well, with cooling, immediately before placed back in the NMR probe.

The sample used to obtain the spectrum in Figure 5 was made in a similar manner (1.00 mmol of t-Bu^{6}Li, 0.25 mmol of diethyl ether, diluted with cyclopentane to 1.00 mL) except it was degassed and sealed under vacuum. The sample was then held at room temperature for over a week. The solution remained clear and free of precipitate, in contrast to samples with higher oxygen to lithium ratios, which contained white precipitate upon reaction.

NMR Parameters and Conditions. All NMR spectra were obtained on a Varian VXR-300 at 75 and 44 MHz for ^{13}C and ^{6}Li, respectively. Typical conditions for ^{13}C NMR were 18° flip angle, 2.857-s repetition rate, 17 500-Hz spectral width, 32K transform, 128-1024 transients, Waltz proton decoupling. All chemical shifts were set relative to TMS by setting the resonance for protonated cyclopentane to 25.8 ppm.

Typical conditions for ^{6}Li spectra were one transient, 90° flip angle, 300-Hz spectral width, and 32K transform. Spectra were run with gated proton decoupling, such that there was proton decoupling but no NOE. All ^{6}Li chemical shifts are relative to (t-Bu^{6}Li)$_4$ at 0.00 ppm.

The temperature within the NMR probe was determined from the difference in the ^{1}H chemical shifts of methanol peaks by using the algorithm supplied by the NMR manufacturer. Decoupling power was kept to a minimum to avoid heating of the sample.

Kinetic Measurements. The change in percent dimer as a function of time was determined from integration of the ^{6}Li NMR spectra. Only single transient spectra with no NOE were used for quantitative measurements. The initial rate of disappearance of dimer was estimated from the concentration of dimer vs time curve at the beginning of the reaction. Rates were determined from only the first 10% of the reaction, or less, to avoid problems with competing reactions such as reaction of the dimer with mixed t-BuLi/LiOEt aggregates. Rates were only measured for samples with sufficient excess of ethyl ether (O:Li $\geq$ 4) to assure rapid formation of the coordinated dimer.

Hydrolysis and GC-MS of Samples. Several of the samples used for NMR analysis were also analyzed by GC-MS. In those cases, the NMR tube was opened and a saturated solution of NH_4Cl was added. Mass spectra of the organic portion was obtained with a Hewlett-Packard 5970A GC-MS and data station.

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Registry No. (t-Bu^{6}Li)$_4$, 36833-94-0; [t-Bu^{6}Li·2OEt$_2$]$_2$, 114719-00-5; OEt$_2$, 60-29-7; t-Bu^{6}Li, 103258-93-1.

Homoaromatic Delocalization in the Transition State for Norcaradiene Formation

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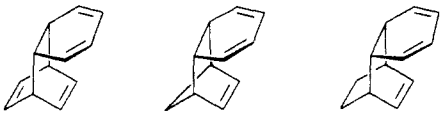
Abstract: The kinetics for the extrusion of benzene from norcaradiene adducts **11** and **12** have been measured. The high **11**/**12** rate ratio, 8.9×10^3, was shown to be due to homoaromatic interactions in the cycloreversion transition state emanating from **11**. This conclusion was reached after studying the benzene extrusion kinetics for several model compounds, including **20**. The syntheses of the requisite compounds are fully described.

For some time we have been studying the relationship between structure and reactivity for [4 + 2] cycloreversions involving the extrusion of benzene. We have shown that, in the case of **1** and its higher condensed analogues, the rate of cycloreversion is a linear function of the developing aromatic resonance energy.[1] We have used this finding as a strong argument for concert in these cycloreversions.

As illustrated by the benzene adducts **2**[2] and **3**,[3] strain energy effects appear to have a large effect on the rate of cycloreversion. At 164 °C, the more strained **2** reacts 1.9×10^5 faster than **3**.



1 **2** **3**

We now report a very large difference in the cycloreversion reactivities of diastereomers **11** and **12** and further experiments aimed at differentiating between steric (strain) and electronic effects in these reactions.

The synthesis of **11** and **12** proceeded from homobarrelene, **4**. Diels-Alder reaction of **4** with dimethoxytetrachlorocyclopentadiene at 100 °C gave adducts **5a** and **6a** in a 5:2 ratio. The endo,endo configurations of **5a** and **6a** were demonstrated via their photocyclizations to the caged derivatives **7a** and **8a**. The mixture of **5a** and **6a** was dechlorinated with Na/NH_3, following which ketals **5b** and **6b** were separated and purified by crystallization and chromatography. Ketones **9** and **10**, obtained via hydrolysis of **5b** and **6b** in 80% acetic acid, were converted to **11** and **12** via flash pyrolysis.

As detailed in the Experimental Section, the distinction between **5a** and **6a** was made on the basis of the upfield NMR shift experienced by the cyclopropyl methylene of **5a**, compared to that of **6a**. The two stereoisomers required vastly different temperatures for cycloreversion. Thus while **11** yielded benzene at 65 °C, the same process for **12** required 165 °C. The kinetic parameters for the cycloreversion of **11** between 77 and 95 °C were measured by monitoring the concentration of evolved cycloheptatriene (at 303 nm). The first-order rate constants (see Table I) were sub-

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[‡] Department of Chemistry, Iowa State University.

(1) Bertsch, A.; Grimme, W.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 377.
(2) Rye, A. R.; Wege, D. *Aust. J. Chem.* **1974**, *27*, 1943.
(3) Grimme, W.; Reinhardt, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 617.

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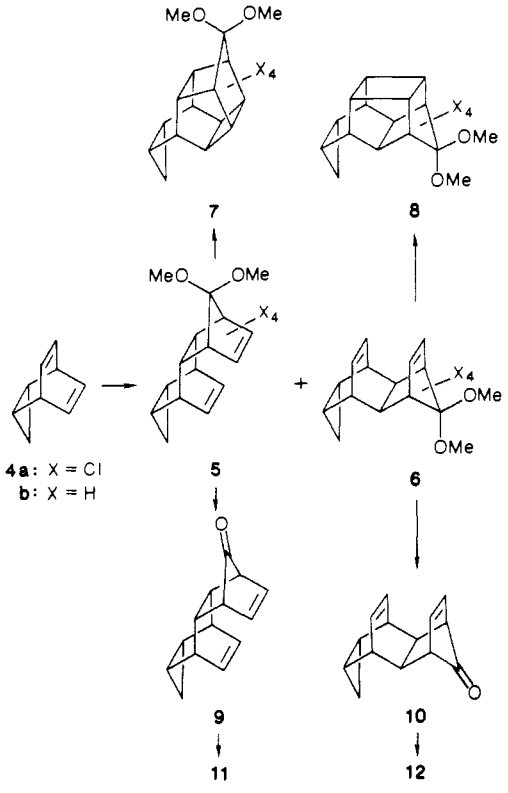
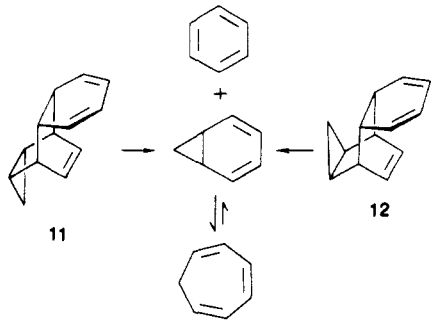


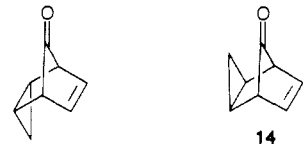
jected to a linear regression analysis to produce the following Arrhenius expression:

$$\log k_{11} = (12.88 \pm 0.65) - (27\,800 \pm 1000)/2.303RT$$



The rate constant for the cycloreversion of **12** was found by NMR in $C_2D_2Cl_4$ at 164.5 °C to be $(1.00 \pm 0.01) \times 10^{-5}$ s^{-1}, which is very similar to that for the "parent" compound, **3** ($k_3 = 5.81 \times 10^{-5}$ s^{-1}). From the observed Arrhenius parameters for **11**, we calculate that $k_{11}/k_{12} = 8.9 \times 10^3$ at 164.5 °C, which corresponds to $\Delta\Delta G^{\ddagger} = 7.9$ kcal/mol. This difference is not thermodynamic in origin, since MMPM1 calculations indicate that the thermally more stable **12** is actually 1.2 kcal/mol less stable than **11**. Clearly the kinetic effect has its origin in the relative stabilities of the cycloreversion transition states emanating from **11** and **12**.

