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combined aqueous layers were extracted with 100 mL of ether and then acidified with concentrated HCl and extracted with dichloromethane (3 × 75 mL). The combined organic extracts were washed with 100 mL of brine and dried ($MgSO_4$). Removal of solvent gave 4.38 g (59.6%) of **11** as a yellow solid. Recrystallization from ether yielded material with mp 136.5–137.5 °C (lit.[11] mp 136–137 °C).

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[3 + 2]- and [5 + 2]-Cycloadditions of the Cyclohepta-2,4-dienyl Cation

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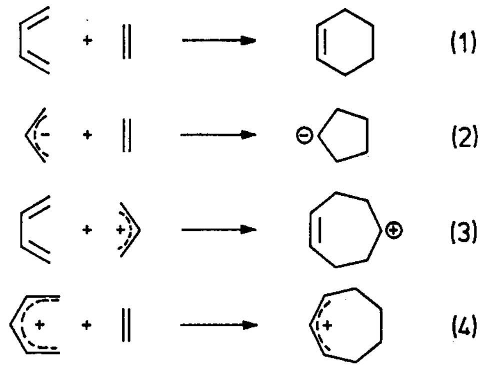
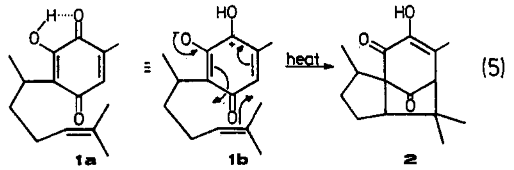
The cyclohepta-2,4-dienyl cation (**9**), generated in situ from 5-chloro-1,3-cycloheptadiene (**10**) and zinc chloride, undergoes a [3 + 2]-cycloaddition with 1-phenylpropyne (**11**) to give the bicyclo[4.2.1]nona-2,7-dien-9-yl cation (**18**), which is stereoselectively trapped by a chloride ion. The corresponding reaction of **10** with 1-methoxy-2-methylpropene (**13**) yields the aldehyde **14** and the bicyclo[3.2.2]nonenes **15a–c** and **16**, which are rationalized by a stepwise [5 + 2]-cycloaddition process. Configurations and conformations of the bicyclo[3.2.2]nonenes are investigated by NMR spectroscopy.

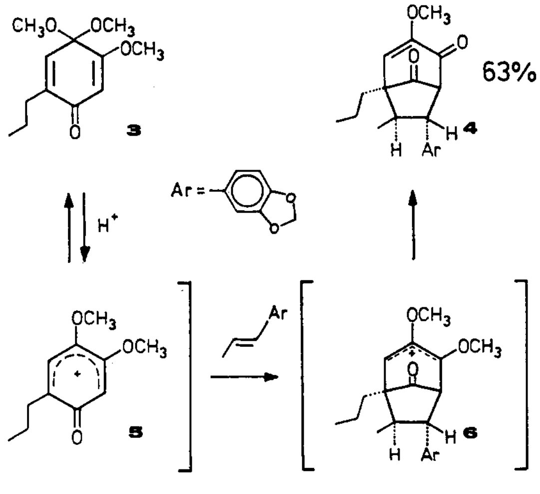
The thermally allowed $[_\pi 4_s + _\pi 2_s]$-cycloaddition reactions[1] can be realized in four different ways (eq 1–4).



Synthetic as well as mechanistic aspects of Diels–Alder reactions (eq 1)[2,3] allyl anion,[4] azallyl anion,[4] and 1,3-dipolar cycloadditions[3,5] (eq 2) have been studied in great detail. Allyl cation cycloadditions with 1,3-dienes (eq 3) offer a synthetic access to seven-membered ring compounds, but the mechanism of these reactions is still questionable.[6] As shown in the following discussion, examples of eq 4 are rare.

