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(61) The different reaction paths for proton attack and attack of other electrophiles, for example, bromine, may be explained by perturbation theory.[62] Calculations on benzvalene[9] and on 2,3-dimethylbenzvalene[63] reveal that these molecules are polarized; the bicyclobutane part bears a negative charge. So, in a charge-controlled reaction one should expect attack at the bicyclobutane moiety. In contrast, an orbital-controlled reaction is expected to take place at a center where the highest occupied molecular orbital has the highest coefficient, that is, at the double bond.
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(64) The reaction products attributed to this kind of catalysis are the same as the ones obtained in acid-catalyzed reactions. To prevent or at least suppress these competing pathways one can use glassware cleaned with ammonia or basic solvents. For example, tricyclo[4.1.0.0^{2,7}]heptane (**53**) rearranges in toluene solution mainly into 2-norcarene (**54**)[65] and only a small amount of bicyclo[3.2.0]hept-6-ene (**55**). Gas-phase pyrolysis[67] affords mainly **54**. Compound **54** was also obtained in the acid-catalyzed reaction of **53**.[68] When the reaction was carried out in a basic solvent, tetramethylethylenediamine (TMEDA), the yield of **55** was raised to 40%.[65]

Of course, an acid or glass surface catalyzed reaction can in principle give rise to the same reaction product as a thermal reaction. However, in that case addition of basic solvents such as TMEDA[65] or triethylamine[66] lowers greatly the reaction rates.[65]
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# Comparison of Diels–Alder Reactivity of a Bicyclobutane and of a Cyclobutane Bridged Diene

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Abstract: Kinetic measurements reveal an unanticipated difference in the Diels–Alder reactivities of dienes bridged by small rings. The bicyclobutane bridged diene **1** is extremely reactive whereas the cyclobutane bridged diene **4** shows a remarkably low reactivity even toward highly reactive dienophiles. Theoretical approaches to explain the reactivity of dienes in Diels–Alder cycloadditions are applied to the dienes at hand. The orbital interactions between the small rings and unsaturated bridges in **1** and **4** and the corresponding Diels–Alder adducts have been examined. The results of ab initio calculations, performed by van Duynen and van der Ploeg, indicate that the HOMO of bicyclobutane has A_2 symmetry which leads to a repulsive interaction with the diene bridge in **1**. As a consequence, **1** has a high-lying HOMO which is confirmed by PES measurements. The reactivity of **1** is shown to be quantitatively in accordance with its HOMO energy. In contrast the reactivity of **4** is much lower than anticipated from its HOMO energy. This is attributed to the existence of repulsive interactions between the filled frontier orbitals of the cyclobutane ring and the ethylene bridge in the Diels–Alder adducts of **4**.

The Diels–Alder reaction,[1] discovered nearly half a century ago, has been the subject of numerous studies.[2–15] As far as the mechanism is concerned the Diels–Alder reaction is generally believed to occur via a concerted pathway.[16] This conclusion, based on experimental observations,[2,17] received a theoretical foundation from the principle of conservation of orbital symmetry as formulated by Woodward and Hoffmann[4] and was corroborated by calculations.[13,15,18] The reactivity of substrates in a Diels–Alder cycloaddition depends greatly on the structural features of the reaction components. In general, rates of addition are the same,[2] within an order of magnitude, in going from a polar to a nonpolar solvent except when the solvent acts as a specific catalyst.[2h] The reactivity of the diene component[2,19,20] depends on its structure and configuration, and on the nature of the substituents at the conjugated chain.[19,20] It is essential that the double bonds of the diene molecule have a coplanar cis configuration. Normally electron-donating groups increase the reactivity of the diene whereas an electron-acceptor group decreases it.[20] An increase in the volume of substituents[19] of the same type results in a decrease of the reactivity of the diene as well as of the dienophile.[2,19,20] Electron-attracting substituents on the carbon–carbon double bond of the dienophile normally increase the rate of the Diels–Alder reaction. This rule, originally proposed by Alder,[21] has been confirmed by many investigations.[22] A more quantitative treatment of reactivity can in principle be performed by using the quantum-mechanical theory of perturbation.[7,23] Especially frontier molecular orbital treatments,[3] which are a first approximation to a complete perturbation treatment of chemical reactivity, have been exceptionally useful for rationalizing substituent effects in cycloaddition reactions.[11,12,14] In this paper we wish to report the reactivity of a diene 2,3 bridged by a bicyclobutane ring (**1**) and a diene
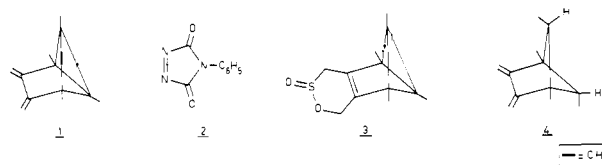
2,3 bridged by a cyclobutane ring (**4**) and to explain the observed differences.