The differential stability pattern found for **11** and **12** is reminiscent of the isomeric homonorbornadienones **13** and **14**.[4] In that case, the rate constant ratio for decarbonylation is $k_{13}/k_{14} = 1 \times 10^5$. The higher reactivity of the anti isomer, **13**, was explained by invoking partial opening of the three-membered ring in the decarbonylation transition state. And the overlap of the Walsh orbitals of the cyclopropane ring with the σ orbitals of the breaking bonds to the carbonyl group is only possible when the cyclopropane ring lies anti, as in **13**.



In the case of our benzene adducts, **11** and **12**, two arguments may be made in opposition to the above explanation:

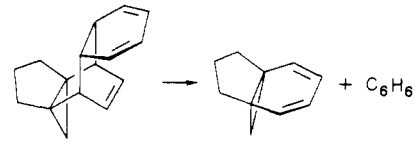
1. On the basis of what is known about the norcaradiene-cycloheptatriene equilibrium,[5] *complete* opening of the three-membered ring would provide no more than about 4 kcal/mol of energy. Thus the ca. 8 kcal/mol energy difference between the two cycloreversion transition states cannot be accounted for by solely a *partial* ring opening.

2. The benzene adduct **11** has the same anti,endo configuration as other Diels-Alder adducts of norcaradiene.[6] In those cases, it is thought that the adducts come from reaction of a dienophile with norcaradiene, which itself is a "reactive intermediate" in equilibrium with cycloheptatriene. Thus if norcaradiene is the ultimate reactant with, for example, maleic anhydride, then the principle of microscopic reversibility would lead one to expect that norcaradiene is the primary product in the reverse Diels-Alder reaction of **11**. A partially opened ring in the cycloreversion transition state is inconsistent with this reasoning.

In order to test whether the high reactivity of **11** was due to (partial) ring opening, we synthesized the anti-endo benzene adduct (**20**) of a fixed norcaradiene (**21**).[7] The synthesis of **20**, as well as that of several additional formal benzene adducts of cyclohexadiene, began with the Diels-Alder reaction between the requisite cyclohexadiene (**15**) and *p*-benzoquinone. Adduct **16a** was reduced to **17a** with Zn/HOAc; the corresponding bis(tosylhydrazone) was converted to **19a** (≡**20**) with *n*-BuLi (Scheme I).[8]

Thermal extrusion of benzene from **20** proceeded about as easily as from unbridged **11**. Therefore, the kinetics were easily followed by monitoring the production of **21** via UV spectroscopy (314 nm). In the range from 85 to 95 °C, the first-order rate constants (Table I) gave the following Arrhenius expression:

$$\log k_{20} = (13.68 \pm 0.32) - (29\,100 \pm 500)/2.303RT$$



Thus, despite the formation of a product with an *intact* cyclopropane ring (**21**), **20** cycloreverts at essentially the same rate as **11**.

There remained the possibility, however, that although the decomposition rates of **11** and **20** were the same, the causes of this similar behavior might be different. In particular, the three-carbon bridge of **20** may sterically interact with the cyclohexadiene ring, thereby facilitating the benzene extrusion to a degree fortuitously the same as the "partial opening" of the cyclopropane ring of **11**.

We thus sought a model compound which would reveal the steric (possibly acceleration) effect of a *syn*-trimethylene bridge; the syn-endo benzene adduct (**19b**) of *cis*-8,9-dihydroindan (**15b** ≡ **27**) seemed like a good choice. Unfortunately, we were thwarted in that Diels-Alder reaction of **15b** proceeded only from the convex

(4) (a) Tanida, H.; Tsuji, T.; Irie, T. *J. Am. Chem. Soc.* **1967**, *89*, 1953. (b) Halton, B.; Battiste, M. A.; Rehberg, R.; Deyrup, C. L.; Brennan, M. E. *J. Am. Chem. Soc.* **1967**, *89*, 5964; **1970**, *92*, 4450. (c) Clarke, S. C.; Johnson, B. L. *Tetrahedron Lett.* **1967**, 617. (d) Birney, D. M.; Berson, J. A. *Tetrahedron* **1986**, *42*, 1561.

(5) (a) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385. (b) Warner, P. M.; Lu, S.-L. *J. Am. Chem. Soc.* **1980**, *102*, 331.

(6) (a) Atasoy, B.; Balci, M.; Büyükgüngör, O. *Tetrahedron Lett.* **1987**, *28*, 555. (b) Adam, W.; Balci, M.; Pietrzak, B. *J. Am. Chem. Soc.* **1979**, *101*, 6285. (c) Tsuji, T.; Teratake, S.; Tanida, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2033.

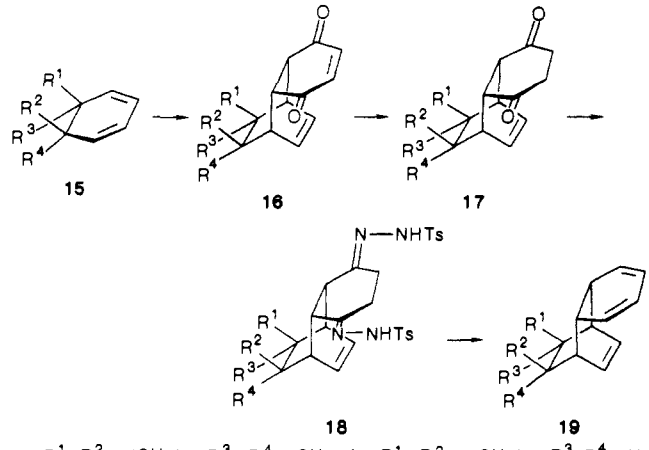
(7) Vogel, E.; Wiedemann, W.; Roth, H. D.; Eimer, J.; Günther, H. *Justus Liebigs Ann. Chem.* **1972**, *759*, 1.

(8) (a) Shapiro, R. H. *Org. React. (N.Y.)* **1978**, *23*, 405. (b) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579.