Woodward and Hoffmann[1] cited the perezon pipitzole rearrangement (eq 5)[7a] as the only representative of reaction 4. Deuterium labeling studies provided arguments for the concerted nature of this reaction[7b] and proved that the rearrangement proceeds stepwise in the presence of a Lewis acid.[7c] Intermolecular analogues of this transformation, e.g., the reaction sequence **3** → **4**,[8d] have been carried out with 2-alkoxybenzoquinone derivatives[8] and 3-hydroxy-4-pyrones.[9,10]





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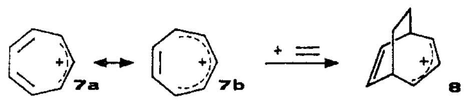
Like 1 and 5, tropylium ions 7 do not incorporate an isolated dienyl cation fragment, and their cycloaddition reactions with alkenes[11] may alternatively be attributed to class (1) or (4). As an extension of our work on allyl[12] and allenyl cation[13] cycloadditions, we have been searching for a clear-cut example of eq 4. [5 + 2]-cycloadditions of

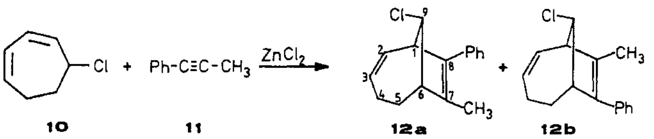


type (4) require U-shaped 2,4-dienyl cations. Acyclic systems, which are forced into U-shape by substituents, are expected to undergo electrocyclic pentadienyl → cyclopentenyl cation ring-closure reactions[1,14] rapidly. Since the same process may take place in cyclic systems with ring size ≥ 8, only six- and seven-membered rings remain. The 2,4-cycloheptadienyl cation 9 was finally selected for our studies, as six-membered ring cations that do not possess special structural features like 1 and 5 will aromatize under ordinary reaction conditions.

9

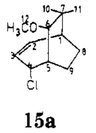
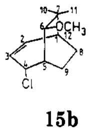
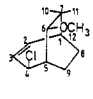
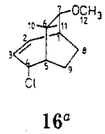
Previously, we have reported that the cycloheptadienyl cation 9 reacts with isobutene and silyl enol ethers with formation of a single new σ-bond, i.e., normal additions, not cycloadditions, take place.[15] We have now obtained bicyclic products when the cycloheptadienyl chloride 10 was reacted with 1-phenylpropyne (11) or the enol ether 13 in the presence of $ZnCl_2$ at −78 °C.

Reaction Products and Structural Assignments.[16] The zinc chloride/ether-catalyzed reaction of 10 with 11 gave 42% of the 1:1 products 12a and 12b (≈10:1). Independent of the way in which the reactants were combined, the yield of **12a,b** was around 40% while the remainder were high molecular weight compounds.



The bicyclo[4.2.1]nonadiene structure of **12a** was derived from ^1H NMR homonuclear spin-decoupling experiments, which showed that the triplet splitting (J = 6.7 Hz) of the proton at the chloro-substituted carbon is due to couplings with both bridgehead hydrogens. The relative positions of methyl and phenyl were determined by NOE experiments: Irradiation at δ 3.45 (1-H) enhanced the intensity of vinyl and phenyl resonances, while irradiation at the second bridgehead position (δ 2.85) yielded a NOE enhancement of the methyl and of a methylene signal. The stereochemistry at C-9 was deduced from a NOE enhancement of 9-H (in addition to 1-H and CH_3) during irradiation of the phenyl resonance.

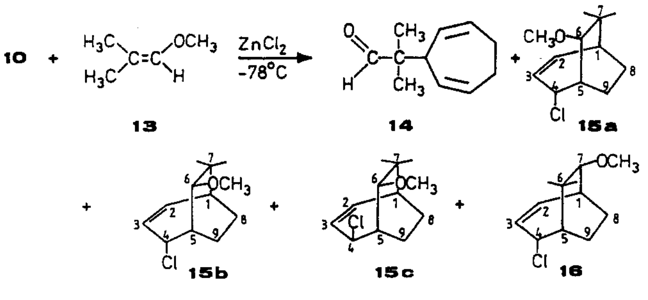
Table I. ^{13}C NMR Chemical Shifts and ^{13}C–^{13}C Coupling Constants (±0.25 Hz, in Parentheses) of the Bicyclo[3.2.2]nonenes 15a–c and 16

