatic ring, is strongly preferred both for very small and for very large substituents at the aromatic interbridge position 11, whereas medium-sized substituents induce the occurrence of minor amounts of the *endo* conformer. In Diels–Alder reactions with dienophiles, compounds **1** behaved like reactive dienes, adding at positions 8 and 11 of the aromatic ring. Substitution by chlorine, though, reduced the reaction rate; the unsymmetrical dienophile acrylonitrile showed little preference for the two possible regioisomeric adducts **8** and **9**. Similarly, compounds **1** were unusually reactive towards acid, and interesting and unforeseen rearrangements were observed. Depending on the substituent at position 11, acid treatment of **1** afforded either *ortho*-annulated analogues such as **12** (with an unexpected substitution pattern) or the spirocyclohexadienone **13h**. Of special interest is the S_N2Ar substitution of 11-halo[5]metacyclophanes, which is without precedent in the chemistry of nonactivated aromatic compounds. Depending on the nucleophile and the halogen, a variety of often unforeseen reaction products were obtained, such as **20(OR)** or **28**, resulting from Meisenheimer adducts being intercepted by protonation. The product of hydroxide attack on the 11-fluoro derivative **1d** was **14**, the oxo isomer of the (nonviable) phenol 11-hydroxy[5]metacyclophane (**35**); **14** was also slowly formed from **20(OMe)** and sodium methoxide. On acid treatment, **14** isomerized to the spirocyclohexadienone **13a**; this transformation is a retro version of the famous dienone–phenol rearrangement, and as such is the first case of its kind. Most of these reactions of **1** are atypical of aromatic compounds, the driving force being the (partial) release of the considerable strain in **1**, which amounts to about 45 kcal/mol.

Introduction

Small cyclophanes display a fascinating dichotomy in structure and reactivity.[1−3] The short bridge prevents the benzene ring from assuming its ideal planar structure. On one hand, one might have expected that this should result in a reduction of its aromatic character. However, a variety of criteria obtained from X-ray crystal structures,[4] NMR spectra,[5] heats of hydrogenation,[6] and theoretical calculations[6,7] indicated that the bent benzene ring of [5]metacyclophanes (**1**) is fully delocalized and aromatic.

On the other hand, the bending goes along with a considerable increase of reactivity that often finds no analogy in ordinary aromatic behavior; rather, it initially seemed[3] to be more in line with a cyclohexatriene-like[8] bond fixation. Thus, several derivatives of **1** react with dienophiles in Diels−Alder reactions with a rate that approaches and sometimes surpasses that of ordinary 1,3-dienes.[3] Similarly high reactivity has been observed towards electrophiles,[3] phosphinidenes,[9] or carbenes[10] under conditions under which simple planar benzene derivatives are unreactive. Nevertheless, it is now clear that this high reactivity is a product of the relief of strain in the transition states and products, and not of bond fixation.[3]



1

a: X = Y = H
b: X = Cl, Y = H
c: X = Y = Cl
d: X = F, Y = H
e: X = F, Y = Cl
f: X = Br, Y = H
g: X = OMe, Y = H
h: X = OMe, Y = Cl
i: X = OCH_2Ph, Y = Cl
j: X = *t*Bu, Y = H

Here we report additional examples of unusual reactivity of halogen derivatives of **1**, which are not only remarkable

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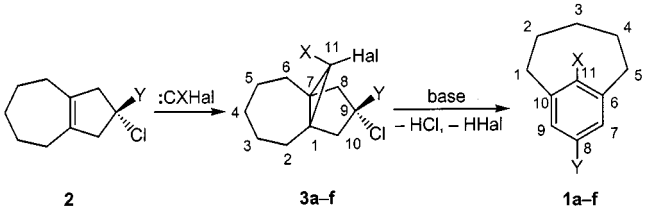
in themselves, but sometimes also provide access to interesting and novel types of structures.

Results and Discussion

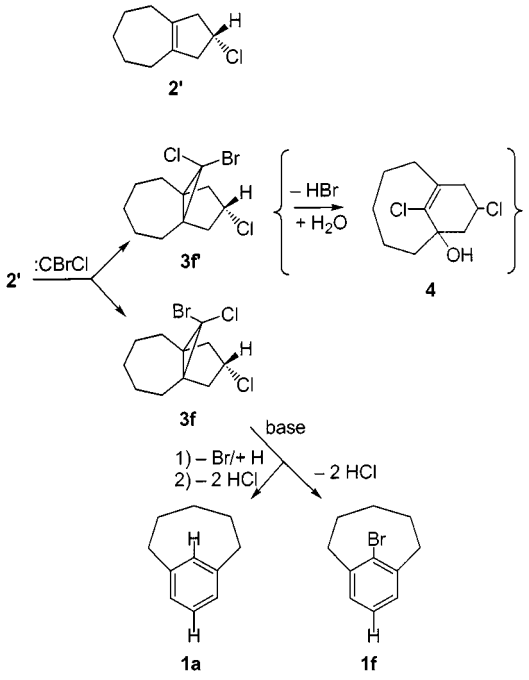
Synthesis and Conformational Analysis of [5]Metacyclophanes (1)

The syntheses of **1a**,[6] **1b** and **1c**,[12] **1g** and **1h**,[11] and **1j**[13] have been reported previously. The preparation of **1i** was achieved by nucleophilic substitution and is described below under this heading. Cyclophanes **1d**−**f** were obtained by our general synthetic approach to [5]metacyclophanes **1**, which is briefly outlined in Scheme 1.[3]



Scheme 1

Addition of a carbene **:**CXHal (X, Hal = halogen) to a 9-halobicyclo[5.3.0]dec-1(7)-ene **2** (Y = H or Cl)[14] gives propellanes **3**, which were subjected to base-catalyzed double elimination of hydrogen halide (HCl and HHal) with concomitant electrocyclic ring-opening to furnish **1**; note that the symmetry-controlled character of the ring-opening requires extrusion of the halogen with an *anti* orientation, and that it is consequently the *syn* substituent X that is retained. As a base, both Ag^+/lutidine and potassium *tert*-butoxide (*t*BuOK) in DMSO have been applied.



Scheme 2

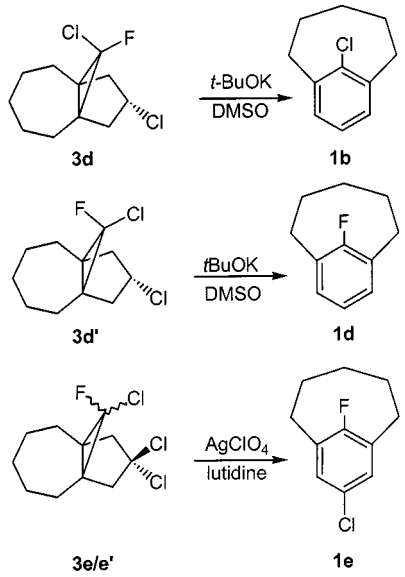
In general, we prefer the latter reagent, because under proper conditions and starting from the easily accessible bromo-substituted **3** (Hal = Br), one may either directly prepare the 11-unsubstituted cyclophanes (**1**, X = H) by in situ reductive removal of the bromine function by the dimsyl anion present in solution,[6,15] or, alternatively, obtain the corresponding 11-bromo derivative (**1**, X = Br). This is illustrated by the reaction of **3f** to furnish either **1a**[6] or **1f** (Scheme 2).

Addition of bromochlorocarbene (**:**CBrCl) to **2′** (**2**, Y = H) gave a 1:1 mixture of the stereoisomeric propellanes **3f** and **3f′**, which was difficult to separate. However, thanks to the higher reactivity of the *anti*-Br in **3f′**, this compound readily reacts by symmetry-allowed ring-opening to furnish, in the presence of some water, the *anti*-Bredt olefin **4** while **3f** remains unchanged; **3f** and **4** can be easily separated by column chromatography.[6] On treatment with base, the pure **3f** thus obtained gave either **1a** or **1f**, or a mixture of both, depending on the reaction conditions, in yields of 60−80%. Slow addition of **3f** to a solution of an excess of *t*BuOK in DMSO gave pure **1a**, apparently by prior reduction of the bromine by dimsyl anion (which is present in minute amounts) followed by base-induced double elimination of HCl.[6,15] Under conditions favoring base-induced elimination rather than build-up of dimsyl anion, in contrast, the normal double HCl elimination involving the *syn*-11-chlorine occurs to furnish **1f**. Thus, addition of solid *i*PrONa to a solution of **3f** in DSMO gave pure **1f**, while addition of *t*BuOK (solid or dissolved in DSMO) gave a 1:1 mixture of **1a** and **1f**.

The 11-fluoro-substituted cyclophanes **1d** and **1e** were obtained after addition of **:**CClF to **2** to furnish **3** and subsequent base-induced elimination (Scheme 3). From **2′**, a 1:1 mixture of **3d** and **3d′** was obtained.[16] This mixture was treated with *t*BuOK/DMSO and gave a 1:1 mixture of **1b** and the desired **1d** in 50% yield, which were separated by preparative GLC. Similarly, treatment of the mixture **3e/e′** [prepared from **2** (Y = Cl)] with $AgClO_4$/lutidine gave **1e** in low yield after preparative GLC.

With a total of 17 representatives of **1** with different substituents X and Y available from this and previous work, it was of interest to reevaluate the phenomenon that these [5]metacyclophanes tend to adopt one or two conformations of the pentamethylene bridge (Figure 1).[3,7] The two conformers are called *exo* or *endo*, depending on whether the bridge carbon atom C-3 (Scheme 1) is pointing away from the benzene ring or towards it, and they can be discerned by NMR spectroscopy at low temperature (220 K); at room temperature, they rapidly interconvert with an activation barrier of $\Delta H^{\neq} \approx 11$ kcal/mol and $\Delta S^{\neq} \approx -5$ cal/mol·K.[12b,17] The positions of the equilibria depend on the substituents, in particular on X at position 11 between the bridge, while Y at the remote position 8 has only a minor influence.

Surprisingly, **1** exists exclusively in the *exo* conformation *both* when X is very small (H) *and* when X is very large (*t*Bu); this was observed for **1a**[12b,17] and **1j** and for their Cl(8) derivatives.[11,13] For **1a**, this is most probably due to



Scheme 3

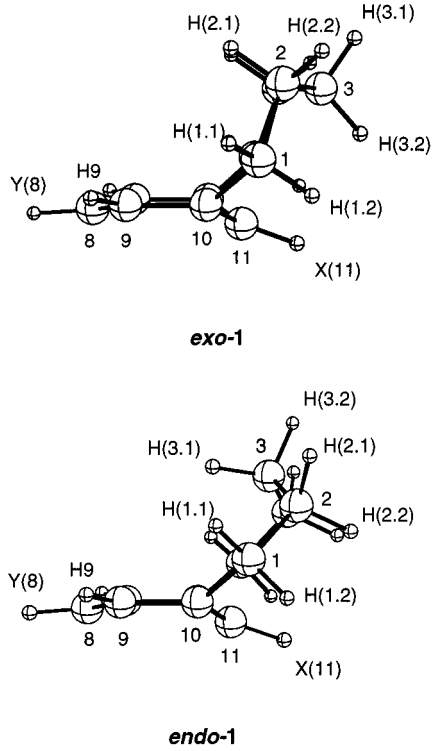


Figure 1. Bridge conformations of [5]metacyclophanes (**1**)

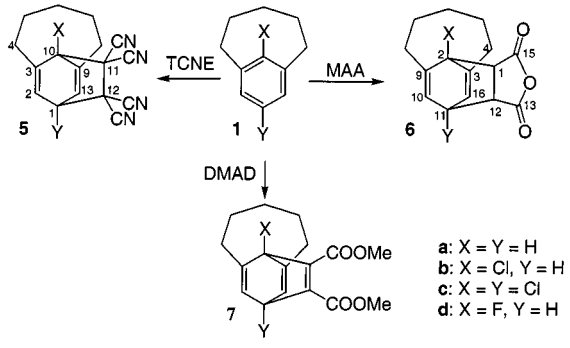
higher strain in the bridge of the *endo* conformer, which has a number of eclipsing interactions.[7][12b,17] When H(11) is replaced by halogen, the percentage of the *endo* conformer increases from 0 (**1a**) to 12 (X = F, **1d**) and 14 (X = Cl, **1b**); in the *exo* conformer, increasing size of the X(11) substituent apparently gives rise to repulsive interactions with H(3.2). MNDO[19] calculations show that the distance Cl(11)−H(3.2) in **1b** is 2.27 Å, the sum of contact radii being 3.15 Å. However, there are nonbonding interactions between X and H(1.2) and H(2.2) in the *endo* conformer too; in ***endo*-1b** these Cl···H distances are 3.1 and 3.06 Å, respectively, and this repulsion will be double, as H(1.2)/H(5.2) and H(2.2)/H(4.2) are equivalent.

This is probably the reason why the trend reverses when X is further enlarged; the percentage of the *endo* conformer decreases for X = Br (**1f**: 10%) and diminishes strongly for X = *t*Bu (**1j**: 0%). In the series with Y = Cl, the 11-alkoxy derivatives also broadly show a decreasing percentage of the *endo* conformer with increasing size of the substituent: 34 (X = OMe, **1g**),[11] 29 (X = OCH_2Ph; **1i**), 25 (X = OEt),[11] 14 (X = O*i*Pr).[11] It is, however, obvious that the actual positions of these equilibria represent a subtle balance between a number of factors, and they are difficult to predict as the energy differences are so small (1−4 kcal/mol).[7,11,17]

An interesting phenomenon observed for ***exo*-1d** is a strong through-space coupling between the 11-fluorine atom and the methylene group at position 3: J[FH(3.1)] = 11.4 Hz, J[FH(3.2)] = 9.5 Hz, and J[FC-3)] = 10.2 Hz. A through-bond coupling [which would be ^6J(FH)] of this magnitude is quite unlikely; furthermore, such couplings are absent in ***endo*-1d**, which shows only a (presumably through-bond) coupling of ^6J(FH) ≈ 1 Hz for H(3.1). A number of through-space couplings involving fluorine have been reported;[20] none of those, however, is as large as in the present case.

