thermodynamic measurements are surprisingly insensitive to the nature of the solvent. This implies that differential solvation effects between solvents are small even though it appears that there may be relatively large differential solvation effects as a function of substituent. Accordingly, the ρ values obtained from these correlations can be used to probe the degree of charge separation at transition states. However, these data must be treated with caution in light of the assumptions and experimental uncertainties implicit in the analysis.

Experimental Section

Acetonitrile (BDH), di-*tert*-butyl peroxide (Aldrich), and tetrabutylammonium perchlorate (Eastman) were purified as previously described.[8] All of the substituted toluenes were available commercially and were purified by distillation prior to use. The substituted cumenes were synthesized by addition of methylmagnesium iodide to the substituted ethyl benzoate followed by dehydration and catalytic hydrogenation of the substituted α-methylstyrene (palladium on carbon, 1 atm of hydrogen). All of these compounds were purified by distillation. The substituted diphenylmethanes were synthesized by Freidel-Crafts substitution of the substituted benzyl chloride on benzne ($AlCl_3$, 0 °C). α-(4-Tolyl)-α-phenylacetophenone and α,α-di-(4-tolyl)acetophenone were a gift from Professor D. R. Arnold (Dalhousie), 2-methoxydiphenylmethane was a gift from Professor P. Maslak (Penn State), 4-methoxy- and 4-cyanocumene were gifts from Dr. P. Mulder (Leiden), and 4-cyanodiphenylmethane was a gift from Professor D. Weir (Notre Dame). The instrument has been described in detail elsewhere.[8]

Unusual Reactivity of Small Cyclophanes: Nucleophilic Attack on 11-Chloro- and 8,11-Dichloro[5]metacyclophane

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Received February 1, 1990

Abstract: Treatment of 11-chloro- (**1a**) and 8,11-dichloro[5]metacyclophane (**1b**) with solutions of sodium alkoxides (NaOMe, NaOEt, and NaO-*i*-Pr) in DMSO at room temperature yielded the 11-alkoxy[5]metacyclophanes **1d–h** by substitution of the chlorine between the bridgeheads. The reaction is believed to proceed via the S_NAr (addition–elimination) mechanism. The unprecedented ease of this reaction in the absence of activating substituents at the aromatic ring is explained by the strained character of the cyclophane; this is confirmed by MNDO/HFS calculations on the reaction of **1a** and chlorobenzene with chloride ion. Contrary to these results, treatment of **1a** or **1b** with sodium hydroxide in DMSO led to the formation of 2-oxobicyclo[6.3.0]undeca-1(8),9-diene (**5a**) or its 10-chloro derivative **5b**, respectively. The formation of **5** can be explained by assuming that the hydroxide anion attacked one of the bridgehead carbon atoms of **1a** or **1b**, followed by a base-induced Wagner–Meerwein rearrangement. A third type of reactivity was observed on treatment of **1b** with sodamide in liquid ammonia, which led to substitution of the "unhindered" chlorine to yield the 8-amino-11-chloro[5]metacyclophane (**1j**), probably via an elimination–addition mechanism. The stereochemistry of **1** is briefly discussed.

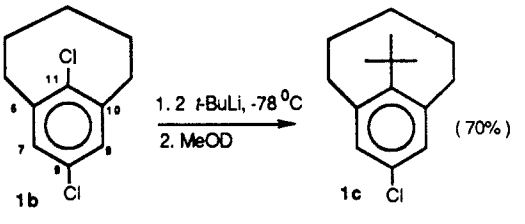
Introduction

In the past few years the synthesis of several small and very small cyclophanes has been achieved.[1] Focusing on the meta series, [5]metacyclophanes can be synthesized with relative ease; the parent compound and several derivatives have been prepared.[1m,n] [4]Metacyclophane, on the other hand, could not be isolated but was detected as a highly reactive intermediate.[1o,p]

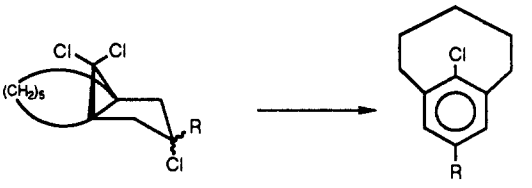
One of our major goals in connection with small cyclophane chemistry was to see whether the aromaticity of the benzene ring could be "broken" as a result of the strong distortion of the normally planar aromatic ring system. Several independent pieces of evidence were found in favor of essentially unperturbed aromaticity: chemical shifts of the aromatic protons fell inside the aromatic region (ring current effect);[1m,n] the quadrupole splitting of deuteriobenzenes at high magnetic fields due to alignment effects showed the characteristic magnetic anisotropy;[2] by X-ray analysis of 8,11-dichloro[5]metacyclophane (**1b**) it was shown that the carbon–carbon bonds of its benzene ring (d = 1.393 ± 0.007 Å) are fully delocalized and typically aromatic.[3]

On the other hand, the reactivity of [5]metacyclophanes was quite unusual. Compared to the typical reaction pattern of normal aromatics, the bent systems were either extremely reactive,[1m,n,4] or underwent reactions that have no counterpart in aromatic chemistry.[1a,4]

Scheme I



Scheme II[a]



2a R = H
2b R = Cl

1a R = H (70%)[a]
1b R = Cl (80%)[b]

[a] **2a**, KO-*t*-Bu, DMSO. [b] **2b**, $AgClO_4$, lutidine, Et_2O.

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[‡] University of Amsterdam.

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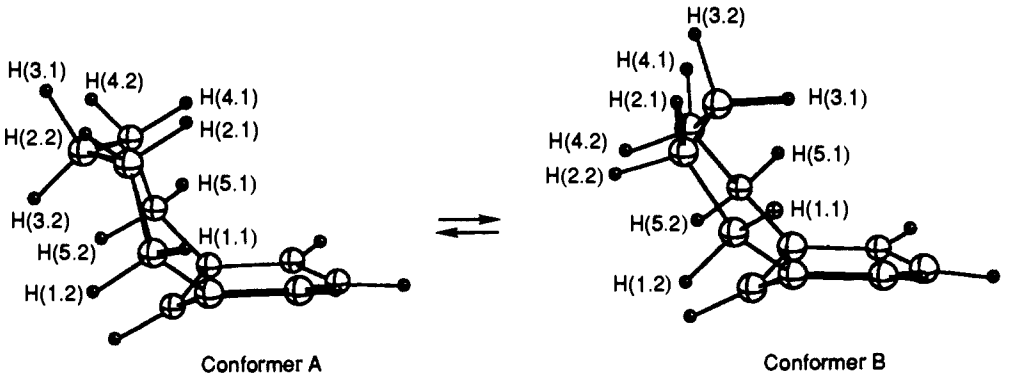


Figure 1. Geometry and numbering of the methylene protons of conformers A and B of **1**.

In this paper we want to focus attention on the reactivity of 11-chloro- (**1a**) and 8,11-dichloro[5]metacyclophane (**1b**) with nucleophiles. One of the motives for this investigation was the observation that **1b**, when treated with *tert*-butyllithium at −78 °C and subsequently quenched with methanol-*O*-*d*, did not yield the "expected" 8,11-dideuterio[5]metacyclophane but a substitution product in which the 11-chlorine atom (between the bridgehead carbons) had been replaced by the sterically demanding *tert*-butyl group, **1c**[5] (Scheme I).

The formation of this unusual product was tentatively explained to proceed via an addition–elimination (S_NAr) mechanism. However, such reactions are not common for organolithium compounds, and other mechanisms could not be fully excluded. Therefore, a more extensive investigation on the reactivity of halogen-substituted cyclophanes toward nucleophiles seemed warranted.

Results

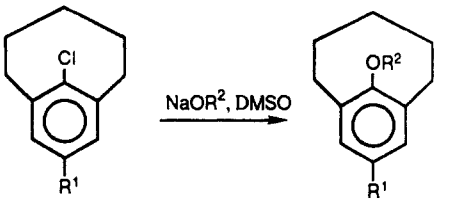
The educts **1a** and **1b** were obtained as follows. Compound **1a** has not been described earlier and was synthesized by treating the trichloro[5.3.1]propellane **2a** with potassium *tert*-butoxide in DMSO (Scheme II); **1b** can be prepared by treating the tetrachloro[5.3.1]propellane **2b** with $AgClO_4$/lutidine in good yield.[1n]

Because of the high reactivity of anions in dipolar aprotic solvents, most of the reactions with nucleophiles described here were performed employing DMSO as solvent. When to a 7-fold excess of a solution of either sodium methoxide or ethoxide in DMSO **1a** was added at room temperature, a dark-colored mixture resulted, which was stirred for several days. After workup a single product was isolated which, on the basis of its spectral data, was characterized as a derivative of **1a** in which the chlorine atom had been replaced by a methoxy or ethoxy group (**1d** or **1e**, respectively). Furthermore, as indicated by ^1H and ^{13}C NMR spectroscopy, the products exhibited overall C_s symmetry and the alkoxy substituent was present at the 11-position, i.e. between the bridgehead carbon atoms, as demonstrated by the chemical shifts and coupling constants of the aromatic protons (Scheme III).

Next, the dichlorocyclophane **1b** was investigated. The comparison of **1a** and **1b** is of interest because the latter contains, in addition to the chlorine at C-11, a second chlorine which may or may not compete in the substitution process; the outcome may be relevant to the question whether the high reactivity observed for **1a** is a general phenomenon of the distorted benzene ring or whether regiochemical differences are discernible.

Compound **1b** was treated with sodium methoxide, ethoxide, or isopropoxide under the same conditions as described for **1a**. It turned out to be much more reactive than **1a**. Stirring overnight was sufficient to convert all of **1b** into the alkoxy-substituted derivatives **1f–h**. As was the case with **1a**, a single product was isolated after workup in fair to good yield. Analysis by mass

Scheme III



1a R^1=H
1b R^1=Cl

1d R^1=H, R^2=Me (90%)
1e R^1=H, R^2=Et (75%)
1f R^1=Cl, R^2=Me (60%)
1g R^1=Cl, R^2=Et (90%)
1h R^1=Cl, R^2=*i*-Pr (55%)

Table I. ^{13}C Chemical Shifts δ (ppm) of the Aromatic Carbon Atoms of **1f,g,h,j**

atom[a]	8-alkoxy-11-chloro[b]	11-alkoxy-8-chloro[b]	**1f**[c]	**1g**[c]	**1h**[c]	**1j**[c]	multiplicity
C11	136.7	168.9	168.9	167.5	166.0	133.4	s
C6/C10	148.8	134.4	137.8	138.8	141.0	147.5	s
C7/C9	109.2	123.6	123.9	123.5	123.2	110.4	d
C8	161.1	130.2	129.0	127.0	127.9	146.8	s
rms 11-substituted-8-chloro[d]			1.8	2.8	3.8	0.9	
rms 8-substituted-11-chloro[d]			10.6	10.9	8.6	9.8	

[a] For numbering see Scheme I. [b] Predicted values with group increments[6] and the values of [5]metacyclophane[7] as a basis. [c] Experimental values from $^{13}C\{^1H\}$ NMR spectra ($CDCl_3$, 300 K, 62.9 MHz). [d] Root mean square value ($\sqrt{(\sum\Delta\delta^2/_4)}$) for the difference between predicted and experimental values.