	 **15a**	 **15b**	 **15c**	 **16**[a]
1	43.81 (39.8, 32.0)	41.05 (39.6, 38.0, 31.1)	41.22 (39.5, 38.3, 32.2)	35.13 (38.8, 35.8, 31.2)
2	134.50 (39.9)	138.16 (39.6)	136.94 (39.6)	134.26 (38.4)
3	129.95 (43.6)	128.19 (43.9)	129.44 (43.3)	130.66 (42.3)
4	63.77 (43.6, 34.2)	65.23 (44.1, 33.9)	66.61 (43.5, 33.0)	66.00 (43.4, 34.4)
5	41.71 (34.7, 34.0)	42.20 (35.2, 34.3)	43.59 (37.7, 32.8, 31.7)	48.53 (33.7, 32.5)
6	86.89 (37.6, 34.7)	86.26 (38.5, 35.3)	82.33 (38.0)	36.80 (36.1, 35.1, 33.9)
7	39.71 (37.6, 35.7, 32.0)	38.28 (38.8, 38.2, 37.1)	40.62 (38.3, 36.7)	87.52 (36.4)
8	23.62 (34.4, 32.0)	25.96 (33.4, 31.0)	25.93 (33.2, 32.3)	21.26
9	19.68 (34.4)	15.78 (34.5, 33.3)	19.64 (33.2, 31.5)	17.70 (31.7)
10	23.62 (35.8)	30.90 36.7)	29.95 (36.6)	30.30
11	30.99 (35.6)	23.22 (37.1)	22.88 (36.3)	25.12
12	58.57	58.29	57.58	58.16

[a] Accuracy of J for this compound ±0.5 Hz.

The minor component **12b** was detected by a set of ^{13}C NMR resonances closely similar to those of **12a**. As expected for the exchange of phenyl and methyl, 1-H was shifted upfield (−0.27 ppm) and 6-H was shifted downfield (+0.37 ppm) relative to **12a**.

When the enol ether 13 was added to a mixture of 10 and $ZnCl_2/Et_2O$ in dichloromethane, 37% of the bicyclic compounds **15a–c** and 16 were obtained in addition to 40% of the aldehyde 14, which has previously been prepared from 10 and 2-methyl-1-siloxypropene.[15b]



The similarity of the ^{13}C NMR chemical shifts of **15a–c** and 16 (Table I) indicates that all of these compounds incorporate the same bicyclic framework. The connectivity of the carbon atoms, i.e., the constitution of **15a–c**, was

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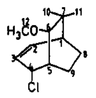
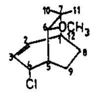
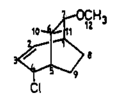
Table II. ^{1}H NMR Chemical Shifts ($CDCl_3$) and H–H Coupling Constants (Hz) of the Bicyclo[3.2.2]nonenes 15a–c and 16

	 **15a**	 **15b**	 **15c**	 **16**
2-H	5.86 $J_{2,3} = 10.8$ $J_{2,1} = 8.9$ $J_{2,4} = 1.8$	6.02 $J_{2,3} = 10.6$ $J_{2,1} = 9.5$ $J_{2,4} = 1.1$	5.93 $J_{2,3} = 11.0$ $J_{2,1} = 9.3$ $J_{2,4} = 1.8$	5.93 $J_{2,3} = 10.8$ $J_{2,1} = 9.3$ $J_{2,4} = 1.6$
3-H	5.61 $J_{3,2} = 10.8$ $J_{3,4} = 2.8$ $J_{3,5} = 1.9$ $J_{3,1} = 0.6$	5.57 $J_{3,2} = 10.6$ $J_{3,4} = 4.4$ $J_{3,5} = 1.5$	5.49 $J_{3,2} = 11.0$ $J_{3,4} = 2.6$ $J_{3,5} = 1.9$	5.59 $J_{3,2} = 10.8$ $J_{3,4} = 2.9$ $J_{3,5} = 1.6$
4-H	5.12 mc $J_{4,5} \approx 3$	4.84 $J_{4,5} = 5.5$ $J_{4,3} = 4.4$ $J_{4,2} = 1.1$	4.73 $J_{4,3} = 2.7$ $J_{4,5} = 2.7$ $J_{4,2} = 1.8$	5.14 $J_{4,5} = 4.5$ $J_{4,3} = 2.9$ $J_{4,2} = 1.6$
6-H	3.18 $J_{6,5} = 5.1$	2.91 $J_{6,5} = 0.7$ $J_{6,9} = 1.9$	3.34 $J_{6,5} = 0.8$ $J_{6,9} = 1.5$	2.93 (7-H) $J_{7,1} = 1.4$ $J_{7,8} = 1.4$
5-H	2.55 mc 1.64–1.87	2.33 mc 1.71–1.95	2.28 mc 1.44–1.50	2.32 (1-H) mc 1.57–1.86 (5-H)
8,9-H	2.17–2.34	2.08–2.19	1.80–2.03	1.99–2.09
10-H	0.91	1.02	1.00	1.08
11-H	1.13	1.05	0.96	1.05
OCH_3	3.39	3.35	3.31	3.26