Diels−Alder Reactions

As indicated in the Introduction, one of the first reactions revealing the unusually high reactivity of **1** was the Diels−Alder reaction, in which **1** behaves like a reactive "diene" towards common dienophiles.[3,12] The addition occurs across the aromatic ring at C-8 and C-11, because only this regiochemistry removes the "Bredt" strain; the alternative 1,4-addition (at C-6 and C-9) would remove only one unfavorable bridgehead double bond while the second anti-Bredt double bond, C-10=C-11, would be retained in the adduct. We investigated Diels−Alder reactions between **1b** and **1d** and the symmetrical dienophiles tetracyanoethene (TCNE), maleic anhydride (MAA), and dimethyl acetylenedicarboxylate (DMAD) in order to compare them with those of **1a**[12] and **1c**[21] (Scheme 4). The reactions were monitored by ^{1}H NMR spectroscopy and found to give quantitatively the adducts **5**, **6**, and **7**, respectively. The times required for completion of the reactions are presented in Table 1.



Scheme 4

Table 1. Times required for completion of Diels–Alder reactions of [5]metacyclophanes

Dienophile	**1a**[12]	**1b**	**1c**[12b][21]	**1d**
TCNE	room temp., < 15 min	room temp., 1 h	room temp., 1 d	room temp., < 15 min
MAA	room temp., < 15 min	room temp., 2 h	room temp., 2 d	room temp., < 15 min
DMAD	room temp., 5 h	room temp., 5 d	60 °C, 5 d	room temp., 1 d

From these semiquantitative results it can be seen that halogen substitution retards the rate of reaction; this is most clearly evident for DMAD, the least reactive dienophile. For chlorine substitution, this effect is obvious in the series **1a** (no chlorine atom: 5 h at room temp.) through **1b** (one chlorine atom: 5 d at room temp.) to **1c** (two chlorine atoms: 5 d at 60 °C). This is in line with studies performed on the Diels–Alder reactivity of 9,10-disubstituted anthracenes with MAA.[22] The rate constant for the reaction between anthracene and MAA was found to be four times higher than that with 9-chloroanthracene and 30 times higher than that with 9,10-dichloroanthracene. These results were explained in terms of electronic deactivation of the diene system rather than by steric repulsion effects, because 9,10-dimethyl- and 9,10-diethylanthracene reacted 200 and 40 times more rapidly, respectively, than anthracene.

This interpretation is further supported by MNDO[19] calculations (Table 2). In a series involving the same dienophile, the rate of addition would be expected to depend mainly on the HOMO of the "diene" **1** (Figure 2). The HOMO energy decreases from **1a** (−8.95 eV) through **1b** (−9.07 eV) to **1c** (−9.28 eV), and so the rate would be expected to decrease in this sequence, as is observed experimentally. Even the slight decrease in rate for X = F (**1d**) compared to X = H (**1a**) is in line with the slightly lower HOMO of **1d** (−8.97), although such subtle differences are obviously too small to allow reliable predictions, and steric effects may also come into play.

Table 2. HOMO energies and orbital coefficients at C-8 and C-11 of [5]metacyclophanes (**1**)

	1a	**1b**	**1c**	**1d**	**1f**	**1h**
Energy [eV]	−8.948	−9.070	−9.284	−8.969	−8.991	−8.854
C-8	−0.517	−0.486	−0.481	−0.507	−0.475	−0.490
C-11	0.600	0.575	0.556	0.546	0.577	0.512
Δ |C-11 − C-8|	0.083	0.089	0.075	0.039	0.102	0.022

We were also interested in the reactions between **1** and acrylonitrile, which can give rise to two modes of addition. Indeed, the two regioisomers **8** (with the cyano group pointing towards position 11) and **9** (with the cyano group pointing towards position 8) were both formed (Scheme 5). Again, the reaction was monitored by ^{1}H NMR spectroscopy, and the products were identified by detailed analysis of these spectra, involving NOEs and coupling patterns (see Exp. Sect.). The **8/9** ratios are presented in Table 3.

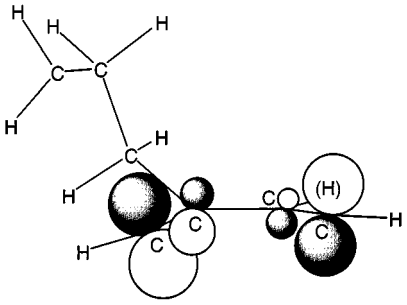
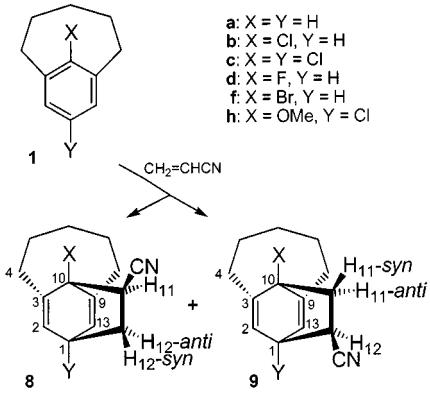


Figure 2. HOMO of [5]metacyclophane (**1a**), calculated by MNDO



Scheme 5

Table 3. Regioselectivity of Diels–Alder reactions of **1** with acrylonitrile

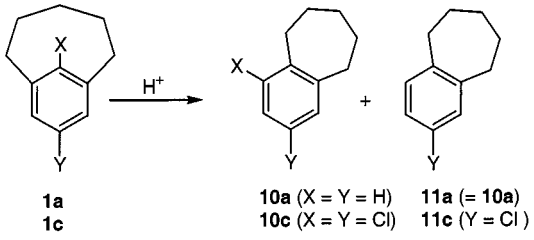
Adduct	**1a**	**1b**	**1c**	**1d**	**1f**	**1h**
8	9	44	15	15	48	70
9	91	56	85	85	52	30

Again, the interpretation of the results must be performed with appropriate caution as the differences in yield of **8** and **9** are small, reflecting minor differences in energy. But the preference of **1** to form **9**, which holds for all cyclophanes with the exception of **1h**, is in line with their HOMO coefficients being higher at C-11 than at C-8; as a result, C-11 will tend to interact with C-2 of acrylonitrile, which has the highest LUMO coefficient. When the HOMO–LUMO difference is rather small, as for **1h** (Δ |C-11 − C-8| = 0.022), the opposite ratio is observed. This is possibly due to steric factors, as the methoxy group of **1h**, in contrast to hydrogen or the halogens, is pushed away by the pentamethylene bridge towards the concave side of the aromatic ring

when the dienophile approaches; the CH_2 group of acrylonitrile is smaller and will experience less steric repulsion than the =CHCN side of the molecule, which results in a higher **8h/9h** ratio (70:30).

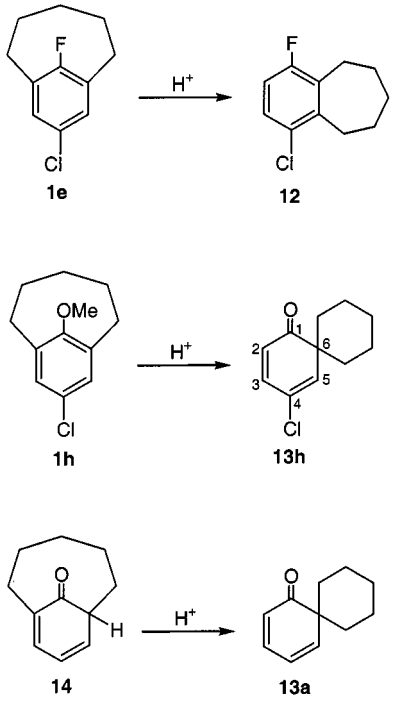
Acid-Catalyzed Rearrangements

Under ordinary conditions, [5]metacyclophanes **1** are at the borderline of stability.[3] Thermally, they slowly decompose on standing at room temperature, and they are particularly sensitive towards acids, which cause instantaneous rearrangement to *ortho* isomers as illustrated in Scheme 6.[3] Thus, the parent **1a** gives benzocycloheptene (**10a**),[23] while **1c** gives both **10c** and, with loss of one chlorine atom, **11c**.[13,21]



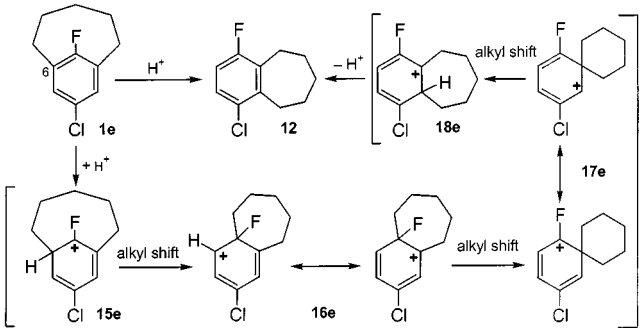
Scheme 6

Against this background, the rearrangement of **1e** to the benzocycloheptene **12** (Scheme 7) was surprising because the relative positioning of the fluorine and chlorine atoms in **12** is 1,4, whereas the two chlorine atoms in **10c** are in a 1,3 relationship. Even more unexpected was the formation of the spirodienone **13h** from **1h**. The corresponding parent compound **13a**, first prepared by Alder et al. in 1957 by a retro-Diels–Alder approach,[24] was obtained from **14** by acid treatment; the synthesis of **14** from **1d** by nucleophilic substitution is described in the next section.



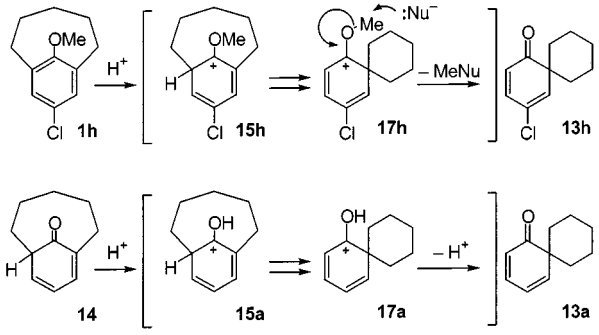
Scheme 7

A mechanistic scheme for the rearrangements described in Scheme 6 has been presented previously,[13,21] and we explain the formation of **12** analogously, as depicted in Scheme 8. The first two steps are analogous to those proposed for acid treatment of **1c**.[13,21] Protonation of **1e** occurs preferentially at C-6 because this makes C-6 tetrahedral, which is accompanied by a considerable reduction of strain. The resulting cation **15e** undergoes a Wagner–Meerwein-type 1,2-alkyl shift to give **16e**. Here, the course of event changes. The dichloro analogue **16c** (Cl instead of F, not shown) goes on reacting by a chlorine 1,2-shift or by extrusion of the tertiary chlorine atom, eventually to furnish **10c** and **11c**, respectively.[13,21] However, a corresponding migration of the fluorine atom (let alone loss of the fluorine atom as an F^+ cation equivalent!) is extremely unlikely; such fluorine migrations have only been observed under special conditions in the gas phase.[25] Thus, **16e** has no pathway available to achieve further stabilization other than a second Wagner–Meerwein rearrangement to afford the spiro cation **17e**; note that the positive charge of **17e** should be somewhat stabilized by resonance with the fluorine atom. Finally, **17e** undergoes a third Wagner–Meerwein shift, resulting in **18e**, followed by loss of a proton to give the observed final product **12**.



Scheme 8

The acid-catalyzed transformation of **1h** into **13h** starts in an analogous fashion, by protonation to give **15h** (Scheme 9). Like **15e**, **15h** is a resonance-stabilized cation and will undergo two consecutive Wagner–Meerwein shifts through **16h** (not shown; cf. Scheme 8) to form **17h**. However, **17h** has a favorable alternative for further stabilization, as loss of the methyl group by attack through a nucleophile directly affords **13h**.



Scheme 9

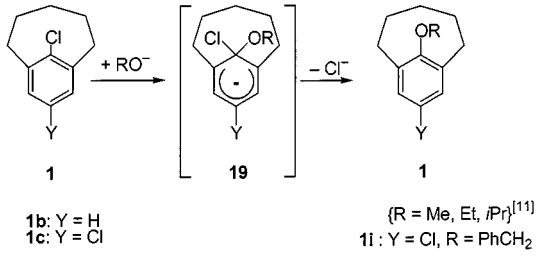
The rearrangement of **14** to **13a** is closely analogous both structurally and mechanistically. Protonation of **14** gives **15a**, from which the further course of events proceeding through **16a** and **17a** is largely analogous, the final deprotonation of **17a** being even more facile than the demethylation of **17h** (Scheme 9). It is of interest to point out that these transformations are related to the well-known dienone−phenol rearrangements.[26] This aspect is discussed below.

Nucleophilic Substitutions

It is typical for aromatic compounds to undergo electrophilic substitution such as the proton-catalyzed reactions described in the previous section. It is equally well established that aromatic compounds are, under normal circumstances, sluggish in reacting with nucleophiles. Thus (halo)aromatics are normally unreactive towards nucleophilic substitution unless the aromatic ring is activated by strongly electron-withdrawing groups such as the nitro group. In that case, the reaction proceeds by the S_N2Ar mechanism, addition of the nucleophile to give the Meisenheimer intermediate, followed by extrusion of the halide anion.

Here, [5]metacyclophanes **1** again constitute an exception, as they are unusually reactive in S_N2Ar substitutions *without* the need for activation by electron-withdrawing groups.[3][4c,11] Here we report further examples of this type of nucleophilic reactivity. In addition, interception of Meisenheimer intermediates provided support for the proposed mechanism, and the interesting bridged cyclohexadienone **14** was obtained.