Table I. Kinetic Parameters for Cycloreversions

compd	η_{obsd}, nm	T, °C	$k \times 10^5$, s^{-1}	log A	E_a, kcal/mol	$\Delta G^{\ddagger}_{164}$, kcal/mol
3		164.5	5.81 ± 0.12			34.31
11	303	77.5	3.77 ± 0.03			
		80.1	4.55 ± 0.01			
		84.8	7.93 ± 0.02	12.88	27.80	27.96
		89.2	13.69 ± 0.02	±0.65	±1.03	
		95.2	24.18 ± 0.05			
12		164.5	1.00 ± 0.01			35.84
20	314	85.0	8.99 ± 0.02	13.68	29.06	27.61
		90.1	15.91 ± 0.04	±0.32	±0.54	
		95.0	27.24 ± 0.05			
25		164.5	0.71 ± 0.01			36.14
26		164.5	14.35 ± 0.33			33.53
28		101.5	0.89 ± 0.01			
		110.5	2.68 ± 0.05	15.71	35.65	30.16
		124.8	11.03 ± 0.90	±0.65	±1.19	
		164.1	110.3 ± 3.70			

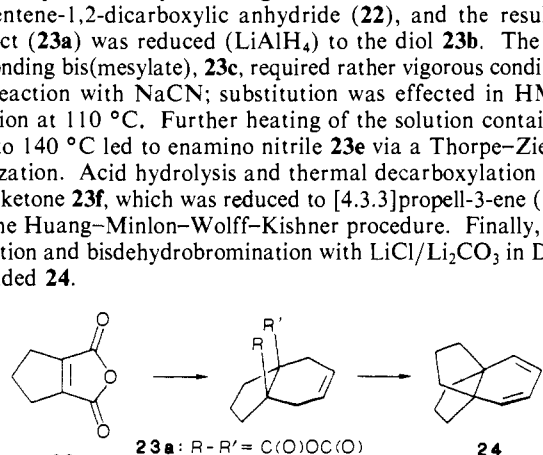
Scheme I



a: R^1-R^2 = $(CH_2)_3$, R^3-R^4 = CH_2; **b**: R^1-R^2 = $(CH_2)_3$, R^3, R^4 = H; **c**: R^1-R^2 = $(CH_2)_3$, R^3-R^4 = $(CH_2)_3$; **d**: R^1, R^2 = H, R^3-R^4 = $(CH_2)_3$; **e**: R^1, R^2 = H; R^3-R^4 = C_5H_8

face to give (via **16d**–**18d**) **19d**. We then turned to **19c** ≡ **25**, the benzene adduct of [4.3.3]propella-2,4-diene (**24**), prepared according to Scheme I.

The previously unknown **24** was prepared according to general methods pioneered by Ginsburg.[9] Butadiene was added to cyclopentene-1,2-dicarboxylic anhydride (**22**), and the resulting adduct (**23a**) was reduced ($LiAlH_4$) to the diol **23b**. The corresponding bis(mesylate), **23c**, required rather vigorous conditions for reaction with NaCN; substitution was effected in HMPT solution at 110 °C. Further heating of the solution containing **23d** to 140 °C led to enamino nitrile **23e** via a Thorpe–Ziegler cyclization. Acid hydrolysis and thermal decarboxylation then gave ketone **23f**, which was reduced to [4.3.3]propell-3-ene (**23g**) via the Huang–Minlon–Wolff–Kishner procedure. Finally, bromination and bisdehydrobromination with $LiCl/Li_2CO_3$ in DMF provided **24**.

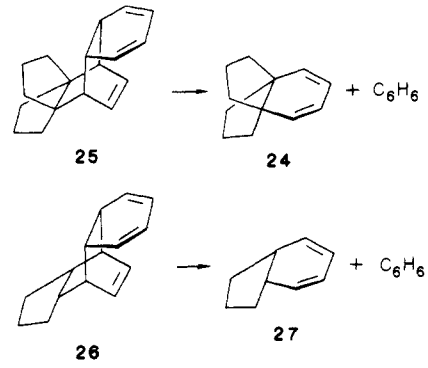


23a: R-R′ = C(O)OC(O)
b: R, R′ = CH_2OH
c: R, R′ = CH_2OMs
d: R, R′ = CH_2CN
e: R-R′ = $C(CN)=C(NH_2)CH_2$
f: R-R′ = $CH_2C(O)CH_2$
g: R-R′ = $(CH_2)_3$

(9) (a) Altman, J.; Babad, E.; Itzchaki, J.; Ginsburg, D. *Tetrahedron* **1966**, Suppl. 8, Part I, 279. (b) Altman, J.; Babad, E.; Pucknat, J.; Reshef, N.; Ginsburg, D. *Tetrahedron* **1968**, *24*, 975.

The benzene extrusion rates for model compounds **19c** ≡ **25** and **19d** ≡ **26** were measured in $C_2D_2Cl_4$ at 164.5 °C by NMR spectroscopy. The rate constants (Table I) are shown below:

$$k_{25} = 6.65 \times 10^{-6}\ s^{-1} \qquad k_{26} = 1.44 \times 10^{-4}\ s^{-1}$$



We see that the sterically more hindered **25** is in fact some 22 times less reactive than the *exo*-indan adduct **26**. Obviously the steric hindrance in **25**, which is lost in the product, is still present at the transition state. This is understandable if we remember that the [4 + 2] cycloreversion and [4 + 2] cycloaddition transition states are the same. For the latter, calculations[10] place the centers of the diene and dienophile only 2.2 Å apart, with the orbitals of one canted 27° from those of the other. In this orientation, the H atoms of the trimethylene bridge of **25** and those of the departing benzene actually come closer together than they are in the ground state. Thus the *syn*-trimethylene bridge of **20** is *not responsible* for its rapid rate of benzene extrusion. On the contrary, one must explain why the decomposition rate of **20** relative to **11** is not *inhibited* by the trimethylene unit. Our explanation is that the steric interaction in **20** is less severe than in **25** because the dihedral angle between the five-membered ring and the bicyclooctene unit of the former is 144° and only 120° in the latter.[11]

The widened dihedral angle in **20**, which is basically due to the constrictive effect of the cyclopropane ring, leads to another consequence. Namely, the dihedral angle between the cyclopropane ring and the bicyclooctene unit is only (360° − 144°)/2 = 108°. This places a cyclopropyl hydrogen in proximity to the bicyclooctenyl π bond in both **20** and **11**. Is this (unfavorable) interaction responsible for the rapid rate of decomposition in those two cases?

We chose **28** as a model to probe this sort of interaction, which is similar to "back strain" in an S_N1 reaction.[12] Molecular models clearly show that the ethano–bicyclooctenyl interaction in **28** is much more severe than the methylene–bicyclooctenyl interactions in **11** and **20**. The preparation of **28** (≡**19e**) proceeded from **29** (≡**15e**) according to the standard methodology given in Scheme I.

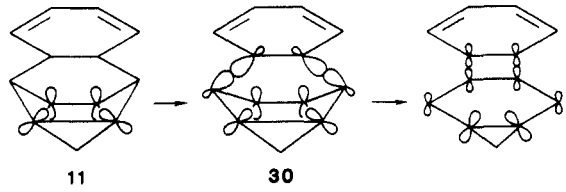
The cycloreversion of **28** occurs readily at 100 °C; the kinetics were studied by NMR in $C_2D_2Cl_4$ between 101 and 164 °C (Table

(10) (a) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. (b) Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1051. (c) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

(11) (a) Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538. (b) Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* **1964**, *42*, 2259.

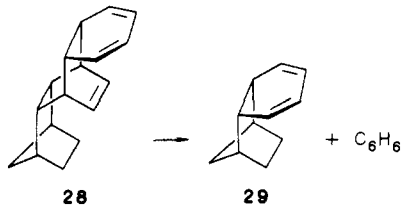
(12) Brown, H. C.; Berneis, H. L. *J. Am. Chem. Soc.* **1953**, *75*, 10.

Scheme II



I). The first-order rate constants obey the following Arrhenius equation:

$$\log k_{28} = (15.71 \pm 0.65) - (35\,700 \pm 1200)/2.303RT$$



On the basis of the above, one calculates that **28** cycloreverts some 35 times faster than indan adduct **26** at 164.5 °C. But at 85 °C, **28** decomposes about 200 times slower than do **11** and **20**. Thus we conclude that the "back strain" effect is operative but cannot fully account for the high relative reactivity of **11** and **20**.