derived from the ^{13}C–^{13}C coupling constants (Table I), which were obtained by one-dimensional INADEQUATE spectroscopy. Because of the similarity of the C-1–C-7 and the C-5–C-6 coupling constants in **15c**, the orientation of the 6,7-ethano bridge in this compound has been ascertained by two-dimensional INADEQUATE spectroscopy.

The isolated quantity of **16** was too small to obtain the ^{13}C–^{13}C coupling constants with high precision. Therefore, the constitution of this isomer was certified by a two-dimensional $\delta\delta$ (^{1}H) correlated spectrum (COSY). Since one bridgehead hydrogen (1-H) is coupled to the vinylic 2-H and to C*H*OCH_3 (7-H), the orientation of the 6,7-ethano bridge must be opposite as in **15a–c**.

The configurations of 15a–c and 16 were assigned on the basis of two-dimensional nuclear Overhauser effect spectroscopy (NOESY). Figure 1 shows a NOE between the C*H*Cl (4-H) and the C*H*OCH_3 (6-H) protons in **15b**. Since a NOE is only possible, if 4-H and 6-H point toward each other, the relative configurations of both C-4 and C-6 can thus be attributed. None of the other compounds showed a NOE between these protons.

In **15c**, one CH_3 group (δ 0.96) shows a NOE with protons of the C_2H_4 bridge, and the other CH_3 group (δ 1.00) shows a NOE with 6-H. These observations imply the OCH_3 group being on the side of the C_2H_4 bridge. The position of Cl is derived from a NOE between C*H*Cl and protons of the C_2H_4 bridge. Similar arguments allowed the stereochemical assignments of **15a** and **16**.

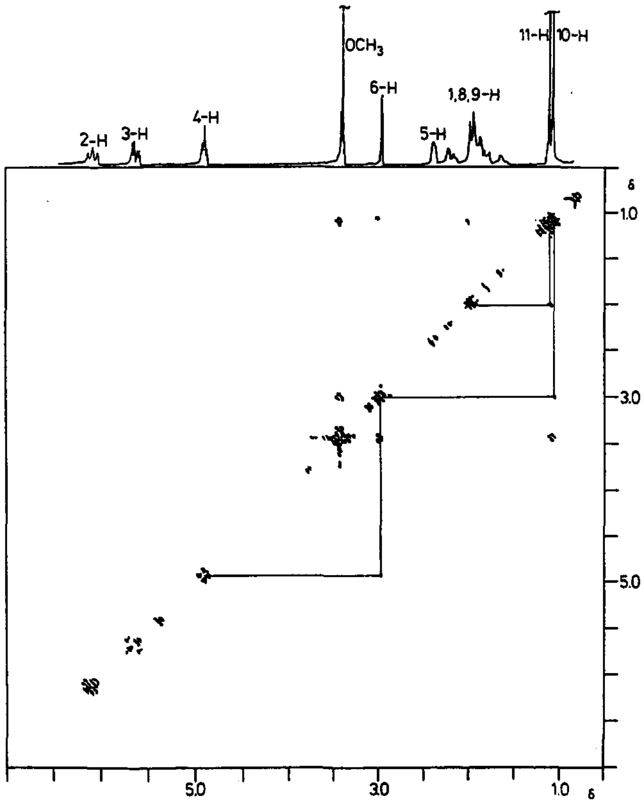


Figure 1. 200-MHz NOESY spectrum of **15b** in $CDCl_3$.