Kinetic Measurements and Discussion. One of the striking properties of the recently synthesized 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**1**)[24] is its high Diels–Alder reactivity. For example, this bicyclobutane bridged diene reacts at a rate too fast to measure with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **2**) even at −70 °C. Competition experiments, carried out at −70 °C, showed that **1** reacts only by a factor of 2–3 slower than cyclopentadiene
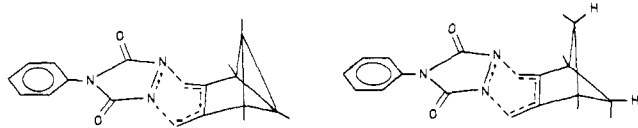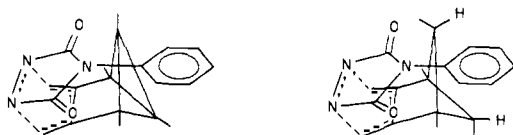
Figure 1. Exo approach.

Figure 2. Endo approach.

with PTAD. Thus, diene **1** competes successfully with cyclopentadiene, one of the most reactive dienes known. The high reactivity of **1** has permitted examination of the mode of addition of sulfur dioxide at low temperature which led to the recognition[25] that sulfur dioxide reacts with **1** via a [2 + 4] [π + $\pi\pi$] mode of addition affording the sulfinic ester **3** under kinetically controlled conditions. On the contrary *endo,endo*-1,4,5,6-tetramethyl-2,3-dimethylenebicyclo[2.1.1]-hexane (**4**)[26] shows a remarkably slow Diels–Alder reactivity. For example, the reaction of tetracyanoethylene (TCNE) with this cyclobutane bridged diene required several hours in refluxing chloroform. The analogous reaction of **1** is complete at room temperature in less than 1 min.

In order to get insight into the quantitative differences of the Diels–Alder reactivity of the bicyclobutane bridged diene **1** and the cyclobutane bridged diene **4** the second-order rate constants were determined for the reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, **2**), tetracyanoethylene (TCNE), maleic anhydride, and dimethyl acetylenedicarboxylate with **1** and **4**, respectively. The results are compiled in Table I. For reason of comparison literature data[2e] on cyclopentadiene and 2,3-dimethylbutadiene are also included.

The results clearly indicate the extreme difference of **1** and **4** in the reactivity toward dienophiles.

How can we explain these differences of **1** and **4**? Both dienes have the ideal fixed coplanar cis configuration as can be deduced from molecular models. Moreover, the ultraviolet spectra of **1** and **4** show maxima at 250 (log ϵ 3.95)[24] and 240 nm (log ϵ 4.29),[26] respectively, which is in good agreement with literature data[27] on cis dienes. The distance between the terminal carbons of the diene moieties in **1** and **4** does not differ significantly. The replacement of the *exo*cyclic diene system by a *endo*cyclic double bond, which results from a Diels–Alder cycloaddition to **1** and **4**, will probably enhance the strain in the rigid small ring skeletons, but there is no reason to expect a larger increase for the case of **4** with respect to that for **1**. A more serious difference arises from the endo methyl groups in **4**. These methyl groups are directed toward the diene system
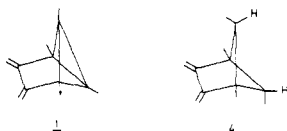
in contrast to those in **1** which are bent away by the central bond of the bicyclobutane moiety. Hence, in principle one might expect a larger hindrance for the incoming dienophile in **4** than in **1**. However, investigation of Dreiding models reveals that the van der Waals radii of the endo methyl groups in **4** hardly reach the central bond of the diene moiety. When a dienophile attacks diene **1** or **4** from the exo side it will be situated above (or below) the plane of the diene moiety in the

	H_5C_6–N (PTAD)	$(CN)_2C{=}C(CN)_2$	maleic anhydride	COOMe C≡C COOMe
cyclopentadiene		43.10^{10}[b]	92.10^{6}[b]	31.10^{4}[b]
1	$>3.10^{13}$	61.10^{9}	11.10^{5}	29.10^{2}
2,3-dimethylbutadiene		24.10^{7}[b]	34.10^{4}[b]	24.10^{2}
4	48.10^{4}	20.10^{2}	$6,5$	$7,2$

[a] Rate constants at 20 °C except for maleic anhydride (30 °C) and dimethyl acetylenedicarboxylate (23 °C). [b] Literature data (taken from Sauer[2e]).

neighborhood of the 1,4 positions in order to permit maximal interaction. This is depicted schematically for the reaction of **1** and **4** with PTAD in Figure 1.

Investigation of Dreiding models gives no indication for strong hindrance of the endo methyl group in **4** toward the exo incoming dienophile. Moreover, steric hindrance of this type would depend on the structural features of the dienophile. One should anticipate that such an effect would be larger using TCNE as dienophile as compared to PTAD. The data of Table I give no compelling support for this assumption.

Appropriately substituted reactants usually form preferentially Diels–Alder adducts with endo stereochemistry.[17a] This has been explained by assuming that better overlap of the orbitals of the dienophile with those on the 1 and 4 positions of the diene can be achieved[28] or alternatively[4,29] that secondary interactions between the orbitals at the 2 and 3 position of the diene and the π orbitals on the substituents of the dienophile can stabilize the transition state. Endo approach of **4** compared to **1** is sterically very hindered by the presence of the endo methyl group. However, the large difference in reactivity of **1** and **4** is also found in the reaction with PTAD (**2**), where endo approach is made sterically impossible in both dienes by the presence of the rings (Figure 2). Hence we do not believe that steric hindrance alone can explain the observed differences in reactivity of **1** and **4**.