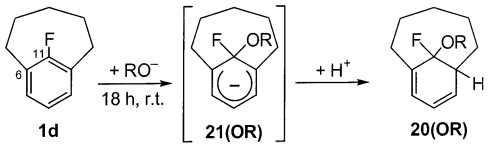
The reaction between the 11-chloro-substituted cyclophanes **1b** and **1c** and alkoxides RONa (R = Me, Et, *i*Pr) in DMSO has been reported to give the corresponding 11-alkoxycyclophanes[11] (Scheme 10). In analogy, we obtained **1i** by treatment with $PhCH_2ONa$. From the observation that **1c**, with its additional electron-withdrawing chlorine substituent at C-8, reacted about five times more rapidly than **1b** (1 d and 5 d, respectively, at room temp.), it had been concluded that the reaction proceeds through the Meisenheimer intermediate **19**; this was supported by theoretical calculations.[11]



Scheme 10

It was expected that the fluoro analogue **1d** would be more reactive in the nucleophilic substitution, as this is generally the case for S_N2Ar reactions. Consequently, its reaction with sodium methoxide with formation of the methoxy substitution product **1g** should proceed much more rapidly.

As 11-fluoro[5]metacyclophane (**1d**) was always obtained together with the 11-chloro analogue **1b** (vide supra; Scheme 3), initial investigations of the nucleophilic substitution were performed on this mixture. However, when a 1:1 mixture of **1d** and **1b** was treated with an eightfold excess of sodium methoxide in DSMO for 18 h, we did not obtain the expected mixture of unchanged **1b** and product **1g**! Instead, after workup, the reaction mixture consisted of only two major components, the expected unchanged **1b** and an unstable adduct **20(OMe)** (Scheme 11). At room temperature, this mixture decomposed within 15−60 min to give a deep purple solution, the identity of which could not be fully established. According to NMR and mass spectrometry and experiments with pure **1d** (vide infra), reaction(s) between **1b** and **20(OMe)** may have occurred, resulting in the formation of purple dimers, trimers, or oligomers.



Scheme 11

Similarly, sodium benzyl oxide gave the corresponding adduct **20(OCH_2Ph)**, although in less pure form. However, when sodium ethoxide or sodium isopropoxide were used as nucleophiles, the adducts **20(OEt)** and **20(O*i*Pr)** were formed in low yield only; the major product (besides unchanged **1b**) was the cyclohexadienone **14**. The formation of **14** is interpreted below (see Scheme 16).

Interestingly, when pure **1d** (obtained by preparative GLC, reactions performed on a milligram scale) was treated with a very large excess of sodium methoxide, a clean mixture of **20(OMe)** and **14** was formed. This reaction mixture was also unstable. At room temperature, it decomposed with formation of MeOH, an unknown compound, and **13a**; the last presumably formed by the acid-catalyzed rearrangement of **14**, induced by traces of acid formed during the decomposition (MeOH, HF?). Now, however, the mixture did not turn purple, which we take as an indication that **1b** is required as a reaction partner to produce the color change mentioned above.

Because of the instability of compounds **20(OR)**, their identification is based on spectroscopic data only. Under GCMS conditions, they decomposed with elimination of HF, presumably to give the originally expected 11-alkoxy derivatives **1** as indicated by retention times and the observation of the molecular ions (e.g., $\mathbf{1g}^+$: m/z = 176 for methoxy). Under direct inlet conditions, however, the expected molecular masses were observed, for **20(OMe)**, for example, m/z = 196 as required for the addition of MeOH (mass 32) to **1d** (mass 164). The ^1H, ^{13}C, and ^{19}F NMR spectra measured at −60 °C were in full agreement with the proposed structures (see Exp. Sect.).

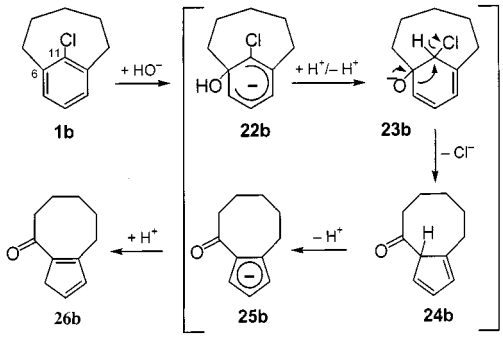
An intriguing question arises: Why does the reaction between 11-chloro[5]metacyclophanes such as **1b** and **1c** and alkoxides proceed smoothly by substitution whereas for their 11-fluoro analogues it stops at the intermediate stage of the Meisenheimer complex to give the addition product? This was all the more surprising as fluorobenzenes are normally better substrates than the corresponding chlorides for substitution by the S_N2Ar mechanism.[27] Here, too, we feel that the high strain of **1** (about 45 kcal/mol[3,6,7]) inverts the normal energetic profile of the reaction.

The first step in S_N2Ar reactions is the addition of the nucleophile to the aromatic ring; this is normally rate-determining.[27] The strongly electron-withdrawing fluorine atom creates a higher positive charge at the *ipso*-carbon atom than the chlorine atom does; this lowers the barrier for attack by the nucleophile. The poorer leaving group properties of fluoride in the second step have no influence on the overall rate.

The situation is completely different for **1**. The attack by the nucleophile is accompanied by the release of a considerable amount of strain in the Meisenheimer intermediates such as **19** or **21(OR)**, because these do not have "anti-Bredt" double bonds involving C-11. Firstly, this lowers the activation barrier sufficiently for the reaction to proceed without an activating electron-withdrawing group. Secondly, the next step, the extrusion of the leaving group, becomes rate-determining. Note that this second step is normally facilitated by the concomitant re-aromatization. Of course, this also holds for the cyclophane reaction. However, the transformation of, for example, **19** to **1** is counteracted by the reintroduction of the [5]metacyclophane strain (vide supra). Under these specific circumstances, the poor leaving group fluoride in **21(OR)** retards this reaction to the extent that the alternative pathway of protonation can prevail, resulting in the formation of **20(OR)**; note that this process occurs in spite of the strongly basic conditions! In contrast, chloride is a much better leaving group, and so **19** is converted into the substitution product **1** more quickly than it can undergo protonation, to furnish an addition product corresponding to **20(OR)**.

Intuitively, one would have expected that the reaction between the hydroxide ion and 11-halo[5]metacyclophanes should proceed by S_N2Ar substitution similar to the attack by alkoxide (see previous section). However, the reaction in fact took a completely different course.[11] Compound **1b**, with its bicyclo[5.3.1]undecane skeleton, gave **26b** with rearrangement to a bicyclo[6.3.0]undecane system; similarly, **1c** gave **26c** (not shown). This was interpreted as indicated in Scheme 12.[11]

Attack of the hydroxide ion occurs at C-6 to give the Meisenheimer complex **22b**. This involves interaction with the LUMO+1 of **1b** (according to MNDO[19] calculations: −0.159 eV; coefficient at C-6: 0.473), which seems less favorable a priori than interaction with the LUMO (−0.531 eV; coefficient at C-11: 0.667). However, this unfavorable aspect is probably overcompensated for by release of strain due to removal of a formal bridgehead double bond and especially by the bridgehead carbon atom C-6



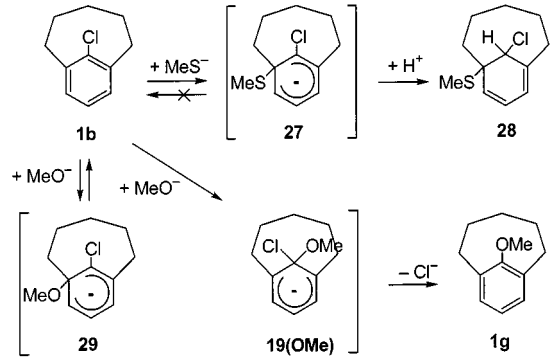
Scheme 12

becoming tetrahedral. Next, protonation/deprotonation affords **23b**, in which the stage is set for a base-induced Wagner−Meerwein-type rearrangement to furnish **24b**, which finally gives **26b** via **25b** as shown.

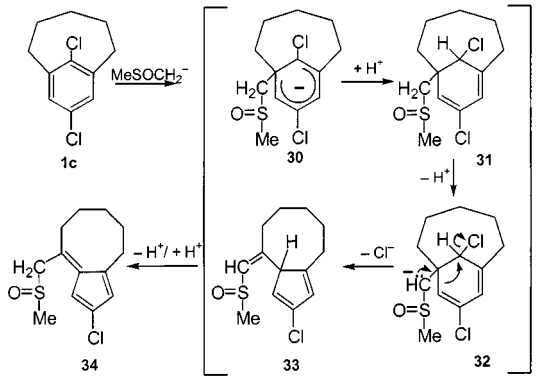
We propose that nucleophilic attack at C-6 is in general the kinetically preferred primary mode of attack, even in the alkoxide reactions of Schemes 10 and 11. In the latter case, however, the primary intermediates analogous to **22b** do not have a rapid follow-up reaction [like the creation of the alkoxide anion functionality (RO^-) in **23b**] available, so the addition of alkoxide at C-6 becomes reversible. On the other hand, the alternative, kinetically less favorable attack of the alkoxide at C-11 opens productive downhill pathways eventually resulting in **1** (Scheme 10) or **20(OR)** (Scheme 11).

This interpretation is supported by two further examples of nucleophilic attack, namely the reaction between sodium methanethioate and **1b** (Scheme 13) and that between dimsylsodium and **1c** (Scheme 14). The first example definitely proves the occurrence of primary attack at the bridgehead carbon atom C-6 with formation of the Meisenheimer complex **27**, because the protonation product **28** is in fact isolated. This result is unique in the [5]metacyclophane series. We feel that this is due to methanethioate being both a very strong nucleophile and a poor leaving group. As a consequence, formation of the primary complex **27** is irreversible, because the barrier for retro-addition is high enough to allow protonation to **28** to proceed. In contrast, methoxide attack at C-6 to afford the analogous Meisenheimer complex **29** is reversible before protonation becomes effective, because methoxide is a better leaving group. Hence, the alternative slower attack at C-11 with formation of **19(OMe)** becomes productive as it is followed by rapid extrusion of chloride with formation of **1g** (Schemes 10 and 13).

In the initial stages, the attack of dimsylsodium at C-6 of **1c** (Scheme 14) resembles the case of methanethioate attack (Scheme 13). Again, the Meisenheimer complex **30** is not prone to undergo retro-addition and instead is protonated to give the adduct **31**. Now, in turn, the situation resembles that of the hydroxide addition (Scheme 12) because deprotonation of the methylene group next to the sulfoxide function gives the anion **32**, which initiates a Wagner−Meerwein-type rearrangement, resulting via **33**



Scheme 13

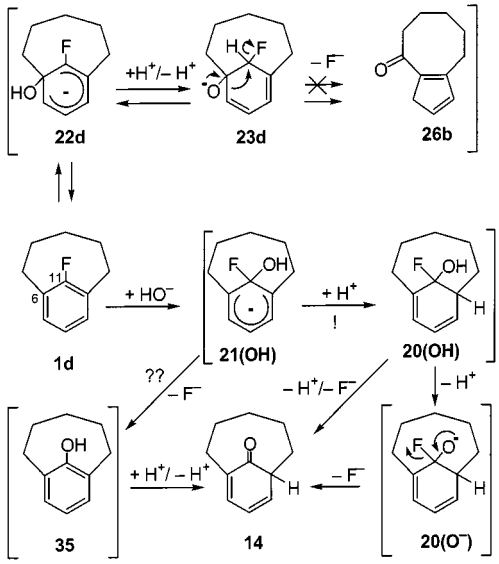


Scheme 14

and a series of protonations and deprotonations in **34**, which has the same combination of an eight-membered and a five-membered ring as **26b**.

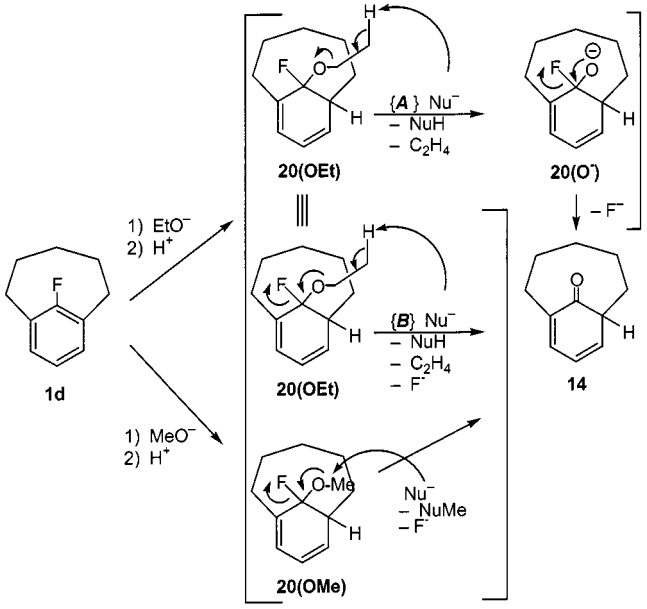
Cyclohexadienones

In its reaction with sodium hydroxide, the fluorocyclophane **1d** was again found to exhibit a reaction behavior (Scheme 15) quite different from that of the chlorocyclophane **1b** (Scheme 12). In the first place, the reaction between **1d** and sodium hydroxide in DMSO, like the reaction with sodium methoxide (Scheme 11), required elevated temperatures to proceed (18 h at 70 °C), and the observed product, the bridged cyclohexadienone **14**, was completely unexpected! This reaction is obviously initiated by attack of hydroxide at C-11. We feel that, as discussed above, the most favorable attack is at C-6, but that this is again not able to produce **26b** because **23d** is not capable of undergoing a base-induced Wagner−Meerwein shift analogous to that of **23b** (Scheme 12) since fluoride is not sufficiently reactive as a leaving group. Consequently, the reaction is reversible and goes back to **1d**. Under these circumstances, in analogy to the alkoxide reactions, attack at C-11 obtains a chance to furnish **21(OH)**, which may react further by two pathways, both affording **14**. Spontaneous extrusion of fluoride anion to give the bridged phenol **35**, followed by dearomatization looks short and attractive, but we feel that fast protonation to give **20(OH)** is more likely, as discussed for the reactions between **1d** and alkoxides (see Scheme 11). Compound **20(OH)** is deprotonated to furnish the alkoxide **20(O⁻)**, which easily expels fluoride to give **14**.