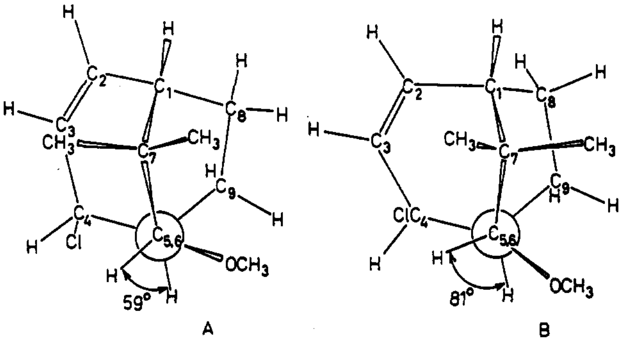


Figure 2. Calculated[17] conformations A and B of the bicyclo[3.2.2]nonene **15b**.

Conformations. Like the ^{13}C NMR chemical shifts, the ^{1}H NMR chemical shifts of corresponding nuclei are closely similar (Table II). There are considerable differences of corresponding H–H coupling constants, however, which indicate unlike dihedral angles in the different isomers. The analysis is complicated by the fact that the bicyclononenes **15** and **16** may exist in two different conformations A and B, depicted for compound **15b** (Figure 2).

The energy differences of the various conformers, which have been calculated by a force-field method (MMPMI[17]),

Table III. Comparison of Calculated[a] Dihedral Angles of Compounds 15a–c and 16 with the Corresponding H–H Coupling Constants

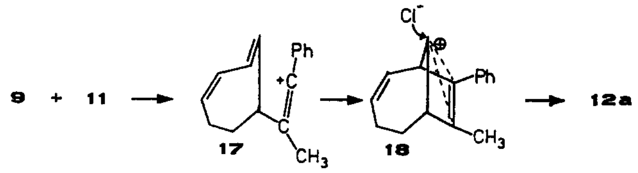
	15a(A)	**15a**(B)	**15b**(A)	**15b**(B)	**15c**(A)	**15c**(B)	**16**(A)	**16**(B)
$\Delta H_f°$, kcal/mol	−58.51	−58.78	−58.01	−58.47	−58.25	−58.73	−57.13	−56.91
θ(H-3–4-H), deg	70.5	51.4	70.1	51.5	51.5	67.9	46.4	63.8
$J_{3,4}$, Hz	2.8			4.4		2.6		≈2.9
θ(H-4–5-H), deg	71.9	54.5	70.2	53.9	52.5	66.7	50.0	65.9
$J_{4,5}$, Hz	≈3			5.5		2.7		4.5
θ(H-5–6-H),[b] deg	58.8	40.5	59.0	80.8	59.2	83.4	56.4	79.1
$J_{5,6}$, Hz	5.1			0.7		0.8		1.4

[a] MMPMI: ref 17. [b] For 16: θ(H-1–7-H) and $J_{1,7}$.

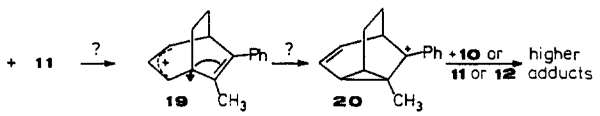
are very small (Table III), and the preferred conformations cannot be derived from the calculated ΔH_f° values. The 5,6-coupling constants of **15b**,**c** and **16**, however, allow us to assign these compounds to conformation B since the J values of approximately 1 Hz are in accord with a dihedral angle of $\approx 80^\circ$ (B). Larger $J_{5,6}$ values would be expected for the dihedral angles of 56–59° (conformation A) on the basis of the Karplus equation.[18]

The conformation of **15a** cannot be assigned on the basis of $J_{5,6}$ as the observed value of ≈ 5 Hz fits the calculated dihedral angles of both conformers (Table III). The coupling constants $J_{3,4} = 2.8$ Hz and $J_{4,5} \approx 3$ Hz, however, are better consistent with dihedral angles of 71° and 72° (A) than with angles of 51° and 55° (conformation B). Therefore, **15a** appears to be the only isomer that prefers conformation A. This conclusion is in accord with the finding that $J_{3,4}$ and $J_{4,5}$ are considerably greater in **15b** than in **15a**, though the configuration of C-4 is identical in both cases.