(1) Reviews: (a) Bickelhaupt, F.; De Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 459. (b) Keehn, P. M.; Rosenfeld, S. M., Eds. *Cyclophanes*; Academic Press: New York, 1983; Vol I. [6]Paracyclophane: (c) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144. (d) Tobe, Y.; Ueda, K.-I.; Kakiuchi, K.; Odaira, Y. *Tetrahedron* **1986**, *42*, 1851. [6]Paracycloph-3-ene: (e) Tobe, Y.; Ueda, K-I.; Kaneda, T.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 1136. [5]Paracyclophane: (f) Jenneskens, L. W.; De Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; De Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. (g) Kostermans, G. B. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1987**, *43*, 2966. [4]Paracyclophane: (h) Kostermans, G. B. M.; Bobeldijk, M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471. (i) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368. [6]-Metacyclophane: (j) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219. (k) Shea, K. J.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305. [6]Metacycloph-3-ene: (l) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5424. [5]Metacyclophane: (m) Turkenburg, L. A. M.; Blok, P. L. M.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1981**, *22*, 3317. (n) Jenneskens, L. W.; De Kanter, F. J. J.; Turkenburg, L. A. M.; De Boer, H. J. J.; De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 4413. [4]Metacyclophane: (o) Kostermans, G. B. M.; Van Dansik, P.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 7887. (p) Kostermans, G. B. M.; Van Dansik, P.; De Wolf, W. H.; Bickelhaupt, F. *J. Org. Chem.* **1988**, *53*, 4531.

(2) Van Zijl, P. C. M.; Jenneskens, L. W. J.; Bastiaan, E. W.; MacLean, C.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1986**, *108*, 1415.

(3) Jenneskens, L. W.; Klamer, J. C.; De Boer, H. J. R.; De Wolf, W. H.; Bickelhaupt, F.; Stam, C. *Angew. Chem.* **1984**, *96*, 236.

(4) Jenneskens, L. W. To be published.

(5) Jenneskens, L. W.; Klamer, J. C.; De Wolf, W. H.; Bickelhaupt, F. *J. Chem. Soc., Chem. Commun.* **1984**, 733.

(6) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Thieme Verlag: Stuttgart, 1984.

(7) Jenneskens, L. W.; De Kanter, F. J. J.; De Wolf, W. H.; Bickelhaupt, F. *Magn. Reson. Chem.* **1986**, *24*, 308.

(8) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

Table II. Mole Fractions of Conformers A and B of **1**[a]

compd	R(11)[b]	R(8)[c]	A[d]	B[d]	$\Delta\Delta H_f°_{(A-B)}$[e]
1'[f]	H	H	1.00		−1.2
1k[g]	H	Cl	1.00		
1c[f]	*t*-Bu	Cl	1.00		−1.0
1j[g]	Cl	NH_2	0.90	0.10	
1a[g]	Cl	H	0.86	0.14	
1h[g]	*i*-PrO	Cl	0.86	0.14	
1b[f]	Cl	Cl	0.85	0.15	−0.4
1g[g]	EtO	Cl	0.75	0.25	
1e[g]	EtO	H	0.70	0.30	
1f[g]	MeO	Cl	0.66	0.33	−0.3
1d[g]	MeO	H	0.58	0.42	

[a] Determined by ^1H NMR spectroscopy at 220 K. [b] R(11) is the substituent present at the 11-position of **1**. [c] R(8) is the substituent present at the 8-position of **1**. [d] Mole fraction. [e] In kcal·mol^{-1}; obtained by MNDO calculation. [f] From ref 1n. [g] This work.

spectrometry indicated that one of the chlorine substituents had been replaced by an alkoxy group; ^1H and ^{13}C NMR spectroscopy indicated the C_s symmetry of the products. This leaves us with two possible positions for the alkoxy (and chlorine) substituent, the position 8 or 11. Distinction between these is not trivial. However, a distinction in favor of the 11-alkoxy-8-chloro isomer could be made on the basis of the following observations.

First, comparison of the experimentally determined ^{13}C chemical shifts of the carbon atoms of the aromatic ring of **1f–h** with those determined by use of standard group increments gave a much better fit with the 11-alkoxy isomers than with the 8-alkoxy isomers (Table I): the root-mean-square value of the difference between the experimentally determined chemical shifts and those of the predicted shifts is significantly lower for the 11-alkoxy-8-chloro isomers than for the 8-alkoxy-11-chloro isomers.

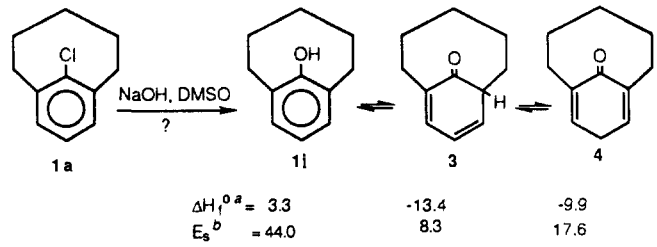
Second, the [5]metacyclophanes exist as a mixture of two conformers. We arbitrarily have designated them as A and B, respectively. The main geometric difference between these two conformers lies in the conformation of the *trans*-cyclooctene ring in **1** containing the pentamethylene bridge and the carbon atoms C6, C10, and C11 of the aromatic ring (Figure 1).

Conformer A has a chair–chair cyclooctene ring with the central methylene group pointing away from the (boat shaped) aromatic ring. Conformer B has a chair–boat cyclooctene ring with the central methylene group pointing toward the benzene ring.

A dynamic equilibrium exists between both conformers. By measuring ^1H NMR spectra at low temperature (220 K), the equilibrium can be frozen on the NMR time scale, and both conformers A and B can be observed separately in the mixture due to characteristic chemical shifts of the aromatic and methylene protons of both conformers. In all cases, conformer A is the most abundant one, its mole fraction varying between 1.0 and 0.6. In Table II the mole fractions of A and B of several derivatives of **1** are shown in order of decreasing A.

The ratio of A:B is not a straightforward one, as is illustrated by a comparison of e.g. **1'**, **1b**, and **1c**, the reason being that the repulsive interaction between the substituent and the "inner" protons H(1.2), H(5.2), and H(3.2) is different in A and B.[1n] Obviously, it depends not only on the size but also on the shape and orientation of the substituent (see also Discussion). However, in line with expectation, it is clear that the ratio A:B is primarily determined by the substituent at position 11 and only to a minor degree influenced by the substituent at position 8. The couple **1'** and **1k**, both having a hydrogen at C11, illustrates this point; similarly a given substituent at C11 has a characteristic and consistent value of A:B. Thus, when we consider the transformations **1a** → **1d** and **1b** → **1f**, the comparable changes of A:B (from 0.86:0.14 to 0.58:0.42 and from 0.85:0.15 to 0.66:0.33, respectively) clearly indicate that it is Cl11 of **1b** that has been replaced by OCH_3. By analogous reasoning, the typical "chlorine" value of **1j** (A:B 0.90:0.10, vide infra) tells us that Cl11 is still present and Cl8 has been substituted (by an amino group). The results obtained from Tables I and II are in agreement in indicating that the alkoxy substituent in **1f**, **1g**, and **1h** must be present at position 11.

Scheme IV[a]



[a] In kcal·mol^{-1}; obtained by MNDO calculations. [b] Strain energy (kcal·mol^{-1}), determined by the difference in $\Delta H_f°$ obtained from MNDO and that obtained by standard group increments.[8]

A logical extension of the series of the alkoxides is the hydroxide anion. Its reaction with **1a** or **1b** has an additional point of interest, because it might lead to a 11-hydroxy[5]metacyclophane, a bridged phenol derivative. Due to the high strain in [5]metacyclophanes, the phenol entity might give up its aromaticity and tautomerize to a cyclohexadienone derivative **3** or **4**. From MNDO calculations on **1i**, **3**, and **4**, it is clear that this would indeed be thermodynamically favorable (Scheme IV). Both the bridged cyclohexa-1,3-dienone **3** and the cyclohexa-1,4-dienone **4** have a much lower heat of formation, and the strain energy in these compounds is also lower than that of **1i**. Compound **3** is more stable and less strained than **4**, which is mainly a consequence of the two strained double bonds in the latter (Bredt's rule). So, one would expect that **1i** would rearrange to **3**.

The synthesis of a [5]methaphenolophane has been claimed by Prelog and co-workers;[9] identification was based on UV absorption spectroscopy. However, the UV spectrum of the pentamethylene isomer differed from that of the higher homologues in showing a *hypsochromic* shift so that an isomerization as indicated in Scheme IV appeared more likely.[9b] We now know that the UV spectra of cyclophanes show an increasing *bathochromic* shift with *decreasing* size of the oligomethylene bridge.[1a,9b] Second, the strongly acidic conditions during the isolation of the compound make the survival of a [5]metacyclophane derivative highly improbable; the small meta- and paracyclophanes undergo a rapid rearrangement to unstrained ortho-bridged isomers or give addition products when treated with even a catalytic amount of acid.[10]

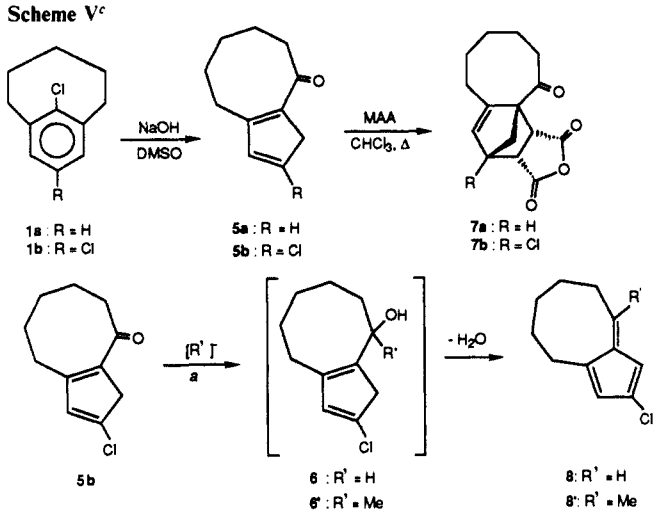
We first examined the reactivity of **1b** toward the hydroxide ion because of its higher reactivity compared to **1a**. Treatment of **1b** with a solution of sodium hydroxide in DMSO and stirring the mixture for several hours at room temperature yielded, after workup, only recovered starting material. However, increasing the temperature to 70 °C and neutralizing the reaction mixture before extraction yielded a bright yellow colored oil as product.