Orbital Interactions of Small Rings and Unsaturated Bridges. Recently, Jorgensen and Borden[30] predicted a low reactivity of dienes 2,3 bridged by a cyclobutane ring on the basis of qualitative considerations of orbital interactions between the cyclobutane ring and the butadiene and ethylene bridge, respectively.[31] This conclusion was corroborated by extended Hückel calculations. In order to explain the differences in the Diels–Alder reactivity of the bicyclobutane bridged diene **1** and the cyclobutane bridged diene **4** ab initio calculations[32] have been performed by van Duynen and van der Ploeg on the model compounds **5, 6, 7, 8,** *cis*-2-butene, *cis*-butadiene, cyclobutane, and bicyclobutane. The molecular orbital energies as obtained by these calculations are displayed in Figure 3. Only the three highest occupied molecular orbitals and the LUMO for each compound are shown.
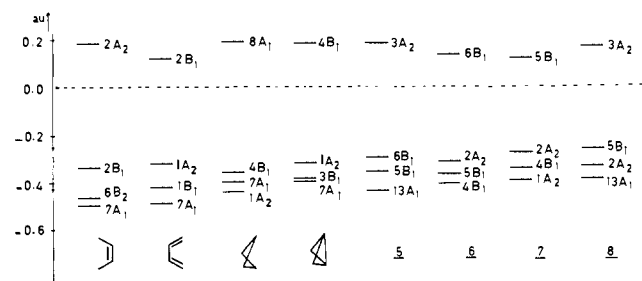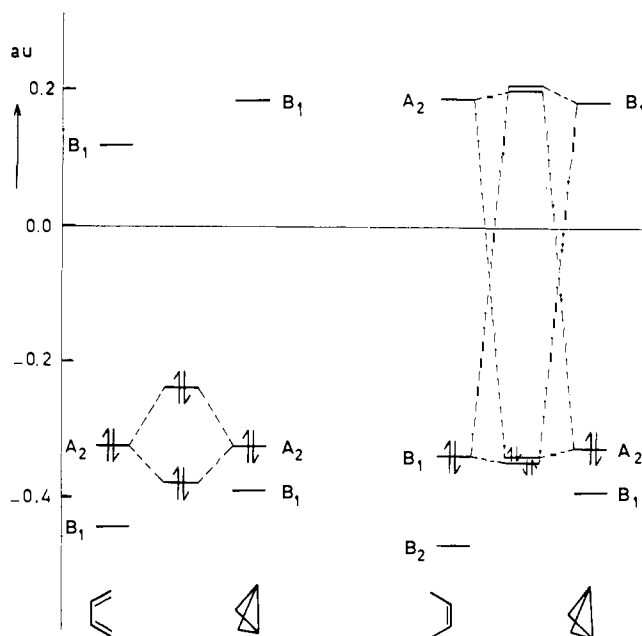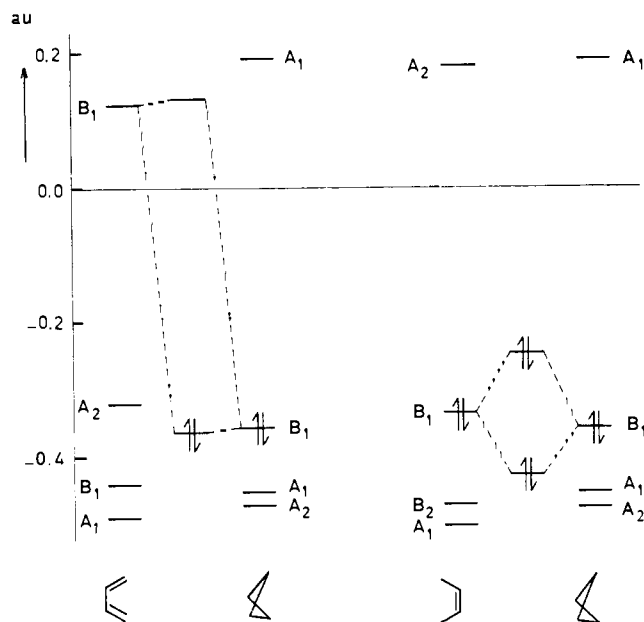
Figure 3. Calculated orbital energies.

Figure 4. Schematic interaction diagrams for the frontier orbital mixings between the bicyclobutane ring and the unsaturated bridges in **5** and **6**, respectively.
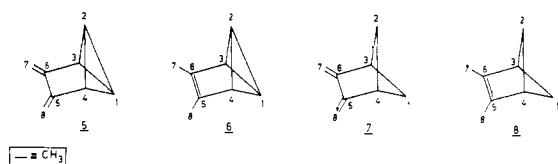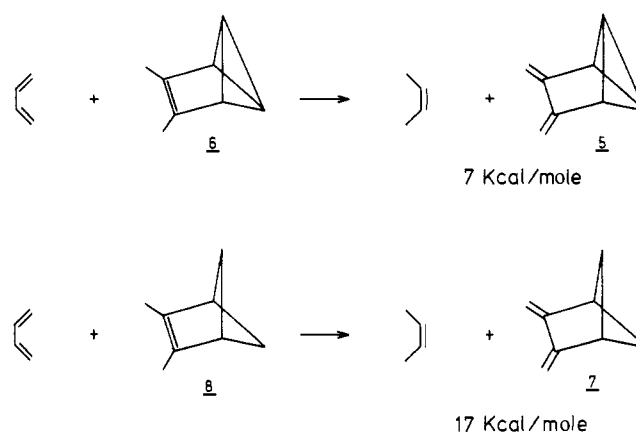

Figure 5. Schematic interaction diagrams for the frontier orbital mixings between the cyclobutane ring and the unsaturated bridges in **7** and **8**, respectively.