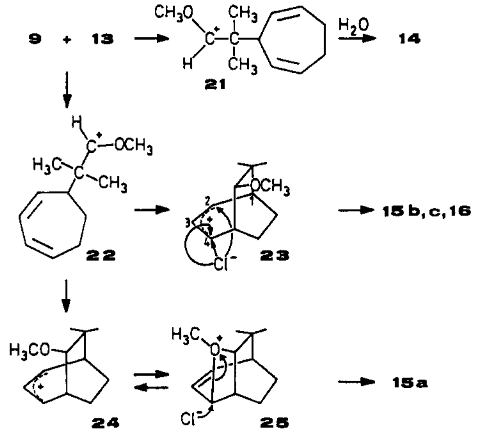
Discussion. Bicyclononadiene **12a**, the major product of the reaction of **10** with **11**, is formed via [3 + 2]-cycloaddition of the cycloheptadienyl cation **9** with 1-phenylpropyne (**11**). Probably, this cycloaddition proceeds stepwise, i.e., phenylpropyne **11** attacks position 1 of the cycloheptadienyl cation **9** to yield vinyl cation **17** as the intermediate. Successive cyclization generates the bridged cation **18**, which reacts stereoselectively at the backside with Cl⁻[19] to form the secondary chloride **12a**. The minor isomer **12b** can be rationalized by initial attack of **11** at C-3 of the cycloheptadienyl cation **9**. Analogous [3 + 2]-cycloaddition reactions of allyl cations with phenylpropyne (**11**) have previously been reported by Miller and Moore.[20]



Products arising from [5 + 2]-cycloaddition of **9** with **11** have not been isolated, possibly because the eventually formed cycloadduct **19** would cyclize to yield the highly stabilized cation **20**. According to previous studies,[21] **20** is expected not to be intercepted by Cl⁻ under these reaction conditions but to react with another π-system (e.g., **10**, **11**, **12**), thus giving rise to the higher boiling products.[21c]



As described above, monocyclic and bicyclic products are formed in almost equal yield by the reaction of **10** with **13**. If the enol ether **13** attacks C-3 of the dienylic cation **9**, the methoxycarbenium ion **21** is produced, which hydrolyzes to give the aldehyde **14**. Attack of the enol ether at C-1 of the cycloheptadienyl cation **9** yields cation **22**, which can cyclize to the stereoisomeric cations **23** and **24**. The formation of **15b** *and* **15c** indicates that Cl⁻ can approach to C-4 of the allyl cation **23** from top and bottom. Topside attack at C-2 of **23** is obviously shielded by one of the geminal methyl groups since only one stereoisomer **16** has been detected. The formation of oxonium ion **25** from **24** and selective backside attack at C-4 may be responsible for the formation of **15a** as the only isomer with the methoxy group pointing toward the propeno bridge.



Since **22** has not been trapped by external nucleophiles, the formation of **23** and **24** *via* concerted [5 + 2]-cycloaddition cannot be excluded. When the cycloheptadienyl cation **9** was reacted with isobutene[15a] or silyl enol ethers,[15b] products derived from 1- and 3-attack were obtained, i.e., the activation energies of 1- and 3-attack are usually of similar magnitude. It is unlikely, therefore, that in this case a concerted cycloaddition mechanism is alone responsible for the formation of the bicyclic products. If the concerted [5 + 2]-cycloaddition mechanism had a significant preference over the stepwise process, **14** would not be formed along with **15** and **16**. We, therefore, suggest **23** and **24** to be formed via a stepwise process, which allows us to treat all presently known dienyl cation–alkene reactions on the basis of a single mechanistic concept.

Experimental Section

General. NMR spectra were recorded on a Varian XL 200 spectrometer. Mass spectra were recorded on a VG 70–250 spectrometer.

The 1D-INADEQUATE spectra were measured in 0.4–0.8 M $CDCl_3$ solutions by using the pulse sequence 90°–τ–180°–τ–90°–Δ–90°–FID(t_2)[22] with $\tau = 6.67 \times 10^{-3}$ s and $t_2 = 10$ s. For a spectral width of 6230 Hz a digital resolution of 0.2 Hz was obtained with 32000 data points. The 2D-INADEQUATE spectrum of **15c** was recorded at 298 K in a 0.7 M $CDCl_3$ solution in the presence of $Cr(acac)_3$ by using the pulse sequence 90°–τ–180°–τ–90°–t_1/2–135°–FID(t_2)[23] with $t_2 = 2.84$ s (based on the maximal value of $t_1 = 0.75$ s) and $\tau = 6.75 \times 10^{-3}$ s. Spectral width was 6230 Hz. Two hundred fifty-six FIDs on 2K data points were taken, and 288 scans were accumulated for each FID resulting in a total acquisition time of 62 h. After a Gaussian multiplication in both dimensions, the FID was transformed. The measured DBQs were in good agreement with the calculated ones.