On the basis of the mass spectrum, it seemed that indeed a net substitution of one of the chlorine atoms by a hydroxy group had taken place. Both ^1H and ^{13}C NMR spectra, however, gave no indication that a hydroxy[5]metacyclophane (or **3**) was formed but were in line with a formylcyclopentadiene derivative **5b** (Scheme V), implying a rearrangement from a [5]metacyclophane or bicyclo[5.3.1]undecane skeleton to a bicyclo[6.3.0]undecane skeleton.

Reduction of **5b** with diisobutylaluminum hydride (DIBAH) yielded the fulvene derivative **8**; reaction with methyllithium gave the 6-methylfulvene derivative **8'**. The intermediates **6** and **6'**, respectively, which are initially formed in these reactions, were not isolated; under the basic reaction conditions they undergo elimination of water yielding the fulvene entity. This is not surprising, because 1-(1'-cyclopentadienyl)alkanols are known to occur as intermediates in the synthesis of a variety of 6-substituted fulvenes by condensation of cyclopentadiene with aldehydes or ketones in the presence of bases such as sodium hydroxide or alkoxides.[11]

(9) (a) Prelog, V.; Wiesner, K. *Helv. Chim. Acta* **1947**, *30*, 1465. (b) Prelog, V.; Barman, P.; Zimmermann, M. *Helv. Chim. Acta* **1950**, *33*, 356.
(10) Kostermans, G. B. M.; Kwakman, P. J.; Pouwels, P. J. W.; Somsen, G.; De Wolf, W. H.; Bickelhaupt, F. *J. Phys. Org. Chem.* **1989**, *2*, 331.

Scheme V[c]



[c] $[R']^-$ = H^- equivalent: DIBAH, 0 °C, 2 h. $[R']^-$ = Me^- equivalent: MeLi, 0 °C, 3 h.

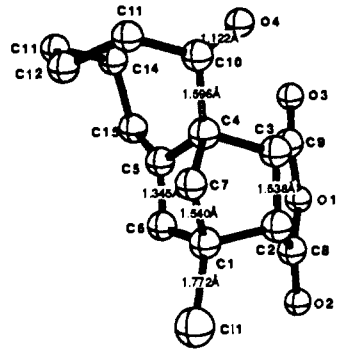


Figure 2. Molecular structure of **7b** from X-ray analysis, with selected bond distances and adopted atom numbering. Hydrogen atoms are omitted for clarity.

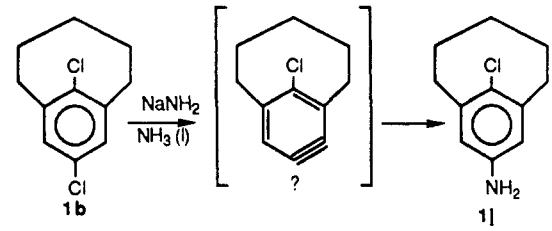
These reactions indicated that the carbonyl group of **5b** is conjugated with the cyclopentadiene system. Distinction between *linear* or *cross* conjugation was unambiguously achieved by an X-ray crystal structure determination of the Diels–Alder adduct **7b**, formed from **5b** and maleic anhydride. The molecular structure of **7b** is depicted in Figure 2.

The anhydride entity of **7b** is expectedly in the endo position. Furthermore, the chlorine atom is attached to one of the bridgehead carbon atoms of the norbornene skeleton. The second bridgehead carbon atom is connected to the carbonyl group which is attached to the pentamethylene chain. The other end of this chain is attached to the olefinic carbon atom at the same side of the norbornene skeleton. These structural data are consistent with the *linear* conjugation of the carbonyl group and confirm the structure of **5b** as drawn in Scheme V.

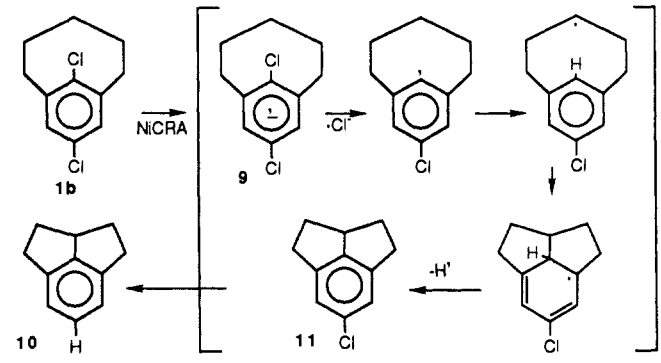
From the spectra of **5b**, no indication was found for the presence of the 6-hydroxyfulvene isomer of **5b**. This is in agreement with the observations of Hafner and co-workers, who found that both formyl- and acetylcyclopentadiene occur exclusively in the carbonylcyclopentadiene form.[12] Contrary to these simple acylcyclopentadienes,[12] which occur as mixtures of the three possible 1,5-H shift tautomers, **5b** was found to be present as the linearly conjugated tautomer exclusively.

As mentioned above, in the workup it was essential to first neutralize the reaction mixture before extraction. Under the basic conditions, **5b** is probably present as its conjugate base and as is difficult to extract from the aqueous layer. This was confirmed by dissolving **5b** in 1 M NaOH; the UV absorption maximum of

Scheme VI



Scheme VII



5b showed a bathochromic shift from pentane to 1 M sodium hydroxide as solvent ($\lambda_{max,pentane}$ = 302 nm, $\lambda_{max,NaOH}$ = 324 nm; formylcyclopentadiene:[13] $\lambda_{max,pH=6}$ = 294 nm, $\lambda_{max,pH=10}$ = 308 nm).

Analogous to the reaction of **1b**, treatment of **1a** with sodium hydroxide yielded **5a**. Its structure was confirmed by the strong analogy of its ^1H and ^{13}C NMR spectra with those of **5b** and by the presence of two olefinic protons. Also, treatment of **1a** with maleic anhydride yielded the Diels–Alder adduct **7a**, which possesses a tertiary bridgehead carbon atom as evidenced from its spectra.

Besides the above-mentioned alkoxide and hydroxide anions we also examined the reactivity of several other nucleophiles toward **1b**. When adding **1b** to a suspension of sodium amide in liquid ammonia and stirring for several hours we found after workup a derivative of **1b** in which one of the chlorines had been replaced by an amino group. On the basis of the ^{13}C NMR spectrum (Table I) and the ratio A:B (Table II), and by arguments analogous to those discussed for the alkoxy isomers, we conclude that the amino group is present at position 8 of the [5]metacyclophane (Scheme VI).

Both the thiophenoxide anion (NaSPh, DMSO) and the cyanide anion (KCN, 18-C-6, DMSO) did not react with **1b**; only starting material was found after workup.

Discussion

Several mechanisms are known by which a formal nucleophilic aromatic substitution can take place.[14] The most common one is the addition–elimination or S_NAr mechanism, which proceeds via a cyclohexadienylide or Meisenheimer complex; however, this mechanism normally requires the presence of strongly electron-withdrawing groups such as nitro or cyano. Second, there is the $S_{RN}Ar$ mechanism that is initiated by single electron transfer from the attacking nucleophile to the aromatic substrate; the resulting aromatic radical anion then extrudes the negatively charged leaving group and turns into a radical that combines with another nucleophile; the resulting new radical anion then transfers its electron to another aromatic molecule. In this way a radical chain mechanism is established. Third, in some cases and under drastic conditions, a direct one-stage substitution is possible.[15] Finally, the elimination–addition or aryne mechanism may occur when there is an ortho hydrogen.

(11) Yates, P. *Adv. Alicyclic. Chem. II* **1968**, 20, Hart, H., Karabatsos, G. J., Eds., Academic Press: New York.
(12) (a) Hafner, K.; Schulz, G.; Wagner, K. *Lieb. Ann. Chem.* **1964**, *678*, 39. (b) Hafner, K.; Kramer, H. E. A.; Musso, H.; Plos, G.; Schulz, G. *Chem. Ber.* **1964**, *97*, 2066.
(13) Kaplan, L.; Wendling, L. A.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1971**, *93*, 3919.
(14) Zoltewicz, J. A. *Top. Curr. Chem.* **1975**, *59*, 35.
(15) Zoltewicz, J. A.; Sale, A. A. *J. Org. Chem.* **1971**, *36*, 1455.

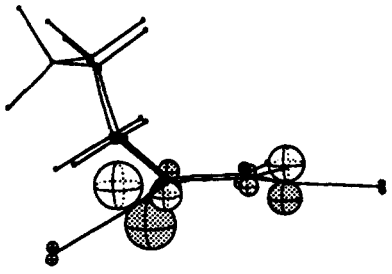


Figure 3. LUMO (21A', ϵ = −0.99 eV) of **1b** (side view).

The aryne mechanism is impossible for substitution at C11 as ortho hydrogens are missing. With some confidence, we can also exclude a $S_{RN}Ar$ mechanism for the alkoxide reactions on the following grounds. Single electron transfer to **1b** would lead to the radical anion intermediate **9** (Scheme VII). We have previously[4] prepared **9** from **1b** by an unambiguous route, i.e. by action of the complex reducing agent $Ni(OAc)_3/NaH/t$-AmOH which is known to reduce aromatic halides by single electron transfer.[16] In this fashion, **1b** was transformed, presumably via **11**, to the tricyclic **10** by transannular ring closure as depicted in Scheme VII.[4] Neither **10** nor **11** were detected as products in our nucleophilic substitutions.