7 Kcal/mole

17 Kcal/mole

Figure 6. Isodesmic reactions.

We can now consider the orbital interactions between ring and bridge in the model compounds **5, 6, 7**, and **8**, respectively. The largest interactions are expected to occur between the frontier orbitals of ring and bridge, provided that they have the correct symmetry for overlap. The HOMO of bicyclobutane has the same symmetry (A_2)[33,37] as the HOMO of butadiene and nearly the same energy and will therefore strongly interact. This interaction leads to destabilization. Replacing the butadiene bridge by ethylene, as in **6**, changes the picture. The HOMO of the ethylene bridge has no longer the same symmetry as the HOMO of the ring; consequently they do not interact. However, the LUMO of ethylene has the correct symmetry to mix with the HOMO of bicyclobutane. Similarly the HOMO of the bridge interacts with the LUMO of the ring. The mixing of a filled molecular orbital and an unfilled one has a stabilizing effect (Figure 4).

These qualitative considerations suggest a preference for *cis*-2-butene over *cis*-butadiene as a bicyclobutane bridging group.[33] The same treatment of **7** and **8** leads to the opposite conclusion. The HOMO of cyclobutane $(4B_1)$ does not interact with the HOMO of butadiene, but can mix with its LUMO (Figure 5). On the contrary, the interaction of cyclobutane and

cis-2-butene results in destabilization because their HOMO's have the same symmetry and will therefore mix. The frontier orbital analysis suggests that a cyclobutane ring is preferentially bridged by butadiene over *cis*-2-butene[33] (Figure 5).

The above analysis, based exclusively on consideration of the frontier orbitals of the small rings and unsaturated bridges, represents an oversimplication of the orbital mixings that exist in these compounds. For example, the destabilization in **5**, due to the interaction of the HOMO's of the butadiene and bicyclobutane moieties, is mitigated by the stabilizing mixing of the penultimate highest occupied orbital of butadiene $(1B_1)$ and the LUMO of bicyclobutane $(4B_1)$. On the other hand, the stabilizing HOMO–LUMO mixings in **7** are weakened by the interacting of the HOMO of cyclobutane and the penultimate highest occupied orbital of butadiene $(1B_1)$. However, the energy gap between these orbitals is relatively high, so that the energetic consequences of their mixing remain relatively small. Another estimation[30] of the energetic preference for *cis*-2-butene as a bicyclobutane bridge as compared to a cyclobutane bridge can be obtained from a calculation of the energy of the isodesmic reactions[39] shown in Figure 6.

The isodesmic reaction which replaces the *cis*-2-butene bridge in **6** by *cis*-butadiene is calculated to be exothermic by about 7 kcal/mol. For the analogous reaction of **8** the exo-
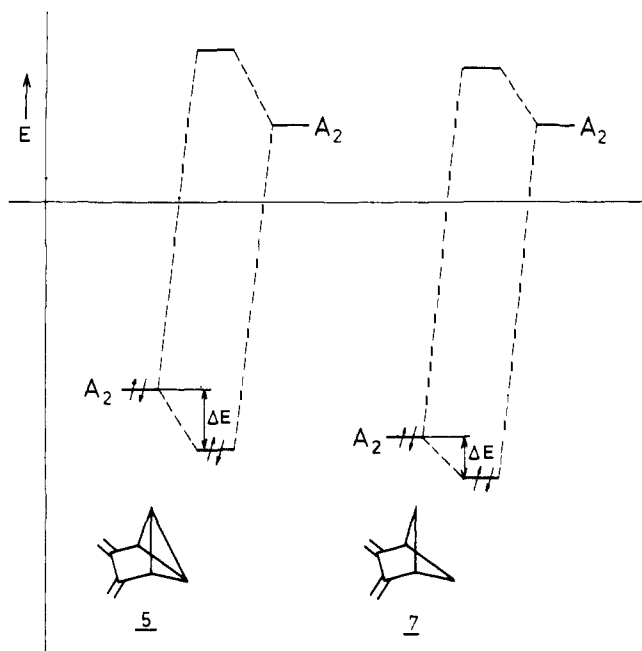
Figure 7. Schematic representation of the interaction of the HOMO's of 5, and 7, with the LUMO of a dienophile.

Figure 8. Correlation of HOMO-LUMO separation with ln k_2 for the Diels–Alder reaction of tetracyanoethylene and maleic anhydride with 1 and 4. The hyperbolic curve drawn is the one reported by Sustmann.[12]

thermicity amounts to 17 kcal/mol. Although no quantitative significance should be attached to these values, one can accept the trends as indicating the energetic preference for *cis*-2-butene as a bicyclobutane bridge as compared to a cyclobutane bridge. By extending these conclusions to dienes 1 and 4 we may conclude that the bicyclobutane bridged diene 1 should undergo the Diels–Alder cycloaddition quite readily in contrast to the cyclobutane bridged diene 4. This is, of course, exactly what is actually observed.