At this point we see that the benzene extrusion rates of **11** and **20** are slightly, but similarly accelerated by "back strain," while that of **20** may be somewhat *decelerated* by "front strain" (i.e., interaction of the trimethylene with the cyclohexadiene). Since **11** and **20** react at about the same rate, partial opening of the cyclopropane ring, only possible for **11**, must, if anything, be slightly decelerative (no effect seems preferable). But none of these steric (strain) factors can explain the large reactivity of **11** and **20** relative to the "parent" **3**, exo cyclopropanated **12**, or endo trimethylenated **26**. We thus turn to an electronic explanation.

In the beginning of this paper, we mentioned that in cycloreversions of aromatic adducts such as **1**, the aromatic resonance energy is partially developed at the transition state. It is, therefore, natural to suppose that some *homoaromatic* resonance energy contributes to the stability of the cycloreversion transition states emanating from the *anti*-norcaradiene adducts. In contrast to the aromatic cases, however, the extent of homoaromatic interaction does not increase after the transition state is traversed, rather it diminishes in the free norcaradiene.[13] An inspection of the orbital overlaps during the reaction course explains this hypothesis (Scheme II). In the starting material (**11**), the π bond and the Walsh orbitals of the cyclopropane ring are separated by the saturated bridgehead atoms. In the transition state (**30**), the formerly σ-bound carbons rehybridize and become available for conjugation with the cyclopropane Walsh orbitals. Importantly, the overall ring conformation and the hybridization and tilting of the incipient p orbitals provide cyclic conjugation with the π bond and the cyclopropane Walsh orbital shown. This orbital array constitutes an almost perfect demonstration of the homoaromatic concept.[14] In the product norcaradiene, however, homoaromatic overlap has diminished due to the flatness of the six-membered ring and the sp^2 hybridization at the carbons next to the cyclopropane ring. Thus the well-known[15] conjugative capabilities of cyclopropane rings are in effect here, but with the new wrinkle that conjugation at the transition state is more effective than in the product ground state.

The above conclusion regarding the transition state for the cycloreversion to norcaradiene and benzene should be applicable to other cases. For example, the decarbonylation of **13** ought to profit from homoaromatic delocalization in the transition state. The same would apply to cycloadditions to the convex face of norcaradienes, and we plan to investigate whether or not the expected higher reactivity of such dienes will be realized.

Experimental Section

General Methods. Melting points were determined with a Tottoli apparatus (Büchi, Flawil) and are uncorrected. Mass spectra were obtained by electron-impact ionization (70 eV) on a Varian 3200 GC/MS machine. IR spectra were measured on a Perkin-Elmer 283 instrument. UV spectra were recorded with a Beckman 25 spectrophotometer, and cycloreversions were monitored in a Zeiss PMQ 3 photometer. ^{1}H NMR spectra were measured on a Varian EM 390 or a Bruker AM 300 instrument and are calibrated to internal TMS. ^{13}C NMR spectra were obtained on the Bruker AM 300 instrument and are calibrated to solvent. Preparative GLPC was done on a Varian Aerograph 90 P with a 0.4 × 50 cm column filled with 20% Reoplex 400 on Chromosorb 0.125–0.150 mm. Analytical GLPC was performed on a Perkin-Elmer Model 8320 instrument with a 0.25 mm × 12.5 m fused silica column, coated with 0.2 μm of GESE-52. We used silica gel (Macherey-Nagel) of particle size 0.063–0.200 and 0.040–0.063 mm for liquid chromatography.

Diels–Alder Adducts of 5,5-Dimethoxytetrachlorocyclopentadiene and Homobarrelene (5a and 6a). Homobarrelene (4)[16] (2.36 g, 20 mmol) and 5,5-dimethoxytetrachlorocyclopentadiene (5.28 g, 20 mmol) were heated under an argon atmosphere for 40 h at 100 °C. The oily product partly crystallized upon cooling to room temperature. It was dissolved in hot hexane (30 mL) from which a first crop of product crystallized on cooling to 10 °C. A second crop was obtained from the concentrated filtrate (15 mL), and a third one from recrystallizing the mother liquor from methanol (20 mL). The three-crystal fractions (6.54 g, 86%) contained the adducts **5a** and **6a** in the same 5:2 ratio. The major product was isolated from an incomplete reaction. In the presence of unreacted 5,5-dimethoxytetrachlorocyclopentadiene, a hexane solution first yielded a crystal fraction rich in the isomer **6a** and on concentration the pure major isomer **5a**.

5a: mp 114 °C; IR (KBr) 1610, 1060, 1040, 980 cm^{-1}; MS, *m/e* 382, 380 (M^+, 0.1), 255, 253 ($C_7H_2Cl_3(OCH_3)_2^+$, 36, 33), 92 ($C_7H_8^+$, 100), 91 ($C_7H_7^+$, 60); ^{1}H NMR (CCl_4) δ 0.18 (AB, $\Delta\nu \approx 10$ Hz, 2 H, 10-H), 0.89 (m, 2 H, 9,11-H), 2.47 (s, 2 H, 2,7-H), 2.90 (XX′ part, 2 H, 1,8-H), 3.46 (s, 3 H, CH_3), 3.57 (s, 3 H, CH_3), 5.54 (AA′ part, 2 H, 12,13-H).

6a (with **5a**): ^{1}H NMR (CCl_4) δ 1.50–1.75 (m, 4 H, 9,10,11-H), 2.43 (s, 2 H, 2,7-H), 2.90 (XX′ part, 2 H, 1,8-H), 3.43 (s, 3 H, CH_3), 3.54 (s, 3 H, CH_3), 6.21 (AA′ part, 2 H, 12,13-H).

The configuration of the two adducts was derived from two facts: (a) When the mixture of the adducts was irradiated with a high-pressure mercury lamp in the presence of xanthone in benzene solution, *both* isomers underwent a rapid intramolecular (2 + 2) photocyclization. After evaporation, the residue was chromatographed with hexane on silica gel (1 × 15 cm) to give a mixture of the cage ketals **7a** and **8a** in a 5:2 ratio. This indicates that both isomers have the endo,endo configuration.

7a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.001 (dt, 1 H), 0.466 (dt, 1 H), 0.942 (dd, 2 H), 2.596 (m, 2 H), 2.77 (m, 4 H), 3.551 (s, 3 H, OCH_3), 3.644 (s, 3 H, OCH_3).

8a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.182 (dt, 1 H), 0.506 (dt, 1 H), 0.901 (dd, 2 H), 2.479 (m, 2 H), 2.77 (m, 4 H), 3.533 (s, 3 H, OCH_3), 3.587 (s, 3 H, OCH_3).

(b) The position of the cyclopropane ring in the major product **5a** follows from the relatively high shift of its methylene protons in the ^{1}H NMR spectrum. They experience the same shielding as do those in homobarrelene, which is caused by the opposing double bond. Therefore, the major product, **5a**, has the anti-endo,endo configuration, and the minor product, **6a**, the syn-endo,endo one.