Scheme 15

As mentioned earlier, **14** was also obtained in the nucleophilic substitution reactions between **1d** and sodium alkoxides in DMSO. Initially, from the results discussed above, we believed that this transformation was caused by traces of water present in the reaction mixture. However, the reaction also occurred when repeated with carefully dried reagents and, more importantly, it did proceed at room temperature, whereas the hydroxide reaction required heating to 70 °C. Therefore, we consider the pathways shown in Scheme 16 to be more likely.



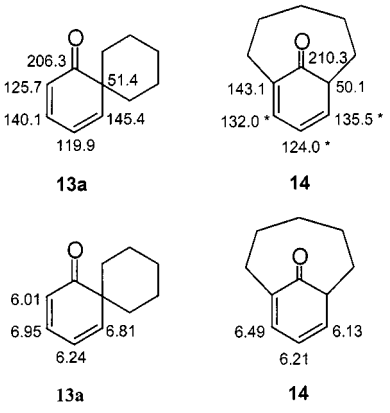
Scheme 16

After the initial formation of the adduct **20(OR)** as depicted in Scheme 11, it is attacked by excess base. For

20(OEt) [and **20(O*i*Pr)**, not shown]**,** this may occur by an E2-type elimination mechanism (pathway {***A***}). The base abstracts a proton from a β-carbon atom with extrusion of the alkoxide **20(O$^-$)** as leaving group, which, as indicated in Scheme 15, extrudes a fluoride anion to form **14**. A priori, this type of base-catalyzed ether cleavage is not very likely under the relatively mild reaction conditions applied in this case. Therefore, one must postulate that E2 elimination and fluoride extrusion occur as a more or less concerted fragmentation (Scheme 16, pathway {***B***}). According to this proposal, **20(OMe)** and **20(OCH$_2$Ph)** should be inert because they do not contain a β-hydrogen atom required for the elimination. This is in line with experimental observation insofar as both react only rather sluggishly under these conditions.

However, the slow transformation of **20(OMe)** into **14** discussed above must proceed by nucleophilic attack at the methyl group in an S_N2-type elimination with extrusion of fluoride anion, either through **20(O$^-$)** or, more probably, as a direct concerted process. The alternative sequence of events, starting with spontaneous extrusion of fluoride anion and followed by attack of the nucleophile, is unlikely in view of the arguments discussed in connection with Schemes 13 and 15 and in view of the important role played by an excess of base.

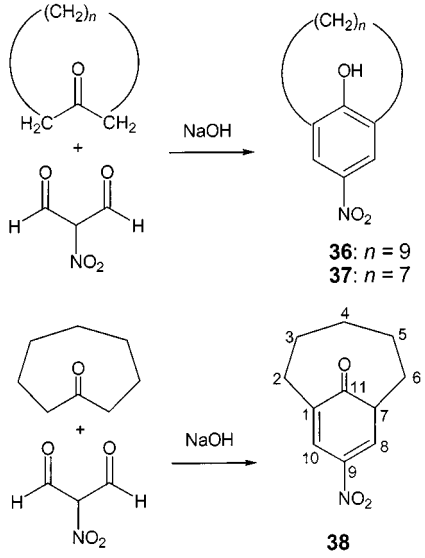
Although a detailed analysis of the geometry of the cyclohexadienone **14** was outside the scope of this investigation, it may be of interest to point out that a comparison of the ^{1}H and ^{13}C chemical shifts of **14** and its isomer **13a** (Scheme 17) clearly indicates the nonplanarity of **14**. In the planar six-membered ring of **13a**, conjugation between the carbonyl group and the diene system gives rise to the expected pattern, with deshielded shifts at the β- and δ-positions alternating with more shielded ones at the α- and γ-positions. In contrast, the short pentamethylene bridge of **14** prevents the cyclohexadienone from being planar. This reduces conjugation and makes the shift pattern more erratic; in particular, the β- and the δ-positions in **14** are less shielded than in **13a**.



Scheme 17

As pointed out in the context of the acid-catalyzed reactions shown in Scheme 9, the products **13** and **14** have an interesting relationship to the cyclohexadienone−phenol rearrangements that have played a prominent role in the development of mechanistic organic chemistry.[26] The important difference is that in our case the rearrangement occurs in the opposite direction, from the aromatic to the alicyclic compound. The driving force is, of course, the reduction of ("Bredt") strain in the cyclohexadienone **14** compared to its phenol tautomer **35**. This overcompensates for the gain in resonance energy in the aromatic system, which makes phenol (C_6H_5OH) about 13 (MNDO) to 17 kcal/mol (flowing afterglow[28]) more stable than cyclohexa-2,4-dienone.

This is in line with previous reports on *meta*-bridged hydroxybenzene derivatives. For the *p*-nitrophenol series, first investigated by Prelog and Wiesner as early as 1947,[29] the borderline of stability lies between the hexamethylene-bridged derivative, which exists as a phenol, and the pentamethylene derivative, which is a cyclohexadienone; this was concluded from the UV spectra. We repeated these syntheses, which start from cycloalkanones and nitromalonaldehyde (Scheme 18). The products were obtained in low yields, and the previous structure assignments, based on UV spectroscopy,[29] were confirmed by IR and NMR spectroscopy. In particular, the phenol structures of **36** and **37** can be deduced from the broad OH signals at 3590 cm^{-1} and by the C_2 symmetry of the ^{1}NMR spectra (both have one aromatic signal at δ = 7.83, for example). On the other hand, **38** has a conjugated carbonyl group (IR signal at 1691 cm^{-1}) and the expected complex ^{1}H and ^{13}C NMR pattern, which was fully analyzed by use of the PANIC program (see Exp. Sect.).



Scheme 18

Conclusions

In an extension of our earlier investigations on the unusual and often unexpected reactivity of [5]metacyclophanes **1**, we have observed several reaction patterns that do not find an analogy in conventional aromatic behavior, such as a great propensity to undergo Diels−Alder reac-

tions. The newly synthesized 11-fluoro-substituted derivatives **1d** and **1e** showed particularly interesting reactions. Thus, treatment of **1e** with acids resulted in rearrangement to the *ortho*-annulated isomer **12** with an unexpected substitution pattern, while the methoxy analogue **1h** gave the spirocyclohexadienone **13h**. Attack on **1d** by alkoxide nucleophiles did not produce the straightforward substitution product, but stopped at the stage of the Meisenheimer intermediate **21**, which was intercepted by protonation to give **20**, the formal adduct of an alcohol to the aromatic ring. Even more surprisingly, the analogous reaction with hydroxide furnished **14**, the oxo isomer of the pentamethylene-bridged phenol **27**; on acid treatment, **14** underwent an equally unforeseen rearrangement to the isomeric spirocyclohexadiene **13a**.

With normal, planar benzene derivatives, none of these reactions takes place; they have their origin in the (partial) release of the considerable strain present in **1** (about 45 kcal/mol). Strain is also a decisive factor in other unusual transformations, such as the reversal of the reactivity of fluoro and chloro derivatives in aromatic nucleophilic substitution reactions.

Experimental Section

General: ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 or MSL 400 spectrometers. Almost all NMR samples were measured in $CDCl_3$, and chemical shifts are reported relative to $CHCl_3$ ($\delta = 7.27$) or $^{13}CDCl_3$ ($\delta = 77.0$) The assignment of signals is based on several 2D NMR techniques (CH correlation, HH-COSY), sometimes NOE and 1D-INADEQUATE experiments. Fluorine magnetic resonance spectra (^{19}F NMR) were recorded in $CDCl_3$ with a Bruker MSL 400 operating at 376.43 MHz; chemical shifts are reported as δ (ppm) relative to hexafluorobenzene. Preparative gas chromatography was performed with an Intersmat P120 apparatus with a 1.5-m 15% SE-30 on Chromsorb W 60/80 mesh column and H_2 as carrier gas. GCMS spectra were recorded with an HP-5971-MSD; where applicable, the expected isotope patterns were observed. High-resolution mass spectra (HRMS) were measured with a Finnigan MAT 90 spectrometer operating at an ionization potential of 70 eV.

11-Fluoro[5]metacyclophane (1d): *t*BuOK (9.7 mmol, 1.09 g) was slowly added over 1 h to a solution of a 1:1 mixture of **3d** and **3d′**[16] (3.8 mmol, 0.90 g) in DMSO (20 mL), followed by stirring for another 1 h at room temp. The dark solution was poured whilst stirring into a cold water/pentane mixture. The layers were separated and the water layer was extracted five times with pentane. The combined organic layers were washed with water (five times), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. After column chromatography, 0.32 g (1.9 mmol, 51%) of an almost 1:1 mixture of **1b** and **1d** remained. Further separation was achieved by preparative GLC (T_{oven} = 160° C, $T_{inj} = T_{det}$ = 190° C). **1d:** ^{1}H NMR: see Table 4. ^{13}C NMR (100.6 MHz, 213 K): ***exo*-1d:** δ = 25.6 ($^1J_{C,H}$ = 125 Hz, $J_{C,F}$ = 10.2 Hz, C-3), 35.1 ($^1J_{C,H}$ = 133 Hz, C-1,-5), 39.4 ($^1J_{C,H}$ = 126 Hz, C-2,-4), 123.8 ($^1J_{C,H}$ = 165, $^3J_{C,F}$ = 5.4 Hz, C-7,-9), 126.8 ($^1J_{C,H}$ = 158, $^4J_{C,F}$ = 5.1 Hz, C-8), 136.1 ($^2J_{C,F}$ = 23 Hz, C-6,-10), 169.9 ($^1J_{C,F}$ = 257 Hz, C-11). ***endo*-1d:** δ = 20.7 ($^1J_{C,H}$ = 125 Hz, C-3), 31.3 ($^1J_{C,H}$ = 132, $^3J_{C,F}$ = 4.6 Hz, C-1,-5), 34.7 ($^1J_{C,H}$ = 129, $^4J_{C,F}$ = 8.2 Hz, C-2,-4), 122.2 ($^1J_{C,H}$ not identified, $^3J_{C,F}$ = 4.2 Hz, C-7,-9), 126.1 ($^1J_{C,H}$ = 165, $^4J_{C,F}$ = 7.0 Hz, C-8), 137.6 ($^2J_{C,F}$ = 20.6 Hz, C-6,-10), C-11 not identified. ^{19}F NMR (376.43 MHz, 213 K): δ = 75.0 (***endo*-1d**), 70.9 (***exo*-1d**); ratio 1:8. MS: *m*/*z* (%) = 164 (53) [$M^{+\cdot}$], 149 (41), 136 (38), 122 (100), 109 (19). HRMS ($C_{11}H_{11}F$): calcd. 164.1001; found 164.0991.

8-Chloro-11-fluoro[5]metacyclophane (1e): According to the method of Dolbier,[30] $TiCl_4$ (22.5 mmol, 4.27 g) was added through a septum to dry THF (40 mL, cooled to −20° C with acetone and dry ice) at such a rate that the temperature did not exceed 5° C. $LiAlH_4$ (22.5 mmol, 0.85 g) was then added (with the aid of a bent glass "adding-tube") to the bright yellow suspension at such a rate that the temperature did not exceed 10° C. The mixture turned green, then brownish, and finally black. It was stirred for 0.5 h at room temp., and the resulting black suspension was transferred to a dropping funnel (under nitrogen) and slowly added to a cooled mixture of $CFCl_3$ (22.5 mmol, 3.08 g) and 9,9-dichlorobicyclo[5.3.0]dec-1(7)-ene (**2**, Y = Cl)[31] (5 mmol, 1.02 g) in dry THF (40 mL) whilst stirring at such a rate that the temperature did not exceed 0° C. After stirring for 0.5 h at 0° C, the mixture was allowed to warm to room temperature and was stirred for another 3 h. It was then poured into a solution of 15 mL of concentrated HCl in 150 mL of ice/water. The mixture was extracted three times with CH_2Cl_2. The combined, black organic layers were washed with 20 mL of a 7.5% $NaHCO_3$ solution, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. This procedure was repeated three times and yielded about 1 g of a mixture of products including a substantial amount of starting material and about 35% of a 1:1 mixture of **3e/e′**; this was used without further purification.

9,9,11-Trichloro-11-fluorotricyclo[5.3.1.0]undecane (3e/3e′): ^{1}H NMR (200 MHz): δ = 3.05 (m, 4 H, 8,10-H), 2.10−1.30 (m, 9 H), 1.15 (m, 1 H). ^{13}C NMR (50.3 MHz): 25.6 ($J_{C,F}$ = 2.8 Hz), 26.2, 27.3, 27.4, 30.7 ($J_{C,F}$ = 1.9 Hz), 32.7 ($J_{C,F}$ = 4.9 Hz), 42.3 ($^2J_{C,F}$ = 9.5 Hz), 43.1($^2J_{C,F}$ = 10 Hz), 56.2 ($^3J_{C,F}$ = 7.4 Hz), 58.8 ($^3J_{C,F}$ = 0.6 Hz), 92.0, 92.0, 102 ($^1J_{C,F}$ = 298 Hz), 105 ($^1J_{C,F}$ = 294 Hz). ^{19}F NMR (376.43 MHz): δ = 22.6 and 20.5. MS: *m*/*z* (%) = 270 (5) [$M^{+\cdot}$], 235 (71) [M − Cl], 214 (100) [M − butene!], 199 (35), 181 (31). HRMS ($C_{11}H_{14}{}^{35}Cl_3F$): calcd. 270.0145; found 270.015. The elimination reaction with **3e/e′** was performed as follows. A solution of the crude mixture containing **3e/e′** (1.5 mmol) in dry THF (3 mL) was added over 5 min, whilst stirring, to a mixture of $AgClO_4$ (6 mmol, 1.24 g) and 2,6-lutidine (3.4 mmol, 0.37 g) in dry THF (6 mL). After stirring for 20 h at room temperature, the reaction mixture was filtered through a glass filter. No traces of silver must remain in the mixture. The filtrate was concentrated and the residue was purified by column chromatography (silica/pentane). A small quantity of impure **1e** was obtained by preparative GLC. The ^{1}H NMR spectrum, measured at room temp., showed broad peaks for the pentamethylene bridge, due to partial coalescence, and was practically identical to that of **1d** under the same conditions, except for the doublet of aryl protons (7-,9-H) at δ = 6.69 ($^4J_{H,F}$ = 5 Hz).