Reactivity of the Dienes 1 and 4 as a Function of HOMO–LUMO Separation. Previously we have discussed the difference in reactivity of 1 and 4 toward dienophiles in terms of the perturbation of the frontier orbitals of the separated parts (ring and unsaturated bridge). Now we will consider the reactivities of 1 and 4 as a function of the separation of their HOMO's and the LUMO of the dienophile. In the normal Diels–Alder cycloaddition reaction the interaction between the HOMO of the diene and the LUMO of the dienophile is the dominant stabilizing factor.[12,40] The Diels–Alder cycloadditions of both dienes 1 and 4 belong to this class because the reaction rates are enhanced by the use of electron-poor dienophiles. The orbital energies of the HOMO's in the model systems 5 and 7 are calculated to be −0.270 and −0.310 au, respectively. Hence the energy of the HOMO of 5 lies about 25 kcal/mol above that of 7. Both HOMO's have the proper symmetry (A_2) to interact with the LUMO of a dienophile and have their highest coefficient on C-7 and C-8. Because of the smaller energy separation between the HOMO and a fixed LUMO of a dienophile this interaction is more favorable for 5 than for 7 (see Figure 7). This reasoning leads also to the conclusion that the bicyclobutane bridged diene 1 is more reactive in Diels–Alder cycloadditions than the cyclobutane bridged diene 4.

The energies of HOMO's can be experimentally determined by photoelectron spectroscopy (PES).[41] The vertical ionization potentials I_v as determined from the photoelectron spectra may be equated with the negative orbital energies providing that Koopman's theorem[42] is valid. By PES measurements[43] values of 7.82 and 8.22 eV were obtained for the π-ionization potentials[44] of 1 and 4, respectively. Thus, the energy of the HOMO of 1 lies 9.2 kcal/mol above that of 4, in reasonable agreement with the calculated value (25 kcal/mol).
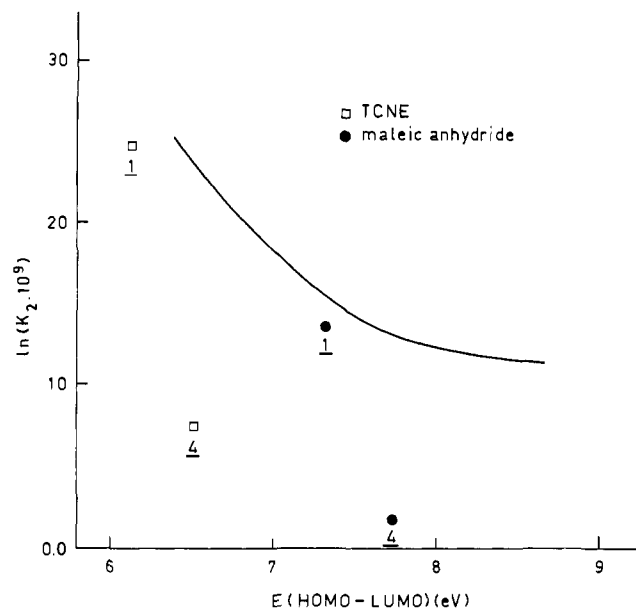
Based on perturbation theory, Sustmann[12] has derived a simple expression[45] which correlates the reaction rate of a Diels–Alder reaction with the energy gap of the frontier orbitals of the reactions. For the normal Diels–Alder reaction the logarithm of the rate constant is inversely proportional to the difference in energy between the HOMO of the diene and the LUMO of the dienophile:

$$\ln k = K \frac{1}{E_{\text{HOMO}} - E_{\text{LUMO}}}$$

The derived relation was tested for the reaction of TCNE and maleic anhydride with a variety of substituted dienes and the expected hyperbolic curve, which is shown in Figure 8, was obtained.[12] The data of dienes 1 and 4 are added to this graph, using the HOMO energies as obtained from the PE spectra, the kinetic data of Table I, and the LUMO energies as used by Sustmann.[12]

We can conclude that the bicyclobutane bridged diene 1 fits quite well in the correlation. Hence, we can conclude that the Diels–Alder reactivity of 1 is largely determined by its electronic properties. In contrast, the cyclobutane bridged diene 4 does not correlate. The reactivity is much lower than anticipated from the HOMO energy. Therefore, we must conclude that the electronic properties of diene 4 cannot be used to explain the Diels–Alder reactivity.

Conclusions

We have discussed the difference in reactivity of 1 and 4 in Diels–Alder cycloadditions on the basis of geometry, strain, and steric factors. The conclusion was reached that these factors alone could not account for the differences actually observed. By considering the interaction between ring and unsaturated bridges in the model compounds 5, 6, 7, and 8, we have concluded that these interactions are stabilizing in diene 4 and Diels–Alder adducts of 1 whereas unfavorable mixings occur in diene 1 and Diels–Alder adducts of 4. We have shown that the electronic properties of 1 are in good agreement with the observed reactivity in contrast to that of 4. The calculations on the isodesmic reactions suggest a difference in exothermicity of about 10 kcal/mol in favor of the Diels–Alder reaction of 1. This may be attributed to the favorable orbital mixing be-

tween the diene bridge and cyclobutane ring in **4.** However, if the reactivity was determined by this interaction, one should expect a reasonable correlation of the reactivity with the HOMO energy of **4.** This is not observed. Alternatively, unfavorable orbitals mixings (orbital repulsion) may largely dictate the reactivity of **1** and **4.** This is in accordance with the observed good correlation of the HOMO energy of **1** and its reactivity. If one accepts that the overlap repulsion in the Diels–Alder adduct of **4** is already felt in the transition state, the poor correlation in the case of **4** is not surprising.