***anti*- and *syn*-14,14-Dimethoxypentacyclo[6.3.2.1^{3,6}.0^{2,7}.0^{9,11}]tetradeca-4,12-diene (5b and 6b).** Ammonia was condensed into a three-necked, round-bottomed flask, equipped with dropping funnel, mechanical stirrer, and dry ice condenser at −78 °C. Sodium (2.0 g, 0.09 mmol) was then added and dissolved with stirring. A solution of the adducts **5a** and **6a** (4.0 g, 10.5 mmol, 5:2 mixture) in ether (20 mL) was slowly added, and the reaction mixture was stirred for 2 h. After addition of solid ammonium chloride until the blue color disappeared, the ammonia was evaporated. The solid residue was dissolved in water and extracted with five 20-mL portions of ether, and the combined extracts were dried over magnesium sulfate and concentrated. The oily residue, on recrystallization from 10 mL of methanol, yielded **5b** (0.8 g). The residue of the

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filtrate was chromatographed on silica gel (65 × 3 cm) with hexane/ethyl acetate (9:1) to give **6b** (R_f 0.26, 0.36 g) and **5b** (R_f 0.23, 0.26 g).

5b: 1.06 g (58%); mp 81 °C; IR (KBr) 1610, 1350, 1280, 1050 cm^{-1}; MS, *m/e* 244 (M^+, 2), 151 [$C_7H_5(OCH_3)_2^+$, 35], 91 ($C_7H_7^+$, 47), 74 [$C(OCH_3)_2^+$, 78], 59 ($CO_2CH_3^+$, 100); ^1H NMR ($CDCl_3$) δ 0.03 (AB, $\Delta\nu$ = 36 Hz, J = 5 Hz, 2 H, 10-H), 0.82 (m, 2 H, 9,11-H), 2.52 (s, 2 H, 2,7-H), 2.59 (m, 4 H, 1,8,3,6-H), 2.94 (s, 3 H, CH_3), 3.14 (s, 3 H, CH_3), 5.13 (t, 2 H, 12,13-H), 5.35 (t, 2 H, 4,5-H).

6b: 0.36 g (49%) of oil; IR (KBr) 1612, 1480, 1370, 1285, 1030 cm^{-1}; MS, almost identical pattern as with **5b**; ^1H NMR ($CDCl_3$) δ 0.89 (m, 2 H, 9,11-H), 1.05 (AB, $\Delta\nu$ = 90 Hz, J = 5.5 Hz, 2 H, 10-H), 2.14 (s, 2 H, 2,7-H), 2.53 (m, 4 H, 1,8,3,6-H), 2.90 (s, CH_3), 3.11 (s, CH_3), 5.28 (t, 2 H, 4,5-H), 5.76 (AA′ part, 2 H, 12,13-H).

***anti-endo,endo*-Pentacyclo[6.3.2.1^{3,6}.0^{2,7}.0^{9,11}]tetradeca-4,12-dien-14-one (9).** A solution of *anti*-dimethyl ketal **5b** (0.76 g, 3.1 mmol) in 7.5 mL of acetic acid was diluted with 1.5 mL of water and stirred at room temperature for 20 h. Then, 25 mL of water and solid $NaHCO_3$ were added, and the mixture was extracted with four 20-mL portions of ether. The combined extracts were washed until neutral with 5% $NaHCO_3$, dried over $MgSO_4$, and evaporated. Filtration of the residue in hexane/ethyl acetate (9:1) over silica gel (5 × 3 cm) afforded colorless crystals of **9**: 0.58 g (94%); mp 56 °C; IR (KBr) 3040, 2920, 1805, 1775, 1025 cm^{-1}; MS, *m/e* 170 (M^+ - CO, 2), 92 ($C_7H_8^+$, 100); ^1H NMR ($CDCl_3$) δ 0.02 (m, 2 H, 10-H), 0.87 (m, 2 H, 9,11-H), 2.59 (narrow m, 2 H, 2,7-H), 2.85 (m, 4 H, 1,8,3,6-H), 5.24 (m, 2 H, 12,13-H), 5.84 (t, 2 H, 4,5-H).

***syn-endo,endo*-Pentacyclo[6.3.2.1^{3,6}.0^{2,7}.0^{9,11}]tetradeca-4,12-dien-14-one (10).** *syn*-Dimethyl ketal **6b** (0.36 g, 1.5 mmol) was hydrolyzed as above, yielding **10** (0.22 g, 75%): mp 119–120 °C dec; IR (KBr) 3025, 2912, 1807, 1779, 1350, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71 (dt, 1 H, 10-H), 1.05 (m, 2 H, 9,11-H), 1.44 (m, 1 H, 10-H), 2.30 (s, 2 H, 2,7-H), 2.85 (m, 4 H, 1,8,3,6-H), 5.87 (t, 2 H, 4,5-H), 5.94 (m, 2 H, 12,13-H).

***anti*-Tetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-3,5,12-triene (11).** Anti ketone **9** (64 mg, 0.32 mmol) was deposited from an ether solution by means of a rotary evaporator onto the walls of the 5-mL distilling flask of a small flash vacuum pyrolysis apparatus. The flask was connected, via an electrically heated reaction tube (40 × 0.4 cm), to a cold trap at −78 °C. A vacuum of 0.9 Torr was maintained in the cold trap while a 2.4 mL/min flow of argon entered the distilling flask through a capillary tube. With the flask at 55 °C and the reactor at 240 °C, the ketone passed through the reactor within 2 h. The product was dissolved from the wall of the trap with pentane and filtered through silica gel (1 × 0.8 cm). Evaporation of the solvent left pure triene **11**; elution with ether afforded an additional fraction of starting ketone **9** (5.3 mg).

11: 39 mg (77% of reacted ketone); mp 81 °C; IR (KBr) 1602, 1030, 740, 680 cm^{-1}; UV (cyclohexane) 262 (sh, 2640), 270 (3250), 280 (3100), 293, (1630) nm; ^1H NMR ($CDCl_3$) δ 0.12 (m, 2 H, 10-H), 0.91 (m, 2 H, 9,11-H), 2.74 (m, 2 H, 1,8-H), 2.92 (s, 2 H, 2,7-H), 5.40 (s, 4 H, 3,4,5,6-H), 5.88 (AA′ part, 2 H, 12,13-H). Triene **11** readily formed an adduct with maleic anhydride (MA) at room temperature, mp 200 °C. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.31; H, 6.04.

***syn*-Tetracyclo[6.3.2.0^{2,7}.0^{9,11}]trideca-3,5,12-triene (12).** By use of the flash vacuum pyrolysis apparatus described above, syn ketone **10** (28 mg, 0.14 mmol) was decarbonylated with a temperature of 65 °C in the flask and 270 °C in the reactor tube. After 2 h, the product was transferred from the trap with pentane and filtered through silica gel (1 × 0.8 cm), yielding crystalline **12**: 21 mg (85%); IR (KBr) 1605, 1360, 1180, 1030, 705, 670 cm^{-1}; UV (cyclohexane) 263 (3300), 273 (3200), 284 (1680) nm; ^1H NMR ($CDCl_3$) δ 0.77 (AB, $\Delta\nu$ = 18 Hz, J = 5 Hz, 2 H, 10-H), 1.08 (m, 2 H, 9,11-H), 2.59 (s, 2 H, 2,7-H), 2.70 (narrow m, 2 H, 1,8-H), 5.34 (AA′BB′, 4 H, 3,4,5,6-H), 6.52 (AA′ part, 2 H, 12,13-H). Compound **12** readily formed an adduct with MA at room temperature, mp 220 °C. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.02; H, 5.96.