A direct substitution of the chlorine atom of **1a** or **1b** is also unlikely. Not only are the reaction conditions rather mild (cf. the harsh conditions of ref 15), but also the difference in reactivity would be difficult to understand for this mechanism. It is, however, easily rationalized if a Meisenheimer complex is involved as an intermediate: the electron-withdrawing chlorine at C8 apparently stabilizes the negative charge in this intermediate.

The regiospecificity of the nucleophilic substitution observed in the case of **1b** shows a preference for attack on the chlorine atom at position 11 and is probably related to the special molecular structure of **1b**, which has been determined by X-ray analysis and reveals a strongly distorted, boat-shaped benzene ring.[3] While the aromatic ring bends down, substituents attached to the benzene ring bend upwards. When we compare C8 and C11, this effect is strongest at C11, resulting in a slight pyramidalization around C11; this effect could in part be responsible for the greater reactivity on this position. Undoubtedly, another important factor in determining regiospecificity will be the release of strain: the Meisenheimer complex formed by attack at C11 has no trans double bonds in the eight-membered ring, while attack at C8 would retain such "anti-Bredt" bonds (e.g. between C6 and C11). Furthermore, FMO interactions will be important, i.e. the LUMO of **1b** (from MNDO), depicted in Figure 3, possesses the correct symmetry (A') for attack on C8 or C11; it resembles a benzene Ψ_4^* MO and has an energy of −0.99 eV. The (degenerate) HOMO of the MeO anion has an energy of −2.45 eV. Hence, the difference between the $LUMO_{1b}$ and $HOMO_{MeO^-}$ is relatively small, so attack will be governed by covalent interactions. Furthermore, the AO coefficients on C11 are greater than those on C8; thus at C11 a more extended p-like orbital results leading to more effective overlap with the HOMO of the attacking nucleophile. Charge effects will not play a decisive role in the observed regiospecificity, because the charge on C8 of **1b** is approximately zero while that on C11 is positive but small (0.04 e).

As already pointed out, nucleophilic aromatic substitutions normally take place only with aromatic rings highly activated, either by the presence of strong electron-withdrawing substituents or by complexation with, for instance, $Cr(CO)_{13}$.[14] Substitution reactions of unactivated chlorobenzenes in dipolar aprotic solvents are known but require much higher temperatures than those described here.[17] In order to gain more insight into the factors that govern the unusual reactivity of the cyclophane, we performed a MNDO analysis of some simplified model systems. In the first place, the chloride anion was chosen as nucleophile to convert **1a** to the Meisenheimer complex **12** (Scheme VIII). Then, while retaining the geometry of **1a** and **12**, the pentamethylene bridge was removed and replaced by two hydrogen atoms; only the C–H distances were optimized. This yielded structures **13** and **14**. For comparison with the normal, unstrained situation, the same calculations were performed for chlorobenzene (**16**) and its Meisenheimer complex **17**. C_s symmetry was imposed throughout these calculations.

Scheme VIII. Structures Used for MNDO and HFS Calculations

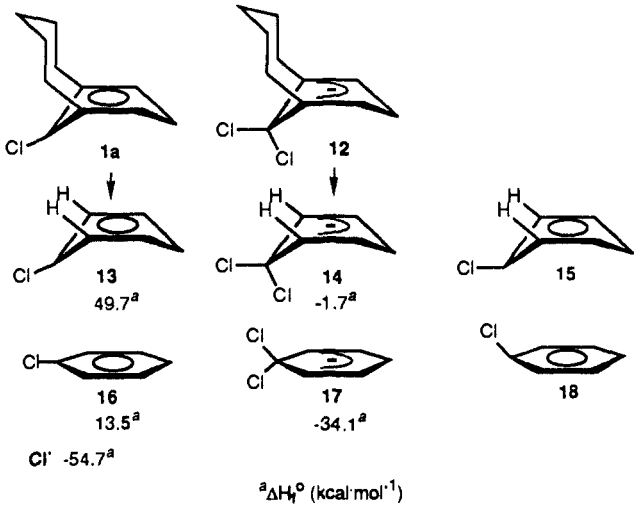


Table III. HFS MO Energies (eV) of **13** and **16**

MO	occupancy	ϵ_{13}	ϵ_{16}
13A'	0	1.19	1.16
12A'[a]	0	−1.20	−0.11
11A'[b]	2	−4.48	−4.88
10A'	2	−6.77	−6.91
9A'	2	−7.24	−7.73
9A''	0	3.20	3.04
8A''	0	−0.20	−0.19
7A''	2	−4.56	−5.39
6A''	2	−6.40	−6.35
5A''	2	−7.96	−7.76

[a](A'-)LUMO. [b](A'-)HOMO.

Next, we performed a single-point HFS[18] calculation on **13**, **14**, **16**, and **17** and, furthermore, on **15** and **18**, which are the frozen structures of **14** and **17** after removal of the chloride anion. A double-ζ basis set was used. We found that the small charge densities on C1 of **13** and **16** cannot explain the greater reactivity of **13** (note that C1 of **13** corresponds to C11 of **1a**). However, an important difference was found in the energies of the LUMO's of **13** and **16** (Table III). The LUMO 12A' of **13** lies 1.1 eV below that of **16**. By analyzing the composition of the MO's of both **14** and **17** in terms of the contributions of the MO's of **15** and **18** and the chloride anion, we could establish that the interaction between the 3p orbitals of the chloride anion and the LUMO 12A' of **15** and **18** plays the most important role in establishing the bond formation in **14** and **17**, respectively. Thus, due to the lower lying LUMO of **13**, acceptance of charge from the incoming nucleophile is more effective in **13** than in **16**. Moreover, the endothermicity of **13** → **14** (ΔH = 3.3 kcal·mol^{-1}) is lower than that of **16** → **17** (ΔH = 7.1 kcal·mol^{-1}). According to the Hammond principle this will also accelerate the nucleophilic attack on **1a**. Clearly, the highly strained character of **1** is responsible for the relative ease by which the nucleophilic substitutions take place.

(16) Caubière, P. *Angew. Chem.* **1983**, *95*, 597.
(17) Shaw, J. E.; Kunerth, D. C.; Swanson, S. B. *J. Org. Chem.* **1976**, *41*, 732.
(18) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52. (c) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4. (d) Baerends, E. J.; Ros, P. *Chem. Phys.* **1975**, *8*, 412. (e) Heijser, W.; Van Kessel, A. Th.; Baerends, E. J. *Chem. Phys.* **1976**, *16*, 371.

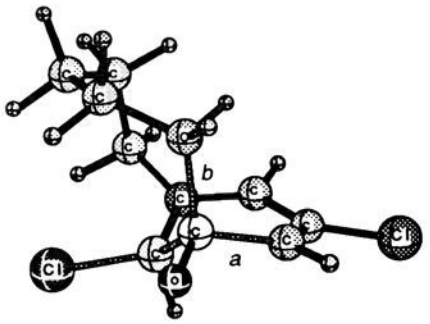
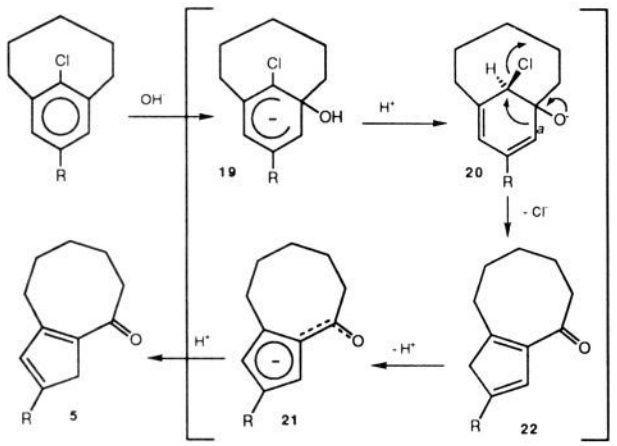


Figure 4. Geometry of **20** obtained by MNDO calculation. The gray tones on the different atoms parallel the charge, black corresponding to −0.66 and white to +0.32 electron charges.

Scheme IX[a]



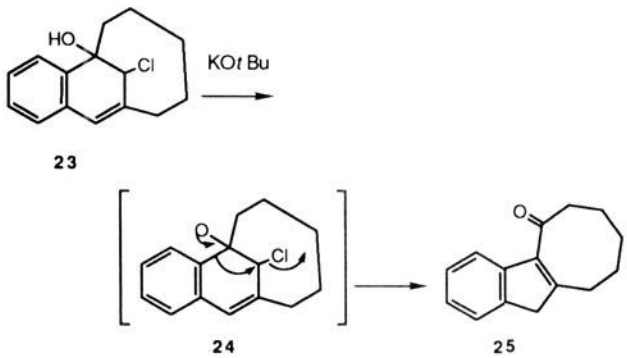
[a] **a**: R = H. **b**: R = Cl.

Attack of the hydroxide anion on both **1a** and **1b** yields a very different product compared to the common behavior of the alkoxide anions. In the hydroxide case a rearrangement of the [5]metacyclophane skeleton takes place, yielding a bicyclo[6.3.0]undecane derivative. We rationalize this by assuming that nucleophilic attack on one of the bridgehead carbons of **1** takes place yielding **19** (Scheme IX). In this process, the LUMO+1 of, for instance, **1b** must be involved, which lies approximately 0.55 eV above the LUMO and possesses A″ symmetry, resembling a benzene Ψ_5* MO. This attack is then followed by protonation at C11 (by another **19**) to give **20**. Then rearrangement takes place in which bond *a* of **20** extrudes the chlorine while the alkoxide oxygen becomes a carbonyl oxygen. Thus, the bicyclo[6.3.0] skeleton is realized. The (MNDO) structure of **20** is depicted in Figure 4. It is clear that bond *a* of **20** is situated anti periplanar to the C11–Cl bond. Therefore bond *a* will be favored for the extrusion of the chlorine anion over bond *b*. The resulting **22** is probably deprotonated under the basic reaction conditions; final quenching then yields **5** as the most stable isomer.

An analogous reaction and mechanism was described by Grice and Reese,[19] who treated **23**, the benzoannealed analogue of protonated **20**, with KO-*t*-Bu in DMSO and obtained **24** (Scheme X). Note that in their case, the carbonyl group stays by necessity *cross* conjugated with the benzocyclopentadiene ring system.