The COSY spectra were measured by using the pulse sequence 90°–t_1–90°–Δ–90°–FID(t_2) with double quantum filtering.[24] Two hundred fifty-six FIDs on 512 data points were recorded, and each FID was obtained from 32 scans. The FIDs were multiplied with a pseudo Gaussian function and zero filled in F_1. The FID was then transformed and symmetrized. The spectral width for **15a**,**b**

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and 16 was $F_1 = F_2 = 1300$ Hz, and $F_1 = F_2 = 1208.5$ Hz for **15c**. With a recycle delay $t_2 = 4.5$ s and $\Delta = 1 \times 10^{-5}$ s the acquisition time was 10 h in each case. Phase cycling for quadrature detection in both dimensions was used.

The NOESY spectra were recorded by using the pulse sequence $90°–t_1–90°–\tau_m–90°$–FID(t_2) with $\tau_m = \tau_m + t_1\kappa$.[25] The mixing times were $\tau_m = 2.7$ s (**15a**), 2.5 s (**15b**), 3.8 s (**15c**), and 1.85 s (**16**), and κ was 0.15. The values of the other parameters were equivalent to those used in the measurements of the COSY spectra.

5-Chloro-1,3-cycloheptadiene (**10**) was prepared from cycloheptatriene and HCl as described previously.[15b] The sample used in the following reactions was contaminated by some 6-chloro-1,3-cycloheptadiene, which is inert under these conditions.[15b] Zinc chloride/ether was prepared according to ref 26.

5-Chloro-1,3-cycloheptadiene (10) and 1-Phenylpropyne (11). A solution of **11** (2.32 g, 20.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise (1.5 h) to a cooled solution (−78 °C) of **10** (2.06 g, 16.0 mmol) and $ZnCl_2$ (3.22 g)/Et_2O (2.7 mL) in 35 mL of CH_2Cl_2. After stirring at −78 °C for 4.5 h, the solution was washed with 25% aqueous NH_4Cl solution and dried over $CaCl_2$, and the solvent was evaporated. Distillation gave a forerun of unreacted **11** and 1.65 g (42%) of **12a** and **12b** (≈10:1 estimated from the NMR signals of the bridgehead protons) with bp 100–105 °C (bath) (0.1 mbar) and 2.10 g of nonvolatile residue.

(1*R,9*S**)-9-Chloro-7-methyl-8-phenylbicyclo[4.2.1]nona-2,7-diene (12a)**: ^{1}H NMR ($CDCl_3$) δ 1.79–1.91 (m, 1 H, 5-H), 1.93 (mc, 3 H, CH_3), 2.03–2.32 (m, 3 H, 4-H_2, 5-H), 2.85 (br t, J = 6.7 Hz, 1 H, 6-H), 3.45 (br t, J = 6.7 Hz, 1 H, 1-H), 4.65 (br t, J = 6.7 Hz, 1 H, 9-H), 5.65–5.77 (m, 1 H, 2-H), 5.86–5.98 (m, 1 H, 3-H), 7.31 (mc, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.50 (q, CH_3), 25.21, 26.79 (2 t, C-4,5), 52.62, 52.99 (2 d, C-1,6), 62.44 (d, C-9), 126.74 (d, C-para), 127.89, 128.14 (2d, C-ortho, meta), 128.20, 133.33 (2 d, C-2,3), 136.48, 136.75, 136.89 (3 s, C-7,8, C-ipso). Anal. Calcd for $C_{16}H_{17}Cl$ (244.8): C, 78.51; H, 7.00. Found: C, 78.37; H, 7.08.