Diels–Alder Adduct (16a) of *p*-Benzoquinone and [4.3.1]Propella-2,4-diene (15a). A solution of [4.3.1]propella-2,4-diene (**21** ≡ **15a**)[7] (2.9 g, 22 mmol) and freshly recrystallized *p*-benzoquinone (2.5 g, 23 mmol) in 10 mL of CCl_4 was heated at 65 °C for 2 h in an argon atmosphere. After the mixture was cooled with ice, the adduct **16a** precipitated as yellow needles, which were recrystallized from ethanol: 4.4 g (83%); mp 101–102 °C; IR (KBr) 1667, 1608 cm^{-1}; MS, *m/e* 240 (M^+, 1), 132 (M^+ - $C_6H_4O_2$, 40), 117 ($C_9H_9^+$, 100); ^1H NMR ($CDCl_3$) δ 0.36 (AB, $\Delta\nu$ = 49 Hz, J = 5 Hz, 2 H, 16-H), 1.65 (m, 6 H, 10,11,12-H), 3.17 (br s, 2 H, 2,7-H), 3.33 (XX′ part, 2 H, 1,8-H), 5.83 (AA′ part, 2 H, 14,15-H), 6.58 (s, 2 H, 3,6-H).

Diels–Alder Adduct (16c) of *p*-Benzoquinone and [4.3.3]Propella-2,4-diene (15c). A degassed solution of [4.3.3]propella-2,4-diene (**24** ≡ **15c**) (283 mg, 1.77 mmol), *p*-benzoquinone (277 mg, 2.57 mmol), and 4-*tert*-butylcatechol (20 mg) in 4 mL of CCl_4 was sealed in vacuo in a glass ampoule and heated at 130 °C for 68 h. After cooling, the solvent was decanted and the glassy residue was dissolved in chloroform and transferred to a flask. After evaporation of solvent and excess dienophile at 40 °C (0.01 Torr), faintly yellow needles were obtained from ether (320 mg, 67%): mp 114–115 °C; IR (KBr) 2938, 1665, 1282, 1092, 860 cm^{-1}; MS, *m/e* 268 (M^+, 9), 108 ($C_8H_{12}^+$, 100); ^1H NMR ($CDCl_3$) δ 1.03–2.10 (m, 12 H, 11,12,13,14,15,16-H), 2.67 (narrow m, 2 H, 3,8-H), 3.11 (XX′ part, 2 H, 2,9-H), 6.19 (AA′ part, 2 H, 17,18-H), 6.63 (s, 2 H, 5,6-H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.76; H, 7.48.

Diels–Alder Adduct (16d) of *p*-Benzoquinone and Bicyclo[4.3.0]nona-2,4-diene (15d). Bicyclo[4.3.0]nona-2,4-diene (**27** ≡ **15d**)[17] (1.2 g, 10 mmol) and *p*-benzoquinone (1.0 g, 9.8 mmol) were refluxed in CCl_4 for 1 h. After evaporation of the solvent, the residue afforded faintly yellow crystals from ether/pentane (1:1): 2.0 g (95%); mp 156–157 °C; IR (KBr) 3055, 2945, 2866, 1665, 1611, 1280, 875 cm^{-1}; MS, *m/e* 228 (M^+, 9), 120 ($C_9H_{12}^+$, 71), 82 ($C_4H_2O_2^+$, 100); ^1H NMR ($CDCl_3$) δ 0.83–1.97 (br m, 6 H, 10,11,12-H), 2.27 (m, 2 H, 9,13-H), 2.93 (narrow m, 2 H, 2,7-H), 3.23 (XX′, 2 H, 1,8-H), 6.17 (AA′, 2 H, 14,15-H), 6.65 (s, 2 H, 4,5-H).

Diels–Alder Adduct (16e) of *p*-Benzoquinone and *endo*-Tricyclo-[6.2.1.0^{2,7}]undeca-3,5-diene (15e). Tricyclo[6.2.1.0^{2,7}]undeca-3,5-diene (**29** ≡ **15e**)[2] (2.17 g, 14.8 mmol) and *p*-benzoquinone (3.5 g, 32.4 mmol) were refluxed overnight in 20 mL of dry ethyl acetate. The solution was then concentrated, the excess dienophile was evaporated at 25 °C (0.01 Torr), and the residue was recrystallized from ethyl acetate to give 2.3 g (61%): mp 170–172 °C; IR (KBr) 3055, 2955, 2935, 1670, 1610, 1282, 1110 cm^{-1}; MS, *m/e* 254 (M^+, 3), 146 (M^+ - $C_6H_4O_2$, 29), 117 ($C_9H_9^+$, 20), 91 ($C_7H_7^+$, 20), 66 ($C_5H_6^+$, 100); ^1H NMR ($CDCl_3$) δ 1.18 (m, 6 H, 11,12,17-H), 2.10 (m, 4 H, 9,10,13,14-H), 2.87 (narrow m, 2 H, 2,7-H), 3.20 (XX′ part, 2 H, 1,8-H), 6.03 (AA′ part, 2 H, 15,16-H), 6.65 (s, 2 H, 4,5-H).

Reduction of the Carbonyl-Flanked Double Bond in the *p*-Benzoquinone Adducts. The same general procedure, illustrated below for pentacyclo[6.5.2.1^{9,13}.0^{2,7}.0^{9,13}]hexadec-14-ene-3,6-dione (**17a**), was used for **17c–e**.

To a solution of **16a** (3.94 g, 16.4 mmol) in 50 mL of acetic acid was added 200-mesh zinc powder (2.5 g, 38 mmol), and the reaction mixture was vigorously stirred for 20 min under an argon atmosphere. After filtration, the zinc and zinc acetate were washed with five 50-mL portions of methylene chloride, and the combined filtrates were concentrated on a rotary evaporator at 40–60 °C (0.01 Torr) to 10 mL. The residue was poured into 25 mL of water and extracted with three 25-mL portions of methylene chloride. The combined extracts were washed with 5% $NaHCO_3$, water, and brine and dried, and the solvent was evaporated. Two recrystallizations from methanol afforded **17a** as colorless crystals: 3.8 g (96%); mp 123 °C; IR (KBr) 1706 cm^{-1}; MS, *m/e* 242 (M^+, 2), 132 (M^+ - $C_6H_6O_2$, 50), 117 ($C_9H_9^+$, 100); ^1H NMR ($CDCl_3$) δ 0.33 (AB, $\Delta\nu$ = 49 Hz, J = 5 Hz, 2 H, 16-H), 1.62 (m, 6 H, 10,11,12-H), 2.48 (AA′BB′, 4 H, 4,5-H), 3.13 (s, 2 H, 2,7-H), 3.33 (XX′ part, 2 H, 1,8-H), 5.88 (AA′ part, 2 H, 14,15-H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.11; H, 7.46.

Formation of Bis(tosylhydrazones) from 1,4-Diketones. The same general procedure, illustrated below for pentacyclo[6.5.2.1^{9,13}.0^{2,7}.0^{9,13}]-hexadec-14-ene-3,6-dione bis(tosylhydrazone) (**18a**), was used for **18c–e**.

A solution of diketone **17a** (1.46 g, 6.03 mmol), tosylhydrazine (2.36 g, 12.7 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 15 mL of dry methanol was stirred under argon at room temperature. After 15 min a thick white precipitate had formed, which was filtered, washed twice with 10 mL of ice-cold methanol, and dried in vacuo over phosphorus pentoxide: 2.96 g (85%); mp 151–152 °C dec; IR (KBr) 3054, 2940, 2882, 1642, 1150 cm^{-1}. Anal. Calcd for $C_{30}H_{34}N_4O_4S_2$: C, 62.26; H, 5.92; N, 9.68. Found: C, 61.23; H, 6.26; N, 9.39.