A striking difference between the reactions of **1a,b** with the alkoxide anions on the one hand and the hydroxide anion on the other is that the latter requires high temperature and reacts by attack on one of the bridgehead carbons, while the alkoxide anions react at lower temperature by attack on C11. It is conceivable that attack on one of the bridgehead carbons of **1a** or **1b** is a reaction common to all oxygen nucleophiles. In the case of the alkoxy anions, however, attack at one of the bridgeheads cannot

Scheme X



be followed by protonation. The basicity of the anion derived from **19** when OH is OR is probably insufficient to facilitate deprotonation of the solvent DMSO.[20] Thus, any further reaction along this path is blocked and the anion will revert to **1**, which can be converted via attack on C11 to the 11-alkoxy product. The lower reactivity of the hydroxide anion as evidenced by the higher reaction temperature is not fully understood at the moment.

Finally, attack of the amino anion on **1b** gives yet another outcome. In this case, substitution of the chlorine at C8 for an amino groupl occurs, indicating that another mechanism is operative. The most obvious one is the elimination–addition mechanism involving a benzyne intermediate,[23] which also occurs when chlorobenzenes are treated with sodamide in liquid ammonia. However, two questions remain. First, can the strained [5]-metacyclophane be converted to an even more strained benzyne derivative? This is not unlikely as even bromo-substituted cyclopropabenzenes can be converted by the amide anion to cyclopropabenzynes and trapped by furan;[24] the strain energy of cyclopropabenzene (68 kcal·mol^{-1}) is significantly higher than that of **1b** (48 kcal·mol^{-1}). Second, if a benzyne intermediate occurs, the reason for the observed regiospecificity of the amination is unclear. In *p*–dichlorobenzenes, the spectator chloro substituent directs the incoming amino substituent predominantly into the para position;[25] the methyl group of a *m*-chlorotoluene, on the other hand, yields both the *o*- and *m*-amino derivative.[26] In our case, both a *p*-chloro and *m*-methylene group are present, thus, besides the 8-amino[5]metacyclophane also the 7-amino derivative might be expected.

Several explanations seem possible, but they remain speculative at this stage. An experimental answer might be obtained by benzyne trapping (with furan or ND_3) or by submitting **1k**, the regioisomer of **1a**, to this reaction; such experiments are being undertaken.

The observation that thiophenolate and cyanide did not react when alkoxide and hydroxide do probably signals that hard and strongly basic nucleophiles[27] are required for this type of reaction; the soft anions are apparently insufficiently capable of forming non-resonance-stabilized Meisenheimer complexes such as the analogues of **12**. We consider this lack of reactivity as an additional argument in favor of the proposed mechanism; it is certainly not in line with a direct one-stage substitution mechanism.

Finally, we would like to briefly comment on the ratio of

(19) Grice, P.; Reese, C. B. *Tetrahedron Lett.* **1979**, 2563.

(20) Cyclohexadienyl anions can be prepared in liquid NH_3 by proton abstraction from 1,3-cyclohexadienes.[21] DMSO is only about 30 times more acidic than NH_3.[22]

(21) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.

(22) Lowry, T. H.; Schueller Ridchardson, K. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1978.

(23) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; McGraw-Hill: New York, 1968.

(24) Apeloig, Y.; Arad, D.; Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4932.

(25) Bunnet, J. F.; Jhong Kook Kim *J. Am. Chem. Soc.* **1973**, *95*, 2254.

(26) Roberts, J. D.; Wheaton Vaughan, C.; Carlsmith, L. A.; Semenow, D. A. *J. Am. Chem. Soc.* **1956**, *78*, 611.

(27) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

Table IV. Chemical Shifts and Coupling Constants of the Protons of Conformers A of 1[a]

proton(s)[c]	1a	1b[d]	1d	1e	1f	1g	1h	1j
			Chemical Shifts δ (ppm)[b]					
H(1.1)[e]	2.48	2.47	2.29	2.27	2.26	2.23	2.21	2.38
H(1.2)	3.69	3.67	3.30	3.34	3.27	3.30	3.34	3.59
H(2.1)	0.33	0.46	0.32	0.33	0.44	0.44	0.43	0.51
H(2.2)	1.94	1.99	1.85	1.86	1.91	1.88	1.89	1.93
H(3.1)	1.36	1.40	1.29	1.30	1.34	1.39	1.28	1.34
H(3.2)	2.07	2.03	2.04	2.07	2.10	2.06	2.02	2.09
H(7)/H(9)	6.77[f]	6.45[g]	6.70[h]	6.70[h]	6.63[g]	6.62[g]	6.63[g]	6.13[g]
H(8)	7.04[f]	*j*			*j*	*j*	*j*	*j*
subst[k]			3.87[g]	4.08[l]	3.85[g]	4.05[l]	4.30[m]	3.74[n]
				1.31[o]		1.30[o]	1.22[p]	
			Coupling Constants J(Hz)[q]					
(1.1)(1.2)	12.7	12.8	12.6	12.5	12.7	12.8	12.4	12.4
(1.1)(2.1)	3.3	3.2	3.2	3.2		3.6	3.3	3.7
(1.1)(2.2)	3.3	3.2	3.2	3.2	3.2	3.5	3.0	3.1
(1.2)(2.1)	12.7	12.7	12.6	12.5	11.0	12.8	12.4	12.7
(1.2)(2.2)	3.0	3.1	3.0	2.7	3.2	2.8	3.0	3.1
(2.1)(2.2)	14.7	14.7				15.3	14.0	15.0
(2.1)(3.1)[r]								
(2.1)(3.2)	10.9	10.7				≈10	≈10	11.0
(2.2)(3.1)	7.9	8.0		7.4	7.8	≈8	7.8	8.5
(2.2)(3.2)[r]								
(3.1)(3.2)	16.7	16.9	14.3	15.3	16.6	15.8	16.0	16.5

[a] Determined by ^{1}H NMR spectroscopy at 220 K. [b] All signals are multiplets unless stated otherwise. [c] For numbering see Figure 1. [d] Values taken from ref 1n. [e] Due to the C_s symmetry of 1 the values for the protons H(4.1), H(4.2), H(5.1), and H(5.2) are identical with those of H(2.1), H(2.2), H(1.1), and H(1.2), respectively. [f] Doublet, J(HH) = 7.0 Hz. [g] Singlet. [h] Very complex multiplet due to the superposition of the two AB_2 systems of conformers A and B. [i] Triplet, J(HH) = 7.0 Hz. [j] Not present. [k] Chemical shifts of the protons of the various substituents. [l] Quartet J(HH) = 7.1 Hz, 2 H. [m] Septet J(HH) = 6.1 Hz, 1 H. [n] Broad singlet. [o] Triplet J(HH) = 7.1 Hz, 3 H. [p] Doublet J(HH) = 6.1 Hz, 6 H. [q] Values not given could not be determined. [r] Too small to be resolved.

conformers A:B of the different isomers of **1**. From Table II, it follows that on changing the substituent on position 8 of **1** while keeping the substituent at position 11 constant, the conformer ratio does not change, or only to a small degree: compare **1′** with **1k** (no change), **1a** with **1b** (0.01 decrease in mole fraction of B), **1d** with **1f** (0.09 decrease in mole fraction of B), and **1e** with **1g** (0.05 decrease in mole fraction of B). Hence, as concluded before, the substituent on the 8 position is not important in determining the ratio A:B. The substituent at position 11, however, *does* play an important role. In the series **1′**, **1a**, and **1d** and in the analogous series **1k**, **1b**, and **1f**, an increasing amount of conformer B is found. Within the series of the alkoxy-substituted cyclophanes, the amount of conformer B decreases in the sequence OMe > OEt > O-*i*-Pr. Thus, cyclophanes having a "small" substituent (i.e. H in **1′**) or a "large" one (i.e. *t*-Bu in **1c**) at position 11 occur only in conformer A; those having "intermediate" substituents (i.e. Cl in **1b**, OR in **1f–h**) occur in both conformers A and B.

When we examine the distances between the various methylene protons and the substituent X present at position 11, strong nonbonded interactions (i.e. distances significantly shorter than the sum of the van der Waals radii[28]) exist between this substituent and the protons H(1.2), H(5.2), and H(3.2) in conformer A, or toward the protons H(1.2), H(5.2), H(2.2), and H(4.2) in conformer B. The sum $\Sigma[d(X,H) - (r(X) + r(H))]$ of these distances and the van der Waals radii for each interaction are only slightly less severe for conformer B compared to those of A (Figure 5). These steric interactions will influence the relative thermodynamic stability of both conformers.

By MNDO calculations the $\Delta\Delta H_f°$(A–B) of **1′**, **1b**, and **1f** were found to be −1.2, −0.4, and −0.3 kcal·mol^{-1}, respectively. For the equilibrium A–B of **1b**, the experimentally determined thermodynamic parameters are $\Delta\Delta H$(A–B) = 0 kcal·mol^{-1} and $\Delta\Delta S$(A–B) = −3.6 cal·mol^{-1}·K^{-1}.[1n] Thus, the ratio A:B is temperature independent and entropy controlled. For **1f**, the A:B ratio was found to be slightly temperature dependent: the experimental values were $\Delta\Delta H$(A–B) = 0.1 ± 0.1 kcal·mol^{-1} and $\Delta\Delta S$(A–B) = −0.3 ± 0.4 cal·mol^{-1}·K^{-1}. These values are not as accurate as those of **1b** because of the much smaller temperature range (220–242 K) examined.

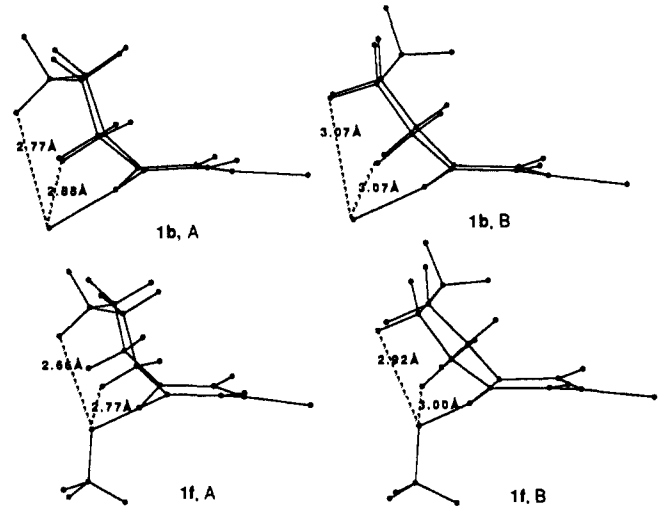


Figure 5. Nonbonded interactions between the methylene protons and the substituent at position 11 in **1b** and **1f**.