This explanation is in qualitative agreement with the Hammond postulate,[23b,46] which states that the less exothermic a reaction, the more the transition state resembles the product in structure. It is thus reasonable to expect that the transition state of a Diels–Alder cycloaddition of **1** can be approximated by using the properties of the reactants whereas the corresponding transition state of **4** is expected to be influenced by the properties of the Diels–Alder adduct. Of course these properties are not reflected in the experimental measurement of the HOMO energy of **4.**

Therefore, we believe that the reactivities of **1** and **4** are largely determined by the existence of repulsive interactions (overlap repulsions) between the filled frontier orbitals of rings and unsaturated bridges in the reacting diene **1** and the Diels–Alder adducts of **4,**[47] respectively (Figure 9).

Experimental Section

Kinetic Measurements. The kinetic measurements were carried out in a ^{1}H NMR tube, by measuring the appropriate absorptions in reagents and/or products as a function of time, on a JEOL C60 H1 spectrometer except for three cases. The reaction of diene **1** with dimethyl acetylenedicarboxylate was carried out in a 5-mL round-bottomed flask with 1 mL of dimethyl acetylenedicarboxylate (solvent) and 63 mg of diene **1** (magnetically stirred). Samples were drawn at measured time intervals and analyzed by ^{1}H NMR spectroscopy. The reaction of diene **1** with TCNE was followed by UV spectroscopy on a Zeiss PMQ II spectrophotometer at 20 °C. The disappearance of the TCNE–benzene (solvent) charge transfer complex at 382 nm was measured as a function of time. The rate of the reaction of diene **1** with PTAD (**2**) was roughly estimated by adding a solution of PTAD (**2**) in 5 mL of benzene (c 7.4 × 10^{-2} mmol/L) to a solution of diene **1** in 10 mL of benzene (c 4.3 × 10^{-2} mmol/L) under vigorous stirring at room temperature. The solution decolorized within 1 s.

Treatment of the Kinetic Data. The addition reactions of diene **1** and diene **4** with TCNE and maleic anhydride and the reaction of diene **4** with PTAD (**2**) were assumed to be second order:

$$\frac{2.303}{a - b} \log \frac{b(a - x)}{a(b - x)} = k_2 t$$

or when $a = b$

$$\frac{x}{a(a - x)} = k_2 t$$

For the Diels–Alder reactions with dimethyl acetylenedicarboxylate, which was used as solvent, the reaction was assumed to be pseudo-first-order:

$$\log \frac{a}{a - x} = k_1 t$$

In all cases plots of log $[b(a - x)]/[a(b - x)]$, $x/[a(a - x)]$, and log $a/(a - x)$ vs. time were linear to at least 70% conversion. The experimentally determined values of the rate constants have an accuracy of about 5%. In the extrapolated values the maximum error is estimated to be 20%. The pseudo-first-order rate constant was converted into the second-order rate constant by taking [dimethyl acetylenedicarboxylate] to be 11.0 mol/L.

Results of the Kinetic Measurements. The k_2 values of the reaction of diene **1** with TCNE, maleic anhydride (solvent o-dichlorobenzene), dimethyl acetylenedicarboxylate, and diene **4** with PTAD (**2**) (solvent acetone-d_6), which are listed in Table I, were obtained at the temperatures indicated. The other k_2 values of diene **4** and 2,3-dimethyl-1,3-diene were calculated by extrapolation of the rate constants determined at higher temperatures. Reaction of diene **4** with
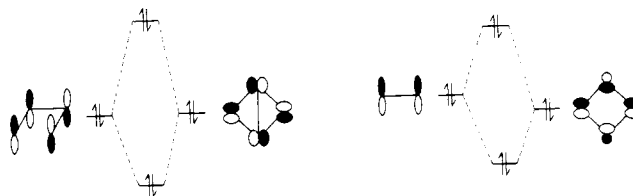

Figure 9. Overlap repulsions between the frontier orbitals of rings and unsaturated bridges in **1** and the Diels–Alder adducts of **4,** respectively.

TCNE (o-dichlorobenzene): $k_2 = 6.59 \times 10^{-4}$ L mol^{-1} s^{-1} (75 °C), 1.29×10^{-3} (83 °C), 3.53×10^{-3} (95 °C). Reaction of diene **4** with maleic anhydride (o-dichlorobenzene): $k_2 = 1.07 \times 10^{-4}$ (145 °C), 2.31×10^{-4} (158 °C), 3.84×10^{-4} (167 °C). Reaction of diene **4** with dimethyl acetylenedicarboxylate (solvent): $k_2 = 8.41 \times 10^{-6}$ (90 °C), 2.10×10^{-5} (101 °C), 4.71×10^{-5} (111 °C), 8.87×10^{-5} (120 °C). Reaction of 2,3-dimethyl-1,3-diene with dimethyl acetylenedicarboxylate (solvent): $k_2 = 9.32 \times 10^{-6}$ (41 °C), 3.18×10^{-5} (52 °C), 6.70×10^{-5} (62 °C).