11-Bromo[5]metacyclophane (1f): Slow addition of solid sodium isopropoxide (3 mmol, 0.25 g) to a solution of **3f**[6] (1 mmol, 0.3 g) in DMSO (15 mL) yielded **1f** free of its reduction product **1a**; some minor olefinic products, presumably intermediates in the reaction, were detected by ^{1}H NMR spectroscopy. This reaction was performed only once and was not optimized. **1f:** ^{1}H NMR: see Table 4. ^{13}C NMR (100.6 MHz, 213 K): ***exo*-1f:** δ = 24.9 ($^1J_{C,H}$ = 121 Hz, C-3), 41.6 ($^1J_{C,H}$ = 126 Hz, C-2,-4), 42.4 ($^1J_{C,H}$ = 134 Hz, C-1,5), 123.2 ($^1J_{C,H}$ = 162 Hz, C-7,-9), 128.8 ($^1J_{C,H}$ = 151 Hz, C-8), 134.8 (C-11), 148.2 (C-6,-10). ***endo*-1f:** the signals were not resolved. MS: *m*/*z* (%) = 224 (21) [$M^{+\cdot}$], 182 (11), 145 (100) [M − Br], 115 (53), 103 (34). HRMS ($C_{11}H_{13}Br$): calcd.: 224.0201; found 224.0199.

Table 4. Proton chemical shifts δ [ppm] and coupling constants J [Hz] of **1** (400 MHz, $CDCl_3$, 213 K; see also Figure 1)

δ	**1d**		**1f**		**1i**		**1j**
	exo ($J_{H,F}$)	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
1.1-H	2.32 (5.0)	2.18	2.68	1.9−1.6	2.31	1.6−1.2	2.68
1.2-H	3.37 (3.8)	3.31	3.67	3.48	3.42	3.28	3.16
2.1-H	0.42 (ca. 0)	1.95	0.27	1.6−1.4	0.48	1.6−1.2	−0.02
2.2-H	1.91 (ca. 0)	2.12	1.94	2.3−2.1	1.90	2.0−1.9	2.0−1.0
3.1-H	1.44 (11.4)	−1.19	1.41	−1.19	1.35	−1.06	2.0−1.0
3.2-H	1.71 (9.5)	1.07	2.19	1.00	2.14	1.03	2.0−1.0
7-H/9-H	6.75 (6.6)	6.75	6.97	6.97	6.67	6.73	6.62
8-H	6.97 (ca. 0)	6.97	7.07	7.07	−	−	6.95
$J_{H,H}$	**1d**		**1f**		**1i**		**1j**
	exo	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*
1.1,1.2	−12.6	[a]	−12.7	−13.9	−12.5	[a]	−12.3
1.1,2.1	3.7	[a]	3.2	[a]	3.3	[a]	3.3
1.1,2.2	3.6	[a]	3.2	[a]	3.3	[a]	3.2
1.2,2.1	12.7	[a]	12.7	small	12.5	[a]	12.3
1.2,2.2	3.0	[a]	3.1	9.7	3.0	[a]	3.1
2.1,2.2	−14.5	[a]	−14.6	[a]	ca. 14	[a]	ca. 14
2.1,3.1	1.0	9.5	small	9.5	small	8	small
2.1,3.2	11.0	small	11.0	small	ca. 9	small	ca. 11
2.2,3.1	8.2	ca. 1	8.1	small	ca. 8	ca. 1	[a]
2.2,3.2	0.8	8.7	small	8.3	small	10	[a]
3.1,3.2	−16.3	−16	−16.7	−16.1	−16	−15.3	[a]

[a] Unresolved.

Diels−Alder Reactions: All reactions were performed on a small scale. The dienophile (1.1 equiv. of TCNE, MAA, or DMAD; 8 equiv. of acrylonitrile) was added to a solution of **1** in $CDCl_3$, and the addition was fmonitored by ^{1}H NMR spectroscopy. The addition reactions were quantitative except for **1f**, with which some by-products were observed.

TCNE Adducts

Reaction with 1b. − 10-Chloro-11,11,12,12-tetracyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (5b): ^{1}H NMR (200 MHz): δ = 6.31 (d, ^3J = 6.7 Hz, 2 H, 2-,13-H), 4.49 (t, ^3J = 6.7 Hz, 1 H, 1-H), 2.8−0.9 (m, 10 H). ^{13}C NMR (50.3 MHz): δ = 23.5 (t, ^1J = 125 Hz, C-6), 33.0 (t, ^1J = 132 Hz, C-4,-8), 36.4 (t, ^1J = 127 Hz, C-5,7), 45.3 (d, ^1J = 150 Hz, C-1), 110.6 (s, CN), 111.6 (s, CN), 124.9 (d, ^1J = 179 Hz, C-2,13), 158.0 (s, C-3,9), signals of C-10, C-11 and C-12 missing due to low intensity. MS: *m/z* (%) = 308 (11) [M$^{+\cdot}$], 273 (3) [M − Cl], 180 (5), 145 (100), 138 (32), 115 (24), 77 (16). HRMS ($C_{17}H_{13}ClN_4$): calcd. 308.0829; found 308.0829.

Reaction with 1d. − 11,11,12,12-Tetracyano-10-fluorotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (5d): ^{1}H NMR (200 MHz): δ = 6.22 (dd, ^3J = 5.9 Hz, $J_{H,F}$ = 5.9 Hz, 2 H, 2-,13-H), 4.53 (td, ^3J = 5.9 Hz, $J_{H,F}$ = 0.8 Hz, 1 H, 1-H), 2.6−0.9 (m, 10 H). ^{13}C NMR (50.3 MHz): δ = 24.5 (td, $J_{C,F}$ = 6.9 Hz!, C-6), 31.0 (t), 35.8 (t), 40 (s), 44 (s), 45.5 (d, C-1), 101 (d, $^1J_{C,F}$ = 208 Hz, C-10), 109.7 (s, CN), 111.3 (s, CN), 123.0 (dd, $J_{C,F}$ = 5.2 Hz, C-2,13), 156.1 (d, $J_{C,F}$ = 23 Hz, C-3,9]. ^{19}F NMR (376.43 MHz): δ = −6.2. GCMS: *m/z* (%) = 292 (28) [M$^{+\cdot}$], 164 (23), 149 (60), 136 (38), 122 (100), 109 (12). HRMS ($C_{17}H_{13}FN_4$): calcd. 292.1124; found 292.1125.

MAA Adducts

Reaction with 1b. − 2-Chloro-14-oxatetracyclo[10.3.1^{3,11}.0.0^{2,9}]pentadeca-3(16),9-diene-13,15-dione (6b): ^{1}H NMR (200 MHz): δ = 6.21 (d, ^3J = 5.9 Hz, 1 H, 2- or 13-H), 6.04 (d, ^3J = 5.5 Hz, 1 H, 2- or 13-H), 4.08 (dddd, ^3J = 5.9, ^3J = 5.5, ^3J = 3.6, ^4J = 5.9 Hz, 1 H, 11-H), 3.52 (m, 2 H, 1-,12-H), 2.85 (ddd, ^2J = −13.3, ^3J = 11.3, ^3J = 3.9 Hz, 1 H, 4- or 8-H*exo*), 2.75 (ddd, ^2J = −13.3, ^3J = 11.3, ^3J = 3.9 Hz, 1 H, 8- or 4-H*exo*), 2.39 (ddd, ^2J = −13.3, ^3J = 4.5, ^3J = 4.5 Hz, 2 H, 4-,8-H*endo*), 2.25 (m, 2 H, 5-,7-H*exo*), 1.98 (dt, ^2J = −16.1, ^3J = 10.6 Hz, 1 H, 6-H), 1.67 (dt, ^2J = −16.1, ^3J = 8.8 Hz, 1 H, 6-H), 0.95 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): 23.7 (t, J = 125 Hz, C-6), 32.1 (t, J = 132 Hz), 32.4 (t, J = 132 Hz), 36.7 (t, J = 132 Hz), 37.0 (t, J = 132 Hz), 38.9 (d, J = 147 Hz), 47.4 (d, J = 147 Hz), 53.7 (d, J = 147 Hz), 74.4 (s, C-2), 125.3 (d, J = 168 Hz, C-10 or C-16), 128.5 (d, J = 168 Hz, C-10 or C-16), 156.9 (s, C-3 or C-9), 158.4 (s, C-3 or C-9), 167.9 (s, CO), 170.1 (s, CO). GCMS *m/z* (%): 278 (19) [M$^{+\cdot}$], 206 (100), 171 (62), 129 (51), 115 (47), 91 (15). HRMS ($C_{15}H_{15}ClO_3$): calcd. 278.0710; found 278.0711.

Reaction with 1d. − 2-Fluoro-14-oxatetracyclo[10.3.1^{3,11}.0.0^{2,9}]pentadeca-3(16),9-diene-13,15-dione (6d): ^{1}H NMR (200 MHz): δ = 6.01 (dd, ^3J = 5.6 Hz, $J_{H,F}$ = 5.6 Hz, 1 H, 2- or 13-H), 5.95 (dd, ^3J = 5.8 Hz, $J_{H,F}$ = 5.8 Hz, 1 H, 13- or 2-H), 4.08 (m, 1 H, 11-H), 3.45 [AB system: δA = 4.47 (dd, ^3J = 7.2 Hz, J = 2.0 Hz), δB = 2.43 (dd, ^3J = 7.2 Hz, J = 1.0 Hz), 2 H, 1-,12-H), 2.6−0.9 (m, 10 H)]. ^{13}C NMR (50.3 MHz): δ = 24.8 (td, $J_{C,F}$ = 6.8 Hz!, C-6), 30.1 (td, $J_{C,F}$ = 2.5 Hz), 30.6 (td, $J_{C,F}$ = 1.5 Hz), 36.3 (td, $J_{C,F}$ = 3.2 Hz), 38.7 (td, $J_{C,F}$ = 1.2 Hz), 45.9 (d, C-11), 45.9 (dd, $J_{C,F}$ = 5.2 Hz, C-12), 48.7 (td, $J_{C,F}$ = 22 Hz, C-1), 98.9 (d, $J_{C,F}$ = 205 Hz, C-2), 123.2 (dd, $J_{C,F}$ = 5.2 Hz), 125.6 (dd, $J_{C,F}$ = 5.2 Hz), 155.8 (td, $J_{C,F}$ = 25 Hz), 156.3 (td, $J_{C,F}$ = 23 Hz), 168.0 (s, CO), 170.3 (s, CO). ^{19}F NMR (376.43 MHz): δ = −16.1. GCMS: *m/z* (%) = 262 (36) [M$^{+\cdot}$] 234 (5), 214 (7), 190 (100), 175 (10), 161 (11), 147 (40), 133 (32), 122 (43), 109 (39). HRMS ($C_{15}H_{15}FO_3$): calcd. 262.1005; found 262.0997.

DMAD Adducts

Reaction with 1b. − Dimethyl 10-Chlorotricyclo[7.3.1. 0^{3,10}]trideca-2,9(13)-diene-11,12-dicarboxylate (7b): ^{1}H NMR (200 MHz): δ = 6.28 (d, ^3J = 5.7 Hz, 2 H, 2-,13-H), 5.02 (t, ^3J = 5.7 Hz, 1 H, 1-

H), 3.77 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 2.7−2.3 (m, 4 H, 4-,8-H), 2.3−1.5 (m, 4 H, 6-H and 5-,7-H*exo*), 1.0−0.8 (m, 2 H, 5-,7-H*endo*). MS: *m*/*z* (%) = 322 (10) [$M^{+\cdot}$], 291 (14), 180 (23), 167 (28), 145 (53), 125 (100), 91 (71). HRMS ($C_{17}H_{19}ClO_4$): calcd. 322.0972; found 322.0972.

Reaction with 1d. − Dimethyl 10-Fluorotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene-11,12-dicarboxylate (7d): ^{1}H NMR (200 MHz): δ = 6.22 (dd, ^3J = 5.8 Hz, $J_{H,F}$ = 6.0 Hz, 2 H, 2-,13-H), 5.04 (td, ^3J = 5.8 Hz, $J_{H,F}$ = 1.2 Hz, 1 H, 1-H), 3.87 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 2.7−2.3 (m, 4 H, 4-,8-H), 2.3−1.5 (m, 4 H, 6-H and 5-,7-H*exo*), 1.0−0.8 (m, 2 H, 5-,7-H*endo*). MS: *m*/*z* (%) = 306 (93) [$M^{+\cdot}$], 293 (77), 247 (60), 207 (91), 194 (100). HRMS ($C_{17}H_{19}FO_4$): calcd. 306.1267; found 306.1266.

Acrylonitrile Adducts: In all cases, a mixture of regioisomers **8** and **9** was obtained. No efforts were made to separate them.

Reaction with 1a: Ratio **8a/9a** = 9:91. MS: *m*/*z* (%) = 199 (32) [$M^{+\cdot}$], 146 (77), 131 (93), 117 (85), 115 (76), 104 (100), 91 (90), 84 (79), 77 (38). HRMS ($C_{14}H_{17}N$): calcd. 199.1361; found 199.1362. **11-Cyanotricyclo[7.3.1. 0^{3,10}]trideca-2,9(13)-diene (8a):** ^{1}H NMR (400 MHz): δ = 6.12 (d, 1 H), 6.07 (d, 1 H), 3.61 (m, 1 H, 1-H), 3.59 (m, 1 H, 10-H), 2.61 (ddd, 1 H, 11-H), 2.5−0.8 (m, 12 H). **12-Cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (9a):** ^{1}H NMR (400 MHz): δ = 5.94 (d, ^3J = 5.6 Hz, 1 H), 5.81 (d, ^3J = 5.8 Hz, 1 H), 3.83 (ddd, ^3J = 5.8, ^3J = 5.6, ^3J = 2.7 Hz, 1 H, 1-H), 3.37 (m, several ^4J unresolved, 1 H, 10-H), 2.75 (ddd, ^3J = 10.3, ^3J = 4.6, ^3J = 2.7 Hz, 1 H, 12-H), 2.44 (ddd, ^2J = −12.3, ^3J = ^3J = 4.2 Hz, 1 H, 8- or 4-H*endo*), 2.35 (ddd, ^2J = −12.3, ^3J = ^3J = 4.2 Hz, 1 H, 4- or 8-H*endo*), 2.26−2.11 (m, 4 H, 4,8-H*exo*, 5,7-H*exo*), 1.90 (ddd, ^2J = −15.8, ^3J = ^3J = 9.5 Hz, 1 H, 6-H), 1.77 [AB system: δA = 1.87 (ddd, ^2J = −12.7, ^3J = 10.3, ^3J = 2.6 Hz, 1 H, 11-H*anti*), δB = 1.67 (ddd, ^2J = −12.7, ^3J = 4.6, ^3J = 2.5 Hz, 1 H, 11-H*syn*)], 1.56 (ddd, ^2J = −15.8, ^3J = ^3J = 9.8 Hz, 1 H, 6-H), 1.10− 0.99 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): δ = 25.1, 27.2, 29.1, 35.0, 35.1, 35.2, 35.2, 40.7 (d), 46.7 (d), 124.5 (d), 125.2 (d), 156.8 (s), 157.4 (s).