Shapiro Elimination[8] of 1,4-Bis(tosylhydrazones) (18) to 1,3-Dienes (19). The same general procedure, illustrated below for pentacyclo-[6.5.2.1^{9,13}.0^{2,7}.0^{9,13}]hexadeca-3,5,14-triene (**19a** ≡ **20**), was used for **19c–e**.

n-Butyllithium in hexane (2.4 M, 20 mL) was slowly added, at −20 °C, to a stirred suspension of bis(tosylhydrazone) **18a** (2.90 g, 5.01 mmol) in 55 mL of dry and deaerated THF under an argon atmosphere. The reaction mixture was stirred at 0 °C overnight and then hydrolyzed at −10 °C with 20 mL of saturated ammonium chloride solution. After addition of 200 mL of pentane, the phases were separated and the organic layer was freed from THF by washing with five 50-mL portions of water. The solution was then dried over magnesium sulfate, concentrated, and chromatographed on silica gel (12 × 2.5 cm) with pentane. The product

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triene **20** eluted with an R_f of 0.2 and was recrystallized from pentane: 242 mg (23%); mp 82–84 °C; UV (hexane) 263 (sh, 2300), 271 (2900), 282 (2750), 294 (1400) nm; MS, *m/e* 210 (M^+, <1), 132 ($M^+ - C_6H_6$, 55), 117 ($C_9H_9^+$, 100); ^1H NMR ($CDCl_3$) δ 0.23 (AB, $\Delta\nu$ = 68 Hz, J = 5 Hz, 2 H, 16-H), 1.65 (m, 6 H, 10,11,12-H), 2.60 (XX′ part, 2 H, 1,8-H), 3.13 (s, 2 H, 2,7-H), 5.35 (AA′BB′, 4 H, 3,4,5,6-H), 5.95 (AA′ part, 2 H, 14,15-H).

Pentacyclo[8.3.3.2^{2,9}.0^{3,8}.0^{1,10}]octadeca-4,6,17-triene (25 ≡ 19c). 17c: 73%; mp 104–105 °C; IR (KBr) 2937, 2864, 1699, 1265, 1162 cm^{-1}; MS, *m/e* 270 (M^+, 10), 108 ($C_8H_{12}^+$, 100), 80 ($C_6H_8^+$, 41); ^1H NMR ($CDCl_3$) δ 0.98–2.07 (m, 12 H, 11,12,13,14,15,16-H), 2.53 (AA′BB′, 4 H, 5,6-H), 2.95 (s, 2 H, 3,8-H), 3.07 (XX′ part, 2 H, 2,9-H), 6.24 (AA′ part, 2 H, 17,18-H).

18c: 96%; mp 122 °C dec; IR (KBr) 3195, 2925, 1601, 1162 cm^{-1}.

25: 10%; mp 88–89 °C; MS, *m/e* 238 (M^+, 1), 160 ($M^+ - C_6H_6$, 70), 131 ($C_{10}H_{11}^+$, 100); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.77–1.68 (m, 10 H, 11,12,13,14,15,16-H), 1.85 (narrow m, 2 H, 14,16-H), 2.32 (XX′ part, 2 H, 2,9-H), 2.82 (s, 2 H, 3,8-H), 5.37 (AA′BB′, 4 H, 4,5,6,7-H), 6.25 (AA′ part, 2 H, 17,18-H).

Tetracyclo[6.5.2.0^{2,7}.0^{9,13}]pentadeca-3,5,14-triene (26 ≡ 19d). 17d: 64%; mp 81–82 °C; IR (KBr) 3048, 2947, 2861, 1696, 1263 cm^{-1}; MS, *m/e* 230 (M^+, 24), 120 ($C_9H_{12}^+$, 93), 91 ($C_7H_7^+$, 78), 56 ($C_3H_4O^+$, 100); ^1H NMR ($CDCl_3$) δ 0.78–2.26 (m, 8 H, 9,10,11,12,13-H), 2.53 (AA′BB′, 4 H, 4,5-H), 2.90 (s, 2 H, 2,7-H), 3.20 (XX′ part, 2 H, 1,8-H), 6.23 (AA′ part, 2 H, 14,15-H).

18d: 68%; mp 122–124 °C dec; IR (KBr) 3208, 3051, 2942, 2866, 1601, 1162 cm^{-1}.

26: 16%; mp 85–86 °C; IR (KBr) 3035, 2925, 2898, 2865, 1604, 1445, 1380 cm^{-1}; UV (pentane) 259 (sh, 2500), 267 (3200), 278 (3100), 290 (1550) nm; MS, *m/e* 198 (M^+, 6), 120 ($C_9H_{12}^+$, 82), 91 ($C_7H_7^+$, 100); ^1H NMR ($CDCl_3$) δ 0.77–1.87 (m, 6 H, 10,11,12-H), 2.17 (m, 2 H, 9,13-H), 2.47 (XX′ part 2 H, 1,8-H), 2.78 (s, 2 H, 2,7-H), 5.42 (AA′BB′, 4 H, 3,4,5,6-H), 6.25 (AA′ part, 2 H, 14,15-H). The MA adduct of **24** was obtained in ether at room temperature; mp 186 °C. Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.64; H, 6.20.

Pentacyclo[6.6.2.1^{10,13}.0^{2,7}.0^{9,14}]heptadeca-3,5,15-triene (28 ≡ 19e). 17e: 64.5%; mp 133–134 °C; IR (KBr) 3051, 2963, 2939, 1706, 1442, 1260, 1189, 743 cm^{-1}; MS, *m/e* 256 (M^+, 27), 146 ($C_{11}H_{14}^+$, 18), 117 ($C_9H_9^+$, 21), 66 ($C_5H_6^+$, 100); ^1H NMR ($CDCl_3$) δ 1.2 (m, 6 H, 11,12,17-H), 2.0 (m, 4 H, 9,10,13,14-H), 2.51 (AA′BB′, 4 H, 4,5-H), 2.85 (narrow m, 2 H, 2,7-H), 3.20 (XX′ part, 2 H, 1,8-H), 6.10 (AA′ part, 2 H, 15,16-H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.69; H, 7.87. Found: C, 79.61; H, 7.54.

18e: 83%; mp 140–141 °C; IR (KBr) 3204, 3052, 2950, 1702, 1162 cm^{-1}.

28: 16%; mp 69–70 °C; IR (KBr) 3067, 3033, 2935, 1603, 791, 750, 730, 671 cm^{-1}; UV (pentane) 261 (sh, 2700), 269 (3250), 280 (3050), 292 (sh, 1600); MS, *m/e* 146 ($C_{11}H_{14}^+$, 73), 117 ($C_9H_9^+$, 32), 78 ($C_6H_6^+$, 100); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02–1.34 (m, 6 H, 11,12,17-H), 1.99 (narrow m, 2 H, 9,14-H), 2.06 (narrow m, 2 H, 10,13-H), 2.48 (XX′ part, 2 H, 1,8-H), 2.77 (s, 2 H, 2,7-H), 5.42 (AA′BB′, 4 H, 3,4,5,6-H), 6.15 (AA′ part, 2 H, 15,16-H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 130.14 (3,6-C), 129.91 (15,16-C), 120.68 (4,5-C), 47.42 (9,14-C), 42.45 (2,7-C), 41.40 (17-C), 41.27 (10,13-C), 39.36 (1,8-C), 24.89 (11,12-C); MA adduct from ether at room temperature; mp 258 °C. Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.02; H, 6.93.