From Tables IV and V, it is evident that the coupling constants between the methylene protons of the bridge do not strongly depend on the substituents of **1**. Thus, on the basis of the Karplus relation,[29] the dihedral angles do not differ much and hence the geometries of the bridges are essentially the same for all substituted [5]metacyclophanes.

By line shape analysis of the coalescence of aromatic and methyl protons of **1f** the activation parameters were determined. These values ($\Delta H^‡$ = 10.6 kcal·mol^{-1}, $\Delta S^‡$ = −6.9 cal·mol^{-1}·K^{-1}) = −6.9 cal·mol^{-1}·K^{-1}) do not differ much from those previously determined for **1b** ($\Delta H^‡$ = 11.6 kcal·mol^{-1}, $\Delta S^‡$ = −5.5 cal·mol^{-1}·K^{-1}).[1n] This is in agreement with the earlier conclusion[1n] that the substituent at position 11 does not influence these activation parameters and hence the flipping of the pentamethylene bridge.

Conclusions

The [5]metacyclophanes **1a** and **1b** undergo, with relative ease, aromatic nucleophilic substitution reactions when treated with

(28) Testa, B. *Principles of Organic Stereochemistry*; M. Dekker: New York, 1979.

(29) Günther, H. *NMR Spektroskopie*; Thieme Verlag: Stuttgart, 1983.

Table V. Chemical Shifts and Coupling Constants of the Protons of Conformers B of **1**[a,b]

proton(s)[d]	1a	1b[e]	1d	1e	1f	1g	1h	1j
			Chemical Shifts δ (ppm)[c]					
H(1.1)[f]	1.83	1.56		1.64		1.63		
H(1.2)	3.50	3.18	3.19	3.20	3.14	3.18	3.20	3.14
H(2.1)	1.55	1.48				1.42		
H(2.2)	2.18	2.31				2.00	2.00	
H(3.1)	−1.20	−1.32	−1.27	−1.27	−1.06	−1.08	−1.10	−0.83
H(3.2)	1.00	0.65	0.97	0.96	1.00	1.00	1.00	
H(7)/H(9)	6.77[g]	6.45[h]	6.70[i]	6.70[i]	6.68[h]	6.66[h]	6.68[h]	6.12[h]
H(8)	7.04[j]	*k*			*k*	*k*	*k*	*k*
subst[l]			3.91[h]	4.07[m]	3.89[h]	4.05[m]	4.30[m]	3.74[o]
				1.31[p]		1.30[p]	1.22[q]	
			Coupling Constants J(Hz)					
(1.1)(1.2)		12.8	12.6		12.3	14.3	12.0	13.5
(1.2)(2.2)	9.7	10.3	3.0		8.8	9.6	9.1	9.8
(2.1)(3.1)	9.4	9.3		7.1	6.7	7.2	8.8	
(2.2)(3.2)	8.3	7.7	7.7			7.7	8.5	
(3.1)(3.2)	15.8	15.9	15.5	16.0	15.9	15.4	16.0	15.9

[a] Determined by ^{1}H NMR spectroscopy at 220 K. [b] Values not given could not be determined; multiplets were concealed under those of conformer A. [c] All signals are multiplets unless states otherwise. [d] For numbering see Figure 1. [e] Values taken from ref 1n. [f] Due to the C_s symmetry of **1** the values for the protons H(4.1), H(4.2), H(5.1), and H(5.2) are identical with those of H(2.1), H(2.2), H(1.1), and H(1.2), respectively. [g] Doublet, J(HH) = 7.0 Hz. [h] Singlet. [i] Very complex multiplet due to the superposition of the two AB_2 systems of conformers A and B. [j] Triplet, J(HH) = 7.0 Hz. [k] Not present. [l] Chemical shifts of the protons of the various substituents. [m] Quartet J(HH) = 7.1 Hz, 2 H. [n] Septet J(HH) = 6.1 Hz, 1 H. [o] Broad singlet. [p] Triplet J(HH) = 6.1 Hz, 3 H. [q] Doublet J(HH) = 7.1 Hz, 6 H.

the alkoxide anions MeO^-, EtO^-, and i-PrO^-. In both cases, the substitution occurs exclusively at position 11. By theoretical calculations, the high reactivity of **1a** compared to that of chlorobenzene can be explained satisfactorily by differnces in LUMO energies and in the endothermicity of the anion attack. The highly strained character of **1a** and the release of it on formation of the Meisenheimer adduct are responsible for this phenomenon.

The hydroxide anion behaves differently: attack on one of the bridgehead carbons takes place, followed by rearrangement and extrusion of the chlorine to yield **5**. The structure of **5b** was unambiguously solved by the X-ray crystal structure determination of the Diels–Alder adduct **7b** formed between **5b** and maleic anhydride. The amide anion reacts with **1b** to yield the 8-amino derivative **1j**. The proposed elimination–addition mechanism remains speculative. Further experiments are underway to clarify this aspect.

It thus seems that the [5]metacyclophanes, although aromatic on the basis of NMR and bond length criteria, exhibit a deviating reactivity toward nucleophiles. However, there is no common reactivity pattern toward nucleophiles; different nucleophiles give rise to different products.

A number of derivaties of **1** have been prepared in this and previous papers. The ratio of conformers A:B is not strongly influenced by the substituent present at position 8 but by substituents at position 11.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer at a frequency of 250.1 MHz. Chemical shifts are reported as δ (ppm) relative to TMS. The temperature was regulated with a Bruker VT-100 variable temperature control unit. Line shape analysis was performed on a Cyber computer with the DNMR program developed by G. Binsch.[30] ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer at a frequency of 62.9 MHz. Chemical shifts are reported as δ (ppm) relative to TMS. GCMS spectra were measured on a Hewlett-Packard 5970/5830 GC/MSD combination; where applicable, the expected isotope patterns were observed. High-resolution mass spectra were measured on a Varian CH-5 DF or a Finnigan MAT 90 spectrometer. UV spectra were recorded on a Beckman DU-70 spectrometer and IR spectra on a Perkin-Elmer 580B spectrometer. Pentane was distilled from NaH, Et_2O from $LiAlH_4$, and DMSO from CaH_2 and stored over mol sieves. Methanol, ethanol and 2-propanol were distilled from Mg/I_2 or CaO and stored over mol sieves. All reactions were performed under a nitrogen atmosphere.

MNDO calculations were performed with versions 1.24 (MOPAC)[31] and 4.1 (VAMP) on a Vax 11/785 computer. HFS calculations were performed with the HFS-LCAO program developed by the department of Theoretical Chemistry, Free University, Amsterdam, on a Cyber 750 or 990 computer.

The ^{1}H NMR spectra of conformers A and B of **1a**, **1b**, **1c–h**, and **1j**, measured at 220 K, are collected in Tables IV and V.

11-Chloro[5]metacyclophane (1a), Compound **2a**[32] (0.98 g, 3.9 mmol) was added to a solution of KO-*t*-Bu (1.1 g, 9.8 mmol) in dry DMSO (48 mL). The resulting mixture was stirred overnight at room temperature. The reaction mixture was then poured into water (100 mL) and extracted with pentane. After drying ($MgSO_4$) and concentration of the organic layer under reduced pressure the residue was purified by flash chromatography (Al_2O_3, pentane). Evaporation of the solvent yielded **1a** as a colorless oil (0.49 g, 2.7 mmol, 70%): ^{13}C NMR ($CDCl_3$, 325 K) δ 147.4 (s, C6/C10), 143.6 (s, C11), 127.3 (d, ^1J(CH) = 162 Hz, C8), 124.3 (d, ^1J(CH) = 165 Hz, C7/C9), 40.2 (t, ^1J(CH) = 126 Hz, C1/C5), 39.3 (t, ^1J(CH) = 131 Hz, C2/C4), 24.8 (t, ^1J(CH) = 127 Hz, C3); MS, m/z (rel intensity) 180 (**1a**$^{\cdot+}$, 37), 145 ([**1a**-Cl]$^+$, 100), 138 (44), 117 (48), 115 (74), 103 (74); HRMS calcd for $C_{11}H_{13}{}^{35}Cl$ 180.0706, found 180.0700.

8,11-Dichloro[5]metacyclophane (1b) was prepared according to the procedure described in ref 1n.

General Prodecure for the Reaction of Alkoxide and Hydroxide Anions with 1a or 1b. NaH (0.49 g, 60% dispersion in mineral oil, 12.3 mmol) was washed three times with dry pentane, Dry DMSO (10 mL) was added and the mixture was heated at 70 °C until all NaH had dissolved. After the mixture was cooled to room temperature the appropiate dry alkanol (MeOH (0.37 g), EtOH (0.53 g), or *i*-PrOH (0.70 g)) or water (0.21 g) was added and the mixture was stirred for another 15 min. An aliquot of this solution (4 mL, 4.9 mmol of RONa, 7-fold excess) was added within 5 min to a solution of **1a** or **1b** (**1a**, 0.13 g; **1b**, 0.15 g; 0.70 mmol) in DMSO (3 mL). In the case of the sodium alkoxides this mixture was stirred for three days for **1a** and 18 h for **1b**. In the case of the sodium hydroxide, the mixture was stirred at 70 °C for 2 days for **1a** and 5 h for **1b**. The mixture was then poured into cold water (10 mL) and extracted three times with pentane (50 mL). In the case of sodium hydroxide, the water layer was first neutralized with 5% acetic acid before extraction. After drying ($MgSO_4$) and concentration of the combined organic layers the residue was purified by flash chromatography (Al_2O_3, pentane).

11-Methoxy[5]metacyclophane (1d): colorless oil (0.11 g, 0.65 mmol, 93%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.72 (AB_2 system, (A) 6.74, (B) 6.69, J(AB) = 7.3 Hz, 3 H, H(7), H(8), and H(9)), 3.88 (s, 3 H, OCH_3), 3.32 (ddd, J = 13.3 Hz, J = 8.1 Hz, J = 5.3 Hz, 2 H, H(1.2)/H(5.2)), 2.22 (ddd, J = 13.3 Hz, J = 5.3 Hz, J = 5.3 Hz, 2 H, H(1.1)/H(5.1)), 1.96 (m, 2 H, H(2.2)/H(4.2)), 1.50–0.95 (bm, 4 H, H(2.1)/H(4.1), H(3.1), and H(3.2)); ^{13}C{^{1}H} NMR ($CDCl_3$, 296 K) δ 169.6 (C11), 136.6 (C6/C10), 124.9 (C9/C7), 122.4 (C8), 59.5 (OCH_3), 38.4 (C1/C5), 35.8 (C2/C4), 23.9 (C3); MS, m/z (rel intensity) 176 (**1d**$^{\cdot+}$, 100), 161 ([**1d**-Me]$^+$, 51), 145 ([**1d**-MeO]$^+$, 77), 133 (25), 117 (39), 115 (39), 105(48), 103(23); HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1210.