Reaction with 1b: Ratio **8b/9b** = 44:56. MS: *m*/*z* (%) = 233 (79) [$M^{+\cdot}$], 198 (88), 156 (55), 145 (100), 115 (70), 103 (50). HRMS ($C_{14}H_{16}ClN$): calcd: 233.0971; found 233.0977. **10-Chloro-11-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (8b):** ^{1}H NMR (400 MHz): δ = 6.13 (d, ^3J = 5.9 Hz, 1 H), 6.09 (d, ^3J = 5.9 Hz, 1 H), 3.62 (tt, ^3J = 5.9, ^3J = 2.9 Hz, 1 H, 1-H), 3.08 (dd, ^3J = 10.5, ^3J = 4.6 Hz, 1 H, 11-H), 2.8−2.6 (m, 2 H, 4-,8-H*exo*), 2.4−2.3 (m, 2 H, 4-,8-H*endo*), 2.2−2.1 (m, 2 H, 5-,7-H*exo*), 2.14 [AB system: δA = 2.22 (dddd, ^2J = −12.5, ^3J = 10.5, ^3J = 2.9, ^4J = 0.8 Hz, 1 H, 12-H*anti*), δB = 2.07 (dddd, ^2J = −12.5, ^3J = 4.6, ^3J = 2.9, ^4J = 0.8 Hz, 1 H, 12-H*syn*)], 1.98 (ddd, ^2J = −15.9, ^3J = ^3J = 10.7 Hz, 1 H, 6-H), 1.56 (ddd, ^2J = −15.9, ^3J = ^3J = 9.0 Hz, 1 H, 6-H), 1.00−0.88 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): δ = 23.7, 28.5 (C-12), 32 (C-4,-8), 37 (C-5,-7), 40.0 (C-1), 41.8 (C-11), 73.4 (C-10), 124.9 (d), 125.7 (d), 158.5 (s), 159.0 (s), signal of CN missing due to low intensity. **10-Chloro-12-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (9b):** ^{1}H NMR (400 MHz): δ = 6.04 (dd, ^3J = 5.9, ^4J = 0.8 Hz, 1 H), 5.91 (d, ^3J = 5.8 Hz, 1 H), 3.83 (td, ^3J = 5.9, ^3J = 2.8 Hz, 1 H, 1-H), 2.94 (ddd, ^3J = 10.4, ^3J = 4.6, ^3J = 2.8 Hz, 1 H, 12-H), 2.8−2.6 (m, 2 H, 4-,8-H*exo*), 2.4−2.3 (m, 2 H, 4-,8-H*endo*), 2.30 [AB system: δA = 2.37 (dd, ^2J = −12.5, ^3J = 10.4 Hz, 1 H, 11-H*anti*), δB = 2.23 (dd, ^2J = −12.5, ^3J = 4.6 Hz, 1 H, 11-H*syn*)], 2.2−2.1 (m, 2 H, 5-,7-H*exo*), 1.98 (dt, ^2J = −15.9, ^3J = 10.7 Hz, 1 H, 6-H), 1.56 (dt, ^2J = −15.9, ^3J = 9.0 Hz, 1 H, 6-H), 1.00− 0.88 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): δ = 23.7, 32 (C-4,-8), 36.9 (C-5,-7), 37.0 (C-12), 39.9 (C-1), 40 (C-11), 77.7, 128.7 (d), 129.8 (d), 154.2 (s), 157.4 (s), signal of CN missing due to low intensity.

Reaction with 1c: Ratio **8c/9c** = 15:85. MS: *m*/*z* (%) = 267 (10) [$M^{+\cdot}$], 232 (100) [$M^{+\cdot}$ − Cl], 214 (12), 196 (20), [$M^{+\cdot}$ − HCl, − Cl], 179 (28), 115 (29). HRMS ($C_{14}H_{15}Cl_2N$): calcd. 267.0582; found 267.0579. **1,10-Dichloro-11-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (8c):** ^{1}H NMR (400 MHz): δ = 6.20 (d, ^4J = 1.1 Hz, 1 H), 6.14 (d, ^4J = 1.1 Hz, 1 H), 3.22 (dd, ^3J = 10.5, ^3J = 4.4 Hz, 1 H, 11-H), 2.8−2.7 (m, 2 H, 4-,8-H*exo*), 2.56 [AB system: δA = 2.62 (ddd, ^2J = −11.2, ^3J = 10.5, ^4J = 1.1 Hz, 1 H, 12-H*anti*), δB = 2.45 (ddd, ^2J = −12.5, ^3J = 4.4, ^4J = 1.1 Hz, 1 H, 12-H*syn*)], 2.4−1.0 (m, 8 H). ^{13}C NMR (50.3 MHz): δ = 23.7 (C-6), 32.3 (C-4,-8), 36.7 (C-5,-7), 41.3 (d, C-11), 42.4 (t, C-12), 64 (s), 74 (s), 120 (CN), 132.9 (d), 134.0 (d), 153 (s), 153.5 (s). **1,10-Dichloro-12-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (9c):** ^{1}H NMR (400 MHz): δ = 6.10 (d, ^4J = 1.0 Hz, 1 H, 2-H), 5.99 (s, 1 H, 13-H), 3.27 (ddd, ^3J = 10.5, ^3J = 4.4, ^4J = 1.0 Hz, 1 H, 12-H), 2.78 (ddd, ^2J = −13.3, ^3J = 11.7, ^3J = 4.0 Hz, 1 H, 8- or 4-H*exo*), 2.74 (ddd, ^2J = −13.3, ^3J = 12.0, ^3J = 4.5 Hz, 1 H, 4- or 8-H*exo*), 2.48 [AB system: δA = 2.55 (dd, ^2J = −12.5, ^3J = 10.5 Hz, 1 H, 11H*anti*), δB = 2.40 (dd, ^2J = −12.5, ^3J = 4.6 Hz, 1 H, 11-H*syn*)], 2.45−2.35 (m, 2 H, 4-,8-H*endo*), 2.24 (m, 2 H, 5-,7-H*exo*), 2.00 (dt, ^2J = −16.1, ^3J = 10.7 Hz, 1 H, 6-H), 1.73 (dt, ^2J = −16.1, ^3J = 9.0 Hz, 1 H, 6-H), 1.03 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): δ = 23.8 (C-6), 32.2 (C-4 or C-8), 32.3 (C-4 or C-8), 36.8 (C-5 or C-7), 36.9 (C-5 or C-7), 39.4 (d, C-12), 43.8 (t, C-11), 65.7 (s), 72.3 (s), 119.2 (CN), 129.7 (d, C-13), 130.2 (d, C-2), 157.6 (s), 158.9 (s).

Reaction with 1d: Ratio **8d/9d** = 15:85. MS: *m*/*z* (%) = 217 (93) [$M^{+\cdot}$], 176 (52), 164 (58), 149 (60), 135 (75), 122 (100), 109 (40). **11-Cyano-10-fluorotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (8d):** ^{1}H NMR (400 MHz): δ = 5.99 (t, ^3J = $J_{H,F}$ = 5.9 Hz, 1 H), 5.91 (t, $J_{H,F}$ = ^3J = 5.9 Hz, 1 H), 3.60 (tt, ^3J = 5.9, ^3J = 2.8 Hz, 1 H, 1-H), 2.90 (ddd, ^3J = 10.6, ^3J = 4.7 Hz, $J_{H,F}$ = 4.4 Hz, 1 H, 11-H), 2.6−1.5 (m, 10 H), 1.0−0.8 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (50.3 MHz): δ = 25.0 ($J_{C,F}$ = 7 Hz!, C-6), 30.7, 31.4, 32.4 ($J_{C,F}$ = 21 Hz, C-11), 36.7, 126.6 ($J_{C,F}$ = 5 Hz), 127.1 ($J_{C,F}$ = 5 Hz), 152.8 ($J_{C,F}$ = 13 Hz), 152.8 ($J_{C,F}$ = 13 Hz), signals of CN and C-10 missing due to low intensity. ^{19}F NMR (376.43 MHz): δ = −11.8. **12-Cyano-10-fluorotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (9d):** ^{1}H NMR (400 MHz): δ = 5.89 (dd, ^3J = 5.9 Hz, $J_{H,F}$ = 5.9 Hz, 1 H, 2-H), 5.75 (dd, $J_{H,F}$ = 5.9, ^3J = 5.8 Hz, 1 H, 13-H), 3.81 (ddd, ^3J = 5.9, ^3J = 5.8, ^3J = 2.8 Hz, 1 H, 1-H), 2.84 (ddd, ^3J = 10.6, ^3J = 4.7, ^3J = 2.8 Hz, 1 H, 12-H), 2.6−2.2 (m, 4 H, 4,8-H], 2.2−2.1 (m, 2 H, 5-,7-H*exo*), 2.02 [AB system: δA = 2.12 (ddd, ^2J = −11.9, ^3J = 10.6 Hz, $J_{H,F}$ = 4.7 Hz, 1 H, 11-H*anti*), δB = 1.92 (ddd, ^2J = −11.9, ^3J = 4.7 Hz, $J_{H,F}$ = 4.7 Hz, 1 H, 11-H*syn*)], 1.72 [AB system: δA = 1.78 (dtd, ^2J = −15.6, ^3J = 9.2 Hz, $J_{H,F}$ = 5.5 Hz), δB = 1.65 (dtd, ^2J = −15.6, ^3J = 10.2 Hz, $J_{H,F}$ = 5.2 Hz, 2 H, 6-H), 1.0−0.8 (m, 2 H, 5-,7-H*endo*]. ^{13}C NMR (50.3 MHz): δ = 25.1 (td, $J_{C,F}$ = 6.9 Hz!, C-6), 26.3 (dd, $J_{C,F}$ = 12 Hz, C-12), 30.3 (t), 34.4 (td, $J_{C,F}$ = 27 Hz, C-11), 36.6 (t), 40.1 (dd, $J_{C,F}$ = 1.6 Hz, C-1), 98.5 (d, $J_{C,F}$ = 194 Hz, C-10), 122.5 (dd, $J_{C,F}$ = 4.9 Hz), 123.3 (dd, $J_{C,F}$ = 5.4 Hz), 157.5 (d, $J_{C,F}$ = 13 Hz), 157.9 (d, $J_{C,F}$ = 13 Hz), signal of CN missing due to low intensity. ^{19}F NMR (376.43 MHz): δ = −12.3.

Reaction with 1f: Ratio **8f/9f** = 48:52. MS: *m*/*z* (%) = 277 (1) [$M^{+\cdot}$], 224 (10), 198 (5) [M − Br], 169 (20), 145 (30), 115 (23), 84 (100). HRMS ($C_{14}H_{16}BrN$): calcd. 277.0466; found 277.0455. **10-Bromo-11-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (8f):** ^{1}H NMR (400 MHz): δ = 6.14 (d, ^3J = 5.9 Hz, 1 H), 6.11 (d, ^3J = 5.9 Hz, 1 H), 3.64 (tt, ^3J = 5.9, ^3J = 3.0 Hz, 1 H, 1-H), 3.25 (dd, ^3J = 9.4,

^3J = 4.4 Hz, 1 H, 11-H), 2.9−2.7 (m, 2 H), 2.6−1.5 (m, 8 H), 1.1−0.9 (m, 2 H). **10-Bromo-12-cyanotricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (9f):** ^{1}H NMR (400 MHz): δ = 6.06 (d, ^3J = 5.9 Hz, 1 H), 5.92 (d, ^3J = 5.9 Hz, 1 H), 3.84 (td, ^3J = 5.9, ^3J = 2.8 Hz, 1 H, 1-H), 2.96 (ddd, ^3J = 10.4, ^3J = 4.6, ^3J = 2.8 Hz, 1 H, 12-H), 2.9−2.7 (m, 2 H), 2.50 [AB system: δA = 2.57 (dd, ^2J = −12.6, ^3J = 10.4 Hz, 1 H, 11-H*anti*), δB = 2.44 (dd, ^2J = −12.5, ^3J = 4.6 Hz, 1 H, 11-H*syn*)], 2.6−1.5 (m, 6 H), 1.1−0.9 (m, 2 H).