Competition Experiment of Cyclopentadiene and Diene 1 with PTAD (2). To a solution of 20 mg of cyclopentadiene (0.31 mmol) and 50 mg of diene **1** (0.31 mmol) in 0.5 mL of acetone-d_6 at −70 °C in a ^{1}H NMR tube was added 37 mg of PTAD (**2**) (0.21 mmol). The mixture was stirred at −70 °C with a rod until all PTAD had dissolved. The tube was placed in the NMR probe (precooled to −70 °C) and the ^{1}H NMR spectrum was recorded. The ratio of cycloadducts (see below) was found to be 2.5 (adduct of cyclopentadiene/adduct of **1**).

Characterization of the Reaction Products. The products of the reactions of diene **1** with maleic anhydride,[52,53] PTAD (**2**),[52,54] TCNE,[24] dimethyl acetylenedicarboxylate,[55] and diene **4** with TCNE[26] and PTAD (see below) were characterized by comparison of the ^{1}H NMR spectra with those of authentic samples. The other adducts were identified by their ^{1}H NMR spectra and exact mass measurements. Diels–Alder adduct of **4** and maleic anhydride: ^{1}H NMR (CDCl$_3$) centered at δ 3.5 (m, 2 H), centered at 2.5 (m, 6 H), 0.93 (s, 6 H), 0.77 (d, 3 H, J = 6 Hz), and 0.72 (d, 3 H, J = 6 Hz); mass m/e found 260.139 (calcd for C$_{16}$H$_{20}$O$_3$, 260.141). Diels–Alder adduct of **4** and dimethyl acetylenedicarboxylate: ^{1}H NMR (dimethyl acetylenedicarboxylate) δ 3.85 (s, 6 H), 3.12 (s, 4 H), 2.47 (q, 2 H, J = 7 Hz), 0.98 (s, 6 H), and 0.90 (d, 6 H, J = 7 Hz); mass m/e found 304.165 (calcd for C$_{18}$H$_{24}$O$_4$, 304.167). Diels–Alder adduct of 2,3-dimethylbutadiene and dimethyl acetylenedicarboxylate: ^{1}H NMR (dimethyl acetylenedicarboxylate) δ 3.85 (s, 6 H), 2.93 (s, 4 H), and 1.70 (s, 6 H); mass m/e found 224.102 (calcd for C$_{12}$H$_{16}$O$_4$, 224.105).

Reaction of Diene 4 with PTAD (2). A solution of 100 mg (0.62 mmol) of diene **4** and 118 mg (0.68 mmol) of PTAD (**2**) in 5 mL of chloroform was stirred for 2 h at room temperature. After removal of the chloroform, the residue was extracted several times with hexane leaving after evaporation 129 mg (60%) of a white solid. Recrystallization (two times) from hexane afforded an analytically pure sample, mp 177–180 °C dec. Anal. Calcd for C$_{20}$H$_{23}$N$_3$O$_2$: C, 71.20; H, 6.87; N, 12.45. Found: C, 70.5; H, 6.9; N, 12.5. Mass spectrum parent peak at m/e 337; ^{1}H NMR spectrum (CDCl$_3$) δ 7.40 (m, 5 H), 4.15 (s, 4 H), 2.48 (q, 2 H, J = 6 Hz), 0.98 (s, 6 H), 0.92 (d, 6 H, J = 6 Hz).

Reaction of Cyclopentadiene with PTAD (2).[57] A solution of 300 mg (4.6 mmol) of cyclopentadiene and 875 mg (5.0 mmol) of PTAD (**2**) in 5 mL of chloroform was stirred for 0.5 h at room temperature. After removal of the chloroform, the residue was extracted with hexane for 20 h in a Soxhlet apparatus. After evaporation of the hexane 800 mg (3.32 mmol) of Diels–Alder adduct (73%) was isolated as a white solid. Recrystallization from ether at −20 °C yielded analytically pure product, mp 143–145 °C. Anal. Calcd for C$_{13}$H$_{11}$N$_3$O$_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.5; H, 4.6; N, 17.5. Mass spectrum parent peak at m/e 241; ^{1}H NMR spectrum (CDCl$_3$) δ 7.19 (m, 5 H), 6.25 (complex multiplet, 2 H) 4.97 (complex multiplet, 2 H), and a AB system centered around 2.02 (2 H, J = 6.0 Hz) with an additional splitting on each peak.

Synthesis of Diene 4. The synthesis[26] of diene **4** was modified in the following way. To 4.4 g of a 1:1 mixture of the bicyclic compound **9** and the tricyclic compound **10** in 40 mL of pyridine was added 6.32
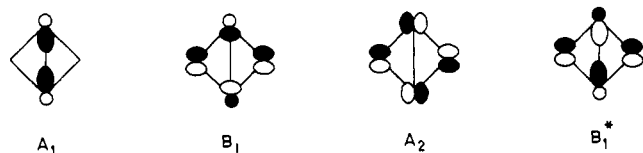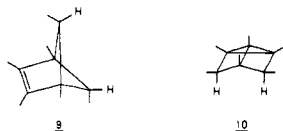
**Figure 10.** Frontier orbitals of bicyclobutane.

g of pyr $H^+Br_3^-$ (1.5 equiv relative to compound **9**) at 0 °C. After 15 min the mixture was poured into ice and extracted with pentane. The pentane layer was washed with water and after drying with $CaCl_2$ and removal of the pentane in vacuo (at 0 °C), compound **4** and **10** were separated by preparative TLC (silica gel PF 254 + 366, Merck) with pentane, leaving 0.75 g (10% overall yield) of **4** (pure according to ^1H NMR).