11-Ethoxy[5]metacyclophane (1e): colorless oil (0.10 g, 0.53 mmol, 75%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.71 (AB_2 system, (A) 6.74, (B) 6.68, J(AB) = 7.1 Hz, 3 H, H(7), H(8), and H(9)), 4.09 (q, J(HH) = 7.0 Hz, 2 H, OCH_2CH_3), 3.35 (ddd, J = 13.1 Hz, J = 8.7 Hz, J = 5.0 Hz, 2 H, H(1.2)/H(5.2)), 2.21 (ddd, J = 13.1 Hz, J = 5.1 Hz, J = 5.1 Hz, 2 H, H(1.1)/H(5.1)), 1.96 (m, 2 H, H(2.2)/H(4.2)), 1.60–0.80 (bm, 4 H, H(2.1)/H(4.1), H(3.1), and H(3.2)), 1.28 (t, J(HH) = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 296 K) δ 168.2 (s, C11), 136.7 (s, C6/C10), 124.5 (d, ^1J(CH) = 164 Hz, C7/C9), 122.6 (d, ^1J(CH) = 160 Hz, C8), 68.2 (t, ^1J(CH) = 144 Hz, OCH_2CH_3), 38.8 (t, ^1J(CH) = 126 Hz, C1/C5), 36.1 (t, ^1J(CH) = 130 Hz, C2/C4), 24.2 (t, ^1J(CH) = 124 Hz, C3), 16.0 (q, ^1J(CH) = 126 Hz, OCH_2CH_3); MS, m/z (rel intensity) 190 (**1e**$^{\cdot+}$, 71), 161 ([**1e**-Et]$^+$, 33), 145 ([**1e**-EtO]$^+$, 37), 133 (39), 118 (25), 105(40); HRMS calcd for $C_{12}H_{18}O$ 190.1358, found 190.1333.

8-Chloro-11-methoxy[5]metacyclophane (1f): colorless oil (88 mg, 0.42 mmol, 60%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.66 (s, 2 H, H(7)/H(9)), 3.86 (s, 3 H, OCH_3), 3.31 (ddd, J = 13.4 Hz, J = 8.7 Hz, J = 5.0 Hz, 2 H, H(1.2)/H(5.2)), 2.20 (ddd, J = 13.0 Hz, J = 5.0 Hz, J = 5.0 Hz, 2 H, H(1.1)/H(5.1)), 1.96 (m, 2 H, H(2.2)/H(4.2)), 1.50–0.90 (bm, 4

(30) Loomes, D. J.; Harris, R. K.; Anstey, P.; Smith, W. *The NMR Program Library*; Science Research Council, Daresbury Laboratory, Daresburey, 1979.

(31) Stewart, J. P. P. *QCPE* **1985**, *5*, 455.

(32) Jenneskens, L. W.; Turkenburg, L. A. M.; De Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 184.

H, H(2.1)/H(4.1), H(3.1) and H(3.2)); ^{13}C NMR ($CDCl_3$, 300 K) δ 168.9 (s, C11), 137.8 (s, C6/C10), 129.0 (s, C8), 123.9 (d, ^1J(CH) = 170 Hz, C7/C9), 59.8 (q, ^1J(CH) = 148 Hz, OCH_3), 38.6 (t, ^1J(CH) = 126 Hz, C1/C5), 36.0 (t, ^1J(CH) = 134 Hz, C2/C4), 24.1 (t, ^1J(CH) = 134 Hz, C3); MS, *m/z* (rel intensity) 210 (**1f**$^{\bullet+}$, 58), 179 ([**1f**-MeO]$^+$ 23), 175 ([**1f**-Cl]$^+$, 100), 145 (39); HRMS calcd for $C_{12}H_{15}O^{35}Cl$ 210.0811, found 210.0803, calcd for $C_{12}H_{15}O$ ([**1f**-Cl]$^+$) 175.1123, found 175.1120.

8-Chloro-11-ethoxy[5]metacyclophane (1g): colorless oil (141 mg, 0.63 mmol, 90%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.64 (s, 2 H, H(7)/H(9)), 4.05 (q, J = 7.1 Hz, 2 H, OCH_2CH_3), 3.32 (ddd, J = 13.4 Hz, J = 9.1 Hz, J = 4.7 Hz, 2 H, H(1.2)/H(5.2)), 2.19 (ddd, J = 13.1 Hz, J = 4.8 Hz, J = 4.8 Hz, 2 H, H(1.1)/H(5.1)), 1.97 (m, 2 H, H(2.2)/H(4.2)), 1.60–0.88 (bm, 4 H, H(2.1)/H(4.1), H(3.1), and H(3.2)), 1.33 (t, J = 7.1 Hz, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 300 K) δ 167.5 (s, C11), 138.8 (s, C6/C10), 127.0 (s, C8), 123.5 (d, ^1J(CH) = 166 Hz, C7/C9), 68.7 (tq, ^1J(CH) = 144 Hz, ^2J(CH) = 4.2 Hz, OCH_2CH_3), 39.0 (t, ^1J(CH) = 129 Hz, C1/C5), 36.3 (t, ^1J(CH) = 129 Hz, C2/C4), 24.3 (t, ^1J(CH) = 122 Hz, C3), 16.0 (q, ^1J(CH) = 127 Hz, OCH_2CH_3); MS, *m/z* (rel intensity) 224 (**1g**$^{\bullet+}$, 76), 195 ([**1g**-EtO]$^+$, 8), 189 ([**1g**-Cl]$^+$, 44), 161 (75), 145 (100); HRMS calcd for $C_{13}H_{17}O^{35}Cl$ 224.0968, found 224.0965.

8-Chloro-11-isopropoxy[5]metacyclophane (1h): colorless oil (92 mg, 0.39 mmol, 55%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.64 (s, 2 H, H(7)/H(9)), 4.28 (septet, J = 7.1 Hz, 1 H, $OCH(CH_3)_2$), 3.37 (ddd, J = 12.6 Hz, J = 10.0 Hz, J = 4.0 Hz, 2 H, H(1.2)/H(5.2)), 2.18 (ddd, J = 12.6 Hz, J = 4.3 Hz, J = 4.3 Hz, 2 H, H(1.1)/H(5.1)), 1.99 (m, 2 H, H(2.2)/H(4.2)), 1.22 (d, J = 7.1 Hz, 6 H, $OCH(CH_3)_2$), 1.60–0.80 (bm, 4 H, H(2.1)/H(4.1), H(3.1) and H(3.2)); ^{13}C NMR ($CDCl_3$, 313 K) δ 166.0 (s, C11), 141.1 (s, C6/C10), 127.9 (s, C8), 123.2 (d, ^1J(CH) = 166 Hz, C7/C9), 76.6 (d, ^1J(CH) = 144 Hz, $OCH(CH_3)_2$), 39.5 (t, ^1J(CH) = 127 Hz, C1/C5), 36.8 (t, ^1J(CH) = 131 Hz, C2/C4), 24.8 (t, ^1J(CH) = 122 Hz, C3), 14.0 (q, ^1J(CH) = 125 Hz, $OCH(CH_3)_2$); MS, *m/z* (rel intensity) 238 (**1h**$^{\bullet+}$, 21), 196 ([**1h**-C_3H_6]$^+$, 9), 161 (100), 91 (24); HRMS calcd for $C_{14}H_{19}O^{35}Cl$ 238.1124, found 238.1127.

8-Amino-11-chloro[5]metacyclophane (1j). Ammonium (20 mL) was condensed at −50 °C. At −35 °C Na (130 mg, 5.6 mmol) was added. after all Na had dissolved a catalytic amount of $Fe(NO_2)_3$ was added. To the resulting greyish suspension of $NaNH_2$ **1b** (172 mg, 0.70 mmol) was added, dissolved in a small amount of Et_2O(0.5 mL). After the mixture was stirred for 3 h, the ammonia was allowed to evaporate. The resulting solid residue was quenched with saturated aqueous NH_4Cl solution. The water layer was extracted with Et_2O/pentane (30:70, v/v). After drying ($MgSO_4$) and evaporation of the solvent, final purification was performed by preparative TLC (Al_2O_3, 1.5 mm, Et_2O/pentane (30:70, v/v) as eluent), which yielded **1j** as a colorless oil (75 mg, 55%). ^{13}C NMR ($CDCl_3$, 243 K, chemical shifts are those of the A conformer) δ 147.5 (s, C6/C10), 146.8 (s, C8), 133.4 (s, C11), 110.4 (d, ^1J(CH) = 159 Hz, C7/C9), 41.2 (t, ^1J(CH) = 127 Hz, C1/C5), 40.3 (t, ^1J(CH) = 132 Hz, C2/C4), 25.1 (t, ^1J(CH) = 122 Hz, C3); MS, *m/z* (rel intensity) 195 (**1j**$^{\bullet+}$, 80), 180 (20), 160 ([**1j**-Cl]$^+$, 50), 145 (51); HRMS calcd for $C_{11}H_{14}N^{35}Cl$ 195.0815, found 195.0796.

2-Oxobicyclo[6.3.0]undeca-1(8),9-diene (5a): bright yellow unstable oil (23 mg, 0.14 mmol, 20%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.71 (dt, ^3J(HH) = 5.2 Hz, ^3J(HH) = 1.3 Hz, 1 H, olefinic H), 6.44 (dt, ^3J(HH) = 5.2 Hz, ^5J(HH) = 0.9 Hz, 2 H, olefinic H), 3.45 (ddt, ^3J(HH) = 1.3 Hz, ^4J(HH) = 1.3 Hz, ^4J(HH) = 1.3 Hz, 2 H, bisallylic CH_2), 2.96 (tt, ^3J(HH) = 7.3 Hz, ^5J(HH) = 0.9 Hz, 2 H), 2.84 (t, ^3J(HH) = 7.3 Hz, 2 H), 1.73 (m, 4 H), 1.50 (m, 2 H); MS, *m/z* (rel intensity) 162 (**5a**$^{\bullet+}$, 16), 125 (14), 119 (50), 105 (47); HRMS calcd for $C_{11}H_{14}O$ 162.1044, found 162.1041.