Reaction with 1h: Ratio **8h/9h** = 70:30. MS: *m*/*z* (%) = 263 (19) [M$^{+\cdot}$], 228 (100) [M − Cl], 210 (87), 175 (64), 145 (32), 129 (27), 115 (36), 103 (20), 91 (26), 77 (32). **1-Chloro-11-cyano-10-methoxytricyclo[7.3.1.0^{3,10}]trideca-2,9(13)-diene (8h):** ^{1}H NMR (400 MHz): δ = 6.09 (s, 1 H), 6.03 (s, 1 H), 3.56 (s, 3 H, OMe), 3.27 (dd, ^3J = 10.5, ^3J = 4.1 Hz, 1 H, 11-H), 2.69 (ddd, ^2J = −12.2, ^3J = 12.2, ^3J = 3.8 Hz, 1 H, 4- or 8-H*exo*), 2.49 (m, 1 H, 8- or 4-H*exo*), 2.48 [AB system: δA = 2.57 (ddd, ^2J = −11.2, ^3J = 10.5, ^4J = 0.9 Hz, 1 H, 11-H*anti*), δB = 2.39 (ddd, ^2J = −11.2, ^3J = 4.1, ^4J = 1.2 Hz, 1 H, 11-H*syn*)], 2.4−2.2 (m, 2 H, 4-,8-H*endo*), 2.2−2.1 (m, 2 H, 5-,7-H*exo*), 1.8−1.5 (m, 2 H, 6-H), 1.0−0.8 (m, 2 H, 5-,7-H*endo*). ^{13}C NMR (100.6 MHz): δ = 24.8 (t, C-6), 29.3 (t, C-4 or C-8), 30.5 (d, C-11), 32.8 (t, C-8 or C-4), 36.3 (t, C-5 or C-7), 37.3 (t, C-7 or C-5), 40.9 (t, C-12), 52.4 (q, MeO), 83 (C-10), 120 (CN), 131.2 (d), 135.3 (d), 154.9, 154.9. **1-Chloro-12-cyano-10-methoxytricyclo[7.3.-1.0^{3,10}]trideca-2,9(13)-diene (9h):** ^{1}H NMR (400 MHz): δ = 5.98 (s), 5.86 (s), 3.45 (s, 3 H, OMe), 3.24 (ddd, ^3J = 10.6, ^3J = 4.4, ^4J = 1.0 Hz, 1 H, 12-H), 2.5−0.8 (m, 12 H). ^{13}C NMR (100.6 MHz): δ = 25, 30.7 (C-4 or C-8), 31.2 (C-8 or C-4), 36.7 (C-5 or C-7), 36.9 (C-7 or C-5), 38.0 (C-12), 52.3 (MeO), 129.2, 129.5, some signals missing due to low intensity.

Acid-Catalyzed Rearrangements: A drop of CF_3COOH was added to a dilute solution of the compound in $CDCl_3$ in an NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy; all rearrangements were quantitative. When concentrated solutions were used, polymerization and unidentified products were observed.

Reaction with 1e. − 1-Chloro-4-fluoro-6,7,8,9-tetrahydro−5*H*-benzo[7]annulene (12): ^{1}H NMR (200 MHz): δ = 7.10 (dd, $^3J_{H,H}$ = 7, $^4J_{HF}$ = 5 Hz, 1 H, 2-H), 6.77 (dd, ^3J = 7.0, $^3J_{H,F}$ = 9 Hz, 1 H, 3-H), 2.98 (m, 2 H), 2.81 (m, 2 H), 1.80 (m, 2 H), 1.58 (m, 4 H). ^{13}C NMR (50.3 MHz): δ = 158.3 ($J_{C,F}$ = 242 Hz, C-4), 143.1 ($J_{C,F}$ = 3 Hz, C-1), 131.8 ($J_{C,F}$ = 16 Hz, C-4a), 127.7 ($J_{C,F}$ = 3 Hz, C-9a), 127.3 ($J_{C,F}$ = 9 Hz, C-2), 113.7 ($J_{C,F}$ = 26 Hz, C-3), 32.1 ($J_{C,F}$ = 7 Hz), 31.0 ($J_{C,F}$ = 2 Hz), 27.0, 26.5, 25.0. ^{19}F NMR (376.43 MHz): δ = 42.2 (dd, $^3J_{H,F}$ = 9, $^4J_{H,F}$ = 5 Hz). MS: *m*/*z* (%) = 198 (83), 163 (100), 156 (62), 133 (40). HRMS ($C_{11}H_{12}ClF$): calcd. 198.0612; found 198.061.

Reaction with 1h. − 4-Chlorospiro[5.5]undeca-2,4-dien-1-one (13h): ^{1}H NMR (400 MHz): δ = 6.89 (dd, ^3J = 10.0, ^4J = 2.7 Hz, 1 H, 3-H), 6.80 (dd, ^4J = 2.7, ^5J = 0.7 Hz, 1 H, 5-H), 6.06 (dd, ^3J = 10.0, ^5J = 0.7 Hz, 1 H, 2-H), 1.8−1.2 (m, 10 H). ^{13}C NMR (100.6 MHz): δ = 203.6 (C-1), 142.1 (d, C-5), 139.4 (d, C-3), 127.2 (d, C-2), 52.7 (s, C-6), 34.3 (t, C-7, C-11), 25.2 (t, C-9), 21.3 (t, C-8,-10), signal of C-4 missing due to low intensity. MS: *m*/*z* (%) = 196 (100) [M$^{+\cdot}$], 161 (63), 141 (34), 128 (26), 105 (20), 91 (57), 81 (65).

Reaction with 14 (vide infra). − Spiro[5.5]undeca-2,4-dien-1-one (13a): ^{1}H NMR (400 MHz): δ = 6.95 (ddd, ^3J = 9.7, ^3J = 5.8, ^4J = 1.8 Hz, 1 H, 3-H), 6.81 (ddd, ^3J = 9.7, ^4J = 1.8, ^5J = 0.9 Hz, 1 H, 5-H), 6.24 (ddd, ^3J = 9.7, ^3J = 5.8, ^4J = 1.0 Hz, 1 H, 4-H), 6.06 (ddd, ^3J = 9.7, ^4J = 1.0, ^5J = 0.9 Hz, 1 H, 2-H), 1.8−1.2 (m, 10 H). ^{13}C NMR (100.6 MHz): δ = 206.3 (C-1), 145.4 (d, C-5) 140.1 (d, C-3), 125.8 (d, C-2), 119.9 (d, C-4), 51.4 (s, C-6), 34.2 (t, C-7,-11), 25.4 (t, C-9), 21.4 (t, C-8,10). GCMS: *m*/*z* (%) = 162 (50) [M$^{+\cdot}$], 147 (15), 133 (21), 120 (32), 107 (57), 91 (100), 81 (97). HRMS ($C_{11}H_{16}O$): calcd. 162.1045; found 162.1042.

Nucleophilic Substitutions

General Procedure: NaH (10 mmol, 0.40 g, 60% dispersion in mineral oil) was washed five times with dry pentane. Dry DMSO (10 mL) was added and the mixture was heated at 70 °C until all the NaH had dissolved (2 h). After the mixture had cooled to room temperature, the appropriate dry reagent [10 mmol: MeOH (0.32 g), EtOH (0.46 g), *i*PrOH (0.60 g), benzyl alcohol (1.08 g), MeSH (0.50 g), or water (0.18 g)] was added and the mixture was stirred for another 15 min. An aliquot of this solution (*x* mL, which is equivalent to *x* mmol of RONa; for *x*, see experiments) was added to a solution of **1** in DMSO (5 mL). The solution was stirred (varying from 1 h to 5 d, at room temperature or 70° C, as indicated) and subsequently poured into cold water (30 mL). The water layer was extracted five times with pentane (30 mL). The combined pentane layers were washed three times with water. After drying with $MgSO_4$ and concentration under reduced pressure, the residue was analyzed by GCMS and NMR spectroscopy. In the case of a reaction with hydroxide, the water layer was neutralized with 0.1 M HCl, and extracted five times with pentane, followed by the usual workup. It was important to perform the workup rapidly, and to cool the products immediately afterwards, as decomposition of concentrated material occurred within several minutes.

Reaction with 1b: According to the general procedure, pure **1b** (1 mmol, 0.18 g) was stirred with 7 mL of the solution of NaSMe in DMSO (7 mmol, sevenfold excess) for 56 h at room temp. After workup, a yellow oil remained, and this, according to ^{1}H NMR analysis, consisted of **28** and some unchanged **1b**. **11-Chloro-7-methylthiobicyclo[5.3.1]undeca-1(10),8-diene (28):** Detection by low-temperature NMR, olefinic part calculated with PANIC. ^{1}H NMR (400 MHz): δ = 6.10 (dd, ^3J = 9.4, ^3J = 5.0 Hz, 1 H, 9-H), 5.80 (ddd, ^3J = 9.4, ^4J = 1.1, ^4J = 1.0 Hz, 1 H, 8-H), 5.67 (dddd, ^3J = 5.0, ^4J = 2.6, ^4J = 1.4, ^4J = 1.1 Hz, 1 H, 10-H), 5.31 (dd, ^4J = 2.6, ^4J = 1.0 Hz, 1 H, 11-H) 2.03 (s, 3 H, SMe), 2.5−1.0 (m, 10 H). ^{13}C NMR (100.6 MHz): δ = 12.5 (q, $J_{C,H}$ = 138 Hz, SMe), 24.7 (t), 25.2 (t), 31.1 (t), 34.1 (t), 37.2 (t, C-2), 55.9 (s, C-7), 64.7 (d, $J_{C,H}$ = 148 Hz, C-11), 120.0 (d, $J_{C,H}$ = 162 Hz, C-8), 127.3 (d, $J_{C,H}$ = 160 Hz, C-9), 134.6 (d, $J_{C,H}$ = 166 Hz, C-10), 140.3 (s, C-1). MS: *m*/*z* (%) = 228 (38) [M$^{+\cdot}$], 213 (16), 193 (77), [M − Cl], 181 (32) [M − SMe], 145 (100), 125 (91) 109 (61), 91 (85). HRMS ($C_{12}H_{17}ClS$): calcd. 228.0739; found 228.0744.

Reactions with 1c

Reaction with Benzyl Alcohol: According to the general procedure, pure **1c** (0.6 mmol, 0.13 g) was stirred with 5 mL of a solution of $NaOCH_2C_6H_5$ in DMSO (5 mmol, 8-fold excess) for 60 h at room temp. After workup, there remained a yellow oil (0.07 g), consisting of **1i** and some by-products. **11-Benzyloxy-8-chloro[5]metacyclophane (1i). − *exo* Conformer:** ^{1}H NMR (400.3 MHz, 213 K): δ = 6.67 (s, 2 H, 7,9-H), 3.42 (ddd, ^2J = −12.5, ^3J = 12.5, ^3J = 3.0 Hz, 2 H, 1-,5-H*exo*), 2.31 (ddd, ^2J = −12.5, ^3J = 3.3, ^3J = 3.3 Hz, 2 H, 1-,5-H*endo*), 2.14 (m, 1 H, 3-H*exo*), 1.90 (m, 2 H, 2-,4-H*exo*), 1.35 (m, 1 H, 3-H*endo*), 0.48 (m, 2 H, 2-,4-H*endo*). ^{13}C NMR (100.6 MHz, 213 K): δ = 25.1 (C-3), 37.3 (C-1,-5!), 40.5 (C-2,-4!), 71.0, 124.7 (C-7,-9), 126−129 (several signals of benzyloxy group), 136, 139, 167.1 (C-11). ***endo* Conformer:** ^{13}C NMR (100.6 MHz, 213 K): δ = 20, 34.1, 33.4, 74.5, 126.6, rest of the signals not assignable. MS: *m*/*z* (%) = 286 (69) [M$^{+\cdot}$], 251 (100), 195 (42), 165 (27), 91 (72), 81 (36).

Reaction with *t*BuOK: *t*BuOK (4 mmol, 0.45 g) was added over 15 min to a solution of **1c** (0.8 mmol, 0.17 g) in dry DMSO (10 mL). After stirring for 3 h at 40° C, the dark mixture was poured into ice/water (50 mL) and extracted five times with pentane. During these extractions a yellow precipitate (**A**) formed and was filtered off. The combined yellow pentane layers were washed three times with water and dried with $MgSO_4$, filtered, and concentrated under reduced pressure. A yellow oil (about 0.1 g) remained, and this rapidly formed a brown tar on concentration. ^{1}H NMR analysis showed the presence of the fulvene **34**, together with some impurities. The yellow precipitate **A** was dissolved in diethyl ether, washed with water, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Yellow crystals remained, but rapidly decomposed in concentrated form. Analysis showed the presence of pure **34**. **10-Chloro-2-[(methylsulfoxy)methyl]bicyclo[6.3.0]undeca-1,8,10-triene (34):** Unstable yellow crystalline compound. ^{1}H NMR (200 MHz): δ = 6.26 (d, ^4J = 1.94 Hz, 1 H, 11-H), 6.01 (br. s, several ^4J = unresolved, 1 H, 9-H), 3.85 [AB system: δA = 3.87, δB = 3.83, ^2J = −12.1 Hz, 2 H, $CH_2S(O)$], 2.9−2.6 (m, 4 H, 3,7-H), 2.61 [s, 3 H, MeS(O)], 1.7−1.2 (m, 6 H). ^{13}C NMR (50.3 MHz): δ = 21.3 (t), 24.2 (t), 27.0 (t), 29.2 (t), 33.0 (t), 38.7 [q, MeS(O)], 63.3 (t, C-12), 115.4 (d), 130.5 (d), 134.9 (s), 138.2 (s), 139.7 (s), 146.9 (s). MS: *m*/*z* (%) = 256 (11) [$M^{+\cdot}$], 240 (7), 194 (41), 193 (79), 165 (21), 157 (39), 151 (52), 142 (32), 129 (77), 115 (100). HRMS ($C_{13}H_{17}{}^{37}ClOS$): calcd. 258.0661 found 258.066. When the reaction was performed in [D_6]DMSO, 3−5 deuterium atoms were incorporated, as indicated by GCMS. In the ^{1}H NMR spectrum, the signal at δ = 2.61 was missing, and the signal at δ = 3.85 was reduced in intensity.