8-Amino-7-cyano[4.3.3]propella-3,7-diene (23e). A mixture of NaCN (63 g, 1.28 mol), *cis*-1,6-bis[(mesyloxy)methyl]bicyclo[4.3.0]non-3-ene (**23c**)[9] (22.6 g, 0.067 mol) and 380 mL of dry HMPT was heated with stirring at 140 °C under argon for 42 h. After cooling, it was poured into 2 L of water and stirred for another hour. The product was collected on a sintered plate, washed with water, and dried in vacuo. Recrystallization from ethanol yielded the amino nitrile **23e**: 8.7 g (65%); mp 143–144 °C; IR (KBr) 3450, 3355, 3040, 2937, 2179, 1645, 1611 cm^{-1}; MS, *m/e* 200 (M^+, 12), 146 ($M^+ - C_4H_6$, 100); ^1H NMR ($CDCl_3$) δ 1.31–1.8 (m, 6 H, 10,11,12-H), 2.0–2.2 (m, 4 H, 2,5-H), 2.35 (narrow m, 2 H, 9-H), 4.33 (br s, 2 H, HN), 5.93 (narrow m, 2 H, 3,4-H).

When the reaction temperature was lowered to 110 °C, *cis*-1,6-bis(cyanomethyl)bicyclo[4.3.0]non-3-ene (**23d**) was obtained instead of **23e**: 79%; mp 118 °C; ^1H NMR ($CDCl_3$) δ 1.83 (narrow m, 6 H, 7,8,9-H), 2.16 (narrow m, 4 H, 2,5-H), 2.30 (s, 4 H, 10,11-H), 5.63 (narrow m, 2 H, 3,4-H).

[4.3.3]Propell-3-en-8-one (23f). A solution of amino nitrile **23e** (8.64 g, 43.2 mmol) in 300 mL of acetic acid and 42 mL of water was first refluxed for 0.5 h and then combined with 120 mL of 85% phosphoric acid and refluxed for another 25 h. After cooling, the mixture was poured onto 900 g of ice and stirred until the ice had melted. The product was extracted with ether, and the organic phase was washed with 5% aqueous sodium carbonate and brine. After being dried with magnesium sulfate, the solution was evaporated and the oily residue was distilled (95–100 °C, 0.01 Torr). Further purification by GLPC (120 °C) yielded ketone **23f**: 4.26 g (56%); mp 67–69 °C; IR (neat) 3021, 2955, 1740 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 1.2–1.6 (2 m, 6 H, 10,11,12-H), 1.75 (AB, $\Delta\nu$ = 34.1 Hz, J = 17.3 Hz, 4 H, 2,5-H), 1.97 (AB, $\Delta\nu$ = 17.0 Hz, J = 17.7 Hz, 4 H, 7,9-H), 5.49 (t, J = 1.9 Hz, 2 H, 3,4-H).

The severe hydrolysis conditions partially induced a shift of the double bond into the 2 position of **23f**. The solvent composition given above led to 27% of this isomer; with a smaller amount of water, this process becomes dominant.

[4.3.3]Propell-3-ene (23g). Ketone **23f** (4.26 g, 24.2 mmol) was dissolved in 25 mL of triethylene glycol. Powdered KOH (5.43 g, 97 mmol) and hydrazine hydrate (7.7 g, 150 mmol) were added, and the mixture was boiled with stirring for 2 h. Then the reflux condenser was changed to a Zincke distillation head, and the bath temperature was slowly raised to 200 °C. When the N_2 evolution had ceased, as indicated by a bubble counter, 30 mL of water was added from a dropping funnel, and the distillation was continued. The distillate was acidified to a pH of 3 and extracted with pentane. After being washed with brine and dried over magnesium sulfate, the extract was concentrated and the residue was distilled (50–55 °C, 1 Torr). Further purification by GLPC (100 °C) gave propellene **23g**: 3.46 g (88%); mp 71–73 °C; IR (neat) 3045, 2942, 2863, 1641, 1451, 715 cm^{-1}; ^1H NMR (CCl_4) δ 1.50 (narrow m, 12 H, 7,8,9,10,11,12-H), 1.92 (d, J = 3 Hz, 4 H, 2,5-H), 5.77 (t, J = 3 Hz, 2 H, 3,4-H).

[4.3.3]Propella-2,4-diene (24). Propellene **23g** (3.35 g, 20.6 mmol) was dissolved in 30 mL of methylene chloride and cooled to −78 °C. Bromine (3.3 g, 20.6 mmol) in 15 mL of dry methylene chloride was slowly added with stirring, and the mixture was allowed to warm to ambient temperature within 1 h. Evaporation of solvent at room temperature left the crude dibromide as a yellow solid. Lithium carbonate (2.74 g, 37.0 mmol) and lithium chloride (1.16 g, 27.3 mmol) were dried in vacuo at 220 °C for 2 h and added to the crude dibromide dissolved in 90 mL of dry DMF. The degassed mixture was heated with stirring at 115–120 °C for 18 h under an argon atmosphere. After cooling, it was poured into 350 mL of water and extracted with four 50-mL portions of pentane. The combined extracts were washed with brine, filtered through alumina (2 × 5 cm), and concentrated by distillation on a Vigreux column (1 × 50 cm) to 4 mL. The residue was separated by low-pressure liquid chromatography (1 × 25 cm silica gel of 60 μm particle size, pentane). The first fraction collected contained [4.3.3]propell-2-ene, which was freed from solvent by GLPC (90 °C): 0.30 g (9%); mp 51–52 °C; ^1H NMR (CCl_4) δ 1.45–1.55 (m, 2 H, 5-H), 1.52 (narrow m, 12 H, 7,8,9,10,11,12-H), 1.8–1.95 (m, 2 H, 4-H), 5.62 (narrow m, 2 H, 2,3-H).

The second fraction contained the desired diene **24** together with vinylic monohalides, from which it was separated by GLPC (90 °C): 1.15 g (35%); mp 33–34 °C; IR (neat) 3021, 2945, 2866, 1647, 1454 cm^{-1}; MS, *m/e* 160 (M^+, 23), 131 ($M^+ - C_2H_5$, 84), 117 ($M^+ - C_3H_7$, 100); HRMS calcd for $C_{12}H_{16}$ 160.1264, found 160.1264; ^1H NMR (CCl_4) δ 1.2–1.4 (m, 4 H, 8,11-H), 1.5–1.9 (m, 8 H, 7,9,10,12-H), 5.57 (s, 4 H, 2,3,4,5-H).

The MA adduct of **24** was obtained by heating the components in CCl_4 at 70 °C for 2 h; mp 157 °C. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.30; H, 7.10.

Kinetic Measurements. The fast cycloreversions of compounds **11** and **20** were followed in dodecane solution (4 × 10^{-4} M) by continuous monitoring of the long-wavelength UV absorption of the products; the yields were quantitative (also verified by NMR). A quartz polarimeter cell with 5-cm path length was used, whose outer jacket was heated with thermostated circulating water. The temperature measured in the cell by means of a thermistor was constant within 0.05 °C. Wavelengths and temperatures of the measurements, as well as the rate constants and the Arrhenius parameters of these cycloreversions, are given in Table I. From the latter, the free enthalpies of activation at 164 °C, $\Delta G^{\ddagger}_{164}$, were calculated.

The slow cycloreversions of compounds **3**, **12**, **25**, **26**, and **28** were followed in $C_2D_2Cl_2$ solution (0.25 M) by ^1H NMR spectroscopy; the yields of the benzene and cyclohexadienes produced were quantitative. The degassed samples were sealed in NMR tubes and heated in a vacuum isolated tube (20 × 1.5 cm) by the vapor of refluxing mesitylene (bp 164.7 °C). At defined intervals, the tubes were taken from the oven, cooled with ice, and measured in the spectrometer. From the integrated signals of educt and product, rate constants were obtained by means of the first-order rate equation.

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