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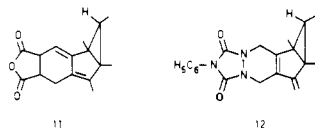
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(56) In this reaction the Diels–Alder cycloadduct was formed in ~50% yield. The other products were not identified but are probably due to an acid-catalyzed rearrangement of diene **4**. The rate constant given in Table I should therefore be regarded as an upper limit.
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# The Aromatic Cope Rearrangement. Thermal Reactions of *cis*-1-Aryl-2-vinylcyclopropanes

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Abstract: At 140–150 °C *cis*-1-phenyl-2-vinylcyclopropane (**1c**) undergoes cis ⇌ trans interconversion with $\Delta H^{\ddagger} = 32$ kcal/mol, $\Delta S^{\ddagger} = -5.8$ eu, and at or above 200 °C formation of 4-phenylcyclopentene occurs. Attempts to trap the Cope rearrangement product, bicyclo[5.4.0]undeca-1,4,8,10-tetraene (**3**), via Diels–Alder adducts failed. Heating **1c** with potassium *tert*-butoxide at 150 °C gave 1-phenyl-1,3-pentadiene (**4**). This product was formed only from **1c**, and in the presence of *tert*-butyl alcohol-*O*-*d* recovered **1c** and **1t** were devoid of deuterium. A route to **4** via formation of a tetraenide ion from **3** followed by ring opening is postulated. Treatment of *cis*-1-(*m*-methoxyphenyl)-2-vinylcyclopropane (**7c**) with ethyl mercaptide gave *cis*-1-(*m*-hydroxyphenyl)-2-vinylcyclopropane (**8c**). Heating **8c** at 120 °C gave 6,9-dihydro-5*H*-benzocyclohepten-1-ol (**10**). Treatment of *cis*-1-(*p*-methoxyphenyl)-2-vinylcyclopropane gave only *trans*-1-(*p*-hydroxyphenyl)-2-vinylcyclopropane. The relevance of these results to the aromatic Cope rearrangement is discussed.

Introduction

Since its discovery by Cope[1] in the early 1940s, the Cope rearrangement has become the prototype for the [3,3] sigmatropic shift. In distinct contrast to the Claisen rearrangement,[2] the Cope rearrangement has been most reluctant to reveal itself if one double bond of the 1,5-hexadiene system is incorporated in an aromatic ring. Thermolysis of 4-phenyl-1-butene produces no *o*-allyltoluene,[3] and the presence of activating substituents on C₄ does not permit observation of the Cope rearrangement.[4] Use of naphthalene or phenanthrene rings with activated molecules such as diethyl α-allyl-α-(2-naphthyl)malonate or diethyl α-allyl-α-(9-phenanthryl)malonate gave products of a complex rearrangement, which might result from further reaction of an initial Cope rearrangement product, though the mechanism is still unknown.[5] The first study productive of isomers interpretable as the direct result of a Cope rearrangement was based on the very reasonable assumption that the rearrangement can indeed proceed (eq 1) but $K \ll 1$ and that observation of the rearrangement
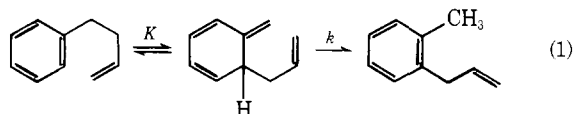
is prevented because the prototropic step does not proceed at a reasonable rate, i.e., $k \rightarrow 0$. To activate the prototropy the 4-phenyl-1-butene was heated with potassium *tert*-butoxide, and *o*-allyltoluene along with *cis*- and *trans*-*o*-propenyltoluenes was obtained.[6] Despite the inviting prospect revealed, the actual mechanism of formation of these products has never been securely tied to the Cope rearrangement.

One further ingredient in the recipe for the present approach to the problem was added by the observation of Doering and

Roth[7] that when C₃ and C₄ of the hexadiene moiety are incorporated into a cyclopropane ring with proper stereochemistry the Cope rearrangement is greatly accelerated. Applied to 4-phenyl-1-butene this principle leads to *cis*-1-phenyl-2-vinylcyclopropane, a substrate of considerable interest in the present context (eq 2). The acceleration of the rearrangement
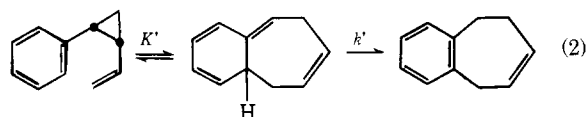
is accompanied by the further advantage that $K' \gg K$, because the relief of strain from opening the cyclopropane will offset a large part of the loss of aromatic resonance energy. Since we expected k' to be about equal to k, we planned to attempt to trap the direct Cope product in other ways.

cis-1-Phenyl-2-vinylcyclopropane. Synthesis and Reactions

An attempt to develop a directed synthesis of *cis*-1-phenyl-2-vinylcyclopropane (**1c**) via the route of Scheme I was

Scheme I