10-Chloro-2-oxobicyclo[6.3.0]undeca-1(8),9-diene (5b): bright yellow oil (110 mg, 0.56 mmol, 80%); ^{1}H NMR ($CDCl_3$, 296 K) δ 6.26 (t, ^4J(HH) = 0.9 Hz, 1 H, olefinic H), 3.52 (td, ^5J(HH) = 1.3 Hz, ^4J(HH) = 0.9 Hz, 2 H, bisallylic CH_2), 2.85 (tt, ^3J(HH) = 7.1 Hz, ^5J(HH) = 1.2 Hz, 2 H), 2.75 (t, ^3J(HH) = 7.1 Hz, 2 H), 1.73 (m, 2 H), 1.65 (m, 2 H), 1.47 (m, 2 H); ^{13}C NMR ($CDCl_3$, 300 K) δ 196.2 (s, *C*=O), 154.4 (s), 142.7 (s), 141.3 (s), 134.3 (d, ^1J(CH) = 168.5 Hz, C9), 46.2 (td, ^1J(CH) = 131.7 Hz, ^3J(CH) = 6.9 Hz), 40.9 (t, ^1J(CH) = 129.8 Hz), 28.7 (t, ^1J(CH) = 128.9 Hz), 24.0 (t, ^1J(CH) = 128.0 Hz), 23.4 (t, ^1J(CH) = 130.4 Hz), 22.6 (t, ^1J(CH) = 126.0 Hz); MS, *m/z* (rel intensity) 196 (**5b**$^{\bullet+}$, 66), 168 ([**5b**-CO]$^+$, 33), 153 (88), 105 (88), 77(100); HRMS calcd for $C_{11}H_{13}O^{35}Cl$ 196.0655, found 196.0649; UV (*n*-pentane) $\lambda_{max}(\epsilon)$ = 302 nm (9050); UV (1 M NaOH) $\lambda_{max}(\epsilon)$ = 324 nm (15.200).

13-Oxa-2,12,14-trioxotetracyclo[8.5.1.0^{1,8}.0^{11,15}]hexadeca-8-ene (7a), Compound **5a** (10 mg, 0.06 mmol) and maleic acid anhydride (6 mg, 0.6 mmol) were dissolved in $CDCl_3$ (400 μL) and transferred to a NMR tube that was sealed under vacuum and heated at 70 °C for 3 h. ^{1}H NMR ($CDCl_3$, 296 K) δ 5.94 (bs, 1 H, olefinic H, H(9)), 4.20 (d, ^3J(HH) = 8.2 Hz, 1 H, H(15)), 3.65 (dd, ^3J(HH) = 8.2 Hz, ^3J(HH) = 4.5 Hz, 1 H, H(11)), 3.55 (m, 1 H, H(10)), 2.68–2.57 (m, 3 H), 2.47–2.16 (m, 5 H), 1.80–1.50 (m, 4 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K) δ 209.4, 170.9, 169.4, 151.6, 136.4, 71.5, 55.8, 48.3, 46.9, 45.7, 42.4, 29.0, 28.3, 24.2, 22.5.

10-Chloro-13-oxa-2,12,14-trioxotetracyclo[8.5.1.0^{1,8}0^{11,15}]hexadeca-8-ene (7b), Compound **5b** (70 mg, 0.36 mmol) and maleic acid anhydride (36 mg, 0.37 mmol) was dissolved in $CHCl_3$ (1.2 mL). This mixture was heated to 70 °C for 2 h. After cooling to room temperature and subsequent concentration under reduced pressure, a darkbrown colored oil resulted which was dissolved in boiling hexane/EtOH (3:1 v/v 20 mL) and treated with decolorzing carbon. After the yellow colored solution was cooled, **7b** crystallized as colorless needles that were collected by vacuum filtration (60 mg, 0.20 mmol, 55%): mp 169.0 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 296 K) δ 5.96 (bs, 1 H, olefinic H, H(9)), 4.07 (AB system, (A) 4.38 (B) 3.77, J(AB) = 8.4 Hz, 2 H, H(11)/H(15)), 2.68–2.50 (m, 3 H), 2.47–2.03 (m, 5 H), 1.95–1.54 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 K) δ 206.8 (s, *C*=O, C2), 167.8 (s, *C*=O, C14 or C12), 167.7 (s, *C*=O, C12 or C14), 151.3 (s, olefinic C, C8), 130.3 (d, ^1J(CH) = 177.9 Hz, olefinic C, C9), 69.9 (s, bridgehead C, C1 or C10), 67.9 (s, bridgehead C, C10 or C1), 63.0 (t, ^1J(CH) = 140.4 Hz, C16), 54.7 (dd, ^1J(CH) = 148.5 Hz, ^2J(CH) = 7.0 Hz, C11 or C15), 49.0 (dd, ^1J(CH) = 147.8 Hz, ^2J(CH) = 8.0 Hz, C15 or C11), 42.2 (t, ^1J(CH) = 125.5 Hz), 28.8 (t, ^1J(CH) = 128.0 Hz), 28.1 (t, ^1J(CH) = 128.7 Hz), 23.7 (t, ^1J(CH) = 125.6 Hz), 22.3 (t, ^1J(CH) = 126.5 Hz); MS (thermal retro-Diels–Alder reaction), the mass spectrum observed is that of **5b**; HRMS calcd for $C_{15}H_{15}O_4{}^{35}Cl$ 294.0659, found 294.0659; IR ($CHCl_3$) 1865, 1785, 1700, 1600 cm^{-1}. Anal. Calcd for $C_{15}H_{15}O_4{}^{35}Cl$: C, 61.10; H, 5.10. Found: C, 61.02; H, 5.22.

10-Chlorobicyclo[6.3.0]undeca-1,8,10-triene (8), To a solution of **5b** (80 mg, 0.41 mmol) in dry benzene (3 mL) was added at 0 °C a solution of DIBAH (0.56 mmol) in *n*-hexane (3 mL). After being stirred for 2 h the reaction mixture was quenched with MeOH. Water was added and the water layer extracted three times with pentane. After drying ($MgSO_4$) of the combined organic layers the solvent was removed under reduced pressure. Final purification was achieved by flash chromatography (Al_2O_3, pentane) which yielded **8** as an unstable yellow oil (58 mg, 0.32 mmol, 78%): ^{1}H NMR ($CDCl_3$, 296 K) δ 6.44 (td, ^3J(HH) = 8.7 Hz, ^4J(HH) = 1.2 Hz, 1 H, H(2)), 6.06 (d, ^4J(HH) = 1.2 Hz, 1 H, olefinic H), 6.01 (m, 1 H, olefinic H), 2.75 (td, ^3J(HH) = 8.7 Hz, ^4J(HH) = 0.9 Hz, 2 H), 2.65 (td, ^3J(HH) = 7.0 Hz, ^3J(HH) = 8.7 Hz, 2 H, H(3.1)/H(3.2)), 1.60 (m, 4 H), 1.41 (m, 2 H); MS, *m/z* (rel intensity) 180 (**8**$^{\bullet+}$, 100), 145 ([**8**-Cl]$^+$, 90), 115 (58), 103 (51); UV (*n*-pentane) λ_{max} (rel ϵ) = 271 nm (1.0), 281 (sh, 0.6), 373 (0.02).

10-Chloro-2-methylbicyclo[6.3.0]undeca-1,8,10-triene (8′). To a solution of **5b** (80 mg, 0.41 mmol) in dry Et_2O (2 mL) was added, at 0 °C, a solution of MeLi (1.3 mL of a 1.6 M solution in hexane, diluted with 2.7 mL of Et_2O). The resulting mixture was stirred for 2 h at °C and 1 h at 20 °C. After the reaction mixture was quenched with water (10 mL) and extraction with Et_2O (3 × 5 mL), the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure yielding **8′** as a bright yellow oil (65 mg, 0.33 mmol, 80%): ^{1}H NMR ($CDCl_3$, 296 K) δ 6.39 (d, ^4J(HH) = 2.0 Hz, 1 H, olefinic H), 5.98 (d, ^4J(HH) = 2.0 Hz, 1 H, olefinic H), 2.78 (td, ^3J(HH) = 7.2 Hz, ^4J(HH) = 0.9 Hz, 2 H, allylic H's), 2.69 (t, ^3J(HH) = 6.8 Hz, 2 H, allylic H's), 2.18 (s, 3 H, CH_3), 1.60 (m, 4 H), 1.36 (m, 2 H); ^{13}C NMR ($CDCl_3$, 270 K) δ 141.7 (s), 136.7 (s), 132.9 (s), 131.3 (s), 128.1 (dq, ^1J(CH) = 170 Hz, ^4J(CH) = 7 Hz, C11), 115.8 (dd, ^1J(CH) = 173 Hz, ^4J(CH) = 5 Hz, C9), 33.4 (t, ^1J(CH) = 126.0 Hz), 29.5 (t, ^1J(CH) = 126 Hz), 26.9 (t, ^1J(CH) = 127 Hz), 24.4 (q, ^1J(CH) = 127 Hz, CH_3), 24.3 (t, ^1J(CH) = 128 Hz), 21.7 (t, ^1J(CH) = 123 Hz); MS, *m/z* (rel intensity) 194 (**8′**$^{\bullet+}$, 100), 179 ([**8′**-Me]$^+$, 38), 159 ([**8′**-Cl]$^+$, 57), 115 (81); HRMS calcd for $C_{12}H_{15}{}^{35}Cl$ 194.0862, found 194.0829, calcd for $C_{12}H_{15}$ ([**8′**-Cl]$^+$) 159.1174, found 159.1193; UV (*n*-pentane) λ_{max} (ϵ) = 274 nm (17.100), 281 (16.600), 292 (sh, 9700), 360 (490).

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands foundation for Scientific Research (NWO). Figures 1–5 were created by the use of the Molecule program developed by Dr. N. J. R. van Eikema Hommes. The services and facilities of the Dutch CAOS/CAMM center are gratefully acknowledged.

Supplementary Material Available: X-ray crystallographic data of compound **7b** including tables of fractional atomic coordinates, bond distances, and bond angles for non-hydrogen and hydrogen atoms (5 pages). Ordering information is given on any current masthead page.