9-Chloro-8-methyl-7-phenylbicyclo[4.2.1]nona-2,7-diene (12b) is assumed to be the minor component of the mixture because of ^{1}H NMR absorptions at δ 3.12–3.27 (m, 1,6-H) and 4.70 (br t, J = 6.7 Hz, 9-H). The relation of these protons was ascertained by spin-decoupling experiments. ^{13}C NMR ($CDCl_3$) δ 15.01 (q, CH_3), 25.45, 27.14 (2 t, C-4,5), 51.55, 54.60 (2 d, C-1,6), 62.52 (d, C-9), 126.89 (d, C-para), 128.00, 128.31 (2d, C-ortho, meta), 127.34, 133.93 (2 d, C-2,3), 133.26, 135.76, 136.79 (3 s, C-7,8, C-ipso).

5-Chloro-1,3-cycloheptadiene (10) and 1-Methoxy-2-methylpropene (13). A solution of **13** (4.30 g, 50.0 mmol) in 30 mL of CH_2Cl_2 was added dropwise (0.5 h) to a rapidly stirred solution of **10** (5.14 g, 40.0 mmol) and $ZnCl_2$ (5.04 g)/Et_2O (4.20 mL) in 60 mL of CH_2Cl_2 (−78 °C). After 1 h the reaction mixture was washed with 50 mL of 25% aqueous NH_4Cl solution and dried with $CaCl_2$. The solvent was evaporated, and the yellow residue was distilled to give 1.29 g of **10** (bp 20–30 °C (bath) (0.4 mbar)), 5.09 g of the 1:1 products **14–16**, and 1.27 g of a nonvolatile residue. Separation of 1.00 g of the 1:1 product mixture by MPLC (silica gel, 15–25 μm, hexane:ether = 98.5:1.5) yielded 153 mg of (1*S**,4*R**,6*S**)-4-chloro-6-methoxy-7,7-dimethylbicyclo[3.2.2]non-2-ene (**15a**), 81 mg of (1*S**,4*R**,6*R**)-4-chloro-6-methoxy-7,7-dimethylbicyclo[3.2.2]non-2-ene (**15b**), 189 mg of (1*S**,4*S**,6*R**)-4-chloro-6-methoxy-7,7-dimethylbicyclo[3.2.2]non-2-ene (**15c**), 54 mg of (1*S**,4*R**,7*S**)-4-chloro-7-methoxy-6,6-dimethylbicyclo[3.2.2]non-2-ene (**16**), and 393 mg of 2-(2,6-cycloheptadienyl)-2-methylpropanal (**14**) (77% total yield with respect to reacted **10**).

NMR data: Tables I and II. Mass spectrum (70 eV) of **15c**: m/z (rel intensity) 216, 214 (0.5%, 1.9%, M^+), 147 (3), 135 (2), 121 (3), 105 (4), 97 (12), 93 (15), 91 (11), 86 (100). Anal. Calcd for $C_{12}H_{19}ClO$ (214.7): C, 67.12; H, 8.92. Found for **15a**: C, 67.56; H, 9.31. Found for **15b**: C, 67.89; H, 8.97. Found for **15c**: C, 67.02; H, 8.78. Spectroscopic data of **14**: see ref 15b.

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Photocycloaddition of 1,4-Dioxene to 3-Methylcyclohex-2-en-1-one: Conformational Analysis, X-ray Crystal Structures, and Acid-Catalyzed Rearrangement of the Photoadducts

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Photochemical cycloaddition of 1,4-dioxene to 3-methylcyclohex-2-en-1-one leads to a mixture of four 11-methyl-1,4-dioxatricyclo[$6.4.0.0^{6,11}$]dodecan-7-one isomers **3–6**. Their structures have been established by X-ray diffraction and ^{13}C NMR, and their conformational properties have been studied by force field calculations. They only differ by the stereochemistry of the cyclobutane–dioxane junction, which is found to have a pronounced influence upon the conformation of the molecules. The four-membered rings are strongly distorted in all cases. These cyclobutane photoadducts undergo an unusual acid-catalyzed rearrangement, affording compounds **19–21**. The structures of two of them, **19** and **20**, have been established by X-ray diffraction. The formation of these rearranged products can be rationalized in terms of a common cationic intermediate **23** stabilized by oxygens.

The photocycloaddition of cyclic α,β-unsaturated ketones to alkenes has been extensively studied. It has become an important tool in the arsenal of the synthetic organic chemist, leading to versatile intermediates that can be subsequently used in a number of ways. For example, the cyclobutane intermediates smoothly undergo an acid-catalyzed rearrangement, providing useful precursors of many natural products.[1]