Reactions with pure 1d: Because the purification of **1d** was achieved by preparative GLC, the reactions were performed on a small, unquantified scale; the amount of **1d** was normally about 8−10 mg (^{1}H NMR). The reaction with methanol was performed several times; one example is described. In this experiment, NaOMe solution (2 mL, 2 mmol, 20-fold excess) was added to **1d** (about 16 mg, 0.1 mmol) in 3 mL of DMSO. The reaction time was 18 h at room temp. Two products, **20(OMe)** and **14**, were observed in a 6:4 ratio by NMR spectroscopy. **11-Fluoro-11-methoxybicyclo[5.3.1]undeca-1(10),8-diene [20(OMe)]:** Very unstable compound, detection by low-temperature NMR spectroscopy. ^{1}H NMR (400 MHz): δ = 6.08 (dd, ^3J = 9.3, ^3J = 5.0 Hz, 1 H, 9-H), 5.91 (dd, $J_{H,F}$ = 5.7, ^3J = 5.0, ^4J = unresolved, 1 H, 10-H), 5.80 (ddd, ^3J = 9.3 Hz, $J_{H,F}$ = 6.0, ^3J = 5.7, ^4J = unresolved, 1 H, 8-H), 3.35 (s, 3 H, OMe), 2.61 (dddd, all ^3J = 5.5−5.7 Hz, $J_{H,F}$ = 2.1 Hz, 1 H, 7-H), 2.5−1.0 (m, 10 H). ^{13}C NMR (100.6 MHz): δ = 22.7 (t, $J_{C,H}$ = 124 Hz), 26.2 (td, $J_{C,H}$ = 124 Hz, $J_{C,F}$ = 4.3 Hz), 27.9 (t, $J_{C,H}$ = 125 Hz), 28.5 (t, $J_{C,H}$ = 124 Hz), 37.3 (t, $J_{C,H}$ = 132 Hz, C-2), 42.3 (dd, $J_{C,H}$ = 153 Hz, $J_{C,F}$ = 25 Hz, C-7), 50.8 (q, $J_{C,H}$ = 145 Hz), 114.2 (d, $J_{C,F}$ = 223 Hz, C-11), 124.2 (dd, $J_{C,H}$ = 158 Hz, $J_{C,F}$ = 7.2 Hz), 124.7 (d, $J_{C,H}$ = 162 Hz), 129.4 (dd, $J_{C,H}$ = 165 Hz, $J_{C,F}$ = 5.4 Hz), 139 (d, $J_{C,F}$ = 34 Hz, C-1). ^{19}F NMR (376.43 MHz): δ = 34.6. MS: *m*/*z* (%) = 196 (100) [$M^{+\cdot}$], 176 (54), 161 (24), 153 (26), 139 (14), 109 (94). HRMS ($C_{12}H_{17}FO$): calcd. 196.1263; found 196.1268. **Bicyclo[5.3.1]undeca-1(10),8-dien-11-one (14):** ^{1}H NMR (400 MHz): δ = 6.49 (ddt, ^3J = 5.4, ^4J = 1.8, ^4J = 1.0 Hz, 1 H, 10-H), 6.21 (dd, ^3J = 9.2, ^3J = 5.4 Hz, 1 H, 9-H), 6.14 (ddd, ^3J = 9.2, ^3J = 5.0, ^4J = 1.8 Hz, 1 H, 8-H), 3.07 (ddd, all ^3J = 5.2 to 5.7 Hz, 1 H, 7-H), 2.50 [AB system: δA = 2.85 (dddd, ^2J = −12, ^3J = 11.7, ^3J = 5.8, ^4J = 1.0 Hz, 1 H, 2-H*exo*), δB = 2.14 (dddd, ^2J = −12, ^3J = 5.8, ^3J = 2.1, ^4J = 1.0 Hz, 1 H, 2-H*endo*], 1.92 (m, 1 H), 1.8 (m, 2 H), 1.7 (m, 2 H), 1.35 (m, 1 H), 1.27 (m, 1 H), 0.95 (m, 1 H). ^{13}C NMR (100.6 MHz): δ = 210.3 (s, C-11), 143.1 (s, C-1), 135.4 (d), 132.0 (d), 124.0 (d), 50.1 (d, C-7), 35.8 (t), 35.7 (t), 30.0 (t, C-2!), 26.9 (t), 24.9 (t). GCMS: *m*/*z* (%) = 162 (100) [$M^{+\cdot}$], 147 (9), 133 (37), 120 (26), 107 (93), 91 (80), 78 (32). HRMS ($C_{11}H_{14}O$): calcd. 162.1045; found 162.1039. The reaction with water was performed on a smaller scale by stirring **1d** for 18 h at 70 °C in 2 mL of a solution of NaOH in DMSO. Compound **14** was obtained without neutralization of the water layer; it turned out to be very sensitive towards traces of acid. Identification was as described above.

Reactions with a Mixture of 1b and 1d: For each reaction, an approximately 1:1 mixture of **1b** and **1c** (together 0.6 mmol, 0.10 g) in 5 mL of DMSO was treated with 5 mL of a solution of NaOR in DMSO (5 mmol, eightfold excess); the reaction time was 18 h at room temp.

With Methanol: After workup, a yellow oil containing **20(OMe)**, **14**, unchanged **1b**, and traces of **1g**[11] remained. The products were very unstable, and a purple compound was formed on standing at room temp. Identification was as described above.

With Ethanol: After workup, a yellow oil consisting of **20(OEt)**, **14**, unchanged **1b**, and some side products remained. The products were very unstable, and a purple compound was formed on standing at room temp. Purification was impossible. Identification was performed in the mixture; the assignment of ^{13}C NMR signals is not unambiguous. **11-Ethoxy-11-fluorobicyclo[5.3.1]undeca-1(10),8-diene [20(OEt)]:** ^{1}H NMR (200 MHz): δ = 6.1−5.7 (m, 3 H), 3.8−3.5 (m, 2 H, OCH_2Me), 2.7−1.0 (m, 11 H), 1.09 (t, ^3J = 7.0 Hz, 3 H, Me). ^{13}C NMR (100.6 MHz): δ = 14.3, 22.5, 26.2, 28.2, 28.6, 37.3, 42.4 (d, $J_{C,F}$ = 25 Hz, C-7), 58.7 (or 56.0?!), 114.4 (d, $J_{C,F}$ = 230 Hz, C-11), 123.8 (d, $J_{C,F}$ = 7 Hz), 124.6, 129.5 (d, $J_{C,F}$ = 5.4 Hz), 139.5 (d, $J_{C,F}$ = 34 Hz, C-1). ^{19}F NMR (376.43 MHz): δ = 36.5. MS: *m*/*z* (%) = 210 (63) [$M^{+\cdot}$], 190 (40), 161 (26), 153 (39), 109 (100), 84 (92). HRMS ($C_{13}H_{19}FO$): calcd. 210.142; found 210.1422.

With 2-Propanol: After workup, a yellow oil consisting of **20(O*i*Pr)**, **52**, unchanged **21c** and **22c** and many side products remained. The products were very unstable, and a purple compound was formed on standing at room temp. Identification was almost impossible, but ^{19}F NMR indicated formation of adduct, along with **1d**. **11-Fluoro-11-isopropoxybicyclo[5.3.1]undeca-1(10),8-diene [20(O*i*Pr)]:** ^{19}F NMR (376.43 MHz): δ = 44.6.

With Benzyl Alcohol: After workup, a yellow oil consisting of **20(O*i*Pr)**, unchanged **22c**, and some side products remained. The products were very unstable, and a purple compound was formed on standing at room temp. Purification was impossible, identification was performed in mixture, and although the formation of adduct was clearly observed, assignment of signals is rather tentative. **11-Benzyloxy-11-fluorobicyclo[5.3.1]undeca-1(10),8-diene [20-($OCH_2C_6H_5$)]:** ^{1}H NMR (200 MHz): δ = 7.4−7.2 (m, 5 H), 6.06 (dd, ^3J = 9.0, ^3J = 5.0 Hz, 1 H, 9-H), 5.93 (dd, $J_{H,F}$ = 5, ^3J = 5.0, ^4J = unresolved, 1 H, 10-H), 5.79 (ddd, ^3J = 9.0 Hz, $J_{H,F}$ = 6.0, ^3J = 5.0, ^4J = unresolved, 1 H, 8-H), 4.63 (AB system: δA = 4.64, δB = 4.61, ^2J = −14 Hz, 2 H, OCH_2Ph), 3.3−1.0 (m, 11 H). ^{13}C NMR (100.6 MHz): δ = 22, 26.3, 28.0, 28.8, 37.4, 42.4 ($J_{C,F}$ = 25 Hz), 65, 114.7 ($J_{C,F}$ = 225 Hz, C-11), 124.6, 124.7, 126−128 (several signals of phenyl of adduct and remaining benzyl alcohol), 130.0 ($J_{C,F}$ = 5 Hz), 137.5, 139.3 ($J_{C,F}$ = 33 Hz, C-1). ^{19}F NMR (376.43 MHz): δ = 39.1.

"Prelog-Type" Reactions

15-Hydroxy-12-nitro[9]metacyclophane (36): Cyclododecanone (4.5 mmol, 0.82 g) was added at room temp. to a solution of sodium nitromalonaldehyde (5 mmol, 0.8 g) and NaOH (65 mmol,

2.6 g) in ethanol (9 mL) and water (3 mL). After this had stirred for 8 d, water (15 mL) was added and the suspension was filtered through a Büchner funnel. The water layer was acidified to pH = 4 with 0.1 M HCl and extracted with diethyl ether. After drying with $MgSO_4$, it was filtered and concentrated under reduced pressure; yellowish crystals remained. **36:** ^{1}H NMR (200 MHz): δ = 7.83 (s, 2 H, 11,13-H) 5.7 (br. s, 1 H, OH), 2.78 [AB system: δA = 3.04 (ddd, ^2J = −13.6, ^3J = 7.4, ^3J = 4.7 Hz), δB = 2.52 (ddd, ^2J = −13.6, ^3J = 9.5, ^3J = 4.7 Hz), 4 H, 1-,9-H], 1.96 (m, 2 H), 1.52 (m, 2 H), 1.23 (m, 2 H), 1.1−0.8 (m, 4 H), 0.42 (m, 2 H). ^{13}C NMR (50.3 MHz): δ = 160.7 (s), 141.3 (s), 130.8 (s, C-10,-14), 125.1 (d, C-11,-13), 30.9 (t, C-1,-9), 26.1 (t), 25.4 (t), 25.1 (t, C-5), 24.4 (t). MS: *m/z* (%) = 263 (100), [$M^{+\cdot}$], 246 (16), 165 (35), 150 (22), 131 (12), 121 (15), 107 (15), 95 (15), 91 (30), 55 (40), 41 (40). HRMS ($C_{15}H_{21}NO_3$): calcd. 263.1521; found 263.151.

13-Hydroxy-10-nitro[7]metacyclophane (37): Cyclodecanone (4.6 mmol, 0.70 g) was added at room temp. to a solution of sodium nitromalonaldehyde (5 mmol, 0.8 g) and NaOH (65 mmol, 2.6 g) in ethanol (9 mL) and water (3 mL). After this had stirred for 8 d, water (15 mL) was added and the suspension was filtered through a Büchner funnel. The water layer was acidified to pH = 4 with 0.1 M HCl and extracted with diethyl ether. After drying with $MgSO_4$, it was filtered and concentrated under reduced pressure, yielding yellow crystals. **37:** ^{1}H NMR (200 MHz): δ = 7.83 (s, 2 H, 9,11-H), 5.7 (br. s, 1 H, OH), 2.97 [AB system: δA = 3.33 (ddd, ^2J = −13.7, ^3J = 10.3, ^3J = 4.4 Hz), δB = 2.60 (ddd, ^2J = −13.7, ^3J = 5.0, ^3J = 4.5 Hz), 4 H, 1,9-H], 1.95 (m, 2 H), 1.5 (m, 2 H), 1.3−1.0 (m, 6 H). ^{13}C NMR (50.3 MHz): δ = 160.8 (s), 142 (s), 129.3 (s, C-10,-14), 122.5 (d, C-11,-13), 31.7, 30.8, 28.0, 26.7. MS: *m/z* (%) = 253 (100) [$M^{+\cdot}$], 218 (39), 189 (44), 165 (55), 91 (14), 77 (12), 65 (11), 41 (11). HRMS ($C_{13}H_{17}NO_3$): calcd. 235.1208; found 235.122.

9-Nitrobicyclo[5.3.1]undeca-1(10),8-dien-11-one (38): A solution of cyclooctanone (4.2 mmol, 0.56 g) in ethanol (30 mL) was added to a solution of sodium nitromalonaldehyde (4.8 mmol, 0.75 g) and NaOH (28 mmol, 1.1 g) in water (10 mL). After this had stirred for 6 d, the ethanol was removed under reduced pressure. Some water was added to the residual red oil, and the solution was extracted four times with CH_2Cl_2 to remove polymers. After acidification to pH = 3 (dropwise with a 0.1 M HCl solution), the water layer was extracted four times with diethyl ether. The combined ethereal layers were dried with $MgSO_4$, filtered, and concentrated. Recrystallization could be achieved from pentane at −20 to −80° C and yielded several mg of reasonably pure **38**. ^{1}H NMR (400 MHz): δ = 7.38 (dd, ^3J = 5.7, ^4J = 2.8 Hz, 1 H, 8-H), 7.09 (dt, ^4J = 2.8, ^4J = unresolved, 1 H, 10-H), 3.55 (ddd, all ^3J = 5.2 to 5.7 Hz, 1 H, 7-H), 2.55 [AB system: δA = 2.84 (ddd, ^2J = −11.9, ^3J = 11.8, ^3J = 6.0 Hz, 1 H, 2-H*exo*), δB = 2.26 (ddd, ^2J = −11.9, ^3J = 6.0, ^3J = 2.3 Hz, 1 H, 2-H*endo*)], 2.0−1.9 (m, 3 H), 1.8−1.7 (m, 2 H), 1.38 (m, 1 H), 1.19 (m, 1 H), 0.96 (m, 1 H). ^{13}C NMR (50.32 MHz): δ = 205.8 (s, C-11), 146.3 (s, C-9), 145.5 (s, C-1), 136.5 (d, C-8), 124.2 (d, C-10), 48.5 (d, C-7), 35.0 (t), 34.9 (t), 30.0 (t, C-2!), 26.4 (t), 25.2 (t). MS: *m/z* (%) = 207 (90) [$M^{+\cdot}$], 179 (23), 165 (60), 153 (65), 136 (27), 132 (48), 117 (24), 105 (29), 91 (10). HRMS ($C_{11}H_{13}NO_3$): calcd. 207.0895; found 207.